

FORMALDEHYDE**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 (CH₃OH), 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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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>
3. CSR internet site; http://csr.com.au/product_homeswork/timber/timber_home.asp
4. James R. FAIR and Richard C. KMETZ; "Formaldehyde" in: John J. McKETTA (Exec. Ed.); Encyclopedia of Chemical Processing and Design; Marcel Dekker; New York; 1985.
5. H. Robert GERBERICH and George C. SEAMAN; "Formaldehyde" in: Jacqueline I. KROSHWITZ (Exec. Ed.); Kirk-Othmer Encyclopedia of Chemical Technology, 4th edition, Vol. 11; John Wiley & Sons; New York; 1994.
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.
9. Günther REUSS, Walter DISTELDORF, Otto GRUNDLER and Albrecht HILT; "Formaldehyde" in: Wolfgang GERHARTZ (Exec. Ed.); Ullmann's Encyclopedia of Industrial Chemistry, 5th edition, Vol. A11; VCH; Weinheim; 1988.

⁴ Credit is due to other members of Group 8, and in particular Miss. Rachel WELDON, for Ref's [1], [2], [3] and [6].

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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.

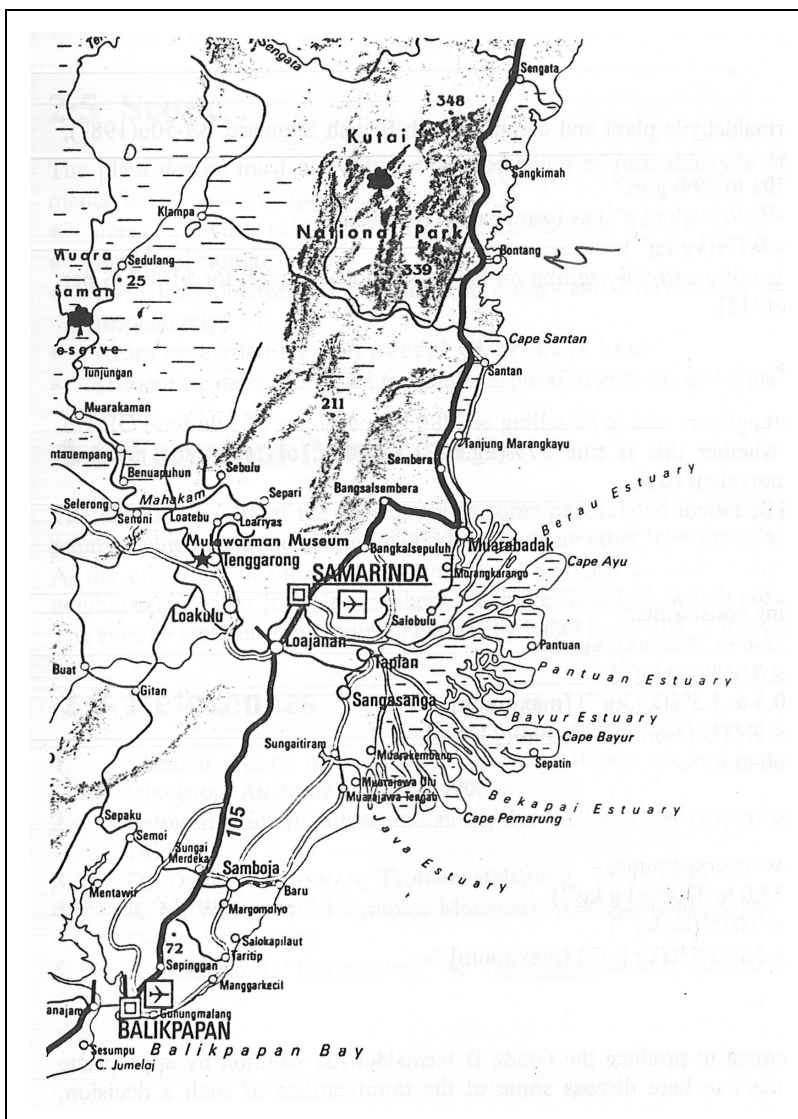


Figure 2-1: Map of Bontang, Indonesia; 1:1500000. [5]

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].

Chapter 2: Problem Definition**FORMALDEHYDE****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 794kg.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 = 46.7MJ.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)	4GJ ⁻¹
Electricity (Elec.)	Directly available at 50Hz and 11kV, 3.3kV and 415V as three-phase	45(MW.h) ⁻¹
Nitrogen (N ₂)	Dry, Pressure = 1000kPa(g)	0.3(Nm ³) ⁻¹
Demineralised water (DMW)	Ambient temperature, p = 300kPa(g)	2.5t ⁻¹
Towns water (TNW)	Ambient temperature, p = 300kPa(g)	0.60t ⁻¹
Steam	Saturated at 1100kPa(g)	12t ⁻¹
Recirculated cooling water (RCW)	300kPa(g) ex-cooling tower	0.06m ⁻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

1. Weather reports on the Indonesian News Report (Siaran Berita, Monday to Saturday, 11:00a.m., SBS television, Australia); 1997–1999.
2. Indonesian international student Mr. Kowil TANRANG (expert opinion); private communication; August 1999.
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.

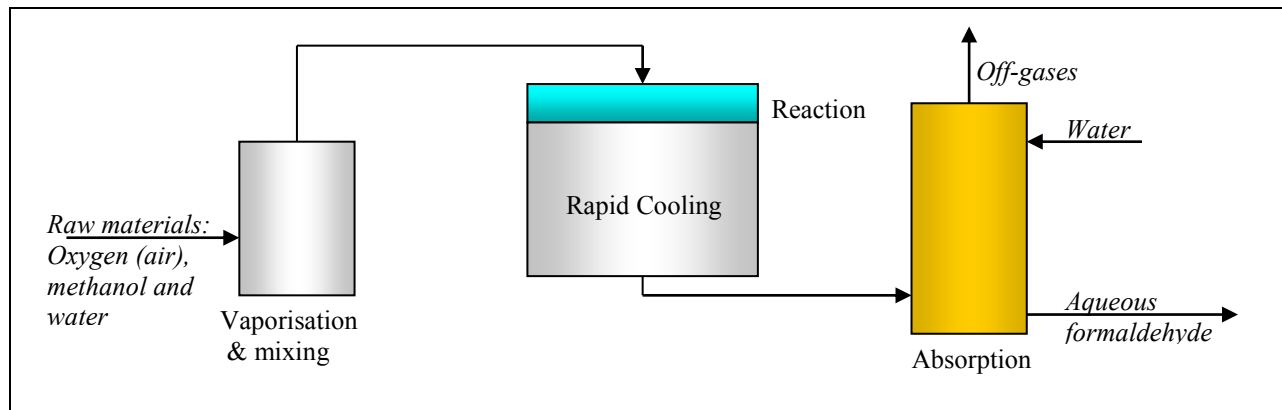


Figure 3-1: Essential process operations in the manufacture of formaldehyde from methanol.

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. < 0.02s [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°C¹. 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:

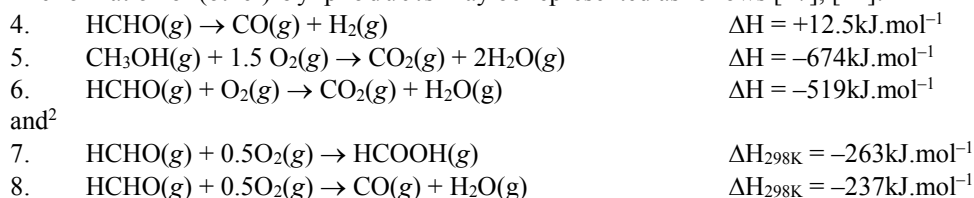
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|----|--|--|-------------------|
| 1. | $\text{CH}_3\text{OH}(\text{g}) + 0.5 \text{O}_2(\text{g}) \rightarrow \text{HCHO}(\text{g}) + \text{H}_2\text{O}(\text{g})$ | $\Delta\text{H} = -159\text{kJ}\cdot\text{mol}^{-1}$ | (oxidation) |
| 2. | $\text{CH}_3\text{OH}(\text{g})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

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.

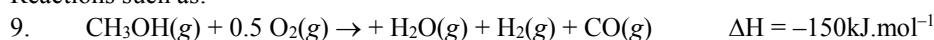
These are carried out at ambient pressure. The precise reaction temperature obtained depends upon the extent to which methanol is in excess in the methanol–air feed mixture.

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

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.

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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).

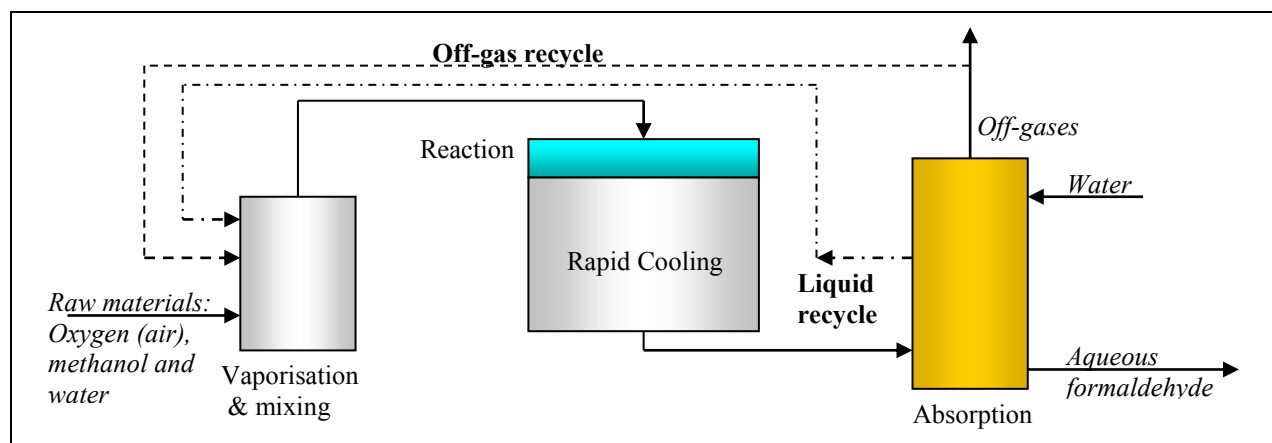


Figure 3-2: Key process flow routes in non-distillative manufacture of formaldehyde from methanol¹⁰.

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.

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.

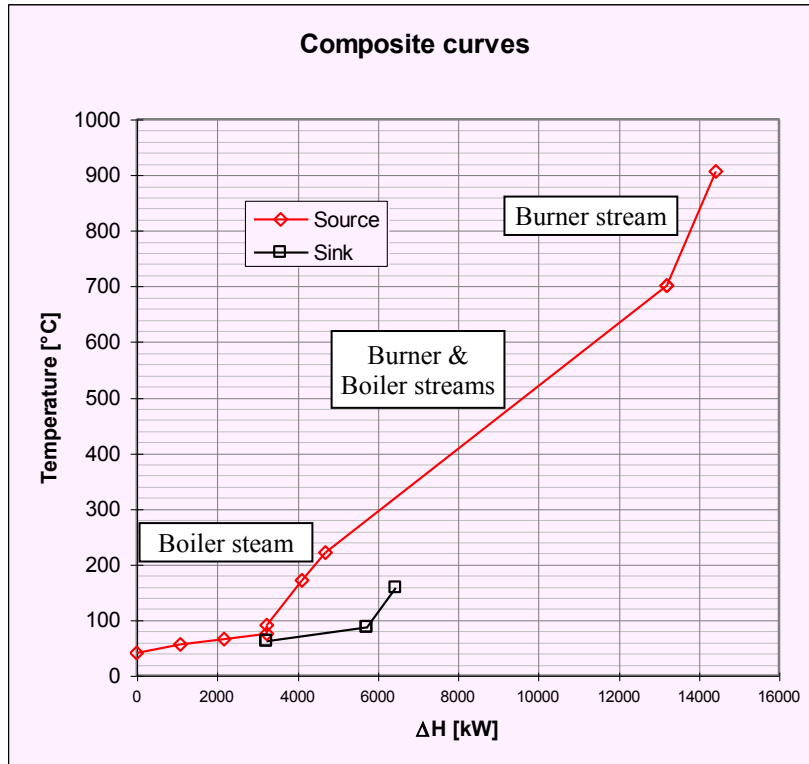


Figure 3-4: Composite curves.

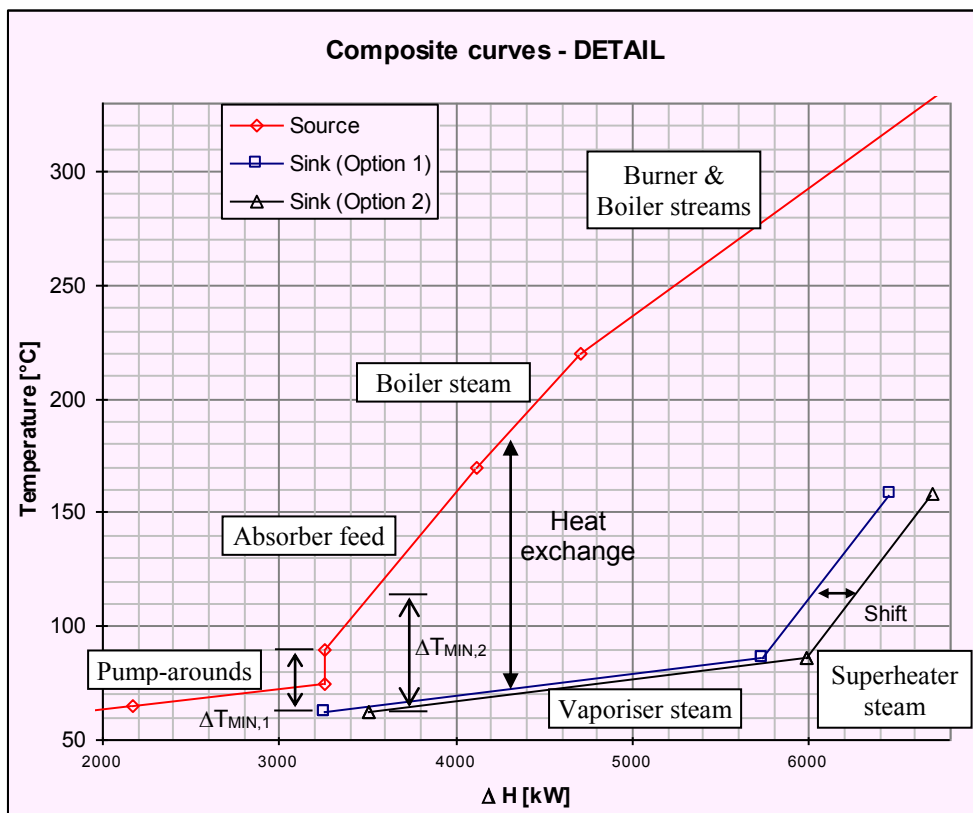


Figure 3-5: Detail of composite curves.

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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 $0.5\text{m}\cdot\text{s}^{-1}$, 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.

3.7 References

1. Albrecht AICHER, Hans HAAS, Hans DIEM, Christian DUDECK, Fritz BRUNNMUELLER and Gunter LEHMANN (all BASF AG); "Manufacture of Concentrated Aqueous Solutions of Formaldehyde;" in: US Patent 4119673; 10 October, 1978. Note: Original patent lodged in Germany (2444586).
2. Albrecht AICHER, Hans HAAS, Heinrich SPERBER, Hans DIEM, Matthias GUENTER and Gunter LEHMANN (all BASF AG); "Production of formaldehyde;" in: US Patent 4010208; 01 March, 1977. Note: Original patent lodged in Germany (2322757).
3. Anecdotal information received on the operation of Orica's Deer Park facility, August 1999.²⁹
4. V. I. ATROSHCHENKO and I. P. KUSHNARENKO; "Kinetics of the catalytic oxidation of methanol to formaldehyde over a silver catalyst;" in: International Chemical Engineering, Vol. 4, No. 4, pp. 581-585; October 1964. Note: Translated from the original Russian in Izvestiya Vysshikh Uchebn, Zavedenii, Khimiya i Khimicheskaya Tekhnologiya, No. 5, pp. 774-780; 1963.
5. P. DAVIES, R. T. DONALD and N. H. HARBORD; "Catalytic Oxidations;" in: Martyn V. TWIGG (Ed.); Catalyst Handbook, 2nd edition; Wolfe Publishing; London; 1989.³⁰
6. Frank J. EVANS (Ed.) and J. S. SWEARINGEN; "Process Machinery Drives - Steam Turbines;" in: Robert Howard PERRY and Don W. GREEN (Ed's); Perry's Chemical Engineers' Handbook, 6th edition; McGraw-Hill Inc.; New York; 1984.
7. James R. FAIR and Richard C. KMETZ; "Formaldehyde" in: John J. McKETTA (Exec. Ed.); Encyclopedia of Chemical Processing and Design; Marcel Dekker; New York; 1985.³¹
8. Presentation by Mr. Simon FARRAR (Orica Adhesives and Resins, Deer Park; ex-West Kalimantan, Indonesia) at Monash University, 04/08/1999. He stated that they had achieved formic acid concentrations of, "0.01 to 0.02%," in their silver catalyst process, "by cooling to below 500°C very rapidly." He also stated that mixing was required along with vaporisation, and that the process gases fed to the reactor

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.

- 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.”
9. H. Robert GERBERICH and George C. SEAMAN; “Formaldehyde” in: Jacqueline I. KROSCWITZ (Exec. Ed.); Kirk-Othmer Encyclopedia of Chemical Technology, 4th edition, Vol. 11; John Wiley & Sons; New York; 1994.
 10. I. HAHNENSTEIN, H. HASSE, Y.-Q. LIU and G. MAURER; “Thermodynamic Properties of Formaldehyde Containing Mixtures for Separation Process Design,” in: Theodore B. SELOVER and Chau-Chyun CHEN (Vol. Ed’s); Thermodynamic Properties for Industrial Process Design, AIChE Symposium Series [298], Vol. 90; American Institute of Chemical Engineers; 1994.³²
 11. Guenter HALBRITTER, Wolfgang MUEHLHALER, Heinrich SPERBER, Hans DIEM, Christian DUDECK and Gunter LEHMANN (all BASF AG); “Manufacture of formaldehyde;” in: US Patent 4072717; 07 February, 1978. Note: Original patent lodged in Germany (2442231).
 12. Elwyn JONES and G. G. FOWLIE; “Thermodynamics of Formaldehyde Manufacture from Methanol;” in: –; Journal of Applied Chemistry, Vol. 3, pp. 206–209; Society of Chemical Industry; London; May, 1953.
 13. Shigeo KIMURA and Kouichi KURATA (both Mitsubishi Gas Chemical Co.); “Process for Recovering Waste Heat from Formaldehyde Product Gas;” in: US Patent 4691060; 01 September, 1987.
 14. Yasuo KURAISHI and Kyugo YOSHIKAWA; “A New Process for the Manufacture of Formalin via Excess Methanol Process (Introduction of Waste Gas Recycle developed by Mitsubishi Gas Chemical Company, Inc. “MGC”);” in: Chemical Economy & Engineering Review, Vol. 14, No. 6 (No. 159), pp. 31–34; June 1982.³³
 15. L. F. MAREK and Dorothy A. HAHN; Catalytic Oxidation of Organic Compounds in the Vapour Phase, American Chemical Society Monograph Series #61; The Chemical Catalogue Co.; New York; 1932.
 16. Raymond MAUX (Societe Chimique des Charbonnages); “Preparation of Formaldehyde;” in: US Patent 3728398; 17 April 1973. Note: Original patent lodged in France.
 17. Günther REUSS, Walter DISTELDORF, Otto GRUNDLER and Albrecht HILT; “Formaldehyde” in: Wolfgang GERHARTZ (Exec. Ed.); Ullmann’s Encyclopedia of Industrial Chemistry, 5th edition, Vol. A11; VCH; Weinheim; 1988.
 18. Robert C. REID, John M. PRAUSNITZ and Bruce E. POLING; The Properties of Gases and Liquids, 4th edition; McGraw-Hill; New York; 1987.
 19. G. F. C. ROGERS and Y. R. MAYHEW (‘Arrangers’); Thermodynamic and Transport Properties of Fluids, SI Units, 5th edition; Basil Blackwell; Oxford; 1995.
 20. Karl SEITHER, Guenter MATTHIAS, Hans DIEM, Oskar HUSSY and Hans HAAS (all BASF AG); “Manufacture of Formaldehyde;” in: US Patent 3932522; 13 January 1976. Note: Original patent lodged in Germany (2114370).
 21. Hosaka SHINGO and Sakaguchi YASUHIKO (both Mitsui Toatsu Chem. Inc.); “Production of Formaldehyde;” in: Japanese Patent 06184035; 05 July, 1994.
 22. R. K. SINNOTT; Chemical Engineering Design, 2nd edition; in: J. F. RICHARDSON and J. M. COULSON; Chemical Engineering, Vol. 6; Butterworth-Heinemann; Oxford; 1997.
 23. Robin SMITH; Chemical Process Design, International edition; McGraw-Hill; New York; 1995.³⁴
 24. J. Frederic WALKER; Formaldehyde, [American Chemical Society Monograph series], 3rd edition; Rheinhold Publishing; New York; 1964.
 25. J. G. M. WINKELMAN, H. SIJBRING and A. A. C. M. BEENACKERS; “Modeling and Simulation of Industrial Formaldehyde Absorbers;” in: Liang-Shih FAN *et alii* (Ed’s); Chemical Engineering Science, Vol. 47, No. 13/14, The First International Conference on Gas-Liquid and Gas-Liquid-Solid Reactor Engineering [Columbus, Ohio, U.S.A.], Session E: Reactor modeling, dynamics, and control, pp. 3785–3792; Pergamon Press; Oxford; 1992.

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.

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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.

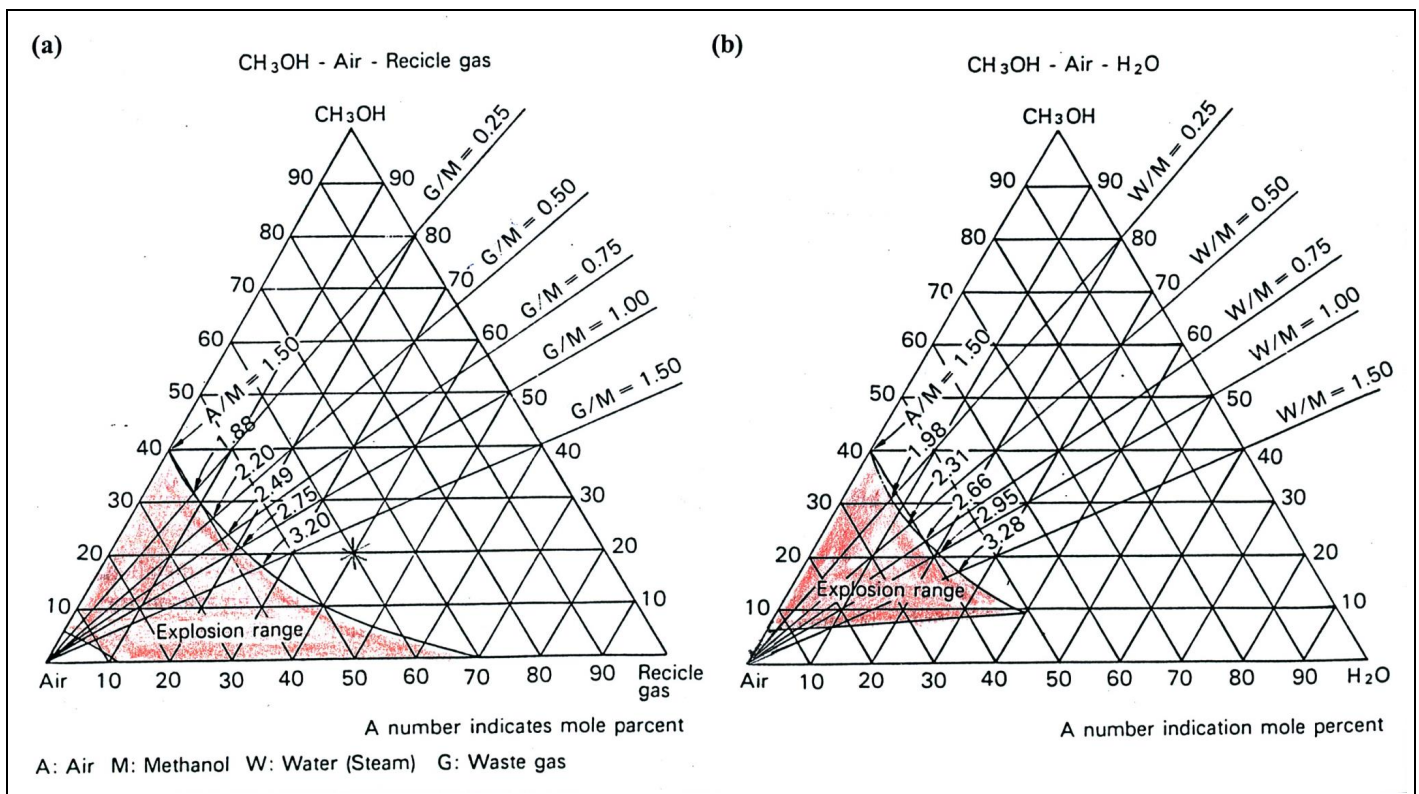


Figure 4-1: (a) Explosion limits for the Methanol –Air–Recycle-gas system; (b) Explosion limits for the Methanol –Air–Water system. [9]

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

1. Dr. David J. BRENNAN; Problem statement; 28/07/1999.
2. Presentation by Mr. Simon FARRAR (Orica Adhesives and Resins, Deer Park; ex-West Kalimantan, Indonesia) at Monash University, 04/08/1999. He stated that at their plant methanol was shipped in “from the Bontang area.”
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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4. Alan ENGLISH, Jerry ROVNER and Simon DAVIES; "Methanol" in: Jacqueline I. KROSCWITZ (Exec. Ed.); Kirk-Othmer Encyclopedia of Chemical Technology, 4th edition, Vol. 11; John Wiley & Sons; New York; 1994.
5. Eckhard FIEDLER, Georg GROSSMAN, Burkhard KERSEBOHM, Günter WEISS, Claus WITTE; "Methanol;" in: Barbara ELVERS, Stephen HAWKINS and Gail SCHULZ (Ed's); Ullmann's Encyclopedia of Industrial Chemistry, 5th edition, Vol. A16; VCH; Weinheim; 1990.
6. Gerhard FRANZ and Roger A. SHELDON; "Oxidation;" in: Barbara ELVERS, Stephen HAWKINS and Gail SCHULZ (Ed's); Ullmann's Encyclopedia of Industrial Chemistry, 5th edition, Vol. A18; VCH; Weinheim; 1991.
7. Guenter HALBRITTER, Wolfgang MUEHLHALER, Heinrich SPERBER, Hans DIEM, Christian DUDECK and Gunter LEHMANN (all BASF AG); "Manufacture of formaldehyde;" in: US Patent 4072717; 07 February, 1978. Note: Original patent lodged in Germany (2442231).
8. Peter HÄUSSINGER, Reiner LOHMÜLLER and Allan M. WATSON; "Hydrogen;" in: Barbara ELVERS and Stephen HAWKINS (Ed's); Ullmann's Encyclopedia of Industrial Chemistry, 5th edition, Vol. A13; VCH; Weinheim; 1989.
9. Yasuo KURAISHI and Kyugo YOSHIKAWA; "A New Process for the Manufacture of Formalin via Excess Methanol Process (Introduction of Waste Gas Recycle developed by Mitsubishi Gas Chemical Company, Inc. "MGC");" in: Chemical Economy & Engineering Review, Vol. 14, No. 6 (No. 159), pp. 31–34; June 1982.¹⁷
10. Harry LEHRER; Private communication; August 1999.
11. Ernest E. LUDWIG; Applied Process Design for Chemical and Petrochemical Plants, 3rd edition, Vol. 1; Gulf Publishing; Houston; 1977.
12. Alan MANZOORI; "Notes on Steam-Power Systems;" in: Martin J. RHODES; CHE3108 Lecture Notes; Monash University; 1998
13. L. F. MAREK and Dorothy A. HAHN; Catalytic Oxidation of Organic Compounds in the Vapour Phase, American Chemical Society Monograph Series #61; The Chemical Catalogue Co.; New York; 1932.
14. W. Eric OLBRICH; Private communication; August 1999.

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

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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:

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

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 Pshchetskii [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 $2.6455\text{kg}\cdot\text{s}^{-1}$, with mass fractions of 0.540 formaldehyde (HCHO), 0.010 methanol (CH₃OH), approximately 0.0002 formic acid (HCOOH) and the remainder water (H₂O) – 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 (CO₂), 0.10 to 0.25 H₂, 0.0002 to 0.001 HCHO and “substantial amounts of nitrogen [N₂] 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).



Using the spreadsheet's "iterate" function

REACTIONS:

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	NETT	
51.3882561	51.3882561	51.3882561	=Total HCHO formed pre-degradation						
-19.2706	-32.1177	0	0	-2.14118	0	0	0	-53.52943	
19.2706	32.11766	0	-0.47476	0	-3.31545	-0.01028	-0.01028	47.5775	
-9.6353	0	-6.423532	0	-3.21177	-3.31545	-0.00514	-0.00514	-22.59632	
0	0	0	0	0	0	0	0	0	
19.2706	0	12.84706	0	4.282355	3.315448	0	0.010278	39.72574	
0	32.11766	-12.84706	0.474756	0	0	0	0	19.74535	
0	0	0	0	2.141177	3.315448	0	0	5.456626	
0	0	0	0.474756	0	0	0	0.010278	0.485033	
0	0	0	0	0	0	0.010278	0	0.010278	
9.635298	32.11766	-6.423532	0.474756	1.070589	0	-0.00514	0.005139	36.87477	
(NOT ZERO)		(NOT ZERO)		(NOT ZERO)				(NOT ZERO)	

Stream: Fresh feed	Recycled off-gas	Total reactor feed
MOLAR FLOWS [mol.s ⁻¹]	FRACTION:	FRACTION:
CH ₃ OH 54.35507 0.3008	0 0.0000	54.3551 0.1837
HCHO 0 0.0000	0 0.0000	0 0.0000
O ₂ 22.65455 0.1254	0.0553 0.0005	22.7099 0.0768
N ₂ 85.48174 0.4731	81.2076 0.7050	166.6894 0.5634
H ₂ O 18.18057 0.1006	9.5298 0.0827	27.7104 0.0937
H ₂ 0 0.0000	18.7581 0.1628	18.7581 0.0634
CO ₂ 0 0.0000	5.1838 0.0450	5.1838 0.0175
CO 0 0.0000	0.4608 0.0040	0.4608 0.0016
HCOOH 0 0.0000	0 0.0000	0 0.0000
TOTAL 180.6719 1.0000	115.1954 1.0000	295.8674 1.0000

(Absorber feed)

Reactor effluent	Absorber water in	Off-gas	Product
FRACTION:	FRACTION:	FRACTION:	FRACTION:
CH ₃ OH 0.8256 0.0025	0 0.0000	0 0.0000	0.8256 0.0072
HCHO 47.5775 0.1430	0 0.0000	0 0.0000	47.5775 0.4156
O ₂ 0.1135 0.0003	0 0.0000	0.0582 0.0005	0 0.0000
N ₂ 166.6894 0.5010	0 0.0000	85.4817 0.7050	0 0.0000
H ₂ O 67.4361 0.2027	18.18057 1.0000	10.0314 0.0827	66.0555 0.5771
H ₂ 38.5034 0.1157	0 0.0000	19.7454 0.1628	0 0.0000
CO ₂ 10.6404 0.0320	0 0.0000	5.4566 0.0450	0 0.0000
CO 0.9458 0.0028	0 0.0000	0.4850 0.0040	0 0.0000
HCOOH 0.0103 0.0000	0 0.0000	0 0.0000	0.0103 0.0001
TOTAL 332.7421 1.0000	18.18057 1.0000	121.2584 1.0000	114.4689 1.0000
		Total out: 235.727267	(SHOULD BE ZERO)

CHECK !

ACC = 0 = IN+GEN-OUT:	Additional fuel/air	Combusted off-gas
FRACTION:	FRACTION:	FRACTION:
0.0000 0.0000	0 0.0000	0 0.0000
0.0000 0.0000	0 0.0000	0 0.0000
0.0000 0.0000	12.0800 0.1991	2.0230 0.0118
0.0000 0.0000	45.5811 0.7513	131.0628 0.7628
0.0000 0.0000	3.0092 0.0496	32.7859 0.1908
0.0000 0.0000	0 0.0000	0 0.0000
0.0000 0.0000	0 0.0000	5.9417 0.0346
0.0000 0.0000	0 0.0000	0 0.0000
0.0000 0.0000	0 0.0000	0 0.0000
0.0000 0.0000	60.6703 1.0000	171.8134 1.0000
(SHOULD BE ZERO)		

MASS FLOWS [kg.s ⁻¹]	FRACTION:	FRACTION:
CH ₃ OH 1.7416 0.3357	0 0.0000	1.7416 0.2200
HCHO 0 0.0000	0 0.0000	0 0.0000
O ₂ 0.7249 0.1397	0.0018 0.0006	0.7267 0.0918
N ₂ 2.3946 0.4615	2.2749 0.8341	4.6695 0.5899
H ₂ O 0.3275 0.0631	0.1717 0.0630	0.4992 0.0631
H ₂ 0 0.0000	0.0378 0.0139	0.0378 0.0048
CO ₂ 0 0.0000	0.2281 0.0837	0.2281 0.0288
CO 0 0.0000	0.0129 0.0047	0.0129 0.0016
HCOOH 0 0.0000	0 0.0000	0 0.0000
TOTAL 5.1887 1.0000	2.7272 1.0000	7.9159 1.0000

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	NETT
-0.61747	-1.02911	0	0	-0.06861	0	0	0	-1.71519
0.578623	0.964371	0	-0.01426	0	-0.09955	-0.00031	-0.00031	1.428571
-0.30832	0	-0.205545	0	-0.10277	-0.10609	-0.00016	-0.00016	-0.723055
0	0	0	0	0	0	0	0	0
0.347164	0	0.231442	0	0.077147	0.059728	0	0.000185	0.715667
0	0.064743	-0.025897	0.000957	0	0	0	0	0.039803
0	0	0	0	0.094233	0.145912	0	0	0.240145
0	0	0	0.013298	0	0	0	0.000288	0.013586
0	0	0	0	0	0	0.000473	0	0.000473
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
(SHOULD BE ZERO)		(SHOULD BE ZERO)		(SHOULD BE ZERO)				

Reactor effluent	Absorber water in	Off-gas	Product
FRACTION:	FRACTION:	FRACTION:	FRACTION:
CH ₃ OH 0.0265 0.0033	0 0.0000	0 0.0000	0.026455 0.0100
HCHO 1.4286 0.1805	0 0.0000	0 0.0000	1.428571 0.5400
O ₂ 0.0036 0.0005	0 0.0000	0.0019 0.0006	0 0.0000
N ₂ 4.6695 0.5899	0 0.0000	2.3946 0.8341	0 0.0000
H ₂ O 1.2149 0.1535	0.3275 1.0000	0.1807 0.0630	1.190003 0.4498
H ₂ 0.0776 0.0098	0 0.0000	0.0398 0.0139	0 0.0000
CO ₂ 0.4683 0.0592	0 0.0000	0.2401 0.0837	0 0.0000
CO 0.0265 0.0033	0 0.0000	0.0136 0.0047	0 0.0000
HCOOH 0.0005 0.0001	0 0.0000	0 0.0000	0.000473 0.00018
TOTAL 7.9159 1.0000	0.3275 1.0000	2.8707 1.0000	2.645503 1.0000
		Total out: 5.51625088	(SHOULD BE ZERO)

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.

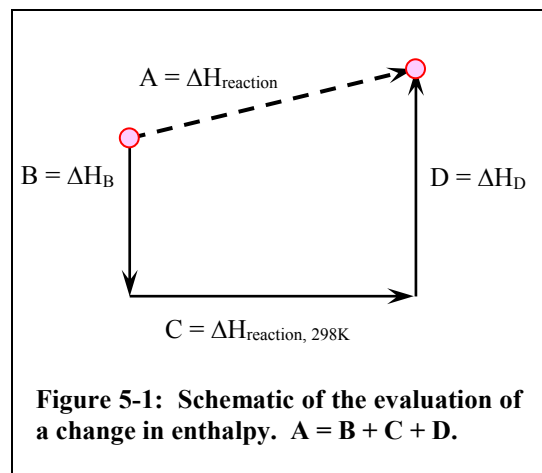
As enthalpy is a 'state' property – *i.e.* it is independent of path – it is possible to calculate a change in enthalpy by constructing a hypothetical path. The method used here took heats of formation¹⁴ of each species, in the relevant phase, at 25°C (298K) and then made adjustments using average specific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

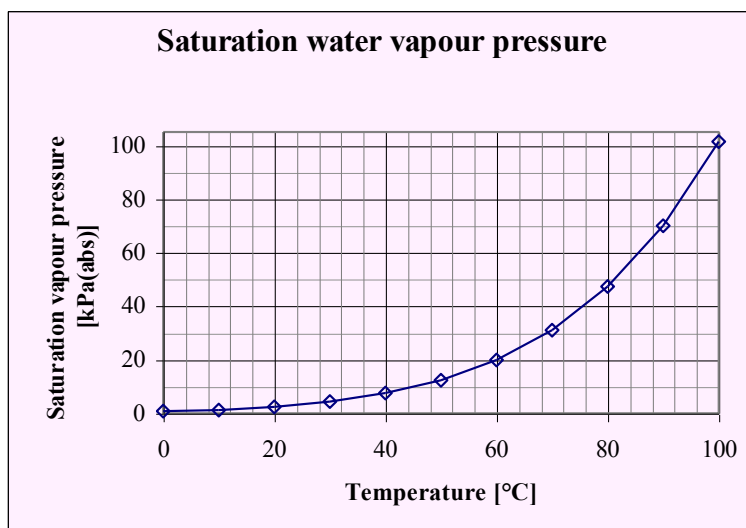


Figure 5-2: Saturation water vapour content of a gas [15].

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

1. V. I. ATROSHCHENKO and I. P. KUSHNARENKO; “Kinetics of the catalytic oxidation of methanol to formaldehyde over a silver catalyst;” in: International Chemical Engineering, Vol. 4, No. 4, pp. 581–585; October 1964. Note: Translated from the original Russian in Izvestiya Vysshikh Uchebn. Zavedenii. Khimiya i Khimicheskaya Tekhnologiya, No. 5, pp. 774–780; 1963.
2. James R. FAIR and Richard C. KMETZ; “Formaldehyde” in: John J. McKETTA (Exec. Ed.); Encyclopedia of Chemical Processing and Design; Marcel Dekker; New York; 1985.²⁷
3. Presentation by Mr. Simon FARRAR (Orica Adhesives and Resins, Deer Park; ex-West Kalimantan, Indonesia) at Monash University, 04/08/1999. He stated oxygen was only present at “trace” levels upon exiting the reactor.
4. V. N. GAVRILIN and B. I. POPOV; “Oxidation of Methanol to Formaldehyde on a Silver Catalyst. I. On the Conditions of the Process;” in: G. K. BORESKOV (Ed. in Chief); Kinetics and Catalysis, Vol. 6, No. 5, pp. 799–803; September–October, 1965. Note: Translated from the original Russian in Kinetika i Kataliz, Vol. 6, No. 5, pp. 884–888; September–October, 1965.
5. I. HAHNENSTEIN, H. HASSE, Y.-Q. LIU and G. MAURER; “Thermodynamic Properties of Formaldehyde Containing Mixtures for Separation Process Design;” in: Theodore B. SELOVER and Chau-Chyun CHEN (Vol. Ed’s); Thermodynamic Properties for Industrial Process Design, AIChE Symposium Series [298], Vol. 90; American Institute of Chemical Engineers; 1994.²⁸
6. Guenter HALBRITTER, Wolfgang MUEHLHALER, Heinrich SPERBER, Hans DIEM, Christian DUDECK and Gunter LEHMANN (all BASF AG); “Manufacture of formaldehyde;” in: US Patent 4072717; 07 February, 1978. Note: Original patent lodged in Germany (2442231).
7. Peter HAWKINS; ECS1610 Lecture Materials; 1995.
8. Elwyn JONES and G. G. FOWLIE; “Thermodynamics of Formaldehyde Manufacture from Methanol;” in: –; Journal of Applied Chemistry, Vol. 3, pp. 206–209; Society of Chemical Industry; London; May, 1953.
9. Chun-Zhu LI; Private communication; August, 1999.
10. Peter E. LILEY, Robert C. REID and Evan BUCK; “Physical and Chemical Data;” in: Robert Howard PERRY and Don W. GREEN (Ed’s); Perry’s Chemical Engineers’ Handbook, 6th edition; McGraw-Hill Inc.; New York; 1984.
11. W. Eric OLBRICH; Private communication; August 1999.
12. David W. OXTOBY and Norman H. NACHTRIEB; Principles of Modern Chemistry, 2nd edition; Saunders College Publishing; Philadelphia; 1990.
13. Robert C. REID, John M. PRAUSNITZ and Bruce E. POLING; The Properties of Gases and Liquids, 4th edition; McGraw-Hill; New York; 1987.
14. Günther REUSS, Walter DISTELDORF, Otto GRUNDLER and Albrecht HILT; “Formaldehyde” in: Wolfgang GERHARTZ (Exec. Ed.); Ullmann’s Encyclopedia of Industrial Chemistry, 5th edition, Vol. A11; VCH; Weinheim; 1988.
15. G. F. C. ROGERS and Y. R. MAYHEW (‘Arrangers’); Thermodynamic and Transport Properties of Fluids, SI Units, 5th edition; Basil Blackwell; Oxford; 1995.
16. R. K. SINNOTT; “Chemical Engineering Design,” 2nd edition; in: J. F. RICHARDSON and J. M. COULSON; Chemical Engineering, Vol. 6; Butterworth-Heinemann; Oxford; 1997.
17. Robin SMITH; Chemical Process Design, International edition; McGraw-Hill; New York; 1995.²⁹
18. J. Frederic WALKER; Formaldehyde, [American Chemical Society Monograph series], 3rd edition; Rheinhold Publishing; New York; 1964.

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.

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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 $2\text{m}\cdot\text{s}^{-1}$ flow of liquids, or half that for liquids under gravity flow, and around $25\text{m}\cdot\text{s}^{-1}$ 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

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

where Q is the heat transfer [kW], U the overall heat transfer [$\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$], 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.

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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

1. Australian Standard 1210; SAA Unfired Pressure Vessels Code; 1989⁸.
2. James R. FAIR and Richard C. KMETZ; "Formaldehyde" in: John J. McKETTA (Exec. Ed.); Encyclopedia of Chemical Processing and Design; Marcel Dekker; New York; 1985.⁹
3. David J. BRENNAN; CHE3109 Lecture Materials; Monash University; Melbourne; 1998.
4. Raymond P. GENEREUX, Charles B. MITCHELL, C. Addison HEMPSTEAD and Bruce F. CURRAN; "Transport and Storage of Fluids;" in: Robert Howard PERRY and Don W. GREEN (Ed's); Perry's Chemical Engineers' Handbook, 6th edition; McGraw-Hill Inc.; New York; 1984.
5. H. Robert GERBERICH and George C. SEAMAN; "Formaldehyde" in: Jacqueline I. KROSCWITZ (Exec. Ed.); Kirk-Othmer Encyclopedia of Chemical Technology, 4th edition, Vol. 11; John Wiley & Sons; New York; 1994.
6. Douglas C. GIANCOLI; Physics for Scientists and Engineers with Modern Physics, 2nd edition; Prentice Hall; Englewood Cliffs, New Jersey; 1989.
7. I. HAHNENSTEIN, H. HASSE, Y.-Q. LIU and G. MAURER; "Thermodynamic Properties of Formaldehyde Containing Mixtures for Separation Process Design;" in: Theodore B. SELOVER and Chau-Chyun CHEN (Vol. Ed's); Thermodynamic Properties for Industrial Process Design, AIChE Symposium Series [298], Vol. 90; American Institute of Chemical Engineers; 1994.¹⁰
8. Guenter HALBRITTER, Wolfgang MUEHLHALER, Heinrich SPERBER, Hans DIEM, Christian DUDECK and Gunter LEHMANN (all BASF AG); "Manufacture of formaldehyde;" in: US Patent 4072717; 07 February, 1978. Note: Original patent lodged in Germany (2442231).
9. Ernest HOLMES; Handbook of Industrial Pipework Engineering; McGraw-Hill; London; 1973.
10. James G. KNUDSEN, Kenneth J. BELL, Arthur G. HOLT, Hoyt C. HOTTEL, Adel F. SAROFIM, F. C. STANDIFORD, David STUHLBARG and Vincent W. UHL; "Heat Transmission;" in: Robert Howard PERRY and Don W. GREEN (Ed's); Perry's Chemical Engineers' Handbook, 6th edition; McGraw-Hill Inc.; New York; 1984.
11. Peter E. LILEY, Robert C. REID and Evan BUCK; "Physical and Chemical Data;" in: Robert Howard PERRY and Don W. GREEN (Ed's); Perry's Chemical Engineers' Handbook, 6th edition; McGraw-Hill Inc.; New York; 1984.
12. Robert C. REID, John M. PRAUSNITZ and Bruce E. POLING; The Properties of Gases and Liquids, 4th edition; McGraw-Hill; New York; 1987.
13. Günther REUSS, Walter DISTELDORF, Otto GRUNDLER and Albrecht HILT; "Formaldehyde" in: Wolfgang GERHARTZ (Exec. Ed.); Ullmann's Encyclopedia of Industrial Chemistry, 5th edition, Vol. A11; VCH; Weinheim; 1988.
14. Martin J. RHODES; CHE3108 Lecture Materials; Monash University; Melbourne; 1998.
15. G. F. C. ROGERS and Y. R. MAYHEW ('Arrangers'); Thermodynamic and Transport Properties of Fluids, SI Units, 5th edition; Basil Blackwell; Oxford; 1995.
16. Frank L. RUBIN, Herbert A. MOAK, Arthur D. HOLT, F. C. STANDIFORD and David STUHLBARG; "Heat-Transfer Equipment;" in: Robert Howard PERRY and Don W. GREEN (Ed's); Perry's Chemical Engineers' Handbook, 6th edition; McGraw-Hill Inc.; New York; 1984.
17. R. K. SINNOTT; "Chemical Engineering Design," 2nd edition; in: J. F. RICHARDSON and J. M. COULSON; Chemical Engineering, Vol. 6; Butterworth-Heinemann; Oxford; 1997.
18. J. Frederic WALKER; Formaldehyde, [American Chemical Society Monograph series], 3rd edition; Reinhold Publishing; New York; 1964.

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		
Inlet temperature [°C]	Liquid	Vapour	
	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		
Main inlet branch nominal diameter [mm]	Liquid	Vapour	
	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
Date:	10/01/1999 [sic!]	Date:	30/09/1999
		Authorised:	—
		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
Fluid description		BFW	Steam	BFW	Steam
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	
		Feed 1	Feed 2	Exit 1	Exit 2
Branch nominal diameter [mm]		25	254	51	356
Connection type		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
Fluid description		BFW	Steam	BFW	Steam
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	
		Feed 1	Feed 2	Exit 1	Exit 2
Branch nominal diameter [mm]		38	305	51	432
Connection type		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
Inlet temperature [°C]	Liquid	Vapour		
	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	22.0		-	
	Formaldehyde	trace		-	
	Oxygen	9.2		-	
	Water	6.3		100	
	Other (including nitrogen)	62.5		trace	
Flowrate [$kg.s^{-1}$]		7.916		0.484	
Vapour fraction		In	Out	In	Out
Temperature [$^{\circ}C$]		62	158	187	187
Pressure [kPa(abs)]		185	170	1200	1185
Density [$kg.m^{-3}$]		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)				
		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	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	0.3			-
	Formaldehyde	18.1			-
	Oxygen	0.1			-
	Water	15.4			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		Shell-side	
Outlet branch nominal diameter [mm]		762		51	
Connection type		610		305	
		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 [$W.m^{-2}.K^{-1}$]	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 [$^{\circ}C$]		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		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 [$W.m^{-2}.K^{-1}$]	126				
Heat transfer area [m^2]	180				
PROCESS DETAILS					
Fluid description		Tube-side Aqueous methanol		Shell-side 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	
		In	Out	In	Out
Vapour fraction		0	0	1	0
Temperature [$^{\circ}C$]		73	81	170	90
Pressure [kPa(abs)]		185	175	1200	1185
Density [$kg.m^{-3}$]		889	882	1.0	1.0
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)	U-tube bundle (U)				
Number of tube passes	6 (six)				
		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	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 [$W.m^{-2}.K^{-1}$]	800				
Heat transfer area [m^2]	75				
PROCESS DETAILS					
Fluid description		Tube-side		Shell-side	
		Stage 3 recirculant		Recirculated cooling water	
Fluid composition [%($kg.kg^{-1}$)]:	Water	79.8		100	
	Formaldehyde	19.9		-	
	Other (including methanol)	0.3		trace	
Flowrate [$kg.s^{-1}$]		13.7		12.8	
Vapour fraction		In	Out	In	Out
Temperature [$^{\circ}C$]		0	0	0	0
Pressure [kPa(abs)]		51	40	30	41
Density [$kg.m^{-3}$]		305	265	400	360
		1050	1050	1000	1000
MECHANICAL DATA					
Maximum design pressure [kPa(abs)]		450			
Minimum design pressure [kPa(g)]		-5			
Maximum design temperature [$^{\circ}C$]		150			
Minimum design temperature [$^{\circ}C$]		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)				
Inlet branch nominal diameter [mm]		Tube-side		Shell-side	
		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 [$W.m^{-2}.K^{-1}$]	700				
Heat transfer area [m^2]	210				
PROCESS DETAILS					
Fluid description		Tube-side		Shell-side	
		Stage 2 recirculant		Recirculated cooling water	
Fluid composition [%($kg.kg^{-1}$)]:	Water	70.6		100	
	Formaldehyde	28.9		-	
	Other (including methanol)	0.5		trace	
Flowrate [$kg.s^{-1}$]		41.2		37.5	
Vapour fraction		In	Out	In	Out
Temperature [$^{\circ}C$]		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 [$^{\circ}C$]		150			
Minimum design temperature [$^{\circ}C$]		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		Shell-side	
		178		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					
Fluid description		Tube-side		Shell-side	
		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 [$^{\circ}C$]		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 [$^{\circ}C$]		170			
Minimum design temperature [$^{\circ}C$]		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 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 [$kg.s^{-1}$]		21.2		4.6	
Vapour fraction		In	Out	In	Out
Temperature [$^{\circ}C$]		1	0.10	1	1
Pressure [kPa(abs)]		188	188	1000	760
Density [$kg.m^{-3}$]		1300	1250	110	106
MECHANICAL DATA					
Maximum design pressure [kPa(abs)]	1350				
Minimum design pressure [kPa(g)]	-10				
Maximum design temperature [$^{\circ}C$]	1100				
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)	To stack (-)				
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	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		Shell-side	
		Aqueous methanol		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 [$^{\circ}C$]		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 [$^{\circ}C$]	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).					
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 [$W \cdot m^{-2} \cdot K^{-1}$]	1000				
Heat transfer area [m^2]	21				
PROCESS DETAILS					
Fluid description		"Shell"-side		Tube-side	
		Stage 4 process fluid		Recirculated cooling water	
Fluid composition [%($kg \cdot kg^{-1}$)]:	Water	In	Out	In	Out
	Formaldehyde	100.0	84	100	100
	Other (including methanol)	0.0	15	-	-
Flowrate [$kg \cdot s^{-1}$]		0.33	0.40	7.32	7.32
		In	Out	In	Out
Vapour fraction		0	0	0	0
Temperature [$^{\circ}C$]		37	42	30	35
Pressure [kPa(abs)]		110	124	143	103
Density [$kg \cdot m^{-3}$]		1000	1000	1000	1000
MECHANICAL DATA					
Maximum design pressure [kPa(abs)]		200			
Minimum design pressure [kPa(g)]		-5			
Maximum design temperature [$^{\circ}C$]		170			
Minimum design temperature [$^{\circ}C$]		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	
	Outlet branch nominal diameter [mm]	25		N/A	
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		
	Suction	Delivery	
Temperature [°C]	37	37	
Pressure [kPa(abs)]	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		
	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 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		
	Suction	Delivery	
Temperature [°C]	62	62	
Pressure [kPa(abs)]	185	245	
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		
	Suction	Delivery	
Branch nominal diameter [mm]	203	127	
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)]:	Water	45.0	
	Formaldehyde	54.0	
	Other (including methanol)	1.0	
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
Date:	23/09/1999	Date:	24/09/1999
		Authorised:	—
		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		
	Suction	Delivery	
Temperature [°C]	51	51	
Pressure [kPa(abs)]	265	305	
Total delivered head, "TDH" [m]	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		
	Suction	Delivery	
Branch nominal diameter [mm]	152	102	
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.			
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		
	Suction	Delivery	
Temperature [°C]	30	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		
	Suction	Delivery	
Branch nominal diameter [mm]	102	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
Date:	24/09/1999	Date:	24/09/1999
		Authorised:	—
		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		
	Suction	Delivery	
Temperature [°C]	37	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		
	Suction	Delivery	
Branch nominal diameter [mm]	19	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			
	Inlet	Outlet	
Fluid description	Process Gas	Process Gas	
Fluid composition [% (kg.kg ⁻¹)]:	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]	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	Outlet	
	610	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	Shell-side			
	Steam circuit	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 [$^{\circ}C$]	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 [$^{\circ}C$]	1000				
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)	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 Methanol feed	Outlet Methanol feed
Fluid composition [% (kg.kg ⁻¹)]:	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 38	Outlet 38
Connection type		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					
Fluid description	Inlet 1	Inlet 2	Inlet 3	Outlet	
	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
Vapour fraction	0	0	0	0	
Temperature [°C] - see Notes	60	37	37	65	
Pressure [kPa(abs)]	110	110	110	110	
Density [kg.m ⁻³]	1100	790	1000	1100	
Mean flowrate [kg.s ⁻¹]	0.187	0.017	0.069	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	
Branch nominal diameter [mm]	Inlet 1	Inlet 2	Inlet 3	Outlet	
Connection type	25	13	13	25	
	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 [m ³]	330		
PROCESS DETAILS			
Fluid description	Inlet 1	Outlet	
	Grade B	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	Outlet	
	25	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 [m ³]	507				
PROCESS DETAILS					
Fluid description	Inlet 1	Inlet 2	Inlet 3	Outlet	
	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
Vapour fraction	0	0	0	0	
Temperature [°C] - see Notes	60	37	37	65	
Pressure [kPa(abs)]	110	110	110	110	
Density [kg.m ⁻³]	1100	790	1000	1100	
Mean flowrate [kg.s ⁻¹] - see Notes	2.458	0.000	0.000	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	
Branch nominal diameter [mm]	Inlet 1	Inlet 2	Inlet 3	Outlet	
Connection type	38	13	13	51	
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 [m ³]	1120		
PROCESS DETAILS			
Fluid description	Inlet 1	Outlet	
	Grade A	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		
Branch nominal diameter [mm]	Inlet 1	Outlet	
	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		
	Suction	Delivery	
Temperature [°C]	152	100	
Pressure [kPa(abs)]	500	102	
Density [kg.m ⁻³]			
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		
	Suction	Delivery	
Branch nominal diameter [mm]			
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:	—
Date:	09/10/1999	Date:	—

SPECIFICATION SHEET:		VALVE	
Equipment item	V-1		
Description	Water let-down valve		
Type	Restriction in line; Isenthalpic		
Quantity	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		
	Inlet	Outlet	
Temperature [°C]	37	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		
	Inlet	Outlet	
Branch nominal diameter [mm]	13	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
Date:	10/01/1999 [sic!]	Date:	30/09/1999
		Authorised:	—
		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.

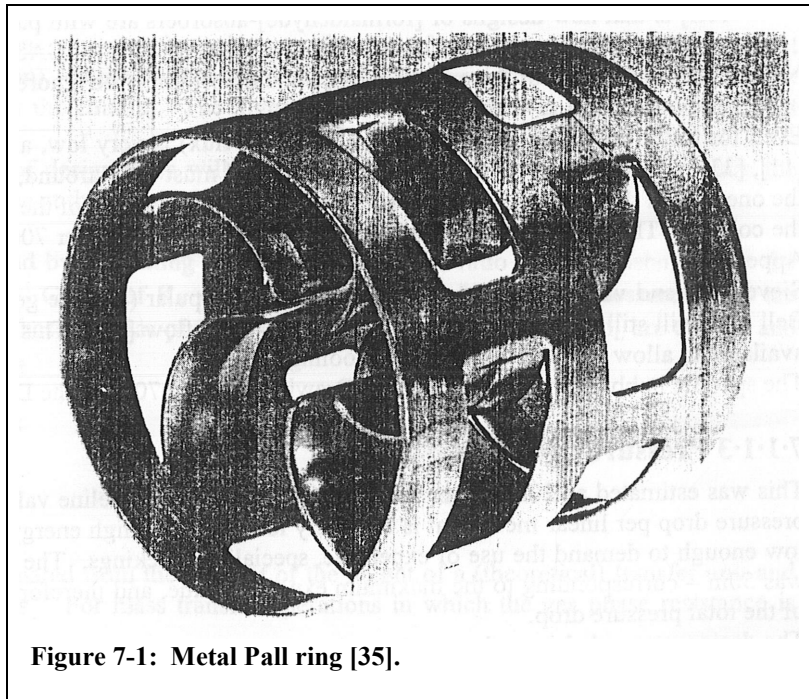


Figure 7-1: Metal Pall ring [35].

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.

Chapter 7: Detailed Design of Formaldehyde Absorber

FORMALDEHYDE

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 serpentines 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.

FORMALDEHYDE**Chapter 7: Detailed Design of Formaldehyde Absorber****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 $K_4 \equiv 13.1 V^2 \cdot F_P \cdot (\mu_L/\rho_L)^{0.1} \div \{\rho_G \cdot (\rho_L - \rho_G)\}$, 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

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

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:

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

The gas phase mole fractions, y_{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.*

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

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

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

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

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

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 [$\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$] and k_L [$\text{m}\cdot\text{s}^{-1}$]. A correlation for the wetted surface area, a_w [$\text{m}^2\cdot\text{m}^{-3}$], 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:

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

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

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

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

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

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

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

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

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 [$\text{dyn}\cdot\text{cm}^{-1}$].

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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

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

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

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

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

and

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

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].

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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].

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.

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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 2×10^{-5} cm².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 2.2×10^{-5} cm².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 $70\text{mN}.\text{m}^{-1}$ 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 $60\text{mN}.\text{m}^{-1}$ 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 OKUMOT. 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].

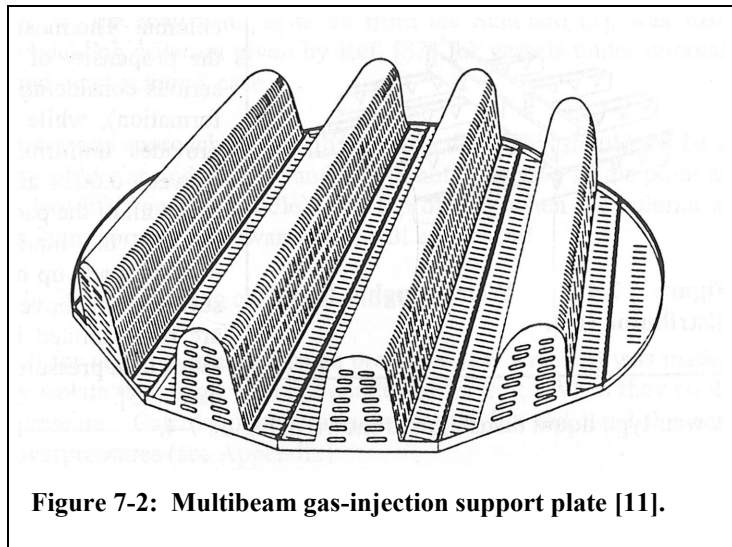


Figure 7-2: Multibeam gas-injection support plate [11].

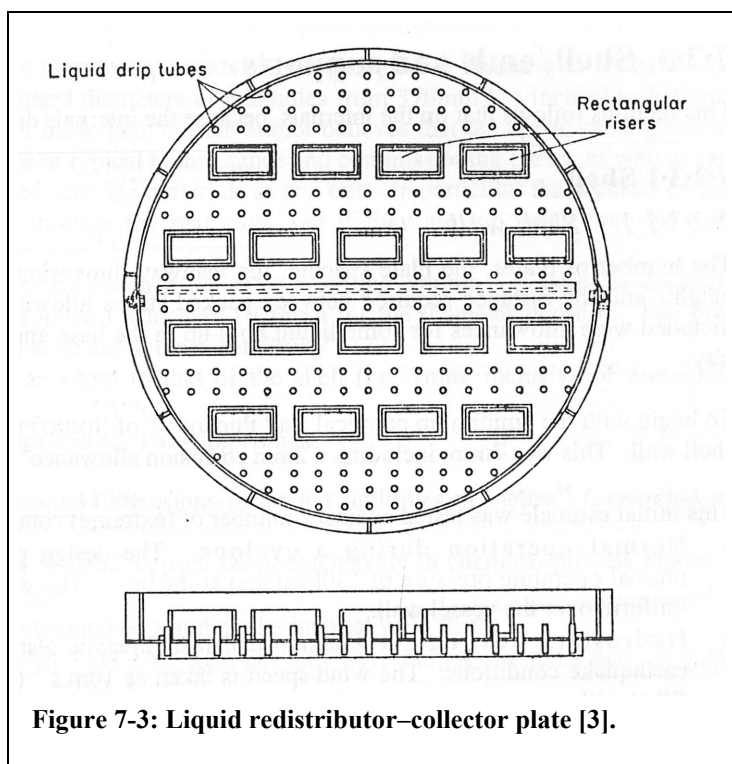


Figure 7-3: Liquid redistributor-collector plate [3].

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.

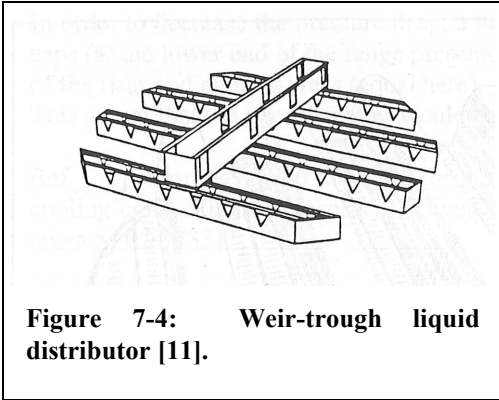


Figure 7-4: Weir-trough liquid distributor [11].

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.

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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].

Chapter 7: Detailed Design of Formaldehyde Absorber**FORMALDEHYDE****7.2.3.1.3 Insulation**

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 + 2mm), 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 .

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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.

7.3 References

1. M. ALBERT, I. HAHNENSTEIN, H. HASSE and G. MAURER; “Vapor–Liquid Equilibrium of Formaldehyde Mixtures: New Data and Model Revision,” in: –; American Institute of Chemical Engineers Journal; Vol. 42, No. 6; Chemical Engineering Research and Development, Thermodynamics; pp. 1741–1752; June 1996.
2. Australian Standard 1210; SAA Unfired Pressure Vessels Code; 1989⁵¹.
3. J. R. BACKHURST and J. H. HARKER; Process Plant Design; Heinemann Educational Books; London; 1973.
4. William L. BOLLES and James R. FAIR; “Improved mass-transfer model enhances packed-column design,” in: Nicholas P. CHOPEY (Ed. in Chief); Chemical Engineering; Vol. 89, N. 14, pp. 109–116; McGraw-Hill; New York; 12 July, 1982.
5. David James BRENNAN; CHE3109 Lecture Materials; Monash University; Melbourne; 1998.
6. J. M. COULSON and J. F. RICHARDSON; Chemical Engineering, Vol. 2 – “Particle Technology and Separation Processes,” 4th edition; Pergamon; Oxford; 1991.
7. J. W. DREW (Chair); “Packed Columns – A Guide to Performance Evaluation,” 2nd edition; in: S. D. FEAGEN (Chair); AICHE Equipment Testing Procedure; AIChE Pub. E28; American Institute of Chemical Engineers; New York; 1990.
8. Markus DUSS (Sulzer Chemtech AG); Private communication; 06 and 07 September, 1999.
9. William M. EDWARDS; “Mass Transfer and Gas Absorption,” in: Robert Howard PERRY and Don W. GREEN (Ed’s); Perry’s Chemical Engineers’ Handbook, 6th edition; McGraw-Hill; New York; 1984.
10. James R. FAIR and Richard C. KMETZ; “Formaldehyde” in: John J. McKETTA (Exec. Ed.); Encyclopedia of Chemical Processing and Design; Marcel Dekker; New York; 1985.⁵²
11. J. R. FAIR, D. E. STEINMEYER, W. R. PENNEY and B. B. CROCKER; “Liquid-Gas Systems,” in: Robert Howard PERRY and Don W. GREEN (Ed’s); Perry’s Chemical Engineers’ Handbook, 6th edition; McGraw-Hill; New York; 1984.
12. Howard M. FEINTUCH and Robert Ewald TREYBAL; “The Design of Adiabatic Packed Towers for Gas Absorption and Stripping,” in: Hugh M. HULBERT (Ed.) Industrial and Engineering Chemistry – Process Design and Development; Vol. 17, No. 4, pp. 505–513; October, 1978.
13. Raymond P. GENEREAUX, Charles B. MITCHELL, C. Addison HEMPSTEAD and Bruce F. CURRAN; “Transport and Storage of Fluids,” in: Robert Howard PERRY and Don W. GREEN (Ed’s); Perry’s Chemical Engineers’ Handbook, 6th edition; McGraw-Hill; New York; 1984.
14. H. Robert GERBERICH and George C. SEAMAN; “Formaldehyde” in: Jacqueline I. KROSCWITZ (Exec. Ed.); Kirk-Othmer Encyclopedia of Chemical Technology, 4th edition, Vol. 11; John Wiley & Sons; New York; 1994.
15. Douglas C. GIANCOLI; Physics for Scientists and Engineers with Modern Physics, 2nd edition; Prentice Hall; Englewood Cliffs, New Jersey; 1989.
16. J. GMEHLING, U. ONKEN and J. R. RAREY-NIES; “Vapor-Liquid Equilibrium Data Collection, Aqueous Systems (Supplement 2),” in: Dieter BEHRENS and Reiner ECKERMANN (Ed’s); Chemistry Data Series; Vol. I, Part 1b; DECHEMA; Frankfurt am Main; circa 1977–1986.
17. Don W. GREEN; “Conversion Factors and Miscellaneous Tables,” in: Robert Howard PERRY and Don W. GREEN (Ed’s); Perry’s Chemical Engineers’ Handbook, 6th edition; McGraw-Hill; New York; 1984.
18. I. HAHNENSTEIN, H. HASSE, Y.-Q. LIU and G. MAURER; “Thermodynamic Properties of Formaldehyde Containing Mixtures for Separation Process Design,” in: Theodore B. SELOVER and Chau-Chyun CHEN

⁵¹ Third amendment is most recent, dated December 1993.

⁵² This reference due to Dr. David J. BRENNAN.

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- (Vol. Ed's); Thermodynamic Properties for Industrial Process Design, AIChE Symposium Series [298], Vol. 90; American Institute of Chemical Engineers; 1994.⁵³
19. Guenter HALBRITTER, Wolfgang MUEHLTHALER, Heinrich SPERBER, Hans DIEM, Christian DUDECK and Gunter LEHMANN (all BASF AG); "Manufacture of formaldehyde;" in: US Patent 4072717; 07 February, 1978. Note: Original patent lodged in Germany (2442231).
 20. Jack P. HOLMAN; Heat Transfer, 7th edition, in SI units; McGraw-Hill; London; 1990.
 21. Ernest HOLMES; Handbook of Industrial Pipework Engineering; McGraw-Hill; London; 1973.
 22. Peter E. LILEY, Robert C. REID and Evan BUCK; "Physical and Chemical Data;" in: Robert Howard PERRY and Don W. GREEN (Ed's); Perry's Chemical Engineers' Handbook, 6th edition; McGraw-Hill; New York; 1984.
 23. Arthur MORLEY; Strength of Materials, 11th edition; Longmans, Green and Co.; London; 1955.⁵⁴
 24. John McMURRY; Organic Chemistry, 3rd edition; Brooks/Cole; Pacific Drive, California; 1992.
 25. W. Erich OLBRICH; CHE3117 Lecture Notes; Monash University; Melbourne; 1998.
 26. W. Erich OLBRICH; CHE4109 Lecture Notes; Monash University; Melbourne; 1999.
 27. Kakusaburo ONDA, Hiroshi TAKEUCHI and Yoshio OKUMOT; "Mass Transfer Coefficients between Gas and Liquid Phases in Packed Columns;" in: –; Journal of Chemical Engineering of Japan; Vol. 1, No. 1, pp. 56–62; 1968.
 28. Robert C. REID, John M. PRAUSNITZ and Bruce E. POLING; The Properties of Gases and Liquids, 4th edition; McGraw-Hill; New York; 1987.
 29. Günther REUSS, Walter DISTELDORF, Otto GRUNDLER and Albrecht HILT; "Formaldehyde" in: Wolfgang GERHARTZ (Exec. Ed.); Ullmann's Encyclopedia of Industrial Chemistry, 5th edition, Vol. A11; VCH; Weinheim; 1988.
 30. Martin J. RHODES; CHE3108 Lecture Materials; Monash University; Melbourne; 1998.
 31. G. F. C. ROGERS and Y. R. MAYHEW ('Arrangers'); Thermodynamic and Transport Properties of Fluids, SI Units, 5th edition; Basil Blackwell; Oxford; 1995.
 32. SHARMA; Private communication; August 1999. He advocated removal to levels under "50ppm."
 33. R. K. SINNOTT; "Chemical Engineering Design," 2nd edition; in: J. F. RICHARDSON and J. M. COULSON; Chemical Engineering, Vol. 6; Butterworth-Heinemann; Oxford; 1997.
 34. Tamarapu SRIDHAR and Sanjay MAHAJANI; CHE4102 Lecture Notes; Monash University; Melbourne; 1999.
 35. Ralph F. STRIGLE Jr. (Norton Chemical Process Products Corporation); Packed Tower Design and Applications – Random and Structured Packings, 2nd edition; Gulf Publishing; Houston; 1994.⁵⁵
 36. [Sulzer Chemtech AG]; Structured Packings for Distillation and Absorption; Sulzer Chemtech AG; Winterthur, Switzerland; [1997?].⁵⁶
 37. Robert Ewald TREYBAL; Mass Transfer Operations, 3rd edition, International edition; McGraw-Hill; Auckland; 1986.
 38. Peter Heinz Theodore UHLHERR; CHE3102 Lecture Notes; Monash University; Melbourne; 1997.
 39. J. Frederic WALKER; Formaldehyde, [American Chemical Society Monograph series], 3rd edition; Reinhold Publishing; New York; 1964.
 40. J. G. M. WINKELMAN and A. A. C. M. BEENACKERS; "Simultaneous Absorption and Desorption with Reversible First-Order Chemical Reaction: Analytical Solution and Negative Enhancement Factors;" in: –; Chemical Engineering Science; Vol. 48, No. 16, pp. 2951–2955; Pergamon Press; Oxford; 1993.
 41. J. G. M. WINKELMAN, H. SIJBRING and A. A. C. M. BEENACKERS; "Modeling and Simulation of Industrial Formaldehyde Absorbers;" in: Liang-Shih FAN *et alii* (Ed's); Chemical Engineering Science, Vol. 47, No. 13/14, The First International Conference on Gas-Liquid and Gas-Liquid-Solid Reactor Engineering [Columbus, Ohio, U.S.A.], Session E: Reactor modeling, dynamics, and control, pp. 3785–3792; Pergamon Press; Oxford; 1992.

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 $2\text{m}\cdot\text{s}^{-1}$ flow of liquid (or a maximum of $1\text{m}\cdot\text{s}^{-1}$ under gravity flow) and $25\text{m}\cdot\text{s}^{-1}$ 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 tapings 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.

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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

1. Australian Standard 1210; SAA Unfired Pressure Vessels Code; 1989²³.
2. James R. FAIR and Richard C. KMETZ; "Formaldehyde" in: John J. McKETTA (Exec. Ed.); Encyclopedia of Chemical Processing and Design; Marcel Dekker; New York; 1985.²⁴
3. David J. BRENNAN; CHE3109 Lecture Materials; Monash University; Melbourne; 1998.
4. Raymond P. GENEREUX, Charles B. MITCHELL, C. Addison HEMPSTEAD and Bruce F. CURRAN; "Transport and Storage of Fluids;" in: Robert Howard PERRY and Don W. GREEN (Ed's); Perry's Chemical Engineers' Handbook, 6th edition; McGraw-Hill Inc.; New York; 1984.
5. H. Robert GERBERICH and George C. SEAMAN; "Formaldehyde" in: Jacqueline I. KROSHWITZ (Exec. Ed.); Kirk-Othmer Encyclopedia of Chemical Technology, 4th edition, Vol. 11; John Wiley & Sons; New York; 1994.
6. Thomas J. GEYER; "Method 301 Validation of Fourier Transform Infrared (FTIR) Spectroscopy for measuring Formaldehyde and Carbonyl Sulfide;" in: –; Proceedings of the 1996 Air & Waste Management Association's 89th Annual Meeting & Exhibition; [AWMA?]; [Nashville]; [June 1996].
7. Thomas J. GEYER; "Performance Specification and Evaluation of Fourier Transform Infrared (FTIR) Continuous Emissions Monitors [CEM's] for measuring Hazardous Air Pollutants [HAP's];" in: –; Pro-

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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- ceedings of the 1996 Air & Waste Management Association's 89th Annual Meeting & Exhibition; [AWMA?]; [Nashville]; [June 1996].
8. Guenter HALBRITTER, Wolfgang MUEHLTHALER, Heinrich SPERBER, Hans DIEM, Christian DUDECK and Gunter LEHMANN (all BASF AG); "Manufacture of formaldehyde;" in: US Patent 4072717; 07 February, 1978. Note: Original patent lodged in Germany (2442231).
 9. Ernest HOLMES; Handbook of Industrial Pipework Engineering; McGraw-Hill; London; 1973.
 10. Mathew JEFFREY; Private communication; August 1999.
 11. Shigeo KIMURA and Kouichi KURATA (both Mitsubishi Gas Chemical Co.); "Process for Recovering Waste Heat from Formaldehyde Product Gas;" in: US Patent 4691060; 01 September, 1987.*
 12. D. R. LAWSON, H. W. BIERMANN, E. C. TUAZON, A. M. WINER, G. I. MACKAY, H. I. SCHIFF, G. L. KOK, P. K. DASGUPTA and K. FUNG; "Formaldehyde measurement methods evaluation and ambient concentrations during the Carbonaceous Species Methods Comparison Study;" in: -; Aerosol Science & Technology; Vol. 12, No. 1, pp. 64-76; -; -; January 1990.
 13. Thomas E. Marlin; Process Control: Designing Processes and Control Systems for Dynamic Performance, International edition; McGraw-Hill; New York; 1995.
 14. John MCMURRY; Organic Chemistry, 3rd edition; Brooks/Cole; Pacific Drive, California; 1992.
 15. Günther REUSS, Walter DISTELDORF, Otto GRUNDLER and Albrecht HILT; "Formaldehyde" in: Wolfgang GERHARTZ (Exec. Ed.); Ullmann's Encyclopedia of Industrial Chemistry, 5th edition, Vol. A11; VCH; Weinheim; 1988.
 16. Dale E. SEBORG, Thomas F. EDGAR and Duncan A. MELLICHAMP; Process Dynamics and Control; John Wiley & Sons; New York; 1989.
 17. R. K. SINNOTT; "Chemical Engineering Design," 2nd edition; in: J. F. RICHARDSON and J. M. COULSON; Chemical Engineering, Vol. 6; Butterworth-Heinemann; Oxford; 1997.
 18. Trevor J. SWEENEY; "Technical Safety;" in: John R. G. ANDREWS (Co-ord.); CHE4115 Lecture Materials; Monash University; Melbourne; 1998.
 19. J. Frederic WALKER; Formaldehyde, [American Chemical Society Monograph series], 3rd edition; Rheinhold Publishing; New York; 1964.
 20. T. C. WHERRY, Jerry R. PEEBLES, Patrick M. MCNEESE, Philip O. TETER Jr., Richard E. WORSHAM and Roy M. YOUNG; "Process Control;" in: Robert Howard PERRY and Don W. GREEN (Ed's); Perry's Chemical Engineers' Handbook, 6th edition; McGraw-Hill Inc.; New York; 1984.

* Thanks to Mr. Phonse Everard for this reference.

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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 $\$500 \times 10^6$) 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

1. Günther REUSS, Walter DISTELDORF, Otto GRUNDLER and Albrecht HILT; "Formaldehyde" in: Wolfgang GERHARTZ (Exec. Ed.); Ullmann's Encyclopedia of Industrial Chemistry, 5th edition, Vol. A11; VCH; Weinheim; 1988.
2. R. K. SINNOTT; "Chemical Engineering Design," 2nd edition; in: J. F. RICHARDSON and J. M. COULSON; Chemical Engineering, Vol. 6; Butterworth-Heinemann; Oxford; 1997.
3. Trevor J. SWEENEY; "Technical Safety;" in: John R. G. ANDREWS (Co-ord.); CHE4115 Lecture Materials; Monash University; Melbourne; 1998.

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.

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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.

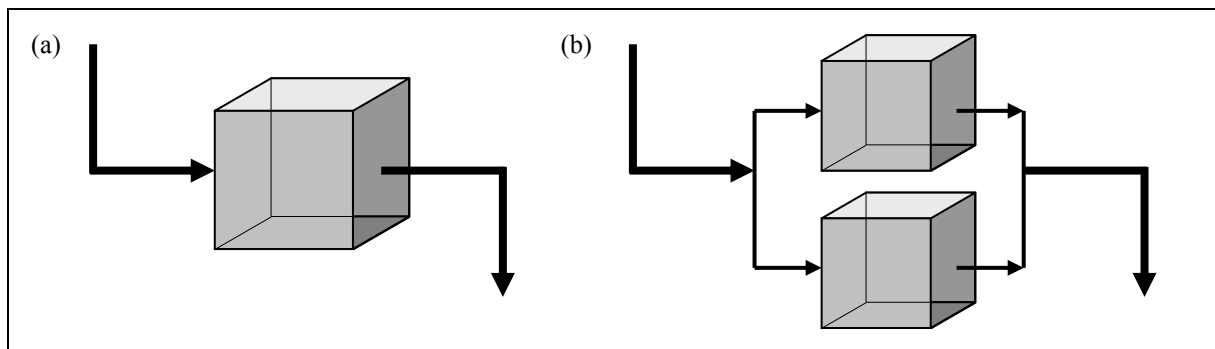


Figure 10-1: Schematic showing (a) single streaming and (b) parallel streaming of a single process.

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 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].

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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.

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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.

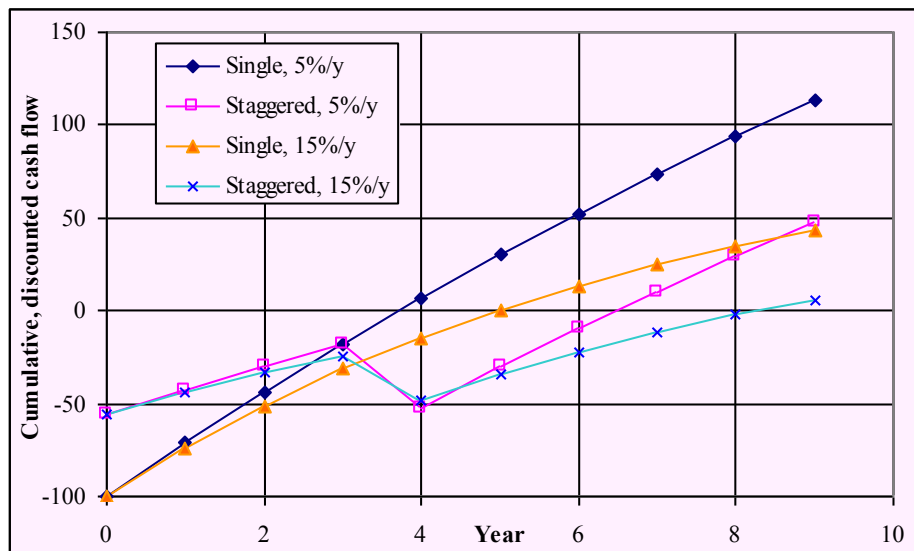


Figure 10-2: The effect of discount rate on the two investment strategies.

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).

Chapter 10: Parallel Streaming**FORMALDEHYDE**

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

1. David J. Brennan; Process Industry Economics: An International Perspective; Institution of Chemical Engineers; Rugby; 1998.
2. Hans DIEM, Guenther MATTHIAS, Albrecht AICHER, Hans HAAS, Hans SCHREIBER and Heinrich SPERBER (all BASF AG); “Production of Formaldehyde;” in: US Patent 3928461; 23 December, 1975. Note: Original patent lodged in Germany (2231248).
3. Donald E. GARRETT; Chemical Engineering Economics; Van Nostrand Reinhold; New York; 1989.
4. Raymond P. GENEREUX, Charles B. MITCHELL, C. Addison HEMPSTEAD and Bruce F. CURRAN; “Transport and Storage of Fluids;” in: Robert Howard PERRY and Don W. GREEN (Ed’s); Perry’s Chemical Engineers’ Handbook, 6th edition; McGraw-Hill Inc.; New York; 1984.
5. H. Robert GERBERICH and George C. SEAMAN; “Formaldehyde” in: Jacqueline I. KROSCHWITZ (Exec. Ed.); Kirk-Othmer Encyclopedia of Chemical Technology, 4th edition, Vol. 11; John Wiley & Sons; New York; 1994.
6. Guenter HALBRITTER, Wolfgang MUEHLHALER, Heinrich SPERBER, Hans DIEM, Christian DUDECK and Gunter LEHMANN (all BASF AG); “Manufacture of formaldehyde;” in: US Patent 4072717; 07 February, 1978. Note: Original patent lodged in Germany (2442231).
7. O. P. KHARBANDA; Process Plant & Equipment Cost Estimation; Sevak Publications; Bombay; 1977.
8. Günther REUSS, Walter DISTELDORF, Otto GRUNDLER and Albrecht HILT; “Formaldehyde” in: Wolfgang GERHARTZ (Exec. Ed.); Ullmann’s Encyclopedia of Industrial Chemistry, 5th edition, Vol. A11; VCH; Weinheim; 1988.
9. R. K. SINNOTT; “Chemical Engineering Design,” 2nd edition; in: J. F. RICHARDSON and J. M. COULSON; Chemical Engineering, Vol. 6; Butterworth-Heinemann; Oxford; 1997.
10. Trevor J. SWEENEY; “Technical Safety;” in: John R. G. ANDREWS (Co-ord.); CHE4115 Lecture Materials; Monash University; Melbourne; 1998.

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 $70\text{m} \times 124\text{m} = 8680\text{m}^2 \equiv 0.868\text{ha}$ [3].¹⁵

The processing plant only occupies $30\text{m} \times 52\text{m} = 1560\text{m}^2 \equiv 0.156\text{ha}$ (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

1. The Castle Group; "Oil, Gas, Plastic and Chemical/Petrochemical Processing;" in: Indonesian Business: The Year in Review; http://www.castleasia.com/yir/Chapter_11.htm. (Accessed August 1999.)
2. Eckhard FIEDLER, Georg GROSSMAN, Burkhard KERSEBOHM, Günter WEISS, Claus WITTE; "Methanol;" in: Barbara ELVERS, Stephen HAWKINS and Gail SCHULZ (Ed's); Ullmann's Encyclopedia of Industrial Chemistry, 5th edition, Vol. A16; VCH; Weinheim; 1990.
3. Don W. GREEN; "Conversion Factors and Miscellaneous Tables;" in: Robert Howard PERRY and Don W. GREEN (Ed's); Perry's Chemical Engineers' Handbook, 6th edition; McGraw-Hill; New York; 1984.
4. Kaltim [East Kalimantan] Industrial Estate; Untitled; <http://www.kie.co.id/tabel.html>. (Accessed 10/08/1999.)
5. J. C. MECKLENBURGH (Chairman); Plant Layout: A Guide to the Layout of Process Plant and Sites; Leonard Hill Books in association with The Institution of Chemical Engineers; Aylesbury, Bucks; 1973.
6. Erich MOSBERGER and coauthors, Lurgi AG [*verbatim*]; "Chemical Plant Design and Construction;" in: Barbara ELVERS, Stephen HAWKINS and Gail SCHULZ (Ed's); Ullmann's Encyclopedia of Industrial Chemistry, 5th edition, Vol. B4; VCH; Weinheim; 1992.
7. R. K. SINNOTT; "Chemical Engineering Design," 2nd edition; in: J. F. RICHARDSON and J. M. COULSON; Chemical Engineering, Vol. 6; Butterworth-Heinemann; Oxford; 1997.
8. Steve WHEELER and Laura ALLEN (Ed's); Monash University Diary/Directory '99; Monash Unicomm; Melbourne; [circa 1999].

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.

Chapter 12: Economic Evaluation**FORMALDEHYDE****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 .

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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.

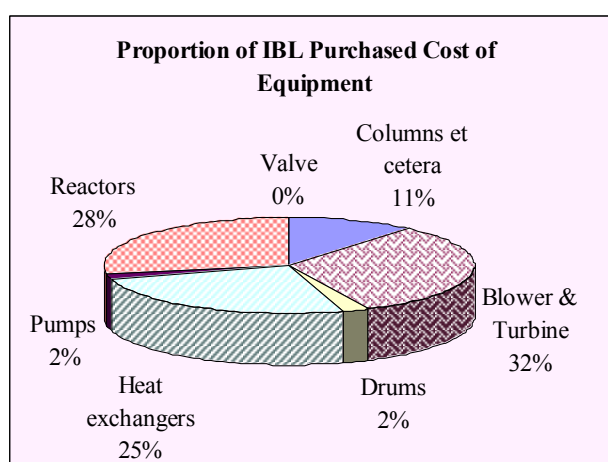


Figure 12-1: The proportion of each IBL purchased cost of equipment (PCE).

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 $1200 \text{kPa}(\text{abs})$ 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.

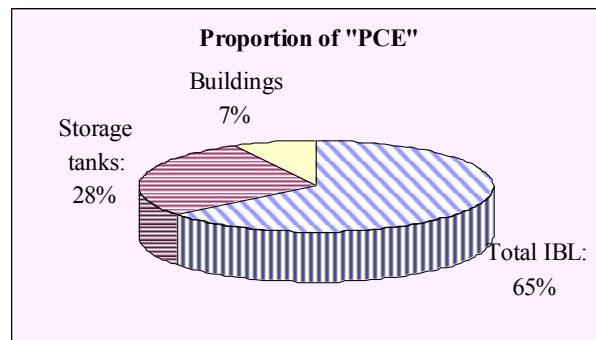


Figure 12-2: The proportion of three purchased costs of equipment (PCE).

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.

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The first thing that springs to ones 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.

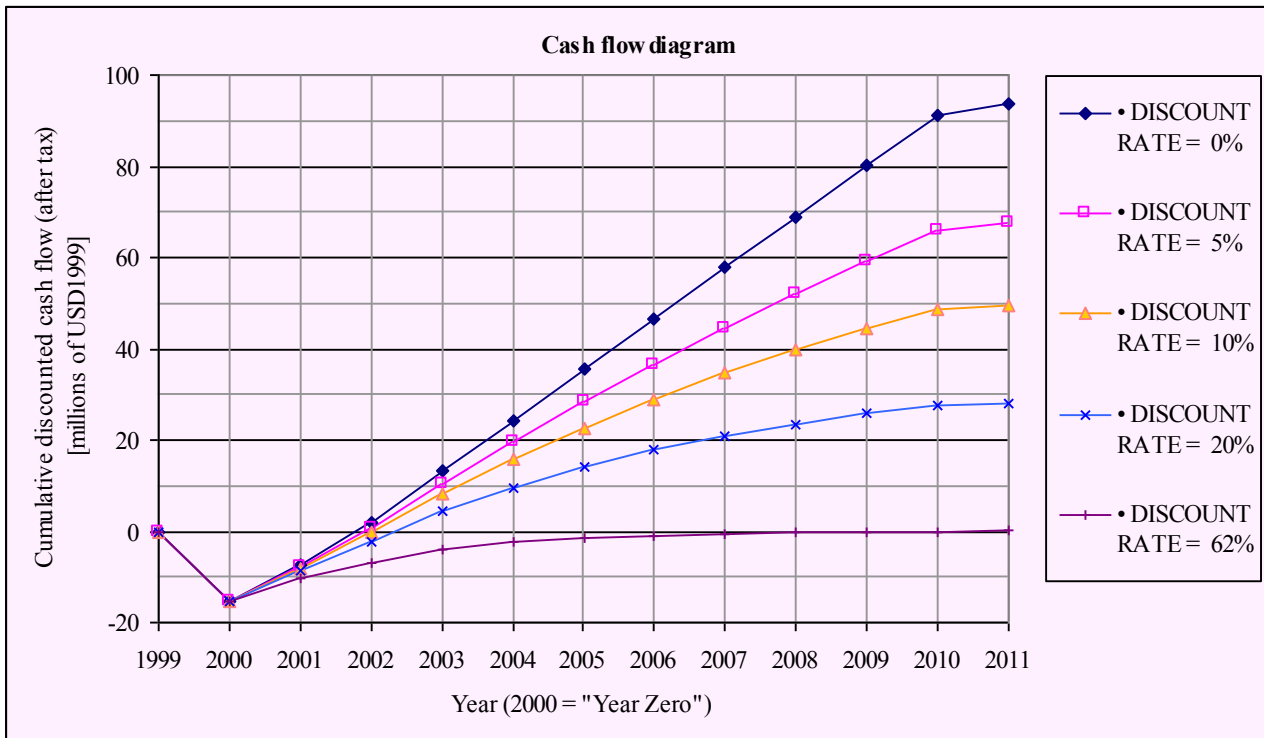


Figure 12-3: Cumulative cash flow diagram (discounted and after tax).

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 $\%.y^{-1}$ 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.

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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 24×10⁶USD₁₉₉₉.y⁻¹ at full capacity utilisation (*i.e.* design flows), with an operating cost of 10.0×10⁶USD₁₉₉₉.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 15.7×10⁶USD₁₉₉₉. 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

1. David J. BRENNAN; CHE4117 Lecture Notes; Monash University; Melbourne; 1999.
2. David J. BRENNAN; Process Industry Economics: An Australian Perspective; Longman Cheshire; Melbourne; 1990.
3. David J. BRENNAN; Process Industry Economics: An International Perspective; Institution of Chemical Engineers; Rugby; 1998.
4. P. L. BREUER and David J. BRENNAN; [Data and Techniques for] Capital Cost Estimation of Process Equipment; The Institution of Engineers, Australia; Melbourne; 1994.
5. "Business;" in: The [Saturday] Age; May to October, 1999.
6. The Castle Group; "Oil, Gas, Plastic and Chemical/Petrochemical Processing;" in: Indonesian Business: The Year in Review; http://www.castleasia.com/yir/Chapter_11.htm. (Accessed August 1999.)
7. Chemical Engineering; McGraw-Hill; New York; July 1999; p. 138.³³
8. Chemical Engineering; McGraw-Hill; New York; August 1999; p. 150.³⁴
9. Chemical Marketing Reporter; "Chemical Profile: Formaldehyde;" in: ChemExpo; <http://www.chemexpo.com/news/PROFile980622.cfm>; 22 June, 1998. (Accessed 07 April, 1999.)
10. Chemical Marketing Reporter; "Chemical Profile: Methanol;" in: ChemExpo; <http://www.chemexpo.com/news/PROFILE980803.cfm>; 03 August, 1998. (Accessed 26 April, 1999.)
11. Donald E. GARRETT; Chemical Engineering Economics; Van Nostrand Reinhold; New York; 1989.
12. H. Robert GERBERICH and George C. SEAMAN; "Formaldehyde" in: Jacqueline I. KROSCWITZ (Exec. Ed.); Kirk-Othmer Encyclopedia of Chemical Technology, 4th edition, Vol. 11; John Wiley & Sons; New York; 1994.
13. Don W. GREEN; "Conversion Factors and Miscellaneous Tables;" in: Robert Howard PERRY and Don W. GREEN (Ed's); Perry's Chemical Engineers' Handbook, 6th edition; McGraw-Hill; New York; 1984.
14. Richard S. HALL, Jay MATLEY and Kenneth J. MCNAUGHTON; "Current costs of process equipment;" in: Chemical Engineering; McGraw-Hill; New York; 05 April 1982; pp. 80–116.³⁵

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.

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15. F. A. HOLLAND, F. A. WATSON and J. K. WILKINSON; "Process Economics;" in: Robert Howard PERRY and Don W. GREEN (Ed's); Perry's Chemical Engineers' Handbook, 6th edition; McGraw-Hill; New York; 1984.
16. Kaltim [East Kalimantan] Industrial Estate; Untitled; <http://www.kie.co.id/tabel.html>. (Accessed 10/08/1999.)
17. O. P. KHARBANDA; Process Plant & Equipment Cost Estimation; Sevak Publications; Bombay; 1977.
18. Günther REUSS, Walter DISTELDORF, Otto GRUNDLER and Albrecht HILT; "Formaldehyde" in: Wolfgang GERHARTZ (Exec. Ed.); Ullmann's Encyclopedia of Industrial Chemistry, 5th edition, Vol. A11; VCH; Weinheim; 1988.
19. R. K. SINNOTT; "Chemical Engineering Design," 2nd edition; in: J. F. RICHARDSON and J. M. COULSON; Chemical Engineering, Vol. 6; Butterworth-Heinemann; Oxford; 1997.
20. Russ SWAN (Ed.); "contract news" [sic!]; in: The Chemical Engineer; Issue 684; The Institution of Chemical Engineers; Rugby; 08 July, 1999; p. 10.
21. Russ SWAN (Ed.); The Chemical Engineer; Issue 685; The Institution of Chemical Engineers; Rugby; 22 July, 1999; pp. 4 ("BASF bounces back") and 11 ("Winning the grand prize").³⁶

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.

