



CHE4117: Design Project (1999)

FORMALDEHYDE FROM METHANOL

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Summary

In early 1999 MonMark Consulting Services was contracted by Rhonnan Worldwide to investigate the potential formaldehyde market in the local region as part of their diversification strategy. That preliminary report, reinforced by the recent closure of a 100t.y^{-1} Australian formaldehyde plant, led to Rhonnan's decision to invest in a new formaldehyde plant. The plant would produce 90% "Grade A" product (54% formaldehyde and 1% methanol by mass) from methanol feedstock, for a neighbouring resins plant. The remaining 10% would be "Grade B" (37% and 7% respectively). MonMark were again invited to advise. Investigations commenced soon after the start of the 1999–2000 financial year.

Initial indications suggested that the best site for such a set up would be Bathurst, N.S.W.. Production of around $125,000\text{t.y}^{-1}$ of Grade A product appeared to be the optimum capacity.

Rhonnan had not ventured into this market before, and so the technology had to be bought into. As the product was to go to resins manufacture, the most favourable production route was identified as the metal oxide process.

Following talks with BASF AG, Rhonnan advised at this stage that a plant in Bontang, Kalimantan, producing the equivalent of $80,000\text{t.y}^{-1}$ of Grade A solution was more in keeping with their Synchronised Operations Paradigm. If possible, a silver catalyst process, similar to that developed by BASF, was to be used.

From this new starting point, more information was sought on BASF's process, in which recycled off-gases are mixed with the reactor feed and passed over a silver catalyst. The equipment items required led to the development of mass and energy balances. Difficulties were encountered in modelling the aqueous formaldehyde system using a computer simulation package, largely due to the tendency of formaldehyde to undergo hydration, but these were overcome by independent spreadsheet calculations. The balances showed that the plant would be self-sufficient in steam, but a consumer of recirculated cooling water (RCW).

The information gathered confirmed that the BASF process was the preferred type of silver catalyst process. Some changes were made in MonMark's suggested optimisation of the process. For example, MonMark recommends that the blower be driven by a steam turbine so as not to be dependent on outside supply.

Based on the mass and energy flows obtained, all the equipment items were specified in sufficient detail to allow economic feasibility studies to go ahead, as well as for piping and instrumentation diagram (P&ID) purposes.

It was felt that the absorber was the key component in the process, given that no distillation column will be present, and so a detailed design of this unit was undertaken. This included both mechanical and process design. As this was to be essentially the final design, subject to approval, much time was spent looking at the vapour–liquid equilibria. In the end a conservative approach was taken, and subsequent safety factors omitted.

Details worked out at this stage of the project indicated that a trayed section would be required at the top of the tower, with cooling coils, to achieve high levels of absorption. This made the column over 30m in height.

Following the detailed design of the absorber, a P&ID for that item was drawn up, which also included the recirculation stream equipment. (The recirculation streams must be cooled due to the high heat of absorption.)

A hazards and operability (HAZOP) study was conducted on the methanol vaporiser. This was seen as one of the priorities, because it contains a significant inventory of methanol, which is flammable. The HAZOP meeting was conducted in a small group, and uncovered around 100 possible improvements to the draft P&ID.

Some confusion in the board room resulted in a move to clarify MonMark's position on parallel streaming. Parallel streaming is generally to be avoided, due to increased capital and operating costs as well as maintenance issues. However in this case the catalytic reactors (and associated items) are specified in parallel to cope with Rhonnan's condition that the plant be capable of operating effectively at only 60% of the design rates. Parallel specification of the reactors, in the ratio 40:60, allows the contact time to remain at the design value.

Parallel streaming can also be required for safety reasons, or due to size limitations.

After the plant layout was determined, it was discovered that the site required only 0.87ha of land, of which the processing plant comprised 18% and the storage area 28%.

Economic evaluation showed that the fixed capital investment required would be approximately 13.4 million US dollars, with an additional 2.4 million working capital. Local financial volatility meant that the contingencies that have been included are higher than normal. However with an annual operating cost of only 10 million compared to expected sales revenues of 24 million at full capacity, the payback time, net present value (NPV) and discounted cash flow rate of return (DCFRR) were all very favourable. And the assumptions made tended to err more on the conservative side. (Note: Costs are in 1999 dollars.)

MonMark Services conclude that the plant is likely to be highly profitable, and recommend investment. Further studies would tie up any 'loose ends' with regard to the specification of items and more accurate economic evaluation. MonMark Services would be pleased to provide further consultation on the project.

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Declaration of Authorship

I, David Verrelli, hereby declare that all of the work presented in this report is due to my own unstinting efforts, except in the various instances in which the work of others has been duly acknowledged and fully referenced, or otherwise specified. Any contributions made by group members, classmates or lecturers are indicated as such.

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David Verrelli

David VERRELLI

Melbourne, 18th October, 1999.

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Preface

This report is the culmination of five years of undergraduate study at Monash University, Clayton. It is therefore only just that any credit associated with this report be distributed to not only myself, but also the lecturers who advised me, other staff who assisted me, the friends who counselled me and provided welcome diversion, and my parents who supported me.

Of course, any errors in fact or omissions remain my own responsibility.

I wish in particular to thank Anthony, Susan, Sylvia, Hasan, Hanny, Juliana, Jo, Angela, Makoto, Mong, Lan, Li Ling, Gareth, Helen, Tu, Katrina, Jeremy, Mary, Manual, Adrian and Yuki.

Also Dr. Peter Uhlherr, Dr. Ross Nicol, Dra. Yacinta Kurniasih, Tina Weller, Dr. W. Erich Olbrich, Dr. Joe Mathews, Dr. Philip Thomson, Dr. Steve Siems, Dr. Paul Webley, Dr. John Andrews, Dr. Tamarapu Sridhar and Nick.

I would like to recognise various of the staff at Wheelers Hill Secondary College and Waverley Meadows Primary School.

Finally a word for all those people who have entertained me – through music, through television and through literature.

David Verrelli

David VERRELLI

Melbourne, 18th October, 1999.

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PART 1: Project Option Considerations

1 RECOMMENDATIONS ON CAPACITY, LOCATION AND PROCESS ROUTE

1.1 Problem Statement

Part 1 of the Design Project looks at the hypothetical situation in which a shortfall in the Australian formaldehyde¹ (HCHO) market of $1 \times 10^5 \text{ t.y}^{-1}$ at 54%(m/m) is to occur due to an imminent plant closure. The task is then to specify relevant plant information in order to meet this new demand, namely initial capacity, location (in Australia) and process route.

The plant will be part of a complex in which the formaldehyde that is produced from methanol will in turn be used to make amino and phenolic resins.

Two grades of formaldehyde are to be produced: “Grade A,” containing 54%(m/m) formaldehyde and 1%(m/m) methanol (CH_3OH), and “Grade B,” containing 37%(m/m) formaldehyde and 7%(m/m) methanol.

Other practical limits on such impurities as formic acid² (HCOOH) are implicit in the nature of the end use of the resins as adhesives in engineered wood products.

There is a requirement to produce nine (9) times more Grade A than Grade B.

Forecast Australian growth rates for formaldehyde over the following five years are said to range from $+2\%.\text{y}^{-1}$ to $+6\%.\text{y}^{-1}$. This growth is of the entire Australian formaldehyde industry, being (initially) approximately $2 \times 10^5 \text{ t.y}^{-1}$.

1.2 Capacity

The following assumptions are made in calculating the initial optimal capacity:

- the calculation will be based on a plant life of 10 years (minimum)
- our plant will come on line just as the other plant closes
- our plant will hold half the market share for the duration of its operating life

The last assumption has been forced due to a lack of information. In a real scenario consideration could be made of the preferences of various buyers according to, for example, their location. However in this situation nothing is known about the competitor(s), except that they produce $1 \times 10^5 \text{ t.y}^{-1}$ of 54%(m/m) formaldehyde in year 1.

There is no reason to assume that they will be unable to increase their market share (particularly being established companies). In fact, it is known that existing plants often operate at low capacity utilisation rates [7], [4].

The market increase will be estimated at $4\%.\text{y}^{-1}$ for the first five (5) years, neither overly conservative nor overly optimistic. However since details of the increase in demand are unknown for years 6 to 10 a conservative estimate of $2\%.\text{y}^{-1}$ is appropriate. Since the market cannot be predicted for this period with any great confidence a cautious approach will be pursued. The total market demand compared with our share of the market is shown in Table 1-1 below (based on 54%(m/m) formaldehyde):

Criteria used in the selection were that the capacity utilisation should not drop below, say, 75% of the design rate at any stage in the project, as this would be highly uneconomical. (It is impracticable to stockpile formaldehyde due storage limitations).

It is known that in practice formaldehyde plants often operate for up to (around) 30 years [7]. However, in order to operate at reasonable capacity utilisation in early years and to minimise capital investment risk, extra capacity which may be required after the initial 10 year period considered would be added on at a later date (depending on market growth).

It is also usually possible to ‘squeeze’ more production out of a plant after it has been operating for a number of years by ‘fine-tuning’ or ‘debottle-necking’.

¹ The International Union of Pure and Applied Chemistry (IUPAC) recognises both “formaldehyde” and “methanal” as acceptable names for the molecule HCHO [8].

² The IUPAC recognises both “formic acid” and “methanoic acid” as acceptable names for HCOOH [8].

Year	Potential Market Share [t.y ⁻¹]	Total Market Capacity [t.y ⁻¹]	Estimated Market Increase [%y ⁻¹]	Capacity Utilisation [%]
1	100,000	200,000	4	80
2	104,000	208,000	4	83
3	108,000	216,000	4	87
4	112,000	225,000	4	90
5	117,000	234,000	4	94
6	119,000	239,000	2	96
7	122,000	243,000	2	98
8	124,000	248,000	2	99
9	127,000	253,000	2	100
10	129,000	258,000	2	100

Table 1-1: Market Forecasts for Australian Formaldehyde Sales.

Based on the above, a plant capacity of 125,000t.y⁻¹ of 54%(m/m) formaldehyde has been selected.

Since the product to be made is a mixture of Grade A and Grade B, the above estimate of 125,000t.y⁻¹ accounts for only 90% of the product mix. The total amount of product that is required is approximately 139,000t.y⁻¹. Thus the capacity of the plant will be 139,000 tonnes per year.

1.3 Process Route

The main alternatives are 'silver catalyst type process(es)' and the 'metal oxide [catalyst] type process' [9], [5]. The preferred process is that using a metal oxide catalyst for the reasons described below:

- The silver catalyst process uses methanol in excess whereas the metal oxide catalyst process uses air in excess. As methanol is toxic and highly flammable, the reduced inventory of the latter process constitutes a lower hazard.
- The metal oxide process may more conveniently produce formaldehyde that is lower in methanol concentration, making it more suitable for resins manufacture [7].
- The metal oxide catalyst process, unlike the silver catalyst process, does not require external steam for start up, which would mean additional expense.
- The yield obtained in the Formox process, 88 to 92%, is higher than the 86 to 90% attainable in the silver catalyst process.
- The metal oxide catalyst process runs at lower temperatures (300 to 400°C) to the silver catalyst processes (600-650°C), requiring less heat energy.
- The metal oxide catalyst process has generally the higher catalyst selectivity.

It is believed that these advantages outweigh the following disadvantages for the metal oxide catalyst process:

- The off-gas is non-combustible, causing substantial costs in controlling environmental pollution.
- The catalyst replacement time is substantially longer (around one (1) week, compared with one (1) day for the silver catalyst process).
- The investment costs for the metal oxide catalyst process are slightly higher.
- The equipment items in the metal oxide catalyst process are larger, due to the large volume of air flowing through the system, and thus more expensive – although there may be fewer items in total.
- The larger volumetric flow rate also leads to larger power consumption by the blower, thus contributing to higher overall operating costs.

1.4 Location

The recommended location³ for our formaldehyde production facility is Bathurst, NSW.

The main reason behind this decision is the close proximity of MDF (medium-density fibreboard) producers CSR and Boral [3], [2]. These companies produce their wood products from radiata pine harvested from nearby plantation forests. CSR is the largest producer of timber products in Australia. They are the leading supplier of

³ One option that could have been considered if the scenario had been more detailed is to operate smaller plants at more than one location.

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Chapter 1: Capacity, Location and Process Route Recommendations

solid timber, particleboard, door skins and hardboard. They also produce large amounts of medium density fibreboard panels and decorative laminates.

In terms of other raw materials, methanol can be brought in by rail following shipment to Sydney. Urea will come from Newcastle by road and phenol is available from Huntsman [6] in Victoria.

With 29,000 inhabitants in Bathurst, accommodation and facilities for employees are readily available [1]. Similarly, all of the required utilities are accessible locally. The land is suitable for plant construction. Specialist labour will be available from Sydney if required.

Local community attitudes are expected to be favourable as the proposed plant will be a major new source of employment. Furthermore, it is anticipated that protests against logging will not be vigorous as this is a pre-existing industry.

Emissions from the plant will be tightly controlled and the plant will be operated according to stringent environmental guidelines.

1.5 References

1. Bathurst internet site; <http://www.bluemt.com.au/hwt/walkabouts.htm>⁴
2. Boral internet site; <http://www.boral.com.au/timber/facts/softwood.htm>
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6. Huntsman internet site; <http://www.huntsman.com>
7. Presentation by Mr. Eric JACOBSEN (Orica Adhesives and Resins, Deer Park) at Monash University, 21/07/1999. He stated that the current capacity utilisation of the Deer Park plant was of the order of, "50 to 60 percent."
8. John McMURRY; Organic Chemistry, 3rd edition; Brooks/Cole; Pacific Drive, California; 1992.
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⁴ Credit is due to other members of Group 8, and in particular Miss. Rachel WELDON, for Ref's [1], [2], [3] and [6].

PART 2: Plant Design for Nominated Capacity, Location and Process Route

2 PROBLEM DEFINITION

2.1 Introduction

Similarly to the scenario in Part 1 of this report, the requirement in Part 2 is to satisfy a perceived demand for formaldehyde (HCHO). However in this case the capacity, location and process route have all been fixed, and it is up to the individual and the group to investigate the best means of achieving the set objective.

Not only is it necessary to specify process details, but also other required infrastructure such as utility requirements.

2.2 Plant

2.2.1 Process Route

The plant is to produce formaldehyde from methanol (CH_3OH) via a silver catalyst type process. No further restrictions were made in this regard.

2.2.2 Location Details

The site is located in on the island of Borneo in Bontang, East Kalimantan (Kalimantan Timur) province, Indonesia (see Figure 2-1 at left).

Bontang is located at 0.05° North (latitude) and 117.31° East (longitude) – *i.e.* essentially directly on the equator. The population was said to be under 10000, although this may not include an ever growing number of expatriate workers at the local petrochemical complex. [4]

The site is flat and there are no space constraints other than those imposed by safety and economic considerations and practicalities of construction, operation and maintenance.

Ambient air temperatures range from 20 to 37°C ¹ and cooling water is available at a “maximum summer temperature” of 30°C .

Natural gas is available to meet fuel needs.



Figure 2-1: Map of Bontang, Indonesia; 1:1500000. [5]

¹ Note that this has been changed from the initial 10 to 47°C range (adjusted by 10°C at each end of the range) that was initially specified, which was judged to be unrealistic on the basis of Ref's [1] and [2].

2.2.3 Capacity

The plant is required to produce “Grade A” product and “Grade B” product in the same 9:1 ratio as before, except that now the total capacity is to be $80 \times 10^3 \text{ t.y}^{-1}$, calculated as the equivalent of 54%(kg.kg⁻¹) formaldehyde solution.

It may be shown that this equates to $74.3 \times \text{t.y}^{-1}$ of Grade A product and $5.7 \times \text{t.y}^{-1}$ of Grade B on a 54%(kg.kg⁻¹) formaldehyde basis.

Equivalently this may be expressed as $8.2 \times \text{t.y}^{-1}$ of Grade B product as 37%(kg.kg⁻¹) formaldehyde basis, giving a total of $82.6 \times \text{t.y}^{-1}$ of formaldehyde solution of the two grades (the apparent discrepancy is due to rounding).

2.2.4 Other Characteristics

The plant is expected to be in operation for 350 days of the year. It must also be able to cope with turn-downs to 60% of the design capacity.

Heat recovery is to be maximised as far as is economical, with any surplus steam generated able to be used elsewhere in the factory complex.

2.3 Feedstock and Product Specifications

2.3.1 Methanol Feedstock

Methanol is supplied by pipeline to the formaldehyde plant and complies with British Standard BS-506(1987), which includes the following specifications.

Density:	791 to 794 kg.m ⁻³
Acidity:	< 0.003%(kg.kg ⁻¹) as formic acid (HCOOH)
Water content:	< 0.1%(kg.kg ⁻¹)

Methanol is “an internationally traded commodity currently selling on the international market for \$100 US per tonne FOB [freight on board] US Gulf Coast” [3].

2.3.2 Formaldehyde Product

Formaldehyde solutions of 37%(kg.kg⁻¹) strength are said to be selling at \$286 US per tonne of solution FOB US Gulf Coast [3]. However it is unclear whether this is true 37%(kg.kg⁻¹) solution, or rather the price of 54%(kg.kg⁻¹) solution on a 37%(kg.kg⁻¹) equivalent basis.

For capacity data please refer to section 2.2.3, above.

2.3.2.1 Grade A

“Formaldehyde 54” is to satisfy the following constraints:

Formaldehyde content:	53.8 to 54.2%(kg.kg ⁻¹)
Formic acid content:	≤ 0.06%(kg.kg ⁻¹)
Methanol content:	0.5 to 1.5%(kg.kg ⁻¹) [maximum]
Turbidity	≤ 5NTU (Nominal Turbidity Units)
Temperature	60 to 67°C

2.3.2.2 Grade B

“Formaldehyde 37/7” is to satisfy the following constraints:

Formaldehyde content:	37.0 to 37.4%(kg.kg ⁻¹)
Formic acid content:	≤ 0.03%(kg.kg ⁻¹)
Methanol content:	6.5 to 7.5%(kg.kg ⁻¹) [maximum]

2.3.2.3 Overall requirements

While it is not, strictly speaking a requirement to produce the Grade B formaldehyde solution by appropriate dilution of Grade A product, it is convenient to here discuss some of the ramifications of such a decision. Namely, assuming no formic acid in additional methanol or water, and further assuming no ion-exchange treatment, the Grade A formaldehyde should be produced with a formic acid content of ≤ 0.0432%(kg.kg⁻¹), rather than the ≤ 0.06%(kg.kg⁻¹) quoted above (taking into account the ranges of acceptable formaldehyde in each).

2.4 Utilities provided

The following utilities are provided outside of the 'battery limits' of the plant:

Utility	Description	Price [1999 Australian dollars]
Natural gas (NG)	Lower calorific value = 46.7 MJ.kg^{-1} Composition: 91%CH ₄ , 6%C ₂ H ₆ , 1%C ₃ H ₈ , 1%N ₂ and 1%CO ₂ (by mass)	4 GJ^{-1}
Electricity (Elec.)	Directly available at 50Hz and 11kV, 3.3kV and 415V as three-phase	$45(\text{MW.h})^{-1}$
Nitrogen (N ₂)	Dry, Pressure = 1000kPa(g)	$0.3(\text{Nm}^3)^{-1}$
Demineralised water (DMW)	Ambient temperature, p = 300kPa(g)	2.5 t^{-1}
Towns water (TNW)	Ambient temperature, p = 300kPa(g)	0.60 t^{-1}
Steam	Saturated at 1100kPa(g)	12 t^{-1}
Recirculated cooling water (RCW)	300kPa(g) ex-cooling tower	0.06 m^{-3}

Table 2-1: Details of utilities provided.

2.5 Scope

The plant design must not only cover production of formaldehyde in accordance with the preceding requirements, but it must also specifically cover:

- consideration of safety and environmental hazards
- methanol storage (if any)
- formaldehyde storage (equivalent to 3 days and 7 days at the design production rate for grades A and B respectively)
- steam generation by 'recovery' of process heat
- effluent treatment facilities to enable disposal of gaseous and aqueous effluents.

2.6 Terminal Points

The terminal points of the project are in some part related to the scope. For this project design begins at the point at which methanol, water, natural gas and any other 'raw materials' enter the plant.

At the other end of the design, formaldehyde product as well as any surplus utilities will be exported to the neighbouring resins plant (or another user in the complex), which point of interface constitutes a terminal point. The storage tank farm for formaldehyde is included inside the 'outside battery limits' section of our plant.

2.7 References

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3. Dr. David J. BRENNAN; Problem statement; 28/07/1999.
4. K. M. WRIGHT (Cartographic Manager); *The Jacaranda Atlas*, 4th edition; The Jacaranda Press; Milton, Queensland; 1992.
5. –; Map No. 4, "Kalimantan;" in: *'Indonesia' Series*; Nelles; München; circa 1980's.

Formaldehyde

3 PROCESS SYNTHESIS AND FLOWSHEET DEVELOPMENT

3.1 Characteristics of ‘Silver Catalyst Processes’

The process by which formaldehyde is produced from methanol over a silver catalyst – commonly abbreviated to ‘the silver process’ – is described in the standard chemical engineering reference texts in reasonable detail (e.g. [17], [7] and [9]). The silver process was also alluded to in section 1.3.

This section presents characteristics that are common to all silver processes.

The silver process has four absolutely essential operations, which are outlined in sections 3.1.1 to 3.1.3 below. See also Figure 3-1.

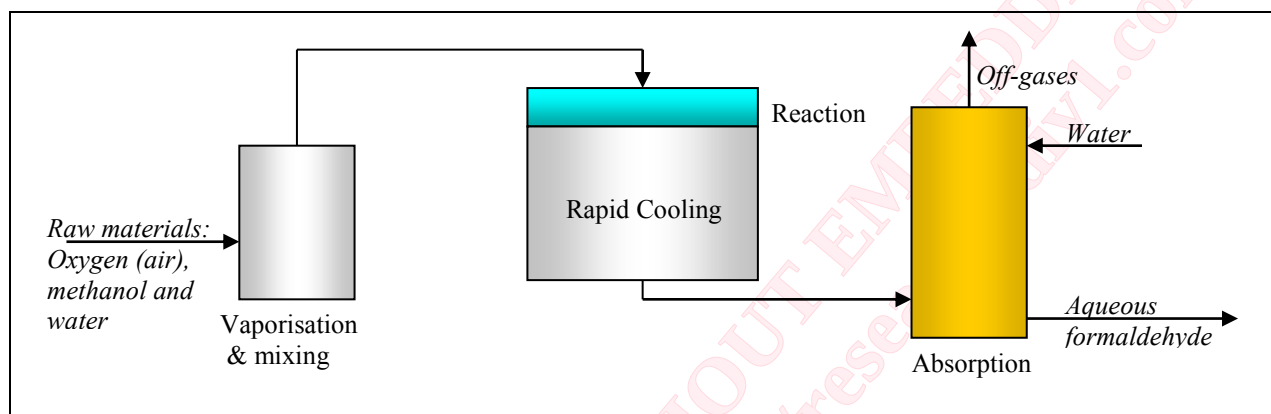


Figure 3-1: Essential process operations in the manufacture of formaldehyde from methanol.

3.1.1 Reactor

To paraphrase SMITH (Ref. [23]), the reactor is always at the heart of any process in which a chemical reaction is to take place. All other unit operations are present to provide support in one way or another for this key unit operation.

3.1.1.1 Physical characteristics

The reactor consists of silver catalyst in the form of either a gauze or small particles (crystals). These are of necessity very shallow in order that the contact time between process gas and catalyst be very short. The contact time must be very short (e.g. $< 0.02\text{s}$ [4]) in order to avoid decomposition of the formaldehyde (HCHO) into formic acid (HCOOH), which is said become significant at temperatures above 350°C [17] (or possibly 500°C [8], or possibly 350 to 450°C [16]), whereas the reaction temperature is typically 590 to 720°C ¹. Typical contact time constraints have given rise to very shallow beds – of the order of a couple of centimetres deep. This means that beds may be up to 4m wide [11].

The variation in terms of physical reactor bed design does not seem to vary much except in terms of details, such as the use of an incolloy catalyst shelf [21], baffle plate on which are deposited impurities by the impinging vapour before entering the catalyst zone [20], and particularly variation in terms of the number and dimensions of catalyst beds.

The most significant variation is probably in terms of the catalyst used, including size distributions for crystals [11], [2].

3.1.1.2 Reactions

The central reactions are as follows:

- | | | | |
|----|--|--|-------------------|
| 1. | $\text{CH}_3\text{OH}(\text{g}) + 0.5 \text{O}_2(\text{g}) \rightarrow \text{HCHO}(\text{g}) + \text{H}_2\text{O}(\text{g})$ | $\Delta H = -159\text{kJ}\cdot\text{mol}^{-1}$ | (oxidation) |
| 2. | $\text{CH}_3\text{OH}(\text{g}) = \text{HCHO}(\text{g}) + \text{H}_2(\text{g})$ | $\Delta H = +84\text{kJ}\cdot\text{mol}^{-1}$ | (dehydrogenation) |
| 3. | $\text{H}_2(\text{g}) + 0.5\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$ | $\Delta H = -243\text{kJ}\cdot\text{mol}^{-1}$ | |

¹ Note that this would most probably refer to the temperature of the gases immediately exiting the catalyst bed. The catalyst surface temperature would be expected to be greater than that of the bulk gas, and clearly a temperature profile must also exist over the bed (however shallow) to account for the incoming process gases at low temperature. Somewhat surprisingly, Ref. [15], pp. 141, 145, teaches that the maximum catalyst temperature occurs closer to the forward end.

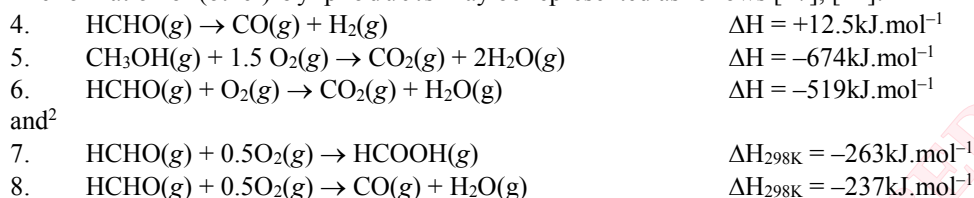
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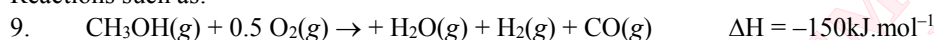
These are carried out at ambient pressure. The precise reaction temperature obtained depends upon the extent to which methanol is in excess in the methanol–air feed mixture.

The endothermic dehydrogenation reaction (2.) is highly temperature dependent in terms of equilibrium constant. Conversions vary from 50% at 400°C, to 90% at 500°C and around 99% at 700°C [17]. Ref. [5] also shows this in graphical form (p. 496), in which plot it is evident that other significant reactions (including those below) are essentially irreversible, with equilibrium constants quoted for some reactions, under certain conditions as up to a whopping 10^{25} .

The formation of (other) by-products may be represented as follows [17], [24]:



Reactions such as:



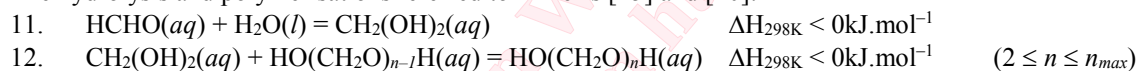
are not considered, as they have only been referred to by Ref. [5], and can be considered to be accounted for by combination of the other reactions above.

Reactions such as [5]:



were not incorporated in the analysis, on the basis that the by-products so produced could equally well be approximated by by-product formation and formaldehyde degradation from the other reactions considered. Further, the conversion of such reactions appears to be quite small compared to the other by-product reactions³. Methane (CH_4) is another example of a ‘minor’ by-product.

The hydrolysis and polymerisations referred to in Ref’s [25] and [10]:



were assumed to be not relevant to the reactor as such, by implication from *e.g.* Ref. [17], in which these reactions were entirely omitted from discussion with regard to the reactor.

However p. 623 of the same reference does include mention of apparently significant polymerisation in the gas phase. It is assumed that neglecting this detail will not introduce significant errors into the process design procedure⁴.

The assumption that these reactions only have a significant effect when formaldehyde is in the liquid phase, such as in the absorption operation (see section 3.1.3 following), is supported by Ref. [24] (p. 55).

3.1.2 Cooling

As noted in the previous section, there is a need to cool the process gases down rapidly following reaction – *e.g.* within less than 0.1s [11]. The exit temperature should be below 300°C [].

3.1.2.1 Waste-heat boiler

The most common means of achieving this quick reduction in temperature is by means of a simple waste-heat boiler, with a typical steam pressure being 500kPa(abs), corresponding to a temperature of approximately 150°C [17]. It was not thought wise to change this parameter in the absence of solid supporting information. There may be disadvantages in terms of reaction by-products if this were changed, and also material costs may increase.

This is generally a ‘standard’ unit⁵, with process gases flowing through in a single pass on the tube-side. The main difference to ‘normal’ units would be that it is typically fabricated as an integral part of the complete ‘reactor unit’.

² Heats of reaction from Ref. [18].

³ This contrasts with the very low conversion to formic acid. However that reaction must be incorporated, due to the importance of formic acid in terms of the quality of the final product.

⁴ Although it would be important to be aware of for more detailed, on-site chemical analyses and assays, for example.

⁵ With typical features, such as an absence of (shell-side) baffles.

3.1.2.2 Quench column

The other common means of achieving a rapid decrease in temperature is to send the reactor effluent into a quench column immediately after the reactor.

While this can offer the fastest means of cooling the process gas mixtures in some situations, due to the extremely rapid mechanism of 'direct heat exchange', the disadvantage lies in the concentration of the final product. That is, in order to sufficiently cool down the mixture it may be necessary to introduce such a large quantity of water that the product would end up being too dilute. This is a particular concern for this Project, which is the reason this technique was not adopted.

3.1.2.3 Novel cooling operations

Ref. [16] outlines a novel procedure whereby the cold process off-gases are, "at least partly," re-injected into the gaseous mixture leaving the catalyst layer. Conceptually this is quite similar to the quench column, except that the quench water is replaced by cold process off-gases.

For reasons that will be made clear later in this chapter, this process was not adopted (see section 3.2.2.2, page 3-6, and following).

3.1.3 Vaporiser & mixer

It is also clear from the section describing the reactor (section 3.1.1, page 3-1), that the relevant reactions take place in the gas phase. To obtain the essentially homogeneous gas-phase mixture, it is necessary to heat the liquid components. This might be achieved by either conventionally by indirect heat transfer, or possibly by direct heat transfer.

In some cases it is seen that the liquid reactants (which may not include water) are heated separately and then the vapour generated blended with an oxygen-containing stream. The mixing may simply be accomplished by their turbulent flow through ductwork (see *e.g.* Ref. [24], p. 20).

In a variation on this idea the oxygen-containing gas is heated to high temperature such that methanol sprayed into that stream can abstract sufficient (thermal) energy to be completely vaporised [3].

Another variation has circulating methanol-containing liquid being heated and 'refluxed' into a packed column, with the oxygen-containing gas flowing counter-currently [17].

This was the technique adopted, for the following reasons:

- It is felt that this process would give the best mixing of the vapours and gas, which is said to be a crucial element of this unit operation [8]. However the other processes considered would probably also be adequate.
- The size of the heater will be smaller, as it involves a liquid-phase on the process side, which has both a higher density, as well as a greater mass transfer coefficient than a gas.
- The size of the heater will be smaller than it would if the liquid were sprayed into heated gas, due to the larger temperature driving force that will be available. In addition, the large specific change in enthalpy upon vaporisation would necessitate a 'very high' gas temperature, which may be difficult to achieve without steam of pressure higher than the 'standard plant supply pressure' of 1200kPa(abs).
- Only one (series of) heat exchanger(s) is required, whereas heating the individual streams separately would require a greater number of units.
- By carrying out the actual heating of aqueous methanol liquid in the absence of any oxygen-containing gas stream it is believed that risks associated with flammability and explosiveness of the mixture would be reduced.
- Two-phase flow in the pipework was avoided.

3.1.4 Absorber

The purpose of the absorber is to extract the formaldehyde from the reactor effluent (vapour phase) into an aqueous liquid phase. In doing so, some amount of methanol will also condense into solution, as well as contaminant species such as formic acid.

Methanol is not considered a contaminant as such, because it also acts as a stabiliser, although it is undesirable in too great a concentration.

As will become apparent to the reader in Chapter 7 of this report, in which the detailed design of this unit is examined, at this preliminary stage of the design there were too many unknown quantities and complicating

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factors for the system to be designed ‘from first principles’. Thus, much as was done for the reactor (for which an extensive literature search failed to uncover relevant kinetic data) the first approach was to investigate current industry practice.

Looking first at features common to all industrial formaldehyde absorbers, they all had more than one stage, and all had liquid pump-arounds for at least the bottom stages (*e.g.* Ref’s [17], [7] and [9]).

In all cases the bottom pump-arounds were cooled, while the top stage pump-around never was. This cooling is required due to the significantly exothermic process that occurs when formaldehyde gas passes into solution. The heat of solution in water is quoted as $62\text{kJ}\cdot\text{mol}(\text{HCHO})^{-1}$ at 23°C [17].

The key differences were:

- The number of stages: Some columns were shown as having two stages, *e.g.* Ref. [9]; some three, *e.g.* Ref. [7]; and some four, *e.g.* Ref. [17].
The value of four was taken preliminarily as it was believed this could accomplish a higher absorption duty (albeit at a higher cost), for a given total height of packing.
- The number of columns: In some cases the absorption is broken up between two columns in series [8], [11], although use of a single column appears to be more wide-spread.
A single column was chosen for simplicity, as meaningful benefits of operating two columns in series were not evident at this point.
- Top-stage pump-around: Some references showed a pump-around over the top stage [17], while many did not [9], [7].
The decision was to pump around the top stage too, because the rate of fresh water to the column would have to be low in order to obtain a sufficiently concentrated product without the need for distillation (see section 3.2).
- Type of internals: Although packing of some description (usually dumped) was common for all references in the bottom sections, some showed a trayed top stage [17], [3] to act as an ‘off-gas scrubber’.
It was felt that a more uniform approach was best, with either dumped packing (or structured packing if necessary) preferred for the top stage. Benefits could include lower pressure drop; ease of replacement; probable cheaper cost due to the need to specify resistant materials; and low liquid hold-up, which would reduce hazards associated with formaldehyde and methanol inventories⁶ [22].
It was later seen that trays were required to handle the low liquid flows arising from not recirculating about the top of the column (Chapter 7).

3.2 Variations and Additions to Silver Catalyst Type Processes

It is important for the reader to realise that the four essential operations presented here will not necessarily result in a product of a given purity or ‘quality’. Rather, these four operations represent the minimum number of major unit operations necessary to produce some kind of aqueous formaldehyde product (which will also contain certain concentrations of methanol, formic acid *et cetera*), from the raw materials water, air and methanol, with off-gas of a certain composition exiting from the absorber. Other operations are required to meet desired composition criteria, and these are now described (section 3.2.4, page 3-7).

There are two main classes of silver catalyst processes for the manufacture of formaldehyde from methanol: those that do not include a distillation column, and those that do. One of the main varieties of the former process is the so-called ‘BASF process’⁷ [17].

3.2.1 With distillation

Ref. [17]⁸ terms the class of silver catalyst process that incorporates a distillation column as “Incomplete Conversion.” This extent of (primary) conversion – around 77 to 87% – leads to the need to distil the product and recycle unreacted methanol.

⁶ Though, according to the design, the material at the top of the column would be reasonable dilute.

⁷ After the German company *Badische Anilin- & Soda-Fabrik AG*, who started production using a crystalline silver catalyst circa 1905, who were the largest manufacturers of formaldehyde “in the Western world” (1983) and hold several patents in production technologies [17].

⁸ One thing to be wary of is the authorship of various of the standard references. One may note, for example, that three of the four authors of Ref. [17], in which BASF and the “BASF process” are ‘talked up’, are BASF employees.

For this process the reaction clearly takes place at a high excess of methanol to oxygen: the primary reaction being oxidation (reaction 1. of section 3.1.1.2, page 3-1). This occurs at between 590 and 650°C, and at pressure just above atmospheric.

The overall yield is said to be of the order of 91 to 92%(mol.mol⁻¹), however it is important to realise that this will vary from plant to plant.

A distillation column usually is accompanied with a 'deacidification unit', typically an ion-exchange resin, as levels of formic acid increase at the normal operating temperatures of distillation columns.

This combination is capable of producing solutions of up to 55%(kg.kg⁻¹) formaldehyde concentration, with less than 1%(kg.kg⁻¹) methanol and under 0.005%(kg.kg⁻¹) formic acid⁹.

3.2.2 Without distillation

If the silver catalyst process is run at higher temperatures (*e.g.* 680 to 720°C), and with only a slight excess of methanol to oxygen (97 to 98% methanol conversion), then it is possible to produce high concentrations of formaldehyde with low methanol levels, without the need for a distillation column [17].

When operating with the correct catalyst contact time, formic acid levels are also low enough to make an ion-exchange unit redundant.

In this process overall yields are of the order of 89.5 to 90.5%(mol.mol⁻¹). The final product may contain approximately 40 to 55%(kg.kg⁻¹) formaldehyde, an "average" of 1.3%(kg.kg⁻¹) methanol and 0.01%(kg.kg⁻¹) formic acid [17].

There are two principal means of operating a non-distillative silver process, recycling either off-gases or dilute formaldehyde solutions from the absorber. These are shown in Figure 3-2 following.

Both are made possible by altering the flammability characteristics of the mixture (see section 3.6.2, page 3-12).

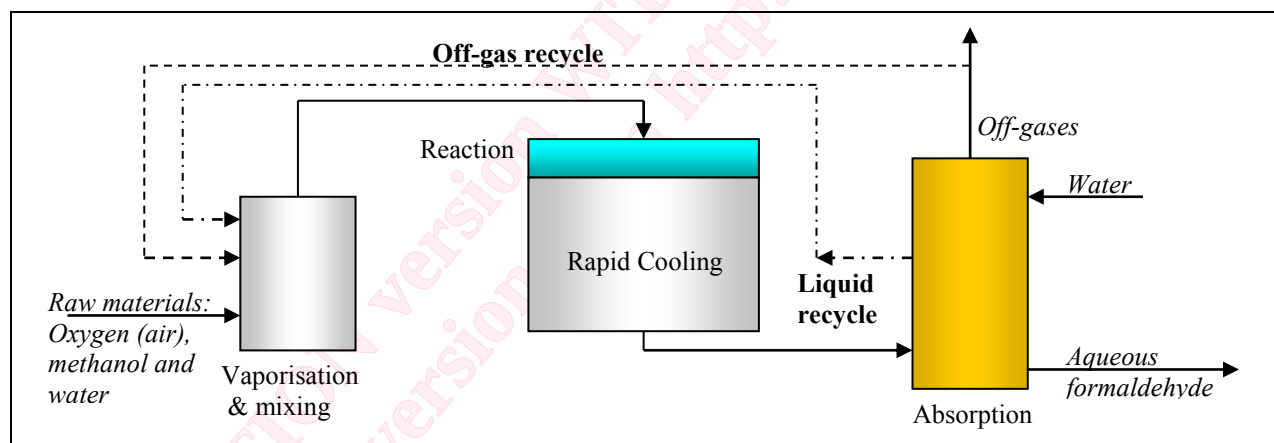


Figure 3-2: Key process flow routes in non-distillative manufacture of formaldehyde from methanol¹⁰.

3.2.2.1 Liquid recycle

In this configuration part of the pump-around liquid from either the third or fourth stage of the absorber is recycled back to a vaporiser [17], [1], and thence into the reactor.

Yields are from 89 to 91% of the theoretical for a single pass. Formaldehyde product solutions obtained from the absorber contain from 50 to 65%(kg.kg⁻¹) formaldehyde and "only" 0.8 to 2.0%(kg.kg⁻¹) methanol [1]. Formic acid is "low, as a rule less than 0.015%"(kg.kg⁻¹).¹¹

Benefits¹² are said to include that the configuration [1]:

- is "simpler" and "less trouble prone"
- "gives a higher and more constant conversion of the starting mixture"

⁹ *I.e.* Below 50ppm (by mass).

¹⁰ Note: Only one of the two alternatives is used at any one time (at a given plant).

¹¹ Based on 50%(kg.kg⁻¹) formaldehyde solution.

¹² These benefits are in comparison to nominal "conventional processes."

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- gives a longer catalyst life
- permits the use of a large catalyst bed cross-section
- does not require “special measures” to “prevent temperature fluctuations in the catalyst”
- causes less pollution, due to lower entrainment of formaldehyde in off-gas and wastewater.

The key to all but the last of these would seem to be the concept of “thermal ballast,” which is mentioned in Ref. [9] with regard to the recycling of tail gas. The idea is based in the addition of what may be considered ‘inerts’ (in that they do not react to a great extent) to the reactor feed. Given that the nett feed of raw materials to the system as a whole is more or less constant, then by doing this the enthalpy of reaction that is released (remembering that the reaction is nett exothermic) is distributed over a larger mass. This means that the temperature change induced must be lower for a given change in enthalpy (*viz.* heat release), and hence fluctuations are reduced and the operation becomes more stable.

It is also said to be more economical.

3.2.2.2 Off-gas recycle

This configuration appears to be more common, and is used by: BASF [17], [11]; the Mitsubishi Gas Chemical Company [14]; and possibly E. I. du Pont de Nemours & Company [9]. It consists of the recycling of a portion of the off-gas from the top absorber stage back to the vaporiser.

Again, the key to the advantages of this process lies in the concept of thermal ballast, outlined in the previous section.

The following information is abstracted from the patent taken out by BASF with regard to this process [11].

Preferably running at 650 to 730°C, yields are 89 to 92% of the theoretical¹³. The aqueous formaldehyde product may contain from 50 to 60%(kg.kg⁻¹) formaldehyde, 0.5 to 1.1%(kg.kg⁻¹) methanol and, “as a rule,” less than 0.015%(kg.kg⁻¹) of formic acid¹⁴.

Compared to “the conventional processes”, benefits of this configuration are that it:

- is simpler and “permits more trouble-free running”
- has a “higher and more constant conversion of the starting mixture”
- gives a longer working life of the catalyst
- has a large catalyst bed cross-section
- does not require “special measures” to “avoid temperature fluctuations in the catalyst”
- is more economical.

The astute reader will already have observed that the claimed benefits for this configuration are almost identical to that for the case of liquid recycle.

3.2.3 That is the question

To distil, or not to distil... Distillation does have some pros, in that the anion-exchange unit allows for a product that could be lower in formic acid, and the system is most probably quite ‘forgiving’, in the sense that operational ‘goofs’ in the reactor or absorber might still be able to be ‘rectified’ in the absorber¹⁵.

However the information that has been presented demonstrates that it is still possible to satisfy the product requirement constraints, defined in Chapter 2 of this report, without distillation.

Distillation columns are control-intensive units, which are relatively expensive compared to the blower and ductwork that would replace it. Ion-exchange resins are a further cost, and may require specialised knowledge to operate. For the sake of minimising costs¹⁶, a non-distillative process is preferred.

To recycle liquid, or to recycle off-gas... As noted earlier, the advantages of the two recycle processes are very similar: 54%(kg.kg⁻¹) methanol is well within the range of capabilities of both classes, and they both have low product formic acid concentrations. While the liquid recycle is said to have an environmen-

¹³ Ref. [14] claims 440kg of methanol produce 370kg of (100%) formaldehyde: *i.e.* an overall yield of 89.7%.

¹⁴ Ref. [14]: 37 to 55%(kg.kg⁻¹) formaldehyde; 0.5 to 8%(kg.kg⁻¹) methanol; less than 0.005%(kg.kg⁻¹) formic acid.

¹⁵ If the reader will excuse this brief moment of punniness.

¹⁶ Capital costs would certainly be reduced, while operating costs would require further, more detailed assessment. Maintenance of (and operating labour for) a distillation column and ion-exchange unit would be a significant cost, and additional cooling and heating would be needed, while recycling would require heating and pumping xor compressing.

tal advantage, it is believed that this is not a deciding factor, because the off-gas that is not recycled is to undergo combustion in any case (see section 3.2.4.4).

Clearly recycling a liquid will induce lower operating costs in terms of pumping (rather than compressing), and also lower capital costs in terms of the piping. However the concern is that recycling a stream with a non-negligible amount of formaldehyde in it will simply cause that formaldehyde to decompose when it passes through the reactor again, thereby reducing the efficiency (although apparently there is not a great difference in the overall yields).

The process in which the off-gas was recycled was also more common. It was also described by Ref. [25] in generic terms as the “silver process,” and one reference even claimed that off-gas recycle processes will, “play a significant role,” and will, “continue to dominate the mainstream” of formaldehyde production [14].

Finally, the principal factor was the methanol content that could be achieved in the product. Although it is true that both processes were capable of achieving the 1%(kg.kg⁻¹) methanol required, this was at the high end of achievable concentrations for off-gas recycle, but at the low end for liquid recycle. Thus, so as to increase the margin between the design value and the ‘best possible’, the off-gas recycling configuration was selected.

3.2.4 Additions

3.2.4.1 Vapour superheater

In order to operate at the optimum reaction temperature (and to exercise more control over this), a vapour superheater is installed following the vaporiser.

This also further reduces the possibility of condensation of liquid (water) onto the catalyst.

3.2.4.2 Absorber feed cooler

The vapours entering the absorber should enter at a temperature below the (approximately) 170°C at which they exit the waste-heat boiler in order to reduce the vapour pressure exerted by the condensable components.

As will be discussed later (section 3.5), for heat-integration reasons it was decided not to go as far as partially condensing the absorber feed, as shown in Ref. [25]. This would also have engendered two-phase flow, which is (apparently¹⁷) something to avoid.

3.2.4.3 Pump-arounds

As mentioned earlier, the absorber unit has pump-arounds which are also cooled by passing through heat exchangers. Thus each would require a ‘standard’ pump and shell-and-tube heat exchanger.

3.2.4.4 Off-gas burner

There are stringent guidelines around the world to limit the quantities of formaldehyde emissions. For this reason some processes run their absorbers at high ‘duties’ to remove as much as possible, while catalytic converters are common in metal-oxide plants.

However in this case the most advantageous option is to fully combust the off-gas leaving the absorber. This means that there is no panic if gas-phase concentrations at the top of the absorber rise 50% above the emission limits, as the high-temperature combustion will certainly handle that.

The other main reason is related to the hydrogen that is present in the off-gases in significant levels. This is highly flammable, and it is more economical to recover this stored energy by liberation in the form of heat, which is used to raise steam. In this case it is not necessary to add any extra fuel to aid combustion (only oxygen/air is required).

This must also have facility for the addition of natural gas, on the occasion of start-up, at which time there would be negligible hydrogen-containing off-gas, as would normally be combusted to raise the steam.

3.2.4.5 Pressurising units

The blower has already been mentioned in passing. This is necessary to overcome the pressure drop through the process. While Ref’s [17] and [11] teach that two separate blowers are used, in this instance a single blower is specified, as it is believed that adequate control can be maintained by appropriate use of valves in the two gas lines¹⁸.

¹⁷ According to, for example, Dr. Andrew HOADLEY.

¹⁸ This idea was originally due to Dr. Paul A. WEBLEY.

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Various pumps are also required around the plant in order to overcome pressure drops through equipment on both the process and utility sides.

3.2.4.6 Turbine

The cost of supplying electricity to the blower is a significant operating cost. Given that the process is a net exporter of steam, consideration was given to installing a turbine to run.

One may evaluate the change in enthalpy upon bringing steam saturated at 1200kPa(abs) down to atmospheric pressure in an isentropic manner [19]¹⁹. Taking a hypothetical basis of 1t of steam, from the costs given in Chapter 2 this would, therefore, equate to alternatively an income of \$12 for the steam xor a cost reduction of \$5.26 by supplying energy to the blower directly. With our 'bean counting' hats on we realise the financial folly of such an investment (which would also have to bear the cost of a turbine). However other pertinent issues arise.

For example, there is a perception that electricity supplies in Bontang may be less reliable than Australian process plant workers are accustomed to [8] (despite the fact that Bontang already has a reasonably developed chemical processing infrastructure). For this operability reason it may be better to have a reliable source of electricity, rather than short-sightedly leaping at the superficially more profitable option.

Now the dollar ratio of the two rough calculations carried out may engender some disbelief that it is not simply more economical to run the turbine only in the event of a blackout. Or that it is not more financially sound to run off, say, diesel. To repudiate these beliefs it would be necessary to have more detailed figures available on the frequency and duration of power outages, *et cetera*. There is one more relevant factor to be considered though.

The same quantity of steam, 1t, at 500kPa(abs) would save \$2.50 in electricity costs²⁰. However it is, apparently, unsaleable. Given that the decision has been made to raise steam at this pressure from the waste-heat boiler following the reactor (section 3.1.2), it may be seen (see section 3.5) that the more effective use of this energy is to drive the turbine, rather than to be used for heating.

3.2.4.7 Storage

The definition of the terminal points of the process also required storage tanks to be included. Separate tanks would be required for the two grades of formaldehyde produced during normal operation.

At this point, the flowsheet has begun to take the form of Figure 3-3, below.

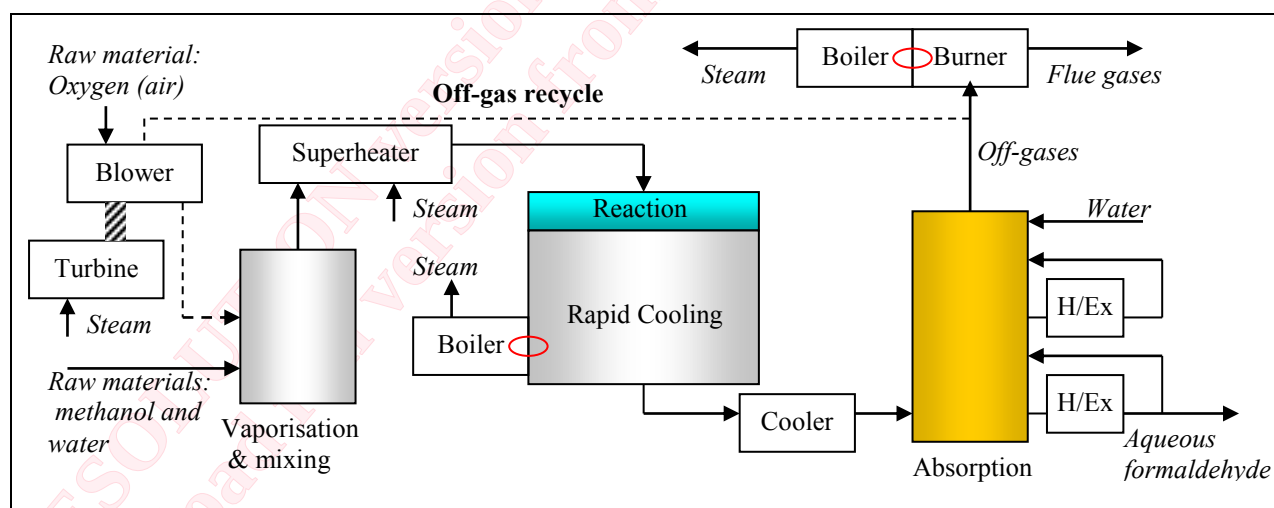


Figure 3-3: A more developed flowsheet. Note: Pumps, boiler feed water, condensate, cooling water omitted. "H/Ex" = Heat Exchanger. Not all stages shown for absorber.

¹⁹ The starting condition is $h_g = 2784 \text{ kJ.kg}^{-1}$, $s_g = 6.523 \text{ kJ.kg}^{-1}.\text{K}^{-1}$, and the end condition $h = 2363 \text{ kJ.kg}^{-1}$ (by linear interpolation) $\Rightarrow \Delta h = 421 \text{ MJ.t}^{-1}$.

²⁰ The starting condition is $h_g = 2749 \text{ kJ.kg}^{-1}$, $s_g = 6.822 \text{ kJ.kg}^{-1}.\text{K}^{-1}$, and the end condition $h = 2475 \text{ kJ.kg}^{-1}$ (by linear interpolation) $\Rightarrow \Delta h = 200 \text{ MJ.t}^{-1}$.

3.3 Separation

The main separation in this process is carried out in the absorber, without the need for a distillation column. This has been discussed in section 3.1.4, page 3-3.

3.4 Recycle

3.4.1 Introduction to recycling philosophy

While the increasing environmental awareness among chemical engineers is unquestionably a great thing, there is a disturbing element of ignorance on some matters. In particular related to ‘buzzwordism’²¹. While no knowledge is no good, a little bit a knowledge can also be dangerous: contrary to popular perception there is no inherent environmental or other advantage to be gained *ipso facto* simply by the act of recycling.

For example, if one considers a process in which 50% conversion is achieved, with half of that conversion being by-products. At least two expensive separations would have to be undertaken, to separate product, by-product and reactant. Then there are the piping or ductwork and pumps or blowers required to return the relevant materials.

And yet, the naïve reader of that process plant’s brochures may view this process – in which around 50% of the materials are recycled – more favourably than a competitor’s process, operating at close to 100% conversion with minimal by-product formation²² – and hence no recycle to speak of.

3.4.2 Recycling as it applies to the current project

Due to the desire to render distillation superfluous, no unreacted methanol is recycled. Instead it all remains as the stabiliser in the final solution²³.

However recycling is an integral component of this project, as the thermally-stabilising effect, which the inerts in the process stream have, allows operation at a lower excess of methanol. At the same time, the mixture remains outside of the flammability limits.

This recycling has been discussed under sections 3.2.1 to 3.2.3 (pages 3-4ff.).

In terms of materials other than the product methanol, there is certainly scope to return the majority of the condensate and recirculated cooling water for reuse. This is subject to the need for blow-down, with any ensuing deficiencies being made up with make-up water.

The pump-arounds on the absorber could possibly also be thought of as recycle streams, though on a more ‘local’ scale. As noted, these were required in order to remove heat. They also ensured that the packing was more easily wetted. (See sections 3.1.4, page 3-3 and 3.2.4.3, page 3-7.)

3.5 Process Integration and Energy Efficiency

3.5.1 Process integration

For this process, the relevant areas in which potential for process integration exists are in terms of heat energy and mechanical or electrical energy.

3.5.1.1 Composite curves

One of the steps²⁴ that was taken to decide where profitable integrations might lie was to construct the ‘composite curves’ of Linnhoff and co-workers [23]. This resulted in the graphs in Figure 3-4 and Figure 3-5 of temperature versus ‘flow enthalpy’ for the sink and source²⁵ streams.

²¹ To coin a new term.

²² Obviously a hypothetical construct for illustrative purposes only.

²³ Assuming that we neglect the vanishingly small quantities passing up out of the absorption tower in the off-gas.

²⁴ Of course, the first step was to construct a preliminary flowsheet, of the sort shown in Figure 3-3, based on guidelines gleaned from the various references – and then perform some mass and energy balances. These are the subject of discussion in later chapters.

²⁵ Source streams being, generally, the hotter.

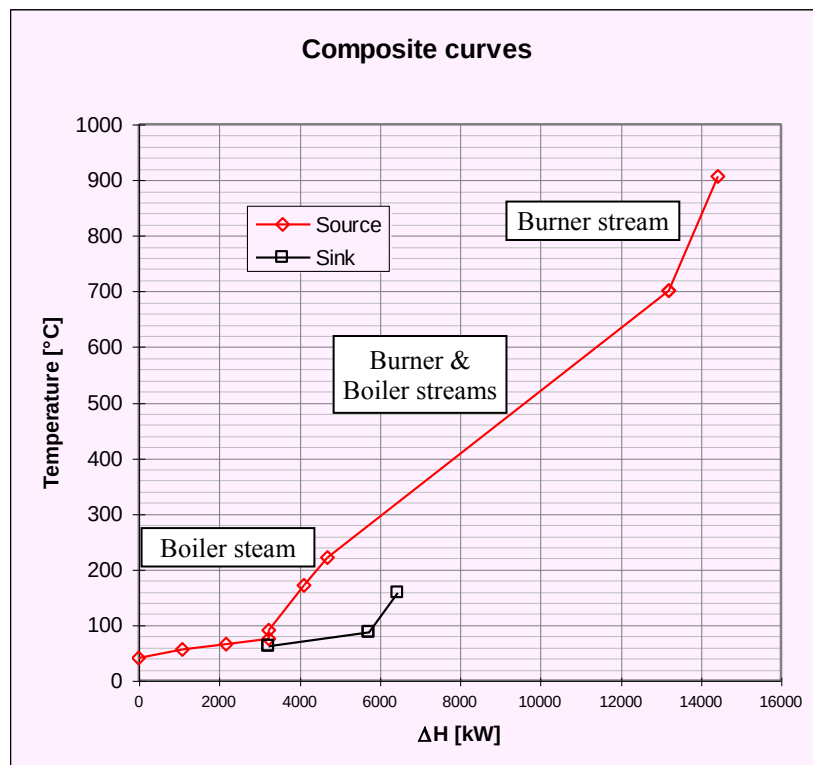


Figure 3-4: Composite curves.

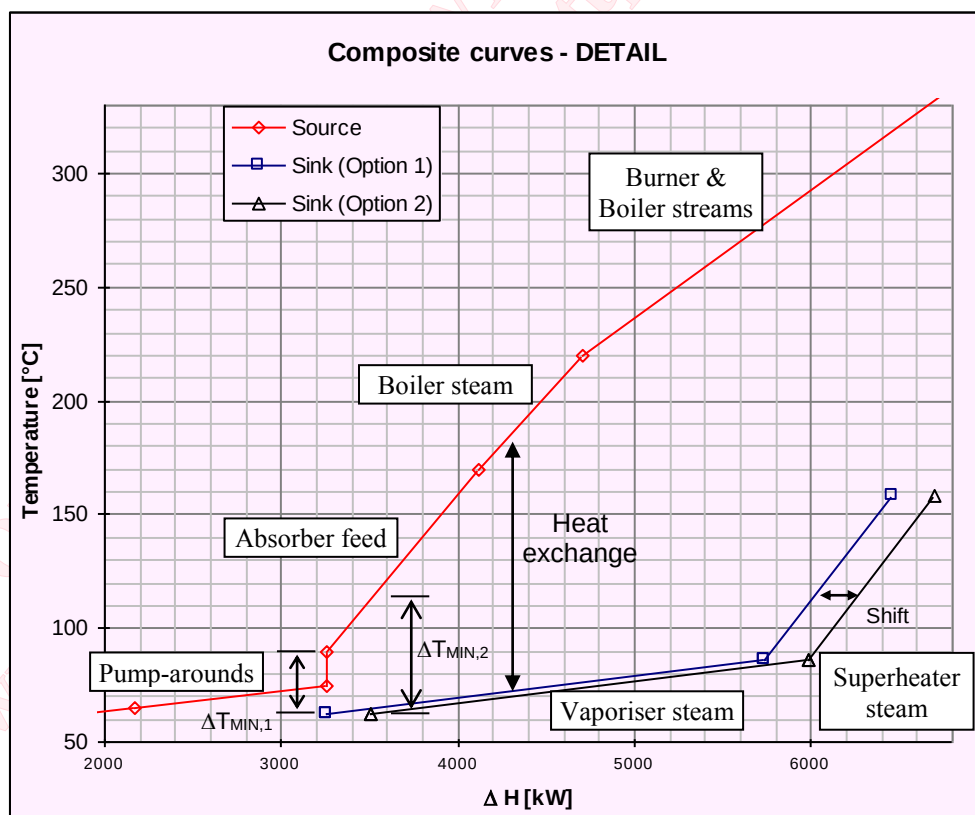


Figure 3-5: Detail of composite curves.

To begin with the curves looked significantly different. Those curves shown are, more or less, the refined version.

The first thing that becomes clear is that the sink curve should be shifted as far to the left as possible in order to use the higher grade heat for raising steam. The nature of this system means that a ‘threshold’ problem is to be considered, in which only cold utilities are required (nett). However, in this case the low temperatures of the source stream at the top of the absorber (*i.e.* the pump-around) mean that the sink curve cannot be shifted far enough left to avoid using cooling utilities on either side of the (process) sink curve.

Initially it was considered advantageous to partially condense the absorber feed before it entered the column, as taught by Ref. [25]. However this meant that the temperature of the absorber feed was of the order of 60°C. Hence the only way that the cooler on the absorber feed line could be integrated with the vaporiser would be to use one exchanger between those two streams, with two additional exchangers to further cool the absorber feed and further heat the vaporiser stream. Thus this option was not attractive.

A further reason not to partially condense the absorber feed²⁶ is found in Ref. [13], wherein it is stated that such an operation will likely lead to paraformaldehyde forming on the heat transfer surface.

Therefore the temperature of the absorber feed was adjusted upward to 90°C. A higher temperature was not selected, in order to avoid excessive cooling duty in the absorber pump-arounds.

The minimum temperature of approach was set higher than 10°C, at almost 30°C, because the source transfer fluid is a gas.

It was also found that the off-gases exiting the absorber should be ‘reasonably cool’ (preferably below 50°C). While this does have some beneficial effect on the equilibrium of absorbing formaldehyde, the main reason is to keep the saturation water content of the gas low.

3.5.2 Start-up issues

On start-up the plant will be cold. Thus any process-to-process heat transfer will have to be supplemented by a heating utility on start-up. A separate cooling utility is not required. This is most easily accomplished by the following:

- An ability to raise the desired amount of 1200kPa(abs) steam from the burner by combustion of natural gas. Any 500kPa(abs) steam that is then required may be obtained by letting this steam down in pressure.
- The design heating of the vaporiser and superheater lines should each have one contribution from an independent utility, namely steam. In this way, when process–process heat transfer is inoperable (*i.e.* on start-up), the utility can take over the full duty in an existing exchanger.

Relevant start-up schemes are described in Ref’s [11] and [13].

3.5.3 Other issues

As noted, the steam generated from the waste-heat boiler was specified as saturated at 500kPa(abs), in order to avoid any product quality problems. The steam generated in the burner was set at 1200kPa(abs), because this was the export pressure.

An attempt to produce high pressure steam in the burner, pass this through the turbine (attached to the blower), and then come out at 1200kPa(abs) failed. Even for steam entering at 5960kPa(abs) and 482°C [6] there was insufficient power obtained from the turbine to drive the blower. On top of this are the extra costs and hazards associated with high pressure steam.

The 500kPa(abs) that is produced is too low to heat anything other than (some of) the vaporiser loop, and it cannot be exported. However it is just the right quantity to run the turbine. It should be noted that Ref. [6] also states that, for turbines that are running, “erosion corrosion is pretty much confined to units that are operating on saturated steam with inadequate boiler-water treatment.”²⁷ As we will be using demineralised water for make-up, this should not be a problem.

A requirement also exists to ensure that formaldehyde-containing solutions are not cooled to too low a temperature, at which paraformaldehyde may be precipitated.

²⁶ Apart from the dogmatic advice of Dr. Andrew HOADLEY.

²⁷ Emphasis added.

3.6 Economic, Safety and Environmental Considerations

3.6.1 Economic factors

The primary economic issue considered was whether or not to include a distillation column, and complementary anion-exchange unit. While it was relatively easy to find the advantages of omitting these items in terms of costs, the disadvantages that might arise were not so apparent. However it was judged that these would be minor.

As discussed, savings can be made with some heat integration of the process. However, heat integration was only considered in case in which the number of heat exchangers would not be increased excessively.

Along with heat integration, some power integration was incorporated, with a steam turbine used to drive the blower. Although the turbine may have appeared an uncertain proposition on purely monetary terms, the advantage of having a secure supply of power was the determining factor.

Probably the major saving is in the use of the large quantity of steam that is raised in our process. This may be considered the recovery and reuse of waste heat.

Another saving was made in combining the recycle and fresh air streams so as to be able to pass them through a single blower. It is believed that adequate control will still be possible through the use of appropriate control valves.

Similarly, the absorption duty was combined into a single column.

The height of the absorption column will determine how much of the formaldehyde (and methanol) are recovered in the liquid product stream. Increasing the height of the tower will have a capital cost penalty, but allows for higher efficiency of operation in terms of yields. If we assume that the burner is always on-line when needed, then environmental penalties for excessive releases of formaldehyde are not a major consideration, although lower quantities are inherently safer. The height of the column, implied by a specified absorption 'duty', is not decided at this stage. However, initially, it is to be selected based on reported industrial practice.

Due to the turn-down requirement for an ability to operate at 60% of the design flows, and due to the importance of contact time on the reaction, it was considered necessary to operate two reactors. The ratio of capacities would be 60:40. Although this will be a more expensive option in terms of initial capital expenditure, it is essentially a prerequisite in this case. There will also be some operability benefits: if one reactor is off-line for maintenance or other reasons then that still leaves one reactor operational.

3.6.2 Safety factors

Both methanol and formaldehyde are flammable, as is the hydrogen that is produced (section 3.1.1.2, page 3-1).

The ability to operate without a distillation column is predicated on feeding a minimal excess of methanol to the reactor. Given that this process operates on the rich side of the flammability limits, this is only possible if inerts are added to the feed, because clearly a certain amount of oxygen is required for the reaction.

Addition of water is effective in this regard, but has the disadvantage of diluting the product, and so it cannot be used on its own. Therefore the oxygen-lean off-gases from the absorber are recycled and combined with the reactor feed stream. A ratio of flows is selected to operate at a safe margin outside of the flammability envelope (see e.g. Ref. [14]).

Flame speed data [5], [12] indicate that the maximum burning velocity of methanol is under 0.5m.s^{-1} , which is much lower than the design gas flowrate. As a consequence, provided the reactant mixture is flowing at around the design flowrate, the reaction will be contained at the catalyst surface. Nevertheless it was thought prudent to include a flame trap on the line between the reactor and the superheater to minimise the hazards of flashback. This is particularly important when there is no forward flow of reactant gases, such as occurs under shut-down and start-up conditions.

Elsewhere in the process, flammable mixtures are avoided by the virtue of the low oxygen availability.

It has been stated that the lower liquid hold-up of packed beds in the absorber is one advantage, because of the reduction in inventory in that vessel. While trays may be used at the top of the column, this is less important, as solutions will be much more dilute there.

Other issues, such as locating the burner away from methanol stores, are not considered at the flowsheet development stage.

3.6.3 Environmental factors

Formaldehyde is a suspected carcinogen, which demands that care be taken to minimise emissions and exposure.

It has been mentioned that the absorber will be designed to remove the majority of the formaldehyde, which is inherently better in environmental terms. However, in any case, the off-gases that are to be released first undergo combustion in a burner–waste heat boiler. This is expected to deliver almost complete oxidation of the formaldehyde to mostly carbon dioxide (CO₂), with some amount of carbon monoxide (CO) formed, along with water (H₂O).

Thus, all gaseous emissions²⁸ will be within world guideline values (see e.g. Ref. [17]).

There will be only very limited quantities of liquid waste generated during normal operation. Product material from start-up that is slightly out of the specified ranges can be stored in a separate tanks and gradually blended in with product produced after steady operation is realised.

Blow-down from boilers and the cooling water circuit should contain negligible levels of formaldehyde, and can be directed to trade waste.

Low concentrations of formaldehyde may be discharged with wastewaters, as formaldehyde is readily degraded by bacteria (e.g. *Escherichia coli*, *Pseudomonas fluorescens*) in non-sterile, natural water to form carbon dioxide and water.

Solid waste is desirably very small. In particular the valuable silver catalyst will be regenerated. Small quantities of waste from filters and the like do not pose an especial risk, and can be disposed of as normal.

Again, although issues such as providing for detection of leaks and operator education are important, they are not considered during development of the flowsheet.

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²⁸ This would include fumes from handling areas (e.g. loading zones), relief valves and venting of process equipment.

²⁹ The author wishes to acknowledge Miss. Michelle HILL and Miss. Jayne BORENSZTAJN for kindly providing this information.

³⁰ This reference due to Dr. David J. BRENNAN.

³¹ This reference due to Dr. David J. BRENNAN.

Chapter 3: Process Synthesis and Flowsheet Development

Formaldehyde

- should be “well-mixed.” Also that it was common for some silver processes to run with two absorption columns, because, having lower volumetric gas flows than metal oxide type processes, “they can afford to do it.”
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³² The author wishes to acknowledge Mr. Adrian DIXON for kindly providing access to this reference.

³³ This reference due to Dr. David J. BRENNAN.

³⁴ This reference kindly made available by Mrs. Hsu-San WARE.

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4 PROCESS FLOWSHEET

4.1 Exhortation

The development of the process flowsheet has been examined in great detail in the preceding chapter. The reader is exhorted to not read any further without having read Chapter 3!

This chapter describes the process that was finally arrived at, without further justification of the major unit operations selected. However some discussion on process variables such as temperature and flowrate is entered into, as well as insertion of minor equipment items.

While reading this chapter, please look to the first drawing in the Drawing Annex (preceding the Appendices), entitled, "Formaldehyde Plant Process Flow Diagram."

4.2 Process Flowsheet Description

4.2.1 Reactor feed system – Part 1

At the front end of the process, methanol, air, recirculated off-gases and water are fed into the vaporiser unit. This comprises:

- the "Methanol Feed Vaporiser," HX-1,
 - the "Liquid Recirculation Pump," P-2,
- and a heat exchange duty split between two exchangers:
- HX-5, the "Reactor Effluent Cooler"
- followed by
- HX-10, the "Vaporiser Recycle Heater."

4.2.1.1 Heat exchange

As discussed in Chapter 3, the configuration chosen was a packed bed over which a large flow of heated aqueous methanol flows. A lesser amount then vaporises in the gas stream flowing counter-currently, achieving good mixing. Conceptually one may equate the small specific sensible heating duty over a large flow to the large specific latent heating duty spread over the lesser flow.

A demister then knocks out any liquid droplets.

Thus we see that no (indirect) heat exchange takes place in HX-1.

It is clear from the description of HX-5 that the primary function of this heat exchanger is to cool down the stream exiting the reactor. To be more precise, the stream exiting the waste-heat boiler integral with the catalytic reactor bed. Given that the reactor process gases are already flowing orthogonally to the catalytic bed, it is commonsense to assume that the reactor effluent will flow on the tube side¹.

As the (equivalent) vaporising duty cannot be achieved exclusively by heat transfer in HX-5, HX-10 is installed following. This is heated by 1200kPa(abs) steam generated in the "Tail Gas Burner," RXN-1. The reason for installing the exchangers in this order is evident from the composite curve construction of Chapter 3. Its presence makes an allowance for the reduced transfer in HX-5 on start-up².

4.2.1.2 Liquid flow

Just as P-2 is required to build up head in stream 10 in order to pass through HX-5 and HX-10, the methanol must be increased in pressure to match that at which the vaporiser is run³.

It is reasonable to assume that methanol supply will be intermittent⁴ [2]. Thus the methanol (supplied by pipeline [1], exiting at just above atmospheric) will be stored in ST-1, which will have a capacity equivalent to 3

¹ I.e. through the tubes.

² It would not be feasible to pass steam through the tube side of HX-5 on start-up, and then switch back to the reactor effluent once steady-state operation was established.

³ In turn, the vaporiser pressure specified is consequent on the exit pressure of the combusted tail-gas (stream 40) – being namely atmospheric – at the 'back end' of the process and the pressure drops specified on the units that the process fluid must flow through.

Chapter 4: Process Flowsheet

Formaldehyde

days usage at design flowrates. Higher capacities are precluded by the hazards associated with increased inventories of flammables, as well as the increased cost.

It may be assumed that this storage tank always has some head of methanol, conservatively taken at 110kPa(abs), whereas stream 6 is at 185kPa(abs).

The water is available at 400kPa(abs), which is more than enough to enter HX-1. For this reason a pressure let-down valve, V-1, is shown on the Process Flow Diagram (see Drawing Annex).

The ratio of water flow to methanol flow may be estimated from Ref. [13]. However the final value is derived from the mass balance, where attention is paid to the need to maintain a minimum liquid flow in the absorber (ABS-1) while avoiding excessive dilution of the product stream.

In fact there is some cause to consider the need to have water feed at all. The main advantage would appear to be the reduction in flammability of the mixture.

4.2.1.3 Gas flow

The air and recycled off-gas streams join at a tee and both are raised in pressure from atmospheric by a blower, CP-1. The blower is driven by a steam turbine, TRB-1.

The ratio of these two streams is a complicated mixture of factors: mass and energy balances, as well as guidelines on desirable ratios between the feed methanol [7].

4.2.1.3.1 Flammability

Another key criterion is the flammability of the mixture. Representative flammability envelopes for a waste-gas recycle process are shown in Figure 4-1 below.

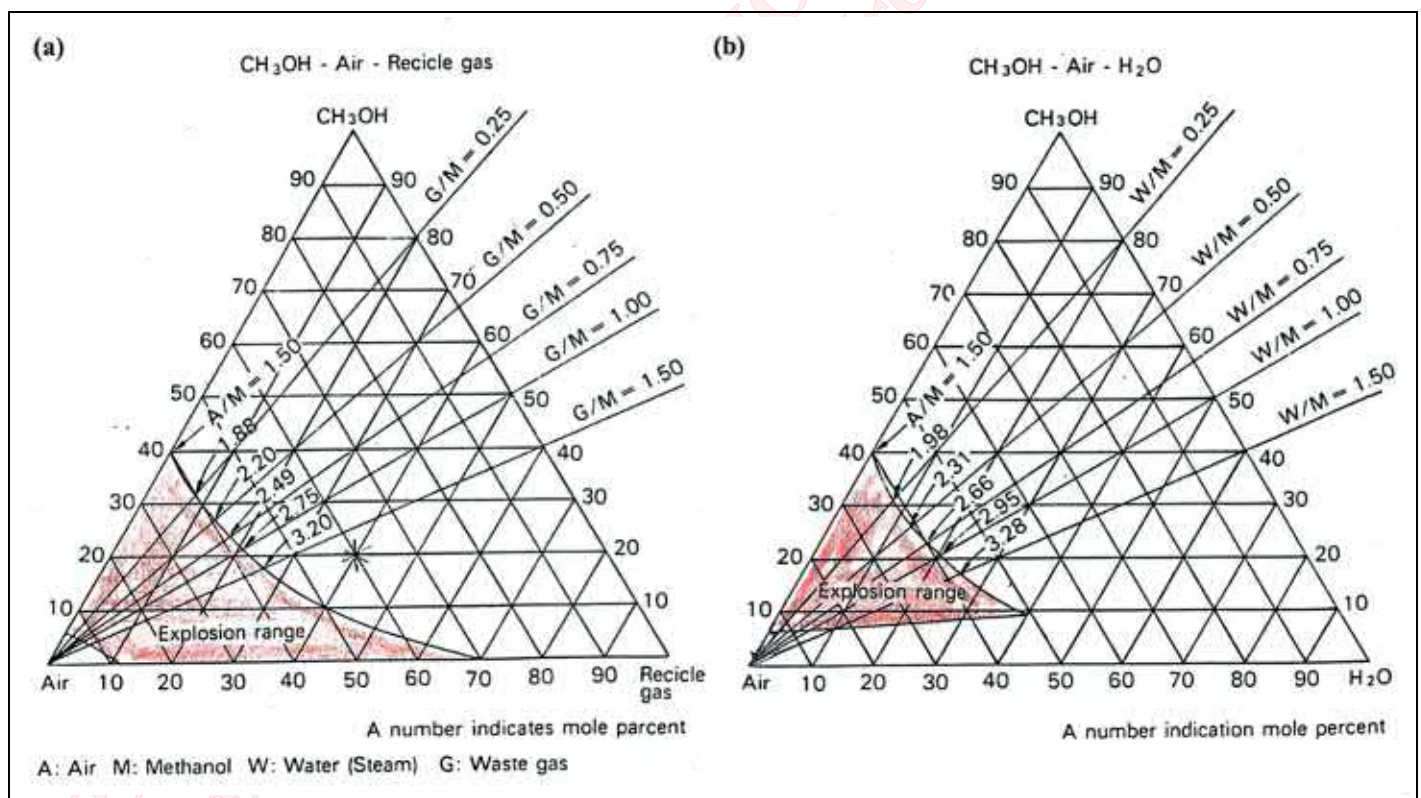


Figure 4-1: (a) Explosion limits for the Methanol –Air–Recycle-gas system; (b) Explosion limits for the Methanol –Air–Water system. [9]

⁴ Or, at least, 'occasionally intermittent'! That is, although the methanol may even be sourced from within the Bontang complex, it is nice to not be at the mercy of another plant's down-time and the vagaries of the policies of another company.

When the methanol is fed from storage it is not flammable as long seal integrity is maintained so that oxygen ingress is not possible. Once the methanol (and water) enters the vaporiser oxygen is present in the incoming fresh air. This would ordinarily be flammable at the ratio of methanol to oxygen specified (with the lower excess of methanol required to operate without a distillation column). However the addition of the oxygen-lean off-gas keeps the point of operation outside of the flammability envelope. This is marked on Figure 4-1.

It is difficult to discover how well the additional complication of the presence of hydrogen in the recycled off-gas affects the flammability of the mixture in the vaporiser, and in the reactor feed. However an independent calculation based on Le Chatelier's Rule may be carried out along the lines of:

$$L_{mixture} = \{ \sum (v_i / L_i) \}^{-1},$$

where L is alternatively the lower explosive limit (lel), or upper explosive limit (uel), v is the volume (*i.e.* mole) fraction of the flammable constituents only, and subscript i is the summation index, being taken over all of the flammable components [11].

Given that the upper flammability limit of hydrogen may be taken as 76% at atmospheric pressure and 20°C [6], while that of methanol may be 36% [4] or 44% [5]⁵ (all by mole). Methanol is present at a mole fraction of around 0.18, with hydrogen approximately 0.06. This gives a value for the mixture of 24% flammables on a mole (*i.e.* volume) basis. Hence the uel of the mixture is around 47% (by mole).

If the mixture were in air then it would indeed be explosive. However the mixture is enriched in nitrogen and water: By stoichiometry⁶ the above mixture would require 28% (pure) oxygen for complete combustion, on a molar basis. The actual oxygen content has been arranged to be 7.7% by mole, and so the mixture should not be flammable – at least not at the moderate temperatures outside of the catalyst bed.⁷

4.2.1.4 Filtering

Due to the sensitivity of the catalyst to impurities, which has necessitated the use of stainless steel in the plant, filters have been installed on all of the feed streams. That for the water is not shown, as demineralised water has been specified, and therefore purification takes place outside of the battery limits of the plant⁸.

4.2.2 Reactor feed system – Part 1

4.2.2.1 Further heat exchange

Once the well-mixed vapour stream containing oxygen, formaldehyde and several other chemicals has passed out of the vaporiser, HX-1, it is superheated in HX-2. This is a steam-heated exchanger operating at 1200kPa(abs) on the shell side.

4.2.2.2 Flame trap

A flame trap, FT-1, is installed on the reactor feed line as a relatively cheap means of further reducing the risk of explosive combustion in the reactor. The aim is to contain any such accident so that it does not flash back to the significant⁹ methanol inventory in the vaporiser, HX-1.

The mechanism of this device is discussed in *e.g.* Ref. [6]: “explosions cannot occur in spaces occupied by packing material,” such as Raschig rings, capillaries or parallel plates.

4.2.3 Reaction system

4.2.3.1 Reactor unit

The reactor system consists of the catalyst bed integral with a waste-heat boiler. The catalyst bed is very shallow, and contains silver crystals with certain size distributions. Due to the turndown requirement (see

⁵ This was the only reference found quoting the higher figure. All other references quoted 36% by mole, 36.5% by mole *et cetera*.

⁶ $\text{CH}_3\text{OH}(\text{g}) + 1.5 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$ and $\text{H}_2(\text{g}) + 0.5\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$.

⁷ Further information on the relationship of methanol and hydrogen flammability with temperature is presented in Ref's [3] and [8] (respectively).

⁸ And outside of the scope of treatment of this report!

⁹ Although the inventory would be less than for a kettle-type reboiler, which would also have methanol at a higher concentration.

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Chapter 2) and the importance of space velocity¹⁰ through the bed [7] two parallel paths were specified. The first combination of RXN-1 and HX-4 handle 40% of the design flow, while the second stream (60% of the design flow) passes through RXN-2 and HX-3.

Both are cooled to 170°C, being approximately 20°C above the saturation temperature of the 500kPa(abs) steam.

4.2.3.2 Steam system

The steam is generated from water fed from a steam drum (D-1 and D-2). This comes in at the saturation temperature and is vaporised. However OLBRICH indicates that the flow immediately exiting the boiler will not be a saturated vapour by any means, but will be in the two-phase region¹¹. Thus this two-phase mixture passes through a steam drum in which any liquid water is captured, with only the vapour passing out into the steam distribution pipework. As noted above, this 500kPa(abs) steam is used to run the turbine (TRB-1) that drives the compressor (CP-1). On start-up it would be possible to supply steam generated in the burner (RXN-3)¹², suitably let down in pressure.

The boiler feed water (streams 100 and 106) is assumed to come from recycled condensate that has undergone purification as needed. Thus the temperature is taken as 100°C.

4.2.4 Absorption**4.2.4.1 The column**

Absorption takes place in a single column, ABS-1. This consists of four stages: stages 1 to 3 at the base of the column are packed, while the top half of the column has trays.

This enables high liquid flowrates, high cooling duties and large amounts of mass transfer to occur in the bottom half of the column, while at the top the saturation vapour pressure is lowered so that removal down to ppm levels is plausible.

4.2.4.2 The rest

Demineralised water is available at 400kPa(abs). However the height of the column means that a pump is required to attain the necessary head. This is P-10 in the Process Flow Diagram (Drawing Annex).

There are three pump-arounds corresponding to the three packed sections of the absorber. Each of these is cooled to remove the heat of absorption¹³: units HX-8, HX-7 and HX-6 going up the column. Pressure drops across these exchangers necessitates centrifugal pumping to keep the inlet and outlet pressures of the column similar. This job is done by pumps P-4, P-6 and P-7 (corresponding to the three heat exchangers listed).

After being cooled from 75°C to 60°C with the recirculation flow around the bottom stage (stage 1), the product stream (stream 25) is then drawn off. This flow is set by the design requirements of Chapter 2: 2.646kg.s⁻¹ of aqueous 54%(kg.kg⁻¹) formaldehyde solution

An energy balance¹⁴ on the trayed section (stage 4) reveals that cooling is required to obtain maximum levels of formaldehyde recovery from the exiting gas stream. For this reason 'serpentine' cooling coils are installed on each tray. As for the demineralised water, the recirculated cooling water must undergo an increase in pressure to reach the top of the column. Pump P-8 is responsible for this task.

4.2.5 Tail-gas treatment**4.2.5.1 Burner**

In the "Tail Gas Burner," RXN-3, the off-gas that is to be 'purged' from the system undergoes almost complete combustion to remove traces of formaldehyde before release to the atmosphere, and to liberate the heat associated with the hydrogen gas present in the stream (stream 39).

¹⁰ Ref. [13] was unique in that "The silver catalyst was characterised by the fact that large variations in gas speed had little effect on the reaction at constant mixture compositions in spite of apparently large temperature differences at the catalyst." However FARRAR also indicated the system was robust in terms of handling turndown [2].

¹¹ And LEHRER suggests a vapour fraction of less than one half for thermosyphon reboilers [10]!

¹² Running on natural gas.

¹³ Equivalently: the heat of condensation plus the heat of dissolution.

¹⁴ Refer to the Detailed Design of the Absorber in Chapter 7.

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Release of the combusted off-gas is then through a stack at a high level (likely to be attached to the absorber support structure).

As noted, the remainder of the off-gas is recycled (stream 38) back to the vaporiser (HX-1) by way of the blower (CP-1).

4.2.5.2 Steam system

Boiler feed water is assumed available at 100°C and 400kPa(abs) from condensate return. This is then pumped up to 1240kPa(abs)¹⁵ by unit P-5, followed by increase of the temperature up to that of the saturated liquid in an economiser, HX-9.

In fact this “Economiser” is simply a series of coils in the burner enclosure which the boiler feed water passes through prior to reaching the steam drum, D-3. The economiser is usually located at the hottest position because the lower temperature of its contents implies a reduction in the tube wall temperature, meaning that materials of construction costs are minimised [12].

Saturated liquid water at 1200kPa(abs) then flows from the base of the steam drum, D-3, to the boiler section of unit RXN-3 where steam is generated. This passes back through D-3 before entering the distribution system.

In the distribution system the steam is diverted in three directions, with flows of similar magnitudes:

- to the “Methanol Superheater,” HX-2;
- to the “Vaporiser Recycle Heater,” HX-10;
- and the remainder to neighbouring plants within the complex.

4.2.6 Storage

There are two grades of formaldehyde produced: the “54/1” Grade A and the “37/7” Grade B (see Chapter 2). Each of these will clearly require separate storage. Thus the two main items in the ‘tank farm’ are ST-5 and ST-3 for Grades A and B, respectively.

These tanks must be heated and kept agitated in order to ensure there is minimal deposition of paraformaldehyde. From ST-3 and ST-5 the formaldehyde product goes to the customer, being the terminal point of this project.

However the additional requirement to manufacture Grade B formaldehyde which is more dilute in formaldehyde, but with a higher methanol mass fraction, means that a buffer tank is required to add the extra water and methanol (streams 41 and 48). This is item ST-2.

A buffer tank is also provided before ST-5. This makes use of the second function of buffer tank ST-2, which is to act as an aid to quality control. The buffer tanks provide a significant residence time which prevents all of the product stream from immediately entering the main storage tanks.

The benefit of this is realised in the event that the product streams (streams 43 and 44) go out of specification. Without the buffer tanks this poor quality material would enter the main storage straight away, possibly causing the entire contents to be corrupted and lost. However with a regular sampling regime in place such deviations out of specification could be detected in time to minimise the risk of contaminating the main storage inventory.

In that instance the poor quality product could be diverted to a third storage tank temporarily, while the process was either adjusted or shut-down, as appropriate. The material in this third storage tank may have to be disposed of, but it is hoped that it could be blended in with the high quality product over a period of several days – rather than a few hours, if it had not been diverted. This third storage tank, and other ‘spare’ tanks, are not shown on the Process Flow Diagram because they are not considered to be a part of normal operation.

4.3 References

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3. P. DAVIES, R. T. DONALD and N. H. HARBORD; “Catalytic Oxidations,” in: Martyn V. TWIGG (Ed.); Catalyst Handbook, 2nd edition; Wolfe Publishing; London; 1989.¹⁶

¹⁵ This includes an allowance for pressure drop in HX-9 and RXN-3.

¹⁶ This reference due to Dr. David J. BRENNAN.

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¹⁷ This reference due to Dr. David J. BRENNAN.

5 MASS AND ENERGY BALANCES & PROCESS SIMULATION

5.1 The Importance of Mass and Energy Balances

Mass and energy balances play a pivotal role in the development of a process design. While it is all well and good to propose to produce certain quantities of ‘stuff’ by feeding in certain quantities of ‘other stuff’, it is even nicer to know that the proposal is physically possible. Therein lies the importance of performing self-consistent mass and energy balances.

5.2 Mass Balances

5.2.1 Development

5.2.1.1 On the problem of reaction mechanisms, or, How come we don’t know much?

The relevant reactions have been given in Chapter 3. However we also realise that very little is known – on a fundamental level – about the reaction mechanisms in the production of formaldehyde from methanol. At this point it is instructive to quote some relevant comments from the references.

“Much attention is being paid to the oxidation of methanol on silver [citing references from 1941 to 1961¹], but many aspects of the process are still unclear. Almost all researchers have studied the reaction in the temperature region below the industrial temperatures [...]. No indications of the system of the process under industrial conditions are cited [in the references given].” [4]

While this reference did give a couple of data points up to 920K (647°C), this is only just approaching the temperature at which our reactor is designed to be operated – namely 700°C.²

If the mechanism were simple then this would not be a problem. However, “the kinetic principles of the process are different in the regions of high and low temperature.” [4] While the other main reactions are essentially irreversible, the tendency towards dehydrogenation “increases rapidly with rising temperature.” [8]

To emphasise that equilibrium data cannot be used exclusively (which would result in a much simpler calculation procedure):

There is a “danger of arguing from chemical-equilibrium data without taking the physical conditions into account. Endothermic reactions, unlike the exothermic kind, can proceed only at a rate, and to an extent, dictated by the heat supplied.” [8]

Again, some progress could be made at this point if the relative proportion in which the endothermic dehydrogenation (and accompanying combustion of hydrogen) and the exothermic oxidation reactions (see below) occur:

1. $\text{CH}_3\text{OH}(\text{g}) + 0.5 \text{O}_2(\text{g}) \rightarrow \text{HCHO}(\text{g}) + \text{H}_2\text{O}(\text{g})$ $\Delta\text{H} = -159\text{kJ}\cdot\text{mol}^{-1}$ (oxidation)
2. $\text{CH}_3\text{OH}(\text{g}) = \text{HCHO}(\text{g}) + \text{H}_2(\text{g})$ $\Delta\text{H} = +84\text{kJ}\cdot\text{mol}^{-1}$ (dehydrogenation)
3. $\text{H}_2(\text{g}) + 0.5\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$ $\Delta\text{H} = -243\text{kJ}\cdot\text{mol}^{-1}$

One of the first ports of call was Ref. [2], which gave a table showing, or claiming to show, a typical mass balance. The data presented there could be ‘regressed’ to fit extents of the various reactions. The finding of this calculation was that reactions 1. and 2. occur roughly in the ratio of 1:1³, with around 20 to 25% conversion⁴ of

¹ It is the considered opinion of the author that because the reaction to produce formaldehyde from methanol over a silver catalyst is a relatively old technology, new research in this area has been diminished in quantity in favour of newer, ‘trendier’ technologies. Further, a mammoth store of proprietary (empirical) knowledge remains ‘in-house’ with the major commercial producers.

² There is also some concern over the temperature recorded, as a profile exists in the catalyst bed. Ref. [4], for example, claims to have measured the “maximum temperature in the reaction zone” – though this is not the catalyst surface temperature.

³ Consistent with the statement made in the body of that text.

⁴ In fact the ratios varied depending on how the regression was performed. For example the following results have been obtained by various colleagues (to whom thanks are expressed), based on the data in Ref. [2] only:

Worker	Result for the ratio of reaction 2. to 1.	Result of the proportion of H ₂ reacted
Miss. Jayne BORENSZTAJN	50:50 (= 1:1)	~20 to 25%
Mr. Saiful ZAINAL ABIDIN	~60:38 (= 1.58:1)	(25%?)
Mr. Michael WHITEMAN	47.5:47.5 (= 1:1)	25%
WHITEMAN and VERRELLI	~55:46 (= 0.84:1)	23%

the hydrogen (reaction 3.). The major problem with this was that it was for a distillative silver catalyst process⁵, which was producing formaldehyde at only 37%(kg.kg⁻¹), though intriguingly with a methanol content of only 0.5%(kg.kg⁻¹).

Further darkness was shed on the subject by Ref. [1]:

“The conversion of methanol to formaldehyde has been the subject of a number of papers, but to this date the process has not been studied thoroughly. The problem of the mechanism has been discussed from three viewpoints. Some authors [3 references from 1935 to 1958] believe that the primary reaction is the endothermic decomposition of methanol into hydrogen and formaldehyde, the heat required for this reaction being supplied by the exothermic oxidation of hydrogen (secondary process). On the other hand, the investigations of Vladovets and Pshezhetskii [1951] confirmed the view that the formation of formaldehyde is a direct oxidation of methanol with oxygen. [Their experiments were carried out temperatures] not in excess of 450–500°C. Some authors [1952 & 1961] have combined the two viewpoints and regard oxidation and dehydrogenation as equally important [...].”⁶

There is also a suggestion that the reaction may change from kinetic control to diffusion control above 600°C.

From the various opinions given in the literature (see References, section 5.5, page 5-11), the author decided that while a 50:50 ratio between the two main reactions may be relevant for lower-temperature silver catalyst processes, at the elevated temperature chosen (700°C), the dehydrogenation reaction would be likely to become more dominant (*e.g.* Ref. [18]). Therefore a ratio of approximately 60:40 was selected for reactions 2. and 1., respectively.

5.2.1.2 That’s one small step for a man....

The author decided that the best way to start a mass balance would be to take a mass balance over the entire plant, because in this way information about the recycle streams would not have to be assumed.

Initially the model was simple, assuming that only the oxidation and dehydrogenation reactions occurred, and in the ratio of 1:1, with all of the condensables recovered in the absorber except for 10% of the water. These assumptions essentially followed Ref. [2].

This was performed using a spreadsheet program, and allowed back-calculation of a required feed for given reactor specifications (including a 98.5% consumption of the oxygen fed), given absorber operating characteristics and the known product requirements. Thus six chemical species (including nitrogen) and three simplified streams were considered: “Fresh feed,” “Off-gas” and “Product.”

5.2.1.3 The development continues

The next step was to incorporate more of the relevant side reactions, as well as adjusting the extents of reaction for each, as described in section 5.2.1.1. The presentation of the reactions was also made more explicit, due to the increased complexity, and showed exactly how much of each species was consumed in a given reaction.

The other major development from the preliminary stage was the inclusion of some recycle flows. Now the reader will be aware that a non-distillative, off-gas recycle process was selected. However at the time that this mass balance was being computed discussion was still on-going within the group as to which of the two recycling processes were better (judging that they were both better than a distillative process).

SMITH [17] presents two different extremes in the way of possible approaches to process flowsheet design:

- “Building an irreducible structure.” This involves following the logic of the “onion model” (briefly described in Chapter 3), starting with the specification of key units in the process and working ‘outwards’ to the ancillaries and utilities. The first specifications must therefore be made from prior experience (either of the designer themselves or extracted from the literature) which suggests to the designer what the effects of certain specification of the central unit operations will have on the supporting equipment items. In some cases several designs may be taken to completion if a decision cannot be made at an earlier stage. The problems with this strategy lie in the impossibility of making exact predictions and the impracticality of evaluating every possible permutation.

and

⁵ Presumably operating at a lower temperature than our process.

⁶ Emphasis added.

- “Creating and optimising a reducible structure.” This involves the creation of a ‘superstructure’ or ‘hyperstructure’ that has embedded within it all of the feasible operations and interconnections. The decisions as to which of these operations and interconnections will remain in the final design is made by expressing the superstructure mathematically using design equations, and then optimising it using standard reduction techniques.

There are two main disadvantages of this process⁷. A compromise must be reached in terms of the number of options initially included: increasing this will increase the likelihood of the optimal structure being contained somewhere within the hyperstructure, but will also increase the complexity of the problem. Also, the many intangibles of design, such as safety and layout are difficult to express mathematically.⁸ For example if the composite curve method had been used exclusively to optimise the heat exchanger network, then the process may have been difficult to start up.

Usually a combination of the two is used in practice.

Given that only two options (the two types of recycle) were to be evaluated, the author decided to attempt to model a ‘reducible’ process in which both a dilute liquid stream and a portion of the off-gases were recycled, with the two parameters representing the proportions of each stream that was recycled. The hope was that optimisation would result in one of the recycle flows (or even both!) being set to zero.

Unfortunately this task was beyond the capabilities of the author in the time available, and so the arguments presented in Chapter 3 were ultimately used to select the off-gas recycle process.

5.2.1.4 Land ho!

The big breakthrough came when a flashback from Ref. [7] struck. Once the “iterate” option in the spreadsheet program was selected, the problem of either creating circular references xor creating practically insoluble optimisation problems (in order to satisfy every component mass balance) was resolved!

With the spreadsheet now working perfectly, and to a surplus number of significant figures, the time was ripe to adjust the reaction scheme parameters in order to satisfy the following guidelines and constraints:

- the product stream must be at 2.6455kg.s^{-1} , with mass fractions of 0.540 formaldehyde (HCHO), 0.010 methanol (CH_3OH), approximately 0.0002 formic acid (HCOOH) and the remainder water (H_2O) – from the problem statement (see Chapter 2) and Ref. [6].
- the off-gas should contain mole fractions of from 0.0025 to 0.010 carbon monoxide (CO), 0.035 to 0.10 carbon dioxide (CO_2), 0.10 to 0.25 H_2 , 0.0002 to 0.001 HCHO and “substantial amounts of nitrogen [N_2] and small amounts of steam, methanol vapour, argon and other rare gases” [6].
- The oxygen consumption in the reactor was initially specified as 98.5% of the fresh feed (after Ref. [2]). This was later increased to 99.5% of the oxygen fed to the reactor [3].
- The conversion of methanol is between 97 and 98% [14].
- The yield of formaldehyde production from methanol is from 89.5 to 90.5% (by mole) [14]⁹.
- The ratio of recycled off-gas to fresh methanol feed will be from 90 to 180% by mass, “preferably” from 105 to 158% [14].
- The water content of the off-gases leaving the absorber, ABS-1, must be essentially saturated, due to the intimate contact and extended contact time. Water vapour will not be removed by demisters or filters¹⁰.

There are a number of points to be made with regard to the preceding... points:

- While it is physically self-evident that not all of the formaldehyde and methanol can be removed from the gas stream in the absorber (ABS-1), the figures above demonstrate that the concentrations become very small. So while, for example, the formaldehyde concentration at the levels quoted may be important on an environmental level, say, it is negligible in the context of an overall mass balance. Therefore the mass balance computed here assumes zero formaldehyde and methanol in the off-gas exiting ABS-1. The precise figures are left to calculation as part of the detailed design assignments (see Chapter 7), but have turned out to be small enough to be recorded as simply “trace” on the stream table accompanying the Process Flow Diagram (stored in the Drawing Annex) discussed in Chapter 4.
- While argon makes up almost 1% of air (by mole) conventional engineering practice treats argon as nitrogen for the purposes of mass and energy balances, given that they are both inert and have similar physico-chemical properties. This simplification is also made here.

⁷ A further disadvantage is the risk of finding a local extremum, rather than the ‘global’ extremum sought.

⁸ And probably difficult to remember to express mathematically!

⁹ Or 89 to 92% according to Ref. [6].

¹⁰ Assuming that these do not have any heat transfer effects. Thanks to Dr. Paul A. WEBLEY.

The keen investigator may wish to know the argon content of some of the streams. This is relatively simple: as neither undergo any chemical reaction, their relative concentrations in a given gas stream remain essentially constant and equal to that of the inlet air¹¹.

- It was initially assumed that the ratio of water exiting the system in the off-gas and product would be in the ratio of 10:90 (after Ref. [2]). However this assumption proved to be inconsistent with the above constraint, and corrections were (eventually) made¹². These corrections included inclusion of water vapour in the incoming air streams (streams 1 and 49).

One final constraint, which was not mentioned explicitly in any reference, was the need for the reaction to be sufficiently exothermic. That is, there was an allowable change in enthalpy per kilogram of total feed to the catalytic reactors, because if the reaction were insufficiently exothermic, then that would imply that the methanol superheater (HX-2) on the feed line (stream 15) was heating to an unrealistically high temperature. Unrealistically high means a temperature that could not be achieved by the moderate steam heating that was known to be in place.

This constraint was satisfied by computer simulation using a commercial package, which was known to give results of sufficient accuracy to satisfy this requirement.

5.2.1.5 The finished article

Now would be a good time to refer to the completed mass balance (A3-sized insert).

The columns in lighter print headed "FRACTION:" give the mole fraction or mass fraction as appropriate. Values in a box represent adjustable input parameters. Comments in italics generally give a reference as to the determination of a parameter or physical data.

Note that "Off-gas" denotes only the tail-gas which is purged from the system.

The shaded box in the bottom right quadrant headed "CHECK!" verifies the integrity of the mass balance, as do the bottom rows ("TOTAL") of the "REACTIONS:" columns. These are explained in the following section.

While every stream is not listed, this is because either calculation is trivial (e.g. stream 14 passes through HX-2 and becomes stream 15), requires a detailed design (e.g. the absorber pump-arounds), or is based on an energy balance (i.e. the utilities). The completed stream tables have been presented accompanying the Process Flow Diagram in the Drawing Annex.

5.2.2 Verification

The mass balances presented have been checked for self-consistency and no discrepancies are present.

Under the heading "CHECK!" the shaded columns calculate the familiar equation

$$\text{ACCumulation} = \text{IN} - \text{OUT} + \text{GENeration} - \text{DISappearance}$$

The disappearance term is subsumed into the generation term (being identical except for sign), and the accumulation set equal to zero, as must be the case at steady-state.

In the first column the calculation is taken over the whole system (excluding the burner). Thus the equation becomes

$$\text{ACC} = \{\text{Fresh feed} + \text{Absorber water in}\} - \{\text{Off-gas} + \text{Product}\} + \{\text{NETT reaction}\}.$$

This is calculated for every component and for the total, on both a mass and mole basis. In all cases zero accumulation is attained as the result.

In the second column under the heading "CHECK!" the reactor-vaporiser section of the plant is excluded from the mass balance, so that the relevant equation is now

$$\text{ACC} = \{\text{Reactor effluent} + \text{Absorber water in}\} - \{\text{Recycled off-gas} + \text{Off-gas} + \text{Product}\} + \{0\}.$$

Again all zeros are returned, confirming the veracity of the mass balance¹³.

¹¹ Discrepancies are due to minor differences in the solubilities of the two species, which is why the same approximation does not apply to liquid streams. However the argon or nitrogen content of liquid streams would be so small as to be... academic!

¹² Thanks due to Dr. Paul A. WEBLEY, who shared the author's surprise at the high saturation water content of the off-gas.

¹³ Because the mass balance over the vaporiser-reactor section of the plant is not independent of those taken over the whole plant and over the absorber section, this mass balance is verified too (by implication).

[illegible]

In the third column a verification of the off-gas burner (RXN-3) is performed. Due to space limitations the individual reactions are not presented in the burner (though they are listed as (1) to (5) immediately above two of the columns pertaining to the mass balance over RXN-3.

Here the equation is

$$ACC = \{\text{Off-gas} + \text{Additional fuel/air}\} - \{\text{Combusted off-gas}\}.$$

Given that the total mass has balanced (to four decimal places), it may be assumed that the mass balance over the burner is verified.

Finally, each reaction that occurs in the catalytic reactors (RXN-1 and RXN-2) is presented separately, allowing detailed analysis. It may be seen that for each reaction the sum of the changes in mass (by generation or disappearance) of the component species summed to zero. This verifies the self-consistency of the reactions presented.

As a note to the reader, the computer simulation program used (see section 5.4, page 5-6) did not violently object to the equality of the mass balances presented here. It is left to the reader to decide whether this would constitute verification of the mass balances.

5.3 Energy Balances

5.3.1 Development

Energy balances were computed after the mass balances were essentially complete, as they depended on mass-balance data for their basic input. The reason their independent calculation could be delayed was that they primarily affected utility streams that were not central to the process, in terms of having other items dependent upon them, and that the computer simulation program (see section 5.4 following) gave adequate results where estimations of recycle flows were required.

5.3.1.1 The early stages

The first step in performing the energy balance was to obtain the needed physico-chemical properties, such as specific heats – as functions of temperature – and (specific) heats of formation. These were obtained from Ref's [13], [5], [10], [12], [14], [15] and [16], and the relevant data is presented in the Appendix.

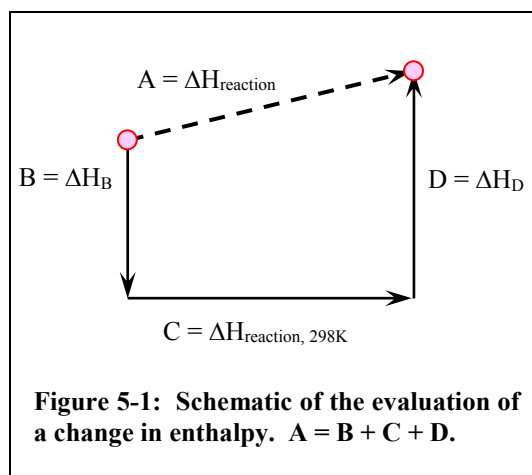
As enthalpy is a 'state' property – *i.e.* it is independent of path – it is possible to calculate a change in enthalpy by constructing a hypothetical path. The method used here took heats of formation¹⁴ of each species, in the relevant phase, at 25°C (298K) and then made adjustments using average specific heats. This is shown schematically in the drawing at right, Figure 5-1.

The average specific heats used were obtained by integrating over the domain from 298K to the temperature of interest. While this was of negligible benefit for moderate temperatures, and of limited benefit for the liquid and aqueous species at any temperature, the computerisation of this process meant that it was not a prohibitively laborious task.

As mentioned, the energy balances were begun using information found from the mass balances. In most cases the temperatures were all known – either from assumption or by (approximate) calculation using the commercial computer simulation program – and the energy balance allowed the heat transfer in a unit to be found. In some cases not all of the temperatures were known, for a process assumed adiabatic, and so calculation of the energy balance proceeded in a way to set the change in total enthalpy over that unit to zero.

5.3.1.2 The final result

Energy balances for key items in the formaldehyde plant are presented in the Appendix at the end of this report.



¹⁴ Implying heats of reaction and dissolution.

Included are the Vaporiser (HX-1), the Absorber (ABS-1), the catalytic reactors (RXN-1 and RXN-2) and the tail-gas burner (RXN-3). Other, minor energy balances are performed as part of the specification of each item, covered in Chapter 6.

5.3.2 Verification

For all of the energy balances the masses input and output are self-consistent, as demonstrated by the mass balances presented earlier (section 5.2, page 5-1) and also independent checks.

The energy balances were also checked to ensure that the sums of the enthalpies of each species in and out added to zero as appropriate, which was the case (within acceptable error ranges). Results were also compared with results from the computer simulation package (see section 5.4, page 5-6), where possible.

The vaporiser calculation has been verified. For all except the recycle streams it is within 1.0%. This figure compares that changes in enthalpy from the feed streams in (streams 3, 6 and 9) to the process vapour that exits (stream 14). An agreement of 99% is very good, and confirms that both methods (spreadsheet and commercial simulator) have performed this portion of the energy balance correctly.

For the recycle streams there is a mismatch of -10%, which is entirely unacceptable. However it is easily seen from the stream table printed out by the computer simulator that the simulator's result is not self-consistent. Due to time constraints this was not recalculated *per se* (see also section 5.4.5, page 5-10), however allowance for the different flows gave a mismatch of +7.6%. This is probably not close enough on its own, but given that the real figure calculated (on the spreadsheet) lies in the middle of the range, this is not enough to discredit the spreadsheet results¹⁵.

The absorber energy balance calculation given in the Appendix is correct. However it does not match up with the values from the simulator. For the recirculating liquid the error is only 1.6%, but this rises to -28% for the other streams into and out of the absorber, which is unacceptable. The reason for this is apparently related to the heat loss.

Using the HYSIM simulator (section 5.4) the absorber streams were adjusted to give operation that was essentially adiabatic. However the recalculated result has shown that in fact the values chosen would require an additional 1528kW cooling duty. Because the HYSIM values were only used as preliminary indicators this does not adversely affect any other units – the correct heat duty has been used in both the specification of items (see Chapter 6) and the detailed design of the absorber (see Chapter 7).

Once the extra cooling duty was incorporated -28% error fell (in magnitude) to +4.8%, which is within the expected range of accuracy.

For the catalytic reactors (calculated together) a good result was obtained. Using the values in the simulation for adiabatic operation gave a total change in enthalpy of only -24.6kW when the energy balance was recalculated independently in the spreadsheet (see Appendix). To demonstrate how close that result is to adiabatic, if operation were truly adiabatic, then the exit temperature of the catalyst bed would have been 975.0K rather than 973.2K, which represents an initial error of only -0.19%.

Care must be taken: the enthalpy values in the simulator package are taken with respect to arbitrary reference points, and will not sum to zero across an adiabatic reactor¹⁶.

Of all the energy balances, that taken over the tail-gas burner is most consistent with the simulator. Proceeding as for the previous case, a heat loss of only -8.3kW was obtained for the assumed adiabatic operation. This is equivalent to adjusting the exit temperature of the adiabatic unit from 1180.8K to 1182.2K – a discrepancy of only -0.11%.

5.4 Process Simulation

Steady-state operation of the formaldehyde plant was simulated on a computer using the commercial package HYSIM, version C2.54.

¹⁵ Furthermore, the spreadsheet calculations were correct in the other cases, and the same method was used in all cases.

¹⁶ It may be noted that the difference in enthalpy for the streams in HYSIM are not heats of reaction – they cannot be. A heat of reaction are usually only defined for isothermal processes, and have no meaning for adiabatic processes, except in hypothetical constructs, as described by Figure 5-1.

5.4.1 Property package

It would be true to say that specification of an appropriate ‘property package’ is crucial in implementing an accurate and meaningful simulation. Property package is used to mean a mathematical model or expression that is used to describe vapour–liquid equilibria. An example would be an equation of state.

SINNOTT [16] provides a helpful review of many of the equations of state and activity coefficient models. The aqueous formaldehyde mixture may be taken as both the most important system to model accurately as well as the most difficult to model satisfactorily¹⁷.

This fits within “Class V” of the reference, “Hydrogen bonding” in which the principle interactions are hydrogen bonds such as in alcohols and water. Given that the pressure is “low” (well under 300kPa), it is acceptable, according to SINNOTT, to use an activity coefficient model to describe the liquid phase fugacity, while the vapour phase may be adequately described by assuming that it behaves as an ideal gas¹⁸ (*i.e.* $pV = nRT$, such that $p_i = f_i$, the fugacity).

Suggested activity coefficient models include Wilson, NRTL, UNIQUAC and UNIFAC. These and other models are now examined. It is possible for all of the models for binary systems to be expanded to handle multi-component systems.

5.4.1.1 Equations of state

The Modified Antoine, PRSV, Virial, Redlich-Kwong and Soave-Redlich-Kwong equations of state were trialed. They were selected because HYSIM supported all of the relevant components for those equations.

5.4.1.2 Margules

This is the simplest of the activity coefficient equations –its advantage lies in its ease of use. It is generally only acceptable for use with “moderately nonideal” mixtures. In particular use of the so-called “two-suffix (one parameter) Margules equation is only justified for simple, binary mixtures in which the components are similar in chemical nature and size[13]. It is not expected to be useful here.

5.4.1.3 Van Laar

This is only slightly more complicated than the Margules equation, but is generally more accurate. It has two parameters [13].

5.4.1.4 Wilson

This is a more complicated equation than that of Margules or van Laar, but can still be handled reasonably easily. It also has two parameters. Ref. [13] states:

“For strongly non-ideal binary mixtures, *e.g.* solutions of alcohols with hydrocarbons, the equation of Wilson is probably the most useful because, unlike the NRTL equation, it contains only two adjustable parameters, and is mathematically simpler than the UNIQUAC equation. For such mixtures the three-suffix [two parameter] Margules equation and the van Laar equation are likely to represent the data with significantly less success, especially in the region dilute with respect to the alcohol, where the Wilson equation is particularly suitable.”

5.4.1.5 NRTL (Non-random two-liquid)

This is a more complicated, three-parameter equation. This is said to be better than the four-suffix (three-parameter) Margules equation [13].

5.4.1.6 UNIQUAC (Universal quasi-chemical)

While this set of equations only contains two independent parameters, it is by far the most complicated of all the models treated here. It has a reputation for being extremely accurate [9], although this may be due in part to deduction from its complexity [13].

¹⁷ As will rapidly become evident, and as noted by OLBRICH [11].

¹⁸ This is in agreement with LI [9].

5.4.1.7 UNIFAC

This is not a model to describe vapour liquid equilibria. It is a so-called group-contribution method that enables parameters used in such models to be calculated, based on regression of all chemical species into representative substituent contributions. It has been found to be quite accurate and reliable, and is normally used with the UNIQUAC model [13], [16].

5.4.1.8 Comparison and selection

The first indication that something was amiss was when the computer simulation package reported vapour in the product pump, which was operating at 75°C, which should have been acceptable¹⁹. The following results were obtained in HYSIM for a 54%(kg.kg⁻¹) formaldehyde, 1%(kg.kg⁻¹) methanol and 45%(kg.kg⁻¹) water mixture:

At 120kPa(abs)

Property package	Bubble point [°C]	Enthalpy ²⁰ at b.p.	Vapour fraction at 75°C	Enthalpy ²¹ at 75°C
Modified Antoine	-15.0520	-3218.8765	0.6232	-568.9592
PRSV	—	—	0.6198	-550.3831
Wilson (I)	—	—	0.1327	-2108.8987
NRTL (RK)	+157.0677	-1715.1731	—	—
NRTL (RK-P)	+148.4017	-1648.1615	0.0000	-2378.9518
NRTL (Virial-P)	+156.2768	-1654.3030	0.0000	-2378.9514
UNIQUAC (I-P)	+42.6327	-2684.7234	0.1436	-2084.7679
UNIQUAC (SRK-P)	+45.8462	-2655.1006	0.1232	-2128.0523
Van Laar (Virial-P)	+90.0567	-228.1504	0.0000	-2378.9437

I = ideal gas; RK = Redlich-Kwong; SRK = Soave-RK; P = Poynting correction (see Ref. [13] or [16]).

Note that the widely varying enthalpy would be mostly dependent on the vapour fraction. It is believed that the enthalpy determination within each model is, at least, reasonably self-consistent.

At 101.325kPa(abs)

Property package	With Poynting correction		Without Poynting correction	
	Bubble point [°C]	Dew Point [°C]	Bubble point [°C]	Dew Point [°C]
Van Laar (I)	81.0377	147.4922	70.0529	137.9438
NRTL (I)	127.0381	175.6683	—	—

The NRTL equation, with ideal gas phase for the low pressure, was initially favoured for its added complexity (from which accuracy is deduced), and to ensure that no vapour was present where it 'should not' be.

Conversely, the van Laar equation (with ideal gas phase) was finally settled on, because it appeared to be closest to the real boiling point²². HYSIM constants for these equations are in the Appendix.

Both had some quirks, including calculation of 700°C streams of two phases – with the liquid phase being mostly carbon dioxide! Obviously such errors were not used for any calculation.

5.4.2 The model

After spending twenty days and twenty nights continually adding – and occasionally deleting – new units and streams from the simulation, the final result given in the Drawing Annex was obtained.

Drawbacks included:

- only one of the four recycle blocks automatically converged all of the time (another converged most of the time) – the others were 'forced' to converge to a consistent result by manually inputting the correct data.
- it was not possible to back-calculate feeds from known product and effluent streams – this too was 'forced' by using the spreadsheet values calculated independently (see section 5.2.1, page 5-1).
- similarly, the absorber could not be specified as adiabatic – instead the recycle flow had to be adjusted to 'force' the energy stream "Q_Abs" to approach zero (while not going positive).

¹⁹ E.g. boiling points [bubble points] from 96 to 100°C (at 101.325kPa(abs)) are quoted for typical solutions [2], [14].

²⁰ In kW, for a mass flow of 2.600kg.s⁻¹ of the mixture.

²¹ In kW, for a mass flow of 2.600kg.s⁻¹ of the mixture.

²² It was also easier to use for independent spreadsheet calculation, and consistency was an objective.

5.4.3 Optimisation

One of the apparent uses of the computer simulation was to optimise the process. This was not a major undertaking in this case because there was really little scope for broad optimisation of the process. What was done was to adjust flows through individual units as substitute short-cut energy balances.

An example of optimisation was in the vaporiser, HX-2. The computer package was expected to allow rapid variation of operating variables in order to optimise the unit²³. The optimisation took the form mainly of deriving a recirculant flow such that it would be of only one phase (namely liquid).

Another use of the simulation was in rapidly assessing the feasibility of using a steam turbine to drive the blower (CP-1). This showed that very high pressure steam from the off-gas burner, let down to 1200kPa(abs) through a turbine, was still insufficient to supply the energy needs of the blower.

HYSIM was also used to help optimise the absorber temperature, as described in the following section. The conclusion was that the top of the column should be as cold as could be achieved using recirculated cooling water (to minimise water content in the off-gas), and the product should be at a temperature close to its storage temperature (say $65 \pm 10^\circ\text{C}$ – see Chapter 2).

5.4.4 Sensitivity analysis

Probably the most sensitive ‘variable’ identified in the simulation was the ‘property package’ that was selected, as described in full in section 5.4.1, page 5-7.

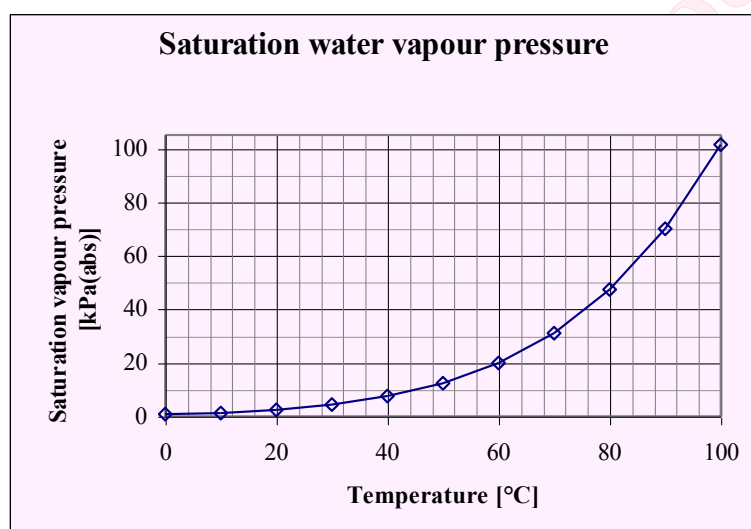


Figure 5-2: Saturation water vapour content of a gas [15].

Another sensitive element was the water vapour content of the off-gas. When this was assumed to be zero, it was relatively easy to match all of the constraints listed in point form under section 5.2.1.4, page 5-3. It should be noted that the off-gas recycle process that was followed is that of BASF, who operate primarily in Germany, where one may expect the temperatures and relative humidities to be far less than equatorial Bontang, where our plant is located. Thus it is likely that the absolute humidity of both the incoming air and also the purged off-gases (stream 39 in the Process Flow Diagram shown in the Drawing Annex) would be comparatively higher for our plant than those values quoted in the references cited (especially Ref. [6]).

The saturation water content of a carrier gas stream as a function of temperature is a highly non-linear, as may be seen from Figure 5-2.

The immediate effect of changing the temperature at the top of the absorber, and hence the water content of the off-gases, was to dramatically affect the amount of demineralised water required to be fed to the absorber (ABS-1) in order to meet product specifications, as well as the reactor feed temperature. See Table 5-1 following.

²³ Although the HYSIM model of aqueous formaldehyde was poor, this stream contained only methanol and water, and was well modelled. However the recycle block “VapRec” and mixer “Mixer4” did not converge automatically.

Situation	Absorber feed water required	Reactor feed temperature
First assumption: off-gases purged contain 10% of the water leaving the system (process-side)	0.392kg.s ⁻¹	462°C
Off-gases contain negligible water	0.249kg.s ⁻¹	164 to 166°C
Top of absorber at approx. 65°C: Off-gases contain 30.8% of the water exiting the system	0.483kg.s ⁻¹	(>>180°C)
Top of absorber at approx. 44°C: Off-gases contain 13.2% of the water exiting the system	0.328kg.s ⁻¹	158°C

Table 5-1: Variation in demineralised water requirement with off-gas water content.

The reactor feed temperature is based on the assumption of a 700°C exit temperature of the effluent gases from the catalyst bed.

From the second to the third row, the yield of formaldehyde for the plant dropped from 90.1% to a maximum of around 87.5%, which was obtained after adjusting variables in line with the prerequisites²⁴ given in section 5·2·1·4, page 5-3.

However the temperature increase over the reactor was still nowhere near great enough, and so the water content in the off-gases was reduced, by assuming a lower top-stage temperature.

Eventually the result in the final row was obtained, which met all of the specifications, but with the new off-gas water content. The yield was then 88.9%.

5·4·5 Failings of the simulation

In retrospect it is easy to wonder whether perhaps time could have been spent more productively in generating a full spreadsheet simulation (*i.e.* not just the mass balance) instead of dogmatically continuing to attempt to ‘force’ the available commercial package to match hand calculations that were known to be correct.

The simulator was of only limited assistance in terms of optimising the process. While it was used to estimate vaporiser recycle flows, this could equally well have been set up in a spreadsheet – which would also allow interaction and would produce essentially instantaneous results – and with greater accuracy²⁵ in the calculation! It was also used to aid in the design of the absorber. However the main contribution was again the independent spreadsheet mass balance, with the simulator only serving in place of short-cut energy balances.

Additionally, the process in question has already had a large number of operating variables specified, either explicitly or by implication (see section 5·2·1·4, page 5-3), and so few variables remained to be optimised.

With respect to sensitivity, the simulator was not particularly helpful. This is largely because insufficient information was known about the reactor, and so the only option was to assume certain reaction mechanisms that fitted known data provided in the references. Hence there was no way of simulating operation of a catalytic at a temperature far from the design operating temperature, for example, such as may occur as the catalyst ages.

The problems of finding an appropriate property package have already been discussed (section 5·4·1, page 5-7). It will be seen later (Chapter 7) that this is because in an aqueous solution formaldehyde exists as a series of hydrolysed polymers, which are far less volatile than formaldehyde.

HYSIM’s main failings involved non-ideal liquid mixtures, which it did not model well, including the energy calculations it performed. This did not effect pure components or gas-phase streams²⁶.

²⁴ But with an off-gas recycle at the high end of the suggested range.

²⁵ Another popular misconception is that numerous significant figures should be shunned in process design. However they are extremely useful for verification of calculations, and have the advantage of not causing significant build-up of rounding errors. Of course, they are less practical for calculations by hand.

²⁶ As the ideal gas equation was selected to model the gas phase.

5.5 References

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²⁷ This reference due to Dr. David J. BRENNAN.

²⁸ The author wishes to acknowledge Mr. Adrian DIXON for kindly providing access to this reference.

²⁹ This reference kindly made available by Mrs. Hsu-San WARE.

6 SPECIFICATION OF EQUIPMENT ITEMS

6.1 Development of the Specification Sheets

Specifications for plant items were developed in accordance with the mass and energy balances. Where additional information was required this was mostly obtained from standard chemical engineering conventions.

These conventions are generally empirically based on finding economic optima.

A brief discussion of some of the representative decisions and calculations follows. Samples of the relevant calculations may be found in the Appendix.

6.1.1 Flowrates

All of the mass flowrates have been obtained from mass and energy balances, as described in Chapter 5. The values for the absorber have been updated based on calculations presented in Chapter 7.

6.1.2 Fluid characteristics

Fluid characteristics such as temperature and pressure were mostly set by the process development summarised in Chapters 3 and 4. From this starting point other properties, such as densities and specific heats, were able to be evaluated in consultation with standard texts [2], [5], [11], [12], [13], [15], [17] as well as some specialised references [6], [7], [18].

6.1.3 Branch sizes

Nominal branch sizes were evaluated on the recommendation of a 2m.s^{-1} flow of liquids, or half that for liquids under gravity flow, and around 25m.s^{-1} for gases (for this plant only low gauge pressures are used) [3], [17].

However the conventional sizing based on the imperial system of measurement (*i.e.* inches *et cetera*) was recognised, and so sizes are given in millimetric equivalents of integer measurements in inches¹ [4], [17]. The flanges will be manufactured to the appropriate standard².

Socket welding flanges are specified in all instances [9].

6.1.4 Power requirements: Pumps and Blower

The power required for pumping a liquid may be evaluated by the equation

$$\text{Pump power} = \{\text{Volumetric flowrate}\} \times \{\text{Pressure differential}\} \div \{\text{Pump efficiency}\}.$$

Pump efficiencies were estimated from typical values in Ref's [14] and [17].

Following this a standard-sized motor was selected by rounding up, after accounting for motor efficiency [14].

All of the pumps were specified as centrifugal as this is the most commonly used type of pump, which is capable of handling the required flowrates and differential pressures [4]. The motors are all totally-enclosed (and fan-cooled) to reduce the flammability hazard.

The blower will be centrifugal also. Although Orica use a Rootes-type blower at their Deer Park facility, both Ref's [4] and [17] suggest that this is not the most appropriate type for the flowrate and pressure differential required. Multiple stages may be required.

6.1.5 Volumes

The vessel volumes have been sized based on rules-of-thumb for residence times that take into consideration control and operability as well as safety concerns. Appropriate safety factors are then applied to allow some contingency volume for uncertainties and abnormal operation.

6.1.6 Heat transfer

Heat transfer is calculated according to the design equation

¹ Two inch increments above 10inches, five inch increments above 25, and so on.

² Probably depending upon the country of purchase, as the plant site is in Bontang, Indonesia.

Chapter 6: Specification of Equipment Items**Formaldehyde**

$$Q = U.A.\Delta T_{\log \text{ mean}}.F_T$$

where Q is the heat transfer [kW], U the overall heat transfer [$\text{W.m}^{-2}.\text{K}^{-1}$], A the heat transfer area, $\Delta T_{\log \text{ mean}}$, the logarithmic mean of the temperature difference³ and F_T a temperature-difference correction factor. F_T is evaluated from standard charts [10], while Ref. [17] gives typical values for U .

Ref. [16] was used in selecting an outside-packed heat exchanger configuration. Although this is relatively expensive, selection was based on:

- need for a removable tube bundle $\Rightarrow$ cannot be fixed tube sheet
- ease of cleaning (including shell side) $\Rightarrow$ preferably not U-tube
- safety considerations $\Rightarrow$ cannot be packed lantern-ring floating head.

The last constraint is present because any leakage through the rings of packing will drop to the floor. Given that the exchangers are operating on flammable materials this is proscribed.

6.1.7 Mass transfer

The packed and trayed sections of the absorber have been designed in Chapter 7 using fundamental rules governing mass transfer, such as mass transfer coefficients, as well as empirical correlations. A full description is to be found in Chapter 7, including the factors influencing the choice of internals.

6.1.8 Reaction

Design of the catalytic reactors, and in particular the catalyst layers, follows the guidelines set out in Ref. [8].

6.1.9 Design temperature and pressure

The maximum design temperatures and pressures were evaluated in a manner similar to that recommended by Ref. [17].

Maximum design was taken as the greater of ten percent of the operating pressure or 50kPa(abs), except that in some cases a higher pressure was selected to allow for the possibility of a 'flow-through' of pressure from one item to another. For example due to by-passing, dead-heading of a pump, or even vapour expansion due to abnormal heating effects⁴.

Maximum temperatures were generally recorded as approximately 50°C above the design operating temperature. This allows for a change in the design operating conditions (*e.g.* as might be recommended after a post-commissioning optimisation study) and gives a safety margin to account for uncertainty. In some places maximums were upgraded to account for the possibility of heat-exchanger failures upstream. For example the column (ABS-1) is rated to withstand 170°C, which is the design temperature exiting the waste-heat boilers (HX-3 and HX-4), despite normal operation being for the reactor effluent to be further cooled (to 90°C) in HX-5. In no case was the maximum design temperature specified below 100°C.

None of the items are designed to operate at negative gauge pressures. Due to the design to withstand internal pressure, the items will have a limited ability to withstand some external pressure (*i.e.* an internal vacuum), but this has not been calculated.

None of the items operates at sub-zero (Celsius) temperatures, and certainly not in cryogenic regions. Thus minimum design temperatures are specified as 10°C or the lowest environmental temperature likely to be encountered. This is recorded only for completeness, to indicate that the minimum temperature requirement does not dictate the (mechanical) design.

6.1.10 Materials of construction

Type 316 stainless steel (316SS) is used throughout the plant, which minimises any poisoning of the catalyst⁵. Stainless⁶ also allows longer storage of formaldehyde solutions without deterioration such as yellowing [18].

³ Taken on a counter-current basis.

⁴ Only a limited allowance is made for this – the equipment is not explosion-proof! Rather, provision of safety valves and bursting discs is made.

⁵ Although modern plants commonly use stainless both before and after catalytic reactor, in our case there is an extra incentive with the recycling of off-gases (though not of methanol).

⁶ Mild steel will cause commercial formaldehyde solutions to yellow in around 2 days. All stainless steels (including types 302, 304 and 316) appear to give inert storage for in excess of 60 days.

Type 316 is more expensive than the commonly used type 304, but has superior corrosion resistance. It is also used throughout Orica's formaldehyde plant in Deer Park.

While type 310 steel gives greater resistance to oxidation at high temperatures, it is prone to forming sigma phases. Both type 310 and type 321, which is also recommended for high temperature use, appear to have lower design tensile strengths than type 316 at the temperature of operation of the reactor, for example, (around 700°C) [1].

Hydrogen embrittlement is another consideration (see Ref. [17]).

For gaskets Teflon is specified due to its resistance to degradation⁷.

6.1.11 Quantity

Generally speaking only one item was specified for each unit. There were a number of exceptions, however.

Some of the pumps are required for safe and continued operation, and so these were specified with an active pump and a stand-by pump. Other pumps, particularly on low-duty absorber pump-arounds, are not essential, and operation could continue without them. This is made clear on each specification sheet (see section 6.2, pages 6-3ff.).

The blower (CP-1) is needed for operation, but it would be too costly and impractical to install a stand-by blower (driven by steam-turbine).

The catalytic reactors (RXN-1 and RXN-2) as well as the associated steam systems are specified separately, although these essentially correspond to two parallel streams in the ratio 40:60, in order to optimise the process to cope with a 60% turndown requirement (as stated in Chapter 2).

The two storage tanks (ST-3 and ST-5) are specified in duplicate because of the potential need to cope with slightly out-of-specification product, as well as unscheduled down-time in the resins plant *et cetera*.

6.2 Specification Sheets

Specification sheets for all of the items named in the process flow diagram (Drawing Annex) are presented in alphanumeric order on the following pages.

While reviewing the specification sheets, the reader is asked to remember that for this section it is considered satisfactory to provide only enough information to enable approximate utility and capital costing, and – where relevant – to enable the process and instrumentation diagram (P&ID – covered in Chapter 8) to be completed. Thus the specifications presented here may be taken as preliminary only.

⁷ Polytetrafluoroethylene; as recommended by staff at Orica's Deer Park facility.

6.3 References

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⁸ Third amendment is most recent, dated December 1993.

⁹ This reference due to Dr. David J. BRENNAN.

¹⁰ The author wishes to acknowledge Mr. Adrian DIXON for kindly providing access to this reference.

SPECIFICATION SHEET:		COLUMN	
Equipment item	ABS-1		
Description	Formaldehyde absorption column		
Quantity	1 (one)		
Vapour process fluid	Reactor effluent (cooled) — Off-gas		
Liquid process fluid	Demineralised water — 54%(kg.kg ⁻¹) HCHO product		
Stages	4 (four), all cooled		
Pump-arounds	On bottom three (3) stages		
PROCESS DETAILS			
Pressure at base [kPa(abs)]			130
Pressure at top [kPa(abs)]			110
	Liquid	Vapour	
Inlet temperature [°C]	37	90	
Outlet temperature [°C]	75	38	
Inlet mass flow [kg.s ⁻¹]	0.3275	7.92	
Outlet mass flow [kg.s ⁻¹]	29.7	5.60	
Inlet density [kg.m ⁻³]	995	1.04	
Outlet density [kg.m ⁻³]	1132	1.01	
Pump-around details	Flow [kg.s ⁻¹]	T _{IN} [°C]	T _{OUT} [°C]
Stage 1 (base)	29.04	60	75
Stage 2	41.99	48	63
Stage 3	13.83	40	51
Stage 4 (top)	0	-	-
MECHANICAL DATA			
Maximum design pressure [kPa(g)]			328
Minimum design pressure [kPa(g)]			-3
Maximum design temperature [°C]			170
Minimum design temperature [°C]			ambient / 10
Internal diameter [mm]			1800
Total column height (excluding support) [mm]			32600
Stage height [mm]			
Stage 1 (base)			2900
Stage 2			2200
Stage 3			2500
Stage 4 (top)			16970
Wall thickness [mm]			7
	Liquid	Vapour	
Main inlet branch nominal diameter [mm]	19	635	
Main outlet branch nominal diameter [mm]	203	559	
Connection type	Socket welding flanges		
SUPPORT			
Type of support structure	Skirt - see Notes		
Height of support structure [mm]	1500		
INSULATION			
Thickness [mm]			25
Extent of coverage	Stage 1 (one) only		
INTERNALS			
Configuration	Bottom 3 (three) stages packed; Stage 4 (four) trayed		
Packing type	50mm pall rings		
Tray type	Bubble-caps on reverse-flow trays with serpentine cooling		
MATERIALS OF CONSTRUCTION			
Shell and branches	Type 316SS		
Lining	None		
Insulation	Fibre-glass blankets		
INTERNALS			
Packing	Type 316SS		
Liquid and gas distributors & plates	Type 316SS		
Trays	Type 316SS		
Gaskets	Teflon		
NOTES			
Support is also provided by scaffolding, incorporating the stair-way.			
REVISION:	"E"		
Designed: David Verrelli	Checked: David Verrelli	Authorised: —	
Date: 01/09/1999	Date: 06/10/1999	Date: —	

SPECIFICATION SHEET:		COMPRESSOR	
Equipment item	CP-1		
Description	Feed gas blower to vaporiser		
Type	Centrifugal		
Quantity	1 (one) - see Notes		
Duty [kW]	539		
PROCESS DETAILS			
Fluid description	Fresh air feed and recycled off-gas		
Fluid composition [(kg.kg ⁻¹):	Nitrogen	78.5	
	Oxygen	12.2	
	Water	4.6	
	Carbon dioxide	3.8	
	Methanol	trace	
	Formaldehyde	trace	
	Other (including hydrogen)	79.3	
Mass flowrate [kg.s ⁻¹]	5.95		
	Suction	Delivery	
Temperature [°C]	44	122	
Pressure [kPa(abs)]	101	185	
Density [kg.m ⁻³]	1.00	1.46	
POWER			
Compressor efficiency [%]	75		
Drive type	Mechanical – connection to shaft of TRB-1		
Motor type	none		
Motor efficiency [%]	-		
Motor power [kW]	-		
MECHANICAL DATA			
Maximum design pressure [kPa(abs)]	210		
Minimum design pressure [kPa(g)]	-1		
Maximum design temperature [°C]	200		
Minimum design temperature [°C]	ambient / 10		
	Suction	Delivery	
Branch nominal diameter [mm]	635	635	
MATERIALS OF CONSTRUCTION			
Casing	Type 316SS		
Lining	None		
Impellor	Type 316SS		
NOTES			
Only one item is specified, as a stand-by compressor is impractical and uneconomical.			
REVISION: "B"			
Designed: Sasha Trandafilovic	Revised: David Verrelli	Authorised: —	
Date: 10/01/1999 [sic!]	Date: 30/09/1999	Date: —	

SPECIFICATION SHEET:		SMALL VESSEL			
Equipment item	D-1				
Description	Steam drum				
Type	Closed				
Quantity	1 (one)				
Volume [m ³]	1.4				
Residence time [s]	300				
PROCESS DETAILS					
		Feed 1	Feed 2	Exit 1	Exit 2
		BFW	Steam	BFW	Steam
Fluid description					
Fluid composition [% (kg.kg ⁻¹)]:	Water	100	100	100	100
Vapour fraction		0	0.35	0	1
Temperature [°C]		100	152	152	152
Pressure [kPa(abs)]		500	500	500	500
Density [kg.m ⁻³]		902	7.2	902.0	0.63
Flowrate [kg.s ⁻¹]		1.2	3.5	3.5	1.2
MECHANICAL DATA					
Maximum design pressure [kPa(abs)]				550	
Minimum design pressure [kPa(g)]				-5	
Maximum design temperature [°C]				200	
Minimum design temperature [°C]				ambient / 10	
Height [mm]				1500	
Diameter [mm]				1100	
Branch nominal diameter [mm]		Feed 1	Feed 2	Exit 1	Exit 2
Connection type		25	254	51	356
		Socket welding flanges			
SUPPORT					
Type of support structure		Scaffolding			
INSULATION					
Thickness [mm]		51			
Extent of coverage		Complete			
MATERIALS OF CONSTRUCTION					
Shell and branches		Type 316SS			
Lining		None			
Insulation		Rock-wool			
NOTES					
One (1) drain and one (1) vent connection are present at the lowest and highest points. BFW = Boiler feed water					
REVISION: "D"					
Designed: Rachel Weldon	Revised: David Verrelli	Authorised: —			
Date: 14/09/1999	Date: 30/09/1999	Date: —			

SPECIFICATION SHEET:		SMALL VESSEL			
Equipment item	D-2				
Description	Steam drum				
Type	Closed				
Quantity	1 (one)				
Volume [m ³]	2.2				
Residence time [s]	300				
PROCESS DETAILS					
		Feed 1	Feed 2	Exit 1	Exit 2
		BFW	Steam	BFW	Steam
Fluid description					
Fluid composition [% (kg.kg ⁻¹):	Water	100	100	100	100
Vapour fraction		0	0.35	0	1
Temperature [°C]		100	152	152	152
Pressure [kPa(abs)]		500	500	500	500
Density [kg.m ⁻³]		902	7.2	902.0	0.63
Flowrate [kg.s ⁻¹]		1.9	5.3	5.3	1.9
MECHANICAL DATA					
Maximum design pressure [kPa(abs)]				550	
Minimum design pressure [kPa(g)]				-5	
Maximum design temperature [°C]				200	
Minimum design temperature [°C]				ambient / 10	
Height [mm]				1500	
Diameter [mm]				1300	
Branch nominal diameter [mm]		Feed 1	Feed 2	Exit 1	Exit 2
Connection type		38	305	51	432
		Socket welding flanges			
SUPPORT					
Type of support structure	Scaffolding				
INSULATION					
Thickness [mm]	51				
Extent of coverage	Complete				
MATERIALS OF CONSTRUCTION					
Shell and branches	Type 316SS				
Lining	None				
Insulation	Rock-wool				
NOTES					
One (1) drain and one (1) vent connection are present at the lowest and highest points.					
BFW = Boiler feed water					
REVISION: "D"					
Designed: Rachel Weldon	Revised: David Verrelli	Authorised: —			
Date: 14/09/1999	Date: 30/09/1999	Date: —			

SPECIFICATION SHEET:		SMALL VESSEL			
Equipment item		D-3			
Description		Steam drum			
Type		Closed, horizontal			
Quantity		1 (one)			
Volume [m ³]		12			
Residence time [s]		300			
PROCESS DETAILS					
		Feed 1	Feed 2	Exit 1	Exit 2
Fluid description		BFW	Steam	BFW	Steam
Fluid composition [% (kg.kg ⁻¹)]:	Water	100	100	100	100
Vapour fraction		0.10	0.15	0	1
Temperature [°C]		188	188	188	188
Pressure [kPa(abs)]		1200	1200	1200	1200
Density [kg.m ⁻³]		835	748	878	6.1
Flowrate [kg.s ⁻¹]		1.7	29.1	29.1	1.7
MECHANICAL DATA					
Maximum design pressure [kPa(abs)]			1350		
Minimum design pressure [kPa(g)]			-10		
Maximum design temperature [°C]			250		
Minimum design temperature [°C]			ambient / 10		
Height [mm]			4000		
Diameter [mm]			2000		
		Feed 1	Feed 2	Exit 1	Exit 2
Branch nominal diameter [mm]		51	254	254	305
Connection type		Socket welding flanges			
SUPPORT					
Type of support structure			Scaffolding		
INSULATION					
Thickness [mm]					
Extent of coverage			Complete		
MATERIALS OF CONSTRUCTION					
Shell and branches			Type 316SS		
Lining			None		
Insulation			Rock-wool		
NOTES					
One (1) drain and one (1) vent connection are present at the lowest and highest points.					
BFW = Boiler feed water					
REVISION: "C"					
Designed: Michael Whiteman		Revised: David Verrelli		Authorised: —	
Date: 07/10/1999		Date: 09/10/1999		Date: —	

SPECIFICATION SHEET:		COLUMN	
Equipment item	HX-1		
Description	Methanol feed vaporiser		
Quantity	1 (one)		
Vapour process fluid	Air and recycled off-gas — Hot reactor feed		
Liquid process fluid	Cool aq. methanol — (Hot aq. methanol)		
Stages	1 (one)		
Pump-arounds	1 (one)		
PROCESS DETAILS			
Pressure at base [kPa(abs)]		185	
Pressure at top [kPa(abs)]		185	
	Liquid		Vapour
Inlet temperature [°C]	37		122
Outlet temperature [°C]	62		62
Inlet mass flow (excl. pump-around) [kg.s ⁻¹]	1.97		5.95
Outlet mass flow [kg.s ⁻¹]	23.9		7.92
Inlet density [kg.m ⁻³]			
Outlet density [kg.m ⁻³]			
Pump-around details	Flow [kg.s ⁻¹]	T _{IN} [°C]	T _{OUT} [°C]
Stage 1	23.9	87	62
MECHANICAL DATA			
Maximum design pressure [kPa(g)]		200	
Minimum design pressure [kPa(g)]		-3	
Maximum design temperature [°C]		170	
Minimum design temperature [°C]		ambient / 10	
Internal diameter [mm]		1800	
Total column height (excluding support) [mm]		3000	
Stage height [mm]			
Stage 1		1000	
Wall thickness [mm]		7	
	Liquid		Vapour
Main inlet branch nominal diameter [mm]			
Main outlet branch nominal diameter [mm]			
Connection type		Socket welding flanges	
SUPPORT			
Type of support structure		Skirt	
Height of support structure [mm]		1000	
INSULATION			
Thickness [mm]			
Extent of coverage			
INTERNALS			
Configuration		Packed	
Packing type		50mm Pall rings	
Tray type		N/A	
MATERIALS OF CONSTRUCTION			
Shell and branches		Type 316SS	
Lining		None	
Insulation		Fibre-glass blankets	
INTERNALS			
Packing		Type 316SS	
Liquid and gas distributors & plates		Type 316SS	
Trays		N/A	
Gaskets		Teflon	
NOTES			
aq. = aqueous			
REVISION: "A"			
Designed: David Verrelli		Checked:	Authorised: —
Date: 06/10/1999		Date:	Date: —

SPECIFICATION SHEET:		HEAT EXCHANGER			
Equipment item		HX-2			
Description		Methanol superheater			
Type		Horizontal shell-and-tube			
Quantity		1 (one)			
Duty [kW]		963			
Log-mean temperature difference [K]		65			
Temperature correction factor, F_T [-]		0.98			
Overall heat transfer coefficient $[W.m^{-2}.K^{-1}]$		111			
Heat transfer area $[m^2]$		148			
PROCESS DETAILS					
Fluid description		Tube-side Reactor feed		Shell-side Steam circuit	
Fluid composition $[(\%)(kg.kg^{-1})]$:		Methanol		-	
		Formaldehyde		-	
		Oxygen		-	
		Water		100	
Other (including nitrogen)		62.5		trace	
Flowrate $[kg.s^{-1}]$		7.916		0.484	
Vapour fraction		In	Out	In	Out
Temperature $[^{\circ}C]$		1	1	1	0
Pressure $[kPa(abs)]$		62	158	187	187
Density $[kg.m^{-3}]$		185	170	1200	1185
		1.78	1.27	5.6	867
MECHANICAL DATA					
Maximum design pressure $[kPa(abs)]$		1300			
Minimum design pressure $[kPa(g)]$		-5			
Maximum design temperature $[^{\circ}C]$		250			
Minimum design temperature $[^{\circ}C]$		ambient / 10			
TYPE OF CONSTRUCTION					
Front end head type (TEMA code)		Bonnet [integral cover] (B)			
Shell type (TEMA code)		One pass shell (E)			
Rear end head type (TEMA code)		Fixed tubesheet [like "B" stationary head] (M)			
Number of tube passes		1 (one)			
Inlet branch nominal diameter [mm]		Tube-side		Shell-side	
Outlet branch nominal diameter [mm]					
Connection type		Socket welding flanges			
SUPPORT					
Type of support structure					
INSULATION					
Thickness [mm]					
Extent of coverage		Complete			
MATERIALS OF CONSTRUCTION					
Shell and branches		Type 316SS			
Lining		None			
Insulation		Fibreglass blanket			
Cladding on insulation					
Channels		Type 316SS			
Tube-sheet		Type 316SS			
Tubes		Type 316SS			
NOTES					
One (1) drain and one (1) vent connection are present on each of the shell side and channels, at the lowest and highest points respectively - in accordance with BS3274(1960). Safety relief valves are also present.					
REVISION: "B"					
Designed: Ho Hai Huynh		Revised: David Verrelli		Authorised: —	
Date: 03/10/1999		Date: 06/10/1999		Date: —	

SPECIFICATION SHEET:		HEAT EXCHANGER			
Equipment item		HX-3			
Description		Waste heat boiler for RXN-2			
Type		Vertical shell-and-tube			
Quantity		1 (one)			
Duty [kW]		3918			
Log-mean temperature difference [K]		156			
Temperature correction factor, F_T [-]		1.00			
Overall heat transfer coefficient $[W.m^{-2}.K^{-1}]$		120			
Heat transfer area $[m^2]$		131			
PROCESS DETAILS					
Fluid description		Tube-side Reactor effluent		Shell-side Steam circuit	
Fluid composition $[(\%)(kg.kg^{-1})]$:		Methanol		-	
		Formaldehyde		-	
		Oxygen		-	
		Water		100	
Other (including nitrogen)		66.2		trace	
Flowrate $[kg.s^{-1}]$		4.74		5.14	
Vapour fraction		In	Out	In	Out
Temperature $[^{\circ}C]$		1	1	0	0.35
Pressure $[kPa(abs)]$		700	170	152	152
Density $[kg.m^{-3}]$		160	145	500	500
		0.5	0.9	902	7.2
MECHANICAL DATA					
Maximum design pressure $[kPa(abs)]$		550			
Minimum design pressure $[kPa(g)]$		-5			
Maximum design temperature $[^{\circ}C]$		750			
Minimum design temperature $[^{\circ}C]$		ambient / 10			
TYPE OF CONSTRUCTION					
Front end head type (TEMA code)		Bonnet [integral cover] (B)			
Shell type (TEMA code)		One pass shell (E)			
Rear end head type (TEMA code)		Fixed tubesheet [like "B" stationary head] (M)			
Number of tube passes		1 (one)			
Inlet branch nominal diameter [mm]		Tube-side 762		Shell-side 51	
Outlet branch nominal diameter [mm]		610		305	
Connection type		Socket welding flanges			
SUPPORT					
Type of support structure		Scaffolding			
INSULATION					
Thickness [mm]		0			
Extent of coverage		-			
MATERIALS OF CONSTRUCTION					
Shell and branches		Type 316SS			
Lining		None			
Insulation		None			
Cladding on insulation		-			
Channels		Type 316SS			
Tube-sheet		Type 316SS			
Tubes		Type 316SS			
NOTES					
One (1) drain and one (1) vent connection are present on each of the shell side and channels, at the lowest and highest points respectively - in accordance with BS3274(1960).					
REVISION: "C"					
Designed: Rachel Weldon		Revised: David Verrelli		Authorised: —	
Date: 14/09/1999		Date: 30/09/1999		Date: —	

SPECIFICATION SHEET:		HEAT EXCHANGER			
Equipment item		HX-4			
Description		Waste heat boiler for RXN-1			
Type		Vertical shell-and-tube			
Quantity		1 (one)			
Duty [kW]		2612			
Log-mean temperature difference [K]		156			
Temperature correction factor, F_T [-]		1.00			
Overall heat transfer coefficient [$\text{W.m}^{-2}.\text{K}^{-1}$]		120			
Heat transfer area [m^2]		87.2			
PROCESS DETAILS					
Fluid description		Tube-side Reactor effluent		Shell-side Steam circuit	
Fluid composition [%(kg.kg^{-1})]:					
Methanol		0.3		-	
Formaldehyde		18.1		-	
Oxygen		0.1		-	
Water		15.4		100	
Other (including nitrogen)		66.2		trace	
Flowrate [kg.s^{-1}]		3.16		3.43	
Vapour fraction		In	Out	In	Out
Temperature [$^{\circ}\text{C}$]		1	1	0	0.35
Pressure [kPa(abs)]		700	170	152	152
Density [kg.m^{-3}]		160	145	500	500
		0.5	0.9	902	7.2
MECHANICAL DATA					
Maximum design pressure [kPa(abs)]				550	
Minimum design pressure [kPa(g)]				-5	
Maximum design temperature [$^{\circ}\text{C}$]				750	
Minimum design temperature [$^{\circ}\text{C}$]				ambient / 10	
TYPE OF CONSTRUCTION					
Front end head type (TEMA code)		Bonnet [integral cover] (B)			
Shell type (TEMA code)		One pass shell (E)			
Rear end head type (TEMA code)		Fixed tubesheet [like "B" stationary head] (M)			
Number of tube passes		1 (one)			
Inlet branch nominal diameter [mm]		Tube-side		Shell-side	
Outlet branch nominal diameter [mm]		635		51	
Connection type		508		254	
		Socket welding flanges			
SUPPORT					
Type of support structure		Scaffolding			
INSULATION					
Thickness [mm]		0			
Extent of coverage		-			
MATERIALS OF CONSTRUCTION					
Shell and branches		Type 316SS			
Lining		None			
Insulation		None			
Cladding on insulation		-			
Channels		Type 316SS			
Tube-sheet		Type 316SS			
Tubes		Type 316SS			
NOTES					
One (1) drain and one (1) vent connection are present on each of the shell side and channels, at the lowest and highest points respectively - in accordance with BS3274(1960).					
REVISION: "B"					
Designed: Rachel Weldon		Revised: David Verrelli		Authorised: —	
Date: 14/09/1999		Date: 30/09/1999		Date: —	

SPECIFICATION SHEET:		HEAT EXCHANGER			
Equipment item		HX-5			
Description		Reactor effluent cooler			
Type		Vertical shell-and-tube			
Quantity		1 (one)			
Duty [kW]		801			
Log-mean temperature difference [K]		35.2			
Temperature correction factor, F_T [-]		0.96			
Overall heat transfer coefficient [$\text{W.m}^{-2}.\text{K}^{-1}$]		126			
Heat transfer area [m^2]		180			
PROCESS DETAILS					
Fluid description		Tube-side		Shell-side	
		Aqueous methanol		Reactor effluent	
Fluid composition [%(kg.kg^{-1})]:		Methanol	31.5	0.3	
		Water	68.5	15.4	
		Formaldehyde	-	18.1	
		Nitrogen	-	59.0	
		Other	trace	7.3	
Flowrate [kg.s^{-1}]		23.9		7.92	
Vapour fraction		In	Out	In	Out
Temperature [$^{\circ}\text{C}$]		0	0	1	0
Pressure [kPa(abs)]		73	81	170	90
Density [kg.m^{-3}]		185	175	1200	1185
		889	882	1.0	1.0
MECHANICAL DATA					
Maximum design pressure [kPa(abs)]		1300			
Minimum design pressure [kPa(g)]		-5			
Maximum design temperature [$^{\circ}\text{C}$]		250			
Minimum design temperature [$^{\circ}\text{C}$]		ambient / 10			
TYPE OF CONSTRUCTION					
Front end head type (TEMA code)		Bonnet [integral cover] (B)			
Shell type (TEMA code)		One pass shell (E)			
Rear end head type (TEMA code)		U-tube bundle (U)			
Number of tube passes		6 (six)			
Inlet branch nominal diameter [mm]		Tube-side		Shell-side	
Outlet branch nominal diameter [mm]					
Connection type		Socket welding flanges			
SUPPORT					
Type of support structure		Scaffolding			
INSULATION					
Thickness [mm]					
Extent of coverage		Complete			
MATERIALS OF CONSTRUCTION					
Shell and branches		Type 316SS			
Lining		None			
Insulation		Fibreglass blanket			
Cladding on insulation					
Channels		Type 316SS			
Tube-sheet		Type 316SS			
Tubes		Type 316SS			
NOTES					
One (1) drain and one (1) vent connection are present on each of the shell side and channels, at the lowest and highest points respectively - in accordance with BS3274(1960).					
REVISION: "B"					
Designed: Saiful D. Zainal Abidin		Revised: David Verrelli		Authorised: —	
Date: 30/09/1999		Date: 09/10/1999		Date: —	

SPECIFICATION SHEET:		HEAT EXCHANGER			
Equipment item		HX-6			
Description		Stage 3 recirculation cooler			
Type	Horizontal shell-and-tube				
Quantity	1 (one)				
Duty [kW]	590				
Log-mean temperature difference [K]	10				
Temperature correction factor, F_T [-]	1.00				
Overall heat transfer coefficient [$\text{W.m}^{-2}.\text{K}^{-1}$]	800				
Heat transfer area [m^2]	75				
PROCESS DETAILS					
		Tube-side		Shell-side	
Fluid description		Stage 3 recirculant		Recirculated cooling water	
Fluid composition [%(kg.kg ⁻¹):		79.8		100	
Water		19.9		-	
Formaldehyde		0.3		trace	
Other (including methanol)					
Flowrate [kg.s ⁻¹]		13.7		12.8	
		In	Out	In	Out
Vapour fraction		0	0	0	0
Temperature [°C]		51	40	30	41
Pressure [kPa(abs)]		305	265	400	360
Density [kg.m ⁻³]		1050	1050	1000	1000
MECHANICAL DATA					
Maximum design pressure [kPa(abs)]		450			
Minimum design pressure [kPa(g)]		-5			
Maximum design temperature [°C]		150			
Minimum design temperature [°C]		ambient / 10			
TYPE OF CONSTRUCTION					
Front end head type (TEMA code)		Channel integral with tube-sheet and removable cover (C)			
Shell type (TEMA code)		One pass shell (E)			
Rear end head type (TEMA code)		Outside-packed floating-head (P)			
Number of tube passes		1 (one)			
		Tube-side		Shell-side	
Inlet branch nominal diameter [mm]		102		102	
Outlet branch nominal diameter [mm]		102		102	
Connection type		Socket welding flanges			
SUPPORT					
Type of support structure		Saddles			
INSULATION					
Thickness [mm]		0			
Extent of coverage		-			
MATERIALS OF CONSTRUCTION					
Shell and branches		Type 316SS			
Lining		None			
Insulation		None			
Cladding on insulation		-			
Channels		Type 316SS			
Tube-sheet		Type 316SS			
Tubes		Type 316SS			
NOTES					
One (1) drain and one (1) vent connection are present on each of the shell side and channels, at the lowest and highest points respectively - in accordance with BS3274(1960).					
REVISION: "B"					
Designed: David Verrelli		Checked: David Verrelli		Authorised: —	
Date: 22/09/1999		Date: 23/09/1999		Date: —	

SPECIFICATION SHEET:		HEAT EXCHANGER			
Equipment item		HX-7			
Description		Stage 2 recirculation cooler			
Type	Horizontal shell-and-tube				
Quantity	1 (one)				
Duty [kW]	2349				
Log-mean temperature difference [K]	18				
Temperature correction factor, F_T [-]	0.88				
Overall heat transfer coefficient [$\text{W.m}^{-2}.\text{K}^{-1}$]	700				
Heat transfer area [m^2]	210				
PROCESS DETAILS					
Fluid description		Tube-side Stage 2 recirculant		Shell-side Recirculated cooling water	
Fluid composition [%(kg.kg ⁻¹):		70.6		100	
Water		28.9		-	
Formaldehyde		0.5		trace	
Other (including methanol)					
Flowrate [kg.s ⁻¹]		41.2		37.5	
Vapour fraction		In	Out	In	Out
Temperature [°C]		0	0	0	0
Pressure [kPa(abs)]		63	48	30	45
Density [kg.m ⁻³]		280	240	400	360
		1100	1100	1000	1000
MECHANICAL DATA					
Maximum design pressure [kPa(abs)]		450			
Minimum design pressure [kPa(g)]		-5			
Maximum design temperature [°C]		150			
Minimum design temperature [°C]		ambient / 10			
TYPE OF CONSTRUCTION					
Front end head type (TEMA code)		Channel integral with tube-sheet and removable cover (C)			
Shell type (TEMA code)		One pass shell (E)			
Rear end head type (TEMA code)		Outside-packed floating-head (P)			
Number of tube passes		2 (two)			
Inlet branch nominal diameter [mm]		Tube-side 178		Shell-side 178	
Outlet branch nominal diameter [mm]		178		178	
Connection type		Socket welding flanges			
SUPPORT					
Type of support structure		Saddles			
INSULATION					
Thickness [mm]		0			
Extent of coverage		-			
MATERIALS OF CONSTRUCTION					
Shell and branches		Type 316SS			
Lining		None			
Insulation		None			
Cladding on insulation		-			
Channels		Type 316SS			
Tube-sheet		Type 316SS			
Tubes		Type 316SS			
NOTES					
One (1) drain and one (1) vent connection are present on each of the shell side and channels, at the lowest and highest points respectively - in accordance with BS3274(1960).					
REVISION: "B"					
Designed: David Verrelli		Checked: David Verrelli		Authorised: —	
Date: 22/09/1999		Date: 23/09/1999		Date: —	

SPECIFICATION SHEET:		HEAT EXCHANGER			
Equipment item		HX-8			
Description		Stage 1 recirculation cooler			
Type		Horizontal shell-and-tube			
Quantity		1 (one)			
Duty [kW]		1620			
Log-mean temperature difference [K]		30			
Temperature correction factor, F _T [-]		0.91			
Overall heat transfer coefficient [W.m ⁻² .K ⁻¹]		600			
Heat transfer area [m ²]		100			
PROCESS DETAILS					
		Tube-side		Shell-side	
Fluid description		Stage 1 recirculant		Recirculated cooling water	
Fluid composition [%(kg.kg ⁻¹):					
Water		45.0		100	
Formaldehyde		54.0		-	
Other (including methanol)		1.0		trace	
Flowrate [kg.s ⁻¹]		29.7		25.9	
		In	Out	In	Out
Vapour fraction		0	0	0	0
Temperature [°C]		75	60	30	45
Pressure [kPa(abs)]		240	200	400	360
Density [kg.m ⁻³]		1150	1150	1000	1000
MECHANICAL DATA					
Maximum design pressure [kPa(abs)]		450			
Minimum design pressure [kPa(g)]		-5			
Maximum design temperature [°C]		170			
Minimum design temperature [°C]		ambient / 10			
TYPE OF CONSTRUCTION					
Front end head type (TEMA code)		Channel integral with tube-sheet and removable cover (C)			
Shell type (TEMA code)		One pass shell (E)			
Rear end head type (TEMA code)		Outside-packed floating-head (P)			
Number of tube passes		1 (one)			
		Tube-side		Shell-side	
Inlet branch nominal diameter [mm]		152		152	
Outlet branch nominal diameter [mm]		152		152	
Connection type		Socket welding flanges			
SUPPORT					
Type of support structure		Saddles			
INSULATION					
Thickness [mm]		0			
Extent of coverage		-			
MATERIALS OF CONSTRUCTION					
Shell and branches		Type 316SS			
Lining		None			
Insulation		None			
Cladding on insulation		-			
Channels		Type 316SS			
Tube-sheet		Type 316SS			
Tubes		Type 316SS			
NOTES					
Co-current flow.					
One (1) drain and one (1) vent connection are present on each of the shell side and channels, at the lowest and highest points respectively - in accordance with BS3274(1960).					
REVISION: "A"					
Designed: David Verrelli		Checked:		Authorised: —	
Date: 23/09/1999		Date:		Date: —	

SPECIFICATION SHEET:		HEAT EXCHANGER			
Equipment item		HX-9			
Description		Economiser (Radiant section of RXN-3)			
Type	Fired boiler (radiant section)				
Quantity	1 (one)				
Duty [kW]	1478				
Log-mean temperature difference [K]	685				
Temperature correction factor, F _T [-]	N/A				
Overall heat transfer coefficient [W.m ⁻² .K ⁻¹]	N/A				
Heat transfer area [m ²]	109				
PROCESS DETAILS					
Fluid description		Tube-side		Shell-side	
		Steam circuit		Combusted off-gas	
Fluid composition [% (kg.kg ⁻¹):		-		trace	
Methanol		-		trace	
Formaldehyde		-		1.4	
Oxygen		100		12.9	
Water		-		80.0	
Nitrogen		trace		5.7	
Other (including CO ₂)					
Flowrate [kg.s ⁻¹]		21.2		4.6	
		In	Out	In	Out
Vapour fraction		1	0.10	1	1
Temperature [°C]		188	188	1000	760
Pressure [kPa(abs)]		1300	1250	110	106
Density [kg.m ⁻³]					
MECHANICAL DATA					
Maximum design pressure [kPa(abs)]		1350			
Minimum design pressure [kPa(g)]		-10			
Maximum design temperature [°C]		1100			
Minimum design temperature [°C]		ambient / 10			
TYPE OF CONSTRUCTION					
Front end head type (TEMA code)		Bonnet [integral cover] (B)			
Shell type (TEMA code)		One pass shell (E)			
Rear end head type (TEMA code)		To stack (-)			
Number of tube passes		1 (one)			
		Tube-side		Shell-side	
Inlet branch nominal diameter [mm]					
Outlet branch nominal diameter [mm]					
Connection type		Socket welding flanges			
SUPPORT					
Type of support structure					
INSULATION					
Thickness [mm]					
Extent of coverage		Complete			
MATERIALS OF CONSTRUCTION					
Shell and branches		Type 316SS			
Lining		Insulated firebrick			
Insulation		Fibreglass blanket			
Cladding on insulation					
Channels		N/A			
Tube-sheet		N/A			
Tubes		Type 316SS			
NOTES					
One (1) drain and one (1) vent connection are present on each of the shell side and channels, at the lowest and highest points respectively - in accordance with BS3274(1960). Safety relief valves are also present.					
REVISION: "C"					
Designed: Michael Whiteman		Revised: David Verrelli		Authorised: —	
Date: 07/10/1999		Date: 09/10/1999		Date: —	

SPECIFICATION SHEET:		HEAT EXCHANGER			
Equipment item		HX-10			
Description		Methanol recycle heater			
Type		Vertical shell-and-tube			
Quantity		1 (one)			
Duty [kW]		1353			
Log-mean temperature difference [K]		108			
Temperature correction factor, F _T [-]		1.00			
Overall heat transfer coefficient [W.m ⁻² .K ⁻¹]		1000			
Heat transfer area [m ²]		13			
PROCESS DETAILS					
Fluid description		Tube-side Aqueous methanol		Shell-side Steam circuit	
Fluid composition [(kg.kg ⁻¹)]:		Methanol	31.5	-	
		Water	68.5	100	
		Other	trace	trace	
Flowrate [kg.s ⁻¹]		23.9		0.68	
Vapour fraction		In	Out	In	Out
Temperature [°C]		0	0	1	0
Pressure [kPa(abs)]		73	87	188	187
Density [kg.m ⁻³]		185	185	1200	1185
MECHANICAL DATA					
Maximum design pressure [kPa(abs)]		1300			
Minimum design pressure [kPa(g)]		-5			
Maximum design temperature [°C]		250			
Minimum design temperature [°C]		ambient / 10			
TYPE OF CONSTRUCTION					
Front end head type (TEMA code)		Bonnet [integral cover] (B)			
Shell type (TEMA code)		One pass shell (E)			
Rear end head type (TEMA code)		Fixed tubesheet [like "B" stationary head] (M)			
Number of tube passes		1 (one)			
Inlet branch nominal diameter [mm]		Tube-side		Shell-side	
Outlet branch nominal diameter [mm]					
Connection type		Socket welding flanges			
SUPPORT					
Type of support structure					
INSULATION					
Thickness [mm]					
Extent of coverage		Complete			
MATERIALS OF CONSTRUCTION					
Shell and branches		Type 316SS			
Lining		None			
Insulation		Fibreglass blanket			
Cladding on insulation					
Channels		Type 316SS			
Tube-sheet		Type 316SS			
Tubes		Type 316SS			
NOTES					
One (1) drain and one (1) vent connection are present on each of the shell side and channels, at the lowest and highest points respectively - in accordance with BS3274(1960).					
REVISION: "B"					
Designed: David Verrelli		Checked: David Verrelli		Authorised: —	
Date: 06/10/1999		Date: 09/10/1999		Date: —	

SPECIFICATION SHEET:		HEAT EXCHANGER				
Equipment item		HX-11				
Description		Serpentine cooling coil				
Type		Serpentine cooling coil				
Quantity		1 (one) - see Notes				
Duty [kW]		153				
Log-mean temperature difference [K]		7				
Temperature correction factor, F _T [-]		1.00				
Overall heat transfer coefficient [W.m ⁻² .K ⁻¹]		1000				
Heat transfer area [m ²]		21				
PROCESS DETAILS						
Fluid description		"Shell"-side		Tube-side		
		Stage 4 process fluid		Recirculated cooling water		
Fluid composition [%(kg.kg ⁻¹)]:		In	Out	In	Out	
		Water	100.0	84	100	100
		Formaldehyde	0.0	15	-	-
Other (including methanol)		0.0	trace	trace	trace	
Flowrate [kg.s ⁻¹]		0.33	0.40	7.32	7.32	
Vapour fraction		In	Out	In	Out	
Temperature [°C]		0	0	0	0	
Pressure [kPa(abs)]		37	42	30	35	
Density [kg.m ⁻³]		110	124	143	103	
		1000	1000	1000	1000	
MECHANICAL DATA						
Maximum design pressure [kPa(abs)]				200		
Minimum design pressure [kPa(g)]				-5		
Maximum design temperature [°C]				170		
Minimum design temperature [°C]				ambient / 10		
TYPE OF CONSTRUCTION						
Front end head type (TEMA code)				N/A		
Shell type (TEMA code)				N/A		
Rear end head type (TEMA code)				N/A		
Number of tube passes				1 (one)		
Inlet branch nominal diameter [mm]		Tube-side		Shell-side		
		25		N/A		
		25		N/A		
Outlet branch nominal diameter [mm]						
Connection type		Socket welding flanges				
SUPPORT						
Type of support structure		None (rests directly on bubble-cap tray)				
INSULATION						
Thickness [mm]		0				
Extent of coverage		-				
MATERIALS OF CONSTRUCTION						
Shell and branches		N/A				
Lining		None				
Insulation		None				
Cladding on insulation		-				
Channels		N/A				
Tube-sheet		N/A				
Tubes		Type 316SS				
NOTES						
Although only one unit is specified, the duty is split between seven (7) trays in each of three (3) sections in stage 4 of the absorber (ABS-1).						
No one flow or composition can be given for the process fluid in stage 4 of the absorber, because two phases are present and both vary – see the specification of item ABS-1.						
REVISION: "A"						
Designed: David Verrelli		Checked:		Authorised: —		
Date: 02/10/1999		Date:		Date: —		

SPECIFICATION SHEET:		PUMP	
Equipment item		P-1	
Description		Methanol feed pump	
Type	Centrifugal		
Quantity	2 (two) - see Notes		
Duty [kW]	0.32		
PROCESS DETAILS			
Fluid description	Boiler feed water		
Fluid composition [% (kg.kg ⁻¹)]:	Methanol	100	
	Other	trace	
Mass flowrate [kg.s ⁻¹]		1.74	
Volumetric flowrate [m ³ .h ⁻¹]		7.93	
Temperature [°C]	Suction		Delivery
Pressure [kPa(abs)]	37		37
	110		185
Total delivered head, "TDH" [m]		9.7	
POWER			
Pump efficiency [%]		70	
Drive type		Electric	
Motor type	T.E.F.C., 50Hz, flange-mounted, 2 pole		
Motor efficiency [%]		80	
Motor power [kW]		0.50	
MECHANICAL DATA			
Maximum design pressure [kPa(abs)]		220	
Minimum design pressure [kPa(g)]		-5	
Maximum design temperature [°C]		100	
Minimum design temperature [°C]		ambient / 10	
Branch nominal diameter [mm]	Suction		Delivery
	38		38
Connection type	Socket welding flanges		
MATERIALS OF CONSTRUCTION			
Casing	Type 316SS		
Lining	None		
Impellor	Type 316SS		
NOTES			
One spare pump is required to be on stand-by for continued operation: this sheet applies to BOTH.			
T.E.F.C. = Totally-enclosed, fan-cooled.			
Provision of pressure let-down valve is included in specification of unit.			
REVISION:	"B"		
Designed:	Sasha Trandafilovic	Revised:	David Verrelli
Date:	10/01/1999 [sic!]	Date:	30/09/1999
		Authorised:	—
		Date:	—

SPECIFICATION SHEET:		PUMP	
Equipment item		P-2	
Description		Vaporiser recycle pump	
Type	Centrifugal		
Quantity	2 (two) - see Notes		
Duty [kW]	2.55		
PROCESS DETAILS			
Fluid description	Boiler feed water		
Fluid composition [% (kg.kg ⁻¹):	Methanol	32	
	Water	68	
	Other	trace	
Mass flowrate [kg.s ⁻¹]	23.9		
Volumetric flowrate [m ³ .h ⁻¹]	96.0		
Temperature [°C]	Suction	62	Delivery
Pressure [kPa(abs)]	185		62
Total delivered head, "TDH" [m]	7.1		
POWER			
Pump efficiency [%]	70		
Drive type	Electric		
Motor type	T.E.F.C., 50Hz, foot-mounted, 2 pole		
Motor efficiency [%]	80		
Motor power [kW]	3.5		
MECHANICAL DATA			
Maximum design pressure [kPa(abs)]	300		
Minimum design pressure [kPa(g)]	-5		
Maximum design temperature [°C]	100		
Minimum design temperature [°C]	ambient / 10		
Branch nominal diameter [mm]	Suction	203	Delivery
Connection type	Socket welding flanges		
MATERIALS OF CONSTRUCTION			
Casing	Type 316SS		
Lining	None		
Impellor	Type 316SS		
NOTES			
One spare pump is required to be on stand-by for continued operation: this sheet applies to BOTH.			
T.E.F.C. = Totally-enclosed, fan-cooled.			
Provision of pressure let-down valve is included in specification of unit.			
REVISION:	"B"		
Designed:	Sasha Trandafilovic	Revised:	David Verrelli
Date:	10/01/1999 [sic!]	Date:	30/09/1999
		Authorised:	—
		Date:	—

SPECIFICATION SHEET:		PUMP	
Equipment item		P-3	
Description		Boiler feed water pump	
Type	Centrifugal		
Quantity	2 (two) - see Notes		
Duty [kW]	0.22		
PROCESS DETAILS			
Fluid description	Boiler feed water		
Fluid composition [% (kg.kg ⁻¹):	Water	100.0	
Mass flowrate [kg.s ⁻¹]		1.09	
Volumetric flowrate [m ³ .h ⁻¹]		3.91	
	Suction	Delivery	
Temperature [°C]	100	100	
Pressure [kPa(abs)]	400	500	
Total delivered head, "TDH" [m]	10.2		
POWER			
Pump efficiency [%]	50		
Drive type	Electric		
Motor type	T.E.F.C., 50Hz, flange-mounted, 2 pole		
Motor efficiency [%]	80		
Motor power [kW]	0.35		
MECHANICAL DATA			
Maximum design pressure [kPa(abs)]	550		
Minimum design pressure [kPa(g)]	-5		
Maximum design temperature [°C]	170		
Minimum design temperature [°C]	ambient / 10		
	Suction	Delivery	
Branch nominal diameter [mm]	25	25	
Connection type	Socket welding flanges		
MATERIALS OF CONSTRUCTION			
Casing	Type 316SS		
Lining	None		
Impellor	Type 316SS		
NOTES			
One spare pump is required to be on stand-by for safety purposes: this sheet applies to BOTH.			
T.E.F.C. = Totally-enclosed, fan-cooled.			
Provision of pressure let-down valve is included in specification of unit.			
REVISION:	"B"		
Designed:	David Verrelli	Checked:	Trandafilovic, Weldon
Date:	30/09/1999	Date:	30/09/1999
		Authorised:	—
		Date:	—

SPECIFICATION SHEET:		PUMP	
Equipment item		P-4A	
Description		Stage 1 recirculation pump	
Type		Centrifugal	
Quantity		1 (one) - see Notes	
Duty [kW]		2.07	
PROCESS DETAILS			
Fluid description		Stage 1 recirculant	
Fluid composition [(kg.kg ⁻¹):		45.0	
Water		54.0	
Formaldehyde		1.0	
Other (including methanol)			
Mass flowrate [kg.s ⁻¹]		29.7	
Volumetric flowrate [m ³ .h ⁻¹]		93	
		Suction	Delivery
Temperature [°C]		75	75
Pressure [kPa(abs)]		200	240
Total delivered head, "TDH" [m]		3.56	
POWER			
Pump efficiency [%]		50	
Drive type		Electric	
Motor type		T.E.F.C., 50Hz, foot-mounted, 2 pole	
Motor efficiency [%]		80	
Motor power [kW]		3.0	
MECHANICAL DATA			
Maximum design pressure [kPa(abs)]		290	
Minimum design pressure [kPa(g)]		-5	
Maximum design temperature [°C]		170	
Minimum design temperature [°C]		ambient / 10	
		Suction	Delivery
Branch nominal diameter [mm]		203	152
Connection type		Socket welding flanges	
MATERIALS OF CONSTRUCTION			
Casing		Type 316SS	
Lining		None	
Impellor		Type 316SS	
NOTES			
Installation is configured such that P-4B may act as a stand-by for either of P-4A xor P-6.			
T.E.F.C. = Totally-enclosed, fan-cooled.			
Provision of pressure let-down valve is included in specification of unit.			
REVISION: "B"			
Designed: David Verrelli		Checked: David Verrelli	Authorised: —
Date: 23/09/1999		Date: 24/09/1999	Date: —

SPECIFICATION SHEET:		PUMP		
Equipment item	P-4B			
Description	Absorber stand-by pump (for P-4A xor P-6)			
Type	Centrifugal			
Quantity	1 (one) - see Notes			
Duty [kW]	3.00			
PROCESS DETAILS				
Fluid description	Stage 1 recirculant	Stage 2 recirculant		
Fluid composition [% (kg.kg ⁻¹):	Water	45.0	70.6	
	Formaldehyde	54.0	28.9	
	Other (including methanol)	1.0	0.5	
Mass flowrate [kg.s ⁻¹]	29.7	41.2		
Volumetric flowrate [m ³ .h ⁻¹]	93	135		
	Stage 1 recirculant	Stage 2 recirculant		
	Suction	Delivery	Suction	Delivery
Temperature [°C]	75	75	63	63
Pressure [kPa(abs)]	200	240	240	280
Total delivered head, "TDH" [m]	3.56		3.72	
POWER				
Pump efficiency [%]	50			
Drive type	Electric			
Motor type	T.E.F.C., 50Hz, foot-mounted, 2 pole			
Motor efficiency [%]	80			
Motor power [kW]	4.5			
MECHANICAL DATA				
Maximum design pressure [kPa(abs)]	330			
Minimum design pressure [kPa(g)]	-5			
Maximum design temperature [°C]	170			
Minimum design temperature [°C]	ambient / 10			
	Suction	Delivery		
Branch nominal diameter [mm]	229	178		
Connection type	Socket welding flanges			
MATERIALS OF CONSTRUCTION				
Casing	Type 316SS			
Lining	None			
Impellor	Type 316SS			
NOTES				
Installation is configured such that P-4B may act as a stand-by for either of P-4A xor P-6.				
T.E.F.C. = Totally-enclosed, fan-cooled.				
Provision of pressure let-down valve is included in specification of unit.				
REVISION: "B"				
Designed: David Verrelli	Checked: David Verrelli	Authorised: —		
Date: 24/09/1999	Date: 05/10/1999	Date: —		

SPECIFICATION SHEET:		PUMP	
Equipment item		P-5	
Description		Boiler feed water pump	
Type	Centrifugal		
Quantity	2 (two) - see Notes		
Duty [kW]	2.76		
PROCESS DETAILS			
Fluid description	Boiler feed water		
Fluid composition [% (kg.kg ⁻¹):	Water	100.0	
Mass flowrate [kg.s ⁻¹]		1.7	
Volumetric flowrate [m ³ .h ⁻¹]		6.2	
	Suction	Delivery	
Temperature [°C]	100	100	
Pressure [kPa(abs)]	400	1200	
Total delivered head, "TDH" [m]		82	
POWER			
Pump efficiency [%]	50		
Drive type	Electric		
Motor type	T.E.F.C., 50Hz, foot-mounted, 2 pole		
Motor efficiency [%]	80		
Motor power [kW]	4.0		
MECHANICAL DATA			
Maximum design pressure [kPa(abs)]	1300		
Minimum design pressure [kPa(g)]	-10		
Maximum design temperature [°C]	250		
Minimum design temperature [°C]	ambient / 10		
	Suction	Delivery	
Branch nominal diameter [mm]	51	38	
Connection type	Socket welding flanges		
MATERIALS OF CONSTRUCTION			
Casing	Type 316SS		
Lining	None		
Impellor	Type 316SS		
NOTES			
One spare pump is required to be on stand-by for safety purposes: this sheet applies to BOTH.			
T.E.F.C. = Totally-enclosed, fan-cooled.			
Provision of pressure let-down valve is included in specification of unit.			
REVISION:	"A"		
Designed:	David Verrelli	Checked:	Sasha Trandafilovic
Date:	30/09/1999	Date:	10/01/1999 [sic!]
		Authorised:	—
		Date:	—

SPECIFICATION SHEET:		PUMP	
Equipment item		P-6	
Description		Stage 2 recirculation pump	
Type		Centrifugal	
Quantity		1 (one) - see Notes	
Duty [kW]		3.00	
PROCESS DETAILS			
Fluid description		Stage 2 recirculant	
Fluid composition [(kg.kg ⁻¹):		Water	
		70.6	
		Formaldehyde	
		28.9	
		Other (including methanol)	
		0.5	
Mass flowrate [kg.s ⁻¹]		41.2	
Volumetric flowrate [m ³ .h ⁻¹]		135	
		Suction	Delivery
Temperature [°C]		63	63
Pressure [kPa(abs)]		240	280
Total delivered head, "TDH" [m]		3.72	
POWER			
Pump efficiency [%]		50	
Drive type		Electric	
Motor type		T.E.F.C., 50Hz, foot-mounted, 2 pole	
Motor efficiency [%]		80	
Motor power [kW]		4.5	
MECHANICAL DATA			
Maximum design pressure [kPa(abs)]		330	
Minimum design pressure [kPa(g)]		-5	
Maximum design temperature [°C]		150	
Minimum design temperature [°C]		ambient / 10	
		Suction	Delivery
Branch nominal diameter [mm]		229	178
Connection type		Socket welding flanges	
MATERIALS OF CONSTRUCTION			
Casing		Type 316SS	
Lining		None	
Impellor		Type 316SS	
NOTES			
Installation is configured such that P-4B may act as a stand-by for either of P-4A xor P-6.			
T.E.F.C. = Totally-enclosed, fan-cooled.			
Provision of pressure let-down valve is included in specification of unit.			
REVISION: "A"			
Designed: David Verrelli		Checked:	Authorised: —
Date: 24/09/1999		Date:	Date: —

SPECIFICATION SHEET:		PUMP	
Equipment item		P-7	
Description		Stage 3 recirculation pump	
Type	Centrifugal		
Quantity	1 (one) - see Notes		
Duty [kW]	1.00		
PROCESS DETAILS			
Fluid description		Stage 3 recirculant	
Fluid composition [% (kg.kg ⁻¹):			
Water		79.8	
Formaldehyde		19.9	
Other (including methanol)		0.3	
Mass flowrate [kg.s ⁻¹]		13.7	
Volumetric flowrate [m ³ .h ⁻¹]		47	
Temperature [°C]		Suction	Delivery
Pressure [kPa(abs)]		51	51
Total delivered head, "TDH" [m]		265	305
		3.90	
POWER			
Pump efficiency [%]		50	
Drive type		Electric	
Motor type		T.E.F.C., 50Hz, foot-mounted, 2 pole	
Motor efficiency [%]		80	
Motor power [kW]		1.5	
MECHANICAL DATA			
Maximum design pressure [kPa(abs)]		350	
Minimum design pressure [kPa(g)]		-5	
Maximum design temperature [°C]		150	
Minimum design temperature [°C]		ambient / 10	
Branch nominal diameter [mm]		Suction	Delivery
Connection type		152	102
		Socket welding flanges	
MATERIALS OF CONSTRUCTION			
Casing		Type 316SS	
Lining		None	
Impellor		Type 316SS	
NOTES			
This pump is not critical; extra cooling can be achieved in the lower stages if necessary.			
T.E.F.C. = Totally-enclosed, fan-cooled.			
Provision of pressure let-down valve is included in specification of unit.			
REVISION: "A"			
Designed: David Verrelli	Checked:	Authorised: —	
Date: 24/09/1999	Date:	Date: —	

SPECIFICATION SHEET:		PUMP	
Equipment item		P-8	
Description		Stage 4 coolant pump	
Type	Centrifugal		
Quantity	1 (one) - see Notes		
Duty [kW]	1.30		
PROCESS DETAILS			
Fluid description		Recirculated cooling water to stage 4	
Fluid composition [% (kg.kg ⁻¹):			
Water		100	
Formaldehyde		-	
Other (including methanol)		trace	
Mass flowrate [kg.s ⁻¹]		7.32	
Volumetric flowrate [m ³ .h ⁻¹]		26.4	
Temperature [°C]		Suction 30	Delivery 30
Pressure [kPa(abs)]		400	525
Total delivered head, "TDH" [m]		12.78	
POWER			
Pump efficiency [%]		70	
Drive type		Electric	
Motor type		T.E.F.C., 50Hz, foot-mounted, 2 pole	
Motor efficiency [%]		80	
Motor power [kW]		2.0	
MECHANICAL DATA			
Maximum design pressure [kPa(abs)]		580	
Minimum design pressure [kPa(g)]		-5	
Maximum design temperature [°C]		100	
Minimum design temperature [°C]		ambient / 10	
Branch nominal diameter [mm]		Suction 102	Delivery 76
Connection type		Socket welding flanges	
MATERIALS OF CONSTRUCTION			
Casing		Type 316SS	
Lining		None	
Impellor		Type 316SS	
NOTES			
This pump is not critical; extra cooling can be achieved in the lower stages if necessary. T.E.F.C. = Totally-enclosed, fan-cooled.			
REVISION: "C"			
Designed: David Verrelli	Checked: David Verrelli	Authorised: —	
Date: 24/09/1999	Date: 24/09/1999	Date: —	

SPECIFICATION SHEET:		PUMP	
Equipment item		P-9	
Description		Boiler feed water pump	
Type	Centrifugal		
Quantity	2 (two) - see Notes		
Duty [kW]	0.32		
PROCESS DETAILS			
Fluid description	Boiler feed water		
Fluid composition [% (kg.kg ⁻¹):	Water	100.0	
Mass flowrate [kg.s ⁻¹]		1.63	
Volumetric flowrate [m ³ .h ⁻¹]		5.86	
	Suction	Delivery	
Temperature [°C]	100	100	
Pressure [kPa(abs)]	400	500	
Total delivered head, "TDH" [m]	10.2		
POWER			
Pump efficiency [%]	50		
Drive type	Electric		
Motor type	T.E.F.C., 50Hz, flange-mounted, 2 pole		
Motor efficiency [%]	80		
Motor power [kW]	0.50		
MECHANICAL DATA			
Maximum design pressure [kPa(abs)]	550		
Minimum design pressure [kPa(g)]	-5		
Maximum design temperature [°C]	170		
Minimum design temperature [°C]	ambient / 10		
	Suction	Delivery	
Branch nominal diameter [mm]	38	38	
Connection type	Socket welding flanges		
MATERIALS OF CONSTRUCTION			
Casing	Type 316SS		
Lining	None		
Impellor	Type 316SS		
NOTES			
One spare pump is required to be on stand-by for safety purposes: this sheet applies to BOTH.			
T.E.F.C. = Totally-enclosed, fan-cooled.			
Provision of pressure let-down valve is included in specification of unit.			
REVISION:	"B"		
Designed:	David Verrelli	Checked:	Trandafilovic, Weldon
Date:	30/09/1999	Date:	30/09/1999
		Authorised:	—
		Date:	—

SPECIFICATION SHEET:		PUMP	
Equipment item		P-10	
Description		Absorber water pump	
Type		Centrifugal	
Quantity		1 (one) - see Notes	
Duty [kW]		0.05	
PROCESS DETAILS			
Fluid description		Demineralised water feed to absorber	
Fluid composition [% (kg.kg ⁻¹):		Water 100	
		Formaldehyde -	
		Other (including methanol) -	
Mass flowrate [kg.s ⁻¹]		0.328	
Volumetric flowrate [m ³ .h ⁻¹]		1.18	
Temperature [°C]		Suction 37	Delivery 37
Pressure [kPa(abs)]		400	495
Total delivered head, "TDH" [m]		9.71	
POWER			
Pump efficiency [%]		60	
Drive type		Electric	
Motor type		T.E.F.C., 50Hz, flange-mounted, 2 pole	
Motor efficiency [%]		80	
Motor power [kW]		0.10	
MECHANICAL DATA			
Maximum design pressure [kPa(abs)]		545	
Minimum design pressure [kPa(g)]		-5	
Maximum design temperature [°C]		100	
Minimum design temperature [°C]		ambient / 10	
Branch nominal diameter [mm]		Suction 19	Delivery 19
Connection type		Socket welding flanges	
MATERIALS OF CONSTRUCTION			
Casing		Type 316SS	
Lining		None	
Impellor		Type 316SS	
NOTES			
Although this is a critical pump to have running, it is small enough for 1 (one) SPARE to be kept ON-SITE, without necessitating the extra pipework of parallel installation.			
T.E.F.C. = Totally-enclosed, fan-cooled.			
REVISION: "A"			
Designed: David Verrelli		Checked:	Authorised: —
Date: 24/09/1999		Date:	Date: —

SPECIFICATION SHEET:		REACTOR	
Equipment item		RXN-1	
Description		Methanol converter	
Quantity		1 (one)	
Type		Catalytic	
PROCESS DETAILS			
Fluid description		Inlet	Outlet
Fluid composition [% (kg.kg ⁻¹)]:		Process Gas	Process Gas
Methanol		22.0	0.3
Formaldehyde		trace	18.1
Oxygen		9.2	0.1
Water		6.3	15.4
Other (including nitrogen)		62.5	66.2
Mass flow [kg.s ⁻¹]		3.16	3.16
Vapour fraction		1	1
Temperature [°C]		158	700
Pressure [kPa(abs)]		170	160
Density [kg.m ⁻³]		1.2186	0.4854
CATALYST DETAILS			
"Duty" [t(CH ₃ OH).h ⁻¹ .m ⁻²]		2	
Area of catalyst bed [m ²]		1.36	
Catalyst bed height [mm]		40	
Residence time [s]		0.02	
Type of catalyst		0.187 part silver granule	
Catalyst support		Copper gauze	
BED ARRANGMENT			
Number of catalyst layers		5	
Particle size distribution		Particle size [mm]	Proportion [% (kg.kg ⁻¹)]
Layer 1		0.6	12.9
Layer 2		0.3	1.2
Layer 3		0.85	5.3
Layer 4		1.5	14.1
Layer 5		2	66.5
MECHANICAL DETAILS			
Maximum design pressure [kPa(abs)]		190	
Minimum design pressure [kPa(g)]		-5	
Maximum design temperature [°C]		750	
Minimum design temperature [°C]		ambient / 10	
Height [mm]		300	
Diameter [mm]		1300	
Wall thickness [mm]		15	
Head Type		Torispherical	
Branch nominal diameter [mm]		Inlet	Outlet
		508	635
Vent		Directly-actuated safety valve	
Emergency vent		Bursting disc	
Internals		Gas distributor and catalyst	
Insulation thickness [mm]		75	
MATERIAL OF CONSTRUCTION			
Shell and branches		Type 316SS	
Insulation		Basic Oxygen Steelmaking (BOS) furnace-brick lining	
REVISION: "E"			
Designed: Rachel Weldon		Revised: David Verrelli	Authorised: —
Date: 14/09/1999		Date: 30/09/1999	Date: —

SPECIFICATION SHEET:		REACTOR	
Equipment item		RXN-2	
Description		Methanol converter	
Quantity		1 (one)	
Type		Catalytic	
PROCESS DETAILS			
Fluid description		Inlet Process Gas	Outlet Process Gas
Fluid composition [% (kg.kg ⁻¹)]:		Methanol	22.0
		Formaldehyde	trace
		Oxygen	9.2
		Water	6.3
Other (including nitrogen)		62.5	66.2
Mass flow [kg.s ⁻¹]		4.74	4.74
Vapour fraction		1	1
Temperature [°C]		158	700
Pressure [kPa(abs)]		170	160
Density [kg.m ⁻³]		1.2186	0.4854
CATALYST DETAILS			
"Duty" [t(CH ₃ OH).h ⁻¹ .m ⁻²]		2	
Area of catalyst bed [m ²]		2.04	
Catalyst bed height [mm]		40	
Residence time [s]		0.02	
Type of catalyst		0.187 part silver granule	
Catalyst support		Copper gauze	
BED ARRANGMENT			
Number of catalyst layers		5	
Particle size distribution		Particle size [mm]	Proportion [% (kg.kg ⁻¹)]
Layer 1		0.6	12.9
Layer 2		0.3	1.2
Layer 3		0.85	5.3
Layer 4		1.5	14.1
Layer 5		2	66.5
MECHANICAL DETAILS			
Maximum design pressure [kPa(abs)]		190	
Minimum design pressure [kPa(g)]		-5	
Maximum design temperature [°C]		750	
Minimum design temperature [°C]		ambient / 10	
Height [mm]		300	
Diameter [mm]		1600	
Wall thickness [mm]		15	
Head Type		Torispherical	
Branch nominal diameter [mm]		Inlet 610	Outlet 762
Vent		Directly-actuated safety valve	
Emergency vent		Bursting disc	
Internals		Gas distributor and catalyst	
Insulation thickness [mm]		75	
MATERIAL OF CONSTRUCTION			
Shell and branches		Type 316SS	
Insulation		Basic Oxygen Steelmaking (BOS) furnace-brick lining	
REVISION: "E"			
Designed: Rachel Weldon		Revised: David Verrelli	Authorised: —
Date: 14/09/1999		Date: 30/09/1999	Date: —

SPECIFICATION SHEET:		HEAT EXCHANGER			
Equipment item		RXN-3			
Description		Tail-gas burner			
Type	Fired boiler (convective section + shield bank)				
Quantity	1 (one)				
		Convective section		Shield bank	
Duty [kW]		1866		251	
Log-mean temperature difference [K]		239		466	
Temperature correction factor, F _T [-]		~1		~1	
Overall heat transfer coefficient [W.m ⁻² .K ⁻¹]		36.5		98	
Heat transfer area [m ²]		116		3.3	
PROCESS DETAILS					
Fluid description		Tube-side Steam circuit		Shell-side Combusted off-gas	
Fluid composition [(kg.kg ⁻¹):					
	Methanol	-		trace	
	Formaldehyde	-		trace	
	Oxygen	-		1.4	
	Water	100		12.9	
	Nitrogen	-		80.0	
	Other (including CO ₂)	trace		5.7	
Flowrate [kg.s ⁻¹]		1.7		4.6	
		In	Out	In	Out
Vapour fraction		1	0.15	1	1
Temperature [°C]		100	188	616	240
Pressure [kPa(abs)]		1250	1200	106	102
Density [kg.m ⁻³]					
MECHANICAL DATA					
Maximum design pressure [kPa(abs)]				1350	
Minimum design pressure [kPa(g)]				-10	
Maximum design temperature [°C]				1000	
Minimum design temperature [°C]				ambient / 10	
TYPE OF CONSTRUCTION					
Front end head type (TEMA code)		Bonnet [integral cover] (B)			
Shell type (TEMA code)		One pass shell (E)			
Rear end head type (TEMA code)		To stack (-)			
		Convective section		Shield bank	
Number of tube passes		24		16	
		Tube-side		Shell-side	
Inlet branch nominal diameter [mm]					
Outlet branch nominal diameter [mm]					
Connection type		Socket welding flanges			
SUPPORT					
Type of support structure		Scaffolding			
INSULATION					
Thickness [mm]					
Extent of coverage		Complete			
MATERIALS OF CONSTRUCTION					
Shell and branches		Type 316SS			
Lining		Insulated firebrick			
Insulation		Fibreglass blanket			
Cladding on insulation					
Channels		N/A			
Tube-sheet		N/A			
Tubes		Type 316SS			
NOTES					
One (1) drain and one (1) vent connection are present on each of the shell side and channels, at the lowest and highest points respectively - in accordance with BS3274(1960). Safety relief valves are also present.					
REVISION:		"C"			
Designed:	Michael Whiteman	Revised:	David Verrelli	Authorised:	—
Date:	07/10/1999	Date:	09/10/1999	Date:	—

SPECIFICATION SHEET:		LARGE VESSEL	
Equipment item	ST-1		
Description	Methanol feed storage		
Type	Closed		
Quantity	1 (one)		
Volume [m ³]	190		
PROCESS DETAILS			
Fluid description	Inlet	Outlet	
Fluid composition [(kg.kg ⁻¹):	Methanol feed	Methanol feed	
Methanol	100	100	
Other	trace	trace	
Vapour fraction	0	0	
Temperature [°C]	37	37	
Pressure [kPa(abs)]	110	110	
Density [kg.m ⁻³]	791	791	
Mean flowrate [kg.s ⁻¹]	1.74	1.74	
MECHANICAL DATA			
Maximum design pressure [kPa(abs)]	250		
Minimum design pressure [kPa(g)]	-5		
Maximum design temperature [°C]	200		
Minimum design temperature [°C]	ambient / 10		
Height [mm]	5000		
Diameter [mm]	7000		
Branch nominal diameter [mm]	Inlet	Outlet	
Connection type	38	38	
	Socket welding flanges		
SUPPORT			
Type of support structure	Bolted to concrete slab foundation		
INSULATION			
Thickness [mm]	None		
Extent of coverage	-		
MATERIALS OF CONSTRUCTION			
Shell and branches	Type 316SS		
Lining	None		
Insulation	None		
NOTES			
One (1) drain and one (1) vent connection are present at the lowest and highest points. Keep away from possible ignition sources.			
REVISION: "C"			
Designed: Sasha Trandafilovic	Revised: David Verrelli	Authorised: —	
Date: 10/01/1999 [sic!]	Date: 02/10/1999	Date: —	

SPECIFICATION SHEET:		LARGE VESSEL				
Equipment item		ST-2				
Description		Grade B formaldehyde buffer tank				
Type		Closed				
Quantity		1 (one)				
Volume [m ³]		183				
PROCESS DETAILS						
		Inlet 1	Inlet 2	Inlet 3	Outlet	
Fluid description		Grade A	Methanol	Water	Grade B	
Fluid composition [(kg.kg ⁻¹):		Formaldehyde	54	0	0	37
		Methanol	1	100	0	7
		Water	45	0	100	56
Other (including formic acid)		trace	trace	trace	trace	trace
Vapour fraction		0	0	0	0	0
Temperature [°C] - see Notes		60	37	37	65	65
Pressure [kPa(abs)]		110	110	110	110	110
Density [kg.m ⁻³]		1100	790	1000	1100	1100
Mean flowrate [kg.s ⁻¹]		0.187	0.017	0.069	0.273	0.273
MECHANICAL DATA						
Maximum design pressure [kPa(abs)]			250			
Minimum design pressure [kPa(g)]			-5			
Maximum design temperature [°C]			200			
Minimum design temperature [°C]			ambient / 10			
Height [mm]			5700			
Diameter [mm]			6400			
		Inlet 1	Inlet 2	Inlet 3	Outlet	
Branch nominal diameter [mm]		25	13	13	25	
Connection type		Socket welding flanges				
SUPPORT						
Type of support structure		Bolted to concrete slab foundation				
AGITATOR						
Type		Turbine pitched blade impeller				
W/D ratio		1/8				
Process requirements		10 minutes mixing per hour				
Required power output [kW]						
Mixing speed [rev.min ⁻¹]						
HEATING COIL						
Duty [kW]		2.7				
INSULATION						
Thickness [mm]		75				
Extent of coverage		Complete				
MATERIALS OF CONSTRUCTION						
Shell and branches		Type 316SS				
Lining		None				
Insulation		Mineral wool				
NOTES						
One (1) drain and one (1) vent connection are present at the lowest and highest points.						
Keep away from possible ignition sources.						
Must be well-agitated and insulated at 65 ± 5°C.						
REVISION:		"E"				
Designed: Sasha Trandafilovic		Revised: David Verrelli		Authorised: —		
Date: 10/01/1999 [sic!]		Date: 02/10/1999		Date: —		

SPECIFICATION SHEET:		LARGE VESSEL	
Equipment item		ST-3	
Description		Grade B formaldehyde storage tank	
Type		Closed	
Quantity		2 (two) - see Notes	
Volume [m³]		330	
PROCESS DETAILS			
Fluid description		Inlet 1 Grade B	Outlet Grade B
Fluid composition [(kg.kg⁻¹)]:	Formaldehyde	37	37
	Methanol	7	7
	Water	56	56
	Other (including formic acid)	trace	trace
Vapour fraction		0	0
Temperature [°C] - see Notes		65	65
Pressure [kPa(abs)]		110	110
Density [kg.m⁻³]		1100	1100
Mean flowrate [kg.s⁻¹]		0.273	0.273
MECHANICAL DATA			
Maximum design pressure [kPa(abs)]		250	
Minimum design pressure [kPa(g)]		-5	
Maximum design temperature [°C]		200	
Minimum design temperature [°C]		ambient / 10	
Height [mm]		8600	
Diameter [mm]		7000	
Branch nominal diameter [mm]		Inlet 1 25	Outlet 25
Connection type		Socket welding flanges	
SUPPORT			
Type of support structure		Bolted to concrete slab foundation	
AGITATOR			
Type		Turbine pitched blade impeller	
W/D ratio		1/8	
Process requirements		10 minutes mixing per hour	
Required power output [kW]			
Mixing speed [rev.min⁻¹]			
HEATING COIL			
Duty [kW]		4	
INSULATION			
Thickness [mm]		75	
Extent of coverage		Complete	
MATERIALS OF CONSTRUCTION			
Shell and branches		Type 316SS	
Lining		None	
Insulation		Mineral wool	
NOTES			
One (1) drain and one (1) vent connection are present at the lowest and highest points.			
Keep away from possible ignition sources.			
Must be well-agitated and insulated at 65 ± 5°C.			
Two tanks provided as contingency for abnormal operation.			
REVISION: "B"			
Designed: Sasha Trandafilovic	Revised: David Verrelli	Authorised: —	
Date: 10/01/1999 [sic!]	Date: 02/10/1999	Date: —	

SPECIFICATION SHEET:		LARGE VESSEL				
Equipment item		ST-4				
Description		Grade A formaldehyde buffer tank				
Type		Closed				
Quantity		1 (one)				
Volume [m³]		507				
PROCESS DETAILS						
		Inlet 1	Inlet 2	Inlet 3	Outlet	
Fluid description		Grade A	Methanol	Water	Grade A	
Fluid composition [(kg.kg ⁻¹):		Formaldehyde	54	0	0	54
		Methanol	1	100	0	1
		Water	45	0	100	45
Other (including formic acid)		trace	trace	trace	trace	trace
Vapour fraction		0	0	0	0	0
Temperature [°C] - see Notes		60	37	37	65	65
Pressure [kPa(abs)]		110	110	110	110	110
Density [kg.m ⁻³]		1100	790	1000	1100	1100
Mean flowrate [kg.s ⁻¹] - see Notes		2.458	0.000	0.000	2.458	2.458
MECHANICAL DATA						
Maximum design pressure [kPa(abs)]			250			
Minimum design pressure [kPa(g)]			-5			
Maximum design temperature [°C]			200			
Minimum design temperature [°C]			ambient / 10			
Height [mm]			8000			
Diameter [mm]			9000			
		Inlet 1	Inlet 2	Inlet 3	Outlet	
Branch nominal diameter [mm]		38	13	13	51	
Connection type		Socket welding flanges				
SUPPORT						
Type of support structure		Bolted to concrete slab foundation				
AGITATOR						
Type		Turbine pitched blade impeller				
W/D ratio		1/8				
Process requirements		10 minutes mixing per hour				
Required power output [kW]						
Mixing speed [rev.min ⁻¹]						
HEATING COIL						
Duty [kW]		23				
INSULATION						
Thickness [mm]		75				
Extent of coverage		Complete				
MATERIALS OF CONSTRUCTION						
Shell and branches		Type 316SS				
Lining		None				
Insulation		Mineral wool				
NOTES						
One (1) drain and one (1) vent connection are present at the lowest and highest points.						
Keep away from possible ignition sources.						
Must be well-agitated and insulated at 65 ± 5°C.						
No methanol or water addition is required for normal operation and designated usage.						
REVISION:		"D"				
Designed: Sasha Trandafilovic		Revised: David Verrelli		Authorised: —		
Date: 10/01/1999 [sic!]		Date: 02/10/1999		Date: —		

SPECIFICATION SHEET:		LARGE VESSEL	
Equipment item		ST-5	
Description		Grade A formaldehyde storage tank	
Type		Closed	
Quantity		2 (two) - see Notes	
Volume [m³]		1120	
PROCESS DETAILS			
Fluid description		Inlet 1 Grade A	Outlet Grade A
Fluid composition [(kg.kg⁻¹)]:	Formaldehyde	54	54
	Methanol	1	1
	Water	45	45
	Other (including formic acid)	trace	trace
Vapour fraction		0	0
Temperature [°C] - see Notes		65	65
Pressure [kPa(abs)]		110	110
Density [kg.m⁻³]		1100	1100
Mean flowrate [kg.s⁻¹]		2.458	2.458
MECHANICAL DATA			
Maximum design pressure [kPa(abs)]		250	
Minimum design pressure [kPa(g)]		-5	
Maximum design temperature [°C]		200	
Minimum design temperature [°C]		ambient / 10	
Height [mm]		11800	
Diameter [mm]		11000	
		Inlet 1	Outlet
Branch nominal diameter [mm]		51	51
Connection type		Socket welding flanges	
SUPPORT			
Type of support structure		Bolted to concrete slab foundation	
AGITATOR			
Type		Turbine pitched blade impeller	
W/D ratio		1/8	
Process requirements		10 minutes mixing per hour	
Required power output [kW]			
Mixing speed [rev.min⁻¹]			
HEATING COIL			
Duty [kW]		4	
INSULATION			
Thickness [mm]		75	
Extent of coverage		Complete	
MATERIALS OF CONSTRUCTION			
Shell and branches		Type 316SS	
Lining		None	
Insulation		Mineral wool	
NOTES			
One (1) drain and one (1) vent connection are present at the lowest and highest points.			
Keep away from possible ignition sources.			
Must be well-agitated and insulated at 65 ± 5°C.			
Two tanks provided as contingency for abnormal operation.			
REVISION: "B"			
Designed: Sasha Trandafilovic	Revised: David Verrelli	Authorised: —	
Date: 10/01/1999 [sic!]	Date: 02/10/1999	Date: —	

SPECIFICATION SHEET:		TURBINE	
Equipment item		TRB-1	
Description		Turbine to drive CP-1	
Type		Centrifugal (multistage condensing)	
Quantity		1 (one) - see Notes	
Duty [kW]		539	
PROCESS DETAILS			
Fluid description		Steam circuit	
Fluid composition [(kg.kg ⁻¹):		Water	100.0
		Other	trace
Mass flowrate [kg.s ⁻¹]		2.72	
Temperature [°C]		Suction	Delivery
Pressure [kPa(abs)]		152	100
Density [kg.m ⁻³]		500	102
POWER			
Turbine efficiency [%]		75	
Drive type		Mechanical – connection to shaft of CP-1	
Generator type		none	
Generator efficiency [%]		-	
Generator power [kW]		-	
MECHANICAL DATA			
Maximum design pressure [kPa(abs)]		1300 - see Notes	
Minimum design pressure [kPa(g)]		-1	
Maximum design temperature [°C]		250	
Minimum design temperature [°C]		ambient / 10	
Branch nominal diameter [mm]		Suction	Delivery
MATERIALS OF CONSTRUCTION			
Casing		Type 316SS	
Lining		None	
Internals (blades, shaft, <i>et cetera</i>)		Type 316SS	
NOTES			
Only one item is specified, as a stand-by turbine is impractical and uneconomical.			
High design pressure to allow safe operation on HP steam that "should" be let down.			
REVISION: "A"			
Designed: David Verrelli		Revised:	Authorised: —
Date: 09/10/1999		Date:	Date: —

SPECIFICATION SHEET:		VALVE	
Equipment item Description		V-1 Water let-down valve	
Type Quantity		Restriction in line; Isenthalpic 1 (one)	
PROCESS DETAILS			
Fluid description		Fresh demineralised water feed	
Fluid composition [(kg.kg ⁻¹)]:		Water	100.0
Mass flowrate [kg.s ⁻¹]		0.226	
Temperature [°C]		Inlet 37	Outlet 37
Pressure [kPa(abs)]		400	185
Density [kg.m ⁻³]		998	998
MECHANICAL DATA			
Maximum design pressure [kPa(abs)]		450	
Minimum design pressure [kPa(g)]		-1	
Maximum design temperature [°C]		100	
Minimum design temperature [°C]		ambient / 10	
Branch nominal diameter [mm]		Inlet 13	Outlet 13
MATERIALS OF CONSTRUCTION			
Casing and restriction		Type 316SS	
Lining		None	
NOTES			
Mains water is available at 400kPa(abs), which is too high for the vaporiser (HX-1) feed.			
REVISION: "B"			
Designed: Sasha Trandafilovic		Revised: David Verrelli	Authorised: —
Date: 10/01/1999 [sic!]		Date: 30/09/1999	Date: —

Formaldehyde

7 DETAILED DESIGN OF FORMALDEHYDE ABSORBER

This chapter deals with the detailed design of one plant item, namely the formaldehyde absorber, ABS-1. The reader may find it helpful to refer to the process flow diagram in the Drawing Annex following this report. Useful calculations are presented in the Appendix (following the Drawing Annex), which may be referred to from time to time.

It might also be helpful for the reader to refer back to the Specification Sheet for ABS-1 that was presented in Chapter 6 of the report. It contains many of the results described in this chapter.

The reader should note that the stages are numbered in ascending order as altitude increases, while the trays are numbered in the opposite direction, in accordance with convention. The three sections into which stage four is divided are labelled A to C as altitude decreases.

7.1 Process Design

Process design essentially deals with sizing the absorber, as well as the specification of additional details, such as inter-stage compositions, temperatures, flows *et cetera*.

7.1.1 Column characteristics

This characterisation of the internals in the absorber could not really take place until the mass and energy balances were commenced. However the following will make more sense if the characteristics of the absorber are presented first. The reader must simply bear in the mind that several processes occurred in parallel.

7.1.1.1 Packing

Random packing is selected for its economical price in comparison to structured packing. Also, trays are avoided in the lower sections because:

- of the difficulty in removing sufficient heat¹
- of the small diameter of the column
- of the corrosive nature of the process fluid
- industry experience should not be completely ignored!

Metal Pall rings² are selected due to their superior mass transfer qualities in comparison to Raschig rings. They are cheaper than Intalox or super Intalox saddles. Ref. [6] indicates that the relative “mass transfer capacity,” $K_{y,a}$, of super Intalox saddles is only marginally better than for Pall rings³. In fact Ref. [3] presents a graph indicating that metal Pall rings have a superior “efficiency” to ceramic Intalox saddles at any given nominal packing size from approximately 15mm or below, to above 50mm.

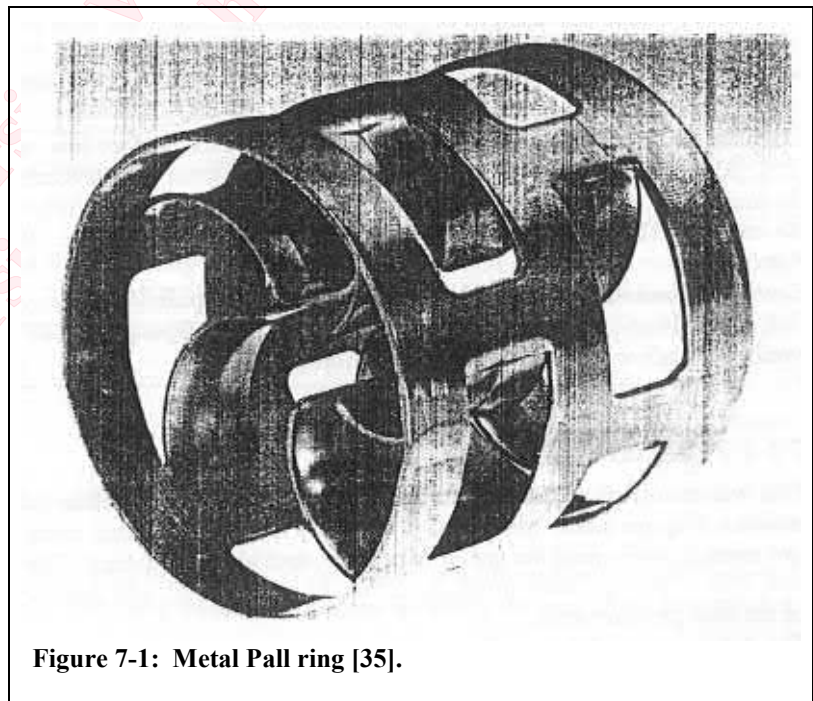


Figure 7-1: Metal Pall ring [35].

¹ Although plates are generally recommended for the removal of heat due to the ability to install cooling coils on the plates, the unusually large heat of absorption of formaldehyde makes this option seem impractical here.

² Interestingly these were also developed by BASF AG [35].

³ At a late stage in the design SHARMA indicated that (super) Intalox saddles would normally be specified, as their superior mass transfer qualities off-set their higher initial cost.

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Type 316 stainless steel is to be used, as elsewhere in the plant, due to its inertness. Also, metal will not be easily broken by attrition (or the initial filling of the column). A metal Pall ring is shown in Figure 7-1. The size chosen is 50mm for the relatively large diameter column (calculated in the Appendix), on the recommendation of Ref. [33].

7.1.1.2 Plate sections

Reverse-flow bubble-cap trays were specified in stage 4, due to the extremely low liquid flow [11], [33].

Initially there was a reluctance to use trays at all – the packed sections appeared to be a simpler means of doing the job more efficiently, with lower liquid hold-up (and hence inventory) and lower pressure drop. However the mass balance showed that it would be difficult to remove formaldehyde down to the very low levels achieved here if recycle was present.

The recycle causes a massive increase in the concentration of formaldehyde in the liquid phase that is entering a stage. Mass transfer is only significant due to the shifting of equilibrium at the reduced temperature. Therefore it seemed that there should be no recycle around the top stage, in order to ‘scrub’ the maximum amount of formaldehyde. This arrangement is shown in, for example, Ref [14].

It may be noted that the decision to remove formaldehyde to around 0.01%(kg.kg⁻¹) in the off-gases was supported by SHARMA, on economic grounds [32].

Once the recycle was removed, the liquid flow was reduced by a factor of around 100 compared to stages 1 and 2 at the base of the column. This was cause enough to consider using a structured packing such as Sulzer Chemtech’s type BX plastic gauze packing, which is claimed to be especially suitable for “processes with small or extremely small liquid rates,” including “formaldehyde absorbers.” [36].

However the energy balance revealed that there was still 153kW of heat to be removed from the system. Thus the decision was made that trays would have to be installed in stage 4 of the absorber (top), similar to the serpentine cooling coils installed in Orica’s absorber in Deer Park.

This decision was made despite few references alluding to cooling coils on trays in the literature as well as comments by DUSS to the effect that

“Cooled trays with serpentine coils were used in former designs. Our experience [at Sulzer Chemtech AG] is that new designs of [formaldehyde]-absorbers are with packing [...], either with structured or dumped packing. This holds [...] for the silver catalyst (or BASF) process.” [8]

Nevertheless the results of the energy balance could not simply be ignored altogether.

Even for trays, the liquid flux (compared to the gas flux) is very low, and reverse-flow trays are recommended [11], [33]. These have a central baffle that the liquid must flow around, such that all of the downcomers are on the one side of the column. The downcomers only lie on one side of the baffle, however, which alternates down the column. This will be clearer with reference to Drawing Number 7002 in the Drawing Annex preceding the Appendix.

Sieve trays and valve trays may have become more popular (and are generally cheaper) than bubble-cap trays. Bell caps will still be specified to handle the low liquid flow [11]. This ensures that sufficient liquid hold-up is available to allow for heat transfer via a cooling coil.

The specific bubble cap used is shown in Drawing Number 7001 in the Drawing Annex.

7.1.1.3 Pressure drop

This was estimated as 20kPa over the entire column using guideline values in Ref. [33]. This corresponds to a pressure drop per linear metre that is relatively low, to avoid high energy demand by the blower (CP-1), but not low enough to demand the use of expensive, specialised packings. The preliminary guess of the column height was 50m – corresponding to the maximum expected value, and therefore yielding a more conservative estimate of the total pressure drop.

The design proceeded in such a way as to attempt to stick to this preliminary value if feasible (so as to avoid a flow-on effect of inconsistencies to other units in the flowsheet), and this was achieved.

7.1.2 Outline of methods used

Several methods were used in conjunction with one another.

7.1.2.1 Mass and energy balances

The overall mass and energy balances presented in Chapter 5 are not sufficient to fully identify all of the absorber streams. Further mass and energy balances were required. However in order to perform these balances some assumptions had to be made.

Assumptions that were made included:

- the pressure varies approximately linearly with altitude in the absorber. This was checked once the various stages were designed, and found to be reasonable. Initial pressure drops per linear meter were estimated from Ref. [33].
- The temperature varies approximately linearly with altitude in the absorber. This was revised due to limitations on the minimum process-side temperature in the absorber.
- Temperature drop in each pump-around would be 15°C. This was chosen to reduce the flow (increase ΔT) without causing deposition of formaldehyde on tube-walls (decrease ΔT). For stage 3 this had to be lowered due to the need to maintain sufficient temperature driving force across the exchanger (HX-6). In HX-8 a cocurrent profile was chosen to increase the (minimum) tube-wall temperature. This was achieved with only a 'penalty' F_T of 0.91.
- At the top of each stage the vapour would be almost at equilibrium with the liquid. This required estimation of temperature and compositions of both phases. The formaldehyde mole fraction in the vapour exiting each stage was assumed to be such that the ratio of $(y_{IN} - y_{OUT})$ to $(y_{IN} - y^*)$ would be 99.5%⁴, where y is the vapour mole fraction, and the superscripted asterisk signifies saturation.

7.1.2.2 Column diameter calculation

The diameter of the column may be found with relative simplicity by assuming a certain approach to 'flooding'⁵. It is related to the design pressure drop described in 7.1.1.3.

While Ref. [3] gives 17 to 33mm(H₂O).m⁻¹ as a rule of thumb, Ref. [33] suggests values below 80, based on the assumption that this will lead to gas flows that are approximately 80% of the flooding velocities. And 66% is "satisfactory."

42mm(H₂O).m⁻¹ was chosen to avoid excessive pressure drop (requiring added cost in driving the blower, CP-1), while still operating reasonably close to flooding.

The need to operate close to flooding was apparent from the specification of the column as being of constant diameter (to reduce the cost of fabrication). In the bottom stage, stage 1, the flow is closest to flooding, and so this will give the minimum diameter for the column. The higher stages must operate at lower percentages of flooding.

On top of this, the turn-down to 60% of design rates will decrease the approach to flooding. Therefore the flooding at the design rates is chosen to be at the high end of the normally accepted range.

The percentage of flooding can be found by evaluating the square root of the ratio of the constant K_4 at the design pressure drop to K_4 at flooding. Charts of K_4 versus $(L/G) \cdot (\rho_G/\rho_L)^{0.5}$ for various pressure drops are available [33]⁶. L and G are the liquid-phase and gas-phase mass fluxes [kg.m⁻².s⁻¹]; ρ_G and ρ_L are the gas and liquid densities [kg.m⁻³].

The calculation is shown in the Appendix.

7.1.2.3 Stage height calculations

7.1.2.3.1 Packed beds

The height of a packed bed may be evaluated from the product of the height of a (theoretical) transfer unit and the number of (theoretical) transfer units⁷. For mass transfer operations in which the gas phase resistance is controlling [9], this is expressed:

$$h_{bed} = H_{OG} \cdot N_{OG} \quad [m] \quad (i)$$

⁴ Initially 99% was selected arbitrarily: 100% would imply infinite packed height, while low values would require to many stages. Only a small alteration was felt to be needed.

⁵ This may be defined, after ECKERT, as "that point in gas-liquid loading where the liquid phase becomes continuous in the voids and the gas phase becomes discontinuous in the same voids of the bed." [3]

⁶ $K_4 \equiv 13.1 V^2 F_P (\mu_L/\rho_L)^{0.1} \div \{\rho_G (\rho_L - \rho_G)\}$, where F_P is the packing factor, characteristic of the size and type of packing.

⁷ The adjective "theoretical" is used to denote that the division into units is hypothetical. It does not imply 'perfect' efficiency.

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or

$$h_{\text{bed}} = H_{\text{Oy}} \cdot N_{\text{Oy}} \quad [\text{m}] \quad (\text{ii})$$

in which the subscript OG indicates calculation based on the overall gas-phase mass transfer coefficient, K_G [$\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$] based on partial pressures as the driving force, while Oy indicates use of K_y [$\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$] as the basis, with mole fractions, y , as the driving force⁸. H is the height [m], N the number of units [–].

Description of methods to obtain H_{Oy} and N_{Oy} are contained in subsequent sections.

The calculation is based on a ‘key component’, namely formaldehyde, with minor transferring components being considered after the initial calculation [12]⁹.

7.1.2.3.2 Trayed sections

The same value of N_{Oy} can also be used to estimate the number of trays required in stage 4 of the column (roughly the top half of the column). Ref. [37] presents KREMSEY’s equation for estimating the number of ideal plates:

$$N_P' = \{ \log_{10} ((y_{\text{NP}+1} / y_1) \cdot (1 - 1/A_E) + 1/A_E) \} \div \{ \log_{10}(A_E) \} \quad [-] \quad (\text{iii})$$

The gas phase mole fractions, $y_{\text{NP}+1}$ and y_1 , are evaluated entering (bottom) and exiting (top), respectively. A is the so-called absorption factor,

$$A = 1 / (m \cdot G_M / L_M) \quad [-] \quad (\text{iv})$$

where G_M and L_M are the superficial¹⁰ gas and liquid molar fluxes, and m is the Henry’s law equilibrium constant defined by

$$y_{\text{equilibrium}} \equiv y^* = m \cdot x \quad [-] \quad (\text{v})$$

with x being the liquid-phase mole fraction of the relevant component.

In fact the first reference used simply A , but to account for non-linearities a weighted average was used:

$$A_E = [A_{\text{BOTTOM}} \cdot (A_{\text{TOP}} + 1) + 0.25]^{0.5} - 0.5 \quad [-] \quad (\text{vi})$$

The subscript E may be taken as ‘effective’ or ‘Edmister’, who first applied this average, for tray-type absorbers and strippers (1943) [12].

It was not considered necessary to use a more sophisticated¹¹ method of calculation, because the heat effects are relatively small, with temperature only varying by 5°C in the liquid phase, and the solution is relatively dilute at the top of the column.

Once the ideal value, N_P' , is found, this can be corrected by use of an efficiency, η , to give the true number of plates, viz.

$$N_P = N_P' / \eta \quad [-] \quad (\text{vi})$$

Ref. [33] reproduces O’Connell’s chart (1946) for the determination of plate efficiencies in absorbers. It is pointed out that “appreciably lower plate efficiencies are obtained in absorption than in distillation.”

However, Ref’s [9] and [11] indicate that for this system, in which the transferring component is highly soluble, efficiencies may be higher than average. Furthermore, a conservative equilibrium relationship was assumed. Therefore the original efficiency obtained was adjusted upwards by a small amount to make it more realistic.

7.1.2.4 Number of transfer units, N_{Oy}

Ref. [9] quotes Colburn’s 1939 formula for the number of theoretical transfer units

$$N_{\text{Oy}} = \ln \{ (1 - (m \cdot G_M / L_M)) \times (y_1 - y_2^*) / (y_2 - y_2^*) + m \cdot G_M / L_M \} \div \{ 1 - (m \cdot G_M / L_M) \} \quad [-] \quad (\text{vii})$$

where the subscripts 1 and 2 refer to the bottom and top of the bed, respectively.

This equation is, strictly speaking, only valid for simple systems where the operating and equilibrium lines are linear. Initially this equation was only to be used to get a preliminary value. To do so, simple arithmetic averages of each variable were used.

⁸ The difference between overall and individual mass transfer coefficients lies in the driving force: for overall coefficients the difference between bulk and saturation (relative to the bulk) values is used, while the difference between interfacial and bulk values are used for the individual coefficients.

⁹ In fact, calculation in spreadsheet form permitted essentially simultaneous treatment.

¹⁰ Based on the empty column cross-sectional flow area.

¹¹ I.e. a more complicated method that could not have been justified, based on inaccuracies in the physical data (see sections 7.1.3 and 7.1.4, from page 7-7 onwards).

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The reader may be somewhat sceptical about the accuracy of applying the above equation – and rightly so. Ref. [12] presents more advanced methods for dealing with heats of absorption and non-linearities.

The rigorous calculation would be too time-consuming for this project, and probably not justified in view of the uncertainties that exist in various of the physical data (see section 7.1.3, page 7-7 and following).

Two short-cut methods were also presented: one using a ‘simple approach’, and the other using an ‘Edmister-type approach’. While the latter was only slightly more complicated than the former, it is said to yield considerably better results, and so it was the method chosen here.

The method makes use of the Edmister average absorption factor, A_E , previously described in section 7.1.2.3.2, page 7-4.

The formula for N_{Oy} is then

$$N_{Oy} = \ln \{ ((y_1 - y_2^*) / (y_2 - y_2^*)) \cdot (1 - 1/A_E) + 1/A_E \} \div (1 - 1/A_E) \quad [-] \quad (\text{viii})$$

When a comparison is made of this Edmister-type approach and Colburn’s formula, the two methods are in very close agreement. Despite apparently large differences between the values of A_{TOP} and A_{BOTTOM} , their arithmetic averages are quite similar to the values of A_E calculated.

7.1.2.5 Height of a transfer unit, H_{Oy}

Two different methods for estimating the (overall) height of a gas-phase transfer unit were examined.

7.1.2.5.1 Fundamental mass transfer correlations of ONDA, TAKEUCHI and OKUMOT

In 1968 ONDA, TAKEUCHI and OKUMOT published a paper [27] giving correlations for the individual gas and liquid phase mass transfer coefficients k_G [$\text{mol.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1}$] and k_L [m.s^{-1}]. A correlation for the wetted surface area, a_w [$\text{m}^2.\text{m}^{-3}$], was also included. These correlations were found so useful that they have been cited and used ever since.

Analysis of the original paper reveals that a better estimation of the individual mass transfer coefficients pertaining to the larger sizes of packing might be made by taking the values around the upper quartile of the range, rather than the mean value¹². This is reflected in the values of the constants used.

The equations eventually used are given below:

$$\{ (k_G.R.T) / (a_t.D_G) \} = 6.00 \{ G / (a_t.\mu_G) \}^{0.7} \cdot \{ \mu_G / (\rho_G.D_G) \}^{1/3} \cdot \{ a_t.D_p \}^{-2.0} \quad [-] \quad (\text{ix})$$

where G is the superficial mass flux of the gas [$\text{kg.m}^{-2}.\text{s}^{-1}$]; a_t is the total surface area of the packing [$\text{m}^2.\text{m}^{-3}$], obtained from the manufacturer; D_p is the nominal packing size [m]; D_G is the gas-phase diffusivity [$\text{m}^2.\text{s}^{-1}$] and the other symbols have their usual meaning, in dimensionally-consistent units¹³.

$$\{ k_L.(\rho_L/(\mu_L.g))^{1/3} \} = 0.0060 \{ L / (a_w.\mu_L) \}^{2/3} \cdot \{ \mu_L / (\rho_L.D_L) \}^{-1/2} \cdot \{ a_t.D_p \}^{0.4} \quad [-] \quad (\text{x})$$

where L is the superficial mass flux of the liquid [$\text{kg.m}^{-2}.\text{s}^{-1}$]; a_w is the wetted surface area of the packing [$\text{m}^2.\text{m}^{-3}$], obtained from the equation below; D_L is the liquid-phase diffusivity [$\text{m}^2.\text{s}^{-1}$] and the other symbols have their usual meaning, in dimensionally-consistent units.

$$a_w/a_t = 1 - \exp \{ -1.45(\sigma_c/\sigma)^{0.75} \cdot (L/a_t.\mu_L)^{0.1} \times (L^2.a_t/(\rho_L^2.g))^{-0.05} \cdot (L^2/(\rho_L.\sigma.a_t))^{0.2} \} \quad [-] \quad (\text{xi})$$

where σ is the surface tension of the liquid [mN.m^{-1}], and σ_c the ‘critical surface tension’ of the packing material [mN.m^{-1}]¹⁴. This latter is given by Ref. [33] as 75mN.m^{-1} for steels.

Some constraints for the applicability of these relations were recorded by Ref. [4]:

- $0.04 < Re_L = \{ L / (a_w.\mu_L) \} < 500$
- $1.2 \times 10^{-8} < We_L < 0.27$
- $2.5 \times 10^{-9} < Fr_L < 1.8 \times 10^{-2}$

and

- $0.3 < (\sigma_c/\sigma) < 2$

All of these conditions are satisfied for the calculations performed in the Appendix.

The individual coefficients may be related back to an overall coefficient by:

¹² Strictly speaking there is no reason to interpret values corresponding to the line-of-best-fit as averages or means. It would be interesting to see the result of analysis of the data in Ref. [27] using a modern curve-fitting computer package.

¹³ Each term in braces is dimensionless.

¹⁴ Please note that this is numerically equal to the commonly quoted [dyn.cm^{-1}].

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$$1/K_y = 1/k_y + m/k_x \quad (\text{xii})$$

where k_y and k_x may be related to k_G and k_L by

$$k_y = k_G \cdot P \quad [\text{mol.m}^{-2}.\text{s}^{-1}] \quad (\text{xiii})$$

$$k_x = k_L \cdot \rho_L \quad [\text{mol.m}^{-2}.\text{s}^{-1}] \quad (\text{xiv})$$

in which P is the total pressure [Pa] and ρ_L the molar density of the liquid phase [mol.m^{-3}] [38].

K_y does not need to be corrected, by means of a Hatta number [34], for reaction that is taking place (see section 7.1.3), because the mass transfer is dominated by the gas phase resistance, whereas the reaction is occurring in the liquid phase [32]. The correction would therefore have little effect.

It is, however, reputed to be a very interesting correction in which the reaction causes a “negative enhancement”¹⁵ of the mass transfer [32], [40].

The overall gas-phase mass transfer coefficient, K_y , obtained can then be used to determine the height of a gas-phase transfer unit by the formula

$$H_{Oy} = G_M / \{(K_y \cdot a_w) \cdot y_{BM}^*\} \quad [\text{m}] \quad (\text{xv})$$

in which y_{BM}^* is the “logarithmic mean inert-gas concentration between bulk-gas value and value in equilibrium with bulk liquid” given by [9]

$$y_{BM}^* = \{(1-y) - (1-y^*)\} / \ln\{(1-y)/(1-y^*)\} \quad [-] \quad (\text{xvi})$$

This is a point average, and here it has been evaluated at the top and bottom of each bed and the average of those two (mean) values used. y_{BM}^* is used to correct for convection in concentrated systems [38].

A comparison may be made with the value calculated based on the tabulated $K_y \cdot a_w \cdot y_{BM}^*$ given by Ref. [9]. Although this is specifically for formaldehyde absorption, the conditions under which it was evaluated may not be representative of the conditions prevailing in ABS-1.

Thus H_{Oy} is known and can be used with N_{Oy} to find h_{bed} as described in the preceding sections.

7.1.2.5.2 Empirical correlations of CORNELL, KNAPP and FAIR

“Cornell’s method” (1960) is presented in Ref. [33]. While the previous method was also empirical, the distinction is made that this method is less closely related to mass transfer fundamentals¹⁶.

CORNELL, KNAPP and FAIR described a method in which the overall height of a gas-phase transfer unit, H_{Oy} , is calculated from the individual film transfer unit heights, H_y [m] and H_x [m]¹⁷. The applicable formula is¹⁸

$$H_{Oy} = H_y + (m \cdot G_M / L_M) \cdot H_x \quad [\text{m}] \quad (\text{xvii})$$

The correlations presented express the individual transfer heights

$$H_y = 0.0190283 \cdot \psi_h \cdot (Sc)_G^{0.5} \cdot (D_c / 0.3048)^{1.24} \cdot (Z / 3.048)^{(1/3)} \div \{L \cdot (\mu_L / \mu_w)^{0.16} \cdot (\rho_w / \rho_L)^{1.25} \cdot (\sigma_w / \sigma_L)^{0.8}\}^{0.6} \quad [\text{m}] \quad (\text{xviii})$$

and

$$H_x = \phi_h \cdot (Sc)_L^{0.5} \cdot K_3 \cdot (Z / 3.048)^{0.15} \quad [\text{m}] \quad (\text{xix})$$

Care must be taken when using these correlations, as the original correlations were given entirely in imperial units (*i.e.* feet *et cetera*)¹⁹.

The correction for the height of the bed, $Z \equiv h_{bed}$ [m], is to be included only when “the distance between liquid redistributors is greater than 3m.”²⁰ For the calculations in the Appendix it was included in some cases and excluded in others.

¹⁵ This is a misleading term, which actually indicates that the Hatta number is less than unity – certainly not negative [32]!

¹⁶ Fundamental methods are to be preferred on principle as providing more insight into the processes occurring. This method appears to at least be more soundly based in principle than equilibrium-stage methods. The HETP (Height Equivalent to a Theoretical Plate) model requires the assumption that gas and liquid temperatures in any horizontal section be identical [7], which clearly will not be the case here [41] (though it will be approached in the trayed stage).

¹⁷ Some of the notation has been changed to be more consistent. The recommended notation is that used by UHLHERR [38], which differentiates between k_x and k_L in the liquid phase, and k_y and k_G in the gas phase. Generally the former of each pair are preferred, as they use (dimensionless) mole fractions to express the driving force. (Use of mass fractions is possible but is generally to be avoided.)

¹⁸ Ref. [3] adds a factor to account for the “degree of wetting.”

¹⁹ The additional significant figures have come from a re-evaluation of the conversion factors.

²⁰ This is not mentioned in Ref. [4].

D_c [m] is a “corrected” diameter: the lesser of the actual diameter of the column or (2×0.3048) .

The subscript w refers to the physical properties of water at 20°C.

K_3 is a “percentage flooding correction factor,” for which a chart is provided of K_3 versus the percentage flooding. The percentage of flooding can be found by evaluating the square root of the ratio of the constant K_4 at the design pressure drop to K_4 at flooding. A chart giving values of K_4 versus $(L/G) \cdot (\rho_G/\rho_L)^{0.5}$ for various pressure drops is given²¹. Recall that L and G are the liquid-phase and gas-phase mass fluxes [$\text{kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$].

Charts are also provided for the H_y factor, ψ_h [m], and the H_x factor, ϕ_h [m]²². These are specific to a certain type of packing, and unfortunately Ref. [33] only gives the original charts for Berl saddles.

All other symbols have their usual meanings, in consistent dimensions.

For the calculations in this report the updated charts of Ref. [4] were used for K_3 , ψ_h and ϕ_h . These are specifically relevant to metal Pall rings of 50mm diameter, as used in the absorber, ABS-1, in our plant.

It is interesting to quote from that reference on accuracy:

Of the two previously available mass transfer models [...] the improved mass-transfer model is better yet, having a safety factor of 1.70. [...] [This] means that commercial columns designed with this model must, on average, have packed heights 70% larger than are really necessary, assuming one wishes a 95% probability of success.”

A safety factor of 1.70 was certainly not used here, and is seldom used in practice. The reason is that most designers introduce ‘individual’ safety factors, which seem to be inherent in the design, at each stage. For example, in this design the equilibrium relationship used was very conservative (see section 7.1.3 following).

7.1.3 Vapour pressures

The vapour pressures play a key part in the design of the formaldehyde absorber, because they are the basis upon which equilibrium mole fractions, y^* , are calculated. (The previous sections demonstrate the importance of the y^* to the design.)

7.1.3.1 On the state of aqueous formaldehyde

Aqueous formaldehyde solutions are very complicated things. Formaldehyde exists only in very low proportions as the monomer, HCHO . For the most part, in solutions of any significant concentration, “formaldehyde” exists as the monohydrate, methylene glycol ($\text{CH}_2(\text{OH})_2$), low molecular mass polymeric hydrates or poly(oxyethylene) glycols ($\text{HO}-(\text{CH}_2\text{O})_n-\text{H}$).²³ The formation of these products is reversible [39].

These hydrates, with their higher molecular masses, are much less volatile than monomeric formaldehyde.

In the gas phase formaldehyde is present predominantly as the monomer [39].

It is true that the initial reaction of the monomer to monohydrate is relatively fast [10]. However the reactions to form higher mass hydrates are slower. This has an impact upon the length of time required for a reasonably concentrated aqueous formaldehyde solution to come to (practical) equilibrium.

A quote from Ref. [39] is pertinent:

“Equilibrium values for formaldehyde [...] solution are readily obtained at room temperatures and above. However, these equilibria are functions of a solution composition which may itself be metastable. The disagreement so often noted in formaldehyde solution data as reported by various investigators is due to the fact that reaction kinetics rather than true equilibria often govern the data obtained.”

Workers in the field have gone to great lengths to ensure their solutions essentially reached equilibrium. For example ILICETO and BEZZI (1951) maintained their solutions at 35°C for at least one month. At around 35°C and below, and normal solution pH values (*i.e.* 3 to 5), the reactions are “slow.” [39]

A quick calculation based on the assumption that liquid hold-up on each tray is equal to the column cross-section multiplied by the weir height (calculated in the Appendix – see also section 7.2, page 7-13). This gives a

²¹ $K_4 \equiv 13.1 V^2 F_P (\mu_L/\rho_L)^{0.1} \div \{\rho_G (\rho_L - \rho_G)\}$, where F_P is the packing factor, characteristic of the size and type of packing.

²² In fact the charts are presented in feet, but values have been converted by the author.

²³ And various other minor constituents such as hemiformals [10].

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volume of $\sim 2.6\text{m}^3$. The nett liquid flowrate may be taken as $1\text{dm}^3\cdot\text{s}^{-1}$ for this calculation. This gives a residence time of just 45 minutes.

While there is significant liquid hold-up in the packed sections, and the pipes and heat-exchangers of the pump-arounds, this does not appear likely to amount to a combined residence time of more than one day. This means that there must be some doubt as to the extent to which equilibrium has been approached²⁴.

It is briefly noted that the statement of DUSS [8] that formaldehyde “shows a maximum boiling azeotrope with water (and methanol)” was not taken into account, due to a lack of detailed information, and a failure to find any other reference to this phenomenon in the literature.

7.1.3.2 Implications for partial pressures

Clearly the formation of less-volatile components in the liquid phase will decrease the partial pressure of condensables in the gas phase. Moreover, the reaction causes a dramatic decrease in the mole fraction of monomeric formaldehyde in the liquid, which leads to the lower saturation partial pressure of formaldehyde.

In some of the literature a distinction is made between “apparent” and “actual” concentrations (or mole fractions *et cetera*) of formaldehyde. Apparent concentrations hypothetical values obtained by calculating the concentration that would exist if all of the hydrates of formaldehyde (as well as minor constituents, such as the hemiformals) reverted back to purely monomeric formaldehyde.

In this report apparent concentrations are used for all of the calculations (including mass and energy balances, and mass transfer computations). Actual concentrations are only considered implicitly insofar as they affect the saturation partial pressures, as discussed in the following section.

7.1.3.3 Modelling of saturation partial pressures of methanol

The vapour–liquid equilibrium of the binary system methanol(1)–water(2) was investigated as a precursor to examining the more important formaldehyde vapour–liquid equilibria. The purpose was twofold: this calculation provided a means of evaluating the method to be used against reliable experimental data; and it served to generate parameters for binary activity coefficient models. In theory the binary model parameters for each of the systems methanol–water, formaldehyde–water and formaldehyde–methanol could be combined to estimate the activity coefficients in the ternary system formaldehyde–methanol–water [28].

The possibility of the solution being ideal was not considered realistic.

One very convenient method for estimating the activity coefficients was to interpolate from the activity coefficients at infinite dilution. Correlations exist for n -primary alcohol(1)–water(2) and water(1)– n -primary alcohol(2) systems [28]. These correlations include temperature dependency.

The van Laar equation was used to model the variation of the activity coefficients with composition, because it is simple to solve for its two parameter from infinite-dilution activity coefficient data, and also because it would give consistency with the HYSIM simulator, in which the van Laar equation was also used²⁵.

To use the van Laar model (and indeed any activity coefficient model), pure-component saturation vapour pressures are needed. These were taken from Ref. [28] in preference to Ref. [33], as the former used the relatively advanced Wagner equation²⁶ (described as “particularly successful”), rather than the Antoine equation. A comparison of the two (see Appendix) shows that the two give significantly different results at higher temperatures: in the absorber either would probably suffice.

Solving for the parameters, using the infinite-dilution data, gave $A = 1840$ and $B = 1530$ at 60°C . This compared to ‘experimental’ values of $A = 2360$ and $B = 1470$ in Ref. [16].

The van Laar parameters used by HYSIM were difficult to determine, however at 60°C they appear to be $A = 0.764$ and $B = 0.626$ (refer to the appendix to Chapter 5). These are clearly completely different from the values given by the other two sources.

²⁴ Though temperatures are higher at the base of the column: it may be that the approach to equilibrium in the liquid phase varies throughout the absorber system.

²⁵ As noted in Chapter 5, the NRTL model was used for much of the original HYSIM work. The problem with using this model, apart from its added complexity, is that it has three parameters instead of two, although the third parameter may be taken as a fixed constant if no other reliable data can be found (or time is short) [28].

²⁶ Though in its “simplest” form.

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The three pairs of parameters were substituted, in turn, into the van Laar equation, and a y - x diagram plotted, which may be seen in the Appendix. For comparison and verification, some experimental data at 59.6°C [22] was also plotted.

The best agreement was between the curve based on the infinite-dilution data and the curve based on 'experimental' parameters, despite the apparently significant differences between their parameters. Both of these curves also matched the experimental data quite well.

Surprisingly, even the very low HYSIM parameters yielded a reasonable match with the other curves – particularly in the region of higher methanol mole fraction. The reason for this is probably that the van Laar equation is not capable of modelling extreme non-ideality, and also that methanol has a high volatility relative to water, and so the activity coefficients would have to be very different from unity to be seen to have a major effect on the relative volatility.

7.1.3.4 Modelling of saturation partial pressures of formaldehyde

7.1.3.4.1 What was done

As mentioned in the previous section, the initial aim was to correlate the three combinations of binary mixtures in order to estimate the vapour–liquid equilibrium of the ternary mixture (ignoring the effect of minor contaminants such as formic acid, HCOOH).

Continuing in the same vein as the previous section on methanol(1)–water(2), activity coefficients at infinite dilution were estimated for the binary formaldehyde(1)–water(2). While a correlation for n -aldehydes(1)–water(2) was available [28], unfortunately there was no correlation for the infinite-dilution activity coefficient for water(1)– n -aldehydes(2).

To get around this problem the idea of modelling formaldehyde (methanal) as a hypothetical single-carbon ketone was hit upon (*i.e.* *methanone). This is justified by the statement that “aldehydes and ketones behave similarly and undergo many of the same reactions.” [24] On the other hand, the results of this approximation may not be as good as first assumed, because the values of the parameter A calculated for both the system n -aldehydes(1)–water(2) and the hypothetical system n -ketones(1)–water(2) were significantly different at 60°C and above. This is shown in the Appendix (worksheet “van Laar VLE” in “DP_VLAR4.XLS”).

Good experimental data was available from Ref. [1]. Comparison showed that the van Laar model based on the infinite-dilution parameters was a very poor approximation of the experimental results.

Both the HYSIM parameters and Raoult's law gave similar results to the infinite-dilution parameters, and all indicated that formaldehyde was far more volatile than water. The difference in saturation partial pressures for the two components clearly dominated the discrepancies in van Laar parameters.

The main problem lies in the model and the inherent assumption that the apparent mole fraction (see section 7.1.3.2) of formaldehyde can be used. The equilibrium partial pressure data for the pure components, water and formaldehyde, indicate conclusively that the relative volatility of formaldehyde to water should be greater than unity. However the experimental data points clearly lie in such positions as to imply that it is the water which is the more volatile of the two substances, based on apparent mole fractions.

The first attempt to fit the parameters of the van Laar model to the experimental points demonstrates the flaws in the application of this to the system. The method used to fit the vapour–liquid equilibrium curve to the data was to minimise the sums of two sets of numbers. The first set of values contained the squares of the difference (*i.e.* error) between the activity coefficient for the formaldehyde partial pressure based on the fitted parameters and that calculated from the experimental data. The second set of values contained the same squares of errors, but for the activity coefficient of the water partial pressure. These two sets were weighted²⁷.

The result of this fitting was a poor match of the experimental line – essentially the equation $y = x$ was obtained, though in an unrecognisable form.

The first attempt at fitting parameters was unsatisfactory, and so a second attempt was made. This followed the example of Ref. [28], in which a linearised form of the van Laar equation was obtained, and the experimental data fitted by minimising the sum of squares of the errors in the relation thus obtained. This gave a value of A that was similar to the previous regression (around –11900 compared to –12200), but the value for B was markedly different (roughly $+1.7 \times 10^{+5}$ compared to $-1.1 \times 10^{+10}$).

²⁷ This was required to give results which both were physically reasonable, as well as close to the experimental results.

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The results of this second fitting may possibly fit the experimental data better below a formaldehyde mole fraction of 0.5, but above that the model becomes physically unrealistic, predicting zero partial pressure of formaldehyde over pure formaldehyde (see Appendix).

In fact the regression is inherently unreliable in this case, because the value of B is found by the difference between two similar numbers, which were obtained by curve-fitting.

A final attempt to fit parameters to the van Laar model was made using the occasionally vaunted UNIFAC method (briefly described in Chapter 5). The calculation is presented in the Appendix. The value of A and B computed were different to those found by all of the previous methods, but again the curve that resulted was most similar to the van Laar curve from infinite-dilution data and from Raoult's law, all of which were very different to the experimental data.

The failure of the above methods and the lie of the experimental data points suggested a linear curve fitting. At 70°C this resulted in $y = 0.7514x$, with an R^2 value of 0.96. An added advantage of this is its simplicity. This was the 'model' used for the design of the absorber.

7.1.3.4.2 What wasn't done

As mentioned, one serious flaw in the van Laar model was its form. Many of the references present empirical correlations directly relating the saturation partial pressure of formaldehyde to the apparent mole fraction of formaldehyde in the liquid.

The formula obtained by LACY based on the data of LEDBURY and BLAIR (1925) [10] was rejected as it did not yield zero partial pressures of formaldehyde over pure water!²⁸ Ref. [39] gives additional information on the original Lacy equation as well as variants of the Lacy equation. These all share the previous fault. Also, the original equation is said to be accurate only for solutions between 10 and 40% (kg.kg⁻¹) formaldehyde, while the variants claimed to be accurate "for solutions of all concentrations below 60°C," but only for solutions below 20% (kg.kg⁻¹) up to 100°C.

Ref. [29] presents a further equation based on the work of LEDBURY and BLAIR, LACY and WALKER. This equation does cause the formaldehyde partial pressure go to zero when there is none present in the liquid. However it was not used for the design of the absorber.

The reasons for not using the equation are that:

- It is more complicated than the straight-line, Henry's law type equation ($y = 0.75x$) derived in the previous section²⁹.
- It is less conservative. It may be shown (see Appendix) that this formula yields partial pressures that are roughly half those taken from the linear approximation (which was from data at 70°C).
- It implies that equilibrium exists between the liquid and vapour, which may not be a reasonable assumption (see section 7.1.3.1, page 7-7).

As noted, the decision was made to use very conservative vapour–equilibrium data and therefore avoid using a 'safety factor'³⁰ at the end.

7.1.4 Other physical property data**7.1.4.1 Densities**

Densities were obtained as follows:

- Densities of water were obtained from a tabulation in Ref. [31].
- The gas was assumed to be ideal, following the law $pV = nRT$.
- Densities of the aqueous formaldehyde solution were evaluated from the formulae presented in Ref's [14] and [29]³¹. These gave similar results, and agreed with the data of Ref's [10] and [39]. The formulae are quoted in the Appendix, where the calculation is performed (under the heading "Diameter computation").

²⁸ Credit is due to Mr. Adrian DIXON, who first noticed this peculiarity.

²⁹ But then again, it was calculated in any case for the purposes of comparison!

³⁰ Please note that the tray efficiency used is not a safety factor.

³¹ Whose formula contained a misprint.

7.1.4.2 Viscosities

7.1.4.2.1 Liquid viscosities

Liquid viscosities were obtained from an empirical correlation against temperature and proportions of formaldehyde and methanol [14]. For dilute solutions this gave results that were up to (approximately) half those of pure water [31], at the same temperature. These values were considered to be highly dubious, and so for the top stage (Stage 4) the values of pure water were taken, and for Stage 3 the two values were averaged.

7.1.4.2.2 Gas viscosities

The gas mixture was assumed to consist of only four components in order to make the computation easier. These were water, formaldehyde, hydrogen and nitrogen. The mole fractions of the first three were exactly as calculated from mass balances *et cetera*, while all other components were taken as nitrogen. However it should be noted that while this assumption will tend to increase the mole fraction of nitrogen recorded, the values were all taken at the bottom of each stage, which has the effect of decreasing the value.

Pure component data were taken from Ref's [22] and [31]. Formaldehyde was assumed to have the same pure component viscosity as methanol. Each of the four pure components, except nitrogen, was found to have very similar gas viscosities (around 1×10^{-5} Pa.s), which varied little with temperature. Nitrogen had a viscosity that was approximately double that of the other components – again relatively invariant with temperature – and so it was an important constituent.

In order to estimate the viscosity of the gas mixture Ref. [28] was consulted. This detailed the method of WILKE, which apparently yields results that are no worse than $\pm 12\%$ (compared to experimental values). This was not a particularly simple method to apply, but it was nevertheless chosen for calculation. REICHENBERG's procedure may be the "most consistently accurate,"³² but it is far too complicated³³ for use in this report.

The results of the computation yielded mixture viscosities that were essentially constant over the range of temperatures in the column, and so the average was taken and used throughout the column.

For comparison the gas viscosity of the mixture was computed by taking an average of the pure-component viscosities that was weighted by the mole fraction of each constituent. Interestingly enough, this gave results that were only around 4% below those calculated by WILKE's method. While this indicates that the values used are at least reasonable, it must surely also demonstrate that some 'sophisticated' calculations – given the uncertainties in physical data – are simply not worth performing!

The calculation is presented in the Appendix (under the heading "Viscosity computation").

7.1.4.3 Diffusivities

Due to uncertainties in the data, and even a lack of data altogether for some components, and the complexity of evaluating diffusion in a multi-component mixture³⁴, binary diffusion is assumed. Further, the effect of concentration on diffusivity coefficients is not considered.

7.1.4.3.1 Liquid-phase diffusivity

For the liquid the two components were assumed to be formaldehyde and water.

The correlation of HAYDUK and MINHAS is used. This is recommended by Ref. [28] as generally yielding the lowest errors³⁵, as well as being reasonably simple to apply. This required the molar volume of formaldehyde at its normal boiling point, which was deduced from Ref. [29].

The value obtained for the liquid diffusivity was found to vary in the column, and could not be taken as constant. In reviewing the value in Stage 1,³⁶ SHARMA [32] commented that he would expect a value of around $2 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ or less, rather than the 3.5×10^{-5} calculated. This is close to the value calculated in the cooler Stage 4 (at the top of the column), namely $2.2 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$.

³² Errors of no more than $\pm 4.8\%$ were recorded.

³³ Requiring, for example, dipole moments of each constituent.

³⁴ "The equations for diffusion in multicomponent systems become very complicated." [37]

³⁵ Average absolute error approximately $\pm 10\%$.

The calculation is presented in the Appendix (under the heading “Liquid-phase diffusivity computation”).

7.1.4.3.2 Gas-phase diffusivity

The gas phase was taken as a binary mixture composed of formaldehyde and nitrogen for the purposes of this calculation.

Two similar methods were tried, which both use the concept of atomic and molecular ‘diffusion volume’ increments, which are additive.

The first method was that of FULLER, GIDDINGS and co-workers (1965–1969) [28]. This was recommended, above all other methods presented, as yielding “the smallest average error.”³⁷ Applying the method yielded a value of approximately $0.174\text{cm}^2.\text{s}^{-1}$, which was essentially invariant over the column.

The second method was described as that of GILLILAND (1934), recommended as “convenient” [20]. This yielded a values in the column that were all close to $0.127\text{cm}^2.\text{s}^{-1}$. The discrepancy would be largely due to the different ‘diffusion volume’ values presented.

Due to the reputation of Ref. [28] and its more comprehensive treatment, and the fact that it presented a more recent ‘method’, the first value was accepted, rather than attempt a verification by one (or more) independent means.

7.1.4.4 Surface tension

The estimation of the liquid surface tension, σ , was difficult due to a paucity of relevant data, in particular that for formaldehyde.

For water at 20°C a value of 70mN.m^{-1} was taken, being an amalgam of values from Ref’s [22], [28] and [33].

It was apparent that the surface tension of water was far higher than that of low-molecular-mass hydrocarbons such as methanol, acetone, formamide and methyl formate [28]. It was assumed that formaldehyde would fit in with this group of chemicals – at least having a surface tension that is closer to those of other similar hydrocarbons than to water.

Furthermore, it was observed that surface tension tended to decrease with increasing temperature [28]. For the aqueous formaldehyde solution a value of 60mN.m^{-1} was therefore settled upon.

As the surface tension of the aqueous formaldehyde is only used in the computation of H_y , in which it is first divided by the water surface tension and then raised to the power of -0.4 , this assumption is reasonable.

7.1.5 Application of the method

Once values for all of the required physical properties has been estimated, as described above, the methods outlined in section 7.1.1, pages 7-1ff., could be applied.

The diameter of the column was taken as 1800mm. This gave flooding of 73% at the bottom stage under normal operating conditions.

The values taken for the packed heights (which are shown in the Specification Sheet of ABS-1 in Chapter 6) were taken as those from ONDA, TAKEUCHI and OKUMOTO. These were generally more conservative than the values of CORNELL, KNAPP and FAIR, though not so conservative as the value derived from Ref. [9]. Again, the more fundamental nature of the approach was also preferred. This selection was another reason not to apply final safety factors.

The heights were also below the maximums recommended by SINNOTT [33].

For the top stage (Stage 4), in which bubble-cap trays were used, the number of ideal trays required for the design separation was 13.5.³⁸ With an efficiency of 65% this became 21 real trays.

³⁶ By implication, the values of the other constants are probably reasonable, as no comment was made on other inaccuracies as they were reviewed.

³⁷ The average absolute error is around $\pm 5\%$.

The mass fraction of formaldehyde in the vapour exiting is only 0.0001, or 100ppm. This is small enough to be described as “trace.” The product fulfils the requirements of the problem statement (given in Chapter 2).

Further details of the compositions of each phase at any point in the absorber may be found in the Appendix, under the heading “(Mass &) Energy Balance over Absorber,” or by deduction from the Specification Sheets of items upstream and downstream of the absorber (see Chapter 6 as well as the Process Flow Diagram in the Drawing Annex).

7.2 Mechanical Design

The reader will find it helpful to refer to drawings 7001 to 7004 in the Drawing Annex while reviewing this section.

7.2.1 Materials and fabrication

As before, all of the construction will be of type 316 (see Chapter 6). The majority of the fabrication will be the welding together of formed sections. These joints will undergo full radiographic or ultrasonic examination in accordance with the Australian Standard [2], to allow a joint efficiency of unity to be valid. Generally the design tensile strength was taken at around 170°C (100MPa).

Teflon will be used for gaskets (as used at Orica’s Deer Park facility), and also for the demister at the top of the tower [37].

Further details and exceptions are given in the following sections.

7.2.2 Internals

7.2.2.1 Bubble-cap trays

7.2.2.1.1 Tray layout

As noted, the trays are reverse flow type to accommodate the low liquid flowrates. Due to the presence of the baffle, the serpentine cooling coils and the bubble-caps, it was decided that employee comfort would dictate a tray spacing of 750mm [3], [33].

Provision was made for a manway in each tray, so that manholes would not have to be installed in the side of the column between every tray. However it is unlikely that many people would enjoy crawling through 21 trays in a row, and so this was split into three sections of 7 trays (A, B and C), with manholes in the shell between each section.

Ref. [11] states that equilateral triangular layouts of bubble-caps are the common arrangement, with spacings between cap centres of 25 to 50mm in excess of the cap diameter. A typical cap diameter is said to be 100mm for a 1.8m column, although there is significant periphery wastage for this configuration. Along with this, there is also a reduction in ‘active area’ due to the presence of the central baffle (and manway), and so 75mm caps will be used on a 125mm equilateral layout.

The cooling coil will fit between the bell caps at the pitch chosen. The required length of the coil (at 25mm diameter) was calculated in Chapter 6 to be 273m, which comes to 13m per tray. The orientation of the coil will be parallel to the central baffle. This gives 8 runs of straight tube, of varying lengths, on each side of the baffle.

7.2.2.1.2 Bubble-caps and pressure drop

In order to evaluate the plate pressure drop, it was found necessary to design the bubble caps. Due to the low liquid flowrate and the need to maintain a height of liquid in the tray, bell caps rather than tunnel caps will be used [11].

By trial and error (see Appendix), the caps were designed to have 40 slots each, of width 3mm and height 10mm. Estimating the typical active area from Ref. [11] resulted in an estimate of 100 caps per tray (rounded down from 124, which was calculated first). It may be seen from Drawing Number 7002 (in the Drawing Annex), that the true number of caps is between 100 and 124, so 100 was a reasonable, slightly conservative estimate.

³⁸ Given that ideal trays are a hypothetical concept, there is no physical reason to round values to integers.

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In order to decrease the pressure drop, a value of 1.0 was taken for the ratio of annular area to riser area for the caps (at the lower end of the range presented by Ref. [11]), with the reversal area equal to 1.35 times the average of the riser and annular areas (equal here).

This meant that the riser diameter would be 53mm.

Ref. [33] recommends 40 to 50mm for the weir height. Given the need to have adequate liquid coverage of the cooling coils, 50mm is specified. Given the low liquid flow, the ratio of weir length to column diameter was taken as 0.70 [33]³⁹.

Taking the height of the slot above the plate floor as 10mm, a total pressure drop of 58mm(H₂O) per plate was calculated. For 21 plates this is 12kPa, which is entirely acceptable, and within the range of the initial assumption (20kPa for the whole column).

7.2.2.1.3 Downcomer design

Some of the information need to calculate the downcomer was found in the previous section. Segmental baffles will be installed [3].

The liquid-seal depth is taken to be 25mm, compared with a design liquid height on the trays of 50mm⁴⁰. Taking foaming into account, the height of aerated liquid in the downcomer is found to be approximately 240mm. This means that the assumed value of 750mm for the plate spacing is more than sufficient.

This compares to the foam height of only 112mm on the trays, so that the baffle height of 200mm is ample.

Finally the residence time in the downcomer is checked: it should be greater than 3 seconds for adequate disengagement [3], [33]. In this case the value calculated was 44s, so this guideline was satisfied too.

It is noted that the downcomer apron will not be sloped, as this will increase the cost unnecessarily – the design given above is valid.

7.2.2.1.4 Tray support

A peripheral support ring welded to the inside of the vessel provides a 'bracket' for the bubble cap trays [3], [33]. (A similar ring will also support the packed column plates.) The width of this ring will be 50mm. It will not extend into the downcomer area [33].

The trays are to be designed to support a mass of 1000N (102kg) acting over an area, in the centre of the plate, that is of a much smaller diameter than the plate (1800mm). This is considered to be a more realistic and more demanding situation than analysing the case of uniform loading over the entire plate. The formula used is taken from MORLEY [23].

A tray thickness of 3mm ("12gauge") was considered reasonable [33], to avoid excess weight. However the deflection under the above load would then be 82mm, which is too great. Therefore two schedule 40 steel pipes (type 316), of 19mm nominal diameter, are welded to the underside of the peripheral support.

The calculations are presented in the Appendix.

It may be noted that the effect of folding the sections of the tray under into a C-beam type of form, in addition to the overlapping of joints, is likely to increase the strength of the trays more than the weakening effect of the holes made for the bell caps.

7.2.2.2 Packed sections

This section begins with a comment on the importance of additional internals that bolster the packed beds:

"The choice [...] can greatly affect the performance of the selected packing. [...] a greater degree of importance is now attached to the design of individual items of equipment within the tower. For example, a support plate is now accepted as a more important component than a mere support for the packing above it – its design can vitally affect the performance of the tower. Similar consideration must be given to distributors and redistributors [...]" [3]

³⁹ There is an error in the chart presented by this reference. The correct relationships may be found in Ref. [17].

⁴⁰ Although the actual height of liquid on the trays will be higher – around 53mm, by the Francis weir equation [11], [33].

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The type of packing (50mm metal Pall rings) has already been specified.

7.2.2.2.1 The bottom of the bed

The packing support plate must possess a high percentage of void area in order to permit free upward flow of the gas. For ease of construction and handling, the plate should be available in sections. Recommended is the gas-injection type of support plate [3]. This will be used below Stage 1, where the liquid collects in the base of the column. However it will not suffice below Stages 2 and 3, as liquid must be drawn off at these points.

For this reason a liquid redistributor-collector plate may be used in conjunction with a gas-injection support plate. The risers on the plate allow liquid to be drawn off [3], while the gas-injection plate avoid the difficulty of trying to pass two phases in opposite directions through the same openings [35].

The type of gas-injection plate to be installed is a multibeam gas injection packing support plate. This has been tested with metal Pall rings, and found to give improved pressure drops. Its modular design allows it to be installed through standard manholes (450mm or larger), while the beam style gives high mechanical strength [35].

Although it is recommended that the redistributor be installed from 150 to 460mm above the packed section below, this is not important in this case, as it is being used primarily for its ability to hold a certain head of liquid to allow draw off.

The liquid collector plate must be of gasketed construction (Teflon will be used) so that it can be sealed to the supporting ledge and be liquid-tight. To provide sufficient head with minimum load a sump is provided.

A multibeam gas-injection support plate is shown in Figure 7-2, and a liquid redistributor in Figure 7-3.

7.2.2.2.2 The top of the bed

The use of a hold-down plate on top of a packed section to restrain the bed under conditions of high gas rates or fluctuating gas flows is not crucial for steel packings [3]⁴¹. A light-weight bed limiter with a mesh backing, resting directly on top of the packed bed, will be sufficient to prevent bed expansion and to keep the top of the bed level [35].

The bed limiter will be restrained by the liquid distributor immediately above it. The construction will be sectional, as for the other internals [35].

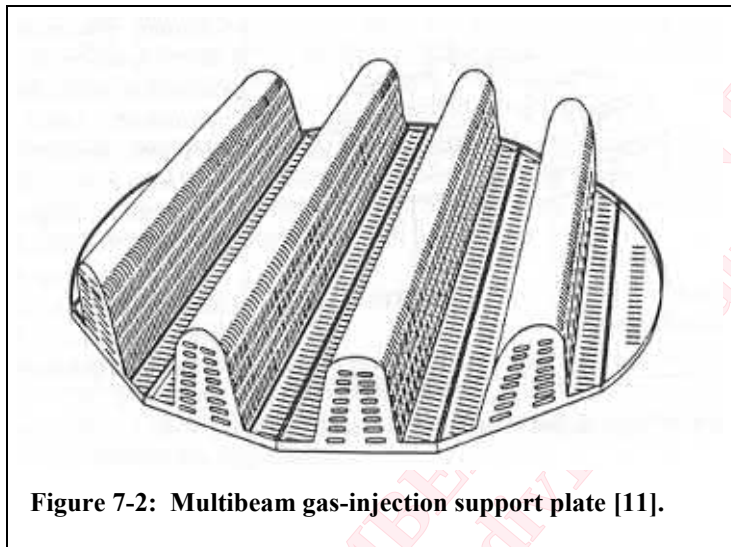


Figure 7-2: Multibeam gas-injection support plate [11].

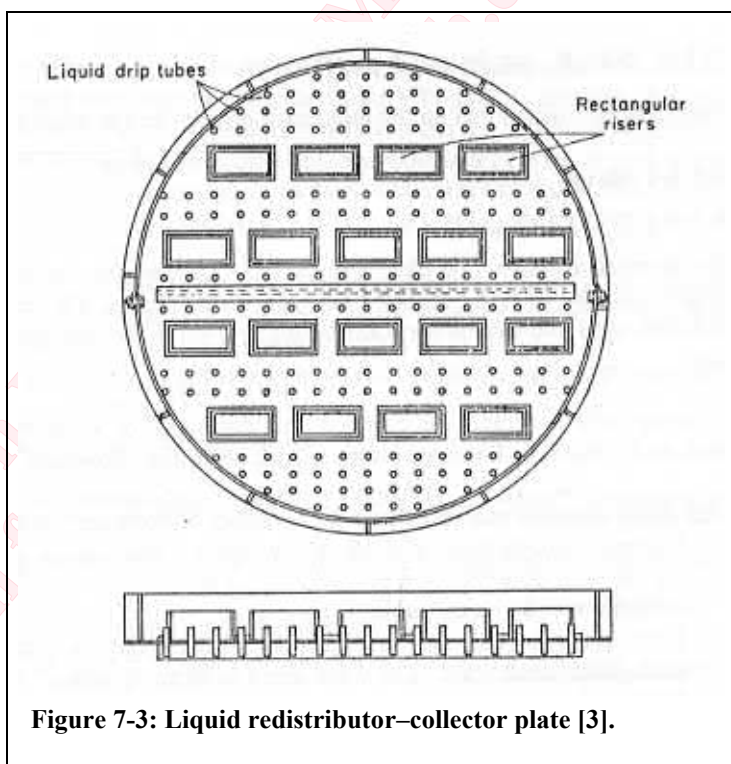


Figure 7-3: Liquid redistributor-collector plate [3].

⁴¹ For carbon or ceramic packings the plate minimises breakage. For plastic packings the plate acts as a bed-limiter, preventing carry-over with the gas.

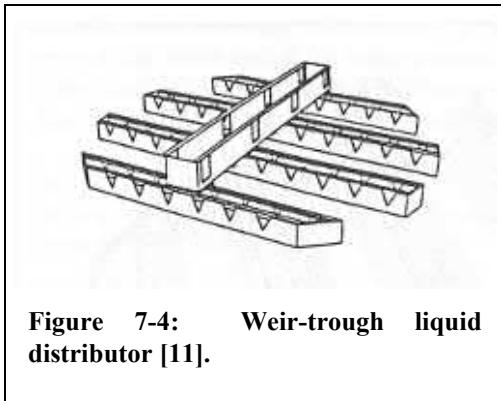


Figure 7-4: Weir-trough liquid distributor [11].

A liquid distributor is needed to prevent maldistribution in the column. The most popular type is the weir type, as it overcomes the propensity of orifice type distributors to block (which is a serious consideration due to the possibility of paraformaldehyde formation), while retaining a high free area for gas flow. It provides uniform, controlled distribution of liquid flowrates between 0.0014 and $0.034 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ [3]. Thus it is suitable for use in all of the packed beds (Stages 1 to 3).

Because the liquid flow into each packed section is almost entirely made up of the recirculant flow, a liquid distributor will suffice even above Stages 1 and 2. While gravity-fed distributors are more limited in their capacity to operate at low turn-down ratios than pressure-fed distributors, a turndown to 60% should be okay [35].

A weir type liquid distributor is shown in Figure 7-4.

As the liquid distributor has little weight to support, fixing may be made to a continuous support ring around the inside of the column. Care must be taken to ensure that the final assembly is completely level [3]. As for the trayed sections, the width of the support ledges will be 50mm [35].

7.2.3 Shell, ends and supports

This sections follows that on the internals, because the internals determine the mass of the vessel to be borne.

7.2.3.1 Shell

7.2.3.1.1 Shell wall

The number of plates, the plate spacing, the manway dimensions (see the following section), the packed bed heights and the distance required between packed stages allowed the height of the vessel to be found. Also included were allowances for some liquid hold-up in the base and a vapour disengagement space above the top tray.

To begin with the “minimum practical wall thickness” of SINNOTT [33] was used to estimate the thickness of the shell wall. This was 7mm, including a 2mm corrosion allowance⁴².

This initial estimate was tested against a number of (extreme) conditions:

- Normal operation during a cyclone. The design pressure was taken as 150kPa(abs), from the normal operating pressure of 130kPa(abs) at the base. The wind speed is taken as $27 \text{ m} \cdot \text{s}^{-1}$ (*i.e.* 100km.h⁻¹), uniform over the vessel wall.
- Hydrostatic testing. It is assumed that hydrostatic testing would not be approved under cyclone or earthquake conditions. The wind speed is taken as $10 \text{ m} \cdot \text{s}^{-1}$ (uniform), but with the vessel now completely filled with water.
- Normal operation during an earthquake. The design is for winds at $10 \text{ m} \cdot \text{s}^{-1}$, with a horizontal force acting due to the earthquake. The data of BROWNELL and YOUNG (1959), as presented by Olbrich [26], are used, and the assumption is that the region is in seismic zone 2 to 3 (medium to high risk).
- Incorrect installation. Installation of the column, when empty, by lifting it from one end, with the other end resting on the ground, in an almost horizontal position. Evaluated at 150°C.

While the cyclone and earthquake loading are not relevant to design in many Australian areas, our site is situated on the Eastern coast of Kalimantan, where such factors should be taken into consideration.

Calculations given in the Appendix treat the vessel as a cantilever, fixed to its foundation. The strengthening effects of scaffolding, closures, peripheral support rings and the like are not considered. As required by the standards, the 2mm corrosion allowance was not included in the strength analysis.

The moment due to small fittings such as ladders, pipes and manways will be small, and is neglected [33].

⁴² Because it is unlikely that significant corrosion of the type 316 steel would occur, this could alternatively be interpreted as a 6mm thick shell wall plus 1mm corrosion allowance.

It was found that the maximum tensile strength of the shell wall, as taken from the Standard [2], was not exceeded in any of the above cases. Also, the buckling criterion given by Ref. [33] for vessels under internal pressure was found to be satisfied for the first, and most extreme, case.

For the last case, the design maximum tensile stress was approached, though not exceeded. This should not be a cause for concern, because correct installation would be at under 50°C, and would not be from a single point at the extreme end of the vessel (a sling would (also) lift from the middle). On top of this, when the column is installed it is reasonable to assume that the extra 2mm corrosion allowance will still be present!

From the above results the shell wall was set to be 7mm, including corrosion allowance.

An attempt to evaluate the suitability of the shell for negative internal gauge pressures (*i.e.* vacuum) was made, on the grounds that someone might accidentally isolate the vessel with hot condensables in it. When they cool, they would condense, decreasing the internal pressure. Calculations were inconclusive, but indicated that the vessel was not suitable for substantial external overpressures (see Appendix).

This is not a major issue, as the vessel is not really designed to withstand external pressure. The remedy would be proper and ongoing training of employees to avoid the damaging situation.

7.2.3.1.2 Manholes and flanges

The manway size is taken from Ref. [3]. This reference presents an intriguing table claiming to be based on British Standard 1500 (1959), which gives standard diameters of manholes from 370mm (14 inches) to 610mm (24 inches). It may be that people were smaller back then, but the author believes that the upper value given is most reasonable. This belief is based on the size of typical maintenance and commissioning crews, as well as the need for ease of access in installing internals and carrying materials in and out – in particular the sections of the bubble-cap trays. The tray sections must fit through the manways, but if they are too small they become impractical.

The height of the manhole – that is, the amount by which it protrudes from the column – is taken as 200mm, which is well below the maximum height given (which is 1070mm for the diameter chosen). The low value is chosen to reduce material costs, as well as to aid in the accessibility⁴³.

The thickness of the manhole walls is taken as equal to that of the shell (*i.e.* 7mm, inclusive of corrosion allowance) [3].

The manways are shown on Drawing Number 7004 in the Drawing Annex.

Just as for the pipes, the flanges are given nominal dimensions in integer multiples of inches⁴⁴ (expressed in millimetres).

The type of flange used will be socket-welding, which, “is used fairly extensively in chemical process piping.” [21] The advantages of this type of flange are that:

- smooth, pocketless bore conditions can be obtained by grinding the internal weld flush
- their static strength is equal to that of welded slip-on flanges, but they have fatigue strengths that are 50% greater
- they cost only about 10% more than slip-on flanges.

From the design pressure, the flanges need only be rated to 6bar [33] or 150psi [13] (whichever is relevant to the standards used by the supplier).

The flanges are shown on the Process and Instrumentation Diagram (P&ID) in the Drawing Annex.

Due to the removal of a portion of the shell for each the instance of a manway or flange installation, there is a need to make up for this by means of some reinforcement. The reinforcement method chosen is the commonly adopted welding of a pad onto the shell, about the outside of the manway or flange. This method is cheaper than a forged ring, but can deliver similar levels of reinforcement, and the problem of thermal stress arising seems unlikely. It also avoids the risk of trapping “crud” and enhancing corrosion by installing inset nozzles. [33]

The “equal area method” is recommended to provide adequate reinforcement, without causing secondary stresses deriving from over-reinforcement. As a simple numerical expression, the outer diameter of the welded pad will be taken as 2.0 times the (inner) diameter of the hole or branch, with the thickness of the pad equal to that of the shell (*i.e.* 7mm).

⁴³ Considering long items passing through the manway, which will be able to be ‘angled’ more.

⁴⁴ Or fractions for small diameters, or multiples of two or five for large diameters, in accordance with the standards [13].

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The calculation of insulation requirement is presented in the Appendix. Insulation is required only at the base of the column (Stage 1), where the temperature is hotter and the solution more concentrated in formaldehyde.

The hotter temperature (75°C at the bottom of the stage) means that insulation is desirable to give some protection to personnel.

The higher solution concentration means that the storage temperature requirements are higher to avoid deposition of paraformaldehyde. At the top of stage 1 the liquid temperature will be 60°C. Assuming the ambient temperature is at the Bontang minimum of 20°C (see Chapter 2), then the average tube-wall temperature will be around 40°C. The combined literature suggests that this is too low a temperature for an unstabilised⁴⁵ solution of 54%(kg.kg⁻¹) formaldehyde.

Given that cooling water utility is required to accomplish the cooling duty, and that increased temperature increases the partial pressure of formaldehyde in the vapour, there is a significant disadvantage in installing excessive or unnecessary insulation, on top of the added capital (and maintenance) cost. Thus insulation is specified for Stage 1 only, with a thickness of 25mm (this is assumed to be a standard thickness). The material will be the fibreglass blankets recommended by Ref. [20] for this type of application.

7.2.3.2 Ends

The top and bottom end of the shell are identical, leading to a cost saving. Initially there was consideration given to a conical base section to facilitate draining, however this would give less liquid hold-up per height,⁴⁶ and were recommended mainly for facilitating the flow of solids (as in hoppers *et cetera*). Thus standard torispherical heads (“dished ends”) were specified for both the top and bottom vessel closures. These are “the most commonly used” up to operating pressures of 1500kPa. They will be the cheapest option up to 1000kPa, as they can be readily formed and require less material than other types of domed heads. [33]

The torispherical head is formed from part of a torus and part of a sphere. The radii of these sections are respectively the ‘knuckle’ radius, R_k , and the ‘crown’ radius, R_c . In order to avoid buckling, guidelines suggest that R_k/R_c be less than 0.06. R_c should be less than the diameter of the shell, D , as this will otherwise approach a flat end, which resists pressures inefficiently. [33]

From these guidelines, and with $D = 1800\text{mm}$, $R_k = 200\text{mm}$ and $R_c = 1400\text{mm}$ were selected.

Calculating the thickness required for the ends using the ‘stress concentration factor’ approach, the minimum thickness was found to be 3.2mm, exclusive of 2mm corrosion allowance. Due to the non-fundamental nature of the design equation, the maximum longitudinal and meridional stresses in the head (which will occur in the toroidal section) were calculated. These were well below the design maximum⁴⁷.

Additional formulae were given in the Standard [2]. The value of 3.2mm for the thickness, t , was checked as it related to buckling. Given that the quantity D/t was equal to 563, much greater than 100,⁴⁸ it was recommended that particular care be exercised with regard to high localised stresses that may give rise to buckling during hydrostatic testing.

At this stage it was decided to form the entire head at the same thickness as the shell ($5 + 2\text{mm}$), to reduce D/t . This has a further advantage in terms of the welding together of the closure and shell. The new thickness resulted in $D/t = 360$ – still greater than 100, but less than before.

Looking to the first amendment (November 1990), a further recommendation regarding the maximum allowable internal pressure is given in the event that $D/t > 300$, as is the case here. That recommendation is found to be satisfied with the thicker value of t (but not for the initial value of t), even for the heavy hydrostatic pressure loading.

⁴⁵ There is no mention of the addition, or presence, of stabilisers in the product, and so it is assumed that they are to be absent. Furthermore, it seems unlikely that the stabilisers would be added before entering final storage.

⁴⁶ Hence a lower residence time, leading to the possibility of more difficult control.

⁴⁷ Implying that an unmentioned safety factor was included in the design equation. The problem with this sort of thing is that designers who are unaware of its inclusion may then apply their own safety factor, which would be excessive.

⁴⁸ The value of 100 strictly applies only when R_k approaches the minimum permitted, *i.e.* 6% of R_c . We have been more conservative here, in selecting designing R_k to be 7% of R_c .

A 'flange' or 'skirt' is included on the formed torispherical head to ensure that the weld line is away from the point of discontinuity between the head and the cylindrical section of the vessel [33] (see Drawing Number 7004, Drawing Annex). The weld will be a double-welded butt joint, as recommended by the Standard [2] to give a maximum welded joint efficiency of unity for the vessel.

Because the head will be formed, the joint efficiency factor can be taken as unity.

7.2.3.3 Supports

7.2.3.3.1 Scaffolding

The description of the skirt support that has been designed follows in the next section. There will also be a further supporting effect of scaffolding which has several functions: it will provide some support to the absorber column (especially strengthening the column against buckling); it will provide some support of the installed pipework entering and exiting the absorber; and it will provide the 'skeleton' for the stair-way up the column.

The design of scaffolding was not included in the terms of the contract, and would require the negotiation of a new contract, or, alternatively, the renegotiation of the existing contract.

7.2.3.3.2 Skirt

A skirt is used to support the absorber column. They are recommended by Ref. [33], because, "they do not impose concentrated loadings on the vessel shell," and, therefore, "they are particularly suitable for use with tall columns subject to wind loading."

The design essentially follows the Australian Standard [2], with incorporation of some material from SINNOTT [33].

The maximum compressive stress will be found from the conditions prevailing during hydrostatic testing. The preliminary assumption is made that the skirt will have the same thickness as the column, *i.e.* 7mm (calculations are carried out using the fully-corroded value of 5mm). This value satisfies both the yield stress and the Young's modulus requirements.

The skirt was assumed to be of the cylindrical type (cheaper), rather than the conical type, and subsequent calculation of the base ring details has been found adequate. The base ring can be shown to have a convenient circumference to take 8 bolts. This number is recommended as a multiple of 4, and gives a realistic bolt cross-sectional area of 590mm² ($D_{\text{bolt}} = 27\text{mm}$). The pitch between the bolts is also above the guideline minimum of 600mm. These bolt dimensions were calculated based on the 'cyclone loading' described previously, as this corresponds to the maximum tension.

Calculations on the width of the base ring gave values below the minimum recommended values⁴⁹ [33], and so the widths shown in Drawing Number 7003 (Drawing Annex) have been increased. The thickness of the base ring is calculated to be 17mm.

The method of connection of the skirt to the shell follows the amended version of option (c) given in Fig. 3.24 of the Standard [2]. This includes recommendations for the position of the skirt-shell weld relative to the shell-end weld. Details are given in Drawing Number 7003 (Drawing Annex).

The skirt has been checked for the possibility of temperature causing discontinuity stresses, but this was found to be negligible.

7.2.3.3.3 Foundation

Ref. [3] presents simple information for the preliminary design of foundations⁵⁰. This essentially involves ensuring that the soil below the foundation is under compression at all points. However there is also a limit on the maximum compressive load that can be borne by the soil. This requires a knowledge of the type of sub-soil below the foundation, which could only be determined by a survey.

⁴⁹ To provide support on the inside edge of the skirt (50mm) and to ensure sufficient provision for the bolt head and spanner.

⁵⁰ Or, at least, it would, if only some [censored] [censored] [censored] had not 'borrowed' some of the pages of the book in a past year.

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This would seem to be a good reason not to design the foundation quantitatively at this stage. A civil engineer may even have to be called in.

Qualitatively, the foundation will be of reinforced concrete. An octagonal shape is recommended because “it combines features of stability and ease of construction with minimum material requirements.” However for our plant it is likely that several equipment items will sit on the one ‘superfoundation’, including the absorber, as is the case at Orica’s Deer Park facility.

The reasoning behind this decision is that the other items will need foundations in any case (they cannot be installed on the ground!), and siting several items on the one foundation would decrease the site area required, as well as inter-piping costs.

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⁵³ The author wishes to acknowledge Mr. Adrian DIXON for kindly providing access to this reference.

⁵⁴ The generosity and thoughtfulness of Mr. Alan FONG and Mr. Anthony FONG is recognised here for the gift of this comprehensive reference.

⁵⁵ The author expresses his sincere thanks to Miss Jayne BORENSZTAJN for making this reference available.

⁵⁶ See also the Sulzer Chemtech website at http://www.sulzerchemtech.com/t1_gauze.htm#BX.

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8 PIPING AND INSTRUMENTATION DIAGRAM (P&ID) AROUND FORMALDEHYDE ABSORBER

The purpose of a piping and instrumentation diagram (P&ID) is multifarious. It must provide piping and valve information; an indication of the instrumentation that is installed, including control; and other fittings. Clearly the purpose of a P&ID is not merely to convey information about the control scheme adopted. The P&ID acts as the foundation for hazard and operability (HAZOP) studies (see Chapter 9) and the mechanics of plant layout activities (see Chapter 11). It is also an invaluable tool in the maintenance, trouble-shooting and optimisation of a plant during and after commissioning.

In this chapter the P&ID for the absorption section of the plant is considered. This includes the formaldehyde absorber, ABS-1, plus the pumps and heat-exchangers on the pump-arounds, as well as the cooling coil and feed water pump.

The completed P&ID is inserted in the Drawing Annex.

8.1 Pipework

8.1.1 Pipes

The pipes are simplest to specify. As everywhere else on the plant, type 316 stainless steel is used for its superior corrosion resistance, which has the additional benefit of providing superior product quality [17], [19]. The diameter is calculated on guideline values of 2m.s^{-1} flow of liquid (or a maximum of 1m.s^{-1} under gravity flow) and 25m.s^{-1} of the gases [3], which are all 'low pressure' in this section of the plant.

The diameter thus calculated is then rounded to a standard nominal diameter [4], based on the imperial system but expressed in integer millimetres.

For the product line and the bottom stage (Stage 1) recirculation, the piping is traced. The tracing on the pipelines was suggested¹ to allow for start-up conditions². On start-up the plant will be cold, including the pipe-walls. This will not be a problem in other parts of the plant. For example, this may be beneficial in the raw methanol handling area, as this would reduce the flammability risk. However where concentrated aqueous formaldehyde solutions³ are concerned, there is a risk⁴ of depositing paraformaldehyde on the walls of the cold tubes [15]. This risk is overcome by installing steam tracing. This is only required for the lower stage.

Some additional piping that was not included on the Process Flow Diagram (see Drawing Annex) includes the bypass lines and kick-back lines⁵. Kick-back lines, when functioning, prevent over-pressure upstream of pumps that would otherwise be 'dead-headed'. A liquid seal is used at the base of packed column ABS-1 to minimise the possibility of getting gas in a pump (P4-A or P4-B) suction line [9].

8.1.2 Joints

Generally all of the 'large' pipes or ducts are flanged, with gaskets of Teflon (as used at Orica's Deer Park plant). 'Large' is roughly any diameter over 40mm [17], although this will vary on a case-by-case basis.

8.1.2.1 Flanged joints

Bolted flanges are used to connect instruments and piping to vessels, which aids disassembly for maintenance work, where either equipment items or piping must be removed⁶. This includes on the isolation valves and on the control valve stations. In some of the longer lengths of pipes additional flanges may be present, as there is a

¹ By Dr. Andrew HOADLEY (private communication).

² The recommended start-up procedure for the plant is discussed in Ref. [8]. Essentially, material can be (mostly) recycled and gradually heated until it comes up to the design operating temperature, at which point the normal ratio of off-take and purge flows is instated. See also Ref. [11].

³ Especially those with low methanol contents, as the "Grade A" product exiting the absorber.

⁴ The risk is decreased at low concentrations. During start-up the concentrations in the lower stage would initially be much lower than during normal operation, and this may obviate the need for tracing! Further study would be required.

⁵ Note that only two kick-back lines are installed on the combination P-4A, P-4B and P-6, as only two are to be active at any one time.

⁶ Large equipment items such as the absorber may still be removed with their thermocouple connections in place.

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practical limit on the length of welded piping sections – these are not shown on the P&ID⁷. Flanges are also used on the manholes in the column (this has been discussed in detail in Chapter 7). Finally, ‘blind’ flanged are used at the ends of pipes to give surety of closure [18].

The flanges selected for use throughout the plant are of the socket welding type. These are, “used fairly extensively in chemical process piping.” [9] The advantages of this type of flange are that:

- smooth, pocketless bore conditions can be obtained by grinding the internal weld flush
- their static strength is equal to that of welded slip-on flanges, but they have fatigue strengths that are 50% greater
- they cost only about 10% more than slip-on flanges.

From the design pressure, the flanges need only be rated to 6bar [17] or 150psi [4] (whichever is relevant to the standards used by the supplier).

8.1.2.2 Screwed joints

Screwed joints are used on smaller pipes, as they are cheaper. For example the pressure indicators are screwed onto valves, and those valves are screwed onto a spool piece. Screwed joints are not indicated by any symbol. Threaded connections will follow the British Standard for Petroleum plants (BSP).

Special ‘threaded’ connections are provided on the shell of ABS-1 (at the base) and on the shell and tube sides of HX-6, HX-7 and HX-8. These connections, shown with a ‘cap’ during normal operation, are designed to take a flexible hose connection for nitrogen inerting when maintenance is required⁸. There is no need to go to the expense of automated nitrogen inerting in the absorption section of the plant. This could be installed in the reaction and vaporisation sections.

8.1.2.3 Welded joints

Many of the joints will simply be welded to further reduce costs. For example the temperature probes are screwed into welded fittings, and the pressure tappings off pipes are simply welded. Welds are also used for the reducers⁹ (shown in the control valve stations). Welds are not indicated by any symbol in the P&ID. Welds will undergo radiographic or ultrasonic examination to verify their integrity [1].

8.1.3 Valves**8.1.3.1 Safety valves**

Safety valves¹⁰ are installed on the absorber, ABS-1. The greatest pressure is expected to be at the base of the column. Maintenance is also easier at low elevations. Common practice is to install safety valves at the top of equipment items. Here a kind of compromise is made, and safety valves installed in both locations. This will handle the possibility of a blockage in the tower (e.g. due to extreme fouling). Given the constant (low) back pressure, the safety valves need not be specified as balanced bellows valves [9].

The reactor has been fitted with bursting disks: the design is directed so that full force of an explosion – if one did occur – would not propagate to the absorber. The heat exchangers are not fitted with safety valves to reduce costs. They will discharge through the column if required.

The process vapour is flammable in air. Formaldehyde is also a possible carcinogen. Therefore the safety valves will discharge to the tail-gas burner (RXN-3 – not shown on the absorber P&ID), from which the safely combusted gases can be released to atmosphere at a ‘high level’. That is, at an elevation where there is no source of ignition (to minimise the hazard of burner malfunction), and at which it can be diluted by the surrounding air before it can be convected or diffuse nearer to the ground.

⁷ That level of detail could only be shown if piping lengths were known, such as on an isometric piping drawing.

⁸ Compressed air could also be connected to ensure the atmosphere in the vessel was breathable in the case of entry by personnel.

⁹ The reducers used are ‘eccentric’ (rather than concentric), to improve drainage.

¹⁰ The nomenclature of Ref. [9] is adopted here, wherein is stated:

“Confusion is sometimes caused by loose interchange of the terms ‘safety valve’ and ‘relief valve’, suggesting they are one and the same thing. There is a difference.

A safety valve is automatically actuated by the static upstream pressure and is used for gas or vapour [...].

It has rapid full opening, or ‘pop’ action, to give immediate protection by release of pressure.

A relief valve automatically operates in a similar manner to a safety valve, but it opens in proportion to the increase in pressure over the operating pressure and it is used for liquids [...].

To complicate matters further, a safety-relief valve [...] can be used either for gas and vapours or liquids.”

Valves leading to safety valves are locked open in normal service, just as major bypass valves are locked closed.

8.1.3.2 Relief valves

On the kick-back lines relief valves¹¹ are installed. This is an innovation of the author's. Common practice has either no kick-back line (increased hazard) or a kick-back line with a restricting orifice plate, "ROP," inserted. This plate allows a small flow through under normal operating conditions, but lets a larger flow through if there is an obstruction downstream of the pump.

An improvement to operation can be made by installing a control valve, which will only allow flow through in response to a certain set overpressure [18]. The disadvantage of this scheme is that capital cost is increased, as well as complexity (and hence maintenance).

The relief valve installed should be cheaper than a control valve station (though more expensive than an ROP), but it will also only be actuated by a certain overpressure, meaning that there is no deterioration in performance during normal operation due to its installation.

A (closed) bypass valve is installed on the kick-back line around the relief valve. This could be opened if the relief valve did not work, or possibly for performing work on the pump.

8.1.3.3 Isolation valves

Spectacle valves are provided on either side of the pumps to achieve positive isolation – an "infallible, leak-proof, visible shut-off" [9]. This is of particular importance for the combination of pumps P-4A, P-4B and P-6. To save money P-4B is configured so as to be able to replace either P-4A xor P-6.¹² If the one pump that is not operating is not properly isolated, then damage may be done to the pump, the effective efficiency of the active pump may be decreased¹³, or – most seriously of all – there may be risk to personnel due to fumes, fire or deflagration.

To minimise the risk of damaging the pump or of causing a loss of containment due to reverse flow, a check valve (or 'non-return valve') is installed upstream of each of the three pumps, but before the isolation valve.

If the pumps in operation are not properly isolated from each other, then some mixing of streams will occur. This is probably not a major hazard, but will cause deterioration of product quality.

For pumps P-7, P-8 and P-10 check valves are not required before the downstream isolation valve. However check valves are installed downstream of the kick-back lines to prevent reverse flow through the overall pump 'installation' [18].

Gate valves are placed in series with each of the line-blind valves, on the "upstream side"¹⁴ of the line-blind valve, to allow the line to be opened or blinded under pressure from that direction [9]. The gate valves are, in fact, integral to the unit.

As noted, valves separate the pressure gauges, to facilitate their removal and replacement.

8.1.3.4 Control valves

"Control valve stations" are arranged such that isolation valves enable easy removal of the control valve proper. Further, the bypass line is oriented to allow access to the underside of the (heavier) control valves, including space underneath for removal by a low trolley or bogey [9].

Line reducers and enlargers (namely reducers fitted 'in reverse') are installed either side of the control valve¹⁵. The control valve size can then be less than the main line size (that is, the line size connected to the control valve station) [9]. This reduces the cost of the control valve, and also improves the controllability¹⁶.

Eccentric reducers and enlargers, rather than concentric ones, are proposed to facilitate drainage. This is important for maintenance work on the control valve.

All of the control valves are likely to come fitted with valve stem positioners.

¹¹ See footnote 10.

¹² Operation is alternated (say monthly) to ensure that both pumps are in good working condition.

¹³ If the unisolated line acts as a kick-back line.

¹⁴ the term 'upstream' may be assigned differently in the case of (say) a valve failure, compared to normal operation.

¹⁵ Presumably the cost of installing larger isolation valves ("A" and "E") either side of the control valve, due to the placement of the reducers, has been found to be off-set by the lower pressure drop. Note that the control valve stations are labelled 'mnemonically' – "B" is for the bypass valve, "C" is the control valve and "D" the drain!

¹⁶ By decreasing the system gain.

For gas streams the 'station' consists of only a butterfly valve, without a bypass line.

8.1.3.5 Drain valves

In all cases the design philosophy is to drain from the lowest point, and to vent from the highest point – whether it be in an item of equipment or in a section of pipe-line. Drain valves are normally closed, and hence are shown 'blacked out'. A drain, which is locked closed and blanked off, is included on the safety-valve discharge line, to drain the line in the event of liquid discharge due to flooding of the tower.

Note that vents and drains are integral with the heat exchanger shells (for both HX-6, HX-7 and HX-8), and therefore are not shown as separate valves on the P&ID. A remotely operated valve (ROV) acts as a vent at the top of the absorber.

A dedicated sample valve is installed on the product line, although samples could be taken from any drain valve. Drains that are not used regularly are blanked off [18].

8.2 Instrumentation and Control

8.2.1 Instrumentation scheme

8.2.1.1 Configuration

Flow measurement devices and control valve stations are installed on the pump delivery lines (rather than the suction lines) to reduce the risk of cavitation.

Also, a sufficient length of straight piping run must be allowed for to give accurate measurement of flowrate [16].

The flowrate measurements will be taken by implication from differential pressure measurements over an ROP. Temperature measurements will come from thermocouples (probably K type, dependent on manufacturer's recommendations). These would not need to measure the temperature at the centre of the column, as the horizontal temperature profile would be relatively flat.

To measure compositions there are a number of possibilities. Standard oxygen detectors may be used on the tail-gas line (Stream 39), but this is more relevant to the tail-gas burner (RXN-3) section of the plant. The oxygen level in the absorber feed (Stream 21) would also always be low during normal operation, which would not be helpful for control.

The formaldehyde content of the product stream would give the most relevant control information. It is also required for quality assurance, and so samples will be taken from the product line, buffer tanks and storage tanks as part of a routine analysis procedure. However the manual sampling regime is relatively slow, and not automated – it would be along the lines of supervisory control. Rapid analysis could be implemented by deducing¹⁷ the composition from measurements of the refractive index and density.

Automated density measuring devices exist, though the accuracy is not known. Therefore there may be scope to automate control. The most readily available and reliable form of on-line formaldehyde analysis appears, however, to be for gas streams,¹⁸ and the more accurate of these seems to be the spectroscopic type [12]. Of these the Fourier Transform Infrared (FTIR) Continuous Emissions Monitors (CEM's) look to have good prospects for implementation [6], [7].

However, without further details on these analysers, including detection range, price and mean time between failures, they will not be specified for the plant. It is assumed that the existing control scheme is adequate, and that the monitors discussed here are to be considered for an upgrade.

8.2.1.2 Locally-mounted instrumentation

Locally-mounted temperature and pressure indicators are installed by every manhole on the absorber, and at the inlet and outlet of every shell-and-tube heat exchanger. Also, local pressure indicators are present up and downstream of every pump.

The purpose of these locally mounted gauges is to provide information to the workers who are actually working on the plant.

The locally mounted gauges will not be electrical, due to considerations of cost, ease of installation and reliability [20].

¹⁷ Namely from correlations, such as those given by [15].

¹⁸ Apparently developed to measure gaseous formaldehyde emissions such as in stack gases and exhaust gases.

8.2.1.3 Panel-mounted instrumentation and alarms

Most of the instrumentation with control room displays are involved in the control of the plant. Control of the plant in the sense of feedback (or feedforward) signals for a controller, but also supervisory control information.

As the control system is likely to be computer-based, instrumentation will be electronic. All output from panel-mounted instruments, controllers, recorders and alarms will be either displayed or else available for display in the control room.

Recorders are installed on the flows of the vapour stream (Stream 21) into the absorber (ABS-1), and for the temperatures of each process-side outlet of the heat exchangers (Streams 24, 29 and 32). In addition to this it is likely that all of the controller variables will have the option of being stored for a period of time.

The benefits of recording information are in verification of performance (possibly for use in case of threatened legal action), for optimisation or troubleshooting, and for diagnosis after a plant upset or accident.

The alarms warn the operators of failures and trips, to allow them to take appropriate action – which means they must be well-trained beforehand. A ‘motor stop alarm’ warns the operators that a pump motor is no longer operating. Obviously all alarms would be recorded.

The trip may have been activated by either the high pressure alarm or low pressure alarm that is installed immediately after each pump. This would send a signal to a relay or ‘actuator’ to stop the pump motor (marked “M” on the P&ID). The high pressure alarm would be activated by a blockage in the line downstream of the pump (including closure of an isolation valve). Low pressure alarms will shut down the pump in the event of gas entering the line, *i.e.* ‘vapour lock’, which could damage the pump¹⁹.

Alarms would be programmed to go off if the process-side temperatures of the streams exiting the shell-and-tube heat exchangers deviated outside of a set range. If the temperature were too high, then that would imply that the recirculated cooling water (RCW) had too high a temperature or too low a flow. If the temperature were too low, then the cooling water may have too great a flowrate, or the process stream too low a flowrate. The problem of a high temperature is that it increases the vapour pressure of formaldehyde, leading to decreased effectiveness of absorption. The problem with low temperature is that paraformaldehyde may form on the cold surfaces.

There is one more alarm, which is installed on the safety-valve discharge line. This line would normally be close to atmospheric pressure, and therefore any pressures significantly above this are likely to be due to safety valve actuation, for whatever reason.

8.2.2 Process control scheme

8.2.2.1 Control systems installed

In the shell-and-tube heat exchangers one fluid is a process fluid, while the other is a utility (RCW). However the flowrate of both streams may be manipulated variables, as the process fluid is simply being recycled around a packed bed. The temperature at the bottom of each bed is largely influenced by the temperature of the recirculant that enters the top of that bed (the recirculant flow being far greater than the flow from the bed above).

Thus the temperature at the bottom of the bed may be adjusted by manipulating the flow of process fluid through the exchanger. In response to this the utility flowrate will need to be adjusted, and this is done by controlling the exit temperature of the RCW.

In each case the control cascaded onto a flow controller, which will provide more stable control [10], [13].

At the bottom of the absorber column (ABS-1) the liquid level is also controlled. The liquid level measurement will be provided by a ‘ball-and-stick’ arrangement, which will float on the surface of the liquid (it will be of type 316SS, of course). This is a cheap option, which has the benefit of not being subject to clogging by paraformaldehyde deposits²⁰, such as may occur with pressure gauges used to determine head of liquid. The manipulated flow is that of the product, Stream 25, rather than the Stage 1 recirculant (which just goes ‘round and ‘round’). The level at the base of the column also implies the liquid temperature at the top of the bed, because that affects how much of the volatile components are condensed or vaporised.

¹⁹ Aside from being symptomatic of other problems, especially a low (or non-existent) liquid level.

²⁰ Although occasional recalibration may be necessitated due to altered buoyancy of the float.

Chapter 8: P&ID around Formaldehyde Absorber**Formaldehyde**

The flow of fresh demineralised water to the top of the column is assumed to be able to varied (using valve CV807C) by simple ratio²¹ with the flow of inlet gas, which is measured.

At the top of the column the main off-gas line (Stream 37) is manipulated by butterfly valve (CV811C) to keep the pressure drop across the column to its design value. Following this is a control valve (CV812C) manipulated by a flow ratio controller to keep the recycled gas to a set proportion.

For the serpentine coolers, the cooling duty is split into three sections (HX-11A, HX-11B and HX-11C), which each cool three trays. Each section consists of seven bubble-cap trays and three temperature probes²². A temperature selector then chooses the highest [10] of these to be controlled. The RCW flow is manipulated.

Some computerised 'interlocks' can be built into the control system (either computer-based or with programmable logic controllers –PLC's). For example, if the feed flow drops below a preset value, then both the off-gas purge (Stream 39) and the product off-take (Stream 25) could be shut off [16].

8.2.2.2 Control valve failure

There will be two electrical lines, one above ground and the other below, to avoid the risk of a loss of power to the control systems. A back-up generator will also be located on the site. However there may still be a controller failure. In that event the following modes of control failure are selected:

- CV807C on the demineralised water feed line (Stream 33) will fail open, as it is better to have a slightly dilute product than a dry (and excessively hot) column.
- CV811C on the main off-gas line (Stream 37) will fail open to avoid overpressurising the absorber.
- CV812C on the tail gas line (Stream 39) will also fail open, to purge contents safely to the burner (RXN-3), for subsequent release at high level.
- CV801C, CV802C and CV803C on the serpentine cooling coils (Stream 129) will fail open to keep the column cool (and hence wetted).
- CV804C, CV806C and CV809C on the recirculant lines (Streams 24, 29 and 32) will fail open to allow cooling.
- CV808C, CV810C and CV813C on the RCW lines (Streams 122, 124 and 126) will hold their position on failure. If they failed closed cooling of the column would cease, but if they failed open, then paraformaldehyde deposition may cause other damage to the plant.
- CV805 on the product line (Stream 25) will hold position on failure. If it failed open then the column may drain, or material that is out of specification may be sent to the tank farm. However, if the valve failed closed then the column may flood.

8.3 References

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²¹ The amount needed would clearly depend also on the water content of the gas stream. However, to account for this a mass-balance approach may need to be taken by the control system, or else a composition analyser installed.

²² They are not too expensive.

²³ Third amendment is most recent, dated December 1993.

²⁴ This reference due to Dr. David J. BRENNAN.

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* Thanks to Mr. Phonse Everard for this reference.

9 HAZARD AND OPERABILITY STUDY FOR VAPORISER

9.1 Introduction

A hazard and operability (HAZOP) study is a procedure for the systematic, critical examination of the operability of a process [2], in order to identify hazards and problems which prevent safe and efficient operation. In this chapter the technique will be applied to a process design, although it may equally well be applied to an existing plant.

Naturally some thought was given to risk minimisation during the preliminary design of the plant, and while drawing up the piping and instrumentation diagram (P&ID – see Chapter 8). However there are bound to be some details that are overlooked without the attention of a formal study¹.

The HAZOP study is traditionally performed by a team of people, with each of its members having expertise in different areas relevant to the section of plant under examination [3]. Analysis proceeds on a line-by-line and item-by-item basis. (or on a step-by-step basis for batch plants²). For each equipment item and for each line the following five headings are filled:

- **Guide word** – this includes the seven guide words³ recommended by the Chemical Industries Association (CIA) [2]: No/Not; More (of); Less (of); As well as; Part of; Reverse; and Other than⁴. Another set of words that may be used as an alternative to, or in conjunction with, these guide words are the ‘critical examination questions’ [3]: What (else); Where (else); When (else); How (else); and Who (else).
- **Deviation** – this is the quantity or element that the guide word refers to. Examples include: Level; Temperature; Pressure; Flow; and Formaldehyde.
- **Possible causes** – this heading identifies the cause of any departure, in the sense of the guide word, of the quantity or element given as the deviation. For example, Less (of) + Level $\Leftarrow$ Leakage. The purpose of this heading is to test whether the deviation can be shown to have a realistic cause.
- **Consequences** – the consequences are the results that follow from a meaningful deviation. This should include an indication of how the operators will find out about the deviation. If none of the consequences are hazardous, then no action need be taken.
- **Action required** – this includes any remedy to the situation that is judged to be merited by the risk that would exist if the action were not taken.

One thing that should be stressed is that a HAZOP study does not magically ‘make a plant safe’. Apart from the obvious potential for the study itself to be flawed, even if conducted rigorously, there remain some hazards that the HazOp study cannot pick up. For example, it may be common practice for the operators to engage in a customary game of poker on the first Sunday night of each month. The diversion of their attention constitutes a hazard, but could not be identified by a HAZOP study. Another example would be the absence of a sanctioned ‘emergency response plan’ (ERP).

Other technical safety procedures must therefore be implemented alongside the HAZOP study, such as hazards analysis (HAZAN) studies and institutionalised hazard management (HAZMAN) methods [3].

The following section looks at the application of a HAZOP study, as described above, to the P&ID for the vaporiser circuit.

9.2 Results of the HAZOP Study

A record of the HAZOP study meeting is given in the Appendix⁵.

In summary of the meeting, eight process streams, two utility streams and four equipment items were examined. These are shown in the pre-HAZOP-study P&ID that is given in the Drawing Annex preceding the Appendix. The post-HAZOP-study P&ID is also given.

¹ For example it is claimed in Ref. [3] that HAZOP studies on the P&ID (in 99 meetings, over 6 months) for the 38th olefines plant (costing \$500 × 10⁶) designed and built by a certain contractor identified 1350 problems.

² This approach would also be relevant to plant start-up and shut-down procedures. However sanity constraints preclude their investigation for this report.

³ Or, more correctly, phrases.

⁴ When referring to time, the guide words Sooner than and Later than may be used.

⁵ Due to the vagaries of the ‘publisher’.

As a result of the study, close to 100 plausible deviations⁶ were identified, with around 100 actions recommended. The reader should not interpret this as meaning that each deviation usually requires only a single action to remedy it. The majority of the deviations had several recommended actions to be taken. However, the several actions taken for one hazard often also served to remedy a potential problem in another line or item.

In some cases this was deliberate, as a sensible economic measure. For example, having judged that there was unlikely to be any significant overpressure in the mains water line (Stream 3), it was necessary only to install a high pressure alarm on one of either Stream 6 or Stream 7, which are in series. (Also, Stream 7 is physically quite short.)

Most of the actions related to the installation of high and low alarms, with associated trips where necessary. An interlock was also recommended for the pair of pumps. Other actions to be taken included the installation of additional instrumentation, particularly panel-mounted instrumentation⁷, and recommendations for the mechanical design of the sections, such as installing a vent, insulating the steam and condensate lines (Stream 118 and 119), and ensuring that the materials of construction and thicknesses are adequate. Maintenance and training were also relevant issues.

9.3 References

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⁶ Deviations that did not appear to be meaningful or that did not have any hazardous consequences are not included in the record of the study.

⁷ All of the instrumentation on the original P&ID appeared to be locally-mounted – or, at least, do distinction was made between locally mounted and panel mounted instrumentation.

10 PARALLEL STREAMING

10.1 Introduction

This chapter covers the “special task” that has been allocated by the project supervisor. And tasks don’t get much more special than this.

10.1.1 Scope of the task

In this study of the advantages and disadvantages of parallel streaming are examined. Considerations include:

- Reliability – How reliable is the one configuration relative to the other? Is this always true?
- Cost – Does one configuration cost more than the other? Is there a trade-off between capital and operating costs?
- Operations – Is one configuration generally easier to operate?
- Maintenance – Does one of the configurations require more maintenance work?

The discussion will be mostly qualitative, but some quantitative examples and estimates are given where it is appropriate.

10.1.2 Definition of parallel streaming

Parallel streaming refers to the processing of materials by the use of two small units, or equipment items, rather than a single, larger unit. When only one stream is present, the configuration is referred to as single-stream. Parallel streaming may also be referred to as multiple streaming.

The schematic in Figure 10-1 illustrates the main conceptual difference between the two processes.

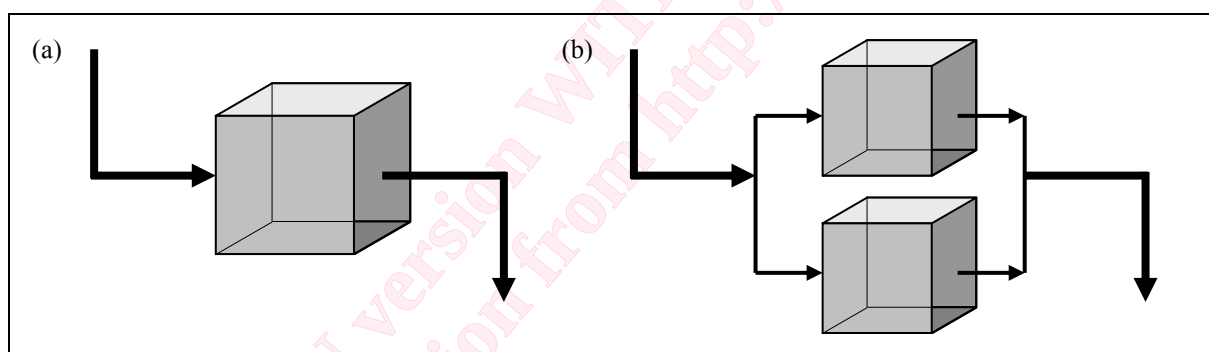


Figure 10-1: Schematic showing (a) single streaming and (b) parallel streaming of a single process.

With reference to the formaldehyde plant that has been designed, there is another possibility: some of the units operations in the plant may be parallel processes, while other unit operations may process in a single-stream configuration.

An example of parallel streaming in our design (see the Process Flow Diagram in the Drawing Annex) is the catalytic reaction operation. The catalyst is split between two beds, RXN-1 and RXN-2. An example of single streaming would be the P-1, the methanol feed pump, in the Process Flow Diagram. Although the Specification Sheet (given in Chapter 6) indicates that there are two pumps installed, P-1A and P-1B, these do not operate in tandem. One pump is a stand-by for the other.

Another case of two items in a single stream process would be two heat exchangers in series, such as HX-5 and HX-10 (with respect to the aqueous methanol stream). This may be seen as two single-stream items forming one single-stream operation.

10.2 Considerations

10.2.1 Cost

Essentially all of the considerations boil down to some sort of cost. In this section operating and capital costs are examined. However the implication is that the later sections on maintenance and so on all infringe on the cost aspect.

10.2.1.1 Capital cost

10.2.1.1.1 Derivation

An estimate of the capital cost of an item may often be obtained from its dimensions. In Figure 10-1 a schematic was given. The pedantic reader will have observed that the volumes of the two smaller cubes are equal to that of the single, larger cube. This means that the ratio of side lengths is $1:2^{1/3}$, or approximately $1:1.260 = 0.794:1$ for (parallel stream):(single stream).

It is reasonable to assume that, for many units, it is the total volumes of all the items that should be equal, rather than, say, the sum of side lengths for each item. This assumption would be almost exactly correct for storage tanks. It would be approximately true for other items, such as the absorber and the steam turbine. (The volume would refer to the process volume, rather than the volume of materials making up the item.)

For an initial estimate, we may suppose that, for the storage tanks, the cost is essentially proportional to the total external surface area. Although the roof may need a vent and the walls may need branches and the underside will need a foundation (and so on), it is assumed that the relative increasing effect that this has on the cost of each will be similar. For the two configurations of cubes¹ given above, the ratio of surface areas for the (two) parallel stream and the single stream processes will be $2(6 \times 1^2):(6 \times (2^{1/3})^2) = 2:2^{2/3} = 1:2^{-1/3} = 1:0.794 = 1.260:1$.

This implies that the cost of a doubling in capacity would be 26% more if a unit was replicated instead of procuring a single, larger unit. Of course, this would not apply to existing operations, where the value of the existing unit must be taken into account.

Of course, the above estimate contains a number of simplifications. For one, the thickness of material required will decrease for a smaller unit. Thicknesses of spheres and cylinders, for a given internal pressure (moderately above atmospheric) may be taken as proportional to the diameter. For a sphere the ratio of diameters for (two) parallel stream units and a single stream unit is also $1:1.260$, with the ratio of surface areas being $1.260:1$, as before. The ratio of thicknesses will be $1:1.260$, and therefore we calculate that the costs would be identical. However this does not take fabrication of the item, such as welding into account. Welding is likely to remain more or less proportional to the surface area, despite the decrease in diameter. Costs of installation, insulation, painting et cetera will also all depend more on the surface area than the thickness. Instrumentation² and piping are more likely to depend on the number of items.

Thus it still seems reasonable to assume that there will be a saving associated with putting in a single stream process in preference to a parallel stream process of the same (total) capacity, which we may estimate to have roughly a 25% greater capital cost.

10.2.1.1.2 Empirical data

Fun though it is to attempt a derivation of the relative costs of the two configurations, the complexities highlighted in the last paragraph mean that surety in the result could never be attained, because each complexity forces the adaptation of new assumptions.

The best way³ of getting around this problem is to use empirical correlations, in which all of the various complexities have been embedded (and then smoothed by curve-fitting).

¹ The same analysis could be applied to cylinders, spheres or another more physically relevant shape. Cubes are only considered here for their simplicity.

² Assuming that, for example, a liquid level controller could control level in either one large tank, or one of the two smaller tanks.

³ With the exception of obtaining actual quotes from a number of vendors! (This would be more specific to the equipment item specified.)

The most popular correlation to use has the form $I = k_i Q^b$ [1]. It indicates an exponential relationship between the capacity, Q , and I , the fixed capital investment. The constant k_i may be replaced, if desired, by expressing the function $I/I_{REF} = (Q/Q_{REF})^b$, where the subscript “REF” stands for a reference condition.

The usefulness of the formula is realised through the values of the exponent, b . For plants which are, “nominally parallel stream,” $b = 0.8$ to 0.9 , but for single stream plants $b = 0.5$ to 0.6 [1]. (Plants that are mixed parallel and single stream have intermediate values of b .⁴)

Thus, we may now consider the case of a doubling in Q_{REF} . The capital investment for the parallel stream process will increase by around $2^{0.85}$, while for the single stream configuration I would only increase by $2^{0.55}$. This gives a ratio of $2^{0.30}:1 = 1.231:1$.

Happily, this predicts that the parallel stream process would be 23% more expensive, which is remarkably similar to the value of 25% found in the previous section. Taking the bounds of the ranges suggested above, the increase may typically range from 15% to 32%.

While the above equations are very neat, the reader should be cautious in generalising the above results to their own circumstances: it is usually difficult to obtain detailed data to confirm the validity of the relationships given [1].

10.2.1.2 Operating cost

Ref. [3] gives a breakdown in typical formaldehyde plant costs, which are claimed to have come from GUTHRIE (1974), via KHARBANDA (1979)⁵. Manufacturing costs are said to be composed of: 59% raw materials costs; 23% depreciation; and 18% utilities and labour.⁶ These figures are supported by Ref. [5], which states that “the cost of methanol represents over 60% of formaldehyde’s production costs.” (The other main raw materials are air, which is ‘free’, and silver catalyst, which is expensive but is ‘consumed’ very slowly.)

10.2.1.2.1 Raw materials

Raw materials may be thought to be identically proportional to the capacity of the plant. The capacity of the plant should be proportional to the (combined) size or volume of the equipment items.

This assumes the same levels of efficiency in, for example, a catalyst bed of larger diameter. This may be difficult to achieve exactly, due to increased maldistribution problems as the bed diameter increases.

As a first estimate, the raw materials will be taken as directly proportional to the plant capacity, and therefore unaffected by the configuration of the plant, in terms of parallel or single streaming (a 1:1 ratio)

10.2.1.2.2 Depreciation

Depreciation depends on the capital cost of the plant, and thus is expected to vary in the manner described in section 10.2.1.1 (supported by Ref. [1]).

10.2.1.2.3 Labour costs

To take a simplified view of things, if it takes one person to sit and stare at one big pressure indicator, it would probably take two people to sit and stare at two smaller pressure indicators. That is, more people are required, in general to run a parallel stream process.

Of course, the above example applies more directly to process labour (operators). Other forms of labour may be almost proportional to the number of operators, such as maintenance labour. These generally constitute the majority of the labour force in the plant [1].

For technical, professional, supervisory, administrative and engineering staff there are large economies of scale are available in both configurations – that is, a doubling in capacity will result in much less than a doubling in the number of those classes of employee.

Again the relationship of costs to capacity may be represented as exponential: $M = k_m Q^a$, where M is the total number of plant employees and Q is the capacity, as before. Of course, for simplicity we assume that the M

⁴ These may be estimated by taking a weighted average of the exponents for purely single-stream and purely parallel stream processing, with the weighting determined by the proportion of capital associated with each configuration [1].

⁵ Ref. [7], which gives identical values (at least for formaldehyde), gives its source as 1965, U.S. conditions. Also, capital related charges were taken as 33% of capital investment.

⁶ For captive production. Otherwise 67%, 18% and 15% respectively [7].

Chapter 10: Parallel Streaming**Formaldehyde**

may equally be interpreted as labour costs. Expressing this with respect to a reference condition permits elimination of the proportionality factor, k_m : $M/M_{REF} = (Q/Q_{REF})^a$.

The exponent, a , is said to be approximately 0.3 to 0.4 for single stream plants, and 0.6 to 0.7 for parallel stream plants.

Thus, a doubling in capacity would, on average, give labour costs for parallel streaming versus single streaming of $2^{0.65}:2^{0.35} = 2^{0.30}:1 = 1.231:1$. That is, total labour costs for parallel stream plants⁷ would be 23% greater than for a single stream plant.

Although the exponents for labour were lower, overall, than for capital cost, the ratios have turned out to be the same, because the difference between exponents for the two configurations was the same for both costs.

10.2.1.2.4 Overall operating cost

The above discussion may be summarised in tabular form:

Cost	Proportion of total	Parallel stream plant	Single stream plant
Raw materials	60%	1	1
Depreciation	22%	1.23	1
Utilities ⁸ and labour	18%	1.23	1
Total	100%	1.09	1

Table 10-1: Relative operating costs for the two configurations (arbitrary units).

This shows that, due to the dominant effect of the raw materials, the total manufacturing cost is only about 9% greater for a parallel stream relative to a single stream plant.

Strictly speaking, the manufacturing cost data estimated above only constitutes one part of the total operating cost. Non-manufacturing costs include “the costs of distribution, selling, research and development, and that share of the cost of running a company which can be allocated to the product or business in question.” [1]

For simplicity these costs were neglected here. In all probability they will be lower than the average, as this plant sells to a captive market using an established technology. Furthermore, the technology has not been developed in-house.

The non-manufacturing costs are not expected to be significantly different for the two configurations.

10.2.1.3 Investment strategy

Wiley entrepreneurs may wish to consider the benefits of a staggered investment, such as may only be obtained through a parallel stream configuration. This strategy involves the initial purchase and commissioning of a process that has a significantly lower capacity than the full design capacity that is projected for the plant. The advantage of this investment is that by the time the second (or subsequent) stage of the project is purchased and commissioned, interest will have been accrued on the capital that would otherwise have been spent, and some income will also have been derived from the existing (smaller scale) operation.

This has the effect of reducing the peak level of indebtedness, which may be important if the availability of start-up capital is problematic.

Such a strategy depends heavily on the prevailing economic circumstances for its success. Of particular importance are the rates of interest and inflation and taxation. These lead to the ‘discount rate’ (see Ref. [1]).

Table 10-2 gives an example of discounted cash flows for a ten year period for two different discount rates and for the two different investment options.

⁷ All of the parallel stream plant calculations here assume that there are two streams, unless otherwise stated.

⁸ Utilities for the formaldehyde process are assumed to be zero. The steam generated is used for heating and driving the blower, with any surplus sold to a neighbouring plant (probably the resins plant). For the purposes of this analysis we will assume that the steam sales exactly balance the recirculated cooling water costs (the only other major utility expense), so that nett utility costs are zero.

Year	Discount rate = 5%.y ⁻¹				Discount rate = 15%.y ⁻¹			
	Single-stream		Staggered		Single-stream		Staggered	
	CF	CDCF	CF	CDCF	CF	CDCF	CF	CDCF
0	-100	-100	-56	-56	-100	-100	-56	-56
1	+30	-71.4	+14	-42.7	+30	-73.9	+14	-43.8
2	+30	-44.2	+14	-30.0	+30	-51.2	+14	-33.2
3	+30	-18.3	+14	-17.9	+30	-31.5	+14	-24.0
4	+30	+6.4	+14-56	-52.4	+30	-14.4	+14-56	-48.0
5	+30	+29.9	+28	-30.5	+30	+0.6	+28	-34.1
6	+30	+52.3	+28	-9.6	+30	+13.5	+28	-22.0
7	+30	+73.6	+28	+10.3	+30	+24.8	+28	-11.5
8	+30	+93.9	+28	+29.3	+30	+34.6	+28	-2.3
9	+30	+113.2	+28	+47.3	+30	+43.1	+28	+5.6

Table 10-2: The effect of discount rate on the two investment strategies. CF = cash flow and CDCF = cumulative, discounted cash flow (both after tax).

This may be graphed as in Figure 10-2.

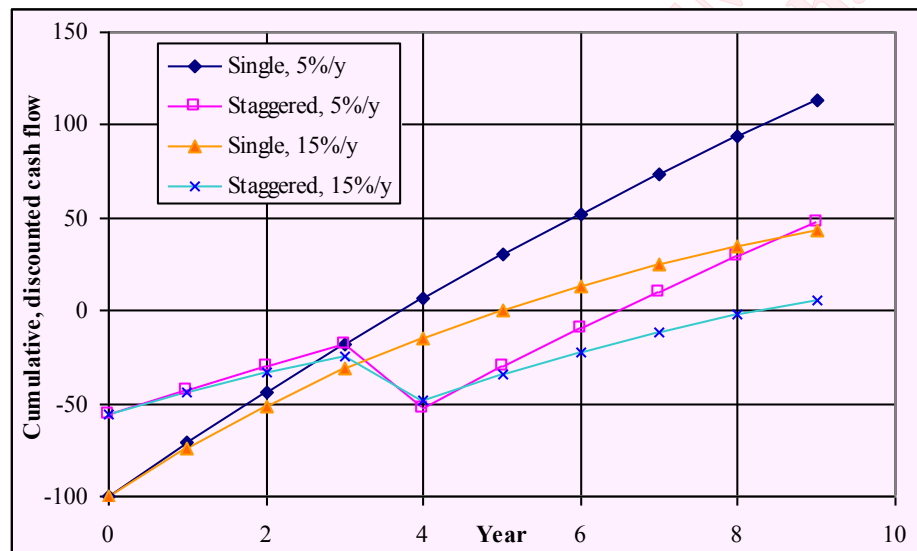


Figure 10-2: The effect of discount rate on the two investment strategies.

This graph shows the single stream option to be preferable in terms of 'net present value' (NPV)⁹. It also retains a positive NPV for greater values of the discount rate¹⁰.

As noted, the advantages of the staggered investment lie in:

- its flexibility
- its lower peak debt.

The above strategy may be regarded as the expansion of an existing plant. From Ref. [1] we observe that expansion in parallel has the benefit of allowing a closer match between plant capacity and market demand. This reveals another advantage: a staggered investment strategy may be more easily adjusted to cope with deviations of reality from the projections that the project was based on.

For example, five years after the initial investment, the company may have planned to put in a second, identical line in parallel. However if they see that the demand has increased much more than they had anticipated, then the capacity of the second line could be increased, or else a third line put in along with the two initially planned. Obviously this is subject to the availability of additional capital and room for expansion.

On the other hand, if the market 'crashed', then work on the proposed second line could be postponed indefinitely.

⁹ The cumulative, discounted value predicted for the end of the project.

¹⁰ The discount rate for which the NPV goes to zero is termed the 'discounted cash flow rate-of-return' (DCFR), or the 'internal rate-of-return' (IRR) [1].

10.2.2 Reliability and risk

The issue of reliability is somewhat confusing: there is a higher probability of something breaking down, but consequences of any one breakdown will be, on average, less severe. For example, if the probability of a large level controller failing is the same as for a small level controller, then the probability of one of two smaller level controllers failing would be double that for the single larger controller. Of course, there is also a possibility (hopefully slim) that the second smaller controller would also fail.

Given that risk is equal to the product of likelihood and severity [10], the two risks approximately balance each other. The risk may be expressed numerically, with probability, severity and risk ranging from 0 (low) to 1 (high).

Case	Probability	Severity	Risk
Failure of one small item	$0.10 \times 0.90 = 0.090$	0.50	0.045
Failure of other small item	$0.10 \times 0.90 = 0.090$	0.50	0.045
Failure of both small items	$0.10 \times 0.10 = 0.010$	1.0	0.010
Total	0.19	(0.526...)	0.10
Failure of one large item	0.10	1.0	0.10

Table 10-3: Risk of failure in parallel and single stream processes. (Arbitrary data.)

The table shows that the risks associated with the two configurations are identical.

Other considerations may be made. For example, if one of the smaller units fails, then it is likely that more attention would be paid to the other smaller unit that was still functioning, thereby reducing the likelihood of a combined failure¹¹. Also, there probably is a higher likelihood of a larger item failing.

These considerations indicate that while the 'reliability' of parallel stream plants is probably less, the risks are probably also reduced.

10.2.3 Maintenance

In terms of maintenance, the malfunctioning of a small level controller (to use the example of the previous section) will not be half as inconveniencing as the malfunctioning of a larger level controller. It is unlikely to take as much as twice as long to unscrew the casing, for example.

To the author's knowledge there is no universally accepted way to represent the level of maintenance required. We will measure it by the number of 'manhours' per week spent doing maintenance work¹². Analysing the situation as in the previous section, Table 10-4 is obtained.

Case	Failures/week	Manhours/failure	Manhours/week
Failure of one small item	$0.10 \times 0.90 = 0.090$	0.7	0.063
Failure of other small item	$0.10 \times 0.90 = 0.090$	0.7	0.063
Failure of both small items	$0.10 \times 0.10 = 0.010$	1.2 ¹³	0.012
Total	0.19	(0.726...)	0.14
Failure of one large item	0.10	1.0	0.10

Table 10-4: Maintenance required for parallel and single stream processes. (Arbitrary data.)

Thus the maintenance required for a parallel plant will be greater than for a single-stream plant.

¹¹ It is assumed that the two events (failure of each small item) are independent of each other. If the plant power supply failed, then obviously all electrical items would fail at once. This is because the power supply would not be a truly parallel system – although parallel wiring is possible.

¹² An alternative may be the irateness of the workers!

¹³ If both fail then we may assume that the maintenance worker will have improved their technique by the time they work on the second item.

10.2.4 Operation

The operability of a plant is a key concern. With parallel catalytic reactors in the plant (RXN-1 and RXN-2 – see the Process Flow Diagram contained in the Drawing Annex), there is the opportunity to regenerate the catalyst in one bed while the other is still producing product. Staggering the regeneration dates in this way would permit the smoothing out of product quality curves, being an average of products from recently regenerated catalyst and older catalyst.

Ref. [2] discusses pluralities of catalytic reactors for silver catalyst processes (*i.e.* ‘desirably’ with stabilising off-gas recycle). Therein is stated that, although the temperatures of reactors within a group may initially be within 10 to 15°C of each other, the temperatures often eventually diverge to 30 to 80°C difference. This is attributed to the nature of the catalyst materials, the catalyst ages, distribution of the silver in the bed, and even pressure drops through different piping. Parallel streams are said to comprise from 2 to 10 units.

That reference states that “A plant with several reactors arranged in parallel and in particular the twin reactors [sic!] represents a preferred embodiment of the process of the invention.” Furthermore, “An additional preferred variation of this embodiment is represented by alternating employment of the process of the invention in the branch lines of a twin reactor [...].”¹⁴ This refers primarily to operation of one catalytic reactor while the other bed is being regenerated: “the catalysts are normally regenerated at different intervals.”

The invention is said to also be relevant to single reactors as well as larger groups of reactors in parallel.

The main reason for including two reactors in this case is the requirement to handle a turndown to 60% of design capacity. With only a single stream, the only way of achieving this would be to reduce the space velocity through the catalyst bed, and hence the contact time. We have seen (Chapter 3) that the contact time is a pivotal parameter controlling the reaction mechanism (along with the temperature). Therefore the preliminary assessment was made that the increased ‘efficiency’ at 60% capacity would offset the increased capital and operating costs (see sections 10.2.1.1 and 10.2.1.2, pages 10-2ff.). Obviously that assumption could be studied in more detail.

Suppose the deterioration in efficiency caused a decrease from the overall yield of 90% at design space velocity to only 80% at the turndown rate for a single stream plant. For the parallel stream there would be no decrease. From this basis Table 10-5 may be constructed (no intermediate turndowns are considered).

Characteristic	Turndown required 10% of time		Turndown required 30% of time	
	Single stream	Parallel stream	Single stream	Parallel stream
Normal yield [%]	90	90	90	90
Turndown yield [%]	80	90	80	90
Average	89	90	87	90

Table 10-5: Variation of average yield with configuration and relative duration of turndown condition.

Thus, on these (somewhat arbitrary) figures the compromise is between a few percentage points of yield and an increased capital cost of around 23%, as well as an increased operating cost of around 9%. However there is an important distinction to be made: the increase in yield for parallel streaming applies to the whole plant, while the increased capital and operating costs apply only to the reactor(s).

Other concerns may not be so easily quantified. For example, if the resins plant wishes to operate at 60% capacity then they will not be too happy if their supplier is only able to produce at full capacity or not at all¹⁵. Given that we (think that we) have a captive market, this is not an insurmountable problem. However if we were attempting to sell in a more competitive market, then customer demands for turndown would be compelling. Ignoring the customers’ wishes could result in the loss of future orders.

The same argument holds for the ability of the dual reactor system to maintain some production while one of the beds is being regenerated.

An important constraint that must always be considered in determining the configuration of unit operations is the maximum (economical) size that the equipment available in. For example, there is no point looking for a

¹⁴ Emphasis added.

¹⁵ The start-up and shut-down penalties here prohibit running at full capacity for three days, and then shutting down for two days, to average 60% production rates (remembering that the storage tanks have a three day capacity at full flow).

company to supply a single pump to handle a flowrate of $4 \times 10^4 \text{ m}^3 \cdot \text{h}^{-1}$ ¹⁶ – clearly a number of pumps in parallel would be needed to handle this requirement [4].

Similarly, there may be legislation or guidelines that prohibit items above a certain size.

In the case of the catalytic reactor considered here there is no such constraint: diameters from 500mm to 4000mm are considered to be feasible [6].

10.3 Recommendations

Where it is possible to avoid parallel streaming, one should do so. However some circumstances make multiple streaming the only feasible option. Such circumstances include:

- Limited availability of investment capital, leading to a constraint on the peak indebtedness allowed
- Uncertainty over the future market demand
- Highly hazardous processes, where the small reductions in risk become justified
- The (anticipated) need to cope with high turndowns
- The desirability of maintaining at least some product output
- Limits on the sizes of equipment.

Even in such cases the number of parallel streams should be kept as low as practical.

10.4 References

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¹⁶ It is left to the reader to wonder why anyone would want or need such a unit operation.

Formaldehyde

11 PLANT LAYOUT¹

Chapter 11 covers development of the plant layout. A description of the philosophy is given, and two general arrangement drawings of the site – in plan view and elevation – are provided in the Drawing Annex (Drawing Numbers 1101 and 1102).

11.1 Procedure

11.1.1 Starting point

There is insufficient information available about the site in Bontang, Indonesia,² and so an exploration of the criteria relevant to site selection would be inappropriate here. From the problem statement (Chapter 2), it is known that the site is flat, and within the bounds of a chemical processing complex³, which includes a formaldehyde resins plant. It is assumed that land area is not a dominant constraint.

Another unknown factor is the local planning permit system: government approval would have to be sought for the plant, which may be a source of unexpected constraints. Thus this design can only be preliminary.

There is also a lack of detailed information as to exactly which facilities would be provided by existing sources in the complex, and which would have to be built specifically for the new formaldehyde plant. Clearly an outside-battery-limits boiler house would not be required, as steam is already generated from the waste heat boilers (HX-3 and HX-4) following the catalytic reactors (RXN-1 and RXN-2) and the off-gas burner (HX-9 and RXN-3)⁴.

A cooling tower may be required, depending on the capacity of the existing unit(s). A possible site for a cooling tower is indicated on the site layout (plan view). In the event that existing facilities have sufficient 'spare' capacity, then that land will be re-allocated as "room for future expansion." The same philosophy is applied to all of the buildings, such as the religious centre⁵.

Given that storage tanks are included on the specification sheets (Chapter 6), these must be shown.

A boiler feedwater treatment and demineralisation plant is not on-site, and neither is an electrical substation [6]. As the majority of the materials entering and exiting the plant travel via pipeline, there is no need for a truck or tanker bay.

11.1.2 Philosophy

Two common philosophies in the laying out of plant items are to design the items according to the sequence in the process flow diagram, and to group similar items together. In this case a compromise procedure is followed.

Due to the large number of recycles (or recirculations) within the process, it is difficult to define one 'process flow sequence'. Rather, some of the flow goes in one direction, and some in another. To this end the layout has followed the 'main' flows, with any equipment for needed for the recycle stream located nearby.

Another factor that has made the layout more difficult is the 'integration' of items. While there is only one process-stream heat integration (HX-5, following the catalytic reactors and in the aqueous methanol recycle), there is also steam sent from the waste heat boilers to the turbine (TRB-1) and the reactor feed heaters (HX-2 and HX-10).

As noted, similar items were grouped together. This was done both on a large scale as well as on a small scale. Thus the storage area, methanol-formaldehyde processing plant and buildings for the employees were all allocated separate areas from the beginning. This initial designation of areas is shown in Figure 11-1.

¹ Although this task was defined as being a being specifically a group activity, Miss Rachel WELDON developed her own plant layout individually.

² Probably because this is a hypothetical project!

³ This much, at least, fits in with what is known about the site: an extensive petrochemical infrastructure exists there [1], [4].

⁴ The reader should be familiar with the Process Flow Diagram (given in the Drawing Annex) by this stage.

⁵ Indonesia is a predominantly Muslim country. Followers of this religion pray five times per day. The religious centre will also have facilities for people of other religions.

Storage area	Methanol–formaldehyde processing plant
	Area for employees

Figure 11-1: Preliminary site area designations.

Room for expansion was intended to be allocated within the methanol–formaldehyde processing plant, and wherever more detailed design indicated that room existed.

On the smaller scale, the 16 pumps (some stand-by) were grouped into three areas, the two catalytic reactors were located side-by-side (literally parallel streams!) and the shell-and-tube heat exchangers were distributed into two groups.

Naturally, the turbine and blower were located in the one enclosure.

In terms of elevations, all items were specified at ground level where possible, due the lower initial cost and ease of maintenance and operation. The packed columns (ABS-1 and HX-1) had to be oriented vertically for gravity flow, as was also the case with the heat exchangers operating on condensing steam (HX-2 and HX-10) and the steam drums (D-1 to D-3).

The plant is an outdoor facility, allowing substantial savings in construction costs, more accessible machinery and reduced dangers of fire or explosion [6]. The blower is housed in an enclosure, however, and thought may be given to an overhead shelter (for operator comfort) above the six pumps near the absorber, for example.

These philosophies are illustrated by the drawings in the Drawing Annex. An attempt has been made to indicate process and utility stream flows (namely steam). A detailed discussion follows.

11.2 Detail of Layout

11.2.1 Buildings⁶

In each case, for safety reasons, at least two means of escape (on different sides) are provided [7]. The walls of the control room and fire shed are to be particularly strong, as these are both close to the storage areas and not too far from the plant, and because these buildings are important in an emergency. (The medical centre is protected by these two.)

The sizes of the buildings are estimated from the guidelines in Ref. [5], based on requirements for no more than 20 persons on site (total)⁷. Other sizings are for roughly 2 operators, 1 laboratory employee and 1 maintenance worker.

The fire shed and medical centre are close to the main entrance. They are as close as is safe to the likely accident areas. While the plant would certainly not have its own vehicle⁸, it should at least have a shed containing fire-fighting equipment. Likewise the “medical centre” is really just a first-aid room, but that is no reason to omit it!

The workshop and store are integrated, as is common practice, and it is located close to the plant, along with the control room and laboratory.

Toilets and showers are provided⁹ in a ‘central’ sort of location – next to the canteen, and not too far from the control room or offices.

⁶ Although this plant is to be part of an existing complex, there are a number of reasons for including buildings on our site: safety (it is never safer to rely on somebody else to maintain a fire-fighting resource, medical facility, *et cetera*); convenience (operators do not like to walk too far to get to a toilet, prayer room or canteen; engineers and visitors like a near-by reception); limitations of existing facilities (the existing canteen/s may already be struggling to seat all of the existing employees). In any case, the buildings do not represent a major cost, as shown in Chapter 12.

⁷ While this may sound high, it actually gave values around the minimum of Ref. [5].

⁸ This is assumed to be established already elsewhere in the complex.

⁹ While these could have been provided in the canteen, it seemed that showers would not be installed in a canteen, and if there was to be a separate shower block, then it ‘may as well’ house the toilets also.

The offices and administration building fronts the car park, so that reception is located in a logical area.

Buildings generally have at least 1.5m clearance between them¹⁰.

11.2.2 Storages

As recommended by Ref. [5], the storage does not occupy, “more than two sides of the process plant area” – it occupies only one side. This arrangement allows adequate safety precautions to be taken. Access to the tanks is still possible if one of the roads is cut off.

Considering the storages as a hazard, they are located at least 15m away from likely sources of ignition in the plant, chiefly the tail-gas burner (RXN-3) and the catalytic reactors operating at 700°C (RXN-1 and RXN-2). The methanol storage tank is a more significant hazard, and therefore a blast wall will be built around it. This is based on the assumption that the wall will be more economical than locating the tank 30m from any other item on the site and from the site boundary, as recommended [5]¹¹. Only authorised employees may enter this area. “Water cannons” may be required for cooling of metal structures in the event of a fire [2].

Each tank will have a bund to collect any leakage, and this bund, too, will have emergency exits [5]. The tanks are grouped, and banded, in such a way that the contents of the tanks in one bund require the same type of fire-fighting equipment. The two ST-3's and the two ST-5's are grouped together. The methanol tank is separate.

The Grade B buffer tank, ST-2, is located closer to the methanol tank, as additional methanol will need to be sent to that tank.

11.2.3 Processing plant

Spacing between items has been taken from BUSH's 1971 values quoted in Ref. [5]. Generally the horizontal spacing recommendation between adjacent items is about 1.5 to 3m. For the shell-and-tube heat exchangers provision is made for removal of the tube bundle¹². The clearances give adequate allowance for safety and maintenance. The clearances are indicated on the drawing by a lighter outline around the item.

Vertical clearances are not relevant to this site.

11.2.3.1 Vaporiser and associated equipment

The equipment items associated with the vaporiser (HX-1) are all located close-by. This includes the various pumps and heat exchangers, each of which are grouped together. The main feed streams are: air (and off-gas), coming from the blower (CP-1); and methanol, coming from the methanol tank (ST-1). These are both located nearby.

As these units contain a significant inventory of methanol, which is quite flammable, they have been located at least 15m away from the most likely sources of ignition, namely RXN-1 to RXN-3.

As indicated, the blower (and turbine) are housed in a compressor building, as typical [6],¹³ for protection against noise pollution. It may also be noted that, “In contrast to the solidly constructed buildings required in Europe, buildings in tropical regions [such as Bontang] can be lightly constructed” for protection against wind and rain only. The compressor building will be well-ventilated to avoid accumulation of flammable vapours.

11.2.3.2 Reactors and associated units

The catalytic reactors and the tail-gas burner are all situated on the downwind side, at least 15m from any equipment other than their associated pumps and steam drums.¹⁴

¹⁰ Except for the fire shed and medical centre, which abut each other.

¹¹ If additional cheap land is available, then ST-1 would simply be moved approximately 20m to the North West.

¹² If applicable.

¹³ An example is Orica's Deer Park plant.

¹⁴ And the cooling tower, if needed. Note that the cooling tower would be located next to its main ‘client’, the absorber.

11.2.3.3 Absorber and associated items

The column, ABS-1, is an important item because of its size. It is supported by a permanent scaffolding structure, which has built-in a stairway. There may also need to be provision for some lifting equipment (especially for the packing). The siting of the absorber is such that heavy lifting vehicles will have good access on two sides (and limited access on the North side). The roads will be built to suit this heavy lifting equipment. The length of the road is also ample to accommodate erection of the column.

The absorber produces the formaldehyde solution that is the product, and so is located closer to the tank farm.

11.2.4 Other

The roads are all through roads to avoid the need for any three-point-turns, particularly of any trucks. They provide access for firefighting vehicles [6], and space for the installation of bulky equipment.

The cooling water tower, if required, would be situated on the downwind side of the plant, downwind of the air intake to the blower (CP-1).

11.3 Area required

As no real site has been allocated, the area needed is simply calculated by looking at the site layout diagram (plan view), given in the Drawing Annex.

This shows that the (fenced) site is $70\text{m} \times 124\text{m} = 8680\text{m}^2 \approx 0.868\text{ha}$ [3].¹⁵

The processing plant only occupies $30\text{m} \times 52\text{m} = 1560\text{m}^2 \approx 0.156\text{ha}$ (or 18% of the total), while the storage area comprises approximately $57\text{m} \times 42\text{m} = 2394\text{m}^2 \approx 0.24\text{ha}$ (28% of the total).

11.4 References

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¹⁵ For comparison, Monash University's "main Clayton campus area covers 101ha." [8]

Formaldehyde

12 ECONOMIC EVALUATION

In this chapter capital and operating costs are estimated, and general conclusions drawn from these. As the plant is not operating in Australia, but rather in Bontang, Indonesia, the costs will be expressed in terms of 1999 U.S. dollars¹ (USD₁₉₉₉). This has a local reputation as a stable currency, which will (hopefully) provide a ‘hedge’ against further fluctuations in the market, possibly due to the immense changes currently occurring in the republic.

Therefore it is recommended that budgeting be done in Australian or American dollars where possible, although Indonesian Rupiah would need to be paid in some instances.

12.1 Capital cost

“Plural perspectives” [1] are used in looking at the capital cost of the site. That is, information from a number of sources, of varying levels of detail, are used to ‘home in’ on an accurate figure.

12.1.1 Definition of boundaries

The capital costs are divided into two categories: inside battery limits (IBL) and outside battery limits (OBL)². Inside battery limits essentially consists of the processing plant, including the reactors, absorbers, pumps and heat exchangers. It would not normally include compressed air supply or steam generation. However, in this case those items are integral in the processing operation. Thus the IBL is considered to include everything that is shown on the Process Flow Diagram (in the Drawing Annex), except for the tanks (ST-1 to ST-5).

Outside battery limits is therefore everything on the site that is not covered under IBL. This includes the tanks, recirculated water cooling tower (if present), and buildings and service facilities for the plant, such as the laboratory, control room, offices, canteen *et cetera*. The OBL facilities can be identified on the plan view of the plant layout (Drawing Number 1101 in the Drawing Annex).

12.1.2 Initial estimates

An initial estimate of the cost of a complete plant may be obtained from the published correlations. These are generally based on information released by companies building news plants.

12.1.2.1 Generalised chart

From Ref. [11] a chart is given for “complete plant costs.” However the reference data is quite old: GUTHRIE (1974); Chemical Engineering (1973/1974); KHARBANDA (1979)³ and Chemical Engineering (1980–1987). It was updated to “early 1987” (CE Index 320)⁴. It is recommended that the data be used as high estimates of IBL and storage costs, rather than low estimates of complete plant costs.

The 1999 CE Index is taken as 390.⁵

Our plant produces 80,000t.y⁻¹ of 54%(kg.kg⁻¹) formaldehyde (HCHO) from methanol, or 229t.d⁻¹, given the 350 days of operation per year specified in Chapter 2.

While the chart specifies no concentration, based on the sources of data used, conventions used in Ref. [1] *et cetera* and the domain of the curve, it is reasonable to assume that this refers to 37%(kg.kg⁻¹) HCHO solution. This gives a plant cost of $4 \times 10^6 \text{USD}_{1987} = 4.9 \times 10^6 \text{USD}_{1999}$.

With a location factor of 0.72 [3] the plant cost comes to $3.5 \times 10^6 \text{USD}_{1999}$.

¹ An average rate over 1999 (real values to date, with the remainder of the year estimated from Ref’s [8] *et cetera*).

² OBL items are also known as ‘off-sites’ [3]. However confusing term is avoided in this report, as OBL items are certainly on the site (or else they would not be considered in the capital cost estimation), just (often) not within the processing plant boundary.

³ This is probably misleading, as Ref. [17] indicates that it took material from data that were already “somewhat obsolete (1965)” at the time of publishing!

⁴ This refers to the index of chemical engineering plant ‘inflation’ published in Ref. [8] and previous issues.

⁵ Based on Ref’s [7] and [8]. Although it initially appears unlikely that the second half peak in 1998 will be replicated in 1999, this is probably seasonal variation. The 1999 Marshall & Swift indices rose significantly above 1998 values.

12.1.2.2 Recent report

A recently reported cost for a new BASF formaldehyde plant, to go on stream at the end of 2000, is given in Ref. [20]. It has a stated capacity of $180,000 \text{ t.y}^{-1}$ ("the world's largest") with a cost of $32 \times 10^6 \text{ DM}_{1999}$. Again the concentration is not given, but reference to Ref. [18] suggests the figure is on a $54\%(\text{kg.kg}^{-1})$ basis. From published exchange rates [5] (see Appendix), this is $17 \times 10^6 \text{ USD}_{1999}$.

The value must now be adjusted down to match our plant capacity. The correct factor to use in the equation $I \propto Q^b$, where I is the capital investment and Q the capacity, is $b = 0.65$ [11], [17], which reflects the parallel streaming component of the process [3] (see also Chapter 11).

Hence the cost of our $80,000 \text{ t.y}^{-1}$ plant is estimated to be 59% less, or approximately $10 \times 10^6 \text{ USD}_{1999}$. With a location factor of 0.6 (estimated from Ref. [3]), the plant cost comes to approximately $6.1 \times 10^6 \text{ USD}_{1999}$.

The difference between the two figures lies in the different natures of the sources. The latter figure probably includes more OBL items, even though it is part of BASF's existing Ludwigshafen complex, described as "mammoth" and "vast" [21].

In both cases expenses such as 'contingencies' and 'supervision' are probably omitted.

12.1.3 Detailed estimate

12.1.3.1 Purchased costs

A more accurate value for the capital cost is obtained by estimating purchased equipment costs individually. This will account for differences in processing technologies. After these are evaluated they can be adjusted to reflect the cost of the entire site using a factored approach. Accuracy is about $\pm 20\%$ [3] (more likely to be low [17]). The correlations are taken from Ref's [4] [11] and [14], and the calculations appear in the Appendix.

The data were updated using the Chemical Engineering Plant Cost index (CE Index), and the historical exchange rate (in the case of the first reference). Location factors were also employed to site the items in Indonesia⁶ [3]. Each of the items was thus brought 'up to date', and subsequently adjusted by the published type, material and pressure factors. Where no factor was quoted for the materials of construction the values in Ref. [3] were used.

Clearly one could not expect each of the sources to give identical results. It was felt that a suitably conservative and yet representative number could be obtained by taking an average in which the maximum value was given a double weighting. It can be seen from the graph in the Appendix that the concordance is generally good. The exception was the case of the storage tanks, where it was felt that the figures of Ref. [3], which were for "pressure vessels," were probably too high⁷. Therefore, for the storage tanks they received a weighting of one half.

In summary, the following costs were obtained:

Item	Cost [1000 × USD ₁₉₉₉]
Columns <i>et cetera</i>	293
Blower & Turbine	848
Drums	54
Heat exchangers	663
Pumps	49
Reactors	733
Valve ⁸	4
Total IBL PCE⁹:	2640

Table 12-1: Purchased cost of equipment (PCE) inside the battery limits (IBL). Detailed in Appendix.

⁶ The exact location in Indonesia is not specified, however it is believed that Bontang is a good example of a modern facility that is quite readily accessible, and is probably typical of the data used for the value in Ref. [3].

⁷ Comparison may also be made to Ref. [14].

⁸ Only included for completeness, as it was shown on the Process Flow Diagram and has a specification sheet.

⁹ Rounded from 2642×10^3 .

The purchased cost of IBL equipment (IBL PCE) was thus found to be around $2.6 \times 10^6 \text{USD}_{1999}$. A detailed breakdown of the costs for each individual item¹⁰ is available in the Appendix.

In addition to the IBL PCE's, costs were also estimated for the storages and the buildings. The values are given in Table 12-2, and detailed breakdowns are again available in the Appendix.

Item	Cost [1000×USD ₁₉₉₉]	Fraction of IBL PCE
Storage tanks	1200	0.44
Buildings	306	0.12

Table 12-2: Purchased cost of items outside battery limits (OBL). Detailed in Appendix.

The key thing to observe in this table is the high cost of the storage tanks relative to the total IBL PCE. This is not entirely unexpected¹¹: “Storage tanks often represent the single largest expense of process plants” [14].

The proportions of the various costs are seen more clearly in the following chart.

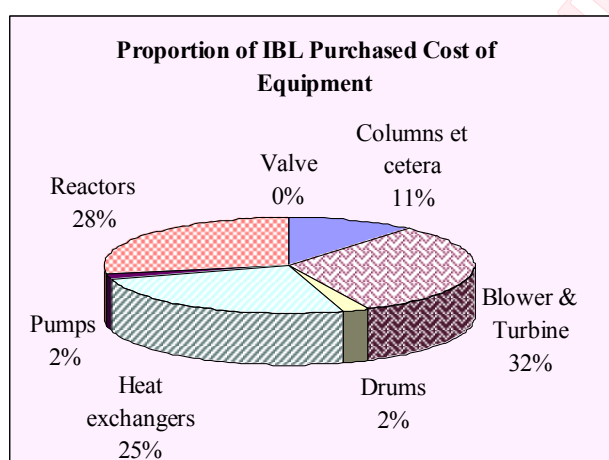


Figure 12-1: The proportion of each IBL purchased cost of equipment (PCE).

There are four significant costs making up the IBL PCE: the columns with their internals; the reactors (mainly the tail-gas burner); the blower with its turbine; and the heat exchangers.

As discussed earlier in this report, it is not imperative that a column be used for the vaporisation unit operation, and so a possible capital cost saving is available here, although some in-line mixing equipment may then need to be installed to ensure uniformity of reactor feed¹².

The reactors are probably all necessary. Removing the tail-gas burner (RXN-3) would require steam to be bought in from existing boilers in the complex. A detailed study¹³ would probably show that this was economically a poor alternative, as steam is not cheap. Moreover, assuming the 100ppm levels of formaldehyde currently exiting the absorber could not be directly released, then another item would have to be added for emission control.

The blower is needed, but there is a trade-off between the operating pressure and the cost of the blower. Although the operating pressure is within guideline recommendations, as discussed in earlier chapters, there may be some merit in looking more closely into the relationship between incremental increase in blower cost and pressure drop through each item. The steam turbine is probably on the order of twice as much as a large motor: it may be that further studies would recommend an alteration of the flowsheet in this regard, dependent on local conditions.

¹⁰ And in some cases further breakdowns, such as absorber shell, packing and trays.

¹¹ It does not appear to be recognised by the references in Table 12-3 – possibly included in their definition of PCE.

¹² Probably not needed if the plant layout is similar to that which has been developed, where the vaporiser unit operation occurs a significant distance from the catalytic reaction.

¹³ Currently 1.72kg.s^{-1} of 1200kPa(abs) steam is produced, at $12 \text{AUD}_{1999} \cdot \text{t}^{-1}$ (Chapter 2). Over the course of 350d (*i.e.* 1y of operation), this equates to a cost of approximately $624 \times 10^3 \text{AUD}_{1999}$. Converting yields $412 \times 10^3 \text{USD}_{1999}$. Although this is less than the capital cost of RXN-3 (see Appendix), presumably RXN-3 would operate for a number of years.

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There is probably little that can be done about the heat exchanger cost, aside from further optimisation of heat transfer coefficients and the heat exchanger network. The more detailed optimisation should include explicit reference to costs, rather than implicit 'rules of thumb'.

12.1.3.2 Total physical plant cost

The total capital cost of the 'physical' plant can be estimated by the application of multiple factors, which combine to form an effective overall LANG-type factor. The factors may be estimated and applied to individual items, but for the purposes of this report application to the combined IBL costs is sufficient [1].

Our formaldehyde plant is classed as a 'fluids processing plant'. Each literature source has presented slightly different factors. These are shown below, along with the factor eventually chosen.

Details	Factor (multiple of IBL PCE):					Comments
	Ref. [3] ¹⁴	Ref. [11] ¹⁵	Ref. [19]	Ref. [15] ¹⁶	Final	
PCE	1.00	1.00	1.00	1.00	1.00	Basis
Complete installation & erection	0.47	0.11 to 0.30	0.4	0.27 to 0.60	0.50	Foundation, insulation, safety, painting & fire-proofing all relevant
Piping (installed)	0.66	0.15 to 0.70	0.70	0.66 to 1.20	0.70	Lots of piping
Instrumentation & controls (installed)	0.18	0.10 to 0.35	0.20	0 [blank]	0.20	Moderate level
Electrical (installed)	0.11	0.10 to 0.15	0.10	0.09 to 0.11	0.10	Low level
Buildings (all)	0.18	0.05 to 1.00	0.30	0.18 to 0.34	0.12	Actual value estimated in previous section
Utilities	0.70	0.30 to 0.75	0.50	0.70	0.10	Few new services need to be provided
Storages ¹⁷	–	–	0.15	–	0.44	Actual value estimated in previous section
Site developments & land	0.16	0.05 to 0.15	0.05 (ex. land)	0.10 (ex. land)	0.10	Purchase of land assumed, but flat land
Environmental provisions	–	0.10 to 0.30	–	–	0.20	Important for a HCHO plant. Accounts for solids/liquid disposal.
Total:	3.46	1.96 to 4.7	3.40	3.00 to 4.05	3.46	

Table 12-3: Factors of the IBL PCE for estimating the total physical plant cost (PPC).

Fascinatingly, the factor finally arrived at by the tortuous route shown is identical to the figure given in Ref. [3]! Using this factor results in a total PPC of $9.14 \times 10^6 \text{ USD}_{1999}$.

The relative importance of the storages and buildings, which were estimated in detail, is indicated by Figure 12-2.

The cost of the buildings is not too high – less than suggested by the general guidelines presented in the following section – as would be expected for a plant that is part of a larger complex. However the cost of the storages is so high that serious consideration should be given to the number and size of storages. In particular:

- Is it possible to reduce the size of the two buffer tanks (ST-2 and ST-3)?
- Is it possible to reduce the size of the 'spare' storage tanks (ST-4B and ST-5B)? How much 'abnormal' product is expected to be produced? How often might the resins plant go off-line, and for how long?
- Is it possible to have only one single 'spare' storage?
- Can the size of the methanol storage be reduced (if not completely eliminated)? How reliable is the supply?

¹⁴ Taken from PETERS and TIMMERHAUS (1991).

¹⁵ This reference did not distinguish between 'fluids processing plants' and other types.

¹⁶ From WOODS (1975).

¹⁷ Only one reference specified a factor for storages. The other references must have either included storages under another factor (e.g. buildings, services) or else under the PCE.

These questions are unable to be answered in full at this stage, and would be the subject of further study.

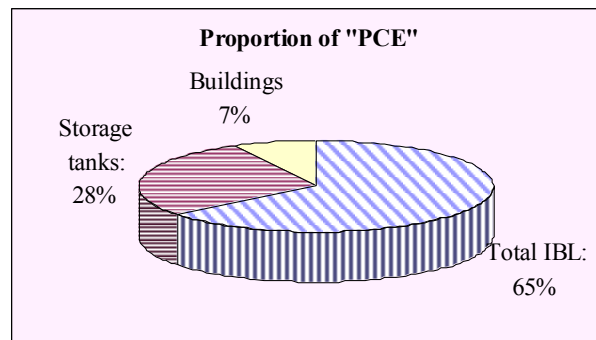


Figure 12-2: The proportion of three purchased costs of equipment (PCE).

12.1.3.3 Total fixed capital

The total capital cost that the company may expect to pay to purchase and erect the plant is given by the 'total fixed capital', or 'total erected cost'. This does not include working capital, which is needed for start-up (covered in section 12.3).

The 'indirect costs' are calculated using factors, in a similar manner to that described in the previous section. They are then added to the total physical plant cost (PPC) already obtained to get the total fixed capital required. The factors used will be as given in Table 12-4.

Details	Factor (multiple of IBL PCE):					Comments
	Ref. [3]	Ref. [11] ¹⁸	Ref. [19]	Ref. [15]	Final	
PCE	N/A	N/A	N/A	N/A	N/A	Basis: 1.00
Design, engineering & supervision	0.33	0.30 to 0.75 ¹⁹	1.02	0.33	0.50	Established technology
Contractor's fee	0.21	0.10 to 0.45	0.17	0.21	0.30	No in-house knowledge or experience
Contingency ²⁰	0.42	0.15 to 0.80	0.34	0.42	0.60	High uncertainty w.r.t. Indonesian 'situation'
Construction / 'field' expenses	0.41	—	—	0.41	0.20	/Considered above
Total:	1.37	0.55 to 2.00	1.53	2.00 to 3.05	1.60	Equivalent to a LANG factor of 5.06

Table 12-4: Factors of the IBL PCE for estimating the indirect costs.

The reader's attention is drawn in particular to the contingency factor, which is set relatively high in order to account for the many uncertainties with respect to the future of the Indonesian nation²¹.

Another factor which has not really been taken into account is the Indonesian regulation that any investment of this type must be a joint venture with an Indonesian company. The precise details of the requirements have changed recently, due largely to the internal and external financial pressure on the country. It is not known exactly how such a prerequisite would affect the calculations.

From the figure found, the indirect costs would be $4.23 \times 10^6 \text{ USD}_{1999}$.

Adding this to the total PPC of $9.14 \times 10^6 \text{ USD}_{1999}$ gives a total fixed capital investment of $13.37 \times 10^6 \text{ USD}_{1999}$, or approximately 13.4 million US dollars in 1999.²²

¹⁸ This reference did not distinguish between 'fluids processing plants' and other types.

¹⁹ Includes construction.

²⁰ Due to company policy and Australian government deterrents, payment of bribes is not considered.

²¹ Notable examples are the future of East Timor and the determination of the president (to occur later in 1999), either of which could lead indirectly to market changes, or more directly (in an extreme case) to sanctions or blockades. If the region is in turmoil, then there may also be problems with (among other things) transportation and finding employees.

While this value was expected to be higher than those found in section 12.1.2, which probably do not consider purchase of land, clearing of land, contractor fee(s) and so on, it has turned out to be larger by factors of 3.8 and 2.2 on the two preliminary estimates. Then again, the two preliminary estimates were themselves different by a factor of 1.7. As the detailed estimate is ‘transparent’ – that is, all the sources and assumptions are visible (see also Appendix) – it will be taken as ‘correct’, or the best estimate.

Clearly the most accurate way to determine the cost would be to decide upon a supplier for each item and get quotes for all work to be done. However that is not possible at this stage: it is both time-consuming and expensive [11], and probably requires still more detailed specification of equipment.

12.2 Operating Cost

Again we endeavour to follow the “plural perspectives” philosophy.

12.2.1 Preliminary estimate

In Chapter 10 we saw that the raw material cost, which is essentially methanol, dominates the manufacturing cost, making up 60%. Depreciation, utilities and labour account for the remaining 40%.

It is difficult to nominate a price for the methanol, upon which the operating cost could be based, due to the wide fluctuations that are observed. For example, in the period 1982 to 1997, its high price was 6.4 times greater than its low price! And this is not due to inflation, as the more recent figure was actually at the low end of that range [10].

The value that will be used is $100\text{USD}_{1999}\cdot\text{t}^{-1}$. This value is given in the problem statement (Chapter 2), and is consistent with the price quoted in the periodical Chemical Marketing Reporter, as at June 1999. It is also consistent with Ref. [10].

The basis is the U.S. Gulf Coast, freight on board (F.O.B.). There is no compelling reason to suppose that the price in Bontang, where a methanol supplier is located, would vary significantly from this value. One would actually suppose that a good deal might be worked out through a contract.

From the mass balance that was performed it may be seen that 0.658t of pure methanol is required for every 1t of 54%(kg.kg⁻¹) formaldehyde solution²³. This is $0.451\text{t}(\text{methanol})\cdot\text{t}(37\%\text{ solution})^{-1}$.

Thus the production costs can be considered to be approximately $75\text{USD}_{1999}\cdot\text{t}^{-1}$, for 37% equivalent formaldehyde. Expressed as the equivalent of 54% solution, this becomes $110\text{USD}_{1999}\cdot\text{t}^{-1}$.

Given the production of 80000t of the more concentrated solution per year, this equates to an annual production cost of $8.8\times 10^6\text{USD}_{1999}$.

12.2.2 Detailed estimates

The technique used to obtain a (hopefully) more accurate estimate follows the method of Ref. [3].

Along with the methanol cost derived above, the selling price of formaldehyde on open market is given as $286\text{USD}_{1999}\cdot\text{t}^{-1}$, for the equivalent of 37%(kg.kg⁻¹) formaldehyde.²⁴ However the formaldehyde product will be largely captive, going to the neighbouring resins plant. For this analysis it will be assumed that the resins plant is a separate entity, such that prices are still paid for the formaldehyde. However, from Ref. [17] it seems that the price that would be paid for the captive product would be only 70% of the ‘free-market’ value. This would give a value of $200\text{USD}_{1999}\cdot\text{t}^{-1}$ for 37% solution.

It will be assumed that all of the 54% “Grade A” solution is sent to the resins plant, and that all of the 37% “Grade B” solution is sold on the free market²⁵. Thus the Grade A sells at $291\text{USD}_{1999}\cdot\text{t}^{-1}$ and the Grade B at $417\text{USD}_{1999}\cdot\text{t}^{-1}$, both on a 54% basis.

²² Equivalent to 20.3 million AUD₁₉₉₉.

²³ From this point onwards the units (kg.kg⁻¹) will be dropped, as all percentage concentrations are on a mass basis.

²⁴ The “equivalent” is in reference to the fact that formaldehyde is actually produced at a strength of 54% (at least initially). So the cost is adjusted proportionally to be ‘equivalent’ to a 37% solution.

²⁵ Hopefully any sales of 54% solution on the free market would be compensated for by sales of 37% solution to the resins plant. In any case, the Grade B product makes up only 10% of the mix (taking each at their respective strengths).

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From the flows found in the mass balance the value associated with any product exiting the absorber will therefore be $300\text{USD}_{1999}\cdot\text{t}^{-1}$ on a 54% basis.

The operating life of the plant is taken as 10y to be more conservative, although lives up to 30y are not unreasonable²⁶, as discussed in Chapter 1. The straight-line method is used, with negligible scrap value assumed [3].

It is not known precisely what quality the “towns water” is. It is no secret that the water quality in Indonesia is, in general, far inferior to that in Australia, and especially in Melbourne. However it will be assumed that the relatively modern Bontang facility, with a high proportion of expatriate workers, has good quality drinking water that can be drunk from the tap, so that it would be acceptable to use this ‘towns water’ to make up recirculated cooling water (RCW) losses. The losses are estimated at 20% [3]²⁷.

The boiler feed water (BFW) make-up is from demineralised water (DMW), also estimated at 20% [3].

Operator wages are taken as 50000AUD_{1999} for shift workers and 40000AUD_{1999} for day workers.

A summary of the results is presented in Table 12-5 (two decimal places are retained throughout for neatness). A full account of the calculations and assumptions made is presented in the Appendix.

Cost	Annual cost [$10^6 \times \text{USD}_{1999}$]	Cost per tonne of 54% product [$\text{USD}_{1999}\cdot\text{t}^{-1}$]
Production costs		
Raw materials: Methanol	5.32	66.48
Utilities: Steam	-0.16	-2.00
Demineralised water (DMW)	0.25	3.15
Recirculated cooling water	0.10	1.25
Towns water	0.20	2.50
Electric power	0.06	0.81
Total	0.46	5.71
Labour: Process labour wages	0.26	3.30
Maintenance labour and overheads	0.75	9.35
Total	1.01	12.65
Maintenance materials	0.67	0.41
Operating supplies / Consumable stores	0.03	1.32
Plant overheads	0.11	1.32
Insurance	0.20	2.51
Property taxes	0.13	1.67
“Book” depreciation ²⁸	1.34	16.71
Total production cost: Fixed	3.49	43.63
Variable	5.78	72.19
Total	9.27	115.82
Non-manufacturing costs:		
Corporate administration	0.23	2.90
Research and development	0.05	0.58
Selling expenses	0.46	5.79
Total non-manufacturing costs	0.74	9.27
hence:		
Total operating cost	10.01	125.08
Also:		
Minimum profit	2.67	33.43
Minimum viable selling price	12.68	158.51

Table 12-5: Operating cost summary. Detailed in Appendix. ²⁹

²⁶ Although they would doubtless involve some further capital investment.

²⁷ Although the temperature in Bontang is generally high, the humidity is also high....

²⁸ This is not a ‘cash cost’ [3].

²⁹ My thanks go to Miss. Jayne BORENSZTAJN for alerting me to additional methanol and DMW flows I originally omitted.

Chapter 12: Economic Evaluation**Formaldehyde**

The first thing that springs to one's attention from the table is the minimum viable selling price calculated (last row). It is calculated based on the reasonable estimation of a minimum profit equivalent to 20% of the fixed capital. However it has come out to be far less than the expected selling price: 159 compared to 300USD₁₉₉₉.t⁻¹ on a 54% basis (Grades A and B combined).

Of course, one also notices the total production cost, 115USD₁₉₉₉.t⁻¹, and the total operating cost, 124USD₁₉₉₉.t⁻¹ (both 54% basis). Both of these agree quite well with the preliminary estimate of the previous section.

This leads to another point regarding the proportion of methanol costs relative to overall on-going costs. For the production costs, which do not include the non-manufacturing costs (see Table 12-5), the methanol accounts for 57% of the costs. For the total operating cost the figure drops slightly to 53%. However both of these are close to 60%, from which we can see the reason for the similarity in values between this section and the previous one.

We notice that there is one 'negative cost' – *i.e.* a cost saving – in the table. This is due to the surplus steam that is produced and 'exported' to neighbouring plants for a fee.

One more value can be extracted from the table. Subtracting the raw materials cost from the total operating cost yields a 'conversion cost' of 58USD₁₉₉₉.t⁻¹ (54% basis).

It is interesting (and useful) to examine what would happen to the operating cost if the turndown requirement to 60% prevailed for an extended period of time. Put simply, the 'fixed' portion of the production cost remains constant on an annual basis (but increases per tonne of solution), while the 'variable' portion of the production cost remains constant relative to the amount of product produced (and hence actually decreases on an annual basis).

The calculation is given in the Appendix. It shows that the total operating cost is 7.51×10^6 USD₁₉₉₉.y⁻¹, or 156USD₁₉₉₉.t⁻¹ of 54% equivalent solution. The former figure shows a decrease, the latter an increase. The minimum viable selling price remains, however, significantly below the expected selling price (even accounting for the fact that it is a captive sale, as discussed earlier).

Clearly the minimum viable selling price is very sensitive to the feedstock cost, which has been shown to constitute roughly 60% of the production cost, and only a slightly lesser proportion of the operating cost. However even if long-term operation at the maximum turndown was needed, the project would still be feasible.

The feedstock cost would have to rise to 2.2 times its current level to bring the minimum viable selling price up to the expected selling price at the maximum turndown, and thrice its current value at full design capacity. Intuitively this seems unlikely.

Of course there was discussion in section 12.2.1 of the variability of the cost of methanol, which had a range in which the maximum price was more than a factor of six greater than its lowest price. However this does not jeopardise the project, as the feedstock costs could not rise independently of the feedstock price. If the feedstock price did triple over a year or two, which is eminently possible, the formaldehyde price would simply follow it closely [12], thus allowing the project to stay profitable.

12.3 Working capital

Working capital can be defined as "capital investment over and above [...] fixed capital required to initiate and sustain operation of a process plant [or other project]" [3]. The main components of working capital are stocks of raw materials, of which an inventory must be accumulated before production can begin, and stocks of finished products and extended credit.

The method followed is taken from Ref. [3], and detailed in the Appendix. A summary is given in Table 12-6.

The methanol storage is 3d, the main storage tanks have a 3d inventory of product and the buffer tanks (ST-2 and ST-3) have an inventory of around 1d.

The value of the finished product stocks in storage is assessed at cash costs [3]. This is the operating cost less the book depreciation (which is not a cash cost). Alternatively, it may be thought of as the raw materials costs plus all of the conversion cash costs (*i.e.* excluding book depreciation).

The value of materials in progress inventory is, in turn, taken as the average of the product value and the raw material value. No definitive data is available for the size of the inventory. Guidelines suggest 1 to 2 weeks of annual production [3]. However, with the final storages being low, the intermediate storage is also low. A value of 1 week will be taken, which is probably still conservative.

Finally, it is assumed that all payments are monthly, giving average credit and indebtedness periods of 6 weeks. The only exception to this are the wages and salaries, which will on average be paid 1.5 weeks in arrears [3].

Component	Value [$10^6 \times \text{USD}_{1999}$]
Production costs	
Raw materials	0.04
Materials in progress inventory	0.13
Product stocks	0.09
Total	0.27
Debtors	
Customers	2.77
Total	2.77
Creditors	
Raw materials	-0.61
Utilities	-0.05
Wages	-0.03
Total	-0.70
hence: Total working capital required	2.35

Table 12-6: Working capital summary. Detailed in Appendix.

The working capital is thereby calculated to be $2.35 \times \text{USD}_{1999}$. The interesting thing about this situation is that there is one dominant factor, which is the unpaid customer debts. One reason is that the time equivalent of the process materials is far less. The other is that the expected selling price is roughly double the operating cost, and so the contribution of the creditors to the working capital is not so great.

We note that the working capital is approximately 10% of the expected sales revenue, which is reasonable.

12.4 Analysis of Project Profitability

While the initial indication of the operating cost relative to the expected selling price look good, this must be looked at in more detail in combination with the fixed capital cost and the working capital requirement. Once again “plural perspectives” are used³⁰.

12.4.1 Return on investment

A simple and widely used indicator of profitability is the return on investment (ROI) parameter [3]. This is defined as the difference between the expected annual sales revenue and the annual operating costs, divided by the sum of the fixed capital and working capital.

The result that is calculated, as the reader may verify, is $(24 - 10.0) \div (13.37 + 2.35) \approx 89\% \cdot \text{y}^{-1}$.

Given that a threshold level of acceptance is said to be $20\% \cdot \text{y}^{-1}$ for this type of project, the value obtained above would indicate that the project is expected to be highly profitable. A more detailed analysis follows.

12.4.2 Cash flow

The cash flow will be estimated using the first approach presented in Ref. [3]. In this method cash flows are estimated on the basis of costs and prices at the present. This may be justified by the “highly unpredictable” nature of inflation rates – their incorporation is certain to add complexity, but will not necessarily increase accuracy. The main disadvantage of this is that it does not allow for the differences in inflation rates for different components, for example tax depreciation and labour costs. It is justified at this stage of the project. The inflation rate is also seen to be relatively low.

The next page shows the cash flow diagram that is estimated (the full cash flow table is in the Appendix). A discussion follows.

³⁰ Giving a plurality of plural perspectives in this chapter.

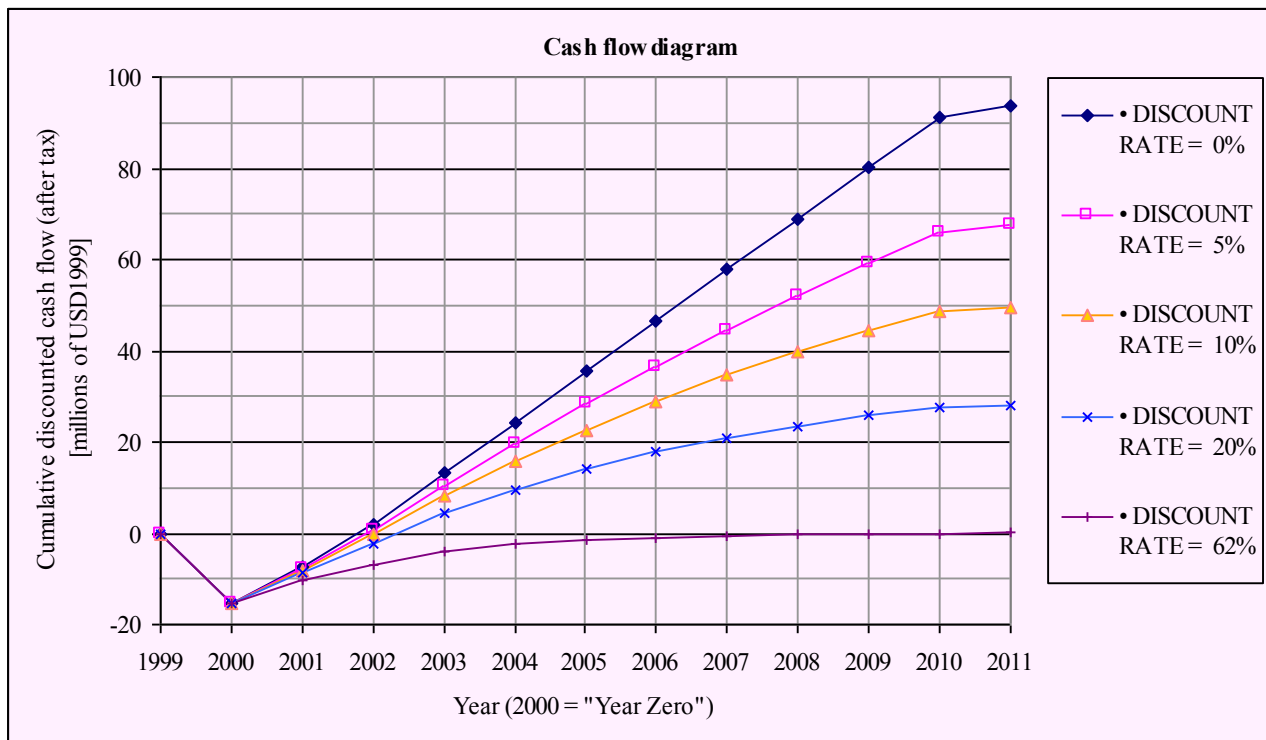


Figure 12-3: Cumulative cash flow diagram (discounted and after tax).

To obtain Figure 12-3 the following assumptions were made:

- Construction of the plant will commence in 2000 and the plant will be producing product in 2001.
- All of the fixed capital will be spent in year zero (2000).
- The production will be 75% of the design capacity in the first year (2001), 90% in the following year and 100% thereafter.
- The working life of the plant will be 10 years (*i.e.* until 2010). It has been explained already that although formaldehyde plants commonly operate for longer than 10 years, for example 30 years, that would not be a suitably conservative first estimate, nor would it account for the further capital expenditure required.
- At the end of ten years the plant is scrapped, with only the working capital recovered (fully).
- The working capital is 80% disbursed in year zero (2000), with the remainder divided equally of the following two years.
- All tax is paid in the year in which the income was incurred. *I.e.* there is minimal 'delay' in collection [3].
- The corporate taxation rate is estimated at 30%. While the Australian rate is around 36%, it is likely that Indonesia has a lower rate³¹.
- The investment allowance is assumed to be zero, and no other incentives (such as tax 'holidays') are allowed for.

12.4.2.1 Discount rate

The discount rate, i , also known as the "cost of capital," is the weighted cost of money from all sources (*viz.* equity and loan) required to fund a project. It is typically expressed in $\% \cdot y^{-1}$ as an interest rate.

Clearly the discount rate must related in some way to the inflation rate (*e.g.* as measured by the consumer price index (CPI)). One means of estimating the rate is given by Ref. [3]. In this method the discount rate is given by:

$$i = L \cdot i_L \cdot (1-t) + E \cdot i_E$$

where L and E refer to the proportion of capital from loan sources and equity sources (*i.e.* internal to the company) respectively, t is the prevailing rate of taxation and i_L and i_E are the individual interest rates³².

³¹ This is deduced by the lack of any social security system *per se* in the Republic of Indonesia, *et cetera*.

³² The equity rate will be estimated internally by company accountants based on how much they think should be earned given the risk of the project.

For example the discount rate may be estimated as follows if the capital investment is derived in equal proportions from equity and loan sources:

$$i = 0.5 \times 10\%.y^{-1} (1 - 0.30) + 0.5 \times 12\%.y^{-1} = 9.5\%.y^{-1}.$$

Note that if the capital was derived entirely from equity sources this would increase to $12\%.y^{-1}$. Alternatively, i would drop to only $7\%.y^{-1}$ (on these figures), if all of the capital came from loans.

Our project presents an interesting problem: although the plant is physically located in Indonesia, the company is not Indonesian – we assume that the company is based in Australia. So on what basis should the discount rate be chosen?

If we suppose lower inflation in Indonesia implies a lower discount rate, then it would be more likely for the project to be assessed as profitable (see the following sections). However the Australian-based company clearly has access to the Australian market (and Australian interest rates), and so company accountants might argue that the project profitability should be compared against the greater potential that exists in Australia.

In both countries inflation is very low, and the current discount rate might be, say, $5\%.y^{-1}$. However it must be remembered that the simplified approach used here uses only a single value for the cost of capital, and so this should reflect some kind of ‘average’ over the entire life of the project.

We will therefore be optimistic (depending on your perspective), and specify a cost of capital of $10\%.y^{-1}$.

Application of the discount rate is explored further in the following sections.

12.4.2.2 Net present value

The net present value (NPV) may be evaluated at any time as the cumulative cash flow which has been ‘discounted’ according to the ‘discount rate’, i . However it is usually used to refer to the NPV at the “completion of economic life.” The relevant formula is [3]:

$$NPV = \sum \{ C_t \div (1 + i)^t \}$$

where the summation is over the time, t , and C_t is the cash flow at time t .

From the cash flow diagram we see that the NPV for all of the discount rates, except for the highest, are positive at the end of the project in the year 2011.

The most relevant curve is of course that corresponding to the discount rate that we believe will predominate over the course of the project, namely $10\%.y^{-1}$. As this has a positive NPV, we assess the project as favourable.

12.4.2.3 Payback time

Not the name of the latest Hollywood blockbuster, the payback time is a measure of, “the time taken to recover investment costs” [3]. For the purposes of this report, it will be the year at which the net present value (NPV) goes to zero, where the reference year (“year zero”) is 2000.

A simple-minded analysis is disproportionately instructive. Our expected sales revenue is $24 \times 10^6 \text{USD}_{1999}.y^{-1}$ at full capacity utilisation (*i.e.* design flows), with an operating cost of $10.0 \times 10^6 \text{USD}_{1999}.y^{-1}$. If all inflation and taxation is ignored, it would seem that barely over a single year is required to make up the combined fixed and working capital of $15.7 \times 10^6 \text{USD}_{1999}$. Of course this also assumes full production capacity and so on, but the indication is undeniably good.

We now turn back to Figure 12-3. From the graph we read that the NPV reaches zero before 2003 for all discount rates under 62%. This is equivalent to a payback time of less than 3 years (and closer to 2), which sounds to be good.

12.4.2.4 Discounted cash flow rate of return

The final indicator of profitability is the ‘discounted cash flow rate of return’ (DCFRR), also known as the internal rate of return (IRR). This is defined as the discount rate at which the final NPV goes to zero [3]. Expressed mathematically, it is the value of i for which

$$NPV = \sum \{ C_t \div (1 + i)^t \} = 0$$

is true.

From the graph we may read that the NPV does not go to zero until the discount rate reaches a massive $62\%.y^{-1}$.

Obviously the first point to make is that $62\%.y^{-1}$ is a fantastic figure, which is far higher than the estimated cost of capital (see section 12.4.2.1). Given that the project could only be less profitable than others of similar risk if the true cost of capital was more than six times greater than the (moderately conservative) value estimated, it would be fair to say that the project is definitely profitable, and indeed far more profitable than comparable investments.

12.5 Conclusions

The total capital cost has been found to be $13.4 \times 10^6 \text{USD}_{1999}$, obtained largely from detailed estimation of the purchased cost of equipment (PCE), multiplied by an overall factor of 5.06. This cost is higher than the preliminary estimates, but these probably do not consider many of the 'extra' costs.

The operating cost has been found to be $9.92 \times 10^6 \text{USD}_{1999}.y^{-1}$, or $124 \text{USD}_{1999}.t^{-1}$ of $54\%(\text{kg.kg}^{-1})$ formaldehyde solution. This gave a minimum viable selling price of $157 \text{USD}_{1999}.t^{-1}$ at full design capacity. Even at the maximum turndown, the minimum viable selling price remained well below the expected selling price of 300USD_{1999} , (which does take account of the majority captive supply). Thus the project would appear viable despite the high sensitivity of the selling price to the feedstock cost.

Working capital was estimated at $2.35 \times 10^6 \text{USD}_{1999}$, which was mostly due to the debtors (customers).

The discounted cash flow showed that the project is highly profitable, even looking at only a 10 year plant life: the net present value (NPV) was positive; the pay-back time was short (approximately 2 years); and the discounted cash flow rate of return (DCFRR) was found to be more than a factor of 6 higher than the estimated cost of capital.

The return on investment (ROI) was also significantly above the threshold level.

Investment in this project is recommended.

12.6 References

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³³ Note that the value of the CE Index shown for May 1998 does not agree with the following reference.

³⁴ Thanks to the Hargrave Library staff who made this copy available.

³⁵ Due to Dr. David BRENNAN.

Formaldehyde

Chapter 12: Economic Evaluation

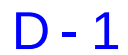
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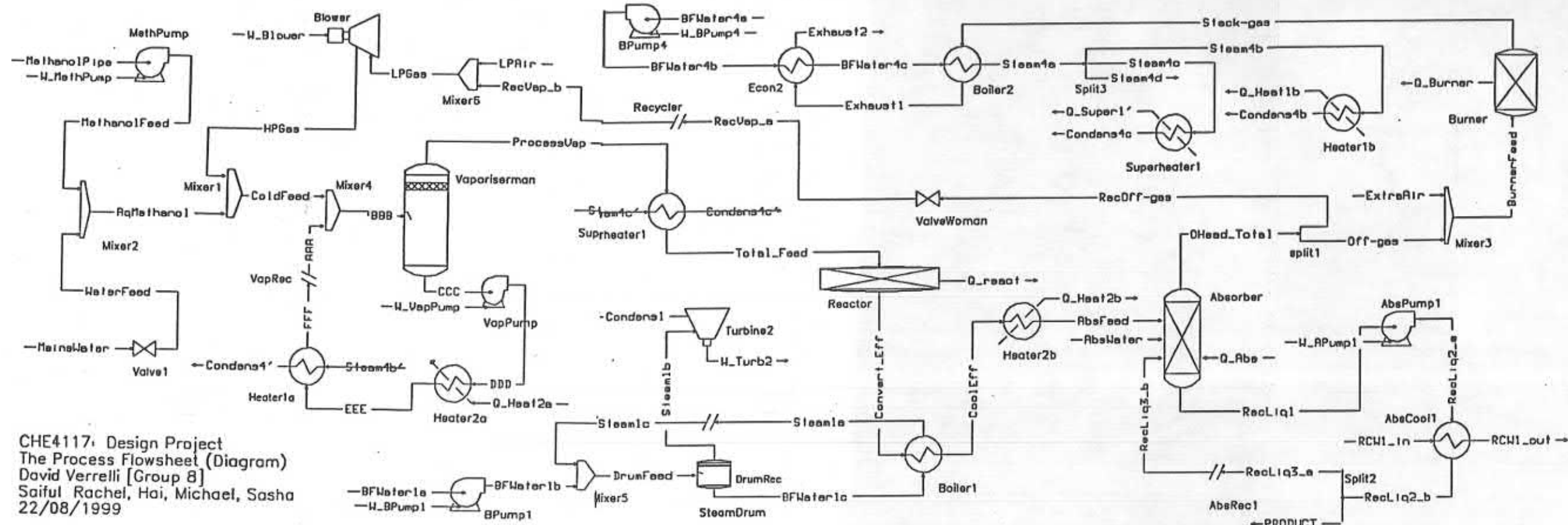
³⁶ This was also the reference from which the management-babble term contained in the Summary was taken ("residue;" p. 32). (A footnote or reference looked 'out of place' on that page.) Other good terms include a Concerted Capability Review, an Incremental Policy Format and a Functional Control Philosophy! There are 1728 possible phrases.



DRAWING ANNEX

1. FORMALDEHYDE PLANT PROCESS FLOW DIAGRAM
2. COMPUTER SIMULATION OUTPUT
3. DRAWING 7001: MECHANICAL DESIGN OF BUBBLE CAP
4. DRAWING 7002: MECHANICAL DESIGN OF BUBBLE CAP TRAYS – COLUMN INTERNALS
5. DRAWING 7003: MECHANICAL DESIGN OF THE BASE OF THE ABSORBER (ABS-1)
6. DRAWING 7004: MECHANICAL DESIGN OF THE ABSORBER (ABS-1) – GENERAL ARRANGEMENT
7. DRAWING 8001: PIPING AND INSTRUMENTATION DIAGRAM (P&ID) OF THE ABSORPTION SECTION OF THE PLANT
8. PIPING AND INSTRUMENTATION DIAGRAM (P&ID) OF THE VAPORISER SECTION OF THE PLANT, VERSION “A” (BEFORE HAZOP)
9. PIPING AND INSTRUMENTATION DIAGRAM (P&ID) OF THE VAPORISER SECTION OF THE PLANT, VERSION “C” (AFTER HAZOP)
10. DRAWING 1101: PLANT LAYOUT – GENERAL ARRANGEMENT DRAWING OF MAIN FORMALDEHYDE PLANT – PLAN VIEW
11. DRAWING 1102: PLANT LAYOUT – GENERAL ARRANGEMENT DRAWING OF MAIN FORMALDEHYDE PLANT – ELEVATION = LOOKING WEST





CHE4117: Design Project
The Process Flowsheet (Diagram)
David Verrilli [Group 8]
Saiful Rachel, Hai, Michael, Sasha
22/08/1999

Stream Name	AAA	AbsFeed	AbsWater	AqMethanol	BBB	BFWater1a	BFWater1b	BFWater1c	BFWater4a	BFWater4b	BFWater4c	BurnerFeed	CCC	ColdFeed	Condens1
Vapour_Frac	0.0000	1.0000	0.0000	0.0000	0.2305	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.8305	0.9417
Temperature	86.5180	90.0000	37.0000	37.0368	62.0833	100.0000	100.0153	151.8571	100.0000	100.1359	189.4517	45.7076	62.0833	38.1968	100.1843
Pressure	185.0000	130.0000	120.0000	185.0000	185.0000	400.0000	500.0000	500.0000	400.0000	1270.0000	1240.0000	185.0000	185.0000	185.0000	102.0000
Flow	957.0421	332.7419	18.1792	66.8933	1252.9148	150.6514	150.6514	221.8490	95.4755	95.4755	95.4755	182.0192	957.0473	295.8688	150.6551
Mass_Flow	20.0000	7.9159	0.3275	1.9675	27.9159	2.7140	2.7140	3.9966	1.7200	1.7200	1.7200	4.5900	20.0000	7.9159	2.7141
LiqVol_Flow	21.6455	10.6550	0.3282	2.4151	31.5978	2.7195	2.7195	4.0047	1.7235	1.7235	1.7235	6.0095	21.6455	9.9523	2.7195
Energy	-26970.2295	3572.8516	-613.5226	-1896.8556	-25984.1970	-4364.6093	-4364.2277	-5547.3923	-2766.0752	-2763.9706	-2103.1497	1680.7712	-28961.0290	738.1688	1402.9055

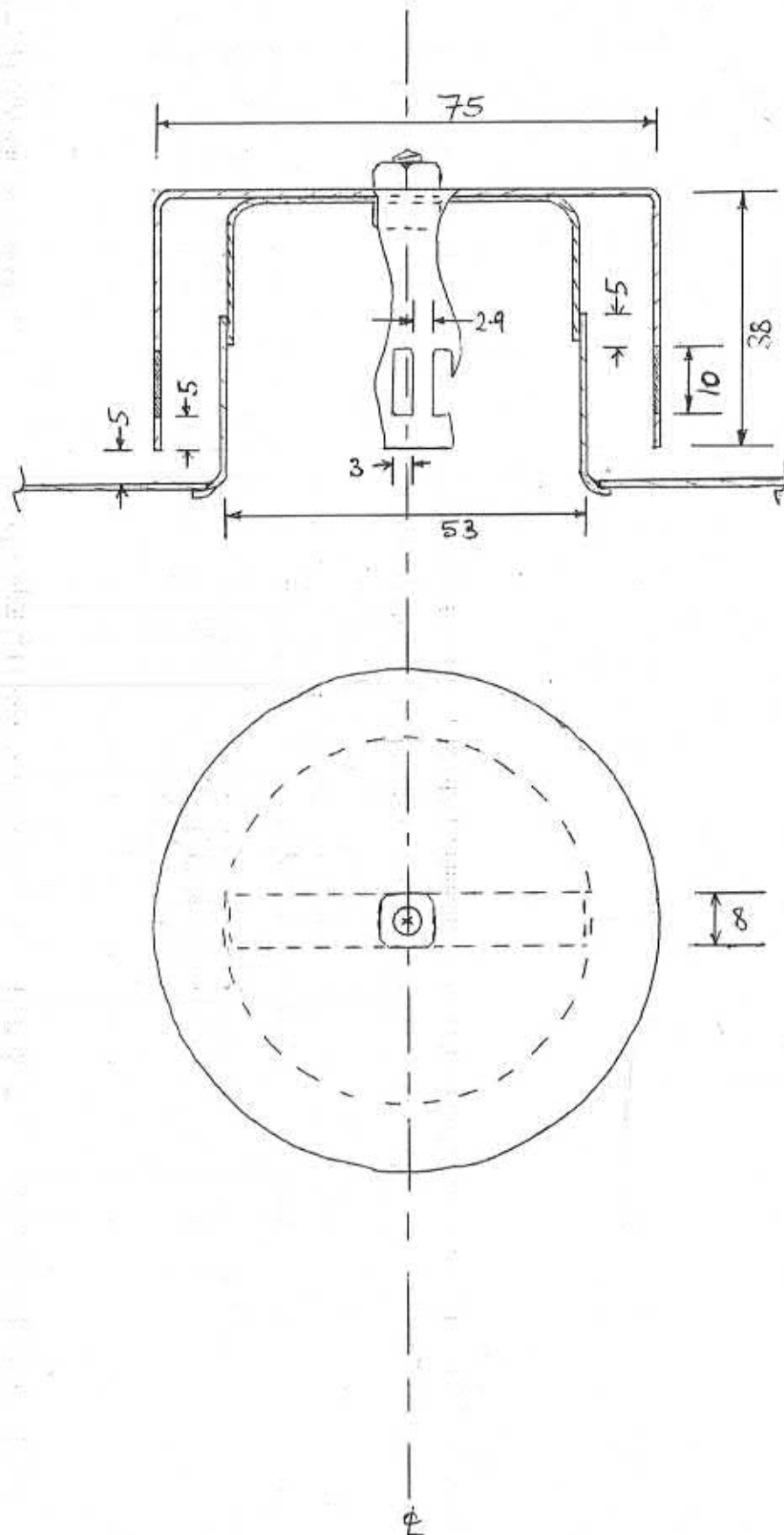
Stream Name	Condens4'	Condens4b	Condens4c	Condens4c'	Convert_Eff	CoolEff	DDD	DrumFeed	EEE	Exhaust1	Exhaust2	ExtraAir	FFF	HPGas	LPAir
Vapour_Frac	0.0000	0.0000	0.0000	0.0000	0.9689	1.0000	0.0000	0.4044	0.0000	1.0000	1.0000	1.0000	0.0000	1.0000	1.0000
Temperature	187.3985	187.3985	187.3985	187.3985	700.0000	170.0000	62.0967	151.8571	72.6444	328.4914	206.3792	37.0000	86.5180	121.5830	37.0000
Pressure	1185.0000	1185.0000	1185.0000	1185.0000	160.0000	145.0000	245.0000	500.0000	215.0000	106.0000	101.0000	110.0000	185.0000	185.0000	101.0000
Flow	31.5819	31.5819	26.8842	26.8842	332.7419	332.7419	957.0473	372.5042	957.0473	171.9008	171.9008	60.6691	957.0473	228.9755	113.7801
Mass_Flow	0.5690	0.5690	0.4843	0.4843	7.9159	7.9159	20.0000	6.7107	20.0000	4.5900	4.5900	1.7176	20.0000	5.9484	3.2212
LiqVol_Flow	0.5701	0.5701	0.4853	0.4853	10.6550	10.6550	21.6455	6.7242	21.6455	5.5203	5.5203	1.9775	21.6455	7.5372	3.7087
Energy	-700.9128	-700.9128	-596.6548	-596.6548	10745.0928	4430.0422	-28959.2476	-3596.7701	-28102.0568	3134.5079	2473.6871	549.2388	-26970.4458	2635.0243	1030.0533

Stream Name	LPGas	MainsWater	MethanolFeed	MethanolPipes	OHead_Total	Off-gas	PRODUCT	ProcessVap	Q_Abs	Q_Burner	Q_Heat1b	Q_Heat2a	Q_Heat2b	Q_Super1'	Q_react
Vapour_Frac	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	1.0000	2.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Temperature	43.5838	37.0000	37.0355	37.0000	50.0000	50.0000	60.0000	82.0833	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Pressure	101.0000	400.0000	185.0000	110.0000	110.0000	110.0000	120.0000	185.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Flow	228.9755	12.5395	54.3538	54.3538	236.5498	121.3501	114.3723	295.8674	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Mass_Flow	5.9484	0.2259	1.7416	1.7416	5.5993	2.8724	2.6441	7.9159	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
LiqVol_Flow	7.5372	0.2264	2.1887	2.1887	7.8596	4.0320	3.1235	9.9523	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Energy	2104.1736	-423.1333	-1473.7222	-1473.9474	2205.7159	1131.5323	-2562.5408	2976.8316	-27.5397	0.0000	1131.6110	857.1907	857.1907	963.2883	0.0000

Stream Name	RCW1_In	RCW1_out	RecLiq1	RecLiq2_a	RecLiq2_b	RecLiq3_a	RecLiq3_b	RecOff-gas	RecVap_a	RecVap_b	Stack-gas	Steam1a	Steam1b	Steam1c	Steam4a
Vapour_Frac	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	1.0000	1.0000	0.9539	0.7500	1.0000	0.7500	1.0000
Temperature	30.0000	45.0000	75.0000	75.0145	60.0000	60.0000	60.0000	50.0000	49.9958	49.9954	907.6920	151.8557	151.8571	151.8557	187.9668
Pressure	400.0000	360.0000	130.0000	170.0000	120.0000	120.0000	120.0000	110.0000	101.0000	101.0000	171.9008	500.0000	500.0000	500.0000	1200.0000
Flow	2885.0285	2885.0285	2569.1488	2569.1488	2569.1488	2454.7765	2454.7776	115.1998	115.1998	115.1954	171.9008	221.8490	150.6551	221.8528	95.4755
Mass_Flow	51.9741	51.9741	59.3941	59.3941	59.3941	56.7500	56.7500	2.7268	2.7268	2.7272	4.5900	3.9966	2.7141	3.9967	1.7200
LiqVol_Flow	52.0790	52.0790	70.1631	70.1631	70.1631	67.0396	67.0396	3.8276	3.8276	3.8286	5.5203	4.0047	2.7195	4.0048	1.7235
Energy	-98890.0260	-95597.3417	-54273.8546	-54269.7600	-57562.4443	-54999.9036	-54999.9279	1074.1837	1074.1837	1074.1202	6539.7038	767.4445	1950.6219	767.4574	1302.0460

Stream Name	Steam4b	Steam4b'	Steam4c	Steam4c'	Steam4d	Total_Feed	W_APump1	W_BPump1	W_BPump4	W_Blower	W_MethPump	W_Turb2	W_VapPump	WaterFeed
Vapour_Frac	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Temperature	187.9668	187.9668	187.9668	187.9668	187.9668	158.2616	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	37.0456
Pressure	1200.0000	1200.0000	1200.0000	1200.0000	1200.0000	170.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	185.0000
Flow	31.5819	31.5819	26.8842	26.8842	37.0093	295.8674	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	12.5395
Mass_Flow	0.5690	0.5690	0.4843	0.4843	0.6667	7.9159	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.2259
LiqVol_Flow	0.5701	0.5701	0.4853	0.4853	0.6681	9.9523	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.2264
Energy	430.6981	430.6981	366.6335	366.6335	504.7143	3940.1198	4.0945	0.3816	2.1046	530.8508	0.2252	547.7165	1.7814	-423.1333

OP_D148.SIM



NOTES

ALL DIMENSIONS IN mm.

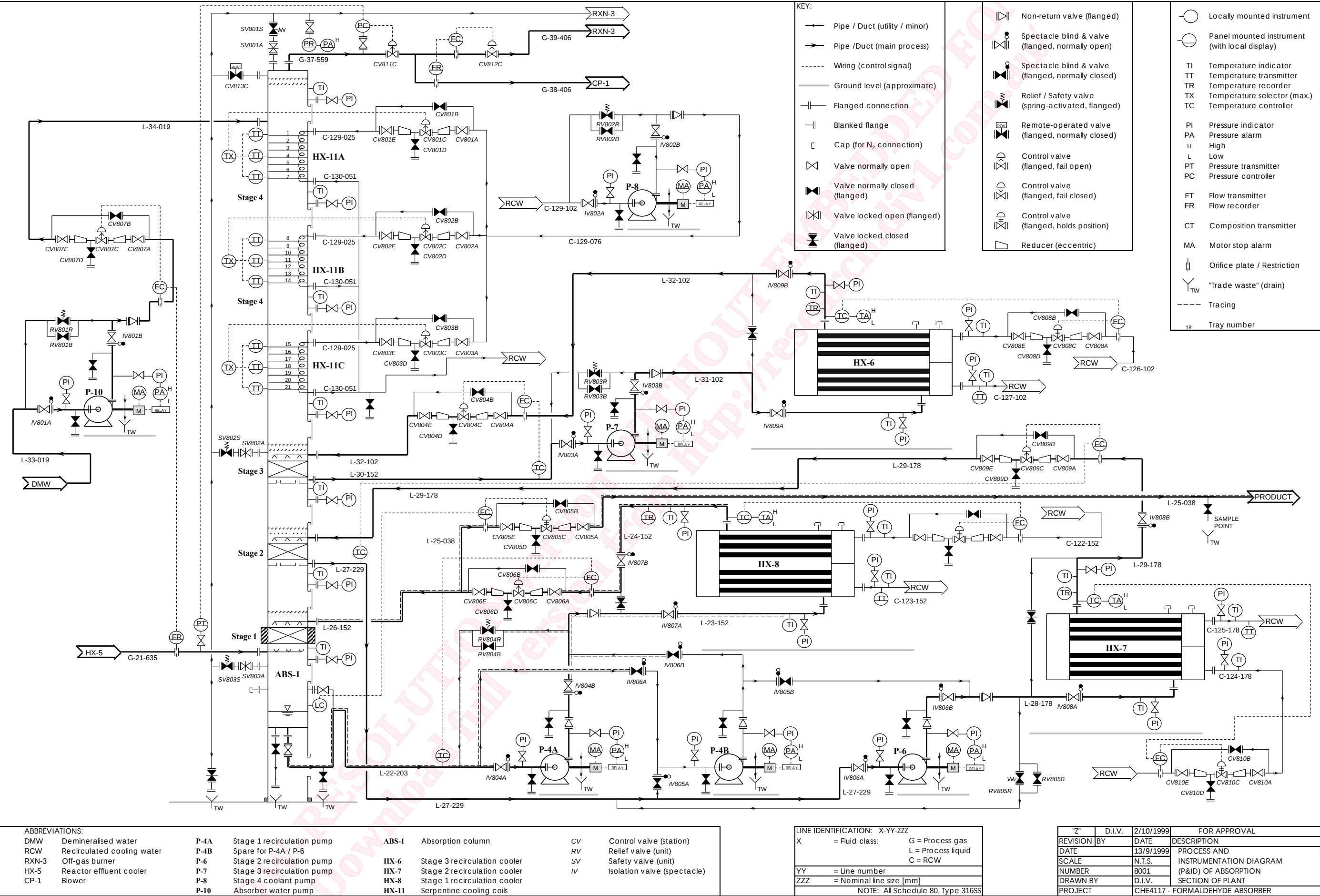
40 SLOTS PER CAP

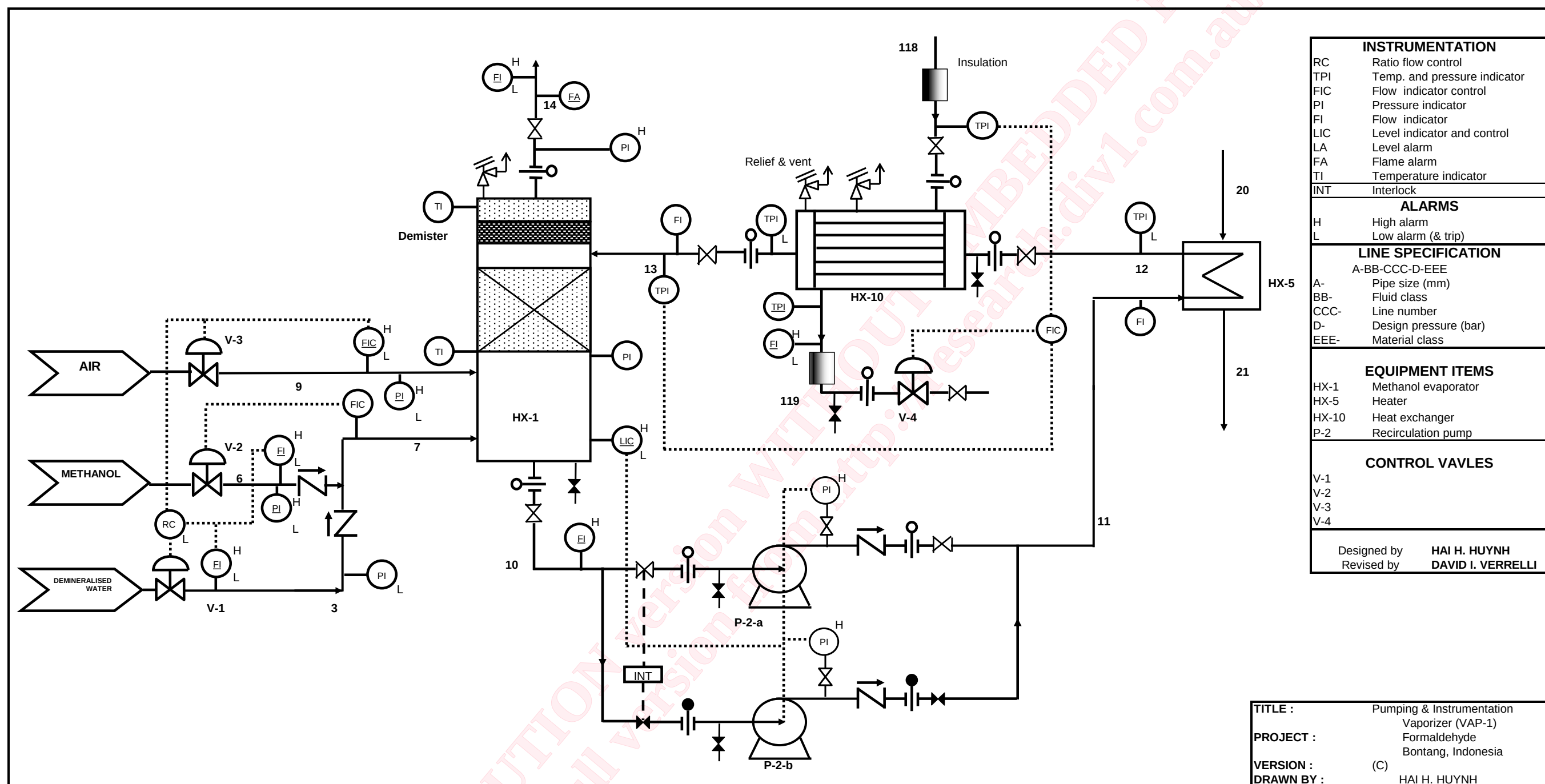
ALL TOLERANCES ± 0.5 mm

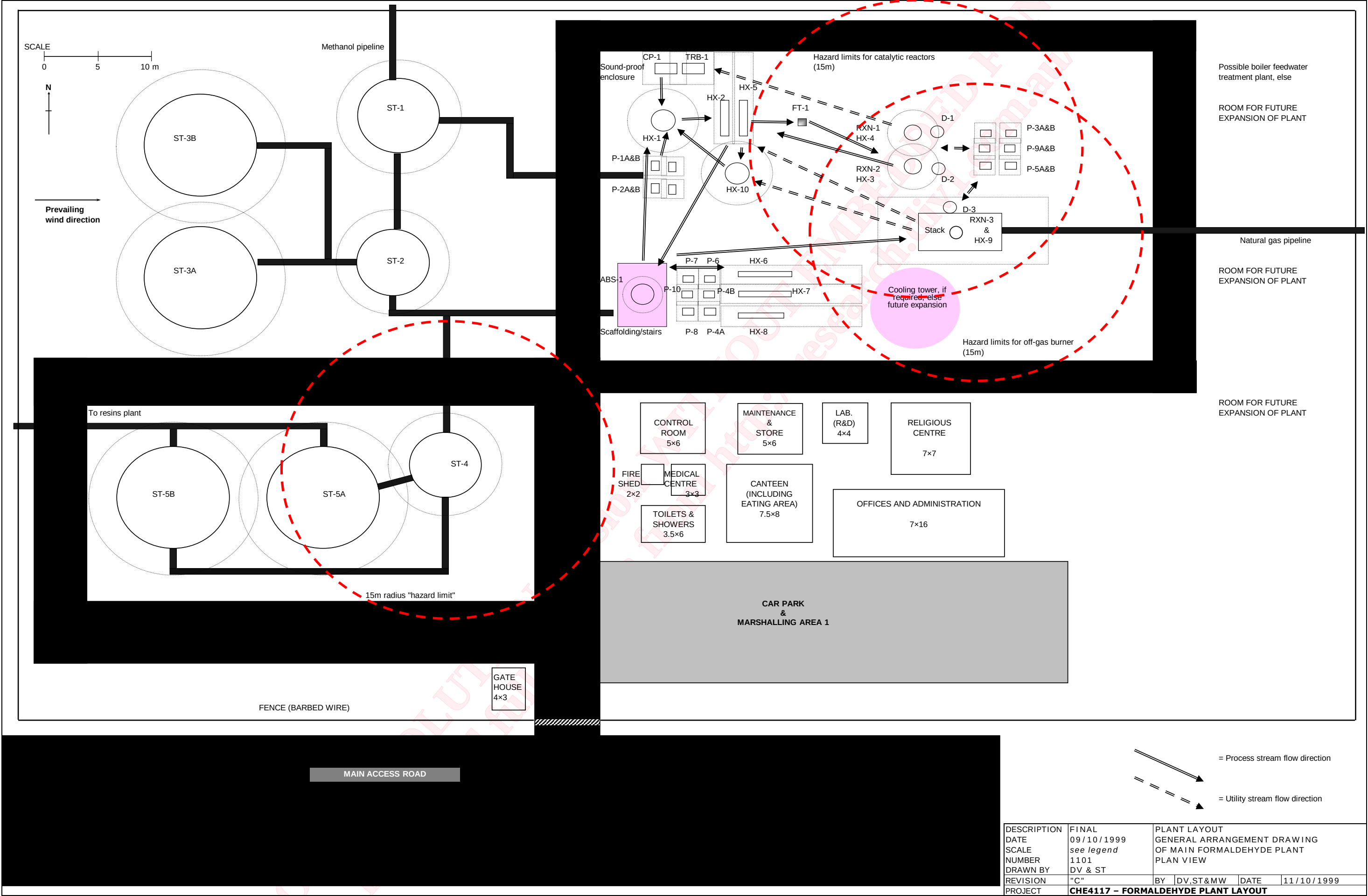
EXCEPT SLOTS: ± 0.1 mm

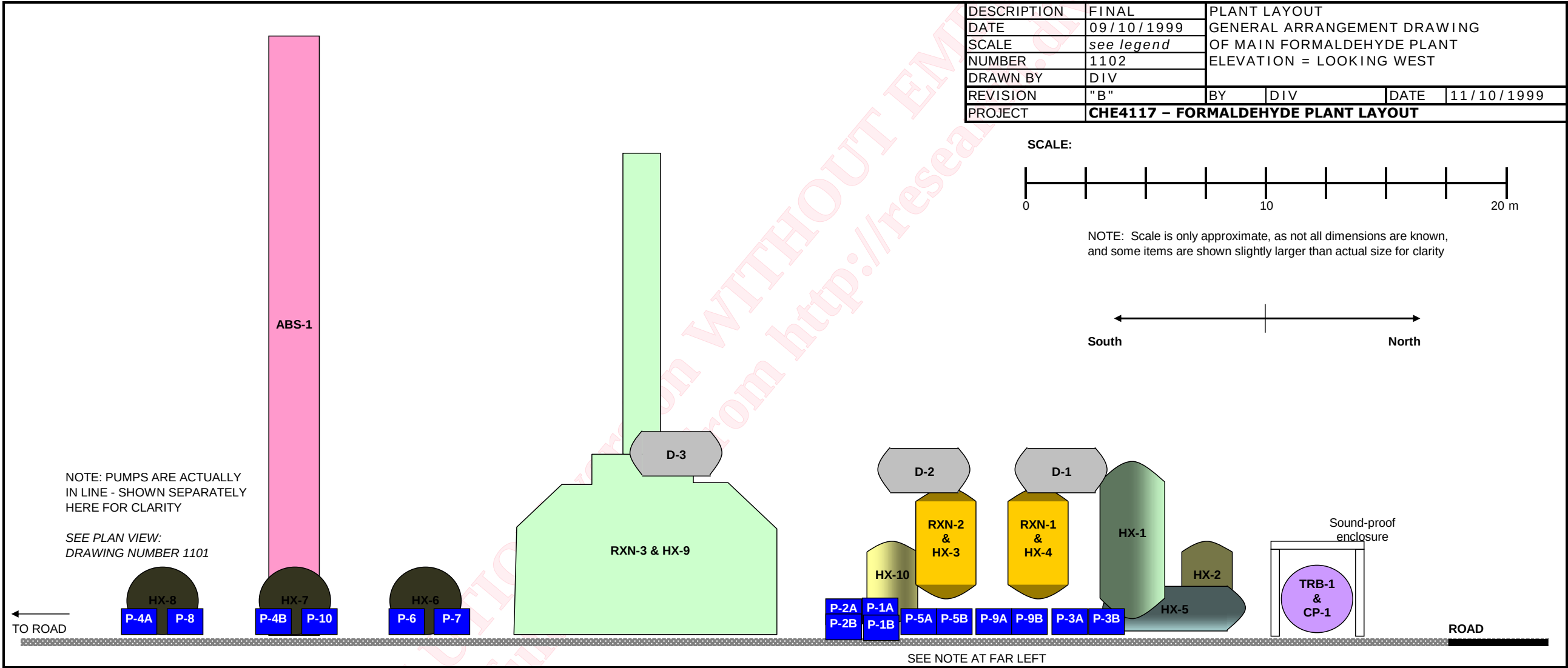
ALL 1.5mm THICK, TYPE 316 STAINLESS

B	DIV	20/09/1999	FOR APPROVAL
REV.	BY	DATE	DESCRIPTION
		12/09/1999	BUBBLE-CAP
		1:1	
		7001	
		DIV	
PROJECT	CHE417 - FORMALDEHYDE ABSORBER		











APPENDIX TO CHAPTER 3

PROCESS SYNTHESIS AND FLOWSHEET DEVELOPMENT

Stream Number(s)	Description	Type	Hot/Cold	T _{IN} [°C]	H' _{IN} [kW]	T _{OUT} [°C]	H' _{OUT} [kW]	m' [t/h]	These are calculated		
									C _p [kJ.kg ⁻¹]	m _{cp}	ΔH'
11,12 (a)	Vaporiser recycle	Sink (sens)	Cold	62.10	-28959.8	86.5	-26970.4	22.5059523	4.07307596	91.6684534	2238.7
11,12 (b)	Vaporiser recycle	Sink (lat)	Cold	86.5	-26970.4	86.5	-37063.3	22.5059523	#DIV/0!	0	0
14.15	Superheating	Sink	Cold	62.08	2976.8	158.3	3940.1	7.9159	1.26525728	10.0156501	963.2882
ex-RXN-1.16	Boiler	Source	Hot	700.0	10745.1	170.0	4430.0	7.9159	1.50522238	11.9151898	-6315.0506
16,17 (a)	Absorber feed	Source (sens)	Hot	170.0	4430.0	90.0	3572.9	7.9159	1.35358993	10.7148825	-857.1906
16,17 (b)	Absorber feed	Source (lat)	Hot	62.1	3572.9	62.0	3572.9	7.9159	#DIV/0!	0	0
19.20	Absorber, stage 1	Source (lat)	Hot	62.1	3572.9	62.0	3572.9	7.9159	#DIV/0!	0	0
28,29	Absorber, stage 2	Source	Hot	75.0	-53691.3	60.0	-56946.9	58.7193	1.232	72.34762	-1085.2143
31,32	Absorber, stage 3	Source	Hot	65.0	-53691.3	50.0	-56946.9	58.7193	1.232	72.34762	-1085.2143
38.40	***FIX Burner	Source	Hot	55.0	-53691.3	40.0	-56946.9	58.7193	1.232	72.34762	-1085.2143
RCW	Utility	Source	Hot	907	6542	220	2550	4.5937	1.266	5.81399228	-3992.0121
TW	Utility	Sink		30.0	30.0	40	40	4.1899	0	0	0
DW	Utility	Sink		30.0	30.0	40	40	4.1899	0	0	0
LP Steam: 500bar(a)	Utility	Source		151.9	151.9	151	151	condensing	infinite		
HP Steam: 1200bar(a)	Utility	Source		188.0	188.0	187	187	condensing	infinite		

2238.6628

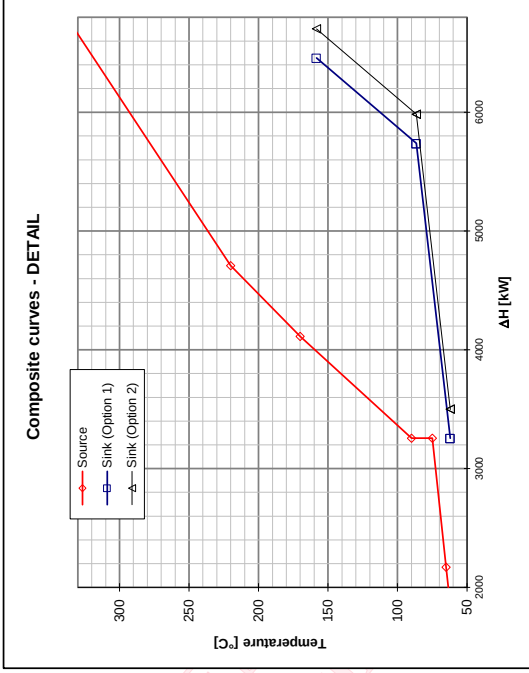
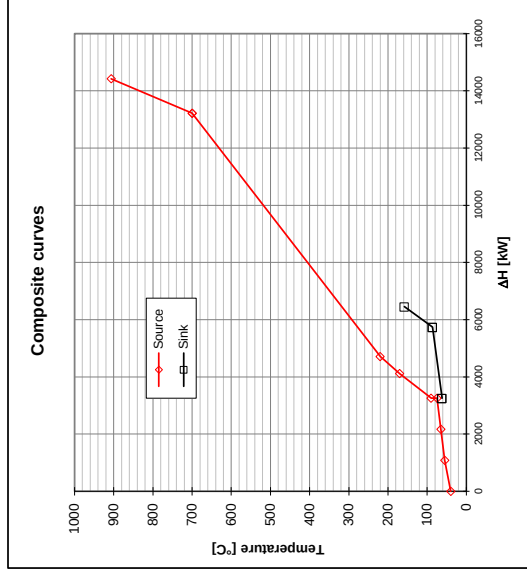
0.0

SOURCE STREAMS Composite Curve

Interval Number	Lower Temp	Upper Temp	Stream	m' _{cp}	ΔH'	Sub-Total ΔH'	Cumul-Total ΔH'
1	40.0	55.0	31.32	72.34762	1085.2143	1085.2143	0
2	55.0	65.0	28.29	72.34762	1085.2143	2160.4286	1085.2143
3	65.0	75.0	19.20	72.34762	1085.2143	3255.6429	2160.4286
4	75.0	90.0	16.17 (a)	10.7148825	857.1906	4112.8335	3255.6429
5	90.0	170.0	ex-RXN-1.16	11.9151898	595.759491	4708.59299	4112.8335
6	170.0	220.0	ex-RXN-1.16	11.9151898	5719.2911	8510.0074	4708.59299
7	220.0	700.0	38.40	5.81399228	2790.71629	13218.6004	8510.0074
8	700.0	907	38.40	5.81399228	1201.29581	14419.8962	13218.6004

SINK STREAMS Composite Curves

Interval Number	Lower Temp	Upper Temp	Stream	m' _{cp}	ΔH'	Sub-Total ΔH'	Cumulative Total ΔH'
1	62.08	62.10	14.15	10.0156501	0.13420971	0.13420971	OPTION 1 3500
2	62.10	86.5	14.15	10.0156501	244.595196	2483.258	DATUM = 3255.6429 3500.13421
3	86.5	158.3	11.12 (a)	91.6684534	2238.6628	5739.03511	3255.77711 3500.13421
			14.15	10.0156501	718.558795	6457.5939	5739.03511 5983.39221





APPENDIX TO CHAPTER 5

MASS AND ENERGY BALANCES & PROCESS SIMULATION

CALCULATION OF DESIGN "GRADE A" AND "GRADE B" CAPACITY

Total capacity: 80 kt(54%).y⁻¹

Percentage of "Grade A": 90 %
Percentage of "Grade B": 10 %

Compositions [%]:

	HCHO	CH ₃ OH	H ₂ O
"Grade A"	54	1	45
"Grade B"	37	7	56

Thus:

Flow of "Grade A":

Flow of "Grade B":

TOTAL flow

Flow of "Grade A":

Flow of "Grade B":

TOTAL flow

350 d _{opm} .y ⁻¹	24 h _{opm} .d _{opn} ⁻¹	3600 s.h _{opn} ⁻¹
212.401 t(54%).d _{opn} ⁻¹	8.850041 t(54%).h _{opn} ⁻¹	2.458345 kg(54%).s ⁻¹
16.17045 t(54%).d _{opn} ⁻¹	0.673769 t(54%).h _{opn} ⁻¹	0.187158 kg(54%).s ⁻¹
<u>228.5714 t(54%).d_{opn}⁻¹</u>	<u>9.52381 t(54%).h_{opn}⁻¹</u>	<u>2.645503 kg(54%).s⁻¹</u>
212.401 t(54%).d _{opn} ⁻¹	8.850041 t(54%).h _{opn} ⁻¹	2.458345 kg(54%).s ⁻¹
23.60011 t(37%).d _{opn} ⁻¹	0.983338 t(37%).h _{opn} ⁻¹	0.273149 kg(37%).s ⁻¹
<u>236.0011 t(solution).d_{opn}⁻¹</u>	<u>9.833379 t(solution).h_{opn}⁻¹</u>	<u>2.731494 kg(solution).s⁻¹</u>

BASIC COMPLETE MATERIAL BALANCE

Assume:

About half of the methanol goes to each of the following reactions [Mechetta, p.358]:

CH₃OH + 0.5O₂ --> HCHO + H₂O

(1)

36%

CH₃OH --> HCHO + H₂

(2)

60%

The former is decreased by the presence of water [Catalyst Handbook, p. 493]
Dehydrogenation (2) is more prevalent for catalysis by silver [Formaldehyde⁽⁹⁾, p. 9]

Atomic masses:

C	12.011	kg.kmol ⁻¹
H	1.0079	kg.kmol ⁻¹
O	15.9994	kg.kmol ⁻¹
N	14.0067	kg.kmol ⁻¹

Sargent-Welch Sci. Co.

Molar masses:

CH ₃ OH	0.032	kg.mol ⁻¹
HCHO	0.030	kg.mol ⁻¹
O ₂	0.032	kg.mol ⁻¹
N ₂	0.028	kg.mol ⁻¹
H ₂ O	0.018	kg.mol ⁻¹
H ₂	0.002	kg.mol ⁻¹
CO ₂	0.044	kg.mol ⁻¹
CO	0.028	kg.mol ⁻¹
HCOOH	0.046	kg.mol ⁻¹

From Simon Farrar (Orica)
G.F.C Rogers & Y. R. Mayhew⁽⁵⁾, p. 2

Assume:

- other (side) reactions are **considered** (as follows):
- nitrogen is inert and approximates any argon present
- methanol is in excess
- oxygen (limiting) consumed to:
- Off gases **released** contain all N₂, O₂ and H₂ and
- by-products form by:

H₂ + 0.5O₂ --> H₂O

(3)

40.0%

HCHO --> CO + H₂

(4)

0.92%

CH₃OH + 1.5O₂ --> CO₂ + 2H₂O

(5)

4.0%

HCHO + O₂ --> CO₂ + H₂O

(6)

6.5%

(once-through)
(nominal) 13.2% of H₂O exiting system

by analogy with Table 4 (p.362) of McKetta
by simplification of Table 4 (p.362) in McKetta
Ullmann's(5), Vol. A11, p. 624.

Assume:

40.0%

of H₂ from (2) [WITHOUT recycled]

0.92%

of HCHO formed by (1) & (2) + recycled

4.0%

of CH₃OH reacted

6.5%

of HCHO formed by (1) & (2) + recycled

*More complete combustion at the elevated temperature? - see Ullmann's⁽⁵⁾, p. 626
Formaldehyde⁽⁹⁾, p. 9

- the formation of formic acid (**during processing!**) is considered here:

HCHO + 0.5O₂ --> HCOOH

(7)

0.020%

cf. HCHO + 0.5O₂ --> CO + H₂O

(8)

0.020%

of HCHO formed by (1) & (2) + recycled
of HCHO formed by (1) & (2) + recycled

cf. Catalyst Handbook, p. 493
Essentially covered by other reactions
Temperature is too high during processing - Simon Farrar.

- the following are not considered:

CH₃OH + 0.5O₂ --> H₂O + H₂ + CO

(9)

HCHO + HCHO --> CH₃OCHO

(10)

- Conversion of methanol is:

- Ratio of total off-gas to that which is recycled is:

- Percentage of fresh water entering the entire system on the process-side that enters the vaporiser (the rest entering the absorber):

- Ambient air: Relative humidity = 80% Temperature = 37 °C hence Mole fraction = 0.049599 at 1atm(abs).

98.5% (once through) (Ullmann) Yield: 88.9%
0.95 ==> Ratio of recycled off-gas to (100%) methanol fed: 157% cf. US patent 4072717, col. 6
50%

NOTE: Compared to a 50:50 split b/n rxn's (1) & (2) with no side reactions, the scheme outlined here requires:

- * less water [now also by (3); & more methanol compensate for red'n in (1)]
- * more methanol [due to "losses" in side-rxn's]
- & * more oxygen (in air) [due to extra methanol consumed]

as fresh feed.

NOTE: "Fresh Feed" is a hypothetical stream - in practice the components of this stream would be added variously at different points in the system.

NOTE (1): Absorber has not been properly modelled at all.

NOTE (2): Trace quantities of NO_x will be present in all gas/vapour process streams except for the fresh feed.

NOTE (3): Water in the incoming methanol has not been considered here.

Formic acid in incoming methanol is negligible, and may be assumed to be completely combusted to "inert" CO₂

FORMULAE:

CH₃OH + 1.5O₂ --> CO₂ + 2H₂O

(1)

HCHO + O₂ --> CO₂ + H₂O

(2)

H₂ + 0.5O₂ --> H₂O

(3)

CO + 0.5O₂ --> CO₂

(4)

HCOOH + 0.5O₂ --> CO₂ + H₂O

(5)

- Excess air supplied: 20%

- Assume **complete** combustion in off-gas burner (except N₂)

Mass fractions [-]:	HCHO	CH ₃ OH	H ₂ O	HCOOH	Mole fraction of air [-]:	O ₂	N ₂	Ar	CO ₂	Approx.	O ₂	N ₂
"Grade A"	0.54	0.01	< 0.45	< 0.001		0.2095	0.7809	0.0093	0.0003		0.2095	0.7905

Using the spreadsheet's "iterate" function				REACTIONS:										(Absorber feed)		CHECK !					Additional fuel/air		Combusted off-gas	
Stream:	Fresh feed	Recycled off-gas	Total reactor feed	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	NETT	Reactor effluent	Absorber water in	Off-gas	Product	ACC = 0 = IN+GEN-OUT:							
MOLAR FLOWS [mol.s ⁻¹]	FRACTION:	FRACTION:	FRACTION:	51.3882561	51.3882561	51.3882561	=Total HCHO formed pre-degradation						FRACTION:	FRACTION:	FRACTION:	FRACTION:								
CH ₃ OH	54.35507 0.3008	0 0.0000	54.3551 0.1837	-19.2706	-32.1177	0	0	-2.14118	0	0	0	-53.52943	CH ₃ OH	0.8256 0.0025	0 0.0000	0.8256 0.0072	0.0000	0.0000	---	0 0.0000	0 0.0000	CH ₃ OH		
HCHO	0 0.0000	0 0.0000	0 0.0000	19.2706	32.11766	0	-0.47476	0	-3.31545	-0.01028	-0.01028	-47.5775	HCHO	47.5775 0.1430	0 0.0000	47.5775 0.4156	0.0000	0.0000	---	0 0.0000	0 0.0000	HCHO		
O ₂	22.65455 0.1254	0.0553 0.0005	22.7099 0.0768	-9.6353	0	-6.423532	0	-3.21177	-3.31545	-0.00514	-0.00514	-22.59632	O ₂	0.1135 0.0003	0.0582 0.0005	0 0.0000	0.0000	0.0000	---	12.0800 0.1991	2.0230 0.0118	O ₂		
N ₂	85.48174 0.4731	81.2076 0.7050	166.6894 0.5634	0	0	0	0	0	0	0	0	0	N ₂	166.6894 0.5010	0 0.0000	85.4817 0.7050	0.0000	0.0000	---	45.5811 0.7513	131.0628 0.7628	N ₂		
H ₂ O	18.18057 0.1006	9.5298 0.0827	27.7104 0.0937	19.2706	0	12.84706	0	4.282355	3.315448	0	0.010278	39.72574	H ₂ O	67.4361 0.2027	18.18057 1.0000	10.0314 0.0827	0.0000	0.0000	---	3.0092 0.0496	32.7859 0.1908	H ₂ O		
H ₂	0 0.0000	18.7581 0.1628	18.7581 0.0634	0	32.11766	-12.84706	0.474756	0	0	0	0	19.74535	H ₂	38.5034 0.1157	0 0.0000	19.7454 0.1628	0.0000	0.0000	---	0 0.0000	0 0.0000	H ₂		
CO ₂	0 0.0000	5.1838 0.0450	5.1838 0.0175	0	0	0	0	2.141177	3.315448	0	0	5.456626	CO ₂	10.6404 0.0320	0 0.0000	5.4566 0.0450	0.0000	0.0000	---	0 0.0000	5.9417 0.0346	CO ₂		
CO	0 0.0000	0.4608 0.0040	0.4608 0.0016	0	0	0	0.474756	0	0	0	0.010278	0.485033	CO	0.9458 0.0028	0 0.0000	0.4850 0.0040	0.0000	0.0000	---	0 0.0000	0 0.0000	CO		
HCOOH	0 0.0000	0 0.0000	0 0.0000	0	0	0	0	0	0	0.010278	0	0.010278	HCOOH	0.0103 0.0000	0 0.0000	0.0103 0.0001	0.0000	0.0000	---	0 0.0000	0 0.0000	HCOOH		
TOTAL	180.6719 1.0000	115.1954 1.0000	295.8674 1.0000	9.635298	32.11766	-6.423532	0.474756	1.070589	0	-0.00514	0.005139	36.87477		332.7421 1.0000	18.18057 1.0000	121.2584 1.0000	114.4689 1.0000	0.0000	0.0000	---	60.6703 1.0000	171.8134 1.0000		
				(NOT ZERO)				(NOT ZERO)				(NOT ZERO)				Total out: 235.727267								
MASS FLOWS [kg.s ⁻¹]	FRACTION:	FRACTION:	FRACTION:	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	NETT	FRACTION:	FRACTION:	FRACTION:	FRACTION:								
CH ₃ OH	1.7416 0.3357	0 0.0000	1.7416 0.2200	-0.61747	-1.02911	0	0	-0.06861	0	0	0	-1.71519	CH ₃ OH	0.0265 0.0033	0 0.0000	0 0.0000	0.026455 0.0100	0.0000	0.0000	---	0 0.0000	0 0.0000	CH ₃ OH	
HCHO	0 0.0000	0 0.0000	0 0.0000	0.578623	0.964371	0	-0.01426	0	-0.09955	-0.00031	-0.00031	1.428571	HCHO	1.4286 0.1805	0 0.0000	0 0.0000	1.428571 0.5400	0.0000	0.0000	---	0 0.0000	0 0.0000	HCHO	
O ₂	0.7249 0.1397	0.0018 0.0006	0.7267 0.0918	-0.30832	0	-0.205545	0	-0.10277	-0.10609	-0.00016	-0.00016	-0.723055	O ₂	0.0036 0.0005	0 0.0000	0.0019 0.0006	0 0.0000	0.0000	0.0000	---	0.3865 0.2250	0.0647 0.0141	O ₂	
N ₂	2.3946 0.4615	2.2749 0.8341	4.6695 0.5899	0	0	0	0	0	0	0	0	0	N ₂	4.6695 0.5899	0 0.0000	2.3946 0.8341	0 0.0000	0.0000	0.0000	---	1.2769 0.7434	3.6715 0.8002	N ₂	
H ₂ O	0.3275 0.0631	0.1717 0.0630	0.4992 0.0631	0.347164	0	0.231442	0	0.077147	0.059728	0	0.000185	0.715667	H ₂ O	1.2149 0.1535	0.3275 1.0000	0.1807 0.0630	1.190003 0.4498	0.0000	0.0000	---	0.0542 0.0316	0.5906 0.1287	H ₂ O	
H ₂	0 0.0000	0.0378 0.0139	0.0378 0.0048	0	0.064743	-0.025897	0.000957	0	0	0	0	0.039803	H ₂	0.0776 0.0098	0 0.0000	0.0398 0.0139	0 0.0000	0.0000	0.0000	---	0 0.0000	0 0.0000	H ₂	
CO ₂	0 0.0000	0.2281 0.0637	0.2281 0.0268	0	0	0	0	0.094233	0.145912	0	0	0.240145	CO ₂	0.4683 0.0592	0 0.0000	0.2401 0.0637	0 0.0000	0.0000	0.0000	---	0 0.0000	0.2615 0.0570	CO ₂	
CO	0 0.0000	0.0129 0.0047	0.0129 0.0016	0	0	0	0.013298	0	0	0	0.000288	0.013586	CO	0.0265 0.0033	0 0.0000	0.0136 0.0047	0 0.0000	0.0000	0.0000	---	0 0.0000	0 0.0000	CO	
HCOOH	0 0.0000	0 0.0000	0 0.0000	0	0	0	0	0	0	0.000473	0	0.000473	HCOOH	0.0005 0.0001	0 0.0000	0 0.0000	0.000473 0.00018	0.0000	0.0000	---	0 0.0000	0 0.0000	HCOOH	
TOTAL	5.1887 1.0000	2.7272 1.0000	7.9159 1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000		7.9159 1.0000	0.3275 1.0000	2.8707 1.0000	2.645503 1.0000	0.0000	0.0000	---	1.7176 1.0000	4.5884 1.0000		
				(SHOULD BE ZERO)				(SHOULD BE ZERO)				(SHOULD BE ZERO)				Total out: 5.51625088								
NOTE: Some water enters with "fresh air"																								
= 5.643335 mol.s ⁻¹																								
= 0.101666 kg.s ⁻¹ ==> 0.225861 in MainsWater																								
Actual reaction conversion: 35.453% 59.089% 25.02% 0.924% 3.939% 6.452% 0.0200% 0.0200%																								
basis: CH ₃ OH CH ₃ OH H ₂ HCHO CH ₃ OH HCHO HCHO HCHO HCHO * Note: HCHO and H ₂ calculated from total generated																								
^ Or 97.5% of the CH ₃ OH remaining after reactions (1) and (5) have proceeded																								

2:23 PM, 10/5/99

1 of 1

DP#MEB19.XLS (Complete Mat. Bal. (2))



CLIENT: CHE4117	SHEET 1 of 1
PROJECT: MASS BALANCE	DATE 01/10/1999
	BY DIV
DESIGN OF: ADDITIONAL GRADE "B" REQUIREMENTS	CHKD:

- ① TOTAL FLOWS.
- From the spreadsheet $\dot{m}_B = 0.273149 \text{ kg.s}^{-1}$ $\dot{m}_B = 0.273 \text{ kg.s}^{-1}$
- Equating formaldehyde content, this requires $\dot{m}_A = 0.187158 \text{ kg.s}^{-1}$ $\dot{m}_A = 0.187 \text{ kg.s}^{-1}$
- ② ADDITIONAL METHANOL
- The feed Grade A contains $(0.01 \dot{m}_A) \text{ kg.s}^{-1}$ of methanol,
but the Grade B product $(0.07 \dot{m}_B) \text{ kg.s}^{-1}$.
- Thus a difference of $0.0172489 \text{ kg.s}^{-1}$ of fresh methanol $\dot{m}_M = 0.0172 \text{ kg.s}^{-1}$
- ③ ADDITIONAL WATER
- Likewise, additional water $\dot{m}_W = \left[(0.45 - 0.0008) \dot{m}_A \right]$
 $+ \left[(0.56 - 0.0008 \times \frac{37}{54}) \dot{m}_B \right]$ $\therefore \dot{m}_W = 0.0687 \text{ kg.s}^{-1}$
 $= 0.0687423 \text{ kg.s}^{-1}$

Table 5a. Thermodynamic & Essential Data of Components

All data from Simmott⁽⁴⁷⁾ unless otherwise stated

	Methanol (CH ₃ OH)	Air	Oxygen (O ₂)	Nitrogen (N ₂)	Formaldehyde (HCHO)	Carbon Dioxide (CO ₂)	Carbon Monoxide (CO)	Water (H ₂ O)	Formic Acid (HCOOH)	Methyl Formate (C ₂ H ₄ O ₂)	Hydrogen (H ₂)
MW	Molecular Weight [g.mol ⁻¹]		32	28.013	30.026	44.01	28.01	18.015	46.025	60.052	2.016
TFP	Normal Freezing Point [°C]		-218.8	-209.9	-117.2	-56.6	-205.1	0	8.3	-99	-259.2
TBP	Normal Boiling Point [°C]		-183	-195.8	-19.2	-78.5	-191.5	100	100.6	31.7	-252.8
TC	Critical Temperature [K]		512.6	126.2	408	304.2	132.9	647.3	580	487.2	33.2
PC	Critical Pressure [bar(abs)]		81	33.9	65.9	73.8	35	220.5		60	13
VC	Critical Volume [m ³ .mol ⁻¹]		0.073	0.09		0.094	0.093	0.056		0.172	0.065
LDEN	Liquid Density [kg.m ⁻³]		791	805	815	777	803	998	1226	974	71
TDEN	Ref. Temp for liquid density [°C]		20	-183	-195	-20	-192	20	15	20	-253
HVAP	Heat of Vaporisation at normal boiling point [J.mol ⁻¹]		35278	5581	23027	17166	6046	40683	21939	28219	904
VISA	Constants in the liquid viscosity eq.		555.3	90.3	319.83	578.08	94.06	658.25	729.35	363.19	13.82
VISB	Constants in the liquid viscosity eq.		260.64	46.14	171.35	185.24	48.9	283.16	325.72	212.7	5.39
DELHF	Standard Enthalpy of formation of vapour at 298K [kJ.mol ⁻¹]		-201.3	0	-115.97	-393.77	-110.62	-242	-378.86	-350.02	0
DELGF	Standard Gibbs energy of formation of vapour at 298K [kJ.mol ⁻¹]		-6282.379	0	-3862.319323	-8947.284708	-3949.30382	-13433.2501	-8231.613254	-5828.6152	0
DELGF	Standard Gibbs energy of formation of vapour at 298K [kJ.mol ⁻¹]		-162.62		-109.99	-394.65	-137.37	-228.77	-351.23	-297.39	
CPVAPA	Constant in ideal gas heat capacity equation (see below)	28.94	28.106	31.15	23.475	19.795	30.869	32.243	11.715	1.432	27.143
CPVAPB	Constant in ideal gas heat capacity equation (see below)	4.15E-03	-3.68E-06	-1.36E-02	3.16E-02	7.34E-02	-1.29E-02	1.92E-03	1.36E-01	2.70E-01	9.27E-03
CVPAPC	Constant in ideal gas heat capacity equation (see below)	2.59E-05	1.75E-05	2.68E-05	2.99E-05	-5.60E-05	2.79E-05	1.06E-05	-8.41E-05	-1.95E-04	-1.38E-05
CPVAPD	Constant in ideal gas heat capacity equation (see below)	-2.58E-08	-1.79E-09	-1.17E-08	-2.30E-08	1.72E-08	-1.27E-08	-3.60E-09	2.02E-08	5.70E-08	7.65E-09
ANTA	Constant in Antoine equation	18.5875	15.4075	14.9502	16.4775	22.5898	14.3886	18.3036	16.9882	16.5104	13.6333
ANTB	Constant in Antoine equation	3626.55	734.55	588.72	2204.13	3103.39	530.22	3816.44	3599.58	2590.87	164.9
ANTC	Constant in Antoine equation	-34.29	-6.45	-6.6	-30.15	-0.16	-13.15	-46.13	-26.09	-42.6	3.19
TMN	Minimum temperature for Antoine constant [°C]	-16	-210	-219	-88	-119	-210	11	-2	-48	-259
TMX	Maximum temperature for Antoine constant [°C]	91	-173	-183	-2	-69	-165	168	136	51	-248

$C_p [J.mol^{-1}.K^{-1}] = A + B.T + C.T^2 + D.T^3$; T in K
 $LOG(Viscosity[mPa.s]) = (VISA).(1/T) - (1/VISB)$; T in K
 $LN(p_{vapour}[satr]) [mmHg(abs)] = ANTA - (ANTB/(T + ANTC))$; T in K

From Oxtoby & Nachtrieb ⁽²⁾	
Heat of formation of the pure liquids at 25°C:	
Methanol	-238.66 -7448.349
Water	-285.83 -15866.22
Formic acid	-424.72 -9228.028
	[kJ.mol ⁻¹] [kJ.kg ⁻¹]
cf. (aq)	
	-245.93 -7675.24
	[kJ.mol ⁻¹] [kJ.kg ⁻¹]
cf. (aq)	
	-425.43 -9243.45
	[kJ.mol ⁻¹] [kJ.kg ⁻¹]
From Ullmann's ⁽⁶⁾	
Heat of solution at 23°C:	
(T = 296.15 K)	62 kJ.mol ⁻¹
HCHO	
=	
1935.927 kJ.kg ⁻¹	

Then with the mean specific heat of HCHO(g):

Mean specific heat of HCHO(l):

Mean specific heat of H₂O(l):

well might the mean c_p of 25%(mol.mol⁻¹) HCHO-H₂O(solution) be (approx.)

*Assuming additive specific heats of the pure liquid constituents (ideal, as per Sinnott⁽²⁾, p. 284.

However, by the same token we would assume that the HCHO component of that mixture would have mean c_p of HCHO(aq) = mean c_p of HCHO(l) =

Heat of formation at 25°C:

Hence:

(cf.)

From Perry⁽⁷⁾

Liquid Phase Heat Capacities					
T in K, c _p in J.kmol ⁻¹ .K ⁻¹					
c _p = C1 + C2.T + C3.T ² + C4.T ³ + C5.T ⁴					
	C1	C2	C3	C4	C5
Methanol	105800	-362.23	0.9379	T_min	T_max
Water	276370	-2090.1	8.125	-0.014116	9.3701E-06
				175.47	400
				273.16	533.15

Liquid Phase Heat Capacity					
T in K, c _p in J.mol ⁻¹ .K ⁻¹					
c _p = A + B.T + C.T ² + D.T ³					
	A	B	C	D	
HCHO	4.16E+02	-2.64E+00	4.98E-03	-	T_min T_max
					? ?

From Perry⁽⁶⁾

Liquid-phase heat capacity of formic acid:

0 °C :

15.5 °C :

20 to 100 °C :

This last row should be sufficiently accurate for the purposes of this report.

1.824224 kJ.kg⁻¹.K⁻¹,

2.129656 kJ.kg⁻¹.K⁻¹,

2.192416 kJ.kg⁻¹.K⁻¹,

83.95991 J.mol⁻¹.K⁻¹,

98.01742 J.mol⁻¹.K⁻¹,

100.9059 J.mol⁻¹.K⁻¹,

Energy Balance over Vaporiser (HX-1)

NOTE: Heat of solution of methanol [implicitly] considered.
Ideal vapour - [& liquid(?)] - phase assumed.

Recirc. liquid flow: **23.945** kg.s⁻¹
23.945

STREAMS IN:

No.	Description	HSYM	Flow [kg.s ⁻¹]	t [°C]	T [K]	Species	State	Mass frac. [⁻]	M _R [kg.mol ⁻¹]	A / C1	B / C2	C / C3	D / C4	C5	c _p [kJ.kg ⁻¹ .K ⁻¹]	ΔH _{f, 298K} [kJ.kg ⁻¹]	ΔH _{f, T} [kJ.kg ⁻¹]	ΔH _{f, T} [kW]	
3	Demin'd water	WaterFeed	0.225861	37.05	310.20	H ₂ O	L	1	0.0180152	276370	-2090.1	8.125	-0.01412	9.37E-06	4.180306924	-15866.04645	-15815.69214	-3572.148043	H ₂ O
6	Methanol	MethanolFeed	1.7416	37.04	310.19	CH ₃ OH	L	1	0.032042	105800	-362.23	0.9379	0	0	2.571789791	-7448.349042	-7417.396266	-12918.13734	CH ₃ OH
9	Air & rec. off-gas	HPCGas	5.948366	121.58	394.73	O ₂	V	0.122168	0.0319988	28.11	-3.68E-06	1.75E-05	-1.07E-08		0.9302	0	89.8450	65.29035916	O ₂
			5.948366		394.73	N ₂	V	0.7850055	0.0280134	31.15	-0.01357	2.68E-05	-1.17E-08		1.042040847	0	100.6434311	469.9545017	N ₂
			5.948366		394.73	H ₂ O	V	0.0459565	0.0180152	32.24	0.001924	1.06E-05	-3.60E-09		1.888880215	-13433.10094	-13250.66722	-3622.281895	H ₂ O
			5.948366		394.73	H ₂	V	0.0063547	0.0020158	27.14	0.009274	-1.38E-05	7.65E-09		14.39067509	0	1389.894573	52.53801484	H ₂
			5.948366		394.73	CO ₂	V	0.0383467	0.0440098	19.8	0.07344	-5.60E-05	1.72E-08		0.890766635	-8948.007035	-8861.974121	-2021.416297	CO ₂
			5.948366		394.73	CO	V	0.0021687	0.0280104	30.87	-0.01285	2.79E-05	-1.27E-08		1.0441883	-3948.533402	-3847.682563	-49.63510507	CO
13	Refluxed liquid	AAA	23.945	86.52	359.67	CH ₃ OH	Aq	0.3151	0.032042	105800	-362.23	0.9379	0	0	2.759445804	-7675.238749	-7505.483162	-56629.16116	CH ₃ OH
			23.945		359.67	H ₂ O	L	0.6849	0.0180152	276370	-2090.1	8.125	-0.01412	9.37E-06	4.183481453	-15866.04645	-15608.68704	-255980.3387	H ₂ O
(average over 298K to T)																			
SUM = -334205.3357																			

Check mass balances: -7.3E-05

STREAMS OUT:

No. Description	HSYIM	Flow	t	T	Species	State	Mass frac.	M _R	A / C1	B / C2	C / C3	D / C4	C5	c _p	ΔH _{f, 298K}	ΔH _{f, T}	ΔH _{f, T}	
		[kg.s ⁻¹]	[°C]	[K]			[-]	[kg.mol ⁻¹]						[kJ.kg ⁻¹ .K ⁻¹]	[kJ.kg ⁻¹]	[kJ.kg ⁻¹]	[kW]	
14 Reactor feed	Process/Vap	7.9159	62.08	335.23	HCHO	V	0	0.0300262	23.48	3.16E-02	2.99E-05	-2.30E-08		1.1904	-3862.293597	-3818.1510	0	HCHO
		7.9159		335.23	CH ₃ OH	V	0.2200129	0.032042	21.15	7.09E-02	2.59E-05	-2.85E-08		1.4137	-6282.379377	-6229.9540	-10850.08793	CH ₃ OH
		7.9159		335.23	O ₂	V	0.0918026	0.0319988	28.11	-3.68E-06	1.75E-05	-1.07E-08		0.9226	0	34.2136	24.86299793	O ₂
		7.9159		335.23	H ₂ O	V	0.0630629	0.0180152	32.24	0.001924	1.06E-05	-3.60E-09		1.8759	-13433.10094	-13363.5378	-6671.078078	H ₂ O
		7.9159		335.23	H ₂	V	0.0047752	0.0020158	27.14	0.009274	-1.38E-05	7.65E-09		14.353614	0	532.2793741	20.12016034	H ₂
		7.9159		335.23	CO ₂	V	0.0288154	0.0440098	19.8	0.07344	-5.60E-05	1.72E-08		0.862979507	-8948.007035	-8916.004907	-2033.740719	CO ₂
		7.9159		335.23	CO	V	0.0016296	0.0280104	30.87	-0.01285	2.79E-05	-1.27E-08		1.042309198	-3948.533402	-3909.881137	-50.43746667	CO
		7.9159		335.23	HCOOH	V	0	0.0460256	11.71	0.1358	-8.41E-05	2.02E-08		1.01930732	-8231.505945	-8193.706665	0	HCOOH
10 Liquid to heater	CCC	23.945	62.08	335.23	N ₂	V	0.5898887	0.0280134	31.15	-0.01357	2.68E-05	-1.17E-08		1.041329524	0	38.61593515	180.3171092	N ₂
		23.945		335.23	CH ₃ OH	Aq	0.3151	0.032042	105800	-362.23	0.9379	0	0	2.660808728	-7675.238749	-7576.567181	-57165.49283	CH ₃ OH
		23.945		335.23	H ₂ O	L	0.6849	0.0180152	276370	-2090.1	8.125	-0.01412	9.37E-06	4.178496813	-15866.04645	-15711.094	-257659.7989	H ₂ O
(average over 298K to T)																		
SUM = -334205.3357																		

Difference in enthalpy between Recirc. liquid in/out:
Difference in/out for others:cf. HYSIM: -1990.7995
cf. HYSIM: 2238.6648
2238.6628

recirc.

1.7814 pump
1131.6109 H/EX1
857.1907 H/EX2

OUT - IN = 0

Recirc. liquid in/out, but HYSIM with "correct" flow:

"ERROR" = -10%
"ERROR" = 1.0%
"ERROR" = 7.6%

nett proc.

1990.583
2238.6628

Energy Balance over Reactor (both RXN-1 and RXN-2)

Ideal vapour-phase assumed.

STREAMS IN:

No. Description	Flow [kg.s ⁻¹]	t [°C]	T [K]	Species	State	Mass frac. [-]	M _R [kg.mol ⁻¹]	A / C1	B / C2	C / C3	D / C4	C5	$\bar{c}_p$ [kJ.kg ⁻¹ .K ⁻¹]	$\Delta H^{\circ}_{f,298K}$ [kJ.kg ⁻¹]	$\Delta H^{\circ}_{f,T}$ [kJ.kg ⁻¹]	$\Delta H^{\circ}_{f,T}$ [kW]
14 Reactor feed	7.9159	158.26	431.41	HCHO	V	0	0.0300262	23.48	3.16E-02	2.99E-05	-2.30E-08		1.2609	-3862.293597	-3694.2703	0 HCHO
	7.9159		431.41	CH ₃ OH	V	0.2200129	0.032042	21.15	7.09E-02	2.59E-05	-2.85E-08		1.5314	-6282.379377	-6078.2973	-10585.9625 CH ₃ OH
	7.9159		431.41	O ₂	V	0.0918026	0.0319988	28.11	-3.68E-06	1.75E-05	-1.07E-08		0.9351	0	124.6193	90.56087089 O ₂
	7.9159		431.41	H ₂ O	V	0.0630629	0.0180152	32.24	0.001924	1.06E-05	-3.60E-09		1.8973	-13433.10094	-13180.2587	-6579.585144 H ₂ O
	7.9159		431.41	H ₂	V	0.0047752	0.0020158	27.14	0.009274	-1.38E-05	7.65E-09		14.41034721	0	1920.345926	72.589076 H ₂
	7.9159		431.41	CO ₂	V	0.0288154	0.0440098	19.8	0.07344	-5.60E-05	1.72E-08		0.906900818	-8948.007035	-8827.151981	-2013.473367 CO ₂
	7.9159		431.41	CO	V	0.0016296	0.0280104	30.87	-0.01285	2.79E-05	-1.27E-08		1.045932979	-3948.533402	-3809.1507	-49.13804402 CO
	7.9159		431.41	HCOOH	V	0	0.0460256	11.71	0.1358	-8.41E-05	2.02E-08		1.106826808	-8231.505945	-8084.008433	0 HCOOH
	7.9159		431.41	N ₂	V	0.5898887	0.0280134	31.15	-0.01357	2.68E-05	-1.17E-08		1.043067619	0	139.0008598	649.0645146 N ₂
SUM = -18415.9446																
(average over 298K to T)																

Check mass balances: 0

STREAMS OUT:

No. Description	Flow [kg.s ⁻¹]	t [°C]	T [K]	Species	State	Mass frac. [-]	M _R [kg.mol ⁻¹]	A / C1	B / C2	C / C3	D / C4	C5	$\bar{c}_p$ [kJ.kg ⁻¹ .K ⁻¹]	$\Delta H^{\circ}_{f,298K}$ [kJ.kg ⁻¹]	$\Delta H^{\circ}_{f,T}$ [kJ.kg ⁻¹]	$\Delta H^{\circ}_{f,T}$ [kW]
14 Reactor effluent	7.9159	700.00	973.15	HCHO	V	0.1804678	0.0300262	23.48	3.16E-02	2.99E-05	-2.30E-08		1.6375	-3862.293597	-2756.9508	-3938.483684 HCHO
	7.9159		973.15	CH ₃ OH	V	0.003342	0.032042	21.15	7.09E-02	2.59E-05	-2.85E-08		2.1308	-6282.379377	-4844.0821	-128.1497527 CH ₃ OH
	7.9159		973.15	O ₂	V	0.000459	0.0319988	28.11	-3.68E-06	1.75E-05	-1.07E-08		1.0100	0	681.7529	2.477099311 O ₂
	7.9159		973.15	H ₂ O	V	0.1534721	0.0180152	32.24	0.001924	1.06E-05	-3.60E-09		2.0506	-13433.10094	-12048.9316	-14637.88172 H ₂ O
	7.9159		973.15	H ₂	V	0.0098049	0.0020158	27.14	0.009274	-1.38E-05	7.65E-09		14.60847417	0	9860.720061	765.3386233 H ₂
	7.9159		973.15	CO ₂	V	0.059157	0.0440098	19.8	0.07344	-5.60E-05	1.72E-08		1.076275079	-8948.007035	-8221.521356	-3849.979696 CO ₂
	7.9159		973.15	CO	V	0.0033468	0.0280104	30.87	-0.01285	2.79E-05	-1.27E-08		1.101087454	-3948.533402	-3205.29937	-84.91653062 CO
	7.9159		973.15	HCOOH	V	5.976E-05	0.0460256	11.71	0.1358	-8.41E-05	2.02E-08		1.466439451	-8231.505945	-7241.659315	-3.42554358 HCOOH
	7.9159		973.15	N ₂	V	0.5898907	0.0280134	31.15	-0.01357	2.68E-05	-1.17E-08		1.089651368	0	735.5146735	3434.497342 N ₂
SUM = -18440.52387																
(average over 298K to T)																

NOTE: For completely adiabatic operation the exit temperature would be:

975.049413 K, which is a difference of only -0.19%

cf. HYSIM: 6804.973
"ERROR" = -27786%
OUT - IN = -2457927093
==> Approx. ADIABATIC

minus feed: -3938
minus feed: 10457.8
minus feed: -88.1
minus feed: -8058.3
minus feed: 692.7
minus feed: -1836.5
minus feed: -35.8
minus feed: -3
minus feed: 2785.4
minus SUM: -24.6

David Verhelst

Formaldehyde

Project

ice over Tail-gas Burner (RXN-3)

-phase assumed.

	Flow	t	T	Species	State	Mass frac.	M _R	A/C1	B/C2	C/C3	D/C4	C5	$\bar{c}_p$	$\Delta H_{f,298K}^0$	$\Delta H_{f,T}^0$	$\Delta H_{f,T}^0$
	[kg.s ⁻¹]	[°C]	[K]			[-]	[kg.mol ⁻¹]						[kJ.kg ⁻¹ .K ⁻¹]	[kJ.kg ⁻¹]	[kJ.kg ⁻¹]	[kW]
gas	Off-gas	2.870748	45.71	318.86	HCHO	V	0	0.0300262	23.48	3.16E-02	2.99E-05	-2.30E-08	1.1785	-3862.293597	-3837.8900	0 HCHO
		2.8707		318.86	CH ₃ OH	V	0	0.032042	21.15	7.09E-02	2.59E-05	-2.85E-08	1.3936	-6282.379377	-6253.5212	0 CH ₃ OH
		2.8707		318.86	O ₂	V	0.0006491	0.0319988	28.11	-3.68E-06	1.75E-05	-1.07E-08	0.9206	0	19.0635	0.035521049 O ₂
		2.8707		318.86	H ₂ O	V	0.0629512	0.0180152	32.24	0.001924	1.06E-05	-3.60E-09	1.8724	-13433.10094	-13394.3273	-2420.58511 H ₂ O
		2.8707		318.86	H ₂	V	0.0138649	0.0020158	27.14	0.009274	-1.38E-05	7.65E-09	14.34216332	0	296.9917812	11.82106887 H ₂
		2.87074824		318.86	CO ₂	V	0.0836524	0.0440098	19.8	0.07344	-5.60E-05	1.72E-08	0.854967694	-8948.007035	-8930.302706	-2144.567625 CO ₂
		2.87074824		318.86	CO	V	0.0047326	0.0280104	30.87	-0.01285	2.79E-05	-1.27E-08	1.04201441	-3948.533402	-3926.955784	-53.35154132 CO
		2.87074824		318.86	HCOOH	V	0	0.0460256	11.71	0.1358	-8.41E-05	2.02E-08	1.003562547	-8231.505945	-8210.724573	0 HCOOH
		2.87074624		318.86	N ₂	V	0.8341498	0.0280134	31.15	-0.01357	2.68E-05	-1.17E-08	1.04135553	0	21.56397378	51.63782648 N ₂
ExtraAir	1.717638	45.71	318.86	HCHO	V	0	0.0300262	23.48	3.16E-02	2.99E-05	-2.30E-08	1.1785	-3862.293597	-3837.8900	0 HCHO	
	1.7176		318.86	CH ₃ OH	V	0	0.032042	21.15	7.09E-02	2.59E-05	-2.85E-08	1.3936	-6282.379377	-6253.5212	0 CH ₃ OH	
	1.7176		318.86	O ₂	V	0.2250448	0.0319988	28.11	-3.68E-06	1.75E-05	-1.07E-08	0.9206	0	19.0635	7.368900182 O ₂	
	1.7176		318.86	H ₂ O	V	0.0315613	0.0180152	32.24	0.001924	1.06E-05	-3.60E-09	1.8724	-13433.10094	-13394.3273	-726.1181003 H ₂ O	
	1.7176		318.86	H ₂	V	0	0.0020158	27.14	0.009274	-1.38E-05	7.65E-09	14.34216332	0	296.9917812	0 H ₂	
	1.71763799		318.86	CO ₂	V	0	0.0440098	19.8	0.07344	-5.60E-05	1.72E-08	0.854967694	-8948.007035	-8930.302706	0 CO ₂	
	1.71763799		318.86	CO	V	0	0.0280104	30.87	-0.01285	2.79E-05	-1.27E-08	1.04201441	-3948.533402	-3926.955784	0 CO	
	1.71763799		318.86	HCOOH	V	0	0.0460256	11.71	0.1358	-8.41E-05	2.02E-08	1.003562547	-8231.505945	-8210.724573	0 HCOOH	
	1.71763799		318.86	N ₂	V	0.7433939	0.0280134	31.15	-0.01357	2.68E-05	-1.17E-08	1.04135553	0	21.56397378	27.5346413 N ₂	
														SUM =	-5246.224418	
Stack-gas	4.588386	907.69</														

NOTE: For completely adiabatic operation the exit temperature would be:

OUT - IN = -8.301638695
====> Approx. ADIABATIC

cf. HYSIM: 4858.9326
"ERROR" = -58630%

DP EB-x3.xls (RXN-3)

Stream	AAA	AbsFeed	AbsWater	AqMethanol	Stream	Q_Heat1b	Q_Heat2a	Q_Heat2b	Q_Super1'
Description					Description				
Vapour frac.	0	1	0	0	Vapour frac.	2.0000*	2.0000*	2.0000*	2.0000*
Temperature C	86.5180*	90.0000*	37.0000*	37.0368	Temperature C	0.0000*	0.0000*	0.0000*	0.0000*
Pressure kPa	185	130	120.0000*	185	Pressure kPa	0.0000*	0.0000*	0.0000*	0.0000*
Molar Flow mol/s*	957.0421	332.7419	18.1792	66.8933	Molar Flow mol/s*	0.0000*	0.0000*	0.0000*	0.0000*
Mass Flow kg/s*	20.0000*	7.9159	0.3275*	1.9675	Mass Flow kg/s*	0.0000*	0.0000*	0.0000*	0.0000*
LiqVol Flow L/s	21.6455	10.655	0.3282	2.4151	LiqVol Flow L/s	0.0000*	0.0000*	0.0000*	0.0000*
Enthalpy kW	-26970.2295	3572.8516	-613.5226	-1896.8556	Enthalpy kW	1131.611	857.1907	857.1907	963.2883
Density kg/m3	876.7156	1.0243	998.2847	794.6892	Density kg/m3	0	0	0	0
Mole Wt.	20.8977	23.7898	18.0151	29.4125	Mole Wt.	0	0	0	0
Spec. Heat kJ/kg-C	4.093	1.3378	4.1901	3.7051	Spec. Heat kJ/kg-C	---	---	---	---
Therm Cond W/m-K	0.5255	0.0359	0.6277	0.2323	Therm Cond W/m-K	---	---	---	---
Viscosity cP	0.3197	0.0157	0.6904	0.497	Viscosity cP	---	---	---	---
Z Factor	0.0015	1	0.0008	0.0027	Z Factor	---	---	---	---
Sur Tension dyne/cm	52.6804	---	70.0165	35.611	Sur Tension dyne/cm	---	---	---	---
Std Density kg/m3	937.6828	---	1014.836	816.5136	Std Density kg/m3	---	---	---	---
Formaldehyde mass frac.	0.0000*	0.1806	0.0000*	0	Formaldehyde mass frac.	0.0000*	0.0000*	0.0000*	0.0000*
Methanol mass frac.	0.3151*	0.0033	0.0000*	0.8852	Methanol mass frac.	0.0000*	0.0000*	0.0000*	0.0000*
Oxygen mass frac.	0.0000*	0.0006	0.0000*	0	Oxygen mass frac.	0.0000*	0.0000*	0.0000*	0.0000*
H2O mass frac.	0.6849*	0.1534	1.0000*	0.1148	H2O mass frac.	0.0000*	0.0000*	0.0000*	0.0000*
Hydrogen mass frac.	0.0000*	0.0098	0.0000*	0	Hydrogen mass frac.	0.0000*	0.0000*	0.0000*	0.0000*
CO2 mass frac.	0.0000*	0.059	0.0000*	0	CO2 mass frac.	0.0000*	0.0000*	0.0000*	0.0000*
CO mass frac.	0.0000*	0.0033	0.0000*	0	CO mass frac.	0.0000*	0.0000*	0.0000*	0.0000*
FormicAcid mass frac.	0.0000*	0.0001	0.0000*	0	FormicAcid mass frac.	0.0000*	0.0000*	0.0000*	0.0000*
Nitrogen mass frac.	0.0000*	0.5899	0.0000*	0	Nitrogen mass frac.	0.0000*	0.0000*	0.0000*	0.0000*
Argon mass frac.	0.0000*	0	0.0000*	0	Argon mass frac.	0.0000*	0.0000*	0.0000*	0.0000*

Stream	BBB	BFWater1a	BFWater1b	BFWater1c	Stream	Q_react	RCW1_in	RCW1_out	RecLiq1
Description					Description				
Vapour frac.	0.2305	0	0	0	Vapour frac.	2.0000*	0	0	0
Temperature C	62.0833	100.0000*	100.0153	151.8571	Temperature C	0.0000*	30.0000*	45.0000*	75.0000*
Pressure kPa	185	400.0000*	500	500.0000*	Pressure kPa	0.0000*	400.0000*	360	130.0000*
Molar Flow mol/s*	1252.9148	150.6514	150.6514	221.849	Molar Flow mol/s*	0.0000*	2885.0285	2885.0285	2569.1488
Mass Flow kg/s*	27.9159	2.7140*	2.714	3.9966	Mass Flow kg/s*	0.0000*	51.9741	51.9741	59.3941
LiqVol Flow L/s	31.5978	2.7195	2.7195	4.0047	LiqVol Flow L/s	0.0000*	52.079	52.079	70.1631
Enthalpy kW	-25984.197	-4364.6093	-4364.2277	-5547.3923	Enthalpy kW	0.0000*	-98890.026	-95597.3417	-54273.8546
Density kg/m3	---	948.0489	948.0807	902.0124	Density kg/m3	0	1003.6873	992.2268	773.2326
Mole Wt.	22.2808	18.0151	18.0151	18.0151	Mole Wt.	0	18.0151	18.0151	23.1182
Spec. Heat kJ/kg-C	---	4.1965	4.1963	4.3193	Spec. Heat kJ/kg-C	---	4.1894	4.1909	3.7574
Therm Cond W/m-K	---	0.6807	0.6807	0.6863	Therm Cond W/m-K	---	0.6182	0.6376	0.3688
Viscosity cP	---	0.279	0.2789	0.1787	Viscosity cP	---	0.7972	0.5939	0.1746
Z Factor	---	0.0024	0.0031	0.0028	Z Factor	---	0.0028	0.0025	0.0013
Sur Tension dyne/cm	---	58.6054	58.6025	48.2944	Sur Tension dyne/cm	---	71.2338	68.6162	41.0466
Std Density kg/m3	---	1014.836	1014.836	1014.836	Std Density kg/m3	---	1014.836	1014.836	839.4352
Formaldehyde mass frac.	0	0.0000*	0	0	Formaldehyde mass frac.	0.0000*	0.0000*	0	0.5407
Methanol mass frac.	0.2881	0.0000*	0	0	Methanol mass frac.	0.0000*	0.0000*	0	0.01
Oxygen mass frac.	0.026	0.0000*	0	0	Oxygen mass frac.	0.0000*	0.0000*	0	0
H2O mass frac.	0.5086	1.0000*	1	1	H2O mass frac.	0.0000*	1.0000*	1	0.4492
Hydrogen mass frac.	0.0014	0.0000*	0	0	Hydrogen mass frac.	0.0000*	0.0000*	0	0
CO2 mass frac.	0.0082	0.0000*	0	0	CO2 mass frac.	0.0000*	0.0000*	0	0
CO mass frac.	0.0005	0.0000*	0	0	CO mass frac.	0.0000*	0.0000*	0	0
FormicAcid mass frac.	0	0.0000*	0	0	FormicAcid mass frac.	0.0000*	0.0000*	0	0.0002
Nitrogen mass frac.	0.1673	0.0000*	0	0	Nitrogen mass frac.	0.0000*	0.0000*	0	0
Argon mass frac.	0	0.0000*	0	0	Argon mass frac.	0.0000*	0.0000*	0	0

Stream	BFWater4a	BFWater4b	BFWater4c	BurnerFeed	Stream	RecLiq2_a	RecLiq2_b	RecLiq3_a	RecLiq3_b
Description					Description				
Vapour frac.	0	0	0.0000*	1	Vapour frac.	0	0	0	0
Temperature C	100.0000*	100.1359	189.4517	45.7076	Temperature C	75.0145	60	60.0000*	60.0000*
Pressure kPa	400.0000*	1270	1240	110	Pressure kPa	170.0000*	120	120	120.0000*
Molar Flow mol/s*	95.4755	95.4755	95.4755	182.0192	Molar Flow mol/s*	2569.1488	2569.1488	2454.7765	2454.7776*
Mass Flow kg/s*	1.7200*	1.72	1.72	4.59	Mass Flow kg/s*	59.3941	59.3941	56.7500*	56.75
LiqVol Flow L/s	1.7235	1.7235	1.7235	6.0095	LiqVol Flow L/s	70.1631	70.1631	67.0396	67.0396
Enthalpy kW	-2766.0752	-2763.9706	-2103.1497	1680.7712	Enthalpy kW	-54269.76	-57562.4443	-54999.9036	-54999.9279
Density kg/m3	948.0489	948.3234	865.0236	1.0463	Density kg/m3	773.2152	790.785	790.785	790.7851
Mole Wt.	18.0151	18.0151	18.0151	25.2173	Mole Wt.	23.1182	23.1182	23.1182	23.1182
Spec. Heat kJ/kg-C	4.1965	4.1946	4.4676	1.1762	Spec. Heat kJ/kg-C	3.7575	3.6248	3.6248	3.6248
Therm Cond W/m-K	0.6807	0.6808	0.6714	0.034	Therm Cond W/m-K	0.3688	0.3747	0.3747	0.3747
Viscosity cP	0.279	0.2786	0.1415	0.0176	Viscosity cP	0.1745	0.2115	0.2115	0.2115
Z Factor	0.0024	0.0078	0.0067	1	Z Factor	0.0018	0.0013	0.0013	0.0013
Sur Tension dyne/cm	58.6054	58.5796	40.1818	---	Sur Tension dyne/cm	41.0438	43.9075	43.9075	43.9075
Std Density kg/m3	1014.836	1014.836	1014.836	---	Std Density kg/m3	839.4352	839.4352	839.4352	839.4353
Formaldehyde mass frac.	0	0.0000*	0	0	Formaldehyde mass frac.	0.5407	0.5407	0.5407	0.5407*
Methanol mass frac.	0	0.0000*	0	0	Methanol mass frac.	0.01	0.01	0.01	0.0100*
Oxygen mass frac.	0	0.0000*	0	0.0847	Oxygen mass frac.	0	0	0	0.0000*
H2O mass frac.	1	1.0000*	1	0.0514	H2O mass frac.	0.4492	0.4492	0.4492	0.4492*
Hydrogen mass frac.	0	0.0000*	0	0.0087	Hydrogen mass frac.	0	0	0	0.0000*
CO2 mass frac.	0	0.0000*	0	0.0522	CO2 mass frac.	0	0	0	0.0000*
CO mass frac.	0	0.0000*	0	0.003	CO mass frac.	0	0	0	0.0000*
FormicAcid mass frac.	0	0.0000*	0	0	FormicAcid mass frac.	0.0002	0.0002	0.0002	0.0002*
Nitrogen mass frac.	0	0.0000*	0	0.8001	Nitrogen mass frac.	0	0	0	0.0000*
Argon mass frac.	0	0.0000*	0	0	Argon mass frac.	0	0	0	0.0000*

Stream	CCC	ColdFeed	Condens1	Condens4'	Stream	RecOff-gas	RecVap_a	RecVap_b	Stack-gas
Description					Description				
Vapour frac.	0	0.8305	0.9417	0.0000*	Vapour frac.	1	1	1	0.9539
Temperature C	62.0833*	38.1968	100.1843	187.3985	Temperature C	50	49.9958	49.9954*	907.692
Pressure kPa	185	185	102.0000*	1185	Pressure kPa	110	101.0000*	101.0000*	110
Molar Flow mol/s*	957.0473	295.8688	150.6551	31.5819	Molar Flow mol/s*	115.1998	115.1998	115.1954*	171.9008
Mass Flow kg/s*	20.0000*	7.9159	2.7141	0.569	Mass Flow kg/s*	2.7268	2.7268	2.7272	4.59
LiqVol Flow L/s	21.6455	9.9523	2.7195	0.5701	LiqVol Flow L/s	3.8276	3.8276	3.8286	5.5203
Enthalpy kW	-28961.029	738.1688	1402.9055	-700.9128	Enthalpy kW	1074.1837	1074.1837	1074.1202	6539.7038
Density kg/m3	898.418	2.3013	0.6286	867.1453	Density kg/m3	0.9691	0.8898	0.89	0.3136
Mole Wt.	20.8976	26.7547	18.0151	18.0151	Mole Wt.	23.6706	23.6706	23.6744	26.7015
Spec. Heat kJ/kg-C	4.0504	1.5864	2.2474	4.4586	Spec. Heat kJ/kg-C	1.26	1.26	1.2597	1.3624
Therm Cond W/m-K	0.5172	---	---	0.6726	Therm Cond W/m-K	0.0382	0.0382	0.0382	---

Viscosity	cP	0.4463	---	---	0.1431	Viscosity	cP	0.017	0.017	0.017	---
Z Factor		0.0015	---	---	0.0064	Z Factor		1	1	1	---
Sur Tension	dyne/cm	56.9883	---	---	40.6386	Sur Tension	dyne/cm	---	---	---	---
Std Density	kg/m3	937.6853	---	---	1014.836	Std Density	kg/m3	---	---	---	---
Formaldehyde	mass frac.	0.0000*	0	0	0.0000*	Formaldehyde	mass frac.	0	0	0.0000*	0
Methanol	mass frac.	0.3151*	0.22	0	0.0000*	Methanol	mass frac.	0	0	0.0000*	0
Oxygen	mass frac.	0.0000*	0.0918	0	0.0000*	Oxygen	mass frac.	0.0008	0.0008	0.0006*	0.0142
H2O	mass frac.	0.6849*	0.0631	1	1.0000*	H2O	mass frac.	0.0632	0.0632	0.0630*	0.1289
Hydrogen	mass frac.	0.0000*	0.0048	0	0.0000*	Hydrogen	mass frac.	0.0139	0.0139	0.0139*	0
CO2	mass frac.	0.0000*	0.0288	0	0.0000*	CO2	mass frac.	0.0834	0.0834	0.0837*	0.0568
CO	mass frac.	0.0000*	0.0016	0	0.0000*	CO	mass frac.	0.0047	0.0047	0.0047*	0
FormicAcid	mass frac.	0.0000*	0	0	0.0000*	FormicAcid	mass frac.	0	0	0.0000*	0
Nitrogen	mass frac.	0.0000*	0.5899	0	0.0000*	Nitrogen	mass frac.	0.8339	0.8339	0.8341*	0.8001
Argon	mass frac.	0.0000*	0	0	0.0000*	Argon	mass frac.	0	0	0.0000*	0

Stream		Condens4b	Condens4c	Condens4c'	Convert_Eff	Stream		Steam1a	Steam1b	Steam1c	Steam4a
Description						Description					
Vapour frac.		0.0000*	0.0000*	0.0000*	0.9689	Vapour frac.		0.7500*	1	0.7500*	1.0000*
Temperature	C	187.3985	187.3985	187.3985	700.0000*	Temperature	C	151.8557	151.8571	151.8557*	187.9668
Pressure	kPa	1185	1185	1185	160	Pressure	kPa	500.0000*	500	500.0000*	1200.0000*
Molar Flow	mol/s*	31.5819	26.8842	26.8842	332.7419	Molar Flow	mol/s*	221.849	150.6551	221.8528	95.4755
Mass Flow	kg/s*	0.569	0.4843	0.4843	7.9159	Mass Flow	kg/s*	3.9966	2.7141	3.9967*	1.72
LiqVol Flow	L/s	0.5701	0.4853	0.4853	10.655	LiqVol Flow	L/s	4.0047	2.7195	4.0048	1.7235
Enthalpy	kW	-700.9128	-596.6548	-596.6548	10745.0928	Enthalpy	kW	767.4445	1950.6219	767.4574	1302.046
Density	kg/m3	867.1453	867.1453	867.1453	0.4855	Density	kg/m3	3.3956	2.5491	3.3956	5.6387
Mole Wt.		18.0151	18.0151	18.0151	23.7898	Mole Wt.		18.0151	18.0151	18.0151	18.0151
Spec. Heat	kJ/kg-C	4.4586	4.4586	4.4586	1.634	Spec. Heat	kJ/kg-C	3.0264	2.5954	3.0264	3.0477
Therm Cond	W/m-K	0.6726	0.6726	0.6726	---	Therm Cond	W/m-K	---	0.0288	---	0.032
Viscosity	cP	0.1431	0.1431	0.1431	---	Viscosity	cP	---	0.014	---	0.0152
Z Factor		0.0064	0.0064	0.0064	---	Z Factor		---	1	---	1
Sur Tension	dyne/cm	40.6386	40.6386	40.6386	---	Sur Tension	dyne/cm	---	---	---	---
Std Density	kg/m3	1014.836	1014.836	1014.836	---	Std Density	kg/m3	---	---	---	---
Formaldehyde	mass frac.	0	0	0	0.1806	Formaldehyde	mass frac.	0.0000*	0	0.0000*	0
Methanol	mass frac.	0	0	0	0.0033	Methanol	mass frac.	0.0000*	0	0.0000*	0
Oxygen	mass frac.	0	0	0	0.0006	Oxygen	mass frac.	0.0000*	0	0.0000*	0
H2O	mass frac.	1	1	1	0.1534	H2O	mass frac.	1.0000*	1	1.0000*	1
Hydrogen	mass frac.	0	0	0	0.0098	Hydrogen	mass frac.	0.0000*	0	0.0000*	0
CO2	mass frac.	0	0	0	0.059	CO2	mass frac.	0.0000*	0	0.0000*	0
CO	mass frac.	0	0	0	0.0033	CO	mass frac.	0.0000*	0	0.0000*	0
FormicAcid	mass frac.	0	0	0	0.0001	FormicAcid	mass frac.	0.0000*	0	0.0000*	0
Nitrogen	mass frac.	0	0	0	0.5899	Nitrogen	mass frac.	0.0000*	0	0.0000*	0
Argon	mass frac.	0	0	0	0	Argon	mass frac.	0.0000*	0	0.0000*	0

Stream		CoolEff	DDD	DrumFeed	EEE	Stream		Steam4b	Steam4b'	Steam4c	Steam4c'
Description						Description					
Vapour frac.		1	0	0.4044	0	Vapour frac.		1	1.0000*	1	1.0000*
Temperature	C	170.0000*	62.0967	151.8571	72.6444	Temperature	C	187.9668	187.9668	187.9668	187.9668
Pressure	kPa	145	245	500	215	Pressure	kPa	1200	1200.0000*	1200	1200.0000*
Molar Flow	mol/s*	332.7419	957.0473	372.5042	957.0473	Molar Flow	mol/s*	31.5819	31.5819	26.8842	26.8842
Mass Flow	kg/s*	7.9159	20	6.7107	20	Mass Flow	kg/s*	0.569	0.569	0.4843	0.4843
LiqVol Flow	L/s	10.655	21.6455	6.7242	21.6455	LiqVol Flow	L/s	0.5701	0.5701	0.4853	0.4853
Enthalpy	kW	4430.0422	-28959.2476	-3596.7701	-28102.0568	Enthalpy	kW	430.6981	430.6981	366.6335	366.6335
Density	kg/m3	0.9362	898.4362	6.2766	889.1826	Density	kg/m3	5.6387	5.6387	5.6387	5.6387
Mole Wt.		23.7898	20.8976	18.0151	20.8976	Mole Wt.		18.0151	18.0151	18.0151	18.0151
Spec. Heat	kJ/kg-C	1.372	4.0504	3.6221	4.0674	Spec. Heat	kJ/kg-C	3.0477	3.0477	3.0477	3.0477
Therm Cond	W/m-K	0.043	0.5172	---	0.5215	Therm Cond	W/m-K	0.032	0.032	0.032	0.032
Viscosity	cP	0.019	0.4462	---	0.3849	Viscosity	cP	0.0152	0.0152	0.0152	0.0152
Z Factor		1	0.002	---	0.0018	Z Factor		1	1	1	1
Sur Tension	dyne/cm	---	56.986	---	55.1394	Sur Tension	dyne/cm	---	---	---	---
Std Density	kg/m3	---	937.6853	---	937.6853	Std Density	kg/m3	---	---	---	---
Formaldehyde	mass frac.	0.1806	0	0	0	Formaldehyde	mass frac.	0	0	0	0.0000*
Methanol	mass frac.	0.0033	0.3151	0	0.3151	Methanol	mass frac.	0	0	0	0.0000*
Oxygen	mass frac.	0.0006	0	0	0	Oxygen	mass frac.	0	0	0	0.0000*
H2O	mass frac.	0.1534	0.6849	1	0.6849	H2O	mass frac.	1	1	1	1.0000*
Hydrogen	mass frac.	0.0098	0	0	0	Hydrogen	mass frac.	0	0	0	0.0000*
CO2	mass frac.	0.059	0	0	0	CO2	mass frac.	0	0	0	0.0000*
CO	mass frac.	0.0033	0	0	0	CO	mass frac.	0	0	0	0.0000*
FormicAcid	mass frac.	0.0001	0	0	0	FormicAcid	mass frac.	0	0	0	0.0000*
Nitrogen	mass frac.	0.5899	0	0	0	Nitrogen	mass frac.	0	0	0	0.0000*
Argon	mass frac.	0	0	0	0	Argon	mass frac.	0	0	0	0.0000*

Stream		Exhaust1	Exhaust2	ExtraAir	FFF	Stream		Steam4d	Total_Feed	W_APump1	W_BPump1
Description						Description					
Vapour frac.		1	1	1	0	Vapour frac.		1	1	2.0000*	2.0000*
Temperature	C	328.4914	206.3792	37.0000*	86.5180*	Temperature	C	187.9668	158.2616	0.0000*	0.0000*
Pressure	kPa	106	101	110	185.0000*	Pressure	kPa	1200	170	0.0000*	0.0000*
Molar Flow	mol/s*	171.9008	171.9008	60.6691	957.0473	Molar Flow	mol/s*	37.0093	295.8674	0.0000*	0.0000*
Mass Flow	kg/s*	4.59	4.59	1.7176*	20	Mass Flow	kg/s*	0.6667	7.9159	0.0000*	0.0000*
LiqVol Flow	L/s	5.5203	5.5203	1.9775	21.6455	LiqVol Flow	L/s	0.6681	9.9523	0.0000*	0.0000*
Enthalpy	kW	3134.5079	2473.6871	549.2388	-26970.4458	Enthalpy	kW	504.7143	3940.1198	4.0946	0.3816
Density	kg/m3	0.5658	0.6764	1.2077	876.7184	Density	kg/m3	5.6387	1.268	0	0
Mole Wt.		26.7015	26.7015	28.3109	20.8976	Mole Wt.		18.0151	26.7549	0	0
Spec. Heat	kJ/kg-C	1.1953	1.1635	1.0368	4.0931	Spec. Heat	kJ/kg-C	3.0477	1.2972	---	---
Therm Cond	W/m-K	0.0442	0.0362	0.0264	0.5255	Therm Cond	W/m-K	0.032	0.037	---	---
Viscosity	cP	0.0273	0.0232	0.0187	0.3197	Viscosity	cP	0.0152	0.0198	---	---
Z Factor		1	1	1	0.0015	Z Factor		1	1	---	---
Sur Tension	dyne/cm	---	---	---	52.6808	Sur Tension	dyne/cm	---	---	---	---
Std Density	kg/m3	---	---	---	937.6853	Std Density	kg/m3	---	---	---	---
Formaldehyde	mass frac.	0	0	0.0000*	0	Formaldehyde	mass frac.	0	0	0.0000*	0.0000*
Methanol	mass frac.	0	0	0.0000*	0.3151	Methanol	mass frac.	0	0.22	0.0000*	0.0000*
Oxygen	mass frac.	0.0142	0.0142	0.2250*	0	Oxygen	mass frac.	0	0.0918	0.0000*	0.0000*
H2O	mass frac.	0.1289	0.1289	0.0316*	0.6849	H2O	mass frac.	1	0.0631	0.0000*	0.0000*
Hydrogen	mass frac.	0	0	0.0000*	0	Hydrogen	mass frac.	0	0.0048	0.0000*	0.0000*
CO2	mass frac.	0.0568	0.0568	0.0000*	0	CO2	mass frac.	0	0.0288	0.0000*	0.0000*
CO	mass frac.	0	0	0.0000*	0	CO	mass frac.	0	0.0016	0.0000*	0.0000*
FormicAcid	mass frac.	0	0	0.0000*	0	FormicAcid	mass frac.	0	0	0.0000*	0.0000*
Nitrogen	mass frac.	0.8001	0.8001	0.7434*	0	Nitrogen	mass frac.	0	0.5899	0.0000*	0.0000*
Argon	mass frac.	0	0	0.0000*	0	Argon	mass frac.	0	0	0.0000*	0.0000*

Stream					Stream				
Description					Description				
Vapour frac.		1	1	0	Vapour frac.		2.0000*	2.0000*	2.0000*
Temperature	C	121.583	37.0000*	37.0000*	Temperature	C	0.0000*	0.0000*	0.0000*
Pressure	kPa	185.0000*	101.0000*	101	Pressure	kPa	0.0000*	0.0000*	0.0000*
Molar Flow	mol/s*	228.9755	113.7801	228.9755	Molar Flow	mol/s*	0.0000*	0.0000*	0.0000*
Mass Flow	kg/s*	5.9484	3.2212*	5.9484	Mass Flow	kg/s*	0.0000*	0.0000*	0.0000*
LiqVol Flow	L/s	7.5372	3.7087	7.5372	LiqVol Flow	L/s	0.0000*	0.0000*	0.0000*
Enthalpy	kW	2635.0243	1030.0533	2104.1736	Enthalpy	kW	2.1046	530.8508	0.2252
Density	kg/m3	1.4644	1.1089	0.9963	Density	kg/m3	0	0	0
Mole Wt.		25.9782	28.3107	25.9782	Mole Wt.		0	0	0
Spec. Heat	kJ/kg-C	1.1508	1.0368	1.1387	Spec. Heat	kJ/kg-C	---	---	---
Therm Cond	W/m-K	0.0382	0.0264	0.032	Therm Cond	W/m-K	---	---	---
Viscosity	cP	0.021	0.0187	0.0179	Viscosity	cP	---	---	---
Z Factor		1	1	1	Z Factor		---	---	---
Sur Tension	dyne/cm	---	---	---	Sur Tension	dyne/cm	---	---	---
Std Density	kg/m3	---	---	---	Std Density	kg/m3	---	---	---
Formaldehyde	mass frac.	0	0.0000*	0	Formaldehyde	mass frac.	0.0000*	0.0000*	0.0000*
Methanol	mass frac.	0	0.0000*	0	Methanol	mass frac.	0.0000*	0.0000*	0.0000*
Oxygen	mass frac.	0.1222	0.2250*	0.1222	Oxygen	mass frac.	0.0000*	0.0000*	0.0000*
H2O	mass frac.	0.046	0.0316*	0.046	H2O	mass frac.	0.0000*	0.0000*	0.0000*
Hydrogen	mass frac.	0.0064	0.0000*	0.0064	Hydrogen	mass frac.	0.0000*	0.0000*	0.0000*
CO2	mass frac.	0.0384	0.0000*	0.0384	CO2	mass frac.	0.0000*	0.0000*	0.0000*
CO	mass frac.	0.0022	0.0000*	0.0022	CO	mass frac.	0.0000*	0.0000*	0.0000*
FormicAcid	mass frac.	0	0.0000*	0	FormicAcid	mass frac.	0.0000*	0.0000*	0.0000*
Nitrogen	mass frac.	0.785	0.7434*	0.785	Nitrogen	mass frac.	0.0000*	0.0000*	0.0000*
Argon	mass frac.	0	0.0000*	0	Argon	mass frac.	0.0000*	0.0000*	0.0000*

Stream					Stream				
Description					Description				
Vapour frac.		0	0	1	Vapour frac.		2.0000*	0	
Temperature	C	37.0355	37.0000*	50.0000*	Temperature	C	0.0000*	37.0456	
Pressure	kPa	185.0000*	110.0000*	110.0000*	Pressure	kPa	0.0000*	185	
Molar Flow	mol/s*	54.3538	54.3538	236.5498	Molar Flow	mol/s*	0.0000*	12.5395	
Mass Flow	kg/s*	1.7416	1.7416*	5.5993	Mass Flow	kg/s*	0.0000*	0.2259	
LiqVol Flow	L/s	2.1887	2.1887	7.8596	LiqVol Flow	L/s	0.0000*	0.2264	
Enthalpy	kW	-1473.7222	-1473.9474	2205.7159	Enthalpy	kW	1.7814	-423.1333	
Density	kg/m3	773.4377	773.4186	0.9691	Density	kg/m3	0	998.2705	
Mole Wt.		32.0419	32.0419	23.6706	Mole Wt.		0	18.0151	
Spec. Heat	kJ/kg-C	3.6422	3.642	1.26	Spec. Heat	kJ/kg-C	---	4.1901	
Therm Cond	W/m-K	0.1747	0.1747	0.0382	Therm Cond	W/m-K	---	0.6277	
Viscosity	cP	0.4623	0.4625	0.017	Viscosity	cP	---	0.6898	
Z Factor		0.003	0.0018	1	Z Factor		---	0.0013	
Sur Tension	dyne/cm	27.6753	27.6809	---	Sur Tension	dyne/cm	---	70.0085	
Std Density	kg/m3	796.4045	796.4045	---	Std Density	kg/m3	---	1014.836	
Formaldehyde	mass frac.	0.0000*	0	0	Formaldehyde	mass frac.	0.0000*	0.0000*	
Methanol	mass frac.	1.0000*	1	0	Methanol	mass frac.	0.0000*	0.0000*	
Oxygen	mass frac.	0.0000*	0	0.0008	Oxygen	mass frac.	0.0000*	0.0000*	
H2O	mass frac.	0.0000*	0	0.0632	H2O	mass frac.	0.0000*	1.0000*	
Hydrogen	mass frac.	0.0000*	0	0.0139	Hydrogen	mass frac.	0.0000*	0.0000*	
CO2	mass frac.	0.0000*	0	0.0834	CO2	mass frac.	0.0000*	0.0000*	
CO	mass frac.	0.0000*	0	0.0047	CO	mass frac.	0.0000*	0.0000*	
FormicAcid	mass frac.	0.0000*	0	0	FormicAcid	mass frac.	0.0000*	0.0000*	
Nitrogen	mass frac.	0.0000*	0	0.8339	Nitrogen	mass frac.	0.0000*	0.0000*	
Argon	mass frac.	0.0000*	0	0	Argon	mass frac.	0.0000*	0.0000*	

Stream					Stream				
Description					Description				
Vapour frac.		0	1	2.0000*	Vapour frac.		0	2.0000*	
Temperature	C	60	62.0833	0.0000*	Temperature	C	60	62.0833	
Pressure	kPa	120	185.0000*	0.0000*	Pressure	kPa	120	185.0000*	
Molar Flow	mol/s*	114.3723	295.8674*	0.0000*	Molar Flow	mol/s*	114.3723	295.8674*	
Mass Flow	kg/s*	2.6441	7.9159	0.0000*	Mass Flow	kg/s*	2.6441	7.9159	
LiqVol Flow	L/s	3.1235	9.9523	0.0000*	LiqVol Flow	L/s	3.1235	9.9523	
Enthalpy	kW	-2562.5408	2976.8316	-27.5397	Enthalpy	kW	-2562.5408	2976.8316	
Density	kg/m3	790.785	1.7759	0	Density	kg/m3	790.785	1.7759	
Mole Wt.		23.1182	26.7549	0	Mole Wt.		23.1182	26.7549	
Spec. Heat	kJ/kg-C	3.6248	1.2336	---	Spec. Heat	kJ/kg-C	3.6248	1.2336	
Therm Cond	W/m-K	0.3747	0.0295	---	Therm Cond	W/m-K	0.3747	0.0295	
Viscosity	cP	0.2115	0.0154	---	Viscosity	cP	0.2115	0.0154	
Z Factor		0.0013	1	---	Z Factor		0.0013	1	
Sur Tension	dyne/cm	43.9075	---	---	Sur Tension	dyne/cm	43.9075	---	
Std Density	kg/m3	839.4352	---	---	Std Density	kg/m3	839.4352	---	
Formaldehyde	mass frac.	0.5407	0.0000*	0.0000*	Formaldehyde	mass frac.	0.5407	0.0000*	
Methanol	mass frac.	0.01	0.2200*	0.0000*	Methanol	mass frac.	0.01	0.2200*	
Oxygen	mass frac.	0	0.0918*	0.0000*	Oxygen	mass frac.	0	0.0918*	
H2O	mass frac.	0.4492	0.0631*	0.0000*	H2O	mass frac.	0.4492	0.0631*	
Hydrogen	mass frac.	0	0.0048*	0.0000*	Hydrogen	mass frac.	0	0.0048*	
CO2	mass frac.	0	0.0288*	0.0000*	CO2	mass frac.	0	0.0288*	
CO	mass frac.	0	0.0016*	0.0000*	CO	mass frac.	0	0.0016*	
FormicAcid	mass frac.	0.0002	0.0000*	0.0000*	FormicAcid	mass frac.	0.0002	0.0000*	
Nitrogen	mass frac.	0	0.5899*	0.0000*	Nitrogen	mass frac.	0	0.5899*	
Argon	mass frac.	0	0.0000*	0.0000*	Argon	mass frac.	0	0.0000*	

STREAM MASS COMPOSITIONS

Stream name **BBB**

Mass Fraction

Component	Total	Vapour	Light Liquid	Heavy Liquid
Formaldehyde	0	0	0	---
Methanol	0.2881	0.1958	0.3232	---
Oxygen	0.026	0.0946	0	---
H2O	0.5086	0.0658	0.6768	---
Hydrogen	0.0014	0.0049	0	---
CO2	0.0082	0.0296	0	---
CO	0.0005	0.0017	0	---
FormicAcid	0	0	0	---
Nitrogen	0.1673	0.6077	0	---
Argon	0	0	0	---

<snip!>

Mass Flows in kg/h

Formaldehyde	0	0	0	---
Methanol	28956.3262	5415.8833	23540.4434	---
Oxygen	2616.1794	2615.8643	0.3154	---
H2O	51110.7188	1819.2366	49291.4844	---
Hydrogen	136.1387	136.1146	0.0241	---
CO2	821.2947	819.3807	1.914	---
CO	46.4667	46.4565	0.0102	---
FormicAcid	0	0	0	---
Nitrogen	16810.0879	16809.3906	0.6961	---
Argon	0	0	0	---
---	---	---	---	---
---	---	---	---	---
Total flow	27.9159	7.684	20.2319	0

STREAM MASS COMPOSITIONS

Stream name **ColdFeed**

Mass Fraction

Component	Total	Vapour	Light Liquid	Heavy Liquid
Formaldehyde	0	0	0	---
Methanol	0.22	0.13	0.6829	---
Oxygen	0.0918	0.1097	0	---
H2O	0.0631	0.0137	0.3171	---
Hydrogen	0.0048	0.0057	0	---
CO2	0.0288	0.0344	0	---
CO	0.0016	0.0019	0	---
FormicAcid	0	0	0	---
Nitrogen	0.5899	0.7046	0	---
Argon	0	0	0	---

<snip!>

Mass Flows in kg/h

Formaldehyde	0	0	0	---
Methanol	6269.7598	3101.2915	3168.4683	---
Oxygen	2616.0107	2615.9941	0.0165	---
H2O	1797.4092	326.3094	1471.0997	---
Hydrogen	136.1388	136.1351	0.0037	---
CO2	821.295	821.1005	0.1945	---
CO	46.4667	46.4646	0.0021	---
FormicAcid	0	0	0	---
Nitrogen	16810.0859	16810.0605	0.0265	---
Argon	0	0	0	---
---	---	---	---	---
---	---	---	---	---
Total flow	7.9159	6.627	1.2888	0

STREAM MASS COMPOSITIONS

Stream name **Convert_Eff**

Mass Fraction

Component	Total	Vapour	Light Liquid	Heavy Liquid
Formaldehyde	0.1806	0.1916 ---		0
Methanol	0.0033	0.0035 ---		0
Oxygen	0.0006	0.0006 ---		0.0001
H2O	0.1534	0.1628 ---		0.0001
Hydrogen	0.0098	0.0104 ---		0
CO2	0.059	0.0018 ---		0.9969
CO	0.0033	0.0034 ---		0.0024
FormicAcid	0.0001	0.0001 ---		0
Nitrogen	0.5899	0.6258 ---		0.0005
Argon	0	0 ---		0
---	---	---		
<snip!>				
---	---	---		

Mass Flows in kg/h

Formaldehyde	5146.2549	5146.1899 ---		0.0651
Methanol	95.2399	95.2387 ---		0.0012
Oxygen	16.6598	16.5632 ---		0.0966
H2O	4371.5361	4371.4492 ---		0.0869
Hydrogen	279.4381	279.4333 ---		0.0049
CO2	1680.9608	48.5047 ---		1632.4562
CO	95.3084	91.3722 ---		3.9362
FormicAcid	1.5783	1.5782 ---		0.0001
Nitrogen	16810.0879	16809.2734 ---		0.8148
Argon	0	0 ---		0
---	---	---		
<snip!>				
---	---	---		
Total flow	7.9159	7.461	0	0.4549

STREAM MASS COMPOSITIONS

Stream name **Stack-gas**

Mass Fraction

Component	Total	Vapour	Light Liquid	Heavy Liquid
Formaldehyde	0	0	0 ---	
Methanol	0	0	0 ---	
Oxygen	0.0142	0.0003	0.1968 ---	
H2O	0.1289	0.1387	0 ---	
Hydrogen	0	0	0 ---	
CO2	0.0568	0	0.8031 ---	
CO	0	0	0 ---	
FormicAcid	0	0	0 ---	
Nitrogen	0.8001	0.861	0.0001 ---	
Argon	0	0	0 ---	
---	---	---		
<snip!>				
---	---	---		

Mass Flows in kg/h

Formaldehyde	0	0	0 ---	
Methanol	0	0	0 ---	
Oxygen	234.4494	4.3651	230.0844 ---	
H2O	2129.9111	2129.8926	0.0185 ---	
Hydrogen	0	0	0 ---	
CO2	939.0356	0	939.0356 ---	
CO	0	0	0 ---	
FormicAcid	0	0	0 ---	
Nitrogen	13219.3457	13219.2148	0.1309 ---	
Argon	0	0	0 ---	
---	---	---		
<snip!>				
---	---	---		
Total flow	4.5897	4.2649	0.3248	0

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Van Laar, IDEAL (DEFAULT PLUS UNIFAC VLE)

Unifac Groups Unavailable for Formaldehyde - Methanol interaction pair

Unifac Groups Unavailable for Formaldehyde - FormicAcid interaction pair

Aij Interaction Parameters				
HOT KEYS	F1_Help	F2_Menu	S_Switch-Matrices	A_UnifacVLE
	H_Henry's Coeff	L_UnifacLLE	C_UnifacLLE	C_UnifacLLE
	I_j immiscible in i	B_all immiscible in i	H2O	
	Formaldehyde	Oxygen		
		-12.1627	-5.7036	
	Methanol	-12.1627	0.6257	
	Oxygen	1480.4229	2570.1833	
	H2O	62.9893	0.7643	
	Hydrogen	693.7556	2.6055	
	CO2	-3918.1270	-3094.8086	
	CO	1192.2665	-4.0521	
	FormicAcid	---	0.2458	
	Nitrogen	-124.3227	1518.7225	
	Argon	1356.6383	2893.7578	

Bij Interaction Parameters									
HOT KEYS	F1_Help	F2_Menu	S_Switch-Matrices						
	Formaldehyde	Oxygen	H2O						
		3.6612	---						
	Methanol	---	---						
	Oxygen	-0.0043	-0.0043						
	H2O	---	---						
	Hydrogen	-0.0010	-0.0009						
	CO2	0.0011	0.0011						
	CO	-0.0024	-0.0036						
	FormicAcid	---	3.6612						
	Nitrogen	-0.0037	-0.0037						
	Argon	-0.0039	-0.0039						

Aij Interaction Parameters									
HOT KEYS	F1_Help	F2_Menu	S_Switch-Matrices	A_UnifacVLE					
	H_Henry's Coeff	L_UnifacLLE	C_UnifacLLE	C_UnifacLLE	A_UnifacVLE				
	I_j immiscible in i	B_all immiscible in i							
		CO2	CO	FormicAcid					
		69.6759	-2.0741	---					
Formaldehyde	11.5578	69.6759	13.8729	0.0257					
Methanol	24.7952	69.6759	1792.9489	-0.7971					
Oxygen	---	---	---	1025.6306					
H2O	-6.5127	-183.6914	266.3600	-3727.8840					
Hydrogen	---	---	---	1542.3230					
CO2	---	---	---	---					
CO	---	---	---	---					
FormicAcid	11.5578	69.6759	-2.0741	---					
Nitrogen	---	---	---	339.0691					
Argon	---	---	---	1772.0728					

Bij Interaction Parameters									
HOT KEYS	F1_Help	F2_Menu	S_Switch-Matrices						
	Formaldehyde	CO2							
		-8.4077							
	Methanol	-1.9464	-8.4077						
	Oxygen	---	---						
	H2O	4.4304	39.0684						
	Hydrogen	---	---						
	CO2	---	---						
	CO	---	---						
	FormicAcid	-0.1687	-8.4077						
	Nitrogen	---	---						
	Argon	---	---						

Aij Interaction Parameters				
HOT KEYS	F1_Help	F2_Menu	S_Switch-Matrices	A_UnifacVLE
	H_Henry's Coeff	L_UnifacLLE	C_UnifacLLE	C_UnifacLLE
	I_j immiscible in i	B_all immiscible in i		
	Formaldehyde	CO2		
		69.6759		
	Methanol	24.7952	69.6759	
	Oxygen	---	---	
	H2O	-6.5127	-183.6914	
	Hydrogen	---	---	
	CO2	---	---	
	CO	---	---	
	FormicAcid	11.5578	69.6759	
	Nitrogen	---	---	
	Argon	---	---	

Bij Interaction Parameters									
HOT KEYS	F1_Help	F2_Menu	S_Switch-Matrices						
	Formaldehyde	CO2							
		-8.4077							
	Methanol	-1.9464	-8.4077						
	Oxygen	---	---						
	H2O	4.4304	39.0684						
	Hydrogen	---	---						
	CO2	---	---						
	CO	---	---						
	FormicAcid	-0.1687	-8.4077						
	Nitrogen	---	---						
	Argon	---	---						

NRTL, IDEAL (DEFAULT)

A:\DP_0080.SIM				
Aij Interaction Parameters				
HOT KEYS	F1_Help	F2_Menu	S_Switch-Matrices	A_UnifacVLE
	H_Henry's Coeff	L_UnifacLLE	C_UnifacLLE	All
I_j	immiscible in i	B_all	immiscible in i	
	Formaldehyde	Methanol	Oxygen	H2O
Formaldehyde	---	-2642.7380	---	321.3200
Methanol	-79.2009	---	---	610.4030
Oxygen	---	---	---	29.1896
H2O	-2806.8950	-48.6725	-80.3697	---
Hydrogen	---	2.6055	---	8.0175
CO2	---	---	---	676.2780
CO	---	-4.0521	---	-12385.0000
FormicAcid	---	---	---	-250.2830
Nitrogen	---	---	---	7.0546
Argon	---	---	---	33.2214

A:\DP_0080.SIM									
Bij Interaction Parameters									
HOT KEYS	F1_Help	F2_Menu	S_Switch-Matrices						
	Formaldehyde	Methanol	Oxygen	H2O					
Formaldehyde	---	---	---	---					
Methanol	---	---	---	---					
Oxygen	---	---	---	-0.0498					
H2O	---	---	19.3401	---					
Hydrogen	---	---	---	-0.0100					
CO2	---	-0.0009	---	-0.0977					
CO	---	-0.0036	---	---					
FormicAcid	---	---	---	---					
Nitrogen	---	---	---	-0.0004					
Argon	---	---	---	-0.0299					

A:\DP_0080.SIM									
NRTL Alpha(i,j) Interaction Parameter									
HOT KEYS		F1_Help	F2_Menu	S_Switch-Matrices	A_UnifacVLE				
		H_Henry's Coeff	L_UnifacLLE	C_UnifacLLE	A_UnifacVLE				
I_j		immiscible in i	B_all	immiscible in i	H2O				
		Formaldehyde	Methanol	Oxygen					
Formaldehyde	---	2.4335	---	---	1.4582				
Methanol	2.4335	---	---	---	0.3001				
Oxygen	---	---	---	---	---				
H2O	1.4582	0.3001	---	---	---				
Hydrogen	---	---	---	---	---				
CO2	---	---	---	---	---				
CO	---	---	---	---	---				
FormicAcid	---	---	---	---	4.3935				
Nitrogen	---	---	---	---	---				
Argon	---	---	---	---	---				

A:\DP_0080.SIM				
Aij Interaction Parameters				
HOT KEYS	F1_Help	F2_Menu	S_Switch-Matrices	A_UnifacVLE
	H_Henry's Coeff	L_UnifacVLE	C_UnifacVLE	A_UnifacVLE
I_j	immiscible in i	B_all	immiscible in i	
	Hydrogen	CO2	CO	FormicAcid
Formaldehyde	---	---	---	---
Methanol	24.7952	---	13.8729	---
Oxygen	---	---	---	---
H2O	-6.5127	-183.6914	266.3600	248.8916
Hydrogen	---	---	---	---
CO2	---	---	---	---
CO	---	---	---	---
FormicAcid	---	---	---	---
Nitrogen	---	---	---	---
Argon	---	---	---	---

A:\DP_0080.SIM									
Bij Interaction Parameters									
HOT KEYS	F1_Help	F2_Menu	S_Switch-Matrices						
	Formaldehyde	Methanol	Oxygen	H2O					
Formaldehyde	---	---	---	---					
Methanol	-1.9464	---	-0.0294	---					
Oxygen	---	---	---	---					
H2O	4.4304	39.0684	-36.7130	---					
Hydrogen	---	---	---	---					
CO2	---	---	---	---					
CO	---	---	---	---					
FormicAcid	---	---	---	---					
Nitrogen	---	---	---	---					
Argon	---	---	---	---					

A:\DP_0080.SIM				
NRTL Alpha(i,j) Interaction Parameter				
HOT KEYS	F1_Help	F2_Menu	S_Switch-Matrices	A_UnifacVLE
	H_Henry's Coeff	L_UnifacLLE	C_UnifacLLE	A_UnifacVLE
I_j	immiscible in i	B_all	immiscible in i	
	Hydrogen	CO2	CO	FormicAcid
	---	---	---	---
{Formaldehyde	---	---	---	---
{Methanol	---	---	---	---
{Oxygen	---	---	---	---
{H2O	---	---	---	4.3935
{Hydrogen	---	---	---	---
{CO2	---	---	---	---
{CO	---	---	---	---
{FormicAcid	---	---	---	---
{Nitrogen	---	---	---	---
{Argon	---	---	---	---

A:\DP_0080.SIM									
Parameters									
	Formaldehyde	Methanol	Oxygen	H2O					
Formaldehyde	---	---	---	---					
Methanol	---	---	---	---					
Oxygen	---	---	---	---					
H2O	---	---	---	---					
Hydrogen	---	---	---	---					
CO2	---	---	---	---					
CO	---	---	---	---					
FormicAcid	---	---	---	---					
Nitrogen	---	---	---	---					
Argon	---	---	---	---					

A:\DP_0080.SIM									
Parameters									
	Formaldehyde	Methanol	Oxygen	H2O					
Formaldehyde	---	---	---	---					
Methanol	---	---	---	---					
Oxygen	---	---	---	---					
H2O	---	---	---	---					
Hydrogen	---	---	---	---					
CO2	---	---	---	---					
CO	---	---	---	---					
FormicAcid	---	---	---	---					
Nitrogen	---	---	---	---					
Argon	---	---	---	---					

A:\DP_0080.SIM									
Parameters									
	Formaldehyde	Methanol	Oxygen	H2O					
Formaldehyde	---	---	---	---					
Methanol	---	---	---	---					
Oxygen	---	---	---	---					
H2O	---	---	---	---					
Hydrogen	---	---	---	---					
CO2	---	---	---	---					
CO	---	---	---	---					
FormicAcid	---	---	---	---					
Nitrogen	---	---	---	---					
Argon	---	---	---	---					

++----- Binary Interaction Parameters -----++

HYSIM displays all binary interaction parameters in the form of two corresponding matrices. Any blanks in the matrix correspond to a stored value of zero. Any element in the matrix may be overwritten by using the cursor to move to that position and either pressing <F2> for a menu or entering the number directly. There are also a series of Hot Keys available in the form.

If you are entering data the components across the top of the menu represent the "i" and the components down the side represent the "j".

		a(i,j)			
		1	2	3	4
j	i-->	ic4	nc4	ic5	nc5
	ic4	---	2,1	3,1	4,1
v	nc4	1,2	---	3,2	4,2
	ic5	1,3	2,3	---	4,3
	nc5	1,4	2,4	3,4	---

more

++----- Binary Interaction Parameters -----++

Each activity model, with the exception of NRTL and Chien-Null has two such matrices, you may use the "S" key to switch between the two. The second matrix corresponds to the bij matrix and is filled in exactly the same manner as the aij matrix. All of the activity models follow this format where

$$A_{ij} = a_{ij} + b_{ij} * T \quad (T = \text{temperature in Kelvin deg})$$

The NRTL model is different in that it contains a third matrix corresponding to the "alpha(i,j)" term. In this case "S" acts as a three way switch, pressing from the Bij matrix will give you the alpha matrix. The units of Aij are different for each activity model and are explained in their corresponding section. If Aijs are not available for all binary parameters you may use the various UNIFAC estimation methods. You have the choice of using the <F2> menu to regress a specific binary pair, or utilize the Hot Keys available in the form.

more

++----- Binary Interaction Parameters -----++

The LLE option is not available for the Wilson model since it is not capable of predicting three phase equilibria. HYSIM's implementation of the NRTL equation contains temperature dependent energy parameters as well as the alpha parameter. After selecting the NRTL equation, the second matrix accessed using the "S" command

is the $B(i,j)$ parameter matrix. Pressing the "S" key a second time will result in HYSIM displaying the $\text{Alpha}(i,j)$ matrix, it is important to note that $\text{Alpha}(i,j) = \text{Alpha}(j,i)$. In order to toggle back to the $A(i,j)$ matrix you must press the "S" key a third time. As with the other activity models, only the a_{ij} parameter is regressed, the α parameter is set equal to 0.3.

----- Paramater Estimation Using Unifac -----

HYSIM uses Unifac to generate A_{ijs} or energy parameters for all of the available activity models. Only A_{ij} and A_{ji} are regressed for each activity model, B_{ij} and B_{ji} are set to zero and the Alpha term for the NRTL is set equal to 0.3. Given a binary HYSIM, will calculate the Unifac activities at the two infinite dilution points, and three intermediate compositions, at a temperature of 298 K and 1 atm pressure. All of the library components in HYSIM carry Unifac structure information, any Hypothetical components should have these groups assigned if the Unifac option is being used. The calculated activities are then used in the internal regression routines to produce the A_{ijs} . There are two important things to note;

First, the parameters are regressed at atmospheric pressure, this will produce better results when using the ideal model for the vapour phase. Second, Unifac is a generalized method and is only going to produce approximate results $\pm (10 - 15 \%)$. The method will work quite well as long as the given binary components are NOT the primary constituents being separated in a fractionation system. **If no other source of A_{ij} data is available this option should be used as opposed to using zero for the energy parameters.**

Hot Keys

Wilson	UNIQUAC	NRTL	VanLaar
Margules	Chien-Null		
VanLaar two or four parameter VanLaar equation [$A_{ij} = a_{ij} + b_{ij} \cdot T$]			
Which activity model do you require			
>			



APPENDIX TO CHAPTER 6

SPECIFICATION OF EQUIPMENT ITEMS



CLIENT: CME4117

SHEET 1 of 2

PROJECT: SPECIFICATION OF ITEMS

DATE 22/09/1999

BY: DIV.

DESIGN OF: HX-6 : STAGE 3 RECIRCULATION COOLER

CHKD: DIV

①

DUTY
From worksheet "Abs'r" of spreadsheet *Detailed Design section.*
 $D_p\text{-eb-04.xls}$:

$$\begin{array}{r} \text{Energy of incoming fluid} = -16148.8 \\ -210.4 \\ -171101.7 \\ -12.7 \\ \hline -187473.6 \text{ kW} \end{array}$$

Similarly
Energy of outgoing fluid = -188061.1 kW

$$\rightarrow \Delta \dot{H} = 587.5 \text{ kW}$$

$$\Delta \dot{H} \doteq 590 \text{ kW}$$

②

TEMPERATURE DRIVING FORCE.

$$(\Delta T)_{lm} = 10^\circ\text{C}$$

$$\text{Perry}^{(6)} : S = \frac{t_2 - t_1}{T_1 - t_1} = \frac{41 - 30}{51 - 30} = \frac{11}{21} = 0.52$$

$$R = \frac{T_1 - T_2}{t_2 - t_1} = \frac{51 - 40}{41 - 30} = \frac{11}{11} = 1$$

$$(\Delta T)_{lm} = 10^\circ\text{C}$$

$$\Rightarrow F_T \doteq 0.8 \rightarrow \text{OKAY ?}$$

$\hookrightarrow$ better : $F_T = 1$ (one tube pass).
two tube passes.

$$F_T = 1$$

③

AREA

$$\Delta \dot{H} = UA(\Delta T)_{lm} \cdot F_T$$

From Sinnott⁽¹⁾ take $U \approx 800 \text{ W.m}^{-2}.\text{K}^{-1}$
aqueous solution

$$\rightarrow A = \frac{587.5}{73.4} \text{ m}^2 \rightarrow \text{OKAY.}$$

$$A \doteq \frac{102}{75} \text{ m}^2$$

④

BRANCH NOMINAL SIZES

$$\text{Process : } \dot{V}_p = (13.830 \text{ kg.s}^{-1}) \div (1050 \text{ kg.m}^{-3}) = 0.0132 \text{ m}^3.\text{s}^{-1}$$

$$\text{Take } v \leq 1 \text{ m.s}^{-1} \Rightarrow A_p \geq \frac{0.00659}{0.0168} \text{ m}^2$$

$$\Rightarrow D_p \geq \frac{0.092}{0.130} \text{ m} = \frac{92}{130} \text{ mm} \rightarrow \text{Take } D_p = \frac{102}{102} \text{ mm} \text{ [Perry}^{(6)}]$$

$$D_p = \frac{102}{102} \text{ mm}$$

$$\text{Utility : } \dot{m}_u = \frac{\Delta \dot{H}}{c_{p,u} \Delta T_u} = \frac{587.5 \text{ kW}}{(4.18)(11) \text{ kJ.kg}^{-1}.\text{K}^{-1}.\text{K}} = 12.8 \text{ kg.s}^{-1}$$

$$\dot{m}_u = 12.8 \text{ kg.s}^{-1}$$

$$\therefore \dot{V}_u \approx 0.0128 \text{ m}^3.\text{s}^{-1} \Rightarrow A_u \geq \frac{0.0064}{0.0168} \text{ m}^2 \text{ (} v \leq 1 \text{ m.s}^{-1} \text{)}$$

$$\Rightarrow D_u \geq \frac{0.090}{0.090} \text{ m} \rightarrow \text{Take } D_u = \frac{102}{102} \text{ mm}$$

$$D_u = \frac{102}{102} \text{ mm}$$

⑤

PRESSURE

As the exchanger is at the base of the tall column, pressure will be affected.

Nominal operating pressure for stage 3 = 124 kPa(abs) at the top, 126 kPa(abs) at the bottom.

The height above the exchanger : 11.6 m (bottom)
14.1 m (top)

$$\Delta H \approx 14.1 \text{ m}$$

With $\rho_c = 995 \text{ kg m}^{-3}$ & $g = 9.78 \text{ m s}^{-2}$ [Ciancioli⁽²⁾]

$$\Rightarrow \Delta p = (995)(9.78)(14.1) = 137 \times 10^3 \text{ Pa (abs)}$$

$$\Rightarrow P_{\text{exiting HX-6}} \geq 137 + 124 = 261 \text{ Pa (abs)}$$

$$P_{\text{exit}} \approx 265 \text{ kPa (abs)}$$

$$\Rightarrow \text{Take } 265 \text{ kPa (abs)} \quad [\text{consider nozzles, 'tortuosity', ...}]$$

$$\hookrightarrow \text{for } (-\Delta p) \text{ across the exchange} = 40 \text{ kPa (abs)} \quad [\text{Sinnott}^{(2)}]$$

$$P_{\text{in}} \approx 305 \text{ kPa (abs)}$$

$$P_{\text{in}} = 305 \text{ kPa (abs)}$$

⑥

DESIGN VALUES

Sinnott⁽²⁾ recommends adding 5 to 10% to pressure:

$$\text{take } P_{\text{DESIGN}} = 450 \text{ kPa (abs)}$$

$$P_{\text{DESIGN}} = 450 \text{ kPa (abs)}$$

$$\text{Take } T_{\text{DESIGN}} = 150^\circ\text{C}$$

$$T_{\text{DESIGN}} = 150^\circ\text{C}$$



CLIENT: CHEM7

PROJECT: SPECIFICATION OF ITEMS

DESIGN OF: HX-7 : STAGE 2 RECIRCULATION COOLER

SHEET L of 1

DATE 22/09/1999

BY DIV

CHECKED DIV

- ① NOTE
See specification of HX-6 for method.
- ② DUTY

$$\Delta H = (+525189.8) - (+522840.7) = 2349 \text{ kW}$$

$$\Delta H = 2349 \text{ kW}$$
- ③ TEMPERATURE DRIVING FORCE

$$(\Delta T)_{LM} = 18^\circ\text{C}$$

$$S = \frac{45-30}{63-30} = \frac{15}{33} = 0.45, R = \frac{63-48}{45-30} = \frac{15}{15} = 1.00$$

$$\Rightarrow F_T = 0.88$$

for 2 tube passes (or 4, ...) $\Rightarrow$ CHOOSE THIS.

$$(\Delta T)_{LM} = 18^\circ\text{C}$$

$$F_T = 0.88$$
- ④ AREA

$$A = \frac{2349 \times 10^3}{700 \times 0.88 \times 18} = \frac{2349 \times 10^3}{11220} = 212 \text{ m}^2 \Rightarrow \text{OKAY (Grassie)}$$

$$A = \frac{2349 \times 10^3}{210} = 11185 \text{ m}^2$$
- ⑤ BRANCHES
 Process: $\dot{V}_p = (41.2 \text{ kg} \cdot \text{s}^{-1}) \div (1100 \text{ kg} \cdot \text{m}^{-3}) = 0.037 \text{ m}^3 \cdot \text{s}^{-1}$
 Then for $v \leq 2 \text{ m} \cdot \text{s}^{-1}$
 $\Rightarrow D_p \geq \frac{0.037}{0.153} \text{ m} \Rightarrow \text{take } D_p = \frac{178}{229} \text{ mm}$
 Utility: $\dot{m}_u = \frac{\Delta H}{c_p \Delta T_u} = \frac{2349}{(4.18)(15)} = 37.5 \text{ kg} \cdot \text{s}^{-1} \Rightarrow \dot{V}_u = 0.0375 \text{ m}^3 \cdot \text{s}^{-1}$
 $\therefore v \leq 2 \text{ m} \cdot \text{s}^{-1} \Rightarrow D_u \geq \frac{0.0375}{0.153} \text{ m} \Rightarrow D_u = \frac{178}{229} \text{ mm}$

$$\dot{m}_u = 37.5 \text{ kg} \cdot \text{s}^{-1}$$

$$D_u = \frac{178}{229} \text{ mm}$$
- ⑥ PRESSURE

$$\Delta p = \rho g \Delta H = (1100)(9.78)(10.1) = 108.7 \text{ kPa}$$

$$\Rightarrow p_{\text{exit}} \approx 109 + 126 = 235 \text{ kPa} \rightarrow \sim 240 \text{ kPa (abs)}$$

$$\therefore p_{\text{in}} = 240 + 40 = 280 \text{ kPa (abs)}$$

$$p_{\text{exit}} = 240 \text{ kPa (abs)}$$

$$p_{\text{in}} = 280 \text{ kPa (abs)}$$
- ⑦ DESIGN VALUES

$$p_{\text{DESIGN}} \approx 450 \text{ kPa (abs)}$$

$$T_{\text{DESIGN}} = 150^\circ\text{C}$$

$$p_{\text{DESIGN}} = 450 \text{ kPa (abs)}$$

$$T_{\text{DESIGN}} = 150^\circ\text{C}$$



CLIENT: CHE4117

PROJECT: SPECIFICATION OF ITEMS

DESIGN OF: HX-8 : STAGE 1 RECIRCULATION COOLER

SHEET 1 of 1

DATE 23/09/1999

BY DJV

CHKD:

①

NOTE
See specification of HX-6 for method

②

DUTY
 $\Delta \dot{H} = (-298663.8) - (-300284.5) = 1620.7 \text{ kW}$

$\Delta H \approx 1621 \text{ kW}$

③

TEMPERATURE DRIVING FORCE

$(\Delta T)_{LM} = 30^\circ\text{C}$

$(\Delta T)_{LM} = 30^\circ\text{C}$

Alternatively, for co-current exchange: $(\Delta T)_{LM,cc} = \frac{(75-30) - (60-45)}{\ln\left(\frac{45}{15}\right)}$

$\therefore (\Delta T)_{LM,cc} = 27.3^\circ\text{C}$

$\rightarrow$ equivalent to $F_T = \frac{27.3}{30} = 0.91 \rightarrow \text{okay}$

Compare: $S = \frac{45-30}{75-30} = \frac{15}{45} = 0.33$, $R = 1.00$

$\rightarrow$ For a 1-2 exchanger, $Perry^{(6)}$ says $F_T \approx 0.96$

Counter-current $\Rightarrow T_{WALL,MIN} \approx \frac{60+30}{2} = 45^\circ\text{C}$

$\rightarrow$ too low for 54% HCHO (by mass) [Kirk-Othmer⁽⁴⁾]

Co-current: $T_{WALL,MIN} \approx \frac{60+45}{2} = 52.5^\circ\text{C}$

$\rightarrow$ better!

$\Rightarrow$ CHOOSE CO-CURRENT ARRANGEMENT.

Recall $(\Delta T)_{LM} = 30^\circ\text{C}$, $F_T = 0.91$

$F_T = 0.91$

④

AREA
 $A = \frac{1621 \times 10^3}{600 \times 27.3} = 98.96 \text{ m}^2$

$A = 100 \text{ m}^2$

⑤

BRANCHES

Process: $\dot{V}_p = (24.7 \text{ kg.s}^{-1}) \div (1150 \text{ kg.m}^{-3}) = 0.0215 \text{ m}^3.\text{s}^{-1}$
 $V \leq 2 \text{ m.s}^{-1} \Rightarrow D_p \geq 128 \text{ mm}$ Take $D_p = 152 \text{ mm}$

$D_p = 152 \text{ mm}$

Utility: $\dot{m}_u = \frac{1621 \text{ kW}}{(4.18 \times 15)} = 25.9 \text{ kg.s}^{-1} \rightarrow \dot{V}_u \approx 0.0259 \text{ m}^3.\text{s}^{-1}$

$\dot{m}_u = 25.9 \text{ kg.s}^{-1}$

$\therefore V \leq 2 \text{ m.s}^{-1} \Rightarrow D_u \geq 128 \text{ mm} \Rightarrow D_u = 152 \text{ mm}$

$D_u = 152 \text{ mm}$

⑥

PRESSURE

$\Delta p = \rho g h \approx (1150 \text{ kg.m}^{-3}) \times (9.78 \text{ m.s}^{-2}) \times (6.4 \text{ m}) = 72 \text{ kPa}$

$\Rightarrow p_{EXT} \approx 72 + 128 = 200 \text{ kPa (abs)}$

$\therefore p_{IN} \equiv p_{EXT} + 40 = 240 \text{ kPa (abs)}$

$p_{EXT} = 200 \text{ kPa (abs)}$
 $p_{IN} = 240 \text{ kPa (abs)}$

⑦

DESIGN VALUES

Take $p_{DESIGN} = 450 \text{ kPa (abs)}$, as before, but increase T_{DESIGN} to 170°C to cope with absorber feed cooler failure

$p_{DESIGN} = 450 \text{ kPa (abs)}$

$T_{DESIGN} = 170^\circ\text{C}$



CLIENT: CHE4117

PROJECT: SPECIFICATION OF ITEMS

DESIGN OF: HX-11: SERPENTINE COOLING COILS

SHEET 1 of 1.

DATE 01/10/1999

BY DIV

CHKD DIV.

①

DUTY

From the specification of P-8, $\dot{M}_H = 153 \text{ kW}$

②

TEMPERATURE

$(\Delta T)_{\min} = 7^\circ\text{C}$ — minimum

$\begin{matrix} 42 \\ 37 \\ 30 \end{matrix}$

$\dot{M}_H = 153 \text{ kW}$

$\Delta T_{\min} = 7^\circ\text{C}$

Counter-current flow can be assumed.

③

AREA

$$A = \frac{153 \times 10^3}{1000 \times 7} = 21.8 \text{ m}^2$$

$A = 21.8 \text{ m}^2$

where $U = 1000 \text{ W.m}^{-2}.\text{K}^{-1}$, after Sinnott⁽²⁾, due to the vigorous agitation, and water on both sides (essentially).

→ If the coil is one inch in diameter (outer)

→ circumference = 79.8 mm

→ Total length = 273 m

Total length = 273 m

At 21 trays, length = 13 m per tray.

Length = 13 m per tray.

④

PRESSURE

See P-8

$P_{\text{in}} = 143 \text{ kPa (abs)}$ } minimum (at top)

$P_{\text{out}} = 103 \text{ kPa (abs)}$

$P_{\text{in}} = 143 \text{ kPa (abs)}$

$P_{\text{out}} = 103 \text{ kPa (abs)}$

There is room for 254 mm coil between trays, with room for 8 lengths of tubing of various lengths on either side of the baffle.

Recall: column diameter = 1.8 m .

①

NOTE:

Refer also to specification of HX-8

②

VOLUMETRIC FLOWRATE

$$\dot{m} = 29.7 \text{ kg} \cdot \text{s}^{-1}, \quad \rho = 1150 \text{ kg} \cdot \text{m}^{-3}$$

$$\Rightarrow \dot{V} = 29.8 \div 1150 \times 3600 = 93.3 \text{ m}^3 \cdot \text{h}^{-1}$$

$$\dot{V} = 93 \text{ m}^3 \cdot \text{h}^{-1}$$

④

PUMP MODEL

From CHE3108, two models cope with $\dot{V} \geq 100 \text{ m}^3 \cdot \text{h}^{-1}$

Take the smaller, with higher efficiency, η : DR-816 (Warrington)

Model = DR-816

⑤

POWER

From the manufacturers graph, taking $\phi = 168 \text{ mm}$

$$\phi = 168 \text{ mm}$$

$$\Rightarrow \eta = 67\%, \quad \text{Power} = 14 \text{ BHP} = 10.4 \text{ kW}$$

$$\text{Alternatively: Power} = \Delta p \cdot \dot{V} = (40 \text{ kPa}) \times (0.0259 \text{ m}^3 \cdot \text{s}^{-1}) = 1036 \text{ W}$$

③

HEAD

$$\text{Total delivered head} = \frac{40 \times 10^3 \text{ Pa}}{(9.78 \text{ m}^3 \cdot \text{s}^{-1}) \times (1150 \text{ kg} \cdot \text{m}^{-3})} = 3.56 \text{ m}$$

$$\text{TDM} = 3.56 \text{ m}$$

Whereas the selected pump delivers $\approx 25 \text{ m}$ of head (hence the extra power).

$P_{\text{req}}^{(b)}$ indicates that the combination of TDM and $\dot{V}$ given here is suitable for a single-stage centrifugal pump.

However, there is concern that pumps capable of handling the relatively large $\dot{V}$ are often designed with a relatively large TDM (design), which must then be let down through a valve while still consuming the higher power.

$\Rightarrow$ "Arbitrarily" take $\eta = 0.5$ [Else typically $\approx 80\%$ - Sinnott⁽¹⁾]

$$\Rightarrow \text{Power} = \frac{1.036 \text{ kW}}{0.5} = 2.07 \text{ kW}$$

$$\eta_p = 50\%$$

$$\text{Power}_p = 2.07 \text{ kW (required)}$$

⑥

MOTOR

From Siemens 1990 catalogue [CHE408], typical drive efficiency is 80%.

Take motor power (round up) as 3 kW.

$$\eta_m = 80\% \\ \text{Power}_m = 3 \text{ kW}$$

⑦

As the section is under gravity flow, take $V_s \leq 1 \text{ m} \cdot \text{s}^{-1}$ here.

$$\therefore A \geq 0.0259 \text{ m}^2 \Rightarrow D_s \geq 181 \text{ mm} \Rightarrow \text{take } D_s = 203 \text{ mm}$$

$$D_s = 203 \text{ mm}$$



CLIENT: CHECHIT

PROJECT: SPECIFICATION OF ITEMS

DESIGN OF: P-6 : STAGE 2 RECIRCULATION PUMP.

SHEET 1 of 1

DATE 24/09/1999

BY DIV

CHKD.

①

NOTE

Refer to specifications of P-4A & HX-7

②

VOLUMETRIC FLOWRATE

$$\dot{m} = 41.2 \text{ kg.s}^{-1} \rightarrow \dot{V} = \frac{41.2}{1100} = 0.0375 \text{ m}^3.\text{s}^{-1}$$

$$\dot{V} = 135 \text{ m}^3.\text{h}^{-1}$$

③

HEAD

$$TDH = \frac{40 \times 10^3}{(9.78)(1100)} = 3.718 \text{ m}$$

$$TDH = 3.72 \text{ m}$$

④

POWER

$$Power = \frac{\Delta p \cdot \dot{V}}{\eta} = \frac{(40 \times 10^3)(0.0375)}{0.5} = 3000 \text{ W}$$

$$Power_p = 3.0 \text{ kW (req'd)}$$

⑤

MOTOR

$$\eta_m = 80\%$$

$$\text{Take } Power_m = 4.5 \text{ kW}$$

$$\eta_m = 80\%$$

$$Power_m = 4.5 \text{ kW}$$

⑥

BRANCH

$$A_s \geq 0.0375 \text{ m}^2 \Rightarrow D_s \geq 218 \text{ mm} \Rightarrow D_s = 229 \text{ mm}$$

$$D_s = 229 \text{ mm}$$



CLIENT: CHEM117

PROJECT: SPECIFICATION OF ITEMS

DESIGN OF: P-7 : STAGE 3 RECIRCULATION PUMP

SHEET 1 of 1

DATE 24/09/1999

BY DIV

CHKD

①

NOTE
Refer to specification of HX-6 and P-6.

②

VOLUMETRIC FLOWRATE

$$\dot{m} = 13.7 \text{ kg.s}^{-1} \Rightarrow \dot{V} = \frac{13.7}{1050} = 0.0130 \text{ m}^3.\text{s}^{-1}$$

$$\dot{V} = 47 \text{ m}^3.\text{h}^{-1}$$

③

HEAD

$$\text{TDH} = \frac{40 \times 10^3}{(9.78)(1050)} = 3.90 \text{ m}$$

$$\text{TDH} = 3.90 \text{ m}$$

④

POWER

$$\text{Power} = \frac{\Delta p \cdot \dot{V}}{\eta} = \frac{(40 \times 10^3)(0.0130)}{0.50} = 1040 \text{ W}$$

$$\text{Power}_p = 1.04 \text{ kW}$$

⑤

MOTOR

$$\eta_m = 80\%$$

$$\text{Take Power}_m = 1.5 \text{ kW}$$

$$\eta_m = 80\% \\ \text{Power}_m = 1.5 \text{ kW}$$

⑥

BRANCH

$$V \leq 1 \text{ m.s}^{-1} \Rightarrow A_s \geq 0.0130 \text{ m}^2 \Rightarrow D_s \geq 129 \text{ mm} \Rightarrow D_s = 152 \text{ mm}$$

$$D_s = 152 \text{ mm}$$

①

PRESSURE DROP:

Assume a pressure drop of 40 kPa due to valves and frictional losses, etc. — both in the coils and in the pipework to and from the coils.

Suppose the exit pressure at the base of the column is $\geq 150 \text{ kPa (abs)}$, to get back to the cooling tower.

The top coil is at a height of $33.57 + 15 \approx 35 \text{ m}$
[See Detailed Design of Absorber]

$$\Rightarrow (\Delta p)_{\text{static}} = (35 \text{ m})(9.78 \text{ m/s}^2)(1000 \text{ kg/m}^3) = 342 \text{ kPa}$$

$$\Rightarrow \text{Exit pressure requirement satisfied.}$$

Thus, to exit the coil, the water undergoes a $(-\Delta p)$ of $\approx 382 \text{ kPa}$

However the water is "only" supplied at 400 kPa (abs), and at no time must the water in the tubes be at a pressure lower than 101 kPa (abs)

$$\Rightarrow \text{Inlet } p \text{ at base of column (after pump)} \Rightarrow \overset{523}{483} \text{ kPa (abs)}$$

$$\text{Take Inlet } p = \overset{525}{485} \text{ kPa (abs)}$$

$$\therefore p_{\text{in}} = 400 \text{ kPa (abs)}, p_{\text{out}} = \overset{525}{485} \text{ kPa (abs)} \text{ w.r.t. P-8}$$

$$p_{\text{in}} = 400 \text{ kPa (abs)}$$

$$p_{\text{out}} = \overset{525}{485} \text{ kPa (abs)}$$

②

TEMPERATURE
 $T = 30^\circ \text{C}$ (assumed const.) for RCW.

$$T = 30^\circ \text{C}$$

③

FLOW
From the Detailed Design of the Absorber, $\dot{A}H = 153.0 \text{ kW}$

$$\Rightarrow \dot{m} = \frac{153.0}{(4.18)(35-30)} = 7.32 \text{ kg/s}$$

$$\therefore \dot{V} = 0.0073 \text{ m}^3/\text{s}$$

$$\dot{A}H = 153.0 \text{ kW (HX-11)}$$

$$\dot{m} = 7.32 \text{ kg/s}$$

$$\dot{V} = 26.4 \text{ m}^3/\text{h}$$

④

$$\text{HEAD}$$

$$\text{TDH} = \frac{\overset{125}{85} \times 10^3}{(1000)(9.78)} = \overset{12.78}{8.69} \text{ m}$$

$$\text{TDH} = \overset{12.78}{8.69} \text{ m}$$

⑤

$$\text{POWER}$$

$$\text{Power} = \dot{V} \cdot \Delta p = \overset{913}{622} \text{ W}$$

From Sinnott², $\eta \approx 70\%$

$$\therefore \text{Power}_p = \frac{1304}{0.7} = \overset{1891}{889} \text{ W}$$

$$\eta \approx 70\%$$

$$\text{Power}_p = \frac{1.30}{0.7} \text{ kW}$$



CLIENT: CHEY/17

SHEET 2 of 2

PROJECT: SPECIFICATION OF ITEMS

DATE 24/09/1999

BY DJV

DESIGN OF: P-8: STAGE 4 COASTAL PUMP

CHKD DJV

- ⑥ Motor Taking $\eta_m = 80\%$
 $\Rightarrow$ say Power_m = $\frac{2.0}{0.8} \text{ kW}$
- ⑦ BRANCHES.
- Suction: Take $V \leq 1.5 \text{ m/s}$
 $\Rightarrow D_s \geq 79 \text{ mm} \Rightarrow D_s = 102 \text{ mm}$
- Delivery: Take $V \leq 2.0 \text{ m/s}$
 $\Rightarrow D_o \geq 68 \text{ mm} \Rightarrow D_o = 76 \text{ mm}$
- $\eta_m = 80\%$
 Power_m = $\frac{1.5 \text{ kW}}{0.8}$
- $D_s = 102 \text{ mm}$
- $D_o = 76 \text{ mm}$



CLIENT: CHE4117

PROJECT: SPECIFICATION OF ITEMS

DESIGN OF: P-10: Absorber water pump.

SHEET 1

DATE: 24/09/1999

BY: JIV

CHECKED:

- ① NOTES
Refer also to specification of P-8
- ② NUMERICAL FLOWRATE
 $\dot{m} = 0.3275 \text{ kg.s}^{-1}$
 $\therefore \dot{V} = 0.00033 \text{ m}^3.\text{s}^{-1}$
- ③ HEAD
 If $\Delta p = 382 \text{ kPa}$ as for P-8, and the column pressure is 110 kPa (abs)
 $\Rightarrow$ Pressure at base of column $= 495 \text{ kPa (abs)}$
 cf. $p_{in} = 400 \text{ kPa (abs)}$

$$TDH = \frac{95 \times 10^3}{(1000)(9.78)} = 9.71 \text{ m}$$
- ④ POWER

$$\text{Power}_p = \frac{(95 \times 10^3)(0.000328)}{\eta_p} = 51.9 \text{ W}$$
 for $\eta_p = 0.60$ [Sinnott⁽¹³⁾]
- ⑤ MOTOR
 $\eta_m = 80\%$
 Take $\text{Power}_m = 0.10 \text{ kW}$ — small motors not in a great range of sizes
 $\rightarrow$ Note: this is small enough for flange mounting.
- ⑥ BRANCHES
 Suction: Take $v \leq 1.5 \text{ m.s}^{-1}$
 $\rightarrow D_s \geq 16.7 \text{ mm} \Rightarrow D_s = 19 \text{ mm} (\frac{3}{4} \text{")}$
- Delivery: Take $v \leq 2 \text{ m.s}^{-1}$
 $\Rightarrow D_D \geq 14.4 \text{ mm} \Rightarrow D_D = 19 \text{ mm} (\frac{3}{4} \text{")}$

$$\dot{m} = 0.3275 \text{ kg.s}^{-1}$$

$$\dot{V} = 1.18 \text{ m}^3.\text{h}^{-1}$$

$$p_{out} = 495 \text{ kPa (abs)}$$

$$p_{in} = 400 \text{ kPa (abs)}$$

$$TDH = 9.71 \text{ m}$$

$$\text{Power}_p = 52 \text{ W}$$

$$\eta_p = 60\%$$

$$\eta_m = 80\%$$

$$\text{Power}_m = 0.10 \text{ kW}$$

$$D_s = 19 \text{ mm}$$

$$D_D = 19 \text{ mm}$$



APPENDIX TO CHAPTER 7

PART 1: VAPOUR—LIQUID EQUILIBRIA

Vapour pressures over solutions, by the van Laar equation(s)

From R, P & $P^{(i)}$, Chapter 8, Table 8-3

$$g^E = A_{12}x_1x_2 / \{x_1(A_{1B}) + x_2\}$$

$$R.T \ln(\gamma_i) = A_{12} \{1 + (A_{1B})/x_1\}^2$$

$$R.T \ln(\gamma_2) = B_{12} \{1 + (B_{1A})/x_2\}^2$$

For the binary system methanol(1)-water(2):

From HYSIM:

$a_{12} =$	0.7643	$b_{12} =$	0
$a_{21} =$	0.6257	$b_{21} =$	0

$$T [^{\circ}\text{C}] = \boxed{60} \quad \therefore T [\text{K}] = 333.15$$

hence: $A_{12} = 0.7643 = A ?$
 $A_{21} = 0.6257 = B ?$

By estimation from *typical* activity coefficients at infinite dilution:
 (From R, P & $P^{(i)}$, Chapter 8, Table 8-17)

Note: species (1) is the solute, at infinite dilution

For n -primary alcohols(1)-water(2):

$T [^{\circ}\text{C}]$	α	ε	ζ	η	θ	Equation
25	-0.995	0.622	0.558	...	0	(a)
60	-0.755	0.583	0.460	...	0	(a)
100	-0.420	0.517	0.230	...	0	(a)

Equations:

$$\log(\gamma_1^{\infty}) = \alpha + \varepsilon N_1 + \zeta/N_1 + \theta/N_2$$

where N_i is the number of carbon atoms in molecule i

$$N_1 = \boxed{1} \quad N_2 = \boxed{0}$$

where A and B may be found by observing that for the van Laar equation:

$$\text{for } x_1 \rightarrow 0 \quad R.T \ln(\gamma_1^{\infty}) = A$$

$$\text{for } x_2 \rightarrow 0 \quad R.T \ln(\gamma_2^{\infty}) = B$$

$$\text{where } R = 8.31451 \text{ J.mol}^{-1} \cdot \text{K}^{-1}$$

For water(1)- n -primary alcohols(2):

$T [^{\circ}\text{C}]$	α	ε	ζ	η	θ	Equation
25	0.760	0	0	...	-0.630	(a)
60	0.680	0	0	...	-0.440	(a)
100	0.617	0	0	...	-0.280	(a)

where N_i is the number of carbon atoms in molecule i

$$N_1 = \boxed{0} \quad N_2 = \boxed{1}$$

NOTE: DECHEMA Chemistry Data Series, Vol. 1, Part 1b (VLE Aq systems, Supp 2) gives:

$$A_{12} = 0.8509 \quad \gamma_1^{\infty} = 2.34$$

$$A_{21} = 0.5291 \quad \gamma_2^{\infty} = 1.70$$

Where these have been correlated for atmospheric pressure (101.325 kPa(abs)).

It is to be assumed that the constants listed here are $A/(R.T)$ and $B/(R.T)$, respectively.

Thus: at 60°C:

$$A_{12} \Rightarrow 2356.975 = A \quad \gamma_1^{\infty} \Rightarrow 2354.9 = A$$

$$A_{21} \Rightarrow 1465.596 = B \quad \gamma_2^{\infty} \Rightarrow 1469.829 = B$$

$$\gamma_1^{\infty}$$

1.531087	$\Rightarrow$	1055.988
1.940886	$\Rightarrow$	1836.896
2.123244	$\Rightarrow$	2336.058

$$\therefore A = T[\text{K}] \times 16.95899 = 3935.17$$

$$\gamma_1^{\infty}$$

1.348963	$\Rightarrow$	742.0455
1.737801	$\Rightarrow$	1530.747
2.172701	$\Rightarrow$	2407.497

$$\therefore B = T[\text{K}] \times 22.19922 = 5972.57$$

Plotting VLE data based on these parameters:

methanol(1)-water(2), T[C] = 60
∴ T [K] = 333.15
From Antoine data, at 60°C:
 $p_{\text{vap},1} \text{ [kPa(aus)]} = 84.65408$
 $p_{\text{vap},2} \text{ [kPa(aus)]} = 19.94065$
 $p_1 + p_2 = y_1 P + y_2 P = P = y_1 x_1 p_{\text{vap},1} + y_2 x_2 p_{\text{vap},2}$
Total pressure = 104.59473 kPa(aus)

x_1	x_2	y_1	y_2	p_1 [kPa(a)]	p_2 [kPa(a)]	P [kPa(a)]
0.001	0.999	1.937802	1.000001	0.164043	19.92073	20.08477
0.05	0.95	1.798037	1.001952	7.610557	18.9806	26.59116
0.1	0.9	1.675797	1.007678	14.18631	18.08438	32.27069
0.2	0.8	1.48052	1.029867	25.06641	16.42897	41.49538
0.3	0.7	1.335354	1.065817	33.91294	14.87715	48.79009
0.4	0.6	1.227125	1.11534	41.55246	13.34437	54.89683
0.5	0.5	1.146843	1.178705	48.54249	11.75207	60.29455
0.6	0.4	1.088265	1.256561	55.27565	10.02266	65.29831
0.7	0.3	1.046995	1.34991	62.04268	8.075424	70.1181
0.8	0.2	1.019909	1.460077	69.07153	5.822977	74.89451
0.9	0.1	1.004774	1.588714	76.55239	3.167999	79.72039
0.999	0.001	1	1.736201	84.56946	0.034621	84.60408

Experimental data from Perry⁽⁶⁾, p. 3-73 (Table 3-26)

Note: Evaluated at 59.4°C

x_1	p_1 [mmHg]	p_2 [mmHg]	P [kPa(a)]	y_1
0.0000	0	145.4	19.38507	0
0.2217	210.1	106.9	42.26319	0.662776
0.2740	240.2	102.2	45.64958	0.701519
0.3324	272.1	96.6	49.15596	0.737998
0.3980	301.9	91.7	52.47568	0.767022
0.4708	335.6	84.8	56.04872	0.798287
0.555	373.7	76.9	60.07506	0.829339
0.692	439.4	57.8	66.28788	0.883749
0.785	486.6	43.8	70.71418	0.917421
0.859	526.9	30.1	74.26056	0.945961
1.000	609.3	0	81.23332	1

Note also the error in the original: they actually quote mole PERCENT

For the binary system formaldehyde(1)-water(2):

From HYSIM:
 $a_{12} = 62.9893$
 $b_{21} = -5.7036$
 $b_{12} = 0$
 $b_{21} = 0$

$T \text{ [°C]} = 60 \therefore T \text{ [K]} = 333.15$

hence: $A_{12} = 62.9893 = A ?$
 $A_{21} = -5.7036 = B ?$

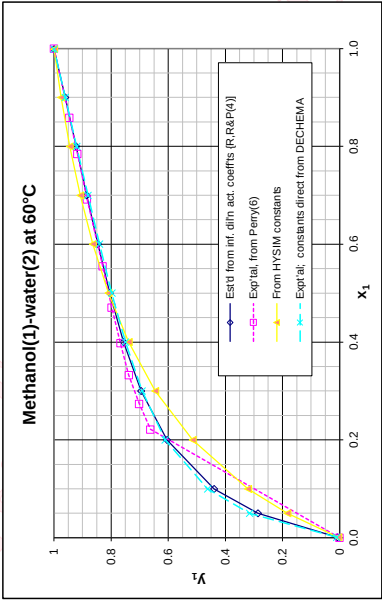
By estimation from typical activity coefficients at infinite dilution:
(From R, P & P⁽⁶⁾, Chapter 8, Table 8-17)

Note: species (1) is the solute, at infinite dilution

For n-aldehydes(1)-water(2):

T [°C]	α	ε	ζ	η	θ	Equation
25	-0.780	0.622	0.320	...	0	(a)
60	-0.400	0.583	0.210	...	0	(a)
100	-0.03	0.517	0	...	0	(a)

γ_1^∞
 $1.452112 \Rightarrow$
 $2.471724 \Rightarrow$
 $3.069022 \Rightarrow$
A
 924.7028
 2506.598
 3479.083



***Note: SAME AS previous

Equations:

(a) $\log(\gamma_1^*) = \alpha + \varepsilon N_1 + \zeta/N_1 + \theta/N_2$

where N_i is the number of carbon atoms in molecule i

$N_1 = \frac{1}{0}$ $N_2 = \frac{0}{0}$

where A and B may be found by observing that for the van Laar equation:

for $x_1 \rightarrow 0$ $R.T.\ln(g_1^*) = A$

for $x_2 \rightarrow 0$ $R.T.\ln(g_2^*) = B$

where $R = 8.31451 \text{ J.mol}^{-1}.\text{K}^{-1}$

This may be COMPARED with the case for a hypothetical single-carbon ketone:

For n -ketones(1)-water(2):

T [°C]	α	ε	ζ	η	θ	Equation
25	-1.475	0.622	0.500	0	...	(b)
60	-1.040	0.583	0.330	0	...	(b)
100	-0.621	0.517	0.200	0	...	(b)

***Note: SAME AS previous

Equations:

(b) $\log(\gamma_1^*) = \alpha + \varepsilon N_1 + \zeta(1/N_1 + 1/N_2) + \eta(N_1 - N_2)^2$

where N_i is the number of carbon atoms in molecule i

$N_1 = \frac{1}{1}$ $N_2 = \frac{0}{0}$

N' , N'' are the number of carbon atoms in respective branches of branched compounds, INCLUDING the "polar grouping."

Thus $N_1 = \frac{1}{1}$ $N'' = \frac{1}{1}$

We observe that this approximation was acceptable for the lowest temperature (25°C), but quite inaccurate for larger deviations from ideality.

For water(1)- n -ketones(2):

T [°C]	α	ε	ζ	η	θ	Equation
25	1.857	0	0	...	-1.019	(c)
60	1.493	0	0	...	-0.73	(c)
100	1.231	0	0	...	-0.557	(c)

Equations:

(c) $\log(\gamma_1^*) = \alpha + \varepsilon N_1 + \zeta(1/N_1 + 1/N_2 + 1/N'') + \theta(1/N_2 + 1/N'')$

where N_i is the number of carbon atoms in molecule i

$N_1 = \frac{0}{0}$ $N_2 = \frac{1}{1}$

N' , N'' are the number of carbon atoms in respective branches of branched compounds, INCLUDING the "polar grouping."

Thus $N_1 = \frac{0}{0}$ $N'' = \frac{0}{0}$

Plotting VLE data based on these parameters:

formaldehyde(1)-water(2), T = 60 °C

$\therefore T [K] = 333.15$

From Antoine data, at 60°C:

$p_{\text{sat},1} [\text{kPa(ats)}] = 1403.154$ $p_{\text{sat},2} [\text{kPa(abs)}] = 19.94065$

$p_1 + p_2 = y_1 P + y_2 P = P = y_1 x_1 p_{\text{sat},1} + y_2 x_2 p_{\text{sat},2}$

$\frac{p_1}{p_1 + p_2} = \frac{y_1 p_1}{P} = \frac{y_1 x_1 p_{\text{sat},1}}{P}$

x_1	x_2	γ_1	γ_2	$p_1 [\text{kPa(a)}]$	$p_2 [\text{kPa(a)}]$	$P [\text{kPa(a)}]$	y_1	y_2
0.0001	0.9999	2.466411	1	0.346076	19.93866	20.28474	0.017061	0.982939
0.001	0.999	2.419887	1.00011	3.395474	19.92092	23.3164	0.145626	0.854374
0.02	0.98	1.796153	1.002909	50.40561	19.59869	70.00429	0.720036	0.279964
0.05	0.95	1.407668	1.011344	98.75878	19.15852	117.9173	0.837526	0.162474
0.1	0.9	1.182532	1.024956	165.9274	18.39447	184.3219	0.900205	0.099795
0.2	0.8	1.058873	1.043499	297.1525	16.64643	313.799	0.946952	0.053048
0.3	0.7	1.024588	1.054564	431.2955	14.72009	446.0156	0.968996	0.033004
0.4	0.6	1.011388	1.061769	567.6535	12.70342	580.3569	0.978111	0.021889
0.5	0.5	1.005445	1.066806	705.3973	10.6364	716.0337	0.985145	0.014855
0.6	0.4	1.002546	1.070518	844.0363	8.53873	852.5751	0.989985	0.010015

$\therefore A = T[K] \times 33.82772$ -9022.62

NOTE: No data is given by R, P & P^(a) for a water(1)-aldehyde(2) system. However information is available for water(1)-ketone(2) systems. It has been assumed that methanal (i.e. formaldehyde) can be modeled as a HYPOTHETICAL single-carbon ketone (i.e. "methanone"). This is based on the statement, "aldehydes and ketones behave similarly and undergo many of the same reactions," in John McMURRY; Organic Chemistry^(a); Brooks/Cole Publishing; Pacific Grove, California; 1992; p. 697.

$\therefore A = T[K] \times 33.82772$ -9022.62

$\therefore A = T[K] \times 17.08944$ -4305.68

$\therefore B = T[K] \times 24.70012$ -8265.62

$N'' = \frac{1}{1}$

$N_2 = \frac{1}{1}$

$N'' = \frac{0}{0}$

$N'' = \frac{0}{0}$

$N'' = \frac{0}{0}$

Constant (Reid, Prausnitz & Poling^(b))

Substance	A	B	C	D	eq'n	T _c [K]	P _c [bar]
Formaldehyde	-7.29343	1.08395	-1.63882	-2.30677	1	408	65.9
Water	-7.76451	1.45838	-2.7758	-1.23303	1	647.3	221.2
Methanol	-8.54796	0.76982	-3.1095	1.54481	1	512.6	80.9

(1) $\ln(p_{\text{sat}}/p_c) = (A(1 - T/T_c)^3 + B(1 - T/T_c)^{1.5} + C(1 - T/T_c)^3)(T_c/T)$

0.7	0.3	1.001093	1.073364	983.2811	6.421076	989.7022	0.993512	0.006488
0.8	0.2	1.000383	1.075615	1122.953	4.289694	1127.243	0.996195	0.003805
0.9	0.1	1.000077	1.077439	1262.937	2.148484	1265.085	0.998302	0.001698
0.999	0.001	1	1.078933	1401.751	0.021515	1401.773	0.999985	1.53E-05

Experimental data from M. Albert, L. Hahnstein, H. Hesse & G. Maurer, *AIChE.J.* p. 1743 (Table 1)

& also, hence recalculated van Laar data

Note: Evaluated at $t^*[C] = 70$, as $T[K] = 343.15$ (approx.) $\Rightarrow$

x_1	p [kPa(a)]	y_1	$\gamma_1 = y_1/p_{\text{sat},1}$	$\gamma_1^{\text{recalc.}}$	ERROR ²	$\downarrow$	but also: $\gamma_2 = Y_2/Y_{\text{sat},2}$	$\gamma_2^{\text{recalc.}}$	ERROR ²
0.030	31	0.029	0.016761	0.013832	8.589E-06	$p_{\text{sat},1} = 1787.843$	0.995006	1	2.494E-05
0.064	30.9	0.054	0.014583	0.013832	5.642E-07	$p_{\text{sat},2} = 31.18772$	1.00136	1	1.849E-06
0.068	31.2	0.056	0.014372	0.013832	2.914E-07	[kPa(abs)]	1.013274	1	0.0001762
0.091	30.9	0.071	0.013485	0.013832	1.204E-07		1.012574	1	0.0001581
0.110	30.9	0.083	0.013041	0.013832	6.251E-07	$A = -12213.6$	1.020832	1	0.000434
0.129	30.7	0.093	0.012379	0.013832	2.109E-06	$B = -1.1E+10$	1.025047	1	0.0006274
0.137	30.5	0.098	0.012203	0.013832	2.652E-06		1.022144	1	0.0004904
									SUM = 0.001913
									(least-squares regression)
									TOTAL SUM = 0.016857599

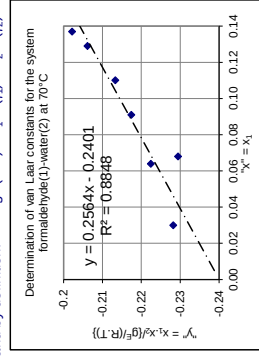
Alternative correlation:

Linearised van Laar equation: [see R.P.&P., Example 8-1]

$x_1 \cdot x_2 [g^2/(R \cdot T)] = D + C \cdot (2x_1 - 1)$

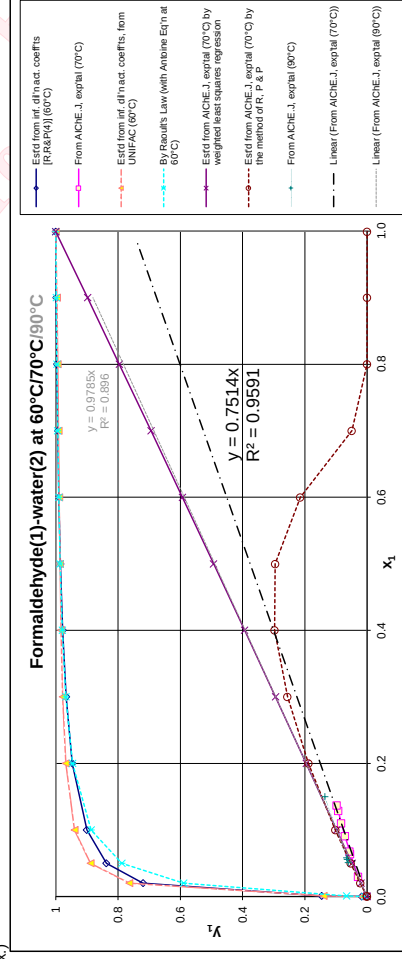
where: $A = R \cdot T / (D - C)$ $B = R \cdot T / (D + C)$

and by definition: $g^E(R \cdot T) = x_1 \cdot \ln(\gamma_1) + x_2 \cdot \ln(\gamma_2)$



Experimental data from M. Albert, L. Hahnstein, H. Hesse & G. Maurer, *AIChE.J.* p. 1743 (Table 1)
Note: Evaluated at $t^*[C] = 90$, as $T[K] = 363.15$ (approx.)

x_1	p [kPa(a)]	y_1
0.051	71.4	0.061
0.056	71.4	0.064
0.058	70.6	0.066
0.150	71.6	0.136



Recalculated van Laar constants:

$T = 70$ °C
 $\therefore T [K] = 343.15$
 From Antoine data, at 70 °C:
 $p_{\text{vap},1} [\text{kPa}(\text{abs})] = 1787.843$ $p_{\text{vap},2} [\text{kPa}(\text{abs})] = 31.18772$
 $A = -12213.6$ $B = -1.1\text{E}+10$
 -9273.5879 -29317.985 -12262.41228 11885.138
 -6805.042 -4113.3916 -1009975.48 174684.34
 (previous "guesses")

$$\text{Total pressure} = 101.325 \text{ kPa}(\text{abs}) \quad p_1 + p_2 = y_1 P + y_2 P = P = y_1 x_1 p_{\text{vap},1} + y_2 x_2 p_{\text{vap},2}$$

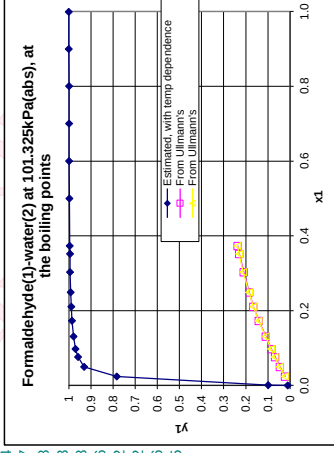
x_1	x_2	y_1	y_2	$p_1 [\text{kPa}(\text{a})]$	$p_2 [\text{kPa}(\text{a})]$	$P [\text{kPa}(\text{a})]$	y_1	y_2	V_1	V_2	V_0	[Est'd from AIChE J. experl (70 °C) by the method of R, P & P]
0.0001	0.9999	0.013832	1	0.001941	19.93866	19.94006	0.973E-05	0.99903	0.000109199			A = -11885.1377
0.001	0.999	0.013832	1	0.019408	19.92071	19.94016	0.000973	0.999027	0.00109134			B = 11128.0122
0.02	0.98	0.013832	1	0.388164	19.54184	19.93	0.019476	0.980524	0.0215527			
0.05	0.95	0.013832	1	0.97041	18.94362	19.91403	0.04873	0.95127	0.052791981			
0.1	0.9	0.013832	1	1.940821	17.94659	19.88741	0.09759	0.90241	0.101888421			
0.2	0.8	0.013832	1	3.881648	15.95252	19.83416	0.195705	0.804295	0.188165947			
0.3	0.7	0.013832	0.999999	5.822482	13.95844	19.78093	0.294348	0.705652	0.255687777			
0.4	0.6	0.013832	0.999998	7.763327	11.96437	19.72769	0.393524	0.606476	0.297156603			
0.5	0.5	0.013832	0.999995	9.704189	9.970278	19.67447	0.493238	0.506762	0.295529612			
0.6	0.4	0.013832	0.999989	11.64508	7.976175	19.62126	0.593493	0.406507	0.21488827			
0.7	0.3	0.013832	0.999974	13.58604	5.98204	19.56808	0.694296	0.305704	0.049001975			
0.8	0.2	0.013832	0.999924	15.52715	3.987826	19.51497	0.795653	0.204347	2.07456E-05			
0.9	0.1	0.013833	0.999614	17.46887	1.993295	19.46217	0.897581	0.102419	2.62666E-76			
0.999	0.001	0.013964	0.008681	19.57402	0.000173	19.57419	0.999991	8.84E-06	2.86146E-23			

From UNIFAC estimation of activity coefficients at infinite dilution (R,P&P and AIChE-J)

$T = 60$ °C
 $\therefore T [K] = 333.15$
 From Antoine data, at 60 °C:
 $p_{\text{vap},1} [\text{kPa}(\text{abs})] = 1403.154$ $p_{\text{vap},2} [\text{kPa}(\text{abs})] = 19.94065$
 $A = 2319.507$ $B = 2851.515$
 NOTE: The previous (initial) estimation was close to this value for A

$$\text{Total pressure} = 101.325 \text{ kPa}(\text{abs}) \quad p_1 + p_2 = y_1 P + y_2 P = P = y_1 x_1 p_{\text{vap},1} + y_2 x_2 p_{\text{vap},2}$$

x_1	x_2	y_1	y_2	$p_1 [\text{kPa}(\text{a})]$	$p_2 [\text{kPa}(\text{a})]$	$P [\text{kPa}(\text{a})]$	y_1	y_2	V_1	V_2	V_0	cf. Y _{Result, 1}
0.0001	0.9999	2.309974	1	0.324125	19.93866	20.26278	0.015996	0.984004	0.006988178			
0.001	0.999	2.307144	1.000001	3.237279	19.92072	23.158	0.139791	0.860209	0.065802063			
0.02	0.98	2.248465	1.000275	63.09888	19.5472	82.64508	0.763483	0.236517	0.589499648			
0.05	0.95	2.159827	1.001737	151.5285	18.97652	170.505	0.888704	0.111286	0.787392424			
0.1	0.9	2.022445	1.007098	283.7802	18.07397	301.8542	0.940124	0.059876	0.886602064			
0.2	0.8	1.782948	1.029835	500.3503	16.42847	516.7788	0.968821	0.03179	0.946212357			
0.3	0.7	1.584723	1.071209	667.0831	14.95242	682.0355	0.978077	0.021923	0.967904568			
0.4	0.6	1.421961	1.135724	798.0925	13.58824	811.6808	0.983259	0.015741	0.979127973			
0.5	0.5	1.28999	1.230139	905.0276	12.26489	917.2925	0.986629	0.013371	0.985987828			
0.6	0.4	1.185169	1.364899	997.7851	10.88512	1008.67	0.989208	0.010792	0.990614716			
0.7	0.3	1.104846	1.555139	1085.189	9.303147	1094.492	0.9915	0.0085	0.993946312			
0.8	0.2	1.047366	1.826335	1175.693	7.283664	1182.977	0.993843	0.006157	0.996459752			
0.9	0.1	1.012168	2.218582	1278.205	4.423997	1282.629	0.996551	0.003449	0.998423456			
0.999	0.001	1.000001	2.792411	1401.753	0.055682	1401.809	0.99996	3.97E-05	0.999985775			



Plotting VLE data based on these parameters:

formaldehyde(1)-water(2)
 Total pressure = 101.325 kPa(abs)
 $T [K] = 273.15$ + $t [^{\circ}C]$
 From Antoine data, at $T [K]$:
 $p_1 + p_2 = y_1 P + y_2 P = P = y_1 x_1 p_{\text{vap},1} + y_2 x_2 p_{\text{vap},2}$
 $A = 33.82772 \times T [K] +$ -9022.62
 $B = 24.70012 \times T [K] +$ -8255.62

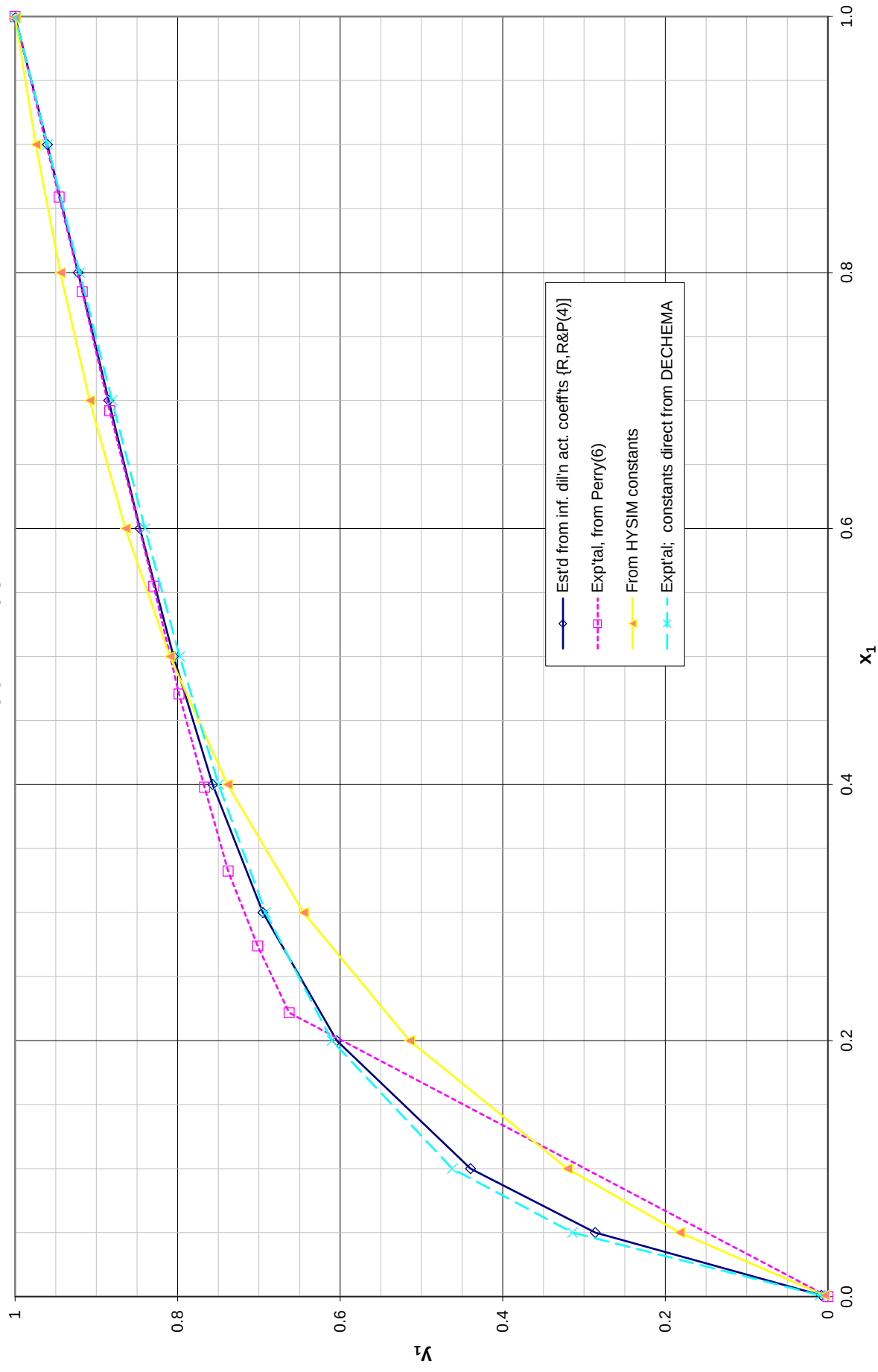
x_1	x_2	guess $T [K]$	A	B	$p_{\text{vap},1}$	$p_{\text{vap},2}$	y_1	y_2	$p_1 [\text{kPa}(\text{a})]$	$p_2 [\text{kPa}(\text{a})]$	$P [\text{kPa}(\text{a})]$	y_1	y_2
0.0001	0.9999	372.84	3589.601	943.4921	3409.471	100.2506	3.180605	1	10.084417841	100.2406	101.325	0.010702	0.989298
0.001	0.999	370.28	3502.945	880.2182	3236.943	91.40732	3.091958	1.000005	10.00849006	91.31633	101.3248	0.098776	0.901224
0.02408	0.97592	335.74	2334.751	2000.0000	1496.138	22.45697	2.203823	1.000562	79.39647307	21.92853	101.325	0.783582	0.216418
0.049585	0.950415	313.04	1566.757	533.5355	822.2511	7.342221	2.315175	0.993312	94.39352083	6.931486	101.325	0.931592	0.068408
0.076291	0.923709	304.51	1278.299	-744.1603	641.2998	4.59191	1.985022	0.991998	97.11739986	4.20765	101.325	0.958474	0.041526
0.097782	0.902218	299.54	1109.996	-867.0508	550.9453	3.443021	1.823689	0.991005	98.24659106	3.078416	101.325	0.969618	0.030382
0.131141	0.868859	293.73	913.4836	-1010.539	458.2639	2.425547	1.651316	0.989724	99.2391977	2.085803	101.325	0.979415	0.020585
0.172983	0.827017	288.39	732.8137	-1142.46	384.192	1.73293	1.503317	0.988625	99.90830338	1.416861	101.3252	0.986017	0.013983

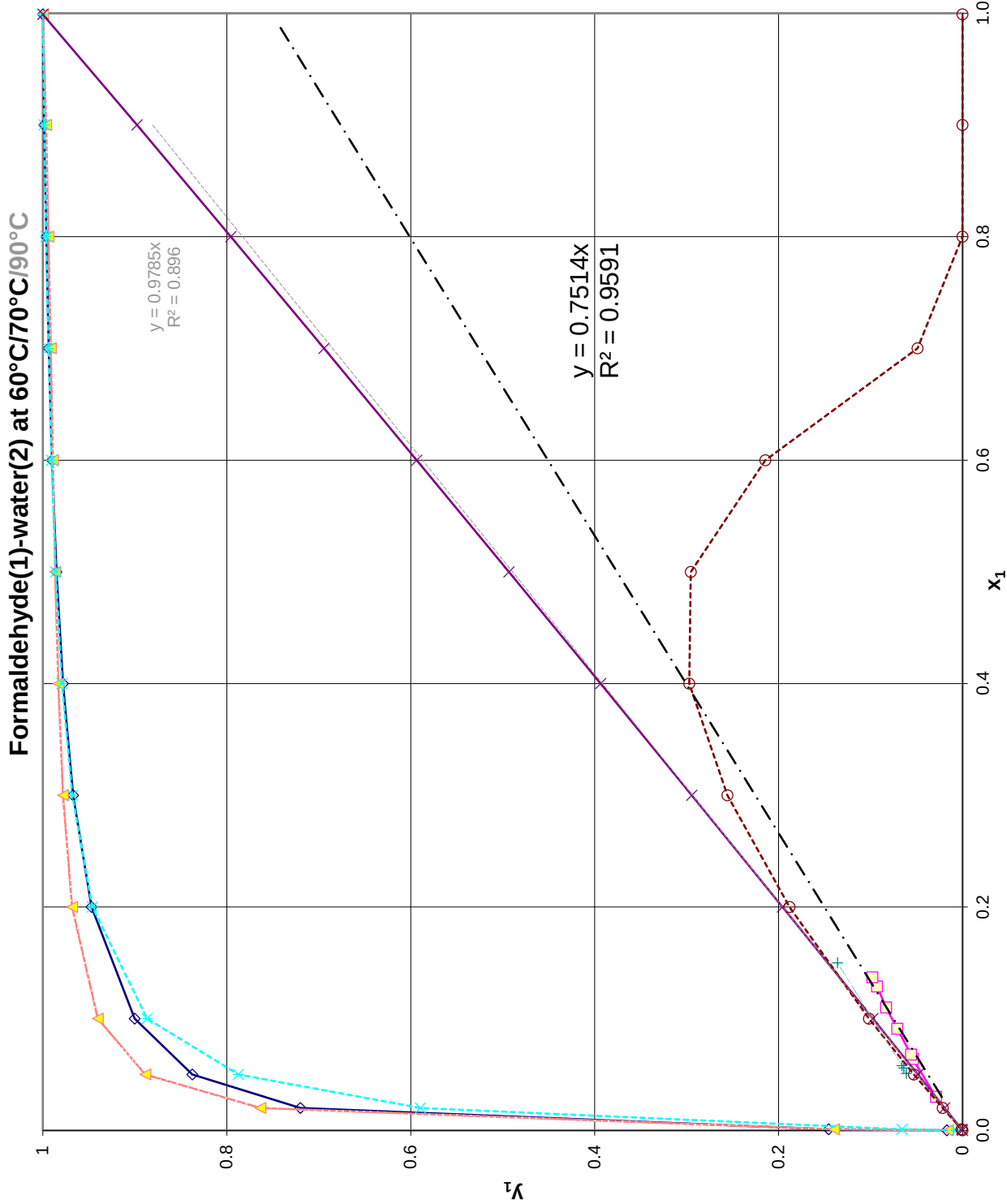
Experimental data from Ullmann's⁽⁵⁾, Vol. A11, p. 622 (Table 3)

Note: Evaluated at the boiling points, at P [kPa(abs)] = 101.325

Note: Evaluated at the boiling points, at P [kPa(abs)] = 101.325

Methanol(1)-water(2) at 60°C





Formaldehyde(1)

0.9183
0.780

 r_i
 q_i

-149.00

 u_{ij} **Water(2)**

0.9200
1.400

240.00

Refer to:

R,P&P; T8-21, T8-3

AIChE.J; T6, T7

0.0001

 x_i

0.9999

60

 $T [^{\circ}\text{C}]$

60

333.15

 $T [\text{K}]$

333.15

9.98E-05

 ϕ_i

0.9999

5.57E-05

 θ_i

0.999944

1.055264

 τ_{ij}

0.917004

10

 z

10

0.7732

 l_i

-2.32

2.310288

 γ_i 1 $\Rightarrow$

1.93E-05 = B (van Laar)

 $\Rightarrow 2319.50663 = A \text{ (van Laar)}$

Similarly:

t [$^{\circ}\text{C}$]	T [K]	γ_1^{∞}	A	γ_2^{∞}	B
60	333.15	2.310288	2319.507	2.799482	2851.515
25	298.15	2.316579	2082.565	2.811124	2562.229
100	373.15	2.304493	2590.208	2.78857	3181.768
0	273.15	2.32201	1913.26	2.821003	2355.352
45	318.15	2.312822	2217.971	2.804196	2727.577
80	353.15	2.307233	2454.867	2.79375	3016.682
120	393.15	2.302023	2725.532	2.783866	3346.785

Hence:

$$A = T[\text{K}] \times 6.76855 + 64.54$$

$$B = T[\text{K}] \times 8.26043 + 2355.78$$

TUTORIAL 4 Question 1

DECHEMA 23/09/1998

DATA Megat Ahmad

David Verrelli

CHE3117

DECHEMA experimental data

PART (a)

PART (b)

PART (c)

x_meth	x_w	T [°C]	PART (a)			PART (b)			PART (c)			ERRORS		
			Methanol	Methanol	Water	Methanol	Methanol	Water	Methanol	Methanol	Water	Part (a) Diff T	Part (b) Diff T	Part (c) Diff T
0.0000	1.0000	100.00	0.0000	0.0000	0	0	0	99.9909	0	0	99.9909	-0.22	0.22	-0.01
0.0089	0.9911	98.43	0.0089	0.008543	99.5691	0.0623018	0.0623018	98.4445	2	0.0089	98.3262	1.14	1.14	0.01
0.0204	0.9796	96.65	0.0204	0.0377609	99.2843	0.132037	0.132037	96.6251	3	0.0204	96.3987	2.63	2.63	-0.02
0.0306	0.9694	95.12	0.0306	0.0572935	99.0172	0.185592	0.185592	95.1575	4	0.0306	94.8657	3.90	3.9	0.04
0.0419	0.9581	93.32	0.0419	0.0793334	98.7061	0.237506	0.237506	93.6702	5	0.0419	93.3407	5.39	5.39	0.02
0.0516	0.9484	92.13	0.0516	0.0985251	98.4288	0.276896	0.276896	92.5002	6	0.0516	92.1495	6.30	6.3	0.02
0.0616	0.9384	91.05	0.0616	0.118515	98.1279	0.313306	0.313306	91.3789	7	0.0616	91.0227	7.08	7.08	-0.03
0.0689	0.9311	90.21	0.0689	0.133208	97.9028	0.337556	0.337556	90.611	8	0.0689	90.2579	7.69	7.69	0.05
0.0759	0.9241	89.54	0.0759	0.147354	97.682	0.359181	0.359181	89.9113	9	0.0759	89.5657	8.14	8.14	0.03
0.0954	0.9046	87.86	0.0954	0.186918	97.042	0.412283	0.412283	88.1297	10	0.0954	87.8234	9.18	9.18	-0.04
0.1242	0.8758	85.72	0.1242	0.245192	96.0386	0.475731	0.475731	85.874	11	0.1242	85.6575	10.32	10.3	-0.06
0.1672	0.8328	83.10	0.1672	0.330091	94.4389	0.547657	0.547657	83.1338	12	0.1672	83.0814	11.34	11.3	-0.02
0.1990	0.8010	81.57	0.1990	0.390082	93.2002	0.589006	0.589006	81.4654	13	0.199	81.5376	11.63	11.6	0.03
0.2348	0.7652	80.01	0.2348	0.453905	91.7707	0.627343	0.627343	79.8584	14	0.2348	80.0628	11.76	11.8	0.05
0.3458	0.6542	76.62	0.3458	0.345798	87.2917	0.713103	0.713103	76.0809	15	0.3458	76.5904	10.67	10.7	-0.03
0.3934	0.6066	75.43	0.3934	0.681376	85.4199	0.740849	0.740849	74.8243	16	0.3934	75.4113	11.86	11.9	-0.02
0.4654	0.5346	73.89	0.4654	0.756025	82.7067	0.777213	0.777213	73.1764	17	0.4654	73.8243	11.53	11.5	-0.07
0.6469	0.3531	70.46	0.6469	0.884807	76.6777	0.854333	0.854333	69.8027	18	0.6469	70.3692	12.25	12.2	-0.09
0.7463	0.2537	68.69	0.7463	0.929978	73.8892	0.893798	0.893798	68.2046	19	0.7463	68.6345	7.99	7.99	-0.06
0.7601	0.2399	68.50	0.7601	0.935239	73.5291	0.899298	0.899298	67.9907	20	0.7601	68.3987	5.39	5.39	-0.10
0.8423	0.1577	67.04	0.8423	0.842281	71.5108	0.8423	0.8423	66.748	21	0.8423	67.0169	6.49	6.49	-0.02
0.8708	0.1292	66.61	0.8708	0.870711	70.8587	0.94261	0.94261	66.3276	22	0.8708	66.5465	4.90	4.9	-0.06
0.9001	0.0999	66.11	0.9001	0.900062	70.2122	0.956535	0.956535	65.9003	23	0.9001	66.0677	4.75	4.75	-0.04
0.9163	0.0837	65.87	0.9163	0.916278	69.8648	0.963407	0.963407	65.666	24	0.9163	65.8052	4.34	4.34	0.06
0.9529	0.0471	65.24	0.9529	0.952897	69.1048	0.979173	0.979173	65.1417	25	0.9529	65.2183	4.62	4.62	-0.02
0.9750	0.0250	64.88	0.9750	0.975021	68.6619	0.988866	0.988866	64.8285	26	0.975	64.8683	4.22	4.22	-0.01
1.0000	0.0000	64.51	1.0000	1	68.1744	1	1	64.4755	27	1	64.4755	4.15	4.15	-0.03
												Mean Deviation		0.06
												Maximum Deviation		0.71
												7.03	0.27	0.25
												12.25	0.71	

Antoine constants from "VLE of Formaldehyde Mixtures: New Data and Model Revision" in AIChEJ, 42(6), p. 1745.

Substance	Constant			Constant (Sinnott ⁽²⁾)			Constant (Reid, Prausnitz & Poling ⁽⁴⁾)				eq'n	T _c [K]	p _c [bar]
	A ₂	B ₂	C ₂	A ₂	B ₂	C ₂	A	B	C	D			
Formaldehyde	14.4625	-2204.13	-30.15	16.4775	-2204.13	-30.15	-7.29343	1.08395	-1.63882	-2.30677	1	408	65.9
Water	16.2886	-3816.44	-46.13	18.3036	-3816.44	-46.13	-7.76451	1.45838	-2.7758	-1.23303	1	647.3	221.2
Methanol	16.5725	-3626.55	-34.29	18.5875	-3626.55	-34.29	-8.54796	0.76982	-3.1085	1.54481	1	512.6	80.9

(sign altered) TO GIVE [mmHg]

(1) $\ln(p_{\text{vap}}/p_c) = \{A(1 - T/T_c) + B(1 - T/T_c)^{1.5} + C(1 - T/T_c)^3 + D(1 - T/T_c)^6\} \cdot (T_c/T)$

(2) $\ln(p_{\text{vap}}) = A - B/T + C \cdot \ln(T) + D(p_{\text{vap}}/T^2)$

Equation: $\ln(p^0 [\text{kPa}]) = A_2 + B_2 / (T[\text{K}] + C_2)$

NOTE: All pressures are absolute

Check pure-component boiling points at atmospheric pressure

==> p ⁰ =	101.325 kPa	t _b [°C] = -273.15 + T[K]
254.0521 K	=	-19.0979 °C
373.1525 K	=	100.0025 °C
337.6612 K	=	64.51121 °C

Now for Raoult's Law:

Composition:

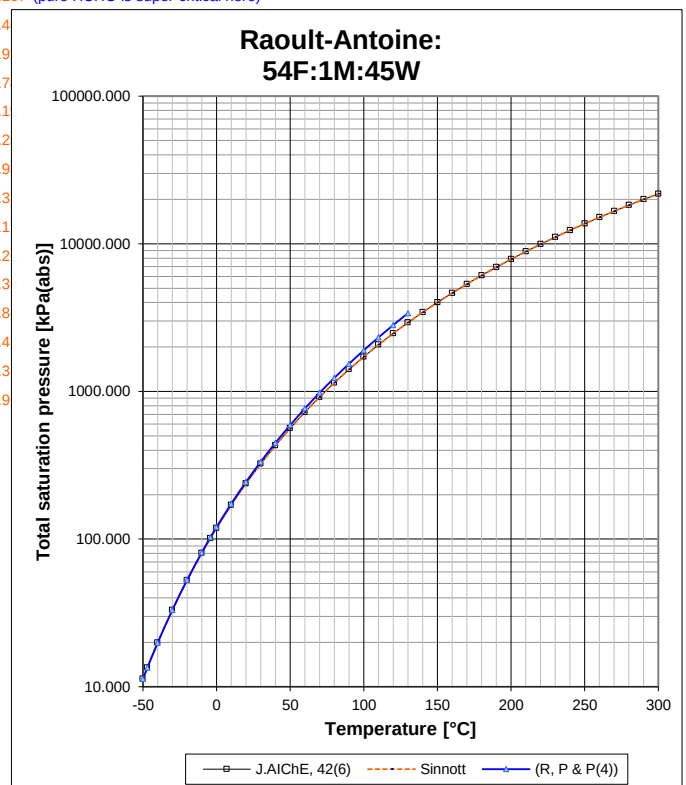
Formaldehyde	0.54
Water	0.45
Methanol	0.01
SUM	1

p ⁰ [kPa]	p [kPa]
t _b [°C] = -20	97.36911
T[K] = 253.15	0.116889
	1.002321
	52.64194

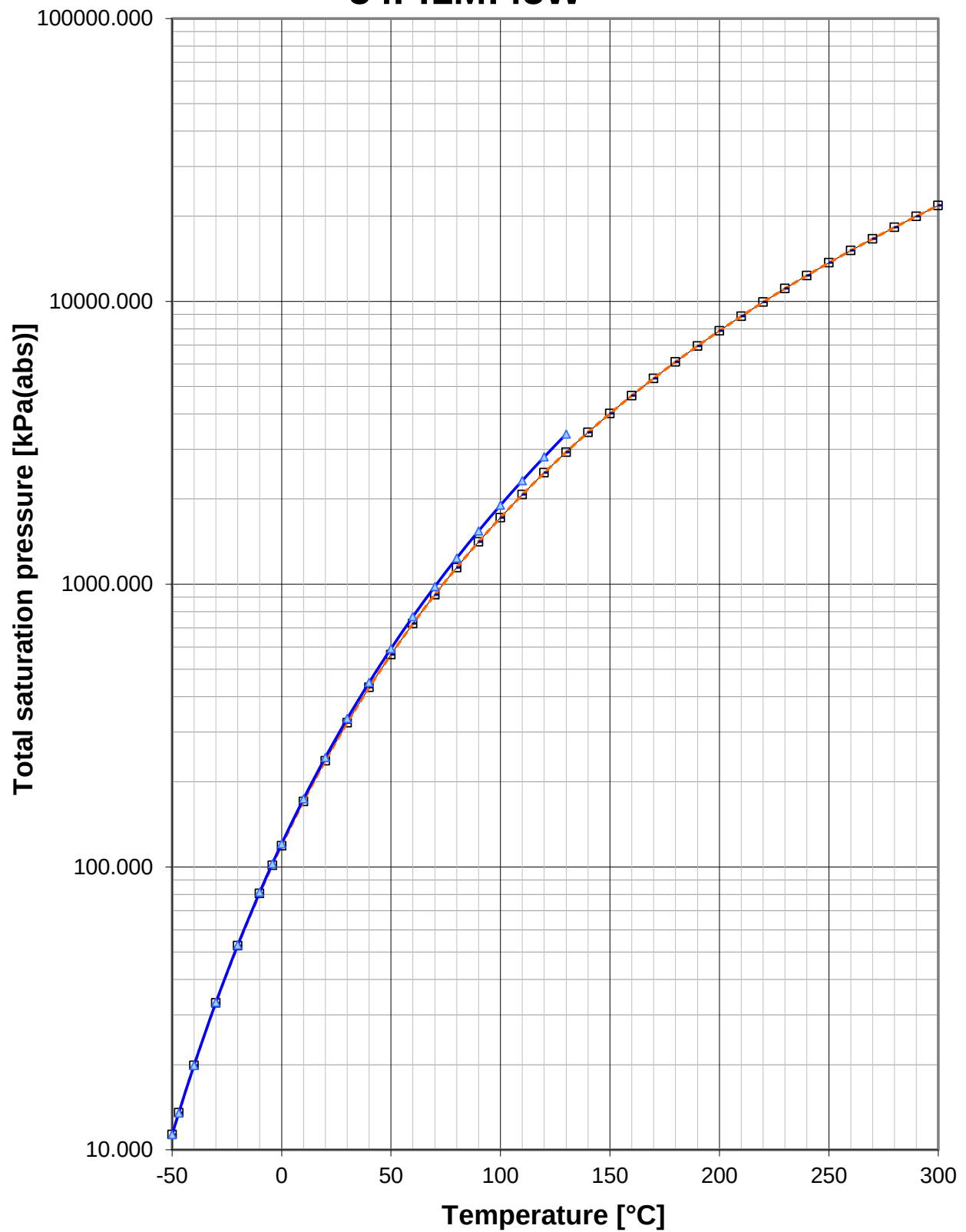
p ⁰ [kPa]	p [kPa]
t _b [°C] = 0	219.6436
T[K] = 273.15	0.593078
	4.013874
	118.9146

		(Sinnott ⁽²⁾)		(R, P & P ⁽⁴⁾)	
t _b [°C] = -50	T[K] = 223.15	p _{TOTAL} = 11.316 kPa(abs)	11.316	11.303	-0.1%
t _b [°C] = -46.9606	T[K] = 226.1894	p _{TOTAL} = 13.509 kPa(abs)	13.509	13.498	= ERROR
t _b [°C] = -40	T[K] = 233.15	p _{TOTAL} = 19.866 kPa(abs)	19.866	19.874	
t _b [°C] = -30	T[K] = 243.15	p _{TOTAL} = 33.084 kPa(abs)	33.084	33.185	
t _b [°C] = -20	T[K] = 253.15	p _{TOTAL} = 52.642 kPa(abs)	52.643	52.985	
t _b [°C] = -10	T[K] = 263.15	p _{TOTAL} = 80.505 kPa(abs)	80.506	81.367	1.1%
t _b [°C] = -4.2046	T[K] = 268.9454	p _{TOTAL} = 101.325 kPa(abs)	101.326	102.688	= ERROR
t _b [°C] = 0	T[K] = 273.15	p _{TOTAL} = 118.915 kPa(abs)	118.916	120.767	
t _b [°C] = 10	T[K] = 283.15	p _{TOTAL} = 170.368 kPa(abs)	170.371	173.960	
t _b [°C] = 20	T[K] = 293.15	p _{TOTAL} = 237.586 kPa(abs)	237.590	244.059	
t _b [°C] = 30	T[K] = 303.15	p _{TOTAL} = 323.482 kPa(abs)	323.487	334.511	3.3%
t _b [°C] = 40	T[K] = 313.15	p _{TOTAL} = 431.129 kPa(abs)	431.135	449.097	= ERROR
t _b [°C] = 50	T[K] = 323.15	p _{TOTAL} = 563.728 kPa(abs)	563.736	591.940	
t _b [°C] = 60	T[K] = 333.15	p _{TOTAL} = 724.578 kPa(abs)	724.589	767.523	
t _b [°C] = 70	T[K] = 343.15	p _{TOTAL} = 917.055 kPa(abs)	917.069	980.723	
t _b [°C] = 80	T[K] = 353.15	p _{TOTAL} = 1144.583 kPa(abs)	1144.599	1236.857	7.5%
t _b [°C] = 90	T[K] = 363.15	p _{TOTAL} = 1410.618 kPa(abs)	1410.639	1541.762	= ERROR
t _b [°C] = 100	T[K] = 373.15	p _{TOTAL} = 1718.635 kPa(abs)	1718.660	1901.913	
t _b [°C] = 110	T[K] = 383.15	p _{TOTAL} = 2072.110 kPa(abs)	2072.141	2324.628	
t _b [°C] = 120	T[K] = 393.15	p _{TOTAL} = 2474.514 kPa(abs)	2474.551	2818.469	
t _b [°C] = 130	T[K] = 403.15	p _{TOTAL} = 2929.300 kPa(abs)	2929.344	3394.358	13.7%
t _b [°C] = 140	T[K] = 413.15	p _{TOTAL} = 3439.900 kPa(abs)	3439.950	#NUM!	= ERROR
t _b [°C] = 150	T[K] = 423.15	p _{TOTAL} = 4009.711 kPa(abs)	4009.770	#NUM!	
t _b [°C] = 160	T[K] = 433.15	p _{TOTAL} = 4642.099 kPa(abs)	4642.167		(pure HCHO is super-critical here)
t _b [°C] = 170	T[K] = 443.15	p _{TOTAL} = 5340.384 kPa(abs)	5340.4		
t _b [°C] = 180	T[K] = 453.15	p _{TOTAL} = 6107.839 kPa(abs)	6107.9		
t _b [°C] = 190	T[K] = 463.15	p _{TOTAL} = 6947.685 kPa(abs)	6947.7		
t _b [°C] = 200	T[K] = 473.15	p _{TOTAL} = 7863.082 kPa(abs)	7863.1		
t _b [°C] = 210	T[K] = 483.15	p _{TOTAL} = 8857.126 kPa(abs)	8857.2		
t _b [°C] = 220	T[K] = 493.15	p _{TOTAL} = 9932.840 kPa(abs)	9932.9		
t _b [°C] = 230	T[K] = 503.15	p _{TOTAL} = 11093.173 kPa(abs)	11093.3		
t _b [°C] = 240	T[K] = 513.15	p _{TOTAL} = 12340.990 kPa(abs)	12341.1		
t _b [°C] = 250	T[K] = 523.15	p _{TOTAL} = 13679.065 kPa(abs)	13679.2		
t _b [°C] = 260	T[K] = 533.15	p _{TOTAL} = 15110.081 kPa(abs)	15110.3		
t _b [°C] = 270	T[K] = 543.15	p _{TOTAL} = 16636.619 kPa(abs)	16636.8		
t _b [°C] = 280	T[K] = 553.15	p _{TOTAL} = 18261.156 kPa(abs)	18261.4		
t _b [°C] = 290	T[K] = 563.15	p _{TOTAL} = 19986.060 kPa(abs)	19986.3		
t _b [°C] = 300	T[K] = 573.15	p _{TOTAL} = 21813.584 kPa(abs)	21813.9		

		p ⁰ [kPa]		p [kPa]	
t _b [°C] = 20	T[K] = 293.15	437.8067	236.4156		
		2.313304	1.040987		
		12.97214	0.129721		
			237.5863		
t _b [°C] = 0.01	T[K] = 273.16				Error:
J.AiChE	p ⁰ [kPa]	0.5935		-2.9%	
Sinnott		0.5935		-2.9%	
R, P & P		0.6120		0.12%	
ACTUAL		0.6112			
t _b [°C] = 100	T[K] = 373.15				Error:
J.AiChE	p ⁰ [kPa]	101.316		-0.0090%	
Sinnott		101.317		-0.0075%	
R, P & P		101.378		0.053%	
ACTUAL		101.325			
t _b [°C] = 373.7	T[K] = 646.85				Error:
J.AiChE	p ⁰ [kPa]	20650		-6.1%	
Sinnott		20651		-6.1%	
R, P & P		22001		0.0065%	
ACTUAL		22000			



Raoult-Antoine: 54F:1M:45W





APPENDIX TO CHAPTER 7

PART 2: DETAILED PROCESS DESIGN

LOW-RESOLUTION version WITHOUT EMBEDDED FONTS
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Property calculation: VLE

Experimental data from M. Albert, L. Hahnenstein, H. Hasse & G. Maurer, AIChE.J., p. 1743 (Table 1)
& also, hence recalculated van Laar data

Note: Evaluated at $t[^\circ\text{C}] =$

70, as $T[\text{K}] = 343.15$ (approx.)

x_1	p [kPa(a)]	y_1
0.030	31	0.029
0.064	30.9	0.054
0.068	31.2	0.056
0.091	30.9	0.071
0.110	30.9	0.083
0.129	30.7	0.093
0.137	30.5	0.098

Substance Constant (Reid, Prausnitz & Poling^(d))

	A	B	C	D	eq'n	T_c [K]	p_c [bar]
Formaldehyde	-7.29343	1.08395	-1.63882	-2.30677	1	408	65.9
Water	-7.76451	1.45838	-2.7758	-1.23303	1	647.3	221.2
Methanol	-8.54796	0.76982	-3.1085	1.54481	1	512.6	80.9

$$(1) \ln(p_{\text{vap}}/p_c) = \{A(1 - T/T_c) + B(1 - T/T_c)^{1.5} + C(1 - T/T_c)^3 + D(1 - T/T_c)^6\} \cdot (T_c/T)$$

Their data:

Note: In all cases HCHO concentration increases down a column.

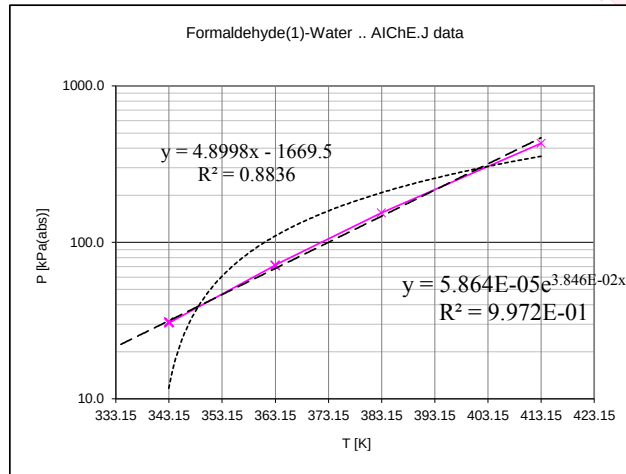
T [K]	t [°C]	P [kPa(abs)]	
343.1	69.95	31.0	
343.1	69.95	30.9	
343.1	69.95	31.2	
343.1	69.95	30.9	
343.2	70.05	30.9	
343.3	70.15	30.7	
343.1	69.95	30.5	
MEAN:	343.1428571	69.99286	30.87143
σ :	0.078679579	0.07868	0.221467

	363.1	89.95	71.4
	363.1	89.95	71.4
	363.2	90.05	70.6
	363.1	89.95	71.6
MEAN:	363.125	89.975	71.25
σ :	0.05	0.05	0.443471

	383.1	109.95	153.1
	383.3	110.15	155.0
	383.1	109.95	155.1
	383.0	109.85	155.1
MEAN:	383.125	109.975	154.575
σ :	0.125830574	0.125831	0.984463

413.2	140.05	405.3
413.2	140.05	414.4
413.1	139.95	423.1
413.2	140.05	423.7
413.2	140.05	432.9

	413.1	139.95	443.1
	413.1	139.95	442.7
	413.1	139.95	449.1
MEAN:	413.15	140	429.2875
σ :	0.053452249	0.053452	15.3195



Hence with:

Henry's law: $y = 0.7514 x$ or $y = x$???
& Total pressure: $P_{\text{BINARY}} = 5.86E-05 \exp(3.85E-02 T[\text{K}])$

Note(1): all pressures in kPa(abs).

Note(2): "with inerts" signifies inert gases present to a TOTAL, COMBINED pressure of "P"

Note(3): obviously the "BINARY" refers to the situation with no inerts, although hydrolysis & polymerisation still occur.

Data for:	x_1	T [K]	P_{BIN} [kPa]	y_1 BINARY	p_1	e.g. y_1 WITH INERTS	Ullmann's ⁽⁵⁾			Ratio of	
						$P = ?$	$x_{\text{Mass } 1}$ [#]	p_1	y_1 w INERTS	y_1 w INERTS	
(bottom)							Assuming a binary solution.				
Abs. Stage 1	0.402006	335.15	23.23769	0.302067	7.019346	128	0.054839	0.528406	3.487933	0.027249	50%
	0.42	348.15	38.3117064	0.312309799	11.96512131	130	0.092039395	0.542435098	7.762824198	0.059714032	65%
Abs. Stage 2	0.195415	323.15	14.64729	0.146835	2.150735	126	0.017069	0.288159	0.943184	0.007486	44%
	0.196488451	336.15	24.14881957	0.147641422	3.565366059	128	0.027854422	0.289558558	2.101505318	0.016418012	59%
Abs. Stage 3	0.129216	315.15	10.76796	0.097093	1.045492	124	0.008431	0.198284	0.407343	0.003285	39%
	0.13020155	324.15	15.22160042	0.097833445	1.489181608	126	0.011818902	0.199676262	0.726852471	0.00576867	49%
Abs. Stage 4	0	313.15	9.970747	0	0	110	0	0	0	0	#DIV/0!
(top)	0.096071711	316.15	11.1901676	0.072188284	0.807798993	124	0.006514508	0.150485765	0.344611498	0.002779125	43%
	0.000001	313.15	9.970746937	7.514E-07	7.49202E-06	110	6.81093E-08	1.66672E-06	1.08208E-05	9.83706E-08	144%

Note(4): Order-of-magnitude concordancy(?) with Ullmann's⁽⁵⁾ - which has lower p_{vap} 's.(1)

$$p_i[\text{kPa}] = 0.1333F \cdot \exp\{-F^* \cdot (a_0 + a_1/T + a_2/T^2)\}$$

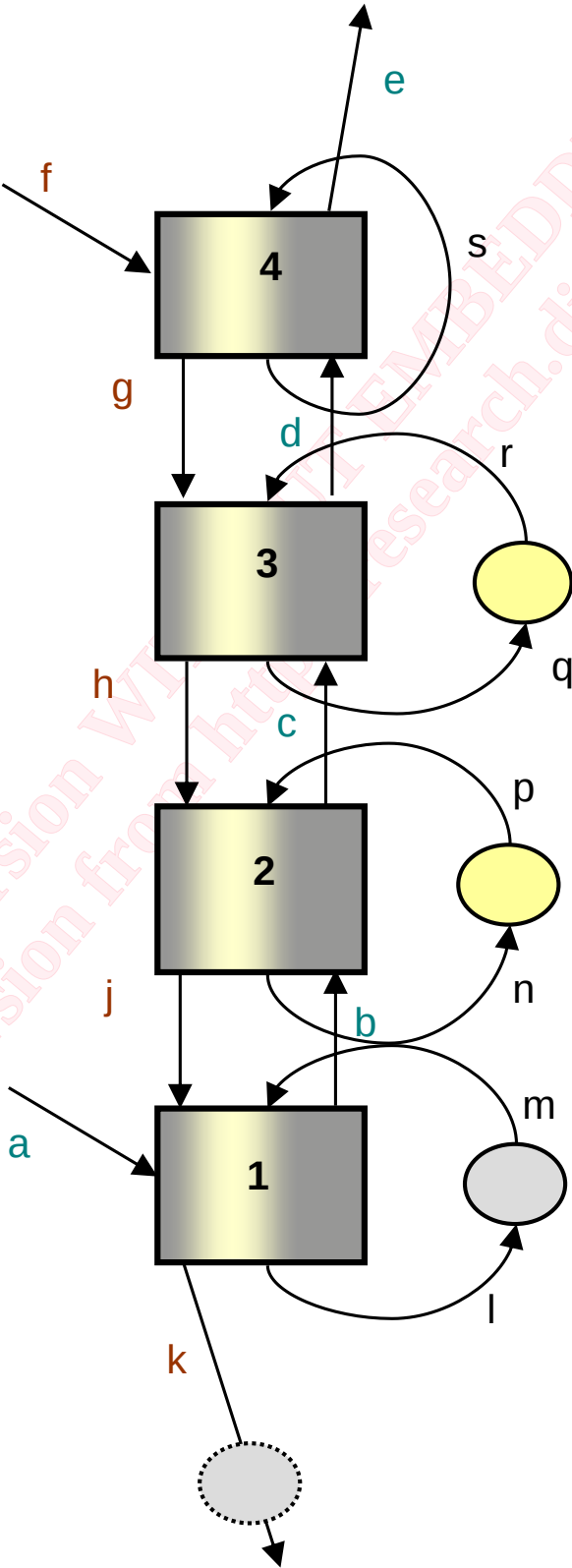
$$\alpha = 0.08760 \pm 0.00950$$

$$a_0 = -12.0127 \pm 0.0550$$

$$a_1 = 3451.72 \pm 17.14$$

$$a_2 = 248257.3 \pm 5296.8$$

TOP Abs. Stage 4	5.86E-05	0	0	#DIV/0!	0	#DIV/0!	#DIV/0!	#DIV/0!
BOTTOM (top)								#DIV/0!



STAGE 2 (LOWER-MIDDLE SECTION OF COLUMN)

Pump-around flow: 41.158 kg s⁻¹ 0.199489 total feed									
Mass fraction of HCHO in liquid from stage above:									
41.158 kg s⁻¹ 0.199489 total feed									

Check mass balances:

0

0

STREAMS OUT:

No. Description	HYSIM	Flow [kg.s ⁻¹]	t [°C]	T [K]	Species	State	Mass frac. [J]	Mass Flow [kg.s ⁻¹]	MR [kmol ⁻¹]
j L from stage 2	-	1.742831	59.24	323.15	HCHO	Aq	0.2888974	0.5034995	0.030026
				323.15	CH ₃ OH	Aq	0.005	0.0087142	0.032042
				323.15	H ₂ O	L	0.7059526	1.2303564	0.018015
				323.15	HCOOH	Aq	0.00015	0.0002614	0.046026
c V from stage 2	-	5.924	50.00	323.15	HCHO	V	0.0718554	0.5042329	0.030026
				323.15	CH ₃ OH	V	0.0012437	0.0087277	0.032042
				323.15	O ₂	V	0.000518	0.0036353	0.031999
				323.15	H ₂ O	V	0.1789649	1.2558551	0.018015
n Pump-around 2	-	41.158	63.00	336.15	HCHO	Aq	0.2888974	11.890551	0.030026
				336.15	CH ₃ OH	Aq	0.005	0.2057919	0.032042
				336.15	H ₂ O	L	0.7059526	29.055867	0.018015
				336.15	HCOOH	Aq	0.00015	0.0061738	0.046026
				336.15	H ₂	V	0.0110662	0.0776551	0.020016
				336.15	CO ₂	V	0.0667666	0.4685232	0.04401
				336.15	CO	V	0.0037773	0.0265063	0.02801
				336.15	HCOOH	V	0.684E-05	0.0002585	0.046026

*Note: Aqueous C_p's taken as those for the pure liquid.

99.50%

Hence "approach to equilibrium" is:

126

kPa(abs)

Mole fraction HCHO in total liquid fed:

0.017069327

given a total pressure of:

2.150755239

kPa(abs)

Hence equilibrium partial pressure in the vapour:

0.017069327

given a total pressure of:

2.150755239

kPa(abs)

Hence equilibrium partial pressure in the vapour:

0.017069327

given a total pressure of:

2.150755239

kPa(abs)

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given a total pressure of:

2.150755239

kPa(abs)

Hence equilibrium partial pressure in the vapour:

0.017069327

given a total pressure of:

2.150755239

kPa(abs)

Hence equilibrium partial pressure in the vapour:

0.017069327

given a total pressure of:

2.150755239

STAGE 3 (UPPER-MIDDLE SECTION OF COLUMN)

Pump-around flow: 13.744 kg.s ⁻¹ (0.0458612)									
Mass fraction of HCHO in liquid from stage above: 0.150415									
STREAMS IN:									
No. Description	HYSIM	Flow [kg.s ⁻¹]	t [°C]	T [K]	Species	State	Mass frac. [-]	Mass Flow [kg.s ⁻¹]	MR [kg.mol ⁻¹]
g L from stage 4	-	0.40	43.00	316.15	HCHO	Aq	0.150417	0.0601659	0.030026
		0.4	WATCH CROSS	316.15	CH ₃ OH	Aq	0.001	0.0004	0.032042
		0.4		316.15	H ₂ O	L	0.8485353	0.3394141	0.018015
		0.4		316.15	HCOOH	Aq	0.00005	0.00002	0.046026
c V from stage 2	-	5.924	50.00	323.15	HCHO	V	0.0220105	0.130401	0.030026
		5.924497		323.15	CH ₃ OH	V	0.0002217	0.0013136	0.032042
		5.924497		323.15	O ₂	V	0.0006136	0.0036353	0.031999
		5.924497		323.15	H ₂ O	V	0.0919008	0.5444662	0.018015
		5.924497		323.15	H ₂	V	0.0131075	0.0776551	0.002016
		5.924497		323.15	CO ₂	V	0.0790824	0.4685232	0.04401
		5.924497		323.15	CO	V	0.004474	0.0265063	0.02801
		5.924497		323.15	HCOOH	V	1.048E-05	6.209E-05	0.046026
		5.924497		323.15	N ₂	V	0.7885791	4.6719343	0.028013
f Pump-around 3	-	13.744	40.00	313.15	HCHO	Aq	0.1994886	2.7417246	0.030026
		13.7437671	WATCH TS APPROACH	313.15	CH ₃ OH	Aq	0.002	0.0274875	0.032042
		13.7437671		313.15	H ₂ O	L	0.7984114	10.973181	0.018015
		13.7437671		313.15	HCOOH	Aq	0.0001	0.0013744	0.046026
Mass fraction of HCHO in total liquid fed: 19.81% (0.00843184) (0.04591577) (4.67E-05)									
Hence equilibrium partial pressure in the vapour: 1.04591577 (4.67E-05)									
Hence equilibrium mole fraction in the vapour: 0.00843184 (given a total pressure of: 124 kPa(abs))									
Check mass balances: 0									
Check mass balances: 0									
STREAMS OUT:									
No. Description	HYSIM	Flow [kg.s ⁻¹]	t [°C]	T [K]	Species	State	Mass frac. [-]	Mass Flow [kg.s ⁻¹]	MR [kg.mol ⁻¹]
h L from stage 3	-	0.65	51	324.15	HCHO	Aq	0.1994886	0.1296676	0.030026
		0.65		324.15	CH ₃ OH	Aq	0.002	0.0013	0.032042
		0.65		324.15	H ₂ O	L	0.7984114	0.5189674	0.018015
		0.65		324.15	HCOOH	Aq	0.0001	0.000065	0.046026
d V from stage 3	-	5.674	42.00	315.15	HCHO	V	0.0107321	0.0608993	0.030026
		5.674497		315.15	CH ₃ OH	V	7.288E-05	0.004136	0.032042
		5.674497		315.15	O ₂	V	0.0006406	0.0036353	0.031999
		5.674497		315.15	H ₂ O	V	0.0643075	0.3649129	0.018015
		5.674497		315.15	H ₂	V	0.0138849	0.0776551	0.002016
		5.674497		315.15	CO ₂	V	0.0825665	0.4685232	0.04401
		5.674497		315.15	CO	V	0.0046711	0.0265063	0.02801
		5.674497		315.15	HCOOH	V	3.011E-06	1.709E-05	0.046026
		5.674497		315.15	N ₂	V	0.8233213	4.6719343	0.028013
q Pump-around 3	-	13.744	51.00	324.15	HCHO	Aq	0.1994886	2.7417246	0.030026
		13.7437671		324.15	CH ₃ OH	Aq	0.002	0.0274875	0.032042
		13.7437671		324.15	H ₂ O	L	0.7984114	10.973181	0.018015
		13.7437671		324.15	HCOOH	Aq	0.0001	0.0013744	0.046026
Mass fraction of HCHO in total liquid fed: 19.81% (0.00843184) (0.04591577) (4.67E-05)									
Hence equilibrium partial pressure in the vapour: 1.04591577 (4.67E-05)									
Hence equilibrium mole fraction in the vapour: 0.00843184 (given a total pressure of: 124 kPa(abs))									
Check mass balances: 0									
Check mass balances: 0									
Pump-around flow: 13.744 kg.s ⁻¹ (0.0458612)									
Mass fraction of HCHO in liquid from stage above: 0.150415									
STREAMS IN:									
No. Description	HYSIM	Flow [kg.s ⁻¹]	t [°C]	T [K]	Species	State	Mass frac. [-]	Mass Flow [kg.s ⁻¹]	MR [kg.mol ⁻¹]
g L from stage 4	-	0.40	43.00	316.15	HCHO	Aq	0.150417	0.0601659	0.030026
		0.4	WATCH CROSS	316.15	CH ₃ OH	Aq	0.001	0.0004	0.032042
		0.4		316.15	H ₂ O	L	0.8485353	0.3394141	0.018015
		0.4		316.15	HCOOH	Aq	0.00005	0.00002	0.046026
c V from stage 2	-	5.924	50.00	323.15	HCHO	V	0.0220105	0.130401	0.030026
		5.924497		323.15	CH ₃ OH	V	0.0002217	0.0013136	0.032042
		5.924497		323.15	O ₂	V	0.0006136	0.0036353	0.031999
		5.924497		323.15	H ₂ O	V	0.0919008	0.5444662	0.018015
		5.924497		323.15	H ₂	V	0.0131075	0.0776551	0.002016
		5.924497		323.15	CO ₂	V	0.0790824	0.4685232	0.04401
		5.924497		323.15	CO	V	0.004474	0.0265063	0.02801
		5.924497		323.15	HCOOH	V	1.048E-05	6.209E-05	0.046026
		5.924497		323.15	N ₂	V	0.7885791	4.6719343	0.028013
f Pump-around 3	-	13.744	40.00	313.15	HCHO	Aq	0.1994886	2.7417246	0.030026
		13.7437671	WATCH TS APPROACH	313.15	CH ₃ OH	Aq	0.002	0.0274875	0.032042
		13.7437671		313.15	H ₂ O	L	0.7984114	10.973181	0.018015
		13.7437671		313.15	HCOOH	Aq	0.0001	0.0013744	0.046026
Mass fraction of HCHO in total liquid fed: 19.81% (0.00843184) (0.04591577) (4.67E-05)									
Hence equilibrium partial pressure in the vapour: 1.04591577 (4.67E-05)									
Hence equilibrium mole fraction in the vapour: 0.00843184 (given a total pressure of: 124 kPa(abs))									
Check mass balances: 0									
Check mass balances: 0									
STREAMS OUT:									
No. Description	HYSIM	Flow [kg.s ⁻¹]	t [°C]	T [K]	Species	State	Mass frac. [-]	Mass Flow [kg.s ⁻¹]	MR [kg.mol ⁻¹]
h L from stage 3	-	0.65	51	324.15	HCHO	Aq	0.1994886	0.1296676	0.030026
		0.65		324.15	CH ₃ OH	Aq	0.002	0.0013	0.032042
		0.65		324.15	H ₂ O	L	0.7984114	0.5189674	0.018015
		0.65		324.15	HCOOH	Aq	0.0001	0.000065	0.046026
d V from stage 3	-	5.674	42.00	315.15	HCHO	V	0.0107321	0.0608993	0.030026
		5.674497		315.15	CH ₃ OH	V	7.288E-05	0.004136	0.032042
		5.674497		315.15	O ₂	V	0.0006406	0.0036353	0.031999
		5.674497		315.15	H ₂ O	V	0.0643075	0.3649129	0.018015
		5.674497		315.15	H ₂	V	0.0138849	0.0776551	0.002016
		5.674497		315.15	CO ₂	V	0.0825665	0.4685232	0.04401
		5.674497		315.15	CO	V	0.0046711	0.0265063	0.02801
		5.674497		315.15	HCOOH	V	3.011E-06	1.709E-05	0.046026
		5.674497		315.15	N ₂	V	0.8233213	4.6719343	0.028013
q Pump-around 3	-	13.744	51.00	324.15	HCHO	Aq	0.1994886	2.7417246	0.030026
		13.7437671		324.15	CH ₃ OH	Aq	0.002	0.0274875	0.032042
		13.7437671		324.15	H ₂ O	L	0.7984114	10.973181	0.018015
		13.7437671		324.15	HCOOH	Aq	0.0001	0.0013744	0.046026
Mass fraction of HCHO in total liquid fed: 19.81% (0.00843184) (0.04591577) (4.67E-05)									
Hence equilibrium partial pressure in the vapour: 1.04591577 (4.67E-05)									
Hence equilibrium mole fraction in the vapour: 0.00843184 (given a total pressure of: 124 kPa(abs))									
Check mass balances: 0									
Check mass balances: 0									
Pump-around flow: 13.744 kg.s ⁻¹ (0.0458612)									
Mass fraction of HCHO in liquid from stage above: 0.150415									
STREAMS IN:									
No. Description	HYSIM	Flow [kg.s ⁻¹]	t [°C]	T [K]	Species	State	Mass frac. [-]	Mass Flow [kg.s ⁻¹]	MR [kg.mol ⁻¹]
g L from stage 4	-	0.40	43.00	316.15	HCHO	Aq	0.150417	0.0601659	0.030026
		0.4	WATCH CROSS	316.15	CH ₃ OH	Aq	0.001	0.0004	0.032042
		0.4		316.15	H ₂ O	L	0.8485353	0.3394141	0.018015
		0.4		316.15	HCOOH	Aq	0.00005	0.00002	0.046026
c V from stage 2	-	5.924	50.00	323.15	HCHO	V	0.0220105	0.130401	0.030026
		5.924497		323.15	CH ₃ OH	V	0.0002217	0.0013136	0.032042
		5.924497		323.15	O ₂	V	0.0006136	0.0036353	0.031999
		5.924497		323.15	H ₂ O	V	0.0919008	0.5444662	0.018015
		5.924497		323.15	H ₂	V	0.0131075	0.0776551	0.002016
		5.924497		323.15	CO ₂	V	0.0790824	0.4685232	0.04401
		5.924497		323.15	CO	V	0.004474	0.0265063	0.02801
		5.924497		323.15	HCOOH	V	1.048E-05	6.209E-05	0.046026
		5.924497		323.15	N ₂	V	0.7885791	4.6719343	0.028013
f Pump-around 3	-	13.744	40.00	313.15	HCHO	Aq	0.1994886	2.7417246	0.030026
		13.7437671	WATCH TS APPROACH	313.15	CH ₃ OH	Aq	0.002	0.0274875	0.032042
		13.7437671		313.15	H ₂ O	L	0.7984114	10.973181	0.018015
		13.7437671		313.15	HCOOH	Aq	0.0001	0.0013744	0.046026
Mass fraction of HCHO in total liquid fed: 19.81% (0.00843184) (0.04591577) (4.67E-05)									
Hence equilibrium partial pressure in the vapour: 1.04591577 (4.67E-05)									
Hence equilibrium mole fraction in the vapour: 0.00843184 (given a total pressure of: 124 kPa(abs))									
Check mass balances: 0									
Check mass balances: 0									
STREAMS OUT:									
No. Description	HYSIM	Flow [kg.s ⁻¹]	t [°C]	T [K]	Species	State	Mass frac. [-]	Mass Flow [kg.s ⁻¹]	MR [kg.mol ⁻¹]
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		0.65		324.15	H ₂ O	L	0.7984114	0.5189674	0.018015
		0.65		324.15	HCOOH	Aq	0.0001	0.000065	0.046026
d V from stage 3	-	5.674	42.00	315.15	HCHO	V	0.0107321	0.0608993	0.030026
		5.674497		315.15	CH ₃ OH	V	7.288E-05	0.004136	0.032042
		5.674497		315.15	O ₂	V	0.0006406	0.0036353	0.031999
		5.674497		315.15	H ₂ O	V	0.0643075	0.3649129	0.018015
		5.674497		315.15	H ₂	V	0.0138849	0.0776551	0.002016
		5.674497		315.15	CO ₂	V	0.0825665	0.4685232	0.04401
		5.674497		315.15	CO	V	0.0046711	0.0265063	0.02801
		5.674497		315.15	HCOOH	V	3.011E-06	1.709E-05	0.046026
		5.674497		315.15	N ₂	V	0.8233213	4.6719343	0.028013
q Pump-around 3	-	13.744	51.00	324.15	HCHO	Aq	0.1994886	2.7417246	0.030026
		13.7437671		324.15	CH ₃ OH	Aq	0.002	0.0274875	0.032042
		13.7437671		324.15	H ₂ O	L	0.7984114	10.973181	0.018015
		13.7437671		324.15	HCOOH	Aq	0.0001	0.0013744	0.046026
Mass fraction of HCHO in total liquid fed: 19.81% (0.00843184) (0.04591577) (4.67E-05)									
Hence equilibrium partial pressure in the vapour: 1.04591577 (4.67E-05)									
Hence equilibrium mole fraction in the vapour: 0.00843184 (given a total pressure of: 124 kPa(abs))									
Check mass balances: 0									
Check mass balances: 0									
Pump-around flow: 13.744 kg.s ⁻¹ (0.0458612)									

Pump-around flow:	0.000	kg.s ⁻¹
Mass fraction of HCHO in liquid from stage above:	0	GOAL SEEK!

Serpentine inter-cooling req'd b/n TRAYS?

ABSORBER DETAILED DESIGN

Model of a simplified case:

Stage 1

Reference(s): Perry⁽⁶⁾, p. 14-20, 14-10.
 "van Laar VLE" worksheet [by D.I.V.], & the relevant references therein.
 "Diam.", "Visc.", "Gdiff" & "Ldiff" worksheets [D.I.V.], & references therein.
 HYSIM material
 I. Hahnenstein, H. Hasse, Y.-Q. Liu and G. Maurer; AIChE Symposium series
 Onda *et alii* - original reference.

Assumptions:

- Assume:**
1. Straight operating line (*i.e.* dilute solutions - small mass transfer)
 2. Straight equilibrium line (*i.e.* Henry's law is valid: $y_i = H_i x_i$)
 3. Absorption heat effects are negligible

Note: Perry's definition of the assumption is ambiguous, if not confusing.

Comment:

This implies constant flowrates.

This may be reasonable, based on data presented in worksheet "van Laar VLE".

This may or may not be valid:

- Hysim's simulation says a large amount of heat [in kW] is evolved
- however the absorber also has pump-around cooling, with large(?) liquid flow and so the actual temperature PROFILES in the absorber will not be great

Additionally, reaction is ignored.

Data:

Temperature at bottom of stage: LIQUID: 75.00 °C GAS: 90.00 °C

Temperature at top of stage: LIQUID: 60.20 °C GAS: 62.00 °C

It is assumed that thermal equilibrium is (almost) reached.

Thus a nominal column temperature of 67.60214 °C will be used here

± 10°C, say.

Pressures:

TOP: 125 kPa(abs)
 BOTTOM: 130 kPa(abs)
 AVERAGE: 127.5 kPa(abs)

Estimate.

Henry's constant: ("m")

By linear regression of AIChE.J data in worksheet "van Laar VLE": 0.7514 (70°C)
 By weighted least squares regression of the above: (approx.) 1 (70°C)
 Data from Ullmann's⁽⁵⁾ & Walker⁽³⁾: << 1
 All other estimates, including Raoult's law: >> 1 (60°C)
 Hence use the value: 0.7514

This was only based on x_{HCHO} under 0.20

This assumes equilibrium of reaction.

This doesn't consider liquid-phase formation of nonvolatiles.

On the conservative side.

THESE DO NOT CONSIDER INERTS PRESENT

Flows:

TOTAL liquid inflow: 1372.037 mol.s⁻¹
 TOTAL liquid outflow: 1401.164 mol.s⁻¹
 RATIO of BOTTOM to TOP liquid flows: 1.021229
 Average stage TOTAL liquid flow: 1386.6 mol.s⁻¹

Thus the flow may be considered constant.

This average is justified by the high pump-around rate.

Vapour inflow: 332.913 mol.s⁻¹
 Vapour outflow: 303.7859 mol.s⁻¹
 RATIO of BOTTOM to TOP vapour flows: 1.09588
 Average (total) vapour flow: 318.3495 mol.s⁻¹

Note: no vapour recirculation.

This is really NOT too large to assume constant flow.

Mean molar masses:

GAS: 0.0231 kg.mol⁻¹
 LIQUID: 0.022944 kg.mol⁻¹

Worksheet "Diam."

Worksheet "Diam."

Mole-fractions:

Mole-fraction of formaldehyde in vapour: TOP: 0.055279
 BOTTOM: 0.1430
 AVERAGE: 0.099133

NOTE: This average for reference only.

(based on a 99.5% nominal approach to equilibrium)

There will be some formaldehyde in the pump-around liquid(!)...

...but too high would cause more formaldehyde to escape more easily.

The similarity is due to the large pump-around.

Mole-fraction of formaldehyde in liquid: TOP: 0.4020
 BOTTOM: 0.4156
 AVERAGE: 0.408822

Mole-fraction IN EQUILIBRIUM WITH liquid: TOP: 0.0548
 BOTTOM: 0.0920
 AVERAGE: 0.073439

Note that temperature is the dominant effect here.

Equilibrium:

Hence "m": TOP: 0.136412
 BOTTOM: 0.221442
 AVERAGE: 0.179636

Defined by $y_{\text{equilibrium}} = m \cdot x$

Actual mean: 0.178927

Diameter:

1.8 m

Calculated in worksheet "Diam."

Flooding:

DESIGN: 73%
 TURNDOWN: 44%

Worksheet "Diam."

Worksheet "Diam."

Internals:

Type: Pall rings
 Material: S.S.
 σ_c : 75 mN.m⁻¹
 Nominal size: 0.051 m
 a_i : 102 m².m⁻³

Sinnott⁽²⁾

i.e. 2 inches.

Fluid properties:

μ_G : 1.66E-05 Pa.s

See worksheet "Visc."

μ_L :	1.89E-03 Pa.s	Worksheet "Diam."
D_G :	0.174 cm ² .s ⁻¹	See worksheet "GDiff".
D_L :	3.5E-05 cm ² .s ⁻¹	See worksheet "LDiff".
ρ_G :	1.04 kg.m ⁻³	Worksheet "Diam."
ρ_L :	1132 kg.m ⁻³	Worksheet "Diam."
σ :	WATER, 303.15K: 71.40 dyn.cm ⁻¹ WATER, 293.15K: 70 mN.m ⁻¹ WATER, 293K: 72.8 dyn.cm ⁻¹ WATER, 303K: 71.18 dyn.cm ⁻¹ METHANOL, 333K: 19.41 dyn.cm ⁻¹ ACETONE, 318K: 21.22 dyn.cm ⁻¹ FORMAMIDE, 338K: 53.66 dyn.cm ⁻¹ METHYL FORMATE, 298K: 24.62 dyn.cm ⁻¹ METHYL FORMATE, 323K: 20.05 dyn.cm ⁻¹ METHYL FORMATE, 373K: 12.90 dyn.cm ⁻¹ ASSUME: 60 dyn.cm ⁻¹	Perry ⁽⁶⁾ Sinnott ⁽²⁾ R, P & P ⁽⁴⁾ R, P & P ⁽⁴⁾ R, P & P ⁽⁴⁾ R, P & P ⁽⁴⁾ R, P & P ⁽⁴⁾ R, P & P ⁽⁴⁾ R, P & P ⁽⁴⁾ Surface tension reduces with T rising.

Mass-transfer coefficients:

Liquid "film":	Calculated; see below.
Vapour "film":	Calculated; see below.
Overall:	Calculated; see below.

Equations:

Height: $h_{bed} = H_{Oy}.N_{Oy}$

H_{Oy} : $H_{Oy} = G_M / [(K_y \cdot a) \cdot y^*_{BM}]$
 where:
 $y^*_{BM} = \{(1 - y) - (1 - y^*)\} / \ln\{(1 - y)/(1 - y^*)\}$
 with y^* the equilibrium gas-phase mole fraction, such that $y^* = m \cdot x$
 and the rate of mass transfer, $N_i = K_y \cdot (y_i - y^*)$, defines the overall gas-phase mass transfer coefficient
 This K_y can also be expressed in terms of the "film" coefficients, viz. :
 $1/K_y = 1/k_y + m/k_x$

NOTE: Prosy W. M. Edwards (& predecessors) use a different notation - care!!

From Onda *et alii* :

$k_L \cdot (\rho_L / \mu_L \cdot g)^{1/3} / \{(\mu_L / \rho_L \cdot D_L)^{-1/2} \cdot (a_t \cdot D_p)^{0.4}\}$ is correlated against $(Re)_L = L / (a_w \cdot \mu_L)$
 $\{(k_G \cdot R \cdot T) / (a_t \cdot D_G)\} / \{(\mu_G / \rho_G \cdot D_G)^{-1/3} \cdot (a_t \cdot D_p)^{-2.0}\}$ is correlated against $(Re)_G = G / (a_t \cdot \mu_G)$
 $a_w / a_t = 1 - \exp\{-1.45(\sigma_w / \sigma)^{0.75} \cdot (L / a_t \cdot \mu_L)^{0.1} \times (L^2 \cdot a_t / (\rho_L^2 \cdot g))^{-0.05} \cdot (L^2 / (\rho_L \cdot \sigma \cdot a_t))^{0.2}\}$
 Where $[G] = [L] = \text{kg.m}^{-2} \cdot \text{s}^{-1}$ a_w is the "effective" - wetted - area per volume

Where: $K_G = K_y / P$ Where: $k_G = k_y / P$ Where: $k_L = k_x / \rho_L$

From Uhlherr, CHE3102 notes.

Alternatively, an estimate may be obtained from Cornell's method (Sinnott⁽²⁾, updated by Bolles/Fair)

$$H_y[m] = 0.0190283 \cdot \psi_h[m] \cdot (Sc)_v^{0.5} \cdot (D_c / 0.3048)^{1.24} \cdot (Z / 3.048)^{(1/3)} / \{L \cdot (\mu_L / \mu_w)^{0.16} \cdot (\rho_w / \rho_L)^{1.25} \cdot (\sigma_w / \sigma_L)^{0.8}\}^{0.6}$$

$$H_x[m] = \phi_h[m] \cdot (Sc)_L^{0.5} \cdot K_3 \cdot (Z / 3.048)^{0.15}$$

Where D_c is a "corrected" diameter: the lesser of {diameter} or $\{2 \times 0.3048\}$.

Where $\mu_w = 1.002 \text{ mPa.s}$ $\rho_w = 998.2032 \text{ kg.m}^{-3}$ $\sigma_w = 70 \text{ mN.m}^{-1}$ (All at 20°C)

And $H_{Oy} = H_y + (m \cdot G_M / L_M) \cdot H_x$ NOTE: use of the coefficient $(m \cdot G_M / L_M)$ implied the subscripts "Oy", "y" and "x" by CHE3102/Uhlherr.

N_{Oy} : Colburn's equation of 1939 is:

$$N_{Oy} = 1 / \{1 - (m \cdot G_M / L_M)\} \times \ln\{[1 - (m \cdot G_M / L_M)] \times \{(y_1 - m \cdot x_2) / (y_2 - m \cdot x_2)\} + m \cdot G_M / L_M\}$$

Note: the G_M and L_M are (moles per time) per unit area (of the column).

"m" is a Henry's law-type constant here:

$$y_{\text{equilibrium } i} = m \cdot x_i$$

Feintuch/Treybal(1978) present an "Edmister-type approach":

$$N_{Oy} = \ln\{[(y_1 - y_2^*) / (y_2 - y_2^*)] \cdot (1 - 1/A_E) + 1/A_E\} / (1 - 1/A_E)$$

where $A_E = [A_{\text{BOTTOM}} \cdot (A_{\text{TOP}} + 1) + 0.25]^{0.5} - 0.5$

and $(1/A_E) = (m \cdot G_i / L_i)$

Calculations:

N_{Oy} : According to Colburn:

$$(m \cdot G_M / L_M) = 0.041243$$

$$\{1 - (m \cdot G_M / L_M)\} = 0.958757$$

$$\therefore N_{Oy} = 5.482$$

According to Feintuch & Treybal:

$$A_{\text{BOTTOM}} = 19.00635$$

$$A_{\text{TOP}} = 33.10883$$

The big difference here means the more sophisticated average is probably worth calculating!

$$A_E = 24.96634 \quad (\text{cf. arithmetic mean of } 26.05759)$$

$$\therefore N_{Oy} = 5.477$$

This non-simple short-cut method has resulted in a **VERY SIMILAR** result to the result from Colburn.

H_{Oy} y_{BM}^* = TOP: 0.944941
 BOTTOM: 0.882242
 AVERAGE: 0.913592

"Averages" are just simple, arithmetic.

G_M = TOP: 130.8265 mol.m⁻².s⁻¹
 BOTTOM: 119.3803 mol.m⁻².s⁻¹
 AVERAGE: 125.1034 mol.m⁻².s⁻¹

From the data of Onda et alii:

$L = 12.5021 \text{ kg.m}^{-2}.\text{s}^{-1}$ **OKAY**
 $(\sigma/\sigma)^{0.75} = 1.1822$ $(L/a_t \mu_L)^{0.1} = 1.5175$ $(L^2 a_t / (\rho_L^2 g))^{0.05} = 1.3958$ **OKAY**
 $(\sigma/\sigma)^{0.75} = 1.1822$ $(L/a_t \mu_L)^{0.1} = 1.5175$ $(L^2 a_t / (\rho_L^2 g))^{0.05} = 1.3958$ $(L^2 / (\rho_L \sigma a_t))^{0.2} = 0.4685$
 Bolles/Fair: $0.3 < \sigma_c / \sigma < 2$ Bolles/Fair: $2.5e-9 < Fr_L < 0.018$ Bolles/Fair: $1.2e-8 < We_L < 0.27$
 $a_w = 83.4 \text{ m}^2.\text{m}^{-3}$
 $(Re)_L = 7.92E+01$ **OKAY** $(\mu_L / \rho_L D_L)^{-1/2} = 0.046027$ $(a_t D_p)^{0.4} = 1.934052$
 Bolles/Fair: $0.04 < Re_L < 500$

Hence: $k_L (\rho_L / \mu_L g)^{1/3} = 0.00985$ where 0.0060 (cf. 0.0051) is the constant for this large, modern packing

Thus, $k_L = 0.00025 \text{ m.s}^{-1}$
 $\rho_B = 49341 \text{ mol.m}^{-3}$
 $\therefore k_x = 12.35 \text{ mol.m}^{-2}.\text{s}^{-1}$

$G = 2.8898 \text{ kg.m}^{-2}.\text{s}^{-1}$
 $(Re)_G = 1.71E+03$ **OFF SCALE!** $(\mu_G / \rho_G D_G)^{-1/3} = 1.027408$ $(a_t D_p)^{-2.0} = 0.036954$
 Hence: $(k_G R T) / (a_t D_G) = 41.708$ where 6.00 (cf. 5.23) is the constant for this large, modern packing

Thus, $k_G = 2.54E-05 \text{ mol.Pa}^{-1}.\text{m}^{-2}.\text{s}^{-1}$ $0.000258 \text{ mol.atm}^{-1}.\text{cm}^{-2}.\text{s}^{-1}$
 $P = 128 \text{ kPa(absolute)}$
 $\therefore k_y = 3.24 \text{ mol.m}^{-2}.\text{s}^{-1}$

We see that the gas-phase resistance is dominant... (...also, "m" is small).

Hence: $K_y = 3.098 \text{ mol.m}^{-2}.\text{s}^{-1}$

$\therefore H_{Oy} = 0.530 \text{ m}$

cf. The data of the Norton Co. (for specific conditions) in Perry⁽⁶⁾, p. 14-34, T14-4:

$K_y \cdot a \cdot y_{BM}^* = 114 \text{ kmol.h}^{-1}.\text{m}^{-3}$
 i.e. $31.667 \text{ mol.m}^{-3}.\text{s}^{-1}$
 Whence $H_{Oy} = 3.951 \text{ m}$

Height: $h_{bed} = 2.91 \text{ m}$

H_{Oy} By Cornell's (updated) method:

Flooding: 73% $K_3 = 0.69$
 (At design percentage flooding, from charts in Bolles/Fair & Sinnott⁽²⁾)
 Flooding: 73% $\psi_h = 140 \text{ ft}$ 42.672 m
 $L [lb_m.h^{-1}.ft^{-2}] = 9.22E+03$ $\phi_h = 0.105 \text{ ft}$ 0.032004 m
 (At design percentage flooding, from charts in Bolles/Fair: specific to metal Pall rings.)
 Estimated height, "Z" = 1.93 m
 $(Sc)_v^{0.5} = 0.960253$ $D_c = 0.6096 \text{ m}$
 $\{L \cdot (\mu_L / \mu_w)^{0.16} \cdot (\rho_w / \rho_L)^{1.25} \cdot (\sigma_w / \sigma_L)^{0.8}\} = 13.37842 \text{ kg.m}^{-2}.\text{s}^{-1}$
 $H_y = 0.333588 \text{ m}$

$(Sc)_L^{0.5} = 21.7266$
 $H_x = 0.447998 \text{ m}$

$\therefore H_{Oy} = 0.352 \text{ m}$
 (We note that the extraordinarily low value of $m \cdot G_M / L_M$ means the contribution of H_x is ~negligible.)

Height: $h_{bed} = 1.93 \text{ m}$ (or 2.25 m without height-correction)

ABSORBER DETAILED DESIGN

Model of a simplified case:

Stage 2

Reference(s): Perry⁽⁶⁾, p. 14-20, 14-10.
 "van Laar VLE" worksheet [by D.I.V.], & the relevant references therein.
 "Diam.", "Visc.", "Gdiff" & "Ldiff" worksheets [D.I.V.], & references therein.
 HYSIM material
 I. Hahnenstein, H. Hasse, Y.-Q. Liu and G. Maurer; AIChE Symposium series
 Onda *et alii* - original reference.

Assumptions:

Assume:

1. Straight operating line (*i.e.* dilute solutions - small mass transfer)
2. Straight equilibrium line (*i.e.* Henry's law is valid: $y_i = H_i x_i$)
3. Absorption heat effects are negligible

Note: Perry's definition of the assumption is ambiguous, if not confusing.

Comment:

This implies constant flowrates.

This may be reasonable, based on data presented in worksheet "van Laar VLE".

This may or may not be valid:

- Hysim's simulation says a large amount of heat [in kW] is evolved
- however the absorber also has pump-around cooling, with large(?) liquid flow and so the actual temperature PROFILES in the absorber will not be great

Additionally, reaction is ignored.

Data:

Temperature at bottom of stage: LIQUID: 63.00 °C GAS: 62.00 °C

Temperature at top of stage: LIQUID: 48.05 °C GAS: 50.00 °C

It is assumed that thermal equilibrium is (almost) reached.

Thus a nominal column temperature of 55.52624 °C will be used here

± 10°C, say.

Pressures:

TOP: 120 kPa(abs)
 BOTTOM: 125 kPa(abs)
 AVERAGE: 122.5 kPa(abs)

Estimate.

Henry's constant: ("m")

By linear regression of AIChE.J data in worksheet "van Laar VLE": 0.7514 (70°C)
 By weighted least squares regression of the above: (approx.) 1 (70°C)
 Data from Ullmann's⁽⁵⁾ & Walker⁽³⁾: << 1
 All other estimates, including Raoult's law: >> 1 (60°C)
 Hence use the value: 0.7514

This was only based on x_{HCHO} under 0.20

This assumes equilibrium of reaction.

This doesn't consider liquid-phase formation of nonvolatiles.

On the conservative side.

THESE DO NOT CONSIDER INERTS PRESENT

Flows:

TOTAL liquid inflow: 2048.583 mol.s⁻¹
 TOTAL liquid outflow: 2100.757 mol.s⁻¹
 RATIO of BOTTOM to TOP liquid flows: 1.025468
 Average stage TOTAL liquid flow: 2074.67 mol.s⁻¹

Thus the flow may be considered constant.

This average is justified by the high pump-around rate.

Vapour inflow: 303.7859 mol.s⁻¹
 Vapour outflow: 251.6118 mol.s⁻¹
 RATIO of BOTTOM to TOP vapour flows: 1.20736
 Average (total) vapour flow: 277.6989 mol.s⁻¹

Note: no vapour recirculation.

This is really NOT too large to assume constant flow.

Mean molar masses:

GAS: 0.023546 kg.mol⁻¹
 LIQUID: 0.020408 kg.mol⁻¹

Worksheet "Diam."

Worksheet "Diam."

Mole-fractions:

Mole-fraction of formaldehyde in vapour: TOP: 0.01726
 BOTTOM: 0.0553
 AVERAGE: 0.03627

NOTE: This average for reference only.

(based on a 99.5% nominal approach to equilibrium)

There will be some formaldehyde in the pump-around liquid(!)...

...but too high would cause more formaldehyde to escape more easily.

The similarity is due to the large pump-around.

Mole-fraction of formaldehyde in liquid: TOP: 0.1954
 BOTTOM: 0.1965
 AVERAGE: 0.195952

Mole-fraction IN EQUILIBRIUM WITH liquid: TOP: 0.0171
 BOTTOM: 0.0279
 AVERAGE: 0.022462

Note that temperature is the dominant effect here.

Equilibrium:

Hence "m": TOP: 0.087349
 BOTTOM: 0.141761
 AVERAGE: 0.11463

Defined by $y_{\text{equilibrium}} = m \cdot x$

Actual mean: 0.114555

Diameter:

1.8 m

Calculated in worksheet "Diam."

Flooding:

DESIGN: 58%
 TURNDOWN: 35%

Worksheet "Diam."

Worksheet "Diam."

Internals:

Type: Pall rings
 Material: S.S.
 σ_c : 75 mN.m⁻¹
 Nominal size: 0.051 m
 a_i : 102 m².m⁻³

Sinnott⁽²⁾

i.e. 2 inches.

Fluid properties:

μ_G : 1.66E-05 Pa.s

See worksheet "Visc."

μ_L :	5.44E-04 Pa.s	Worksheet "Diam."
D_G :	0.174 cm ² .s ⁻¹	See worksheet "GDiff".
D_L :	2.9E-05 cm ² .s ⁻¹	See worksheet "LDiff".
ρ_G :	1.05 kg.m ⁻³	Worksheet "Diam."
ρ_L :	1071 kg.m ⁻³	Worksheet "Diam."
σ :	WATER, 303.15K: 71.40 dyn.cm ⁻¹ WATER, 293.15K: 70 mN.m ⁻¹ WATER, 293K: 72.8 dyn.cm ⁻¹ WATER, 303K: 71.18 dyn.cm ⁻¹ METHANOL, 333K: 19.41 dyn.cm ⁻¹ ACETONE, 318K: 21.22 dyn.cm ⁻¹ FORMAMIDE, 338K: 53.66 dyn.cm ⁻¹ METHYL FORMATE, 298K: 24.62 dyn.cm ⁻¹ METHYL FORMATE, 323K: 20.05 dyn.cm ⁻¹ METHYL FORMATE, 373K: 12.90 dyn.cm ⁻¹ ASSUME: 60 dyn.cm ⁻¹	Perry ⁽⁶⁾ Sinnott ⁽²⁾ R, P & P ⁽⁴⁾ R, P & P ⁽⁴⁾ R, P & P ⁽⁴⁾ R, P & P ⁽⁴⁾ R, P & P ⁽⁴⁾ R, P & P ⁽⁴⁾ R, P & P ⁽⁴⁾ Surface tension reduces with T rising.

Mass-transfer coefficients:

Liquid "film":	Calculated; see below.
Vapour "film":	Calculated; see below.
Overall:	Calculated; see below.

Equations:

Height: $h_{bed} = H_{Oy}.N_{Oy}$

H_{Oy} : $H_{Oy} = G_M / [(K_y \cdot a) \cdot y^*_{BM}]$
 where:
 $y^*_{BM} = \{(1 - y) - (1 - y^*)\} / \ln\{(1 - y)/(1 - y^*)\}$
 with y^* the equilibrium gas-phase mole fraction, such that $y^* = m \cdot x$
 and the rate of mass transfer, $N_i = K_y \cdot (y_i - y^*)$, defines the overall gas-phase mass transfer coefficient
 This K_y can also be expressed in terms of the "film" coefficients, viz. :
 $1/K_y = 1/k_y + m/k_x$

NOTE: Prox W. M. Edwards (& predecessors) use a different notation - care!!

From Onda *et alii* :

$k_L \cdot (\rho_L / \mu_L \cdot g)^{1/3} / \{(\mu_L / \rho_L \cdot D_L)^{-1/2} \cdot (a_t \cdot D_p)^{0.4}\}$ is correlated against $(Re)_L = L / (a_w \cdot \mu_L)$
 $\{(k_G \cdot R \cdot T) / (a_t \cdot D_G)\} / \{(\mu_G / \rho_G \cdot D_G)^{-1/3} \cdot (a_t \cdot D_p)^{-2.0}\}$ is correlated against $(Re)_G = G / (a_t \cdot \mu_G)$
 $a_w / a_t = 1 - \exp\{-1.45(\sigma_w / \sigma)^{0.75} \cdot (L / a_t \cdot \mu_L)^{0.1} \times (L^2 \cdot a_t / (\rho_L^2 \cdot g))^{-0.05} \cdot (L^2 / (\rho_L \cdot \sigma \cdot a_t))^{0.2}\}$
 Where $[G] = [L] = \text{kg.m}^{-2} \cdot \text{s}^{-1}$ a_w is the "effective" - wetted - area per volume

Where: $K_G = K_y / P$ Where: $k_G = k_y / P$ Where: $k_L = k_x / \rho_L$

From Uhlherr, CHE3102 notes.

Alternatively, an estimate may be obtained from Cornell's method (Sinnott⁽²⁾, updated by Bolles/Fair)

$$H_y[m] = 0.0190283 \cdot \psi_h[m] \cdot (Sc)_v^{0.5} \cdot (D_c / 0.3048)^{1.24} \cdot (Z / 3.048)^{(1/3)} / \{L \cdot (\mu_L / \mu_w)^{0.16} \cdot (\rho_w / \rho_L)^{1.25} \cdot (\sigma_w / \sigma_L)^{0.8}\}^{0.6}$$

$$H_x[m] = \phi_h[m] \cdot (Sc)_L^{0.5} \cdot K_3 \cdot (Z / 3.048)^{0.15}$$

Where D_c is a "corrected" diameter: the lesser of {diameter} or $\{2 \times 0.3048\}$.

Where $\mu_w = 1.002 \text{ mPa.s}$ $\rho_w = 998.2032 \text{ kg.m}^{-3}$ $\sigma_w = 70 \text{ mN.m}^{-1}$ (All at 20°C)

And $H_{Oy} = H_y + (m \cdot G_M / L_M) \cdot H_x$ NOTE: use of the coefficient $(m \cdot G_M / L_M)$ implied the subscripts "Oy", "y" and "x" by CHE3102/Uhlherr.

N_{Oy} : Colburn's equation of 1939 is:

$$N_{Oy} = 1 / \{1 - (m \cdot G_M / L_M)\} \times \ln\{[1 - (m \cdot G_M / L_M)] \times \{(y_1 - m \cdot x_2) / (y_2 - m \cdot x_2)\} + m \cdot G_M / L_M\}$$

Note: the G_M and L_M are (moles per time) per unit area (of the column).

"m" is a Henry's law-type constant here:

$$y_{\text{equilibrium}} = m \cdot x_1$$

Feintuch/Treybal(1978) present an "Edmister-type approach":

$$N_{Oy} = \ln\{[(y_1 - y_2^*) / (y_2 - y_2^*)] \cdot (1 - 1/A_E) + 1/A_E\} / (1 - 1/A_E)$$

where $A_E = [A_{\text{BOTTOM}} \cdot (A_{\text{TOP}} + 1) + 0.25]^{0.5} - 0.5$

and $(1/A_E) = (m \cdot G_i / L_i)$

Calculations:

N_{Oy} : According to Colburn:

$$(m \cdot G_M / L_M) = 0.015343$$

$$\{1 - (m \cdot G_M / L_M)\} = 0.984657$$

$$\therefore N_{Oy} = 5.365$$

According to Feintuch & Treybal:

$$A_{\text{BOTTOM}} = 48.78104$$

$$A_{\text{TOP}} = 93.21043$$

The big difference here means the more sophisticated average is probably worth calculating!

$$A_E = 67.29331 \quad (\text{cf. arithmetic mean of } 70.99574)$$

$$\therefore N_{Oy} = 5.363$$

This non-simple short-cut method has resulted in a **VERY SIMILAR** result to the result from Colburn.

$$H_{Oy}: \quad Y_{BM}^* = \begin{array}{l} \text{TOP: } 0.982835 \\ \text{BOTTOM: } 0.958368 \\ \text{AVERAGE: } 0.970601 \end{array}$$

"Averages" are just simple, arithmetic.

$$G_M = \begin{array}{l} \text{TOP: } 119.3803 \text{ mol.m}^{-2}.\text{s}^{-1} \\ \text{BOTTOM: } 98.8772 \text{ mol.m}^{-2}.\text{s}^{-1} \\ \text{AVERAGE: } 109.1288 \text{ mol.m}^{-2}.\text{s}^{-1} \end{array}$$

From the data of Onda et alii:

$$\begin{array}{l} L = 16.6389 \text{ kg.m}^{-2}.\text{s}^{-1} \quad \text{OKAY} \\ (\sigma_L/\sigma)^{0.75} = 1.1822 \quad (L/a_L \mu_L)^{0.1} = 1.7689 \quad (L^2 a_L / (\rho_L^2 g))^{0.05} = 1.3490 \quad (L^2 / (\rho_L \sigma a_L))^{0.2} = 0.5311 \quad \text{OKAY} \\ \text{Bolles/Fair: } 0.3 < \sigma_L / \sigma < 2 \quad \text{Bolles/Fair: } 2.5e-9 < Fr_L < 0.018 \quad \text{Bolles/Fair: } 1.2e-8 < We_L < 0.27 \\ a_w = 90.4 \text{ m}^2.\text{m}^{-3} \\ (Re)_L = 3.38E+02 \quad \text{OKAY} \quad (\mu_L / \rho_L D_L)^{-1/2} = 0.075777 \quad (a_L D_p)^{0.4} = 1.934052 \end{array}$$

$$\text{Hence: } k_L (\rho_L / \mu_L g)^{1/3} = 0.04270 \quad \text{where } 0.0060 \text{ (cf. } 0.0051) \text{ is the constant for this large, modern packing}$$

$$\begin{array}{l} \text{Thus, } k_L = 0.000729 \text{ m.s}^{-1} \\ \rho_B = 52479 \text{ mol.m}^{-3} \\ \therefore k_x = 38.26 \text{ mol.m}^{-2}.\text{s}^{-1} \end{array}$$

$$\begin{array}{l} G = 2.5696 \text{ kg.m}^{-2}.\text{s}^{-1} \\ (Re)_G = 1.52E+03 \quad \text{OFF SCALE!} \quad (\mu_G / \rho_G D_G)^{-1/3} = 1.032485 \quad (a_G D_p)^{-2.0} = 0.036954 \\ \text{Hence: } (k_G R.T) / (a_G D_G) = 38.606 \quad \text{where } 6.00 \text{ (cf. } 5.23) \text{ is the constant for this large, modern packing} \end{array}$$

$$\begin{array}{l} \text{Thus, } k_G = 2.5E-05 \text{ mol.Pa}^{-1}.\text{m}^{-2}.\text{s}^{-1} \quad 0.000253 \text{ mol.atm}^{-1}.\text{cm}^{-2}.\text{s}^{-1} \\ P = 123 \text{ kPa(abs)} \\ \therefore k_y = 3.06 \text{ mol.m}^{-2}.\text{s}^{-1} \end{array}$$

We see that the gas-phase resistance is dominant.... (...also, "m" is small).

$$\text{Hence: } K_y = 3.033 \text{ mol.m}^{-2}.\text{s}^{-1}$$

$$\therefore H_{Oy} = 0.410 \text{ m}$$

cf. The data of the Norton Co. (for specific conditions) in Perry⁽⁶⁾, p. 14-34, T14-4:

$$\begin{array}{l} K_y \cdot a \cdot Y_{BM}^* = 114 \text{ kmol.h}^{-1}.\text{m}^{-3} \\ \text{i.e. } 31.667 \text{ mol.m}^{-3}.\text{s}^{-1} \\ \text{Whence } H_{Oy} = 3.446 \text{ m} \end{array}$$

$$\text{Height: } h_{bed} = 2.20 \text{ m}$$

H_{Oy} : By Cornell's (updated) method:

$$\begin{array}{l} \text{Flooding: } 58\% \quad K_3 = 0.90 \\ \text{(At design percentage flooding, from charts in Bolles/Fair \& Sinnott}^{(2)}) \\ \text{Flooding: } 58\% \quad \psi_h = 140 \text{ ft} \quad 42.672 \text{ m} \\ L [lb_m.h^{-1}.ft^{-2}]: 1.23E+04 \quad \phi_h = 0.120 \text{ ft} \quad 0.036576 \text{ m} \\ \text{(At design percentage flooding, from charts in Bolles/Fair: specific to metal Pall rings.)} \\ \text{Estimated height, "Z" = } 1.53 \text{ m} \\ (Sc)_v^{0.5} = 0.953179 \quad D_c = 0.6096 \text{ m} \\ \{L \cdot (\mu_L / \mu_w)^{0.16} \cdot (\rho_w / \rho_L)^{1.25} \cdot (\sigma_w / \sigma_L)^{0.8}\} = 15.63202 \text{ kg.m}^{-2}.\text{s}^{-1} \\ H_y = 0.279133 \text{ m} \\ (Sc)_L^{0.5} = 13.19657 \\ H_x = 0.391743 \text{ m} \\ \therefore H_{Oy} = 0.285 \text{ m} \\ \text{(We note that the extraordinarily low value of } m.G_M/L_M \text{ means the contribution of } H_x \text{ is ~negligible.)} \end{array}$$

$$\text{Height: } h_{bed} = 1.53 \text{ m} \quad (\text{or } 1.93 \text{ m without height-correction})$$

ABSORBER DETAILED DESIGN

Model of a simplified case:

Stage 3

Reference(s): Perry⁽⁶⁾, p. 14-20, 14-10.
 "van Laar VLE" worksheet [by D.I.V.], & the relevant references therein.
 "Diam.", "Visc.", "Gdiff" & "Ldiff" worksheets [D.I.V.], & references therein.
 HYSIM material
 I. Hahnenstein, H. Hasse, Y.-Q. Liu and G. Maurer; AIChE Symposium series
 Onda *et alii* - original reference.

Assumptions:

Assume:

1. Straight operating line (*i.e.* dilute solutions - small mass transfer)
2. Straight equilibrium line (*i.e.* Henry's law is valid: $y_i = H_i x_i$)
3. Absorption heat effects are negligible

Note: Perry's definition of the assumption is ambiguous, if not confusing.

Comment:

This implies constant flowrates.

This may be reasonable, based on data presented in worksheet "van Laar VLE".

This may or may not be valid:

- Hysim's simulation says a large amount of heat [in kW] is evolved
- however the absorber also has pump-around cooling, with large(?) liquid flow and so the actual temperature PROFILES in the absorber will not be great

Additionally, reaction is ignored.

Data:

Temperature at bottom of stage: LIQUID: 51.00 °C GAS: 50.00 °C

Temperature at top of stage: LIQUID: 40.09 °C GAS: 42.00 °C

It is assumed that thermal equilibrium is (almost) reached.

Thus a nominal column temperature of 45.54601 °C will be used here

± 10°C, say.

Pressures:

TOP: 115 kPa(abs)
 BOTTOM: 120 kPa(abs)
 AVERAGE: 117.5 kPa(abs)

Estimate.

Henry's constant: ("m")

By linear regression of AIChE.J data in worksheet "van Laar VLE": 0.7514 (70°C)
 By weighted least squares regression of the above: (approx.) 1 (70°C)
 Data from Ullmann's⁽⁵⁾ & Walker⁽³⁾: << 1
 All other estimates, including Raoult's law: >> 1 (60°C)
 Hence use the value: 0.7514

This was only based on x_{HCHO} under 0.20

This assumes equilibrium of reaction.

This doesn't consider liquid-phase formation of nonvolatiles.

On the conservative side.

THESE DO NOT CONSIDER INERTS PRESENT

Flows:

TOTAL liquid inflow: 722.1627 mol.s⁻¹
 TOTAL liquid outflow: 734.4732 mol.s⁻¹
 RATIO of BOTTOM to TOP liquid flows: 1.017047
 Average stage TOTAL liquid flow: 728.318 mol.s⁻¹

Thus the flow may be considered constant.

This average is justified by the high pump-around rate.

Vapour inflow: 251.6118 mol.s⁻¹
 Vapour outflow: 239.3013 mol.s⁻¹
 RATIO of BOTTOM to TOP vapour flows: 1.051444
 Average (total) vapour flow: 245.4566 mol.s⁻¹

Note: no vapour recirculation.

This is really NOT too large to assume constant flow.

Mean molar masses:

GAS: 0.023713 kg.mol⁻¹
 LIQUID: 0.019585 kg.mol⁻¹

Worksheet "Diam."

Worksheet "Diam."

Mole-fractions:

Mole-fraction of formaldehyde in vapour: TOP: 0.008476
 BOTTOM: 0.0173
 AVERAGE: 0.012868

NOTE: This average for reference only.

(based on a 99.5% nominal approach to equilibrium)

There will be some formaldehyde in the pump-around liquid(!)...

...but too high would cause more formaldehyde to escape more easily.

The similarity is due to the large pump-around.

Mole-fraction of formaldehyde in liquid: TOP: 0.1292
 BOTTOM: 0.1302
 AVERAGE: 0.129709

Mole-fraction IN EQUILIBRIUM WITH liquid: TOP: 0.0084
 BOTTOM: 0.0118
 AVERAGE: 0.010125

Note that temperature is the dominant effect here.

Equilibrium:

Hence "m": TOP: 0.06525
 BOTTOM: 0.090774
 AVERAGE: 0.078061

Defined by $y_{\text{equilibrium}} = m \cdot x$

Actual mean: 0.078012

Diameter:

1.8 m

Calculated in worksheet "Diam."

Flooding:

DESIGN: 53%
 TURNDOWN: 32%

Worksheet "Diam."

Worksheet "Diam."

Internals:

Type: Pall rings
 Material: S.S.
 σ_c : 75 mN.m⁻¹
 Nominal size: 0.051 m
 a_i : 102 m².m⁻³

Sinnott⁽²⁾

i.e. 2 inches.

Fluid properties:

μ_G : 1.66E-05 Pa.s

See worksheet "Visc."

μ_L :	6.28E-04 Pa.s	Worksheet "Diam."
D_G :	0.174 cm ² .s ⁻¹	See worksheet "GDiff".
D_L :	2.4E-05 cm ² .s ⁻¹	See worksheet "LDiff".
ρ_G :	1.04 kg.m ⁻³	Worksheet "Diam."
ρ_L :	1050 kg.m ⁻³	Worksheet "Diam."
σ :	WATER, 303.15K: 71.40 dyn.cm ⁻¹ WATER, 293.15K: 70 mN.m ⁻¹ WATER, 293K: 72.8 dyn.cm ⁻¹ WATER, 303K: 71.18 dyn.cm ⁻¹ METHANOL, 333K: 19.41 dyn.cm ⁻¹ ACETONE, 318K: 21.22 dyn.cm ⁻¹ FORMAMIDE, 338K: 53.66 dyn.cm ⁻¹ METHYL FORMATE, 298K: 24.62 dyn.cm ⁻¹ METHYL FORMATE, 323K: 20.05 dyn.cm ⁻¹ METHYL FORMATE, 373K: 12.90 dyn.cm ⁻¹ ASSUME: 60 dyn.cm ⁻¹	Perry ⁽⁶⁾ Sinnott ⁽²⁾ R, P & P ⁽⁴⁾ R, P & P ⁽⁴⁾ R, P & P ⁽⁴⁾ R, P & P ⁽⁴⁾ R, P & P ⁽⁴⁾ R, P & P ⁽⁴⁾ R, P & P ⁽⁴⁾ Surface tension reduces with T rising.

Mass-transfer coefficients:

Liquid "film":	Calculated; see below.
Vapour "film":	Calculated; see below.
Overall:	Calculated; see below.

Equations:

Height: $h_{bed} = H_{Oy}.N_{Oy}$

H_{Oy} : $H_{Oy} = G_M / [(K_y.a).y^*_{BM}]$

where:

$$y^*_{BM} = \{(1-y) - (1-y^*)\} / \ln\{(1-y)/(1-y^*)\}$$

with y^* the equilibrium gas-phase mole fraction, such that $y^* = m.x$
 and the rate of mass transfer, $N_i = K_y.(y_i - y^*)$, defines the overall gas-phase mass transfer coefficient
 This K_y can also be expressed in terms of the "film" coefficients, viz.:

$$1/K_y = 1/k_y + m/k_x$$

NOTE: Prosy W. M. Edwards (& predecessors) use a different notation - care!!

From Onda *et alii*:

$k_L.(\rho_L/\mu_L.g)^{1/3} / \{(\mu_L/\rho_L.D_L)^{-1/2}.(a_t.D_p)^{0.4}\}$ is correlated against $(Re)_L = L/(a_w.\mu_L)$
 $\{(k_G.R.T)/(\rho_G.D_G)\} / \{(\mu_G/\rho_G.D_G)^{-1/3}.(a_t.D_p)^{-2.0}\}$ is correlated against $(Re)_G = G/(\rho_G.\mu_G)$
 $a_w/a_t = 1 - \exp\{-1.45(\sigma_w/\sigma)^{0.75}.(L/a_t.\mu_L)^{0.1} \times (L^2.a_t/(\rho_L^2.g))^{-0.05}.(L^2/(\rho_L.\sigma.a_t))^{0.2}\}$
 Where $[G] = [L] = \text{kg.m}^{-2}.\text{s}^{-1}$ a_w is the "effective" - wetted - area per volume

Where: $K_G = K_y / P$ Where: $k_G = k_y / P$ Where: $k_L = k_x / \rho_L$

From Uhlherr, CHE3102 notes.

Alternatively, an estimate may be obtained from Cornell's method (Sinnott⁽²⁾, updated by Bolles/Fair)

$$H_y[m] = 0.0190283.\psi_h[m].(Sc)_v^{0.5}.(D_c/0.3048)^{1.24}.(Z/3.048)^{(1/3)} / \{L.(\mu_L/\mu_w)^{0.16}.(\rho_w/\rho_L)^{1.25}.(\sigma_w/\sigma_L)^{0.8}\}^{0.6}$$

$$H_x[m] = \phi_h[m].(Sc)_L^{0.5}.K_3.(Z/3.048)^{0.15}$$

Where D_c is a "corrected" diameter: the lesser of {diameter} or $\{2 \times 0.3048\}$.

Where $\mu_w = 1.002 \text{ mPa.s}$ $\rho_w = 998.2032 \text{ kg.m}^{-3}$ $\sigma_w = 70 \text{ mN.m}^{-1}$ (All at 20°C)

And $H_{Oy} = H_y + (m.G_M/L_M).H_x$ NOTE: use of the coefficient $(m.G_M/L_M)$ implied the subscripts "Oy", "y" and "x" by CHE3102/Uhlherr.

N_{Oy} : Colburn's equation of 1939 is:

$$N_{Oy} = 1/\{1 - (m.G_M/L_M)\} \times \ln\{[1 - (m.G_M/L_M)] \times \{(y_1 - m.x_2)/(y_2 - m.x_2)\} + m.G_M/L_M\}$$

Note: the G_M and L_M are (moles per time) per unit area (of the column).

"m" is a Henry's law-type constant here:

$$y_{\text{equilibrium } i} = m.x_i$$

Feintuch/Treybal(1978) present an "Edmister-type approach":

$$N_{Oy} = \ln\{[(y_1 - y_2^*)/(y_2 - y_2^*)].(1 - 1/A_E) + 1/A_E\} / (1 - 1/A_E)$$

where $A_E = [A_{\text{BOTTOM}}.(A_{\text{TOP}} + 1) + 0.25]^{0.5} - 0.5$

and $(1/A_E) = (m_i.G_i/L_i)$

Calculations:

N_{Oy} : According to Colburn:

$$(m.G_M/L_M) = 0.026308$$

$$\{1 - (m.G_M/L_M)\} = 0.973692$$

$$\therefore N_{Oy} = 5.414$$

According to Feintuch & Treybal:

$$A_{\text{BOTTOM}} = 32.15762$$

$$A_{\text{TOP}} = 46.24948$$

The big difference here means the more sophisticated average is probably worth calculating!

$$A_E = 38.48309 \quad (\text{cf. arithmetic mean of } 39.20355)$$

$$\therefore N_{Oy} = 5.413$$

This non-simple short-cut method has resulted in a **VERY SIMILAR** result to the result from Colburn.

$$H_{Oy}: \quad Y_{BM}^* = \begin{array}{l} \text{TOP: } 0.991547 \\ \text{BOTTOM: } 0.985458 \\ \text{AVERAGE: } 0.988502 \end{array}$$

"Averages" are just simple, arithmetic.

$$G_M = \begin{array}{l} \text{TOP: } 98.8772 \text{ mol.m}^{-2}.\text{s}^{-1} \\ \text{BOTTOM: } 94.03947 \text{ mol.m}^{-2}.\text{s}^{-1} \\ \text{AVERAGE: } 96.45834 \text{ mol.m}^{-2}.\text{s}^{-1} \end{array}$$

From the data of Onda et alii:

$$\begin{array}{l} L = 5.6055 \text{ kg.m}^{-2}.\text{s}^{-1} \quad \text{OKAY} \\ (\sigma_L/\sigma)^{0.75} = 1.1822 \quad (L/a_L \mu_L)^{0.1} = 1.5638 \quad (L^2 a_L / (\rho_L^2 g))^{0.05} = 1.5011 \quad (L^2 / (\rho_L \sigma a_L))^{0.2} = 0.3450 \quad \text{OKAY} \\ \text{Bolles/Fair: } 0.3 < \sigma_L / \sigma < 2 \quad \text{Bolles/Fair: } 2.5e-9 < Fr_L < 0.018 \quad \text{Bolles/Fair: } 1.2e-8 < We_L < 0.27 \\ a_w = 76.6 \text{ m}^2.\text{m}^{-3} \\ (Re)_L = 1.17E+02 \quad \text{OKAY} \quad (\mu_L / \rho_L D_L)^{-1/2} = 0.063423 \quad (a_L D_p)^{0.4} = 1.934052 \\ \text{Bolles/Fair: } 0.04 < Re_L < 500 \end{array}$$

$$\text{Hence: } k_L (\rho_L / \mu_L g)^{1/3} = 0.01756 \quad \text{where } 0.0060 \text{ (cf. } 0.0051) \text{ is the constant for this large, modern packing}$$

$$\begin{array}{l} \text{Thus, } k_L = 0.000317 \text{ m.s}^{-1} \\ \rho_B = 53626 \text{ mol.m}^{-3} \\ \therefore k_x = 16.98 \text{ mol.m}^{-2}.\text{s}^{-1} \end{array}$$

$$\begin{array}{l} G = 2.2873 \text{ kg.m}^{-2}.\text{s}^{-1} \\ (Re)_G = 1.35E+03 \quad \text{OFF SCALE!} \quad (\mu_G / \rho_G D_G)^{-1/3} = 1.028897 \quad (a_L D_p)^{-2.0} = 0.036954 \\ \text{Hence: } (k_G R T) / (a_L D_G) = 35.462 \quad \text{where } 6.00 \text{ (cf. } 5.23) \text{ is the constant for this large, modern packing} \end{array}$$

$$\begin{array}{l} \text{Thus, } k_G = 2.37E-05 \text{ mol.Pa}^{-1}.\text{m}^{-2}.\text{s}^{-1} \quad 0.00024 \text{ mol.atm}^{-1}.\text{cm}^{-2}.\text{s}^{-1} \\ P = 118 \text{ kPa(abs)} \\ \therefore k_y = 2.78 \text{ mol.m}^{-2}.\text{s}^{-1} \end{array}$$

We see that the gas-phase resistance is [VERY!] dominant.... (...also, "m" is small).

$$\text{Hence: } K_y = 2.746 \text{ mol.m}^{-2}.\text{s}^{-1}$$

$$\therefore H_{Oy} = 0.464 \text{ m}$$

cf. The data of the Norton Co. (for specific conditions) in Perry⁽⁶⁾, p. 14-34, T14-4:

$$\begin{array}{l} K_y \cdot a \cdot Y_{BM}^* = 114 \text{ kmol.h}^{-1}.\text{m}^{-3} \\ \text{i.e. } 31.667 \text{ mol.m}^{-3}.\text{s}^{-1} \\ \text{Whence } H_{Oy} = 3.046 \text{ m} \end{array}$$

$$\text{Height: } h_{bed} = 2.51 \text{ m}$$

H_{Oy} : By Cornell's (updated) method:

$$\begin{array}{l} \text{Flooding: } 53\% \quad K_3 = 0.94 \\ \text{(At design percentage flooding, from charts in Bolles/Fair \& Sinnott}^{(2)}) \\ \text{Flooding: } 53\% \quad \psi_h = 140 \text{ ft} \quad 42.672 \text{ m} \\ L [lb_m.h^{-1}.ft^{-2}]: 4.13E+03 \quad \phi_h = 0.088 \text{ ft} \quad 0.026822 \text{ m} \\ \text{(At design percentage flooding, from charts in Bolles/Fair: specific to metal Pall rings.)} \\ \text{Estimated height, "Z" = } 3.95 \text{ m} \\ (Sc)_v^{0.5} = 0.958168 \quad D_c = 0.6096 \text{ m} \\ \{L \cdot (\mu_L / \mu_w)^{0.16} \cdot (\rho_w / \rho_L)^{1.25} \cdot (\sigma_w / \sigma_L)^{0.8}\} = 5.522268 \text{ kg.m}^{-2}.\text{s}^{-1} \\ H_y = 0.718652 \text{ m} \\ (Sc)_L^{0.5} = 15.76725 \\ H_x = 0.413303 \text{ m} \end{array}$$

$$\therefore H_{Oy} = 0.730 \text{ m} \quad \text{(We note that the extraordinarily low value of } m.G_M/L_M \text{ means the contribution of } H_x \text{ is ~negligible.)}$$

$$\text{Height: } h_{bed} = 3.95 \text{ m} \quad \text{(or } 3.62 \text{ m without height-correction)}$$

ABSORBER DETAILED DESIGN

Model of a simplified case:

Stage 4

Reference(s): Perry⁽⁶⁾, p. 14-20, 14-10.
 "van Laar VLE" worksheet [by D.I.V.], & the relevant references therein.
 "Diam.", "Visc.", "Gdiff" & "Ldiff" worksheets [D.I.V.], & references therein.
 HYSIM material
 I. Hahnenstein, H. Hasse, Y.-Q. Liu and G. Maurer; AIChE Symposium series
 Onda *et alii* - original reference.

Assumptions:

Assume:

1. Straight operating line (*i.e.* dilute solutions - small mass transfer)
2. Straight equilibrium line (*i.e.* Henry's law is valid: $y_i = H_i x_i$)
3. Absorption heat effects are negligible

Note: Perry's definition of the assumption is ambiguous, if not confusing.

Comment:

This implies constant flowrates.

This may be reasonable, based on data presented in worksheet "van Laar VLE".

This may or may not be valid:

- Hysim's simulation says a large amount of heat [in kW] is evolved
- however the absorber also has pump-around cooling, with large(?) liquid flow and so the actual temperature PROFILES in the absorber will not be great

Additionally, reaction is ignored.

Data:

Temperature at bottom of stage: LIQUID: 43.00 °C GAS: 42.00 °C

Temperature at top of stage: LIQUID: 37.00 °C GAS: 37.50 °C

It is assumed that thermal equilibrium is (almost) reached.

Thus a nominal column temperature of 40 °C will be used here

± 10°C, say.

Pressures:

TOP: 110 kPa(abs)
 BOTTOM: 115 kPa(abs)
 AVERAGE: 112.5 kPa(abs)

Estimate.

Henry's constant: ("m")

By linear regression of AIChE.J data in worksheet "van Laar VLE": 0.7514 (70°C)
 By weighted least squares regression of the above: (approx.) 1 (70°C)
 Data from Ullmann's⁽⁵⁾ & Walker⁽³⁾: << 1
 All other estimates, including Raoult's law: >> 1 (60°C)
 Hence use the value: 0.7514

This was only based on x_{HCHO} under 0.20

This assumes equilibrium of reaction.

This doesn't consider liquid-phase formation of nonvolatiles.

On the conservative side.

THESE DO NOT CONSIDER INERTS PRESENT

Flows:

TOTAL liquid inflow: 18.17909 mol.s⁻¹
 TOTAL liquid outflow: 20.85713 mol.s⁻¹
 RATIO of BOTTOM to TOP liquid flows: 1.147314
 Average stage TOTAL liquid flow: 19.51811 mol.s⁻¹

Thus the flow may NOT be considered constant.

Not justified, due to the absence of any (high) pump-around.

Vapour inflow: 239.3013 mol.s⁻¹
 Vapour outflow: 236.6233 mol.s⁻¹
 RATIO of BOTTOM to TOP vapour flows: 1.011318
 Average (total) vapour flow: 237.9623 mol.s⁻¹

Note: no vapour recirculation.

This is really NOT too large to assume constant flow.

Mean molar masses:

GAS: 0.023675 kg.mol⁻¹
 LIQUID: 0.018015 kg.mol⁻¹

Worksheet "Diam."

Worksheet "Diam."

Mole-fractions:

Mole-fraction of formaldehyde in vapour: TOP: 0.000103
 BOTTOM: 0.0085
 AVERAGE: 0.004289

Entering zero here would give infinite height.

Mole-fraction of formaldehyde in liquid: TOP: 0.0000
 BOTTOM: 0.0961
 AVERAGE: 0.048036

NOTE: This average for reference only.

(based on a 99.5% nominal approach to equilibrium)

There will be some formaldehyde in the pump-around liquid(!)...

...but too high would cause more formaldehyde to escape more easily.

The dissimilarity is due to the absence of a (large) pump-around.

Mole-fraction IN EQUILIBRIUM WITH liquid: TOP: 0.0000
 BOTTOM: 0.0065
 AVERAGE: 0.003257

Note that temperature is the dominant effect here.

Equilibrium:

Hence "m": TOP: 0.068109
 BOTTOM: 0.067809
 AVERAGE: 0.067809

Defined by $y_{\text{equilibrium}} = m \cdot x$

We see that for this reducing concentration which varies little absolutely,

"m" is quite constant. Thus bottom value can be taken as value everywhere at top.

Actual mean: 0.067959

Calculated in worksheet "Diam."

Diameter:

1.8 m

Flooding:

DESIGN: 179% Minute liquid flow!
 TURNDOWN: 107% Minute liquid flow!

Worksheet "Diam."

Worksheet "Diam."

Internals:

Type: Pall rings
 Material: S.S.
 σ_c : 75 mN.m⁻¹
 Nominal size: 0.051 m
 a_t : 102 m².m⁻³

???

?

?

???

???

Sinnott⁽²⁾

i.e. 2 inches.

Fluid properties:

μ_G : 1.66E-05 Pa.s

See worksheet "Visc."

μ_L :	7.58E-04 Pa.s	Worksheet "Diam."
D_G :	0.174 cm ² .s ⁻¹	See worksheet "GDiff".
D_L :	2.2E-05 cm ² .s ⁻¹	See worksheet "LDiff".
ρ_G :	1.01 kg.m ⁻³	Worksheet "Diam."
ρ_L :	995 kg.m ⁻³	Worksheet "Diam."
σ :	WATER, 303.15K: 71.40 dyn.cm ⁻¹ WATER, 293.15K: 70 mN.m ⁻¹ WATER, 293K: 72.8 dyn.cm ⁻¹ WATER, 303K: 71.18 dyn.cm ⁻¹ METHANOL, 333K: 19.41 dyn.cm ⁻¹ ACETONE, 318K: 21.22 dyn.cm ⁻¹ FORMAMIDE, 338K: 53.66 dyn.cm ⁻¹ METHYL FORMATE, 298K: 24.62 dyn.cm ⁻¹ METHYL FORMATE, 323K: 20.05 dyn.cm ⁻¹ METHYL FORMATE, 373K: 12.90 dyn.cm ⁻¹ ASSUME: 60 dyn.cm ⁻¹	Perry ⁽⁶⁾ Sinnott ⁽²⁾ R, P & P ⁽⁴⁾ R, P & P ⁽⁴⁾ R, P & P ⁽⁴⁾ R, P & P ⁽⁴⁾ R, P & P ⁽⁴⁾ R, P & P ⁽⁴⁾ R, P & P ⁽⁴⁾ Surface tension reduces with T rising.

Mass-transfer coefficients:

Liquid "film":	Calculated; see below.
Vapour "film":	Calculated; see below.
Overall:	Calculated; see below.

Equations:

Height: $h_{bed} = H_{Oy}.N_{Oy}$

H_{Oy} : $H_{Oy} = G_M / [(K_y.a).y^*_{BM}]$

where:

$$y^*_{BM} = \{(1-y) - (1-y^*)\} / \ln\{(1-y)/(1-y^*)\}$$

with y^* the equilibrium gas-phase mole fraction, such that $y^* = m.x$
 and the rate of mass transfer, $N_i = K_y.(y_i - y^*)$, defines the overall gas-phase mass transfer coefficient
 This K_y can also be expressed in terms of the "film" coefficients, viz.:

$$1/K_y = 1/k_y + m/k_x$$

NOTE: Prosy W. M. Edwards (& predecessors) use a different notation - care!!

From Onda *et alii*:

$k_L.(D_L/\mu_L.g)^{1/3} / \{(D_L/\rho_L.D_L)^{-1/2}.(a_t.D_p)^{0.4}\}$ is correlated against $(Re)_L = L/(a_w.\mu_L)$
 $\{(k_G.R.T)/(\rho_G.D_G)\} / \{(G/(\rho_G.D_G))^{-1/3}.(a_t.D_p)^{-2.0}\}$ is correlated against $(Re)_G = G/(\rho_G.\mu_G)$
 $a_w/a_t = 1 - \exp\{-1.45(\sigma/\sigma_w)^{0.75}.(L/a_t.\mu_L)^{0.1} \times (L^2.a_t/(\rho_L^2.g))^{-0.05}.(L^2/(\rho_L.\sigma.a_t))^{0.2}\}$
 Where $[G] = [L] = \text{kg.m}^{-2}.\text{s}^{-1}$ a_w is the "effective" - wetted - area per volume

Where: $K_G = K_y / P$ Where: $k_G = k_y / P$ Where: $k_L = k_x / \rho_L$

From Uhlherr, CHE3102 notes.

Alternatively, an estimate may be obtained from Cornell's method (Sinnott⁽²⁾, updated by Bolles/Fair)

$$H_y[m] = 0.0190283.\psi_h[m].(Sc)_v^{0.5}.(D_c/0.3048)^{1.24}.(Z/3.048)^{(1/3)} / \{L.(\mu_L/\mu_w)^{0.16}.(\rho_w/\rho_L)^{1.25}.(\sigma_w/\sigma_L)^{0.8}\}^{0.6}$$

$$H_x[m] = \phi_h[m].(Sc)_L^{0.5}.K_3.(Z/3.048)^{0.15}$$

Where D_c is a "corrected" diameter: the lesser of {diameter} or $\{2 \times 0.3048\}$.

Where $\mu_w = 1.002 \text{ mPa.s}$ $\rho_w = 998.2032 \text{ kg.m}^{-3}$ $\sigma_w = 70 \text{ mN.m}^{-1}$ (All at 20°C)

And $H_{Oy} = H_y + (m.G_M/L_M).H_x$ NOTE: use of the coefficient $(m.G_M/L_M)$ implied the subscripts "Oy", "y" and "x" by CHE3102/Uhlherr.

N_{Oy} : Colburn's equation of 1939 is:

$$N_{Oy} = 1/\{1 - (m.G_M/L_M)\} \times \ln\{1 - (m.G_M/L_M)\} \times \{(y_1 - m.x_2)/(y_2 - m.x_2)\} + m.G_M/L_M$$

Note: the G_M and L_M are (moles per time) per unit area (of the column).

"m" is a Henry's law-type constant here:

$$y_{\text{equilibrium } i} = m.x_i$$

Feintuch/Treybal(1978) present an "Edmister-type approach":

$$N_{Oy} = \ln\{[(y_1 - y_2^*)/(y_2 - y_2^*)].(1 - 1/A_E) + 1/A_E\} / (1 - 1/A_E)$$

where $A_E = [A_{\text{BOTTOM}}.(A_{\text{TOP}} + 1) + 0.25]^{0.5} - 0.5$

and $(1/A_E) = (m_i.G_i/L_i)$

Calculations:

N_{Oy} : According to Colburn:

$$(m.G_M/L_M) = 0.826716$$

$$\{1 - (m.G_M/L_M)\} = 0.173284$$

$$\therefore N_{Oy} = 14.978$$

According to Feintuch & Treybal:

$$A_{\text{BOTTOM}} = 1.285356$$

$$A_{\text{TOP}} = 1.127999$$

The big difference here means the more sophisticated average is probably worth calculating!

$$A_E = 1.227783 \quad (\text{cf. arithmetic mean of } 1.206677)$$

$$\therefore N_{Oy} = 14.961 \quad (\text{Note: using } A_{\text{BOTTOM}} \text{ only yields: } 13.264)$$

This non-simple short-cut method has resulted in a VERY CLOSE result to the result from Colburn.

However previous results so close to Colburn, that we will assume that result is good here too.

H_{Oy} : $Y_{BM}^* =$ TOP: 0.999948
 BOTTOM: 0.992505
 AVERAGE: 0.996227 "Averages" are just simple, arithmetic.

$$G_M = \text{TOP: } 94.03947 \text{ mol.m}^{-2}.\text{s}^{-1}$$

$$\text{BOTTOM: } 92.98707 \text{ mol.m}^{-2}.\text{s}^{-1}$$

$$\text{AVERAGE: } 93.51327 \text{ mol.m}^{-2}.\text{s}^{-1}$$

From the data of Onda et alii:

OKAY $L = 0.1382 \text{ kg.m}^{-2}.\text{s}^{-1}$ OKAY $(\sigma_w/\sigma)^{0.75} = 1.1822$ $(L/a_t \mu_L)^{0.1} = 1.0599$ $(L^2 a_t / (\rho_L^2 g))^{0.05} = 2.1622$ OKAY $(L^2 / (\rho_L \sigma a_t))^{0.2} = 0.0793$
 Bolles/Fair: $0.3 < \sigma_w / \sigma < 2$ Bolles/Fair: $2.5e-9 < Fr_L < 0.018$ Bolles/Fair: $1.2e-8 < We_L < 0.27$
 $a_w = 27.3 \text{ m}^2.\text{m}^{-3}$
 $(Re)_L = 6.68E+00$ OKAY $(\mu_L / \rho_L D_L)^{-1/2} = 0.053323$ $(a_t D_p)^{0.4} = 1.934052$
 Bolles/Fair: $0.04 < Re_L < 500$

$$\text{Hence: } k_L (\rho_L / \mu_L g)^{1/3} = 0.00220 \quad \text{where } 0.0060 \text{ (cf. } 0.0051) \text{ is the constant for this large, modern packing}$$

$$\text{Thus, } k_L = 4.29E-05 \text{ m.s}^{-1}$$

$$\rho_B = 55255 \text{ mol.m}^{-3}$$

$$\therefore k_x = 2.37 \text{ mol.m}^{-2}.\text{s}^{-1}$$

$$G = 2.2139 \text{ kg.m}^{-2}.\text{s}^{-1}$$

$$(Re)_G = 1.31E+03$$
 OFF SCALE! $(\mu_G / \rho_G D_G)^{-1/3} = 1.018091$ $(a_t D_p)^{-2.0} = 0.036954$
 Hence: $(k_G R.T) / (a_t D_G) = 34.298$ where 6.00 (cf. 5.23) is the constant for this large, modern packing

$$\text{Thus, } k_G = 2.34E-05 \text{ mol.Pa}^{-1}.\text{m}^{-2}.\text{s}^{-1} \quad 0.000237 \text{ mol.atm}^{-1}.\text{cm}^{-2}.\text{s}^{-1}$$

$$P = 113 \text{ kPa(absolute)}$$

$$\therefore k_y = 2.63 \text{ mol.m}^{-2}.\text{s}^{-1}$$

We see that the gas-phase resistance is dominant... (...also, "m" is small).

$$\text{Hence: } K_y = 2.443 \text{ mol.m}^{-2}.\text{s}^{-1}$$

$$\therefore H_{Oy} = 1.407 \text{ m}$$

cf. The data of the Norton Co. (for specific conditions) in Perry⁽⁶⁾, p. 14-34, T14-4:

$$K_y \cdot a \cdot Y_{BM}^* = 114 \text{ kmol.h}^{-1}.\text{m}^{-3}$$

$$\text{i.e. } 31.667 \text{ mol.m}^{-3}.\text{s}^{-1}$$

$$\text{Whence } H_{Oy} = 2.953 \text{ m}$$

Height: $h_{bed} = 21.08 \text{ m}$

H_{Oy} : By Cornell's (updated) method:

Flooding: 179% $K_3 = 1$??? - Off chart!
 (At design percentage flooding, from charts in Bolles/Fair & Sinnott⁽²⁾)
 Flooding: 179% $\psi_h = 150 \text{ ft}$ 45.72 m ??? - Off chart!
 $L [lb_m.h^{-1}.ft^{-2}]: 1.02E+02$ $\phi_h = 0.051 \text{ ft}$ 0.015545 m ??? - [Just] Off chart!
 (At design percentage flooding, from charts in Bolles/Fair: specific to metal Pall rings.)
 Estimated height, "Z" = 529.71 m
 $(Sc)_v^{0.5} = 0.973464$ $D_c = 0.6096 \text{ m}$
 $\{L \cdot (\mu_L / \mu_w)^{0.16} \cdot (\rho_w / \rho_L)^{1.25} \cdot (\sigma_w / \sigma_L)^{0.8}\} = 0.149992 \text{ kg.m}^{-2}.\text{s}^{-1}$
 $H_y = 34.84471 \text{ m}$

$$(Sc)_L^{0.5} = 18.75357$$

$$H_x = 0.631935 \text{ m}$$

$$\therefore H_{Oy} = 35.367 \text{ m}$$

(We note that the extraordinarily low value of $m \cdot G_M / L_M$ means the contribution of H_x is ~negligible.)

Height: $h_{bed} = 529.71 \text{ m}$ (or 94.92 m without height-correction)

Diameter computation

Design for a pressure drop of 42 mm(H₂O).m⁻¹ at the design condition.
 ==> approx. 412 Pa.m⁻¹
 i.e. 20.58 kPa for a 50 m column.

Note: Assuming a CONSTANT DIAMETER for the entire column, this would have to be evaluated for all stages, for the full range of possible operating conditions.
 Each evaluated at the top of the stage (the lower values).

	STAGE 1		STAGE 2		STAGE 3		STAGE 4: Option a		STAGE 4: Option b	
	Design	0.6×Design	Design	0.6×Design	Design	0.6×Design	Design	0.6×Design	Design	0.6×Design
Lower gas flow rate [mol.s ⁻¹]	303.79	182.27	251.61	150.97	239.30	143.58	236.62	141.97	236.62	141.97
Lower gas flow rate [kg.s ⁻¹]	7.0173	4.2104	5.9245	3.5547	5.6745	3.4047	5.6020	3.3612	5.6020	3.3612
Mean M _g [kg.mol ⁻¹]	0.02310	0.02310	0.02355	0.02355	0.02371	0.02371	0.02367	0.02367	0.02367	0.02367
Lower liquid flow rate [mol.s ⁻¹]	1372.04	823.22	2048.58	1229.15	722.16	433.30	18.18	10.91	18.18	10.91
Lower liquid flow rate [kg.s ⁻¹]	31.4798	18.8879	41.8084	25.0850	14.1438	8.4863	0.3275	0.1965	0.3275	0.1965
Mean M _L [kg.mol ⁻¹]	0.02294	0.02294	0.02041	0.02041	0.01959	0.01959	0.01802	0.01802	0.01802	0.01802
p [kPa(abs)]	125	125	120	120	115	115	110	110	110	110
Temperature [K]	335.15	335.15	323.15	323.15	315.15	315.15	310.65	310.65	310.65	310.65
	62.00	62	50.00	50	42.00	42	37.50	37.5	37.50	37.5
Ideal gas density [mol.m ⁻³]	44.857	44.857	44.662	44.662	43.888	43.888	42.588	42.588	42.588	42.588
Ideal gas density [kg.m ⁻³]	1.036	1.036	1.052	1.052	1.041	1.041	1.008	1.008	1.008	1.008
Liquid mass fraction HCHO [-]	0.526098	0.526098083	0.287507	0.287507374	0.198101	0.198100722	0	0	0	0
Liquid mass fraction CH ₃ OH [-]	0.009723	0.009723183	0.004953	0.004953359	0.001972	0.001971719	0	0	0	0
a	1.151	1.151	1.092	1.092	1.092	1.092	1.092	1.092	1.092	1.092
b	0.5015	0.5015	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30
c	0.0161	0.0161	0	0	0	0	0	0	0	0
Liquid density [kg.m ⁻³]	1132.1	1132.1	1071.0	1071.0	1050.3	1050.3	995.4	995.4	995.4	995.4
$\rho/1000 = a + 0.30(X_F - b) - 0.25(X_M - c) - 10^{-4} \cdot [5.5(X_F - 0.30) + 5.4] \cdot (t[^\circ\text{C}] - 20)$ (Ullmann's ⁽⁹⁾)										
And note the misprinted exponent in the original. Compare with Walker ⁽³⁾ : Values greater than 1000 okay.										
Compare with K-O ⁽⁴⁾ :	1134.8	1134.8	1071.9	1071.9	1050.4	1050.4	993.5	993.5	993.5	993.5
$\rho/1000 = \{1.119 + 0.30(X_F - 0.45) - 0.27(X_M)\} \cdot \{1.0 + 0.00055 \cdot (55 - t[^\circ\text{C}])\}$										
$\therefore (L/G) \cdot (\rho_V / \rho_L)^{0.5}$	1.36E-01	1.36E-01	2.21E-01	2.21E-01	7.85E-02	7.85E-02	1.86E-03	1.86E-03	1.86E-03	1.86E-03
From Fig. 11.44: K ₄	1.2	1.2	1.2	1.2	1.3	1.3	0.13	0.13	???	???
cf. K ₄ at flooding	2.8	2.8	3.2	3.2	3.5	3.5	0.32	0.32	???	???
Percentage of flooding	65%	65%	61%	61%	61%	61%	64%	64%	#VALUE!	#VALUE!
Sinnott ⁽²⁾ calls 66% "satisfactory"							(out of range)	(out of range)	(out of range)	(out of range)
Liquid viscosity [mPa.s]	1.892	1.892	1.226	1.226	1.054	1.054	0.380	0.380	0.380	0.380
From Ullmann's ⁽⁵⁾ = K-O ⁽⁴⁾ : $\eta = 1.28 + 3.9XF + 5X_M - 0.024t[^\circ\text{C}]$	0.450	0.450	0.544	0.544	0.628	0.628	0.758	0.758	0.758	0.758
Hence:	1.892	1.892	1.226	1.226	0.841	0.841	0.758	0.758	0.758	0.758
Packing Size [mm]	Pall rings	Pall rings	Pall rings	Pall rings	Pall rings	Pall rings	Pall rings	Pall rings	Plastic gauze (e.g. Sulzer, Type BX)	or trays???
F _p [m ⁴] Table 11.3, Sinnott ⁽²⁾	50	50	50	50	50	50	50	50		
a [m ² .m ³] Table 11.3, Sinnott ⁽²⁾	66	66	66	66	66	66	66	66		
	102	102	102	102	102	102	102	102		
$\therefore G^2 = [K_L \cdot \rho_L \cdot (\rho_L - \rho_V)] / \{13.1 F_P \cdot (\mu_L / \rho_L)^{0.1}\}$ [kg.m ² .s ⁻¹] ²	6.151	6.151	6.134	6.134	6.683	6.683	0.617	0.617	Largest A	Smallest A
G [kg.m ² .s ⁻¹]	2.480	2.480	2.477	2.477	2.585	2.585	0.785	0.785	0.6	5
Whence A [m ²]	2.829	1.698	2.392	1.435	2.195	1.317	7.133	4.280	0.6025	5.0206
$\therefore L$ [kg.m ² .s ⁻¹]	11.126	11.126	17.477	17.477	6.443	6.443	0.046	0.046	9.29837	0.669482656
G _M [mol.m ² .s ⁻¹]	107.369	107.369	105.182	105.182	109.019	109.019	33.173	33.173	2.5447	m ²
L _M [mol.m ² .s ⁻¹]	484.927	484.927	856.378	856.378	328.996	328.996	2.549	2.549		
Thus diameter [m]	1.898	1.470	1.745	1.352	1.672	1.295	3.014	2.334		
Say diameter of column (bottom 3 stages) is 1.8 m										
Column area [m ²]					2.5447				2.5447	2.5447
Packing size to column diameter ratio:					36.0				2.2014	1.3209
Sinnott ⁽²⁾ : "a larger packing size could be considered"									2.1834	1.3101
Percentage flooding at selected diameter:	72.8%	43.7%	57.6%	34.5%	52.6%	31.5%	178.7%	107.2%	0.128699	0.0772
This should be okay.							CLEARLY PALL RINGS DON'T APPLY		0.465441	0.2793
G [kg.m ² .s ⁻¹]	2.7576	1.6546	2.3282	1.3969	2.2299	1.3380	2.2014	1.3209		
L [kg.m ² .s ⁻¹]	12.371	7.422	16.430	9.858	5.558	3.335	0.129	0.077		
G _M [mol.m ² .s ⁻¹]	119.380	71.628	98.877	59.326	94.039	56.424	92.987	55.792		
L _M [mol.m ² .s ⁻¹]	539.176	323.506	805.042	483.025	283.792	170.275	7.144	4.286		
									13.2	6.3
									6.4	6.8
Note: This is NOT for the (reacting) HCHO-H ₂ O system										

Gas viscosity computation

Using the method of Wilke, given by R, P & P⁽⁴⁾

Molar mass:	Water (1)	18.0152 g.mol ⁻¹
	Formaldehyde (2)	30.0262 g.mol ⁻¹
	Hydrogen (3)	2.0158 g.mol ⁻¹
	Nitrogen (4)	28.0134 g.mol ⁻¹

	STAGE 1	STAGE 2	STAGE 3	STAGE 4
Temperature:				
t [°C]	76	56	46	39.75 Average for gas.
T [K]	349.15	329.15	319.15	312.9

Composition: mole fraction

Water (1)	0.202668	0.229474	0.120116	0.084646
Formaldehyde (2)	0.142986	0.055279	0.01726	0.008476
Hydrogen (3)	0.115716	0.12681	0.153106	0.160982
Nitrogen (4)	0.538631	0.588437	0.709518	0.745897

This is entering, so not at equilibrium.
 Nitrogen mole fraction decreased by taking value at bottom of stage, but increased by assuming all other components as nitrogen.

Approx. pure component viscosity [Pa.s]:

Water (1)	1.11E-05	1.04E-05	1.00E-05	9.87E-06 From Y&R ⁽⁵⁾ , rounded to nearest 5°C
Formaldehyde (2)	1.12E-05	1.05E-05	1.02E-05	1.00E-05 Assume as for methanol: Perry ⁽⁶⁾ , to nearest 10°C
Hydrogen (3)	1.00E-05	9.50E-06	9.50E-06	9.00E-06 Perry ⁽⁶⁾ , to nearest ~25K
Nitrogen (4)	2.00E-05	1.90E-05	1.90E-05	1.80E-05 Perry ⁽⁶⁾ , to nearest ~25K

Wilke's parameter's:

$$\phi_{ij} = \{1 + (\eta_i/\eta_j)^{1/2} \cdot (M_j/M_i)^{1/4}\}^2 / \{8(1 + M_i/M_j)\}^{1/2}$$

i = 1

ϕ_{i1}	1	1	1	1
ϕ_{i2}	1.269471	1.269066	1.262202	1.266702
ϕ_{i3}	0.290487	0.288971	0.284755	0.289163
ϕ_{i4}	0.925623	0.919832	0.90374	0.920565

i = 2

ϕ_{i1}	0.768523	0.768739	0.772445	0.770009
ϕ_{i2}	1	1	1	1
ϕ_{i3}	0.209955	0.208986	0.206894	0.209371
ϕ_{i4}	0.739786	0.735653	0.726742	0.737295

i = 3

ϕ_{i1}	2.338808	2.359044	2.417614	2.356457
ϕ_{i2}	2.792292	2.816461	2.870285	2.8068
ϕ_{i3}	1	1	1	1
ϕ_{i4}	1.910394	1.910394	1.910394	1.910394

i = 4

ϕ_{i1}	1.072542	1.080692	1.104258	1.07965
ϕ_{i2}	1.415965	1.426829	1.451003	1.422487
ϕ_{i3}	0.274938	0.274938	0.274938	0.274938
ϕ_{i4}	1	1	1	1

Terms in series:

i = 1	2.45E-06	2.72E-06	1.45E-06	1.01E-06
i = 2	2.22E-06	8.4E-07	2.68E-07	1.29E-07
i = 3	5.73E-07	6.18E-07	7.87E-07	8.01E-07
i = 4	1.09E-05	1.18E-05	1.48E-05	1.5E-05
∴ SUM = viscosity of mixture [Pa.s]:				
	1.61E-05	1.59E-05	1.73E-05	1.7E-05

It turns out that the decrease in temperature (⇒ decreasing viscosity) almost exactly compensates for the increase in mole fraction of nitrogen (which has double the viscosity of the others)!

Thus, in ALL cases in the absorber, take the gas viscosity as: **1.66E-05 Pa.s**

Comparison with mole-fraction weighted means:

	1.58E-05	1.54E-05	1.63E-05	1.58E-05
"ERROR"	-2.1%	-3.7%	-5.9%	-6.9%

Hence the viscosity would have been underestimated by an average factor of 4.7%

However we see that, although in some cases Wilke's method gives identical values as experiment (methane-propane at 498K), in other cases errors may be +12% (nitrogen-hydrogen at 373K, $y_N = 0.2$) or -12% (ammonia-hydrogen at 306K, $y_A = 0.399$).

Only Reichenberg's method is consistently accurate to no more than ±4.8% w.r.t. experiment (these extremes occur for the same conditions as for Wilke's method, above).

As may be guessed, Reichenberg's method is more involved.

Gas-phase diffusivity computation

Assuming binary diffusion:

Formaldehyde in nitrogen (main constituent)

Use the method of Fuller *et alii* (1965–1969), recommended by R, P & P⁽⁴⁾

(Average abs. error = 5.4%)

$$D_{AB}[\text{cm}^2 \cdot \text{s}^{-1}] = 0.00143 T[\text{K}]^{1.75} / \{P[\text{bar}] \cdot M_{AB}[\text{g} \cdot \text{mol}^{-1}]^{1/2} \cdot [(\Sigma_v)_A^{1/3} + (\Sigma_v)_B^{1/3}]^2\}$$

where $M_{AB} = 2 / (1/M_A + 1/M_B)$

and Σ_v is the "diffusion volume" sum - atoms (xor =molecule):

Σ_v

Atomic and Structural Diffusion Volume Increments

C	15.9
H	2.31
O	6.11
N	4.54
Aromatic ring	-18.3
Heterocyclic ring	-18.3
F	14.7
Cl	21.0
Br	21.9
I	29.8
S	22.9

Diffusion Volumes of Simple Molecules

He	2.67
Ne	5.98
Ar	16.2
Kr	24.5
Xe	32.7
H ₂	6.12
D ₂	6.84
N ₂	18.5
O ₂	16.3
Air	19.7
CO	18.0
CO ₂	26.9
N ₂ O	35.9
NH ₃	20.7
H ₂ O	13.1
SF ₆	71.3
Cl ₂	38.4
Br ₂	69.0
SO ₂	41.8

Thus, for formaldehyde:

(Sv)A 26.63

M_A 30.0262 g.mol⁻¹

For nitrogen:

(Sv)B 18.5

M_B 28.0134 g.mol⁻¹

(cf. 9.08 for individual contributions)

Hence: $[(\Sigma_v)_A^{1/3} + (\Sigma_v)_B^{1/3}] = 5.631019$

	STAGE 1	STAGE 2	STAGE 3	STAGE 4
p [kPa(abs)]	125	120	115	110
Temperature [K]	335.15	323.15	315.15	310.65
Temperature [°C]	62.00	50.00	42.00	37.50
M _{AB}	28.98	28.98	28.98	28.98
Hence DAB[cm ² .s ⁻¹] =	0.176	0.172	0.172	0.175

Again this is so invariant that it may be taken as constant across the entire column:

0.174 cm².s⁻¹

(We note that the decreasing temperature is compensated for by [commensurately?] decreasing pressure.)

Use the method of Gilliland (1934), recommended by Holman⁽⁷⁾

$$D_{AB}[\text{cm}^2 \cdot \text{s}^{-1}] = 435.7 T[\text{K}]^{1.5} / \{P[\text{Pa}] \cdot M_{AB}[\text{g} \cdot \text{mol}^{-1}]^{1/2} \cdot [(\Sigma v)_A^{1/3} + (\Sigma v)_B^{1/3}]\}^2$$

where $M_{AB} = 2 / (1/M_A + 1/M_B)$

and Σv is the molecular volume - summation of atomic contributions:

Σv

Atomic and Structural Diffusion Volume Increments

	C	14.8
	H	3.7
	O	
	in aldehydes/ketones	7.4
	in methyl esters	9.1
	in ethyl esters	9.9
	in higher esters/ethers	11
	in acids	12
	in union with S/P/N	8.3
	N	
	in primary amines	10.5
	in secondary amines	1.20
	F	8.7
	Cl	
	terminal	21.6
	medial	24.6
	Br	27.0
	I	37.0
	S	25.6
	P	27.0

Diffusion Volumes of Simple Molecules

H ₂	14.3
N ₂	15.6
O ₂	7.4
Air	29.9
CO ₂	34.0
H ₂ O	18.8

Thus, for formaldehyde:

(Sv)A 29.6

M_A 30.0262 g.mol⁻¹

For nitrogen:

(Sv)B 15.6

M_B 28.0134 g.mol⁻¹

Hence: $[(\Sigma v)_A^{1/3} + (\Sigma v)_B^{1/3}] = 5.592027$

	STAGE 1	STAGE 2	STAGE 3	STAGE 4
p [kPa(abs)]	125	120	115	110
Temperature [K]	335.15	323.15	315.15	310.65
Temperature [°C]	62.00	50.00	42.00	37.50
M _{AB}	28.98	28.98	28.98	28.98
Hence DAB[cm ² .s ⁻¹] =	0.127	0.125	0.126	0.129

Again this is so invariant that it may be taken as constant across the entire column:

0.127 cm².s⁻¹

(We note that the decreasing temperature is compensated for by [commensurately?] decreasing pressure.)

Note: Due to the obvious errors in estimating BINARY gas diffusion coefficients, computation of diffusivities for the MIXTURE would clearly **not** be justified.

Liquid-phase diffusivity computation

Assuming binary diffusion:

Formaldehyde in water (main constituent)

NOTE: While the correlations are for **dilute** solute diffusion, the hydrolysis of HCHO renders this **valid** here.

Use the correlation of Hayduk and Minhas (1982), recommended by R, P & P⁽⁴⁾

In aqueous solutions:

(Average abs. error = ~10%)

$$D_{AB}^0 [\text{cm}^2 \cdot \text{s}^{-1}] = 1.25 \times 10^{-8} \cdot (V_A^{-0.19} - 0.292) \cdot T [\text{K}]^{1.52} \cdot \eta_w^{\epsilon^*}$$

where $\epsilon^* = (9.58/V_A) - 1.12$

η_w is the viscosity of water [mPa.s]

and V_A is the molar volume of the solute at its normal b.p. [$\text{cm}^3 \cdot \text{mol}^{-1}$]

From Ullmann's⁽⁵⁾:

"Formaldehyde liquefies at -19.2°C, the density of the liquid being 0.8153 g.cm⁻³ at 20°C [...]"

Given a molar mass of: 30.026 g.mol⁻¹

This yields $V_A = 36.828 \text{ cm}^3 \cdot \text{mol}^{-1}$

whence $\epsilon^* = -0.85987$

	STAGE 1	STAGE 2	STAGE 3	STAGE 4
p [kPa(abs)]	125	120	115	110
Temperature [K]	335.15	323.15	315.15	310.65
Temperature [°C]	62.00	50.00	42.00	37.50
From Rogers & Mayhew ⁽³⁾				
Viscosity of liquid water (to nearest 5°C) = η_w [mPa]:	0.463	0.544	0.651	0.718
Hence $D_{AB}^0 [\text{cm}^2 \cdot \text{s}^{-1}] =$	3.5E-05	2.9E-05	2.4E-05	2.2E-05

This probably should **not** be taken as constant across the whole column:

2.8E-05 cm².s⁻¹



APPENDIX TO CHAPTER 7

PART 3: DETAILED MECHANICAL DESIGN

①

NUMBER OF IDEAL STAGES

From the method of Treybal & Feintuch presented in worksheet "Bed 4", it has been shown that

$$N_{og} = \frac{\ln \left[\left(\frac{y_1 - y_2^*}{y_2 - y_2^*} \right) \cdot \left(1 - \frac{1}{A_E} \right) + \frac{1}{A_E} \right]}{1 - \frac{1}{A_E}} \doteq 15$$

Treybal⁽¹⁾ presents the relevant Kremser equation for calculating the number of ideal plates:

$$N_p = \frac{\log_{10} \left[\left(\frac{y_{n+1}}{y_1} \right) \cdot \left(1 - \frac{1}{A_E} \right) + \frac{1}{A_E} \right]}{\log_{10}(A_E)}$$

for the absorption section, with pure water "solvent".

As before $A_E \doteq 1.2278$

$$\begin{aligned} y_{n+1} &= 0.0085 & \text{(entering)} \\ y_1 &= 0.0001032 & \text{(exiting)} \end{aligned}$$

$$\Rightarrow N_p = 13.54$$

13.54 ideal trays.

We see that this is of the same order of magnitude as N_{og} , as expected.

Sinnott⁽²⁾ gives a correlation specifically for the plate efficiency of absorbers, due to O'Connell (1946).

$$\text{given } \kappa = 0.062 \left(\frac{P_s}{\mu_s K M_s} \right)$$

$$\Rightarrow \kappa = 0.062 \left(\frac{1000 \text{ kg.m}^{-3}}{0.8 \text{ mPa.s} \times 0.067459 \times 18.015 \text{ g.mol}^{-1}} \right)$$

$$\kappa = 6.33 \times 10^4$$

From Fig. 11.14 of Sinnott⁽²⁾

$$\text{Efficiency} \approx 56\% \quad (\text{bubble-caps}).$$

$$E_o = 56\%$$

While this may seem quite low, it is higher than it might have been, had K been much larger.

Hence the actual number of plates required is

$(13.54)(0.56)^{-1} = 24$ actual trays
 $P_{eff}^{(6)}$ & VLE data indicate 56% too low: take 21 trays ($E_o = 64.5\%$)

~~24 real trays.~~
 $E_o = 64.5\%$
 21 real trays

②

PLATE SPACING

Sinnott⁽²⁾, p. 510 recommends plate spacings of 0.3 to 0.6 m for this diameter column (1.8m), which can be adjusted after detailed design, with larger spacings for manholes/"manways". Typically estimate 0.5m

J.R. Beckhurst & J.R. Harker (1973) recommend plate spacings of 0.46m for sieve trays in columns of diameter $\leq 1.2m$ to avoid mechanical problems of "supporting a tall, slender column," with spacings down to 0.15m possible. Larger columns have sieve tray spacings of 0.6 to 0.9m. [p.166]

For valve trays the sieve tray recommendations may be used, except that 1.22m spacings are preferred for "very large diameter columns". However this may be able to be reduced based on subsequent calculation of hydraulic parameters, subject to acceptable entrainments.

With these recommendations in mind, and also remembering that bubble-cap trays (for the low liquid flow and heat exchange) will be used with "serpentine" cooling coils, a spacing of 0.75m is selected.

Normal spacing
 $= 0.75m = 1.5$

However there shall be manhole spacing every 7 trays (or 5.25m). Manholes may be a significant cost, and so provision is made for access through tray sections. Manholes must accommodate a person and tray sections. Bachhurst & Harder list sizes from 0.37 m to 0.61 m, inner diameter. As manholes are not installed between each plate, a diameter of 0.61 m (24 inches) can be afforded. Say total tray-to-tray manway spacing is $(0.61 \text{ m} + 0.75 \text{ m}) = 1.36 \text{ m}$

manholes every 7 trays

0.61 m internal diameter manholes

1.36 m tray-to-tray manway spacing.

③ PLATE LAYOUT.

Perry⁽⁶⁾, p 18-8 gives equilateral triangle layouts of bubble-caps as the general arrangement, with spacings between cap centres of {diameter + 25mm} to {diameter + 50mm} as the general arrangement.

A typical cap diameter is said to be 100 mm for a 1.8 m diameter column. There is significant periphery waste.

For the low liquid flow Sinnott⁽²⁾, p. 514 recommends Reverse flow:  — see also Figure of p. 523.

Reverse flow baffle.

However this will again reduce the number of available caps. Thus 75 mm caps will be used at 125 mm equilateral spacing

Cap diameter = 75 mm

Cap spacing = 125 mm

④ PLATE PRESSURE DROP.

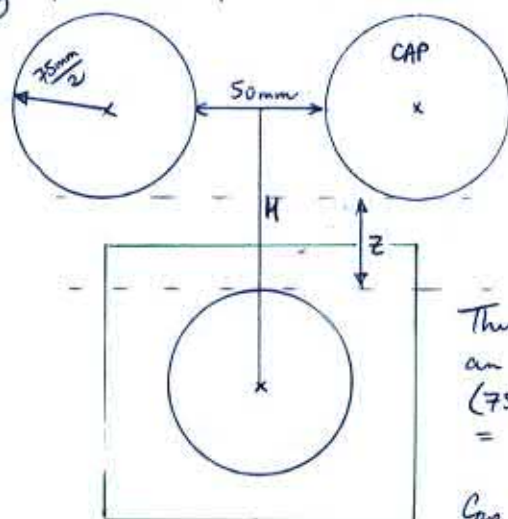
Perry⁽⁶⁾ gives pressure drop correlation equations, from Smith, for bubble-caps [p. 18-9]. However dimensions of the caps are required.

④(a) BUBBLE CAP DIMENSIONS.

Dimensions will be assumed as follows:

For the 75mm diameter caps selected

Say 40 slots of width 3mm and height 10mm



$$H = \left(125^2 - \left(\frac{125}{2} \right)^2 \right)^{\frac{1}{2}}$$

$$\therefore H = 108 \text{ mm}$$

$$\Rightarrow Z = 33 \text{ mm} \quad (\text{assumed})$$

Thus each cap fits into an area
 $(75 + 33) \text{ mm} \times (75 + 50) \text{ mm}$
 $= 13532 \text{ mm}^2$

$$\text{Cap area} = 4418 \text{ mm}^2$$

From Table 18-3 of Perry⁽⁶⁾, a typical "active area" would be $0.66 \times \{\text{total cross sectional area}\}$.

Note: Increase in this fraction due to selecting a lower cap size would be compensated for by decrease due to the reverse flow baffle.

$$\text{Total area} = \frac{\pi}{4} \times (1.8)^2 = 2.545 \text{ m}^2$$

$$\Rightarrow \text{Active area} \approx 1.679 \text{ m}^2$$

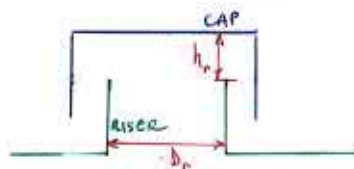
Hence we might estimate $\frac{1.679 \times 10^6}{13532} = 124$ caps per tray,
 or, rounding down 100 caps per tray.

$$40 \times \begin{matrix} h_{sh} = 10 \text{ mm} \\ 3 \text{ mm} \times 10 \text{ mm slots} \end{matrix}$$

100 caps per tray

$$\text{Slot area} = 40 \times 3 \times 10 = 1200 \text{ mm}^2 \text{ per cap}$$

By assumption from Fig. 18-13b of Perry⁽⁶⁾, it will be assumed that the ratio of annular area to riser area is 1.0, with the reversal area equal to 1.35 times {average of riser and annular areas} (equal here).



Reversal area is taken as $(\pi d_r) \cdot h_r$.

PRESSURE DROP

With these specifications the head-loss coefficient for dry bubble-caps, K_2 , is approx. 16.6

$$K_2 = 16.6$$

Given that cap area = riser area + annular area, here riser area = $4418 \div 2 = 2209 \text{ mm}^2$

$$\Rightarrow d_r = 53 \text{ mm}$$

$$(\text{reversal area} = 2982 \text{ mm}^2) \Rightarrow h_r = 18 \text{ mm}$$

$$\text{Riser diameter} = 53 \text{ mm}$$

Hence linear gas velocity through risers:

$$U_h = \frac{(238 \text{ mol.s}^{-1})(43 \text{ mol.m}^{-3})^{-1}}{100 \times (2209 \times 10^{-6}) \text{ m}^2} = 25 \text{ m.s}^{-1}$$

$$U_h = 25 \text{ m.s}^{-1}$$

Given $\rho_L = 1000 \text{ kg.m}^{-3}$ (as for water)
 $\rho_G = 1.02 \text{ kg.m}^{-3}$

$$\Rightarrow K_2 \frac{\rho_G}{\rho_L} U_h^2 = 10.6 \text{ mm (liquid)} \sim 10.6 \text{ mm (H}_2\text{O)}$$

As linear velocity through the slots, U_s is

$$U_s = \frac{(238)(43)^{-1}}{1200 \times 10^{-4}} = 46 \text{ m.s}^{-1}$$

$$U_s = 46 \text{ m.s}^{-1}$$

$$\text{then } K_1 = 3.73 \left(\frac{\rho_G}{\rho_L - \rho_G} \right)^{\frac{1}{2}} h_{st}^{\frac{1}{2}} U_s^{\frac{3}{2}} = 27.4 \text{ mm (H}_2\text{O)}$$

Hence the pressure drop across the disperser is

$$h_d = K_1 + K_2 \frac{\rho_G}{\rho_L} U_h^2 = 27.4 + 10.6 = 38.0 \text{ mm (H}_2\text{O)}$$

$$h_d = 38.0 \text{ mm (H}_2\text{O)}$$

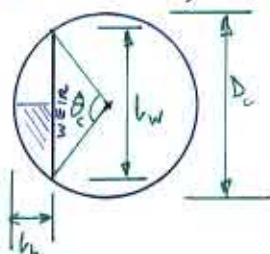
④(b)

WEIR DIMENSIONS are needed to find the pressure drop through the aerated liquid.

Sinnott⁽²⁾, p. 526, recommends 40 to 50 mm as weir height.

Given the need to cool, we will specify 50 mm.

Given the low liquid flow, from Sinnott⁽²⁾, p. 527, take $\frac{l_w}{D_c} \approx 0.70$, $\frac{l_h}{D_c} \approx 0.10$, $\theta_c \approx 89^\circ$ (approx.)



$$\Rightarrow l_w \approx 1.26 \text{ m}$$

$$\frac{l_h}{D_c} \approx 0.10$$

Reference to Perry⁽⁶⁾, p. 1-26

shows that $\frac{l_h}{l_w} \approx 0.205$

$$\Rightarrow l_h \approx 258 \text{ mm}$$

(while $\frac{l_h}{D_c} \approx 0.143$).

$$l_w = 50 \text{ mm}$$

$$l_w = 1.26 \text{ m}$$

$$\frac{l_h}{D_c} \approx 0.10$$

$$l_h = 258 \text{ mm}$$

DYNAMIC SEAL HEIGHT.

This is the calculated height of clear liquid (equivalent) above dispersers. From Perry⁽⁶⁾, pp. 18-10f.:

$$h_s = h_s + h_{ow} + \frac{1}{2} h_{hg}$$

$h_s \equiv$ static slot seal $\equiv$ {weir height} - {height of top of slot above floor}

If the bottom of the slot is assumed 10 mm above the plate floor

$$h_s = 50 - (10 + 10) = 30 \text{ mm}$$

$$h_s = 30 \text{ mm}$$

$h_{ow} \equiv$ height of crest above weir

From the Francis weir equation: $h_{ow} = 664 \left(\frac{V_L}{l_w} \right)^{\frac{2}{3}}$

$$\therefore h_{ow} = 664 \left(\frac{0.35 \text{ kg} \cdot \text{s}^{-1}}{1000 \text{ kg} \cdot \text{m}^{-3} \times 1.26 \text{ m}} \right)^{\frac{2}{3}} = 2.83 \text{ mm (H}_2\text{O)}$$

$$h_{ow} = 2.8 \text{ mm (H}_2\text{O)}$$

$h_{hg} \equiv$ hydraulic gradient across plate.

From Fig. 18-17

$$h_{hg}' \approx 0.05 \text{ inches}$$

With $U_a \equiv$ linear gas velocity through active area

$$U_a = \frac{(238)(43)}{0.66 \pi (1.8)^2} \approx 3.3 \text{ m s}^{-1}$$

$$\text{say } C_{vf} = 15$$

$$\Rightarrow h_{hg} \approx 1.9 \text{ mm (H}_2\text{O)}$$

$$h_{hg} = 1.9 \text{ mm (H}_2\text{O)}$$

$$\text{Thus } h_{ds} = 30 + 2.8 + 1.9 = 34.7 \text{ mm (H}_2\text{O)}$$

$$h_{ds} = 34.7 \text{ mm (H}_2\text{O)}$$

From Fig. 18-15, the correction factor, $\beta \approx 0.58$

$$\beta = 0.58$$

and the relative froth density, $\rho_t \approx 0.18$

Hence the pressure drop through the aerated liquid is

$$h_l' = \beta \cdot h_{ds} = 20.1 \text{ mm (H}_2\text{O)} \approx 20 \text{ mm (H}_2\text{O)}$$

$$h_l' \approx 20 \text{ mm (H}_2\text{O)}$$

Hence the actual height of froth on the plates is

$$h_p = h_l' \div \phi_t \approx 112 \text{ mm}$$

$$h_p \approx 112 \text{ mm}$$

Though this was larger than anticipated, the tray spacing of 0.75m is still valid.

Finally, the total pressure drop across one plate is thus

$$h_t = h_d + h_l' = 38 + 20 = 58 \text{ mm (H}_2\text{O)} \cdot \text{plate}^{-1}$$

$$h_t = 58 \text{ mm (H}_2\text{O)} \cdot \text{plate}^{-1}$$

For 21 plates $h_t \approx 12 \text{ kPa}$

$$(\Delta p) \approx 12 \text{ kPa for all 21 plates}$$

This is acceptable.

⑤

DOWNCOMER DESIGN. — Assumed segmental.

From Perry⁽⁶⁾, p. 18-7 $h_{dc}' = \frac{1}{\phi_{dc}} \cdot h_{dc} = \frac{1}{\phi_{dc}} [h_t + h_w + h_{ow} + h_{da} + h_{hg}]$

$$h_t = 58 \text{ mm}, h_w = 50 \text{ mm}, h_{ow} = 2.8 \text{ mm} \text{ from (4).}$$

$$\text{and } h_{hg} = 1.9 \text{ mm}$$

ϕ_{dc} is the average relative froth density in the downcomer, and is taken as 0.5

h_{da} = head loss due to liquid flow under downcomer apron
[From p. 18-10]

Taking a liquid-seal depth of 25mm from top of liquid on plate to bottom of downcomer.

$$\text{Liquid seal} = 25 \text{ mm} = h_{ap}$$

Thus the minimum flow area under the apron is

$$A_{da} = \left(\frac{1}{2} \times 1.26 \text{ m}\right) \times (50 - 25) \times 10^{-3} \text{ m} = 0.01575 \text{ m}^2$$

$$\text{Whence } h_{da} = 165.2 \left(\frac{3.5 \text{ kg} \cdot \text{s}^{-1}}{1000 \text{ kg} \cdot \text{m}^{-3} \times 0.01575 \text{ m}^2} \right)^2 = 8.2 \text{ mm}$$

$$h_{da} = 8.2 \text{ mm (H}_2\text{O)}$$

Thus $h_{dc} \approx 121 \text{ mm (clear liquid)}$

$$\rightarrow h_{dc}' = 242 \text{ mm (aerated liquid)}$$

$$h_{dc}' = 242 \text{ mm (aerated liquid)}$$

So again the plate spacing of 0.75m is satisfactory
[see Sinnott⁽²⁾, p. 532]

Check downcomer residence time (should be greater than 3 seconds for adequate disengagement — Sinnott⁽²⁾, p. 532)

$$t_r = \frac{A_{da} \cdot h_{dc} \cdot \rho_L}{L} = \frac{(0.01575 \text{ m}^2)(0.121 \text{ m})(1000 \text{ kg} \cdot \text{m}^{-3})}{(0.35 \text{ kg} \cdot \text{s}^{-1})} = 44 \text{ s}$$

$$t_r = 44 \text{ s.}$$

[Also Bachhurst & Harker, p. 177]

plenty.

①

THICKNESS OF ABSORBER TRAYS.

Assume that the tray may be modeled as a circular plate, freely supported and loaded concentrically, as per Mooney⁽¹⁾, Art. 151, pp. 460ff.

Supposing the load to be 1000 N (or just over 100 kg), distributed over an area much smaller than that of the tray, then the maximum deflection is given (approximately) by:

$$\delta_{\max} \approx \frac{5}{3\pi} \frac{Pr^3}{Et^3}$$

in which P is the load (1000 N)
 r the radius of the plate (0.9 m)
 E is the Young's modulus of elasticity
 t the thickness

[Poisson's ratio is assumed $\nu = \frac{1}{m} = \frac{1}{3}$.]

From AS 1210 (1989), Table 3.3.7, for austenitic stainless steels $E \approx 0.194 \times 10^6$ MPa at 50°C.

$\therefore$ For a deflection of 0.010 m, $t \approx 6$ mm

For comparison, $t = 3$ mm yields a heart-attack-inducing $\delta_{\max} \approx 0.082$ m.

Suppose two 25 mm pipes were welded to the underside of the support ring, parallel to the weir. This places it approximately 325 mm off-centre, giving a length of 1650 mm.

length = 1650 mm

If this is subject to a uniformly distributed load, then

$$\delta_{\max} = \frac{5}{384} \frac{PL^3}{EI}, \text{ whence } I = \frac{1.51 \times 10^{-8} \text{ m}^4}{2} \text{ for } \delta_{\max} = 0.010 \text{ m}$$

$\leftarrow$ two bars.

[Mooney⁽¹⁾, p. 187].

For the hollow pipe $I = \frac{\pi}{64} (d_o^4 - d_i^4)$
 for $d_o = 25$ mm $\Rightarrow d_i = 0.022$ m = 22 mm
 $\Rightarrow$ i.e. thickness = 1.5 mm

Hence specify 3 mm thick plate with two supports, 325 mm of centre, parallel to the weir, with $d_o = 25$ mm and thickness at least 1.5 mm $\rightarrow$ 2 mm.

From Perry⁽⁶⁾, p. 6-42, $\frac{3}{4}$ " schedule 40 is ample.
 $\leftarrow$ (nominal)

3 mm thick trays
 2 supports
 325 mm off-centre
 parallel to weir
 $d_o = 25$ mm
 thickness = 2 mm
 $\frac{3}{4}$ " schedule 40.



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①

COLUMN DIMENSIONS

The column has an internal diameter of 1.8m and a height of

$$\begin{aligned}
 H = & 2.90 \quad (\text{Bed 1}) \\
 & + 2.20 \quad (\text{Bed 2}) \\
 & + 2.50 \quad (\text{Bed 3}) \\
 & + 21 \times 0.75 + 2 \times 0.61 \quad (\text{Stage 4 including manways}) \\
 & + 1.50 \quad (\text{Vapour space above stage 4}) \\
 & + 1.50 \quad (\text{Between bed 3 and stage 4}) \\
 & + 3 \times (0.5 + 1.5) \quad (\text{Below beds 1 to 3, including liquid hold-up})
 \end{aligned}$$

$$\therefore H = 33.57 \text{ m, without ends}$$

$$D_i = 1.8 \text{ m}$$

$$H = 33.57 \text{ m}$$

②

WALL THICKNESS

This will be taken as constant for the cylindrical shell.

②(a)

PRELIMINARY ESTIMATE

Taking a corrosion allowance of 2mm, Sinnott⁽²⁾, p 739, recommends a "minimum practical wall thickness" of 7mm for this diameter vessel.

$$t \geq 7 \text{ mm}$$

②(b)

DESIGN PRESSURE

Operating pressure of the absorber may be taken at a maximum of 130 kPa (abs), at the base. [CHE4109]

Design pressure will be taken above Sinnott⁽²⁾'s recommended +5 to 10% in view of the added explosion risk
 $\Rightarrow P_{\text{DESIGN}} = 150 \text{ kPa (abs)}$

$$P_{\text{DESIGN}} = 150 \text{ kPa (abs)}$$

As Bontang may be prone to hurricanes of wind speed up to $\sim 100 \text{ km.h}^{-1}$, wind speed will be set at a fixed 27 m.s^{-1}

Given $C_D \approx 1.0$ for cylinders [Potter and Wiggert⁽¹⁾], the drag coefficient.

$$\text{Equivalent wind pressure, } p_{\text{WIND}} = \frac{1}{2} \rho_{\text{AIR}} V^2$$

As $\rho_{\text{AIR}} \approx 1 \text{ kg.m}^{-3} \Rightarrow p_{\text{WIND}} \approx 365 \text{ Pa}$

This acts on the projected area.

$$\text{For the column } \frac{A_{\text{PROJ}}}{L} = D_o = 1.8 \text{ m}^2.\text{m}^{-1}$$

$$\Rightarrow \text{Treat the wind as a uniformly distributed load, } F_{\text{WIND}} = 656 \text{ N.m}^{-1}$$

$$\text{Treating the vessel as a cantilever, } M_{\text{base}} = F_{\text{WIND}} \cdot \frac{L^2}{2} = 370 \text{ kN.m (at the base)}$$

For a cylinder (ignoring end effects) $I_z = \frac{\pi}{64} (D_o^4 - D_i^4)$

For a thickness of 5mm (ie. without corrosion allowance):

$$I_z = \frac{\pi}{64} [(1.8\text{m})^4 - (1.8 + 0.010\text{m})^4] = 0.0115\text{m}^4$$

$$\text{Thus } \sigma_{z \text{ bend}} = \pm \frac{M_{\text{bend}} \cdot D_o}{2I_z} \doteq \begin{cases} +29.3\text{ MPa, upwind} \\ -29.3\text{ MPa, downwind} \end{cases}$$

where negative signifies compression.

$$\sigma_{\text{HOOP}} = \frac{P_{\text{DESIGN}} D_i}{2t} = +8.8\text{ MPa}$$

$$\sigma_{\text{AXIAL}} = \frac{\sigma_{\text{HOOP}}}{2} = +4.4\text{ MPa}$$

$$P_{\text{DESIGN}} = 49\text{ kPa (g)}$$

$$\sigma_{z \text{ bend}} = \pm 29.3\text{ MPa}$$

$$\sigma_{\text{HOOP}} = +8.8\text{ MPa}$$

$$\sigma_{\text{AXIAL}} = +4.4\text{ MPa}$$

There must also be some self-weight:

$$\text{Mass of shell} \approx (33.57\text{m}) \frac{\pi}{4} (D_o^2 - D_i^2) (\rho)$$

and $\rho \approx 7.7 \times 10^3\text{ kg}\cdot\text{m}^{-3}$ [Carnegie (6)]

$$\Rightarrow m_{\text{SHELL}} \approx 7.3\text{ t}$$

$$\text{Mass of liquid} \approx (21 \times 0.050\text{m} + 3 \times 0.50\text{m}) \times \frac{\pi}{4} (1.8\text{m})^2 \rho$$

$$m_{\text{LIQUID}} \doteq 6.5\text{ t}$$

There is also packing, trays and other internals
say $m_{\text{INTERNALS}} \doteq 10\text{ t}$

$$\Rightarrow m_{\text{TOTAL}} \approx 23.8\text{ t}$$

$$\therefore \sigma_{\text{SELF-WEIGHT}} = \frac{(23.8 \times 10^3\text{ kg})(9.78\text{ ms}^{-2})}{\frac{\pi}{4} [(1.8\text{m})^2 + (1.81\text{m})^2]} \doteq -8.3\text{ MPa}$$

$$\sigma_{\text{SELF-WEIGHT}} = -8.3\text{ MPa}$$

where the value for gravity used is for sealevel,
at the equator [Carnegie (2)].

Thus, at the base of the column:

	UPWIND	DOWNWIND
σ_z [MPa]	+25.4	-33.2
σ_{HOOP} [MPa]	+8.8	+8.8
σ_{RADIAL} [MPa]	~0	~0 (thin shell)

Here the danger of assuming internal pressure to be the dominant factor is clear.

In summary, $\sigma_{\text{MAX}} \doteq -33.2\text{ MPa}$

$$\sigma_{\text{MAX}} = -33.2\text{ MPa}$$

For type F316 "high alloy" (stainless) steel, we abstract a value of ~ 100 MPa as the design tensile strength from AS 1210 (1989).

$$\sigma_{\text{MAX, TENSILE}} \doteq 100 \text{ MPa}$$

This is evaluated at a design temperature of 170°C , corresponding to a complete failure of the cooler on the absorber feed line.

$$T_{\text{DESIGN}} = 170^\circ\text{C}$$

As $\sigma_{\text{MAX}} \ll \sigma_{\text{MAX, TENSILE}} \Rightarrow$ this analysis shows 5mm to be an adequate thickness.

Okay for normal operation during cyclone

②(c)

WATER TESTING

For a completely flooded column,

$$m_{\text{WATER}} = \frac{\pi}{4} \cdot (1.8\text{m})^2 \cdot (33.57\text{m}) \cdot (1000\text{kg}\cdot\text{m}^{-3}) \doteq 85.4 \text{ t}$$

$$\text{So now } m_{\text{total}} = 7.3 + 85.4 + 10 = 102.7 \text{ t}$$

$$\therefore \sigma_{\text{SELF-WEIGHT}} = -35.6 \text{ MPa}$$

$$\sigma_{\text{SELF-WEIGHT}} = -35.6 \text{ MPa}$$

Obviously hydraulic testing would not take place during a cyclone. Taking $v_{\text{WIND}} = 10 \text{ m}\cdot\text{s}^{-1}$

$$\Rightarrow p_{\text{WIND}} = 50 \text{ Pa}$$

Analysing as before,

$$\sigma_{z, \text{bend}} = (\pm 29.3) \left(\frac{50}{365} \right) = \pm 4.0 \text{ MPa}$$

$$\sigma_{z, \text{bend}} = \pm 4.0 \text{ MPa}$$

At the base of the column the pressure due to the hydrostatic head is $p = \rho gh$
 $\Rightarrow p_{\text{WATER}} = 328 \text{ kPa (g)}$

$$\text{Thus, now } \sigma_{\text{HOOP}} = \frac{p_{\text{WATER}} D_i}{2t} = +58.8 \text{ MPa}$$

$$\sigma_{\text{HOOP}} = +58.8 \text{ MPa}$$

$$\sigma_{\text{AXIAL}} = \frac{\sigma_{\text{HOOP}}}{2} = +29.3 \text{ MPa}$$

$$\sigma_{\text{AXIAL}} = +29.3 \text{ MPa}$$

where again $t = 5\text{mm}$ has been used.

Hence, at the base of the column:

	UPWIND	DOWNWIND	
σ_z [MPa]	-2.3	-10.3	
σ_{HOOP} [MPa]	+58.8	+58.8	
σ_{RADIAL} [MPa]	~ 0	~ 0	(thin wall)

Here $\sigma_{\text{MAX}} = +58.8 \text{ MPa}$ is larger than the previous case, but still substantially below the maximum allowable.

$$\sigma_{\text{MAX}} = +58.8 \text{ MPa}$$

$\Rightarrow 7\text{mm}$ thickness (total) is adequate.

Okay for hydrostatic testing.

②(d)

EARTHQUAKE LOADING.

Bontang may be subject to earthquakes.

From Brownell & Young (1959), cited in CHE4101 by Obirich,

$$F_{\text{HORIZ}} = C \cdot m_{\text{VESSEL}} \cdot g$$

where C will be taken as 0.10 (empirical correlation)

Assuming hydraulic testing does not take place, $m_{\text{VESSEL}} = 23.8 \text{ t}$.

$$\Rightarrow F_{\text{HORIZ}} = 23.3 \text{ kN}$$

The average shear stress due to this force:

$$\tau_{\text{ave}} = \frac{23.3 \times 10^3 \text{ N}}{\frac{\pi}{4} (1.8^2 + 1.81^2) \text{ m}^2} = 822 \text{ kPa}$$

From Morley⁽¹⁾, Art. 71, p. 161, we observe $\tau_{\text{max}} = 2\tau_{\text{ave}}$ due to F_{HORIZ} .

$$\Rightarrow \tau_{\text{max}} \approx 1.65 \text{ MPa}.$$

Even allowing for the fact that the actual maximum shear stress will be increased by the effect of other forces acting, it is evident that this is not a significant factor.

→ the suggested design is satisfactory from an earthquake-loading perspective.

②(e)

BUCKLING

Neglecting the stiffening effects of the internals, Sinnott⁽²⁾, p. 760, gives the following equation for buckling:

$$\sigma_c = 2 \times 10^4 \left(\frac{t}{D_o} \right) \text{ MPa}.$$

This is the maximum allowable compressive stress.

$$\text{Here } \sigma_c = 55 \text{ MPa, taking } t = 5 \text{ mm}.$$

From section ②(b), page 2, we found that the maximum compressive stress was $\approx 33 \text{ MPa}$, so the buckling criterion is satisfied.

$$C = 0.10$$

$$F_{\text{HORIZ}} = 23.3 \text{ kN}$$

$$\tau_{\text{max}} \approx 1.65 \text{ MPa}$$

OKay for earthquakes.

$$\sigma_c = 55 \text{ MPa}.$$

OKay for buckling.
(normal operation at high wind speed).



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Alternatively, in the absence of high wind load,

$$\sigma_{z, \text{bend}} = \pm 4 \text{ MPa}, \quad \sigma_{\text{SELF-WEIGHT}} = -8.3 \text{ MPa}$$

Thus the limit of maximum compressive stress $= \sigma_c = 55 \text{ MPa}$ is reached when

$$\text{for which } \sigma_{\text{HOOP}} = -55 \text{ MPa}, \quad \sigma_{\text{AXIAL}} = -27.5 \text{ MPa}$$

$$\text{Given } \sigma_{\text{HOOP}} = \frac{p D_i}{2t}, \quad \text{this implies } p = -306 \text{ kPa(g)}$$

Thus, this implies the vessel would withstand even an absolute vacuum inside, with atmospheric pressure outside.

Okay for buckling (vacuum). ?

Comparison with AS1210 (1984), § 3.9.3

$$\text{gives } \frac{D_o}{t} \approx 360, \quad \frac{L}{D_o} \approx 20 \Rightarrow A \approx 10^{-5} \Rightarrow B \approx 0.94$$

$$\text{And } P = \frac{4B}{3(D_o/t)} \approx 0.003 \text{ MPa net external overpressure} = 3 \text{ kPa(g)}$$

Equation (13.51) of Sinnott⁽²⁾, $P_c = 2.2E \left(\frac{t}{D_o}\right)^3$, gives $P_c \approx -9 \text{ kPa(g)}$

and the recommended safety factor of 3 then yields a maximum (magnitude) overpressure $P_c = -3 \text{ kPa(g)}$, as before.

Maximum external overpressure = 3 kPa(g)

⇒ NOT SUITABLE FOR NON-NEGUGIBLE VACUUM (Note: stiffening effects not considered).

Will fail due to buckling at moderate vacuum.

②(f)

INSTALLATION

Consider the installation of the empty vessel, transported horizontally to site.

If it is raised according to 

$$\text{then, taking the empty mass as } 8t \Rightarrow F = \frac{78.2 \text{ kN}}{2}$$

$$\text{Thus } M_{\text{bend}} = (2F) \cdot \frac{L}{2} = 1313 \text{ kN.m}$$

$$\text{Given } I_z = 0.0115 \text{ m}^4 \quad (\text{as before})$$

$$\Rightarrow \sigma_{z, \text{bend}} = \frac{\pm M_{\text{bend}} \cdot D_o}{2I_z} = \pm 103 \text{ MPa}$$

$$\sigma_{z, \text{bend}} = \pm 103 \text{ MPa}$$



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This is right at the suggested allowable maximum for tensile stress.

However:

- * the maximum tensile stress was evaluated at 150°C, however installation at 50°C gives a design tensile strength of 129 MPa [AS1210(1989)] $\Rightarrow$ OKAY.
- * when installed, the 2mm corrosion allowance will still be entirely present $\Rightarrow$ OKAY
- * in practice the vessel may not be lifted from a single point, and certainly would not be lifted from its end. $\Rightarrow$ OKAY.

OKAY for installation.



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DESIGN OF: ABSORBER ENDS (MECHANICAL)

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①

CHARACTERISTICS

Diameter is 1.8m (internal)
 $\Delta p_{max} = 328 \text{ kPa}$ {see design of ABSORBER SHELL}

$D = 1.8 \text{ m}$
 $\Delta p_{max} = 328 \text{ kPa}$

②

TYPE

Sinnott⁽²⁾ recommends standard torispherical heads
 "dished ends". Formed head (no joints)

Torispherical
 Formed (no joints)

Take ratio of knuckle to crown radius $\geq \frac{6}{100}$

$\frac{R_k}{R_c} \geq \frac{6}{100}$

Also crown radius $\leq$ Diameter of cylinder

$R_c \leq D$

→ Physically $R_c > \frac{D}{2}$

$R_c > \frac{D}{2}$

③

DIMENSIONS.

$0.9 \text{ m} < R_c \leq 1.8 \text{ m}$

Say $R_c = 1.4 \text{ m}$

$R_c = 1.4 \text{ m}$

If $\frac{R_k}{R_c} = \frac{7}{100} \Rightarrow R_k = 0.2 \text{ m}$

$R_k = 0.2 \text{ m}$

④(a)

THICKNESS

Calculate using the "stress concentration factor", C_s , of Sinnott⁽²⁾:

$$C_s = \frac{1}{4} \left(3 + \sqrt{\frac{R_c}{R_k}} \right) = 1.41 (\sim \sqrt{2})$$

$C_s = 1.41$

$J = 1.0$ (formed)

$J = 1.0$

$$\therefore \text{Thickness}_{max} = \frac{(328 \text{ kPa})(1.4 \text{ m})(1.41)}{2\sigma_{max}(1.0) + (328 \text{ kPa})(1.41 - 0.2)}$$

From AS1210(1989) $\Rightarrow \sigma_{max, TENSILE} \doteq 100 \text{ MPa}$

$\sigma_{max, TENSILE} = 100 \text{ MPa}$

$$\Rightarrow \text{Thickness}_{max} = \frac{0.648}{200 + 0.397} = 0.00323 \text{ m}$$

$\text{Thickness}_{max} = 3.2 \text{ mm}$

Add 2mm Corrosion allowance: Thickness $\approx 5.2 \text{ mm}$

Thickness $\approx 5.2 \text{ mm}$

④(b)

CHECK STRESS

Maximum stress is in toroidal section.

From Sinnott⁽²⁾

For the maximum stress = hypothetical inner edge of torus:

$$\sigma_2 = \frac{PR_k}{2t} \left[\frac{D - R_k}{\frac{D}{2} - R_k} \right] = 1.58 \frac{PR_k}{2t} = 1.58 \sigma_1 = 16.2 \text{ MPa}$$

$\sigma_1 = 10.25 \text{ MPa}$

$\sigma_2 = 16.2 \text{ MPa}$



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(5)

Both values are far below the maximum allowable

OKAY.

AUSTRALIAN STANDARD.

Check the above with AS1210(1989)

§ 3.12

$$\frac{D}{t} = \frac{1800}{3.2} = 563 > 100 \Rightarrow$$

particular case should be exercised (buckling)

CARE! (buckling)

Suppose $t = 5\text{mm}$ (+2mm corrosion allowance)

$$\Rightarrow \frac{D}{t} = \frac{1800}{5} = 360 > 100 \Rightarrow \text{Case still required.}$$

↳ However this would match the existing shell better.

Thickness = 5mm
+ 2mm Corrosion allowance

AMENDMENT 1 :

$$\text{As } \frac{D}{t} > 300 \Rightarrow \frac{P_{\max}}{\sigma_{\max, \text{TENSILE}}} \leq \frac{150 \left(\frac{R_h}{D} \right)^{0.84}}{\left(\frac{D}{t_k} \right)^{1.53} \cdot \left(\frac{R_c}{D} \right)^{1.1}}$$

is recommended.

Current dimensions give

$$\frac{P_{\max}}{100 \text{ MPa}} \leq \frac{23.69}{6181.}$$

$$\Rightarrow P_{\max} \leq 0.383 \text{ MPa}$$

$$\text{i.e. } P_{\max} \leq 383 \text{ kPa}$$

$$P_{\max} \leq 383 \text{ kPa}$$

OKAY

Note that the initial 3.2mm thickness would have been too low.

THICKNESS:

$$t = \frac{P R_c C_s}{2 \sigma_{\max, \text{TENSILE}} S - 0.2 P} = \frac{0.649}{200 - 0.068} = 0.003248$$

= 3.2mm
(as before).

① TYPE : Skirt

Skirt.

② REFERENCE : AS1210 (1989)

AS1210 (1989)

③ TEMPERATURE
Check for excessive discontinuity stresses :

$$t \cdot D_o \cdot (T - T_{amb})_{max} \approx (5mm)(1800mm)(90-20) = 6.3 \times 10^5$$

$$6.3 \times 10^5 < 16 \times 10^6$$

OKAY FOR TEMPERATURE.

④ (a) AXIAL COMPRESSIVE STRESS — HYDROSTATIC TEST CONDITION

$$S_a = \left(\frac{4M}{\pi D_o^2 t} + \frac{W}{\pi D_o t} \right) \frac{1}{\cos(\alpha)}$$

$$W = (102.7t)(9.78ms^{-2}) = 1004 kN \div 10^6 N$$

$$\text{take } M = (S_a)(1.8m^2 \cdot m^{-1}) \left(\frac{34m}{2} \right) = 52020 N \cdot m$$

$$\div 5.2 \times 10^7 N \cdot mm$$

Suppose a cylindrical cell of the same thickness as the column:

$$D_o \div 1810 mm, t = 5mm, \alpha = 0^\circ$$

$$\Rightarrow S_a = (4.04 + 35.2)(1) = 39.2 MPa.$$

④ (b) YIELD
 $2S_a < \text{yield strength} \Rightarrow \text{OKAY}$

YIELD OKAY.

④ (c) YOUNG'S MODULUS
 $0.125 \frac{Et}{D_o} = 0.125 \times \left[\frac{(0.191 \times 10^6 MPa)(5mm)}{1810 mm} \right] \div 66 < S_a$

$\Rightarrow \text{OKAY}$

MODULUS OKAY.

⑤ CHECK BASE RING $\left[\frac{S_{min} t^{(b)}}{C} \right]$
Circumference (cylindrical) $\div 1800 \pi$ mm

$$8 \text{ bolts} \Rightarrow \text{pitch} = 706.9 mm > 600 mm$$

PITCH OKAY.

$$\therefore A_b \div \frac{1}{(8)(125MPa)} \left[\frac{4 \times 52020}{1.8} - 10^6 \right] \rightarrow \text{none required FOR HYDRO. TEST.}$$

$$A_b \div \frac{1}{(8)(125)} \left[\frac{4 \times 370000}{1.8} - (23.8 \times 10^3)(9.78) \right] = 589 mm^2$$

$$\Rightarrow D_b = 27.4 mm$$

CYCLONE LOADING.

$$D_b = 27.4 mm$$



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⑥

WIDTH OF BASE RING

From Sinnott ^(*):

$$F_b = \left[\frac{4M_s}{\pi D_s^2} + \frac{W}{\pi D_s} \right] \leq t S_u$$

$$\therefore F_b = 196 \text{ N.m}^{-1}$$

$$\Rightarrow L_b = \frac{196 \times 10^3}{5} \times \frac{1}{10^3} = 39.2 \text{ mm}$$

$$L_b \geq \dots 40 \text{ mm}$$

⑦

THICKNESS

Choose simple anchor (AS1210 (1989)) ... plus gusset [Sinnott ^(*)]

$$\Rightarrow L_r \rightarrow L_b = 39.2 \text{ mm} \leq 40 \text{ mm}$$

$$\therefore t_b = L_r \sqrt{\frac{3f_c'}{f_r}} \leq 40 \sqrt{\frac{3 \cdot (8.75)}{140}}$$

$$\text{As } f_c' \approx \frac{10^6 \text{ N}}{\frac{\pi}{4} [1840^2 - 1800^2] \text{ mm}^2} = 8.74 \text{ N.mm}^{-2}$$

$$\therefore t_b = 17.3 \text{ mm} \rightarrow 17 \text{ mm}$$

$$t_b = 17 \text{ mm.}$$

$\rightarrow L_b$ must be greater : - to accommodate bolt head + spacer
- for inside-skirt provision (same)



CLIENT: CHE4117

PROJECT: FORMALDEHYDE

DESIGN OF: INSULATION on ABSORBER

SHEET 1 of 1

DATE 03/10/1999

BY DIV

CHKD

①

CONVECTIVE HEAT TRANSFER COEFFICIENT.

From Holman⁽⁹⁾, fiber-glass blankets for wrapping are recommended, with $k \approx 0.05 \text{ W.m}^{-2}.\text{K}^{-1}$.

Fiber-glass blankets.
 $k = 0.05 \text{ W.m}^{-2}.\text{K}^{-1}$

For a vertical cylinder

$$h = \begin{cases} 1.42 \left(\frac{\Delta T}{L} \right)^{1/4} & , \text{ laminar} \\ 1.31 (\Delta T)^{1/2} & , \text{ turbulent} \end{cases}$$

where L is "vertical or horizontal dimension".

②

TEMPERATURES

if $T_a = 20^\circ\text{C}$ (minimum of range)

and $T_{\text{ABS-1}} = 75^\circ\text{C}$

$\rightarrow T_{\text{wall min}} \approx 48^\circ\text{C} \dots \text{okay}$

But, at the top of stage 1

$T_{\text{AB-1}} = 60^\circ\text{C} \rightarrow T_{\text{wall min}} \approx 40^\circ\text{C} \dots \text{Too Low}$

In that case $\Delta T = 40^\circ\text{C}$

$\therefore$ take $h \approx 3 \text{ W.m}^{-2}.\text{K}^{-1}$

$h = 3 \text{ W.m}^{-2}.\text{K}^{-1}$

$$h A \Delta T_{\text{surface}} = \dot{Q} = \frac{k}{\Delta x} A \Delta T_{\text{ins}}$$

THICKNESS

Suppose the outer surface of the insulation were at 40°C

$$\Rightarrow (3)(40 - 20) = \frac{0.05}{\Delta x} (60 - 40)$$

$$\therefore \Delta x \div 0.0167 \text{ m} = 16.7 \text{ mm}$$

$\Rightarrow$ Take insulation thickness as 25mm.

$$\Delta x = 25 \text{ mm}$$

Tube wall temperature is thus $T_{\text{wall min}} \rightarrow 60^\circ\text{C}$.

$T_{\text{wall min}} \rightarrow 60^\circ\text{C}$
okay.



APPENDIX TO CHAPTER 9

RECORD OF HAZOP MEETING

Stream 3

GUIDE WORD	DEVIATION	POSSIBLE CAUSES	CONSEQUENCES	ACTION REQUIRED
No	Flow	- Pipe blockage - Control valve V-1 malfunction - Pipe rupture or leakage	- Possibility of entering the explosive limits - Visible on flow indicator - Reactor feed will be outside design composition ==> product may be out of spec. - Reactor temperature may increase (less thermal ballast)	- Display flow reading of Stream 3 on panel (control room) - Have alarm for low flow - Have temperature indicator and alarm in reactor - Regular maintenance and inspection of control valve and piping
More	Flow	Control valve V-1 failure (fail-open to avoid previous deviation)	- Deterioration of catalyst - Decrease in yield	Install alarm for high flow
Less	Flow Pressure	- As for "No Flow" - Control valve V-1 failure - Upstream pipe rupture or leakage	- As for "No Flow" - Reverse flow, possibly including methanol ==> flammability hazard	- As for "No Flow" - Install low pressure alarm and indicator - Install non-return valve
What else?	Instrument air failure	As for "More Flow"	As for "More Flow"	Regular inspection

Stream 6

GUIDE WORD	DEVIATION	POSSIBLE CAUSES	CONSEQUENCES	ACTION REQUIRED
No	Flow	- Upstream pump failure or trip - Pipe blockage - Control valve V-2 failure (fail closed to avoid following deviation) - Pipe rupture or leakage	- Visible on flow indicator - Reactor feed will be outside design composition ==> product will be out of spec. - Reactor temperature will decrease (no reaction), catalyst degradation	- Regular maintenance and inspection - Stand-by pump installed
More	Flow	Control valve V-2 malfunction	- Product out of specification - Visible on flow indicator	- Install alarm for high flow - Have panel-mounted indicator
	Pressure	Downstream blockage AND pump-trip failure	Increased likelihood of rupture and leakage ==> flammability risk	- Pressure indicator and high alarm - Regular maintenance and testing of pump motor trip
	Temperature	Pump dead-heading, as for "More Pressure"	As for "More Pressure"	As for "More Pressure"
Less	Flow	As for "No Flow"	As for "No Flow"	As for "No Flow"
	Pressure	- Control valve V-2 failure - Upstream pipe rupture or leakage - Upstream pump failure or trip	- Reverse flow of methanol ==> flammability hazard - Loss of feedstock	- Install low pressure alarm and indicator (panel mounted) - Install non-return valve - Regular inspection and maintenance
What else?	Instrument air failure	As for "More Flow"	As for "More Flow"	Regular inspection

Stream 7

GUIDE WORD	DEVIATION	POSSIBLE CAUSES	CONSEQUENCES	ACTION REQUIRED
No	Flow	- Upstream pump failure or trip - Pipe blockage - Malfuction of V-1 AND V-2 - Pipe rupture or leakage	- No product - Reactor temperature will decrease (no reaction)	- Provision for indicator on flow controller - Regular maintenance and inspection - Stand-by pump installed
More	Flow	Malfuction of V-1 AND V-2	- Product out of specification (contact time in reactor affected) - Visible on flow indicators - Possible level increase in vaporiser	- Install alarms for high flow on Streams 3 AND 6 - Have panel-mounted indicators
	Pressure	Downstream blockage AND pump-trip failure	Increased likelihood of rupture and leakage ==> flammability risk	- Pressure indicator and high alarm on stream 6 - Regular maintenance and testing of pump motor trip
	Temperature	Pump dead-heading, as for "More Pressure"	As for "More Pressure"	As for "More Pressure"
Less	Flow	As for "No Flow"	- Less product - Reactor temperature will decrease (less reaction)	As for "No Flow"
	Pressure	- Control valve V-1 OR V-2 malfunction - Upstream pipe rupture or leakage - Upstream pump failure or trip	Reverse flow of methanol ==> flammability hazard	- Install low pressure alarm and indicator (panel mounted) - Install non-return valve - Regular inspection and maintenance

Stream 9

GUIDE WORD	DEVIATION	POSSIBLE CAUSES	CONSEQUENCES	ACTION REQUIRED
No	Flow	- Upstream blower (CP-1) failure or trip of steam turbine (TRB-1) - Duct blockage - Duct rupture or leakage - Failure of control valve V-3 (fails closed to avoid feeding a fire)	- Reactor feed will be outside design composition ==> product will be out of spec. - Reactor temperature will decrease (no reaction)	- Provision for indicator on flow controller - Regular maintenance and inspection (Stand-by compressor and turbine too expensive and impractical)
More	Flow	- Malfunction of V-3 - Steam turbine (TRB-1) goes haywire - Too much off-gas recycle	- Product out of specification (contact time in reactor affected) - Visible on flow indicators - Possibly enter flammability limits	- Install alarm for high flow - Have panel-mounted indicators - Remove all ignition sources - Adjust off-gas recycle
	Pressure	Downstream blockage (e.g. V-3 failure) AND turbine-trip malfunction	Increased likelihood of rupture and leakage ==> flammability risk (contains hydrogen)	- Pressure indicator and high alarm - Regular maintenance and testing of turbine trip system
	Temperature	Compressor dead-heading, as for "More Pressure"	As for "More Pressure"	As for "More Pressure"
Less	Flow	As for "No Flow"	- Less product - Reactor temperature will decrease (less reaction) - Product out of spec.	As for "No Flow"
	Pressure	- Control valve V-3 failure - Upstream pipe rupture or leakage - Upstream blower/turbine failure or trip	- Reverse flow of vapour, possibly including methanol ==> flammability hazard - Product out of spec.	- Install low pressure alarm and indicator (panel mounted) - Regular inspection and maintenance (Non-return valve impractical)

Stream 10

GUIDE WORD	DEVIATION	POSSIBLE CAUSES	CONSEQUENCES	ACTION REQUIRED
No	Flow	- Downstream pump (P-2A / P-2B) failure - Pipe blockage - Pipe rupture or leakage - Upstream feed system failure - Accidental closure of isolation valves	- No vaporisation due to zero heat transfer ==> Level in vaporiser rises ==> increased rupture risk of vaporiser ==> flammability hazard - Visible on vaporiser level indicator - composition ==> product will be out of spec. - Reactor temperature will decrease (no reaction) - More cooling required in absorber (control system will detect this)	- Provision for panel display of level - Regular maintenance and inspection - Training of operators not to close isolation valves during operation AND interlocks
More	Flow	- Increase in upstream flow - Lower temperature on exit of HX-10 (Stream 13)	- No increase in vaporisation due to limited utility capacity ==> Level in vaporiser rises ==> increased rupture risk of vaporiser ==> flammability hazard - Visible on vaporiser level indicator - Product out of spec.	- Install alarm for high flow - Have panel-mounted indicators
Less	Pressure	- Downstream blockage of pipe - Accidental closure of isolation valves	Increased likelihood of rupture and leakage ==> flammability risk (contains methanol)	High pressure alarm on pump discharges (to existing indicators)
	Temperature	High temperature of Stream 9 OR 13	Vapour in pump suction ==> damage to pump	Install low level alarm to trip pump
	Flow	As for "No Flow"	- Less product - Reactor temperature will decrease (less reaction) - Product out of spec. - More cooling required in absorber (control system will detect this)	As for "No Flow"
	Pressure	- Low level in vaporiser (HX-1) - Upstream rupture or leakage - Upstream blower/pump failure or trip	As for "More Temperature"	As for "More Temperature"
	Temperature	- Inadequate heat transfer in heat exchangers (HX-5 OR HX-10) - Steam utility failure	Level in vaporiser rises ==> increased rupture risk of vaporiser ==> flammability hazard	Install panel-mounted temperature indicators and alarms on exits of heat exchangers HX-5 AND HX-10

		On start-up temperatures of Streams 20 and 21 will be low	- Visible on vaporiser level indicator - Product out of spec.	- Attempt to make up additional duty in OTHER exchanger, ELSE reduce flow of vaporiser feed - Recycle until operating temperature reached
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Stream 11

GUIDE WORD	DEVIATION	POSSIBLE CAUSES	CONSEQUENCES	ACTION REQUIRED
No	Flow	- Upstream pump (P-2A / P-2B) failure - Pipe blockage - Pipe rupture or leakage - Upstream feed system failure - Accidental closure of isolation valves	As for “No Flow” of Stream 10	As for “No Flow” of Stream 10
More	Flow	As for “More Flow” of Stream 10	As for “More Flow” of Stream 10	As for “More Flow” of Stream 10
	Pressure	- Downstream blockage of pipe (including fouling of heat exchangers, HX-5 OR HX-10) - Accidental closure of isolation valves	Increased likelihood of rupture and leakage ==> flammability risk (contains methanol)	High pressure alarm on pump discharges (to existing indicators)
	Temperature	High temperature of Stream 9 OR 13	Vapour in pump suction ==> damage to pump	Install low level alarm to trip pump
Less	Flow	As for “No Flow”	As for “Less Flow” of Stream 10	As for “No Flow”
	Pressure	- Low level in vaporiser (HX-1) - Upstream rupture or leakage - Upstream blower/pump failure or trip	As for “More Temperature”	As for “More Temperature”
	Temperature	As for “Less Temperature” of Stream 10	As for “Less Temperature” of Stream 10	As for “Less Temperature” of Stream 10

Stream 12

GUIDE WORD	DEVIATION	POSSIBLE CAUSES	CONSEQUENCES	ACTION REQUIRED
No	Flow	As for “No Flow” of Stream 11	As for “No Flow” of Stream 10	As for “No Flow” of Stream 10
More	Flow	As for “More Flow” of Stream 10	As for “More Flow” of Stream 10	As for “More Flow” of Stream 10
	Pressure	- Downstream blockage of pipe (including fouling of heat exchangers, HX-5 OR HX-10) - Accidental closure of isolation valves	Increased likelihood of rupture and leakage ==> flammability risk (contains methanol)	High pressure alarm on pump discharges (to existing indicators)
	Temperature	High temperature of Stream 9 OR 13	Vapour in pump suction ==> damage to pump	Install low level alarm to trip pump
Less	Flow	As for “No Flow”	As for “Less Flow” of Stream 10	As for “No Flow”
	Pressure	- Low level in vaporiser (HX-1) - Upstream rupture or leakage - Upstream blower/pump failure or trip	As for “More Temperature”	As for “More Temperature”
	Temperature	As for “Less Temperature” of Stream 10	As for “Less Temperature” of Stream 10	As for “Less Temperature” of Stream 10

Stream 13

GUIDE WORD	DEVIATION	POSSIBLE CAUSES	CONSEQUENCES	ACTION REQUIRED
No	Flow	As for “No Flow” of Stream 11	As for “No Flow” of Stream 10	As for “No Flow” of Stream 10
More	Flow	As for “More Flow” of Stream 10	As for “More Flow” of Stream 10	As for “More Flow” of Stream 10
	Pressure	- Downstream blockage of pipe (including fouling of heat exchangers, HX-5 OR HX-10) - Accidental closure of isolation valves	Increased likelihood of rupture and leakage ==> flammability risk (contains methanol)	High pressure alarm on pump discharges (to existing indicators)
	Temperature	High temperature of Stream 9 OR 13	Vapour in pump suction ==> damage to pump	Install low level alarm to trip pump
Less	Flow	As for “No Flow”	As for “Less Flow” of Stream 10	As for “No Flow”
	Pressure	- Low level in vaporiser (HX-1) - Upstream rupture or leakage - Upstream blower/pump failure or trip	As for “More Temperature”	As for “More Temperature”
	Temperature	As for “Less Temperature” of Stream 10	As for “Less Temperature” of Stream 10	As for “Less Temperature” of Stream 10

Stream 14

GUIDE WORD	DEVIATION	POSSIBLE CAUSES	CONSEQUENCES	ACTION REQUIRED
No	Flow	- Upstream blockage (including accidental closure of isolation valves) - Upstream leakage or rupture	- No reaction ==> reactor temperature decrease ==> visible on reactor temperature indicator (with alarm) - No product	- Display flow reading of Stream 14 on panel - Have alarm for low flow - Regular maintenance and inspection of ductwork
More	Flow	More flow of feed streams into vaporiser (HX-1) – see Streams 3, 6, 7 and 9	- Product out of spec. (altered contact time in reactor) - Temperature at inlet to reactor will decrease due to limited heat transfer in Superheater (HX-2) ==> possible degradation of catalyst; product out of spec.	- Install a flow indicator, to be displayed in the control room with integral high flow alarm - Size vaporiser unit and steam system to handle some contingency (say 20% above design) - Temperature indicator AND controller will exist on exit of superheater (HX-2)
	Pressure	- Downstream blockage of duct - Accidental closure of isolation valves downstream	- Increased likelihood of rupture and leakage ==> flammability risk (contains methanol) - Discharge through safety valve at top of vaporiser (HX-1)	Install high pressure alarm
	Temperature	High temperature of Stream 9 OR 13	- Vapour in pump suction ==> damage to pump (P-2) - Less heating required in superheater (HX-2) - Composition may be different ==> product out of spec.	- Install low level alarm to trip pump - Temperature indicator AND controller on HX-2
Less	Flow	As for “No Flow”	- Less reaction ==> reactor temperature decrease ==> visible on reactor temperature indicator (with alarm) - Less product	As for “No Flow”
	Pressure	- Upstream rupture or leakage - Upstream blower (CP-1) failure OR trip	- Reaction may be affected via a shift in equilibrium (principally of the dehydrogenation reaction) - Saturation mole fractions of condensables in absorber (ABS-1) will increase ==> less effective	- Install low flow alarm - Make the ducts strong

			- absorption ==> lower plant yield; product out of spec. - Identifiable by blower trip alarm	
Temperature	As for “Less Temperature” of Stream 13	As for “Less Temperature” of Stream 13	As for “Less Temperature” of Stream 13	As for “Less Temperature” of Stream 13
Percentage of methanol	- Inadequate vaporisation (e.g. insufficient steam OR temperature of Stream 20 too low, as on start-up) - Malfunction of ratio controller	- Less reaction - Enter the flammability limits (no longer above the upper limit)	Have alarm on ratio controller – increase the ratio of methanol supplied, if possible, ELSE feed less feed to process and recycle more off-gas	

Stream 118

GUIDE WORD	DEVIATION	POSSIBLE CAUSES	CONSEQUENCES	ACTION REQUIRED
No	Flow	- Blockage in steam lines (including accidental closure of isolation valves; including build-up of deposits ["fouling"] in HX-10) - Upstream leakage or rupture - Failure to add additional fuel (natural gas) to the off-gas burner (RXN-3) on start-up	- No heating in HX-10 ==> less vaporisation occurring ==> less product / out of spec. - Likely to be registered by the pressure indicator on Stream 118	- Display flow reading of Stream 119 on panel - Have alarm for low flow on Stream 119 - Indicate pressure on panel - Regular maintenance and inspection of ductwork
More	Flow	Malfunction in steam system control valves (including V-4 – which should be fail-open to vaporise methanol out of vaporiser)	Over heating of vaporiser recycle stream (in HX-10) ==> gas phase in Stream 13 ==> liquid hold-up in base of vaporiser drops ==> cavitation in pump (P-2)	- Install a flow indicator, to be displayed in the control room with integral high flow alarm on Stream 119 - Temperature indicator AND controller will exist on exit of superheater (HX-2), and duty in this exchanger will decrease as required - Low pressure/Level alarms will trip pump (P-2)
Less	Pressure	- Downstream blockage of line - Accidental closure of isolation valves downstream - Malfunction in steam system control valves (including V-4)	- Increased likelihood of rupture and leakage ==> risk to personnel - Discharge through safety valve on shell-side of HX-10	Install high pressure alarm at boiler (RXN-3)
	Temperature	- As for "More Pressure" - Very low boiler feed water flow leading to super-heating of the 1200kPa(abs) steam	Increased risk of materials failures ==> risk to personnel	Construct steam lines of rugged material
	Flow	As for "No Flow"	- Less heating in HX-10 ==> less vaporisation occurring ==> less product / out of spec. - Likely to be registered by the pressure indicator on Stream 118	As for "No Flow"
	Pressure	- Upstream rupture or leakage - Upstream pump (on boiler feed water to off-gas burner) failure OR trip	Control system would attempt to increase the flow (IF necessary), however there is a limit to the flow that can be handled by HX-10	- Detect with low temperature alarm on Stream 13 AND low flow alarm Stream 119 - Ease off on the flow of feedstock to

			- Temperature of Stream 13 would decrease ==> less vaporisation ==> less feed to reactor ==> less product / out of spec. - Control system would attempt to increase the flow (IF necessary), however there is a limit to the flow that can be handled by HX-10 - Temperature of Stream 13 would decrease ==> less vaporisation ==> less feed to reactor ==> less product / out of spec. - Employees suffer burns to their persons	the vaporiser (HX-1)
Temperature	- Inadequate heating in boiler (RXN-3) - Heat loss through steam lines			- Cover steam lines with adequate insulation and ensure its upkeep - Control temperature of steam at point of generation (RXN-3) - Detect with low temperature alarm on Stream 13 AND low flow alarm Stream 119 - Ease off on the flow of feedstock to the vaporiser (HX-1)
What else?	Personnel performing maintenance on OR near steam lines	- Regular maintenance - Equipment break-down		Cover steam lines with adequate insulation ("Personnel Protection") and ensure its upkeep

Stream 119

GUIDE WORD	DEVIATION	POSSIBLE CAUSES	CONSEQUENCES	ACTION REQUIRED
No	Flow	As for “No Flow” of Stream 118	As for “No Flow” of Stream 118	As for “No Flow” of Stream 118
More	Flow	As for “More Flow” of Stream 118	As for “More Flow” of Stream 118	As for “More Flow” of Stream 118
	Pressure	As for “More Pressure” of Stream 118	As for “More Pressure” of Stream 118	As for “More Pressure” of Stream 118
Less	Temperature	- Low flow of Stream 12 ($q.v.$) - As for “More Pressure” - Very low boiler feed water flow leading to super-heating of the 1200kPa(abs) steam	Increased risk of materials failures ==> risk to personnel	Construct condensate lines of rugged material
	Flow	As for “Less Flow” of Stream 118	As for “Less Flow” of Stream 118	As for “Less Flow” of Stream 118
	Pressure	As for “Less Pressure” of Stream 118	As for “Less Pressure” of Stream 118	As for “Less Pressure” of Stream 118
What else?	Temperature	As for “Less Temperature” of Stream 118	As for “Less Temperature” of Stream 118	As for “Less Temperature” of Stream 118
	Personnel performing maintenance on OR near condensate lines	As for “What else?” of Stream 118	As for “What else?” of Stream 118	As for “What else?” of Stream 118

Vaporiser (HX-1)

GUIDE WORD	DEVIATION	POSSIBLE CAUSES	CONSEQUENCES	ACTION REQUIRED
No	Level	- No inlet flows (blockage of inlet lines/closed control valves) - Inlet flows are too hot (vapour)	- Vapour to suction port of pump (P-2) ==> Damage to pumps - Product out of spec.	Automatic trip on pumps
More	Level	Inadequate heating in recirculation loop (including due to blockage in pipes)	- Flooding of vaporiser - Blower may have to work harder to blow gas stream (Stream 9) through the increased head of liquid	Install high level alarm on existing liquid level controller
	Pressure	Downstream blockage	Pressure will be relieved through existing safety valve on top of HX-1	Ensure regular maintenance, testing AND inspection of safety valve
	Temperature	- Upstream blockage or disturbance - High inlet temperatures on streams 9 OR 13 (q.v.)	Increased risk of materials failures ==> risk to personnel; flammability risk	Construct vaporiser shell of heavy duty materials
Less	Level	- Less inlet flows (blockage of inlet lines/closed control valves) - Inlet flows are too hot (e.g. two-phase)	As for "No Level"	As for "No Level"
	Pressure	- Blower (CP-1) or pump (P-1) failure - Blockage in lines 7 OR 9 (upstream)	- Reaction may be affected via a shift in equilibrium (principally of the dehydrogenation reaction) - Saturation mole fractions of condensables in absorber (ABS-1) will increase ==> less effective absorption ==> lower plant yield; product out of spec. - Identifiable by blower/pump trip alarm	Install low flow alarm
	Temperature	Inadequate heating in recirculation loop (including due to blockage in pipes)	- Flooding of vaporiser - Blower may have to work harder to blow gas stream (Stream 9) through the increased head of liquid	Install high level alarm on existing liquid level controller

Methanol Heater (HX-10)

GUIDE WORD	DEVIATION	POSSIBLE CAUSES	CONSEQUENCES	ACTION REQUIRED
No	Level (shell-side)	- Blockage in Stream 118 (including Less inlet flows: blockage of inlet lines) - Steam trap failure - Leak in HX-10	- No heat transfer - Loss of containment ==> risk to personnel	- Low flow alarm on Stream 119 - Install liquid level controller with low level alarm
More	Level	- Blockage in Stream 119 (including closed control valves) - Insufficient flow of steam through Stream 118	- Flooding of exchanger shell - Evident due to low flow indicator on stream 119 - Heat transfer [coefficient] would decrease ==> evident due to low temperature indicator on Stream 13	Install liquid level controller with high level alarm
Less	Pressure	As for "More Pressure" of Stream 118	As for "More Pressure" of Stream 118	As for "More Pressure" of Stream 118
	Temperature	As for "More Temperature" of Stream 118	As for "More Temperature" of Stream 118	As for "More Temperature" of Stream 118
	Level	As for "No Level"	As for "No Level"	As for "No Level"
	Pressure	If the exchanger were isolated (shell-side) with steam initially present, then the steam would condense ==> decrease in pressure	This may cause material failure in extreme cases	- Train employees to NOT isolate exchanger while it still contains steam – it must be vented - Install vent if not already present (not marked) ELSE discharge through safety valve
	Temperature	As for "Less Temperature" of Stream 118	As for "Less Temperature" of Stream 118	As for "Less Temperature" of Stream 118

Pumps (P-2A AND P-2B)

GUIDE WORD	DEVIATION	POSSIBLE CAUSES	CONSEQUENCES	ACTION REQUIRED
More	Pressure	Dead-heading of pump due to downstream obstruction in line	Possible material failure in extreme cases	- Design pressures rated above operating pressures - Trip pump in case of high pressure alarm (to be installed)
	Temperature	- As for "More Pressure" - High inlet temperatures (see Stream 7)	Possible material failure in extreme cases (due to reduction in the yield strength of metals at elevated temperatures)	Design temperatures rated above operating temperatures
Less	Pressure	Low level in vaporiser (HX-1) ==> Insufficient Net Positive Suction Head (NPSH)	Cavitation ==> Damage to pump	Automatic trip on pump, activated by low level alarm on vaporiser (HX-1)
Reverse	Flow	Check-valve failure	Damage to pump(s)	Make sure that those responsible check the check valves to make sure that the check valves will check the flow, as required



APPENDIX TO CHAPTER 11

ECONOMIC EVALUATION

1999 currency exchange rates:

Source: The Saturday Age, Business section (from CBA - not for currency notes)

One Australian dollar was worth:

DATE	German DM			US \$		
	Buy	Sell	AVERAGE	Buy	Sell	AVERAGE
08 May	1.2290	1.2004	1.215	0.6718	0.6668	0.669
22 May	1.2289	1.2003	1.215	0.6620	0.6570	0.660
10 July	1.2910	1.2610	1.276	0.6692	0.6642	0.667
24 July	1.2209	1.1923	1.207	0.6506	0.6456	0.648
09 October	1.2188	1.1904	1.205	0.6620	0.6570	0.660
Average	1.238	1.209	1.22	0.663	0.658	0.66

So a German DM is equal to	0.5400	US \$.
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PURCHASED EQUIPMENT COSTS

Indonesian, USD₁₉₉₉ basis.

ABBREVIATIONS: n.a. = not available, N/A = not applicable, s-at = shell-and-tube (heat exchanger)

REFERENCE:

Current location factor [B & B; BRENNAN]: 0.769

Historical currency conversion factor [B & B]: 0.769

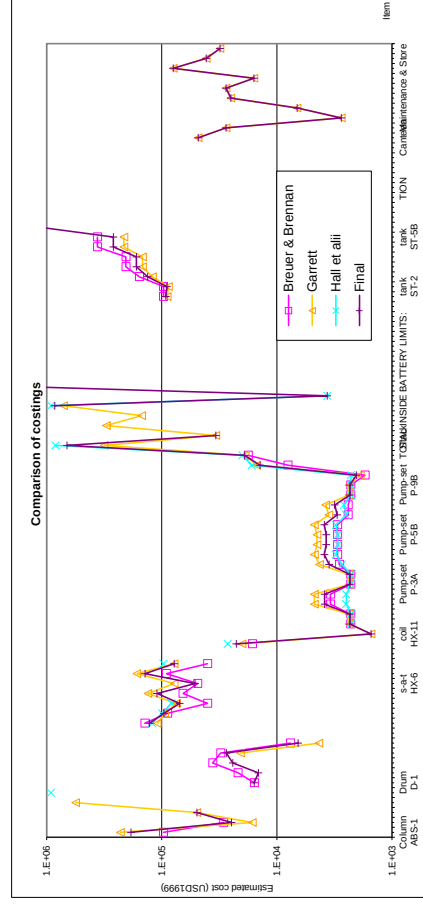
CE index for original date [BRENNAN; CE]: 363.0

CE index for 1999 [CE]: 390

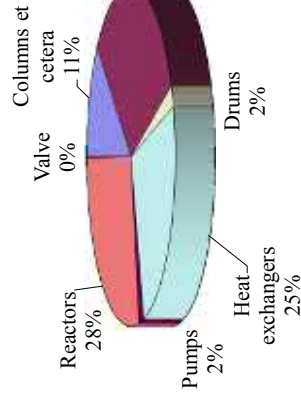
Inflation factor: 1.074

REFERENCE:			BREUER & BRENNAN			GARRETT			HALL, MATLEY & MCNAUGHTON			COMMENTS		
Current location factor [B & B; BRENNAN]:	0.769		0.97		0.97		1		0.97					
Historical currency conversion factor [B & B]:	0.769		1		1		300		1					
CE index for original date [BRENNAN; CE]:	363.0		320		390		390		390					
CE index for 1999 [CE]:	390		390		390		390		390					
Inflation factor:	1.074		1.219				1.3							
ITEM	DESCIP- TION	DIMENSION & TYPE	Original cost [AUD ₁₉₉₉]	Updated cost [USD ₁₉₉₉]	FACTORS Type [-]	FACTORS Materials [-]	FACTORS Pressure [-]	Final cost [USD ₁₉₉₉]	Original cost [USD ₁₉₉₉]	Updated cost [USD ₁₉₉₉]	FACTORS Type [-]	FACTORS Materials [-]	FACTORS Pressure [-]	Final cost [USD ₁₉₉₉]
INSIDE BATTERY LIMITS														
ABS-1	Column	1.8m diameter, 33m height	80.0E+3	50.9E+3	1	1.9	1	96.6E+3	92.0E+3	108.8E+3	1	2.1	1	228.5E+3
Packing	Trays	19.3 m³, 50mm Pall	13.1E+3	8.3E+3	1	3.5	1	29.0E+3	13.1E+3	15.5E+3	1	1.05	1	16.3E+3
CP-1	Blower	21 x 1.8m dia, b-caps	n.a.						22.1E+3	26.1E+3	1	1.9	1	49.5E+3
Blower WITH turbine	539kW	Centrifugal 6 m³.s⁻¹ 85kPa	N/A						190.0E+3	224.6E+3	1	2.5	1	561.5E+3
D-1	Drum	1.4 cubic metres	13.0E+3	8.3E+3	1	1.9	1	15.7E+3	N/A					see below
D-2	Drum	18.0E+3 11.4E+3	18.0E+3	11.4E+3	1	1.9	1	21.7E+3	n.a.					see below
D-3	Drum	2.2 cubic metres	30.0E+3	19.1E+3	1	1.9	1	36.2E+3	n.a.					see below
HX-1	Column	1.8m diameter, 3m height	25.0E+3	15.9E+3	1	1.9	1.02	30.7E+3	8.4E+3	9.9E+3	1	2.1	1	20.8E+3
Packing		5.1 m³, 50mm Pall	3.4E+3	2.2E+3	1	3.5	1	7.6E+3	3.5E+3	4.1E+3	1	1.05	1	4.3E+3
HX-2	s-a-t	Fixed-tube, 148 m²	60.0E+3	38.1E+3	1	3.5	1.05	140.2E+3	32.0E+3	37.8E+3	0.79	3.48	1.05	109.1E+3
HX-3	s-a-t	Fixed-tube, 131 m²	40.0E+3	25.4E+3	1	3.5	1	89.0E+3	29.0E+3	34.3E+3	0.79	3.48	1	94.2E+3
HX-4	s-a-t	Fixed-tube, 87.2 m²	18.0E+3	11.4E+3	1	3.5	1	40.1E+3	23.0E+3	27.2E+3	0.79	3.48	1	74.7E+3
HX-5	s-a-t	U-tube, 180 m²	28.0E+3	17.8E+3	1	3.5	1.05	65.4E+3	36.0E+3	42.6E+3	0.85	3.48	1.05	132.1E+3
HX-6	s-a-t	Floating, 75 m²	22.0E+3	14.0E+3	1	3.5	1	49.0E+3	19.0E+3	22.5E+3	1	3.48	1	78.1E+3
HX-7	s-a-t	Floating, 210 m²	41.0E+3	26.1E+3	1	3.5	1	91.2E+3	40.0E+3	47.3E+3	1	3.48	1	164.4E+3
HX-8	s-a-t	Floating, 100 m²	18.0E+3	11.4E+3	1	3.5	1	40.1E+3	19.0E+3	22.5E+3	1	3.48	1	78.1E+3
HX-9	fired boiler	see RXN-3 (1478kW)	see RXN-3						see RXN-3					see RXN-3
HX-10	s-a-t	Fixed-tube, 13 m²	7.0E+3	4.5E+3	1	3.5	1.05	16.4E+3	5.9E+3	7.0E+3	0.79	3.48	1.05	20.1E+3
HX-11	coil	25mm	n.a.						627.0E+3	741.2E+3	1	2.05	1	1.5E+3
P-1A	Pump-set	0.32kW 7.9 m³.h⁻¹ 9.7m	2.0E+3	1.3E+3	1	1.8	1	2.3E+3	1.0E+3	1.2E+3	1	2.0	1	2.4E+3
P-1B	Pump-set	0.32kW 7.9 m³.h⁻¹ 9.7m	2.0E+3	1.3E+3	1	1.8	1	2.3E+3	1.0E+3	1.2E+3	1	2.0	1	2.4E+3
P-2A	Pump-set	2.55kW 96 m³.h⁻¹ 7.1m	3.0E+3	1.9E+3	1	1.8	1	3.4E+3	2.0E+3	2.4E+3	1	2.0	1	4.7E+3
P-2B	Pump-set	2.55kW 96 m³.h⁻¹ 7.1m	3.0E+3	1.9E+3	1	1.8	1	3.4E+3	2.0E+3	2.4E+3	1	2.0	1	4.7E+3
P-3A	Pump-set	0.22kW 3.9 m³.h⁻¹ 10.2m	2.0E+3	1.3E+3	1	1.8	1	2.3E+3	1.0E+3	1.2E+3	1	2.0	1	2.4E+3
P-3B	Pump-set	0.22kW 3.9 m³.h⁻¹ 10.2m	2.0E+3	1.3E+3	1	1.8	1	2.3E+3	1.0E+3	1.2E+3	1	2.0	1	2.4E+3
P-4A	Pump-set	2.1kW 93 m³.h⁻¹ 3.6m	2.5E+3	1.6E+3	1	1.8	1	2.9E+3	1.8E+3	2.1E+3	1	2.0	1	4.3E+3
P-4B	Pump-set	3.0kW 135 m³.h⁻¹ 3.7m	2.6E+3	1.7E+3	1	1.8	1	3.0E+3	2.0E+3	2.4E+3	1	2.0	1	4.7E+3
P-5A	Pump-set	2.76kW 6.2 m³.h⁻¹ 82m	2.6E+3	1.7E+3	1	1.8	1	3.0E+3	1.9E+3	2.2E+3	1	2.0	1	4.5E+3
P-5B	Pump-set	2.76kW 6.2 m³.h⁻¹ 82m	2.6E+3	1.7E+3	1	1.8	1	3.0E+3	1.9E+3	2.2E+3	1	2.0	1	4.5E+3
P-6	Pump-set	3.0kW 135 m³.h⁻¹ 3.7m	2.6E+3	1.7E+3	1	1.8	1	3.0E+3	2.0E+3	2.4E+3	1	2.0	1	4.7E+3
P-7	Pump-set	1.0kW 47 m³.h⁻¹ 3.9m	2.1E+3	1.3E+3	1	1.8	1	2.4E+3	1.5E+3	1.8E+3	1	2.0	1	3.5E+3
P-8	Pump-set	1.3kW 26 m³.h⁻¹ 13m	2.1E+3	1.3E+3	1	1.8	1	2.4E+3	1.6E+3	1.9E+3	1	2.0	1	3.8E+3
P-9A	Pump-set	0.32kW 5.9 m³.h⁻¹ 10.2m	2.0E+3	1.3E+3	1	1.8	1	2.3E+3	1.0E+3	1.2E+3	1	2.0	1	2.4E+3
P-9B	Pump-set	0.32kW 5.9 m³.h⁻¹ 10.2m	2.0E+3	1.3E+3	1	1.8	1	2.3E+3	1.0E+3	1.2E+3	1	2.0	1	2.4E+3
P-10	Pump-set	0.05kW 1.2 m³.h⁻¹ 9.7m	1.5E+3	953.6E+0	1	1.8	1	1.7E+3	800.0E+0	945.8E+0	1	2.0	1	1.9E+3
RXN-1	Cat. Bed	Take as 20% of HX-4						80E+3	14.9E+3					16.5E+3
RXN-2	Cat. Bed	Take as 20% of HX-3						17.8E+3	18.9E+3					19.9E+3
RXN-3	Burner	12.3 x 10⁶	N/A						200.0E+3	236.4E+3	1	1.34	1	316.8E+3
Stack	15m	Fired, box 3.595MW btu/h	n.a.						12.5E+3	14.8E+3	2.3	1	1	34.0E+3
Steam tur	539kW	centrifugal 3600rpm	n.a.						85.0E+3	100.5E+3	1.04	2.9	1	303.1E+3
Corresponding motor			N/A						42.0E+3	49.7E+3	1.04	2.9	1	149.8E+3
.. Blower + Turbine:														714.9E+3

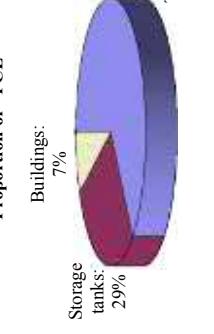
V-1	Exp. Valve (under 1 inch)	n.a.	n.a.	n.a.	1.0E+3	1.3E+3	1	2.9	1	3.7E+3	4E+3 IF h.p. butterfly (negl.)
TOTAL INSIDE BATTERY LIMITS:											
ITEM	DESCIP- TION	DIMENSION & TYPE	Original cost [AUD ₁₇₉₃]	Updated cost [USD ₁₉₉₉]	FACTORS Type [-]	Materials [-]	Pressure [-]	Original cost [USD ₁₉₉₉]	Updated cost [USD ₁₉₉₉]	Final cost [USD ₁₉₉₉]	COMMENTS
STORAGE TANKS											
ST-1	tank	closed 190 m ³	80.0E+3	50.9E+3	1	1.9	1	96.6E+3	1	2.0	92E+3 B&B "pressure vessels"
ST-2	tank	closed 183 m ³	80.0E+3	50.9E+3	1	1.9	1	96.6E+3	1	2.0	91E+3 Garrett cone roof
ST-3	tank	closed 330 m ³	130.0E+3	82.6E+3	1	1.9	1	157.0E+3	1	2.0	133E+3 (cf. ellipsoidal)
ST-4A	tank	closed 507 m ³	170.0E+3	108.1E+3	1	1.9	1	205.3E+3	1	2.0	168E+3
ST-4B	tank	closed 507 m ³	170.0E+3	108.1E+3	1	1.9	1	205.3E+3	1	2.0	168E+3
ST-5A	tank	closed 1120 m ³	300.0E+3	190.7E+3	1	1.9	1	362.4E+3	1	2.0	263E+3 B&B extrapolated
ST-5B	tank	closed 1120 m ³	300.0E+3	190.7E+3	1	1.9	1	362.4E+3	1	2.0	263E+3 B&B extrapolated
TOTAL STORAGE:											
											1.2E+6
ITEM	DESCIP- TION	DIMENSION & TYPE	Original cost [AUD ₁₇₉₃]	Updated cost [USD ₁₉₉₉]	FACTORS Type [-]	Materials [-]	Pressure [-]	Original cost [USD ₁₉₉₉]	Updated cost [USD ₁₉₉₉]	Final cost [USD ₁₉₉₉]	COMMENTS
BUILDINGS											
Canteen		60 m ² : ft ²	646 n.a.								
Control Room		30 m ² : ft ²	323 n.a.								
Fire Shed		4 m ² : ft ²	43 n.a.								
Gate House		12 m ² : ft ²	129 n.a.								
Laboratory		16 m ² : ft ²	172 n.a.								
Maintenance & Store		30 m ² : ft ²	323 n.a.								
Medical Centre		9 m ² : ft ²	97 n.a.								
Offices & Admin.		112 m ² : ft ²	1206 n.a.								
Religious Centre		49 m ² : ft ²	527 n.a.								
Toilets & Showers		21 m ² : ft ²	226 n.a.								
TOTAL BUILDINGS:											
											305.6E+3



Proportion of IBL Purchased Cost of Equipment



Proportion of "PCE"



SUMMARY:

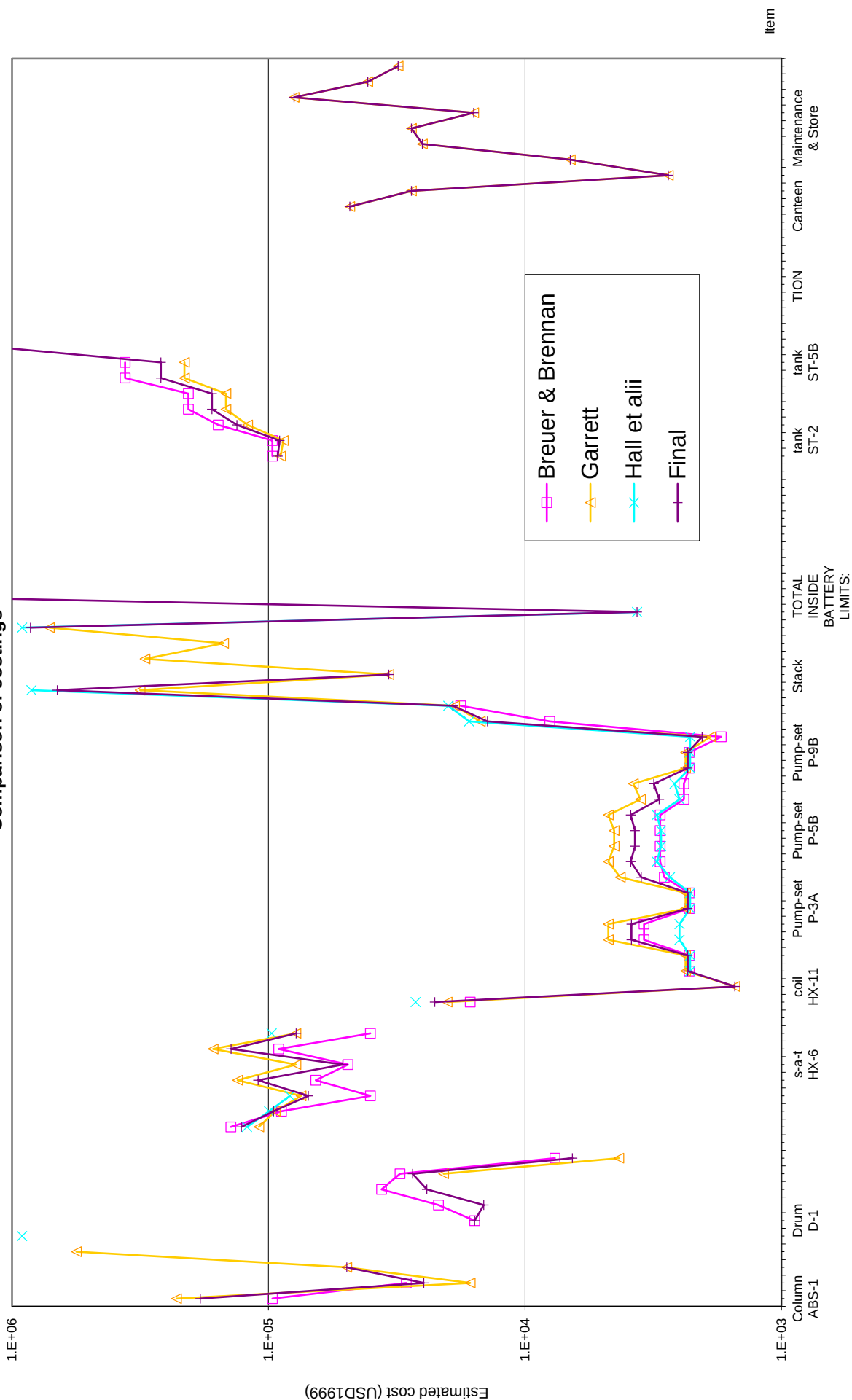
Columns et cetera	292.8E+3
Blower & Turbine	847.8E+3
Drums	54.4E+3
Heat exchangers	662.5E+3
Pumps	48.5E+3
Reactors	732.6E+3
Valve	3.7E+3
Total IBL:	2.6E+6
Storage tanks:	1.2E+6
Buildings:	305.6E+3
SUM:	4.1E+6

Fraction of:

0.44

0.12

Comparison of costings



OPERATING & PRODUCTION COSTS: 100% capacity utilisation

Formaldehyde Production from methanol via a silver catalyst-type process, with off-gas recycle		
PRODUCT PROCESS ROUTE		
GENERAL DATA		
	VALUE	UNITS COMMENTS
PLANT CAPACITY	80000	ty ⁻¹
CAPACITY UTILISATION	1.00	(ty ⁻¹)/(ty ⁻¹)y ⁻¹
FIXED CAPITAL: Inside Battery Limits	2.64 × 10 ⁶	\$
FIXED CAPITAL: Outside Battery Limits	6.50 × 10 ⁶	\$
TOTAL FIXED CAPITAL	13.37 × 10 ⁶	\$
PRODUCT SELLING PRICE	300	\$.t _{product} ⁻¹
EXPECTED ECONOMIC PLANT LIFE	10	y
All "\$" symbols denote USD ₁₉₉₉ . 1AUD ₁₉₉₉ = 0.66USD ₁₉₉₉ . "Expected" price, Freight On Board. 54%(kg.kg ⁻¹) basis. Minimum value (conservative).		

All "\$" symbols denote USD₁₉₉₉. 1AUD₁₉₉₉ = 0.66USD₁₉₉₉.

"Expected" price, Freight On Board. 54%(kg.kg⁻¹) basis.

Minimum value (conservative).

ANNUAL COST COST PER TONNE OF PRODUCT (54% basis)
[×10⁶ \$.y⁻¹] [\$t_{product}⁻¹]

PRODUCTION COST		UNITS	UNIT COST	UNIT USAGE		COMMENTS
			[\$ unit ⁻¹]	[unit.t _{product} ⁻¹]		
RAW MATERIALS						
Methanol	t	100	0.6648	5.32	66.48	From a neighbouring plant in Bontang, by pipeline. The unit cost is adjusted so that the minimum viable selling price equals the expected selling price. There are two inlets streams!
TOTAL RAW MATERIALS COSTS						
				5.32	66.48	
		UNITS	UNIT COST	UNIT USAGE		COMMENTS
			[\$ unit ⁻¹]	[unit.t _{product} ⁻¹]		
UTILITIES						
Steam	t	7.92	-0.252	-0.16	-2.00	Surplus steam is exported for profit.
Nitrogen	Nm ³	0.198	0.000	0.00	0.00	Not required during normal operation.
Demineralsed water	t	1.65	1.912	0.25	3.15	20% of BFW (Streams 100, 105 and 112) + Streams 2, 33 and 41.
Recirculated cooling wate	m ³ ≈ t	0.0396	31.57	0.10	1.25	Streams 122, 124, 126 and 128.
Towns water	t	0.396	6.314	0.20	2.50	Taken as 20% of the RCW flow.
Electric power	MWh	29.7	0.0271	0.06	0.81	From actual pump motor requirements (only): 19.95 kW.
Natural gas	GJ	2.64	0.000	0.00	0.00	Only required on start-up.
TOTAL UTILITIES COSTS						This is only 9% of the Raw Materials cost.
				0.46	5.71	
		NUMBER	COST PER "UNIT"			COMMENTS
			[\$.y ⁻¹]			
PROCESS LABOUR						
Operators per shift	2					(Ignoring time required during shift change-over)
(Hours required per day)	(24)					
(Days required per week)	(7)					
(Hours per shift)	(8)					
Shift teams	4					
TOTAL shift operators	8	33000		0.26	3.30	
TOTAL day operators	0	26400		0.00	0.00	
TOTAL PROCESS LABOUR WAGES						It is assumed that all operators are on a rotating shift, such that none are classed as "day" operators
				0.26	3.30	

FRACTION OF TOTAL PROCESS LABOUR WAGES

PAYROLL OVERHEADS	0.08	0.99	Plant is not in a highly "developed" country	0.30 ≤	0.30	≤ 0.50
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FRACTION OF TOTAL FIXED CAPITAL

MAINTENANCE LABOUR	0.67	8.36	See, e.g. , Brenna ¹ , p. 126, and cf. p. 118.			
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NETT "OPERATING" LABOUR COSTS

Assuming "equal division between materials and labour." See also below

This is 19% of the Raw Materials cost.

FRACTION OF TOTAL FIXED CAPITAL FRACTION OF NETT "OPERATING" LABOUR COSTS

MAINTENANCE MATERIALS	0.67	8.36				
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OPERATING SUPPLIES ≈ CONSUMABLE STORES	0.125	0.41	See Brenna ¹ , p. 118: here the two fractions sum to 0.02 ≤ 100%	0.10	≤ 0.12	
cf.	0.0075	0.10028	The fraction is increased due to high capacity utilisation: and due to the corrosive process fluid (though 316SS is used) which precipitates. Moderately "dirty" and "complicated" process	0.05 ≤	0.13	≤ 0.20

PLANT OVERHEADS	0.4	1.32	Alternative to the above	0.005 ≤	0.008	≤ 0.01
INSURANCE	0.015	2.51	Plant is part of a larger petrochemical complex	0.3 ≤	0.4	≤ 1.0
PROPERTY TAXES	0.01	1.67	Moderate risk	0.001 ≤	0.015	≤ 0.03
"BOOK" DEPRECIATION (not a cash cost)	0.10	16.71	Relatively undeveloped industrial area; incentive	0.01 ≤	0.01	≤ 0.04
TOTAL FIXED COSTS	3.49	43.63	Calculated based on a 10 y plant life	0.05 ≤	0.10	≤ 0.2

TOTAL PRODUCTION COST

FIXED	3.49	43.63	Raw materials & Utilities			
VARIABLE	5.78	72.19	Check: Methanol makes up	57%	of the total "production cost."	✓
TOTAL	9.27	115.82				

NON-MANUFACTURING COSTS

FRACTION OF TOTAL PRODUCTION COST (above)

Corporate administration	0.025	2.90	Relatively simple division; mostly central admin.	0.02 ≤	0.03	≤ 0.06
cf.		2.30	Alternative to the above	0.01 ≤	0.014	≤ 0.04
Research & Development	0.005	0.58	An established technology, largely bought into	0.00 ≤	0.01	≤ 0.05
cf.		1.80	Expected sales revenue = $24 \times 10^6 \text{ \$ (gr)} \cdot y^{-1}$	0.00 ≤	0.006	≤ 0.06
Selling expenses	0.05	5.79	Relatively one major customer (contract)	0.05 ≤	0.05	≤ 0.025
cf.		6.00	Alternative to the above	0.02 ≤	0.020	≤ 0.2
TOTAL NON-MANUFACTURING COSTS	0.020	9.27				

TOTAL OPERATING COST

	10.01	125.08	Check: Methanol makes up	53%	of the total "operating cost."	✓
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MINIMUM PROFIT	Fraction of total fixed capital =	0.20	This is a (pseudo)-commodity ==> Profit margin not so high			
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MINIMUM VIABLE SELLING PRICE

Recall:

TOTAL RAW MATERIALS COSTS

Hence:

"CONVERSION COST"

NOTE: The expected selling price i

300 $\text{\$} \cdot t_{\text{product}}^{-1}$

Which is only methanol.

66.48 $\text{\$} \cdot t_{\text{product}}^{-1}$

58.61 $\text{\$} \cdot t_{\text{product}}^{-1}$

OPERATING & PRODUCTION COSTS TO "BREAK EVEN": 100% capacity utilisation

Formaldehyde Production from methanol via a silver catalyst-type process, with off-gas recycle			
PRODUCT PROCESS ROUTE			
GENERAL DATA			
PLANT CAPACITY	VALUE	UNITS	COMMENTS
CAPACITY UTILISATION	80000	t.y ⁻¹	
FIXED CAPITAL: Inside Battery Limits	1.00	(t.y ⁻¹)(t.y ⁻¹) ⁻¹	All "\$" symbols denote USD ₁₉₉₉ . 1AUD ₁₉₉₉ = 0.66USD ₁₉₉₉ .
FIXED CAPITAL: Outside Battery Limits	2.64 × 10 ⁶	\$	
TOTAL FIXED CAPITAL	13.37 × 10 ⁶	\$	
PRODUCT SELLING PRICE	300	\$.t _{product} ⁻¹	"Expected" price, Freight On Board. 54%(kg.kg ⁻¹) basis.
EXPECTED ECONOMIC PLANT LIFE	10	y	Minimum value (conservative).

ANNUAL COST COST PER TONNE OF PRODUCT (54% basis)

[×10⁶ \$.y⁻¹] [\$t_{product}⁻¹]

PRODUCTION COST	UNITS	UNIT COST	UNIT USAGE		COMMENTS
RAW MATERIALS		[\$ unit ⁻¹]	[unit.t _{product} ⁻¹]		
Methanol	t	297.09	0.6648	15.80	From a neighbouring plant in Bontang, by pipeline. The unit cost is adjusted so that the minimum viable selling price equals the expected selling price.
TOTAL RAW MATERIALS COSTS				15.80	There are two inlets streams!

UTILITIES	UNITS	UNIT COST	UNIT USAGE		COMMENTS
		[\$ unit ⁻¹]	[unit.t _{product} ⁻¹]		
Steam	t	7.92	-0.252	-0.16	Surplus steam is exported for profit.
Nitrogen	Nm ³	0.198	0.000	0.00	Not required during normal operation.
Demineralised water	t	1.65	1.912	0.25	20% of BFW (Streams 100, 105 and 112) + Streams 2, 33 and 41.
Recirculated cooling water	m ³ ≈ t	0.0396	31.57	0.10	Streams 122, 124, 126 and 128.
Towns water	t	0.396	6.314	0.20	Taken as 20% of the RCW flow.
Electric power	MWh	29.7	0.0271	0.06	From actual pump motor requirements (only): 19.95 kW.
Natural gas	GJ	2.64	0.000	0.00	Only required on start-up.
TOTAL UTILITIES COSTS				0.46	This is only 3% of the Raw Materials cost.

PROCESS LABOUR	NUMBER	COST PER "UNIT"		COMMENTS
		[\$.y ⁻¹]		
Operators per shift	2			
(Hours required per day)	(24)			
(Days required per week)	(7)			
(Hours per shift)	(8)			(Ignoring time required during shift change-over)
Shift teams	4			
TOTAL shift operators	8	33000	0.26	
TOTAL day operators	0	0.00	0.00	It is assumed that all operators are on a rotating shift, such that none are classed as "day" operators
TOTAL PROCESS LABOUR WAGES		26400	0.26	

FRACTION OF TOTAL PROCESS LABOUR WAGES

PAYROLL OVERHEADS	0.08	0.99	Plant is not in a highly "developed" country	0.30 ≤	0.30	≤ 0.50
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FRACTION OF TOTAL FIXED CAPITAL

MAINTENANCE LABOUR	0.67	8.36	See, e.g., Brennan ¹ , p. 126, and cf. p. 118.			
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NETT "OPERATING" LABOUR COSTS

Assuming "equal division between materials and labour." See also below

This is 6% of the Raw Materials cost.

FRACTION OF TOTAL FIXED CAPITAL FRACTION OF NETT "OPERATING" LABOUR COSTS

MAINTENANCE MATERIALS	0.67	8.36				
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OPERATING SUPPLIES ≈ CONSUMABLE STORES	0.125	0.41	See Brennan ¹ , p. 118: here the two fractions sum to 0.02 ≤ 100%	0.10	≤ 0.12	
cf.	0.0075	0.10028	The fraction is increased due to high capacity utilisation: and due to the corrosive process fluid (though 316SS is used) which precipitates.	100%		

PLANT OVERHEADS	0.4	1.32	Moderately "dirty" and "complicated" process	0.05 ≤	0.13	≤ 0.20
INSURANCE	0.015	2.51	Alternative to the above	0.005 ≤	0.008	≤ 0.01
PROPERTY TAXES	0.01	1.67	Plant is part of a larger petrochemical complex	0.3 ≤	0.4	≤ 1.0
"BOOK" DEPRECIATION (not a cash cost)	0.10	16.71	Moderate risk	0.001 ≤	0.015	≤ 0.03
TOTAL FIXED COSTS	3.49	43.63	Relatively undeveloped industrial area; incentive	0.01 ≤	0.01	≤ 0.04
			Calculated based on a 10 y plant life	0.05 ≤	0.10	≤ 0.2

TOTAL PRODUCTION COST

FIXED	3.49	43.63	Raw materials & Utilities			
VARIABLE	16.26	203.20	Check: Methanol makes up	80%	of the total "production cost."	✓
TOTAL	19.75	246.83				

NON-MANUFACTURING COSTS

FRACTION OF TOTAL PRODUCTION COST (above)

Corporate administration	0.025	6.17	Relatively simple division; mostly central admin.	0.02 ≤	0.03	≤ 0.06
cf.		2.30	Alternative to the above	0.01 ≤	0.014	≤ 0.04
Research & Development	0.005	1.23	An established technology, largely bought into	0.00 ≤	0.01	≤ 0.05
cf.		1.80	Expected sales revenue = $24 \times 10^6 \$(\text{gr})\text{y}^{-1}$	0.00 ≤	0.006	≤ 0.06
Selling expenses	0.05	12.34	Relatively one major customer (contract)	0.05 ≤	0.05	≤ 0.025
cf.		6.00	Alternative to the above	0.02 ≤	0.020	≤ 0.2
TOTAL NON-MANUFACTURING COSTS	0.020	19.75				

TOTAL OPERATING COST

	21.33	266.58	Check: Methanol makes up	74%	of the total "operating cost."	✓
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MINIMUM PROFIT	Fraction of total fixed capital =	0.20	This is a (pseudo)-commodity ==> Profit margin not so high			
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MINIMUM VIABLE SELLING PRICE

	24.00	300 \$t _{product} ⁻¹	NOTE: The expected selling price			
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Recall:

TOTAL RAW MATERIALS COSTS

Hence:

"CONVERSION COST"

Which is only methanol.

15.80 197.49 \$t_{product}⁻¹

5.53 69.09 \$t_{product}⁻¹

OPERATING & PRODUCTION COSTS: 60% capacity utilisation

Formaldehyde Production from methanol via a silver catalyst-type process, with off-gas recycle			
PRODUCT PROCESS ROUTE			
GENERAL DATA			
	VALUE	UNITS	COMMENTS
PLANT CAPACITY	80000	t.y ⁻¹	
CAPACITY UTILISATION	0.60	(t.y ⁻¹)(t.y ⁻¹) ⁻¹	The possibility of turndown to 60% is a required attribute.
FIXED CAPITAL: Inside Battery Limits	2.64 × 10 ⁶	\$	All "\$" symbols denote USD ₁₉₉₉ . 1AUD ₁₉₉₉ = 0.66USD ₁₉₉₉ .
FIXED CAPITAL: Outside Battery Limits	6.50 × 10 ⁶	\$	
TOTAL FIXED CAPITAL	13.37 × 10 ⁶	\$	
PRODUCT SELLING PRICE	300	\$.t _{product} ⁻¹	"Expected" price, Freight On Board. 54%(kg.kg ⁻¹) basis.
EXPECTED ECONOMIC PLANT LIFE	10	y	Minimum value (conservative).

ANNUAL COST COST PER TONNE OF PRODUCT (54% basis)

[×10⁶ \$.y⁻¹] [\$t_{product}⁻¹]

PRODUCTION COST		COMMENTS	
UNITS	UNIT COST	UNIT USAGE	
	[\$ unit ⁻¹]	[unit.t _{product} ⁻¹]	
RAW MATERIALS			
Methanol	t	100	0.6648
TOTAL RAW MATERIALS COSTS			
			3.19
			3.19
UTILITIES			
Steam	t	7.92	-0.252
Nitrogen	Nm ³	0.198	0.000
Demineralsed water	t	1.65	1.912
Recirculated cooling wate	m ³ ≈ t	0.0396	31.57
Towns water	t	0.396	6.314
Electric power	MWh	29.7	0.0271
Natural gas	GJ	2.64	0.000
TOTAL UTILITIES COSTS			
			0.27
			5.71
PROCESS LABOUR			
Operators per shift	2		
(Hours required per day)	(24)		
(Days required per week)	(7)		
(Hours per shift)	(8)		
Shift teams	4		
TOTAL shift operators	8	33000	5.50
TOTAL day operators	0	26400	0.00
TOTAL PROCESS LABOUR WAGES			
			0.26
			5.50
COMMENTS			
From a neighbouring plant in Bontang, by pipeline.			
The unit cost is adjusted so that the minimum viable selling price equals the expected selling price.			
There are two inlets streams!			
COMMENTS			
Surplus steam is exported for profit.			
Not required during normal operation.			
20% of BFW (Streams 100, 105 and 112) + Streams 2, 33 and 41.			
Streams 122, 124, 126 and 128.			
Taken as 20% of the RCW flow.			
From actual pump motor requirements (only):			
Only required on start-up.			
This is only 9% of the Raw Materials cost.			
COMMENTS			
(Ignoring time required during shift change-over)			
It is assumed that all operators are on a rotating shift, such that none are classed as "day" operators			

FRACTION OF TOTAL PROCESS LABOUR WAGES

PAYROLL OVERHEADS	0.08	1.65	Plant is not in a highly "developed" country	0.30 ≤	0.30	≤ 0.50
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FRACTION OF TOTAL FIXED CAPITAL

MAINTENANCE LABOUR	0.67	13.93	See, e.g., Brennan ¹ , p. 126, and cf. p. 118.			
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NETT "OPERATING" LABOUR COSTS

Assuming "equal division between materials and labour." See also below

This is 32% of the Raw Materials cost.

FRACTION OF TOTAL FIXED CAPITAL FRACTION OF NETT "OPERATING" LABOUR COSTS

MAINTENANCE MATERIALS	0.67	13.93	See Brennan ¹ , p. 118: here the two fractions sum to 0.02 ≤	0.10	≤ 0.12	
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The fraction is increased due to high capacity utilisation: 60%

and due to the corrosive process fluid (though 316SS is used) which precipitates.

OPERATING SUPPLIES ≈ CONSUMABLE STORES	0.03	0.69	Moderately "dirty" and "complicated" process	0.05 ≤	0.13	≤ 0.20
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cf. Alternative to the above 0.005 ≤ 0.008 ≤ 0.01

PLANT OVERHEADS	0.11	2.2	Plant is part of a larger petrochemical complex	0.3 ≤	0.4	≤ 1.0
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INSURANCE	0.20	4.18	Moderate risk	0.001 ≤	0.015	≤ 0.03
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PROPERTY TAXES	0.13	2.79	Relatively undeveloped industrial area; incentive	0.01 ≤	0.01	≤ 0.04
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"BOOK" DEPRECIATION (not a cash cost)	1.34	27.85	Calculated based on a 10 y plant life	0.05 ≤	0.10	≤ 0.2
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TOTAL FIXED COSTS	3.49	72.71				
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TOTAL PRODUCTION COST

FIXED	3.49	72.71	Raw materials & Utilities			
VARIABLE	3.47	72.19	Check: Here methanol makes up	46%	of the total "production cost."	*
TOTAL	6.96	144.90				

NON-MANUFACTURING COSTS

FRACTION OF TOTAL PRODUCTION COST (above)

Corporate administration	0.025	3.62	Relatively simple division; mostly central admin.	0.02 ≤	0.03	≤ 0.06
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cf. Fraction of total fixed capital	0.01375	3.83	Alternative to the above	0.01 ≤	0.014	≤ 0.04
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Research & Development	0.005	0.72	An established technology, largely bought into	0.00 ≤	0.01	≤ 0.05
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cf. Fraction of sales revenue	0.006	1.80	Expected sales revenue = $14.4 \times 10^6 \text{ \$ (gr)} \cdot \text{y}^{-1}$	0.00 ≤	0.006	≤ 0.06
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Selling expenses	0.05	7.24	Relatively one major customer (contract)	0.05 ≤	0.05	≤ 0.025
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cf. Fraction of sales revenue	0.020	6.00	Alternative to the above	0.02 ≤	0.020	≤ 0.2
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TOTAL NON-MANUFACTURING COSTS	0.56	11.59				
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TOTAL OPERATING COST

	7.51	156.49	Check: Here methanol makes up	42%	of the total "operating cost."	*
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MINIMUM PROFIT	Fraction of total fixed capital =	0.20	This is a (pseudo)-commodity ==> Profit margin not so high			
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MINIMUM VIABLE SELLING PRICE

	10.19	212.20	NOTE: The expected selling price i	$300 \text{ \$} \cdot t_{\text{product}}^{-1}$		
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Recall:

TOTAL RAW MATERIALS COSTS

Hence:

"CONVERSION COST"

Which is only methanol.

$66.48 \text{ \$} \cdot t_{\text{product}}^{-1}$

$90.02 \text{ \$} \cdot t_{\text{product}}^{-1}$

OPERATING & PRODUCTION COSTS TO "BREAK EVEN": 60% capacity utilisation

Formaldehyde Production from methanol via a silver catalyst-type process, with off-gas recycle			
PRODUCT PROCESS ROUTE	VALUE	UNITS	COMMENTS
GENERAL DATA			
PLANT CAPACITY	80000	t.y ⁻¹	
CAPACITY UTILISATION	0.60	(t.y ⁻¹)(t.y ⁻¹) ⁻¹	The possibility of turndown to 60% is a required attribute. All "\$" symbols denote USD ₁₉₉₉ . 1AUD ₁₉₉₉ = 0.66USD ₁₉₉₉ .
FIXED CAPITAL: Inside Battery Limits	2.64 × 10 ⁶	\$	
FIXED CAPITAL: Outside Battery Limits	6.50 × 10 ⁶	\$	
TOTAL FIXED CAPITAL	13.37 × 10 ⁶	\$	
PRODUCT SELLING PRICE	300	\$.t _{product} ⁻¹	"Expected" price, Freight On Board. 54%(kg.kg ⁻¹) basis.
EXPECTED ECONOMIC PLANT LIFE	10	y	Minimum value (conservative).

ANNUAL COST PER TONNE OF PRODUCT (54% basis)

[×10⁶ \$.y⁻¹] [\$t_{product}⁻¹]

PRODUCTION COST	UNITS	UNIT COST	UNIT USAGE	COMMENTS
		[\$ unit ⁻¹]	[unit.t _{product} ⁻¹]	
RAW MATERIALS	t	222.30	0.6648	From a neighbouring plant in Bontang, by pipeline. The unit cost is adjusted so that the minimum viable selling price equals the expected selling price. There are two inlets streams!
Methanol				
TOTAL RAW MATERIALS COSTS				
				COMMENTS
UTILITIES				
Steam	t	7.92	-0.252	Surplus steam is exported for profit.
Nitrogen	Nm ³	0.198	0.000	Not required during normal operation.
Demineralised water	t	1.65	1.912	20% of BFW (Streams 100, 105 and 112) + Streams 2, 33 and 41.
Recirculated cooling water	m ³ ≈ t	0.0396	31.57	Streams 122, 124, 126 and 128.
Towns water	t	0.396	6.314	Taken as 20% of the RCW flow.
Electric power	MWh	29.7	0.0271	From actual pump motor requirements (only): 19.95 kW.
Natural gas	GJ	2.64	0.000	Only required on start-up.
TOTAL UTILITIES COSTS		0.27	5.71	This is only 4% of the Raw Materials cost.
				COMMENTS
PROCESS LABOUR	NUMBER	COST PER "UNIT"		
		[\$.y ⁻¹]		
Operators per shift	2			
(Hours required per day)	(24)			
(Days required per week)	(7)			
(Hours per shift)	(8)			(Ignoring time required during shift change-over)
Shift teams	4			
TOTAL shift operators	8	0.26	5.50	
TOTAL day operators	0	0.00	0.00	It is assumed that all operators are on a rotating shift, such that none are classed as "day" operators
TOTAL PROCESS LABOUR WAGES		0.26	5.50	

FRACTION OF TOTAL PROCESS LABOUR WAGES

PAYROLL OVERHEADS	0.08	1.65	Plant is not in a highly "developed" country	0.30 ≤	0.30	≤ 0.50
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FRACTION OF TOTAL FIXED CAPITAL

MAINTENANCE LABOUR	0.67	13.93	See, e.g., Brennan ¹ , p. 126, and cf. p. 118.			
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NETT "OPERATING" LABOUR COSTS

Assuming "equal division between materials and labour." See also below

This is 14% of the Raw Materials cost.

FRACTION OF TOTAL FIXED CAPITAL FRACTION OF NETT "OPERATING" LABOUR COSTS

MAINTENANCE MATERIALS	0.67	13.93	See Brennan ¹ , p. 118: here the two fractions sum to 0.02 ≤	0.10	≤ 0.12	
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The fraction is increased due to high capacity utilisation: 60% and due to the corrosive process fluid (though 316SS is used) which precipitates. Moderately "dirty" and "complicated" process 0.05 ≤ 0.13 ≤ 0.20

Alternative to the above 0.005 ≤ 0.008 ≤ 0.01

Plant is part of a larger petrochemical complex 0.3 ≤ 0.4 ≤ 1.0

Moderate risk 0.001 ≤ 0.015 ≤ 0.03

Relatively undeveloped industrial area; incentive 0.01 ≤ 0.01 ≤ 0.04

Calculated based on a 10 y plant life 0.05 ≤ 0.10 ≤ 0.2

3.49 72.71

TOTAL PRODUCTION COST

FIXED	3.49	72.71	Raw materials & Utilities			
VARIABLE	7.37	153.49	Check: Here methanol makes up	65%	of the total "production cost."	*
TOTAL	10.86	226.20				

NON-MANUFACTURING COSTS

FRACTION OF TOTAL PRODUCTION COST (above)

Corporate administration	0.025	5.65	Relatively simple division; mostly central admin.	0.02 ≤	0.03	≤ 0.06
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cf. Fraction of total fixed capital 3.83 Alternative to the above 0.01 ≤ 0.014 ≤ 0.04

Research & Development 0.005 1.13 An established technology, largely bought into 0.00 ≤ 0.01 ≤ 0.05

cf. Fraction of sales revenue 1.80 Expected sales revenue = 14.4 × 10⁶ \$(gr)/y 0.00 ≤ 0.006 ≤ 0.06

Selling expenses 0.05 11.31 Relatively one major customer (contract) 0.05 ≤ 0.05 ≤ 0.025

cf. Fraction of sales revenue 6.00 Alternative to the above 0.02 ≤ 0.020 ≤ 0.2

TOTAL NON-MANUFACTURING COSTS 0.87 18.10

TOTAL OPERATING COST

11.73 244.29

MINIMUM PROFIT Fraction of total fixed capital = 0.20 2.67 55.71 \$t_{product}⁻¹ This is a (pseudo)-commodity ==> Profit margin not so high

MINIMUM VIABLE SELLING PRICE

14.40 300 \$t_{product}⁻¹ NOTE: The expected selling price 300 \$t_{product}⁻¹

Recall:

TOTAL RAW MATERIALS COSTS

Hence:

"CONVERSION COST"

Which is only methanol.

7.09 147.77 \$t_{product}⁻¹

4.63 96.52 \$t_{product}⁻¹

WORKING CAPITAL: 80000t.y⁻¹ plant with 100% capacity utilisation

PRODUCT		Formaldehyde	
PROCESS ROUTE		Production from methanol via a silver catalyst-type process, with off-gas recycle	
GENERAL DATA			
	VALUE	UNITS	COMMENTS
PLANT CAPACITY	80000	t.y^{-1}	All based on a solution of equivalent conc'n 54% by mass.
CAPACITY UTILISATION	1.00	$(\text{t.y}^{-1})/(\text{t.y}^{-1})^{-1}$	Assumed to be "normal" operation.
FIXED CAPITAL: Inside Battery Limits	2.64×10^6	\$	All "\$" symbols denote USD ₁₉₉₉ . 1AUD ₁₉₉₉ = 0.66USD ₁₉₉₉ .
FIXED CAPITAL: Outside Battery Limits	6.50×10^6	\$	
TOTAL FIXED CAPITAL	13.37×10^6	\$	
PRODUCT SELLING PRICE	300	$\text{\$} \cdot \text{t}_{\text{product}}^{-1}$	"Expected" price, Freight On Board. 54% $(\text{kg} \cdot \text{kg}^{-1})$ basis.
EXPECTED ECONOMIC PLANT LIFE	10	y	Minimum value (conservative).
RAW MATERIAL STOCKS			
INVENTORY	UNIT USAGE	UNIT COST	VALUE
[weeks]	$[\text{t} \cdot \text{t}_{\text{product}}^{-1}]$	$[\text{\$} \cdot \text{t}^{-1}]$	$[\times 10^6 \text{\$}]$
0.43	0.6583	100	0.043
From a neighbouring plant in Bontang, by pipeline, with small storage tank.			
MATERIALS IN PROGRESS INVENTORY			
INVENTORY	UNIT VALUE	VALUE	COMMENTS
[weeks of production]	$[\text{t}]$	$[\text{\$} \cdot \text{t}^{-1}]$	$[\times 10^6 \text{\$}]$
1.0	1276	104	0.133
This low value may still be conservative for such a "short" process. Take "unit value" as average between product and (mean) raw materials. Tonnes composed of average of (contributions from each raw material) and {product}.			
PRODUCT STOCKS			
INVENTORY	PRODUCT CASH COST	VALUE	COMMENTS
[weeks]	$[\text{\$} \cdot \text{t}^{-1}]$	$[\times 10^6 \text{\$}]$	
0.57	108.37	0.095	By pipeline to neighbouring resins plant, with moderate storage.
*NOTE: valued at "cash operating cost" (no depreciation)			
TOTAL = 54% formaldehyde solution			
SUB-TOTAL (process materials)			0.272
DEBTORS			
PERIOD	PRODUCT SELLING PRICE	VALUE	COMMENTS
[weeks]	$[\text{\$} \cdot \text{t}^{-1}]$	$[\times 10^6 \text{\$}]$	
6	300	2.769	Assume monthly payments (every ~ 4 weeks)
*Using the expected price			
TOTAL = Customers			
SUB-TOTAL (debtors)			2.769
NOTE: Other debtors exist (e.g. insurance, et cetera), but are not considered here			
CREDITORS			
PERIOD	COST PER TONNE OF PROD	VALUE	COMMENTS
[weeks]	$[\text{\$} \cdot \text{t}_{\text{product}}^{-1}]$	$[\times 10^6 \text{\$}]$	
6	66.48	(0.614)	Monthly payments assumed (every ~ 4 weeks)
6	5.71	(0.053)	Monthly payments assumed (every ~ 4 weeks)
1.5	12.65	(0.029)	"Paid, say on average, 1.5 weeks in arrears" - Brennan, p. 90
NOTE: Other creditors exist (e.g. "operating supplies"), but are not considered here			
SUB-TOTAL (creditors)			(0.696)
TOTAL WORKING CAPITAL			
			2.345
= {Process materials} + {Debtors} - {Creditors}			

Cash flows

Note: Basis is USD₁₉₉₉ and 54% formaldehyde solution (by mass).
All cash flows in millions of USD₁₉₉₉.

Calendar year Year number	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
Fixed capital													
Working capital		-13.37 -1.88	-0.23	-0.23									2.35
Sales volume [t.y ⁻¹]		0	60000	72000	80000	80000	80000	80000	80000	80000	80000	80000	0
Selling price [USD ₁₉₉₉ .t ⁻¹]													
Sales revenue		0	18	21.6	24	24	24	24	24	24	24	24	0
Variable cost [USD ₁₉₉₉ .t ⁻¹]*													
Variable costs		0	-4.33	-5.20	-5.78	-5.78	-5.78	-5.78	-5.78	-5.78	-5.78	-5.78	0
Fixed costs†		0	-2.89	-2.89	-2.89	-2.89	-2.89	-2.89	-2.89	-2.89	-2.89	-2.89	0
CASH FLOW BEFORE TAX‡		0	10.77	13.51	15.33	15.33	15.33	15.33	15.33	15.33	15.33	15.33	0
Investment allowance†													
Tax depreciation rate													
Tax depreciation allowance			0										
Taxable income			1.34	1.34	1.34	1.34	1.34	1.34	1.34	1.34	1.34	1.34	0
Tax rate													
Tax payments¶			0	9.44	12.17	13.99	13.99	13.99	13.99	13.99	13.99	13.99	0
CASH FLOW AFTER TAX			0	-2.83	-3.65	-4.20	-4.20	-4.20	-4.20	-4.20	-4.20	-4.20	0
CUMULATIVE CASH FLOW AFTER TAX													
• DISCOUNT RATE = 0%		-15.25	-7.54	2.08	13.22	24.35	35.48	46.61	57.75	68.88	80.01	91.14	93.49
• DISCOUNT RATE = 5%		0	-15.25	-7.90	0.82	10.44	19.60	28.32	36.63	44.54	52.07	59.25	67.46
• DISCOUNT RATE = 10%		0	-15.25	-8.24	-0.29	8.08	15.68	22.59	28.88	34.59	39.78	44.50	49.62
• DISCOUNT RATE = 20%		0	-15.25	-8.82	-2.14	4.30	9.67	14.14	17.87	20.98	23.57	25.73	27.84
• DISCOUNT RATE = 62% (annual)		0	-15.25	-10.47	-6.79	-4.15	-2.52	-1.50	-0.88	-0.49	-0.10	-0.01	0.00

* All non-manufacturing costs are assumed to be fixed.

† This therefore 125.08 – 72.19 – 16.71\$ USD₁₉₉₉.t⁻¹.

‡ This is assumed to be zero. § This is book depreciation.

¶ No tax is paid on the working capital recovered, after Brennan.

♣ Similarly, this does not include the working (or fixed) capital.

We assume all tax is paid in the same year (no delay)

We assume production is 75% in the first year, 90% in the following year and 100% thereafter.

We assume all fixed capital is disbursed in "year zero", along with 80% of the working capital, with the remainder distributed equally over the following two years, with full recovery. Tax rate estimated at 30%, slightly lower than the 36% corporate rate in Australia.

Formaldehyde

Acknowledgements

Just a quick word to all my friends and colleagues that did not get a mention in the Preface – sorry, but I couldn't list everyone!

A couple of people not mentioned so far who deserve some recognition:

Mr. Andrew Sahely for his insightful and helpful answers to my several questions;

Mrs. Zong Li Xie for providing access to her report of 1998;

Dr. Sanjay Mahajani for suggesting the incredibly helpful source of patents;

the civil fourth year students who gave access to their binding machine;

and finally due recognition of Mr. Saiful Zainal Abidin for patiently and diligently working by my side through the work on the HYSIM program, including weekends and after hours.

Finally, just because you weren't mentioned, don't (necessarily) mean you don't mean anything to me!

INPUT FILES





