FVO Nr. 3164

Preliminary Plant Design
Chemical Process Technology

Subject

Production of Acetic Acid from Methanol

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Keywords

Acetic Acid, Carbonylation, Homogeneous Catalysis, Methanol, Rhodium Catalyst, Bubble Column

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Summary

In this preliminary plant design the production of acetic acid from methanol and carbon monoxide is studied. An acetic acid plant is designed with a capacity of 100 kton per year located in Rozenburg the Netherlands The purity of the produced acetic acid is 100%, which meets the requirements. The only by-products formed are the water-gas shift products, carbon dioxide and hydrogen.

The process can be divided into four sections. The first section is the reaction section. In this section methanol is carbonylated with carbon monoxide, which is homogeneously catalysed with a rhodium iodide complex. The exothermic carbonylation occurs in a bubble column at low water concentrations. The other three sections are the off-gas treatment section, the catalyst recovery section and the purification section. Carbon monoxide is used in excess amounts, which exit the off-gas treatment, recommendations are done with regard to this excess amount. Both the off-gas treatment section and purification section assure that iodide is kept within the process.

All units in the reaction, catalyst recovery and off-gas treatment section are simulated in Chemcad III.2. Almost all units are calculated and designed.

In this preliminary plant design process control is included. Also a safety, health and environmental analysis is made. If process control is applied well, the process will have no environmental impact. Corrosion prevention is an important aspect, since the process involves iodide components and acetic acid. This is done by the use of Hastelloy C as construction material.

The process is economically evaluated with the characteristic parameters; the return on investment and the internal rate of return. The investments are calculated according to the Lang (67 MHfl) and Taylor (104 MHfl) method. The total costs, based on the Taylor method, are 71 MHfl. The net year profit is 42 Mhfl, with a return on investment of 47% and a internal rate of return 39%. The results of this economical evaluation are positive and indicate a profitable and healthy plant.

Contents

1. Introduction

1.1. Background of the design

The goal of this process-design is the production of 100,000 tons per year of acetic acid from methanol and carbon monoxide, with a purity of at least 99.85 wt%. The process design was performed by four students. It contains a simulation of the process, calculations of the equipment, an economic and an environmental study of the process.

In the Dutch chemical industry acetic acid is used as raw material at a large scale. This acetic acid comes from Germany or Great Britain. Since the raw materials for the production of acetic acid, carbon monoxide and methanol, are available in the Netherlands, it seems very logical to build such a plant in the Netherlands.

1.2. Process

1.2.1. Raw materials

As raw materials carbon monoxide and methanol are used. Methanol is produced in Delfzijl, the Netherlands. Carbon monoxide is produced together with hydrogen as syn-gas. An interesting combination for a plant can be made, together with an ammonia producing plant. Syn-gas can be produced from natural gas and oxygen, which is separated from air. The nitrogen from the same air can be used with hydrogen from the syn-gas for the production of ammonia. The carbon monoxide from the syn-gas can be used in the acetic acid production. Clear is that basically carbon monoxide can be taken from any syn-gas plant.

1.2.2. Processroutes

In the 1960's acetic acid was produced according to the BASF process, which used a cobalt iodide catalyst and operated under very severe conditions (P 100-150 bar and T 180-240 °C). Towards the end of the 1960's at the Monsanto Company in Texas a new process was developed, using a rhodium catalyst with methyl iodide as promoter, and operation under less severe conditions conditions (P 30-60 bar and T 150-230 °C). For this process a 100% yield on methanol was achieved. In the 1990's this process is still considered to be the most effective way of manufactering acetic acid. With the addition of a catalyst stabiliser, it is possible to work at low water concentrations, and reduce the amount of by-products formed.

1.3. Acetic acid

Acetic acid is a colourless corrosive organic liquid, with a sharp odour and a burning taste. It reacts well with oxidation materials and bases with a considerable heat production. It attacks many metals, forming flammable gases. Therefore acetic acid is stored and transported in containers lined with stainless steel, glass or polyethylene [lit.1]. All storage tank vents should be steam traced to prevent plugging by acetic acid crystals, that are formed at 16°C. Also tank cars must be fitted with heating coils. Some more properties are given in appendix A.

Acetic Acid is a raw material for a number of commercial processes. Most is converted to vinyl acetate (49%), used in industrial plastic products and surface coatings, and to

acetic anhydride (9%) and cellulose acetate(16%). Several other end-use applications also exist and are given in figure 1[lit.1].

1.4. Market capacity

The production of acetic acid amounts 5.6 million tons per year in 1993 [lit.20], of which 60% is based on methanol carbonylation using a rhodium catalyst. The demand over the years is shown in table 1.1.

Table 1.1 Acetic acid demand

year	capacity(10^6 tons/yr.)
1977 [lit.15]	2.5
1989 [lit.23]	4.0
1992 [lit.20]	5.0
1993 [lit.20]	5.6

1.5. Environmental and sustainability aspects

Since acetic acid is a very corrosive and biting liquid, care should be taken in handling acetic acid to avoid spillage. Also the vent streams should not contain any acid, this must be removed by scrubbing or chilling. Other waste streams should be neutralised, if they contain acid. In this process design there is only one product stream containing pure acetic acid, and one vent streams that is scrubbed before going out of the process.

The process also contains iodide components, which are highly corrosive and harmful to the environment. Therefore the system should be closed with regard to the iodide components.

Further environmental aspects of the process are discussed in chapter 8.
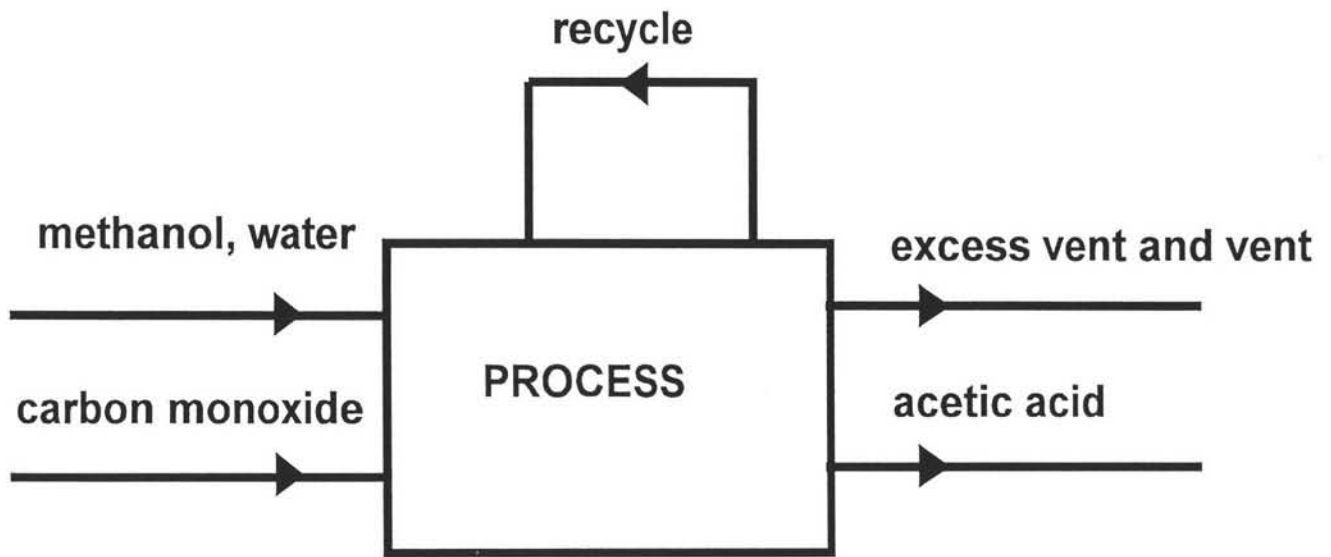
figure 2.1 Input - output structure
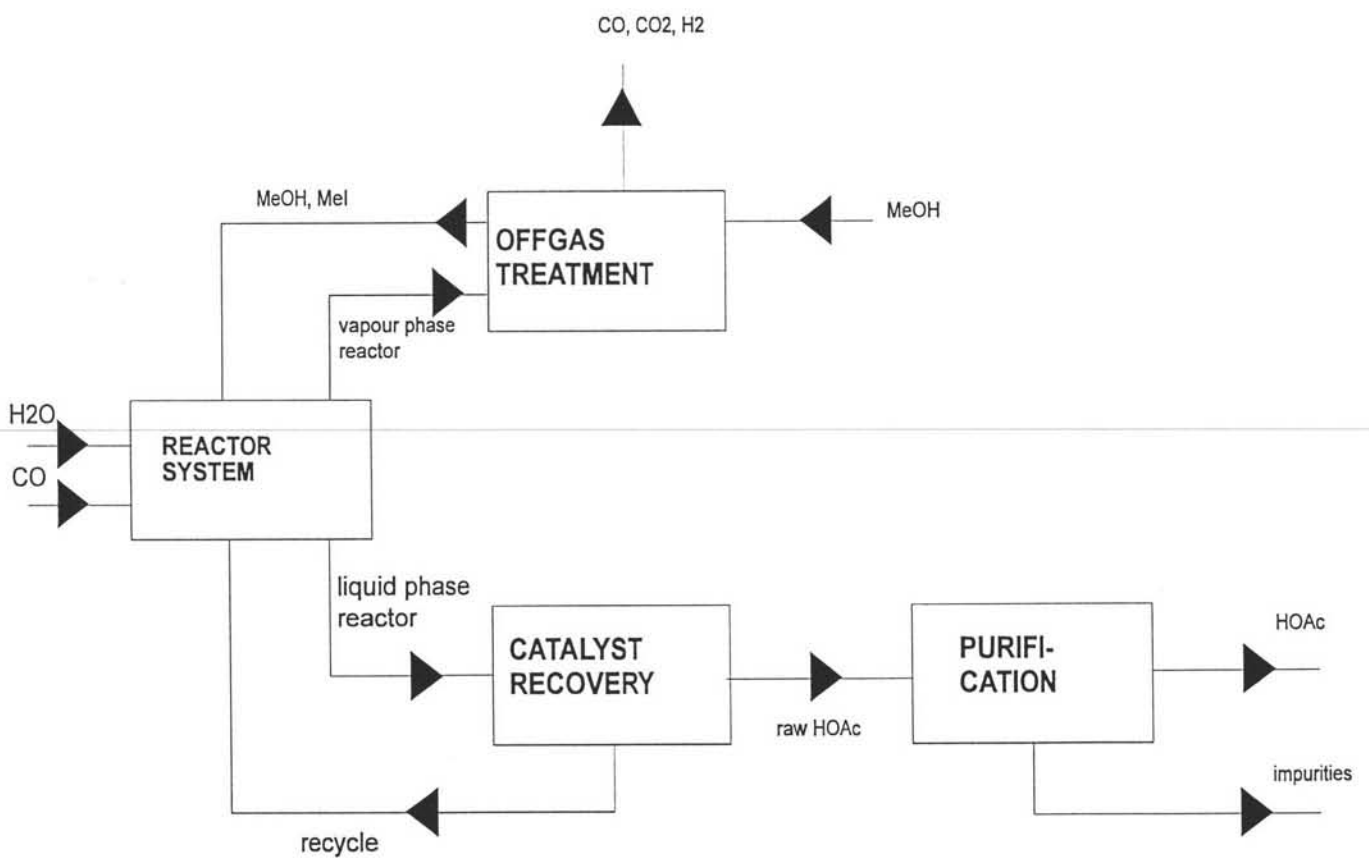
figure 2.2 Block diagram

2. Starting criteria

In this chapter the starting criteria of the design based on the literature studies are described. This chapter will also mark the borders in which this process is designed.

2.1. Choice of the process route

In order to be able to make a choice for the process route for the production of acetic acid from methanol, the guidelines given by Douglas [lit.13] can be used. A detailed description is given in appendix C.

The first decision to be made is whether the process will take place batch-wise or continuous. Douglas [lit.13] gives a few rough guidelines that help indicate whether the process should be performed batch-wise or continuous. In this process the production is more than 4.5 ktons/year, the product is not seasonal, the plant is not a multi-product plant and the reaction time is relatively fast. Therefore a continuous operation has to be chosen for.

Secondly, the input-output structure has to be determined. For this structure, the in- and outgoing streams of the process need to be grouped. For each component entering the process a destination code is determined. In this process, there are two product streams, and two in-going streams. These streams give the input-output structure of the flowsheet, as given in Fig 2.1.

The third decision involves the recycle structure of the process. A few facts are specified before determining the structure. Only one reactor is needed in the process, and one total recycle stream, bringing the reaction intermediates, reversible by-products, catalyst and catalyst stabiliser back to the reactor. An excess of carbon monoxide is supplied to the reactor, and the reactor is operated adiabatically. Clear is that from all units the recycles are brought back to the reactor in one total recycle stream.

The fourth decision is determining the separation system of the process. The vapour recovery system will consist of a flash, after which the gas is being scrubbed in an absorber, to remove all the iodide components from the excess gas (carbon monoxide, carbon dioxide and hydrogen). The liquid recovery system consists of one flash and one distillation column, where the acetic acid product is separated from reaction intermediates and water. Distillation is the least expensive means of separating mixtures.

After all these decisions have been made, a block diagram can be made of the process. Some units have been put together in a block, to make the block diagram clear. The diagram is given in figure 2.2. The process flow scheme given in figure 2.2 has four blocks. The first block is the reactor section, which consists of a reactor, where the carbonylation of methanol is homogeneous catalysed with rhodium complex, and a flash, which separates off-gas from the gaseous reactor liquid. The only side reaction that occurs in minimal amounts is the water-gas shift reaction. The off-gas treatment consists of an absorber, to clean the off-gas. The catalyst recovery system also consists of a flash and a distillation column, where pure acetic acid is removed from the bottom of the column. The purification section consists of two ion exchange resin beds, first one strong cationic exchanger to remove trace quantities of metals, secondly one strong metal exchanged cation exchanger to remove the iodides.

2.2. External specifications

There are given specifications for the raw materials, products and utilities, that are worked with in this process simulation. The specifications are given in the following tables.

Table 2.1 Specifications of the raw materials

Raw material	From	Specifications
Carbon monoxide	Kemira, Rozenburg	100% pure, 30.5 bar, 20 °C
Methanol	Methanor, Delfzijl	100% pure, 1 bar, 20 °C
Demi water	Supplier	100% pure, 7 bar, 20 °C

Table 2.2 Specifications of the products

Product	Specifications
acetic acid	99.85% pure, 1 bar, 20-50 °C
off-gas	CO2/ H2 /CO

Table 2.3 Specifications of the utilities

Utility	Specifications
Steam	MP Steam, 10 bar, 220 °C
Cooling water	1 bar, 20 °C
Electricity	220 V

2.3. Location

Up until now there is no production of acetic acid as an industrial raw material in the Netherlands, although there is a demand for acetic acid, for example for the production of acetic anhydride by Akzo Nobel. There are a few possible locations for the possible production of acetic acid:

Raw materials:
Methanol   Methanor, Delfzijl
Carbon monoxide   Kemira, Rozenburg/ any other syn-gas plant

Clients final product:
Akzo Nobel, Hengelo
Akzo Nobel, Botlek

Harbours:
Delfzijl (KNSI)
Rozenburg (ICI)

Based on the facts above, there are two options for a location, depending on whether the carbon monoxide is produced on the plant itself, or supplied by another manufacturer.

When the theory from Weber [lit. 29] is taken into account for the choice of a location, the following is important. When the mass balance of the process is looked at, it can be concluded that the process deals with "Reinrohstoffe", which means it is favoured placing the plant close to the client of the product. If the condition of the raw materials is looked at, then carbon monoxide shows some problems with transportation, since it is in the gas phase. The easiest way for the transportation of carbon monoxide is by

pipeline, which is quite expensive for long distances. The location is therefore best close to the production of carbon monoxide, unless a transportation net already exists.

Location 1: Rozenburg, supply of carbon monoxide by Kemira
As British Petroleum has shown an interesting combination of the production of acetic acid and acetic anhydride, in Hull, England, with the ammonia plant from Kemira, it seems a good option, placing the acetic acid plant in Rozenburg. Methanol can be supplied from Delfzijl by boat, and carbon monoxide can be supplied from the neighbouring Kemira plant by pipeline. There are ample possibilities for transportation of acetic acid to Hengelo.

Location 2: Delfzijl, production of carbon monoxide on the plant
In this preliminary plant design it is assumed that carbon monoxide is supplied at a pressure of 30.5 bar. The production of syn-gas from natural gas is not very complicated, and good for heat integration in the plant. If location Delfzijl is chosen, then the syn-gas plant can be placed next to the acetic acid plant, and methanol can be transported directly from Methanor. Methanol is a "Reinrohstoffe", and therefore it is easy to place production close to the clients. Both Hengelo and Botlek are easy for transport by waterways.

At this moment, the location in Rozenburg seems most logic, since there already is an existing syn-gas plant, and the transportation of methanol has no problems.

2.4. The catalyst

The production of acetic acid from methanol is a homogeneous catalysed carbonylation of methanol with carbon monoxide. Three catalyst systems are recognised as being capable of giving fast reaction rates for the methanol carbonylation. Halogen promoted cobalt, rhodium and iridium. Rhodium will be used, since the cobalt-catalysed system requires high temperatures and partial pressure of carbon monoxide. The iridium- and rhodium-catalysed systems give comparable high rates at mild conditions, the advantage of rhodium is the insensitivity to hydrogen and a less complicated system than iridium [lit.15]. The required high iridium-methyl complex concentrations result in a production of by-product methane due to hydrogenation of the iridium-carbon bond [lit.20]. The preferred amount of rhodium catalyst is between 4 -5 mol/l [lit.33,43] and 200 - 500 ppm [lit.2].

Iodide is chosen as halogen promoter, since the effectiveness decreases as follows [lit.38]: I > Br > Cl. The replacement of iodide by bromide will result in a major drawback in the carbonylation rate. A large molar excess of methyl iodide promoter over rhodium is required to give commercially viable rates [lit.20]. The preferred amount of promoter, methyl iodide is between 18 - 22 w% [lit.2,42,43].

2.5. The additives

Stability of the rhodium catalyst is sensitive to the reactor composition. The reason for this is the relatively simple transformation of soluble rhodium complexes to insoluble RhI_3 in certain reaction regimes [lit.20].

Water is necessary in the rhodium-catalysed methanol carbonylation in order to attain high reaction rates and maintaining a rhodium-catalyst stability. Though high reaction rates and increased catalyst stability at high water concentrations are attractive, the

separation of the acetic acid from appreciable quantities of water requires substantial expenditure of energy [lit.43]. The separation is difficult because acetic acid forms an azeotrope with water, an azeotropic distillation is involved. The more water there is in the stream the greater will be the operating costs and required capital investment in product recovery-purification system [lit.2].

The desired reaction rates and catalyst stability are obtained at low water concentrations (0.1 - 5 w%) by including in the reaction medium methyl acetate and an additional iodide salt, which is over and above the iodide which is present as a catalyst promoter. The additional iodide is preferably lithium iodide, because of its superior solubility characteristics [lit.42] and good promotional effect on the reaction rate. The presence of the relative volatility suppresser lithium iodide does allow the concentration of water to be controlled to the level necessary to achieve acetic acid product purification with a single distillation column [lit.2]. So methanol carbonylation to acetic acid with catalyst solutions to low water concentrations provide considerable savings and by the addition of lithium iodide and operating at significant concentrations of methyl acetate the same reaction rates are obtained and even better catalyst stability and carbon monoxide selectivity [lit.43].

The high reaction rates are guaranteed by operation at low water concentration by the addition of lithium iodide and operating at significant concentrations of methyl acetate. Rate enhancement by methyl acetate occurs through the reaction with hydrogen iodide (2.1), and through the reaction with lithium iodide to form lithium acetate (2.2).

$$MeOAc + HI \quad \rightarrow \quad MeI + HOAc \qquad\qquad (2.1)$$
$$MeOAc + LiI \quad \rightarrow \quad MeI + LiOAc \qquad\qquad (2.2)$$

Lithium acetate can react with hydrogen iodide to acetic acid or act as promoter for the carbonylation itself (2.3). The rate enhancement is caused by lithium acetate and to a lesser extent by lithium iodide.

$$LiOAc + HI \quad \rightarrow \quad LiI + HOAc \qquad\qquad (2.3)$$

The majority of the promotional effect when lithium iodide is added is due to the formation of lithium acetate rather than lithium iodide. So lithium iodide will promote the carbonylation mainly by its reaction with methyl acetate to produce lithium acetate, which is a more effective promoter. However lithium iodide is very important for maintaining catalyst stability.

Water concentration and carbon monoxide partial pressure are important for maintaining catalyst stability and preventing catalyst precipitation. This due to the fact that water and carbon monoxide help maintain the catalyst as $[RhI_2(CO)_2]^-$ which is very soluble under carbonylation conditions. The rate of RhI_3 precipitation increases as the water concentration decreases. This precipitation is slowed down effectively by the addition of lithium iodide. There is even improved rhodium catalyst stability in the presence of excess iodide. Rhodium catalyst stability is also aided, as mentioned before, by high carbon monoxide partial pressure.

The solvent for the catalyst and catalyst stabiliser, lithium iodide is the product, acetic acid. The reasons for the use of the product as solvent are:
• the high selectivity of carbon monoxide (>90 mol%) and methanol (100 mol%) to acetic acid [lit.12].

- acetic acid as solvent results in zero-order kinetics in the reactants (section 2.8).
- the solubility of carbon monoxide in the liquid phase of the reactor will not be influenced by a higher product concentration, since the product, acetic acid is used as solvent. Another solvent then the product could due to an increase of the product concentration cause a decrease of solubility of carbon monoxide in the liquid phase of the reactor and so cause a decrease in the conversion of carbon monoxide.

The following table shows the preferred weight percentages of lithium iodide, methyl acetate, water and acetic acid in the liquid phase of the reactor [lit.2,42,43].

Table 2.4 Preferred weight percentages of additives in the liquid phase of the reactor

	weight percentage [w%]
lithium iodide	12 - 16
methyl acetate	2 - 4
water	0.1 - 5
acetic acid	50 - 60

2.6. The by-products

The by-products formed during the methanol carbonylation with the high-water method are the products of the water-gas shift and propionic acid, all by-products are formed in small quantities.
An unexpected advantage of operating the reaction system according to the low-water method, described above, is the great reduction in the rate of formation of by-products, propionic acid and water-gas shift products [lit.43]. The yield of water-gas shift products is reduced from approximate 2 to 0.2 mol per 100 mol acetic acid for operation at low instead of high water concentrations. The by-product propionic acid which used to be detected in small quantities (1500 ppm) with operation at high water concentrations is hardly no more detected (90 ppm) with operation at low water method [lit. 42,43].

The extremely short lifetime of any methyl-rhodium species in the catalytic cycle, exclude the possible formation of methane in the presence of hydrogen. Therefore the presence of hydrogen due to impurity of the carbon monoxide feed has no significant influence on the amount of by-products formed during reaction, not even with 50% hydrogen in the feed [lit.15,38].

Considering the above, the production of by-product propionic acid is neglected and the assumed rate of the water-gas shift is 0.002 of the carbonylation rate. Consequently the selectivity of carbon monoxide to the water-gas shift products is 0.002. The selectivity of methanol to acetic acid is 100 mol% [lit.20,33,42,43].

2.7. The reactions

The occurring reactions are:

$$(1-s_{CO})\ CO + (1-s_{CO})\ H_2O \quad \rightarrow (1-s_{CO})\ CO_2 + (1-s_{CO})\ H_2 \qquad (2.4)$$
$$s_{CO}\ CO + s_{CO}\ CH_3OH \quad \rightarrow s_{CO}\ CH_3COOH \qquad (2.5)$$

The overall reaction in the reactor is:

$$(1-s_{CO})\ CO + (1-s_{CO})\ H_2O + s_{CO}\ CH_3OH \rightarrow s_{CO}\ CH_3COOH + (1-s_{CO})\ CO_2 + (1-s_{CO})\ H_2 \qquad (2.6)$$
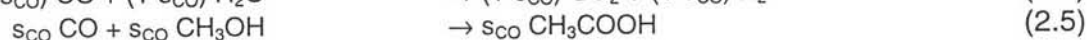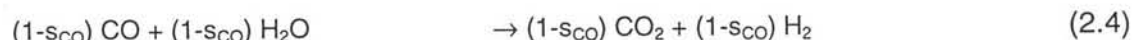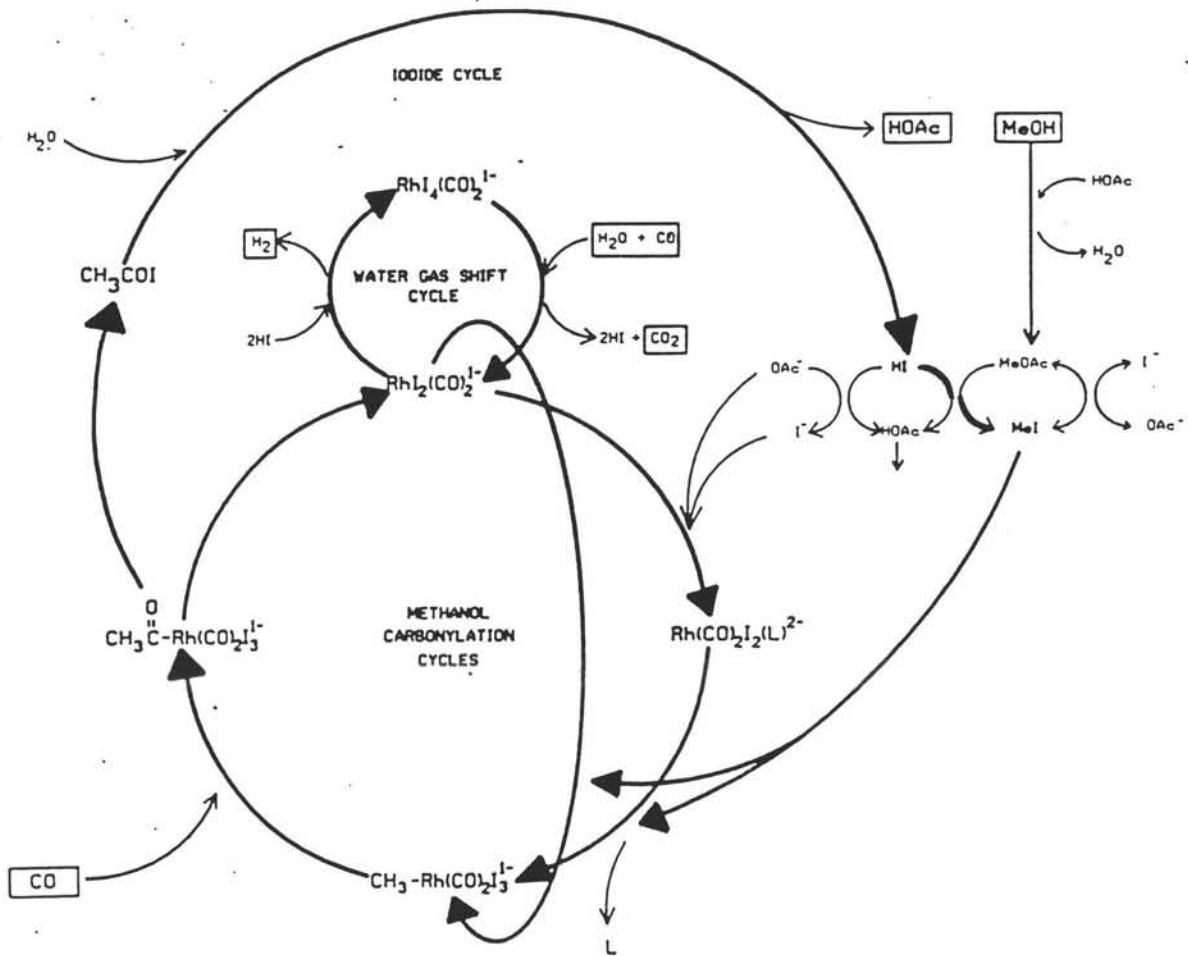
Figure 2.3 The reaction mechanism of methanol carbonylation

As mentioned in the previous section the selectivity of methanol to acetic acid is 1 and the selectivity of carbon monoxide to acetic acid is 0.998 (=1-0.002). Therefore the overall reaction in the reactor is:

$$(1.002)\ CO + 0.002\ H_2O + CH_3OH \quad \rightarrow CH_3COOH + 0.002\ CO_2 + 0.002\ H_2 \qquad (2.7)$$
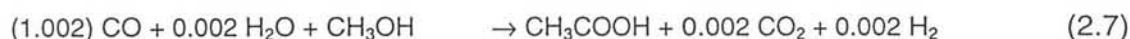
The reaction mechanism of the methanol carbonylation and the water-gas shift are shown in figure 2.3 [lit.43] and is described similar in lit.15, 20 and 43. The methanol fed to the process rapidly esterifies with excess acetic acid. The methyl acetate produced reacts with hydrogen iodide to form methyl iodide. The oxidative addition of methyl iodide to the active catalyst $[Rh(CO)_2I_2]^-$ is the rate determining step in the catalytic cycle. The rhodium(III) methyl complex undergoes rapid methyl migration to form a rhodium(III) acyl species. Reductive elimination of acyl iodide regenerates $[Rh(CO)_2I_2]^-$, and produces acetic acid and hydrogen iodide. Under reaction conditions only $[Rh(CO)_2I_2]^-$ is detected, no iodide hydrogen is detected because of its high reactivity.

2.8. The reaction kinetics

In aqueous media the rate is found to be dependent on carbon monoxide and methanol concentrations. However with respect to carbon monoxide concentration the rate is first order at low partial pressures of carbon monoxide and zero order at high partial pressure (above 3 bar [lit.20]). In acetic acid media the rate shows a zero-order dependence with respect to methanol concentration, while the rate dependence with respect to carbon monoxide partial pressure is similar to that in aqueous media [lit.31]. The addition of hydrogen has no effect the reaction rate [lit.38].

In table 2.5 the reaction kinetics of methanol carbonylation with carbon monoxide in an acetic acid medium and a high partial pressure of carbon monoxide are listed [lit.19,31,38,43].

Table 2.5 The reaction kinetics in acetic acid medium and high CO partial pressures

reaction variables	order
methanol	zero
partial pressure carbon monoxide	zero
methyl iodide	first
Rh complex	first

The reaction rate for the production of acetic acid is given by equation (2.8), according to the above described kinetics.

$$-r = k[CH_3I][Rh-complex] \qquad (2.8)$$

$$k = k_0\ EXP\left(\frac{-E_{act}}{RT}\right) \qquad (2.9)$$

In this equation the reaction rate coefficient, k_0 has a value of 3.5e6 l/mol*s and the activation energy, E_{act} has a value of 61.5 kJ/mol.

As mentioned in section 2.6 the reaction rate of the water-gas shift is 0.002 times the reaction rate of the methanol carbonylation.

2.9. The materials involved in the process

In the following table the most important properties of the materials involved in the process are given.

Table 2.6 Materials involved in the process

Material	Formula	Molecular weight[g/mol]	Melting point [°C]	Boiling point [°C]	Density [kg/l] [20°C]
Hydrogen	H_2	2.0	-259	-253	0.089
Carbon monoxide	CO	28.0	-205	-191	0.001
Carbon dioxide	CO_2	44.0	n.a.	-79	0.001
Methyl iodide	CH_3I	141.9	-66	42	2.279
Methyl acetate	$CH_3CO_2CH_3$	74.1	-98	57	0.934
Water	H_2O	18.0	0	100	1.000
Acetic acid	CH_3COOH	60.1	17	118	1.049
Lithium iodide	LiI	134.0			n.a.
Rhodium catalyst	Rh complex	413.0	n.a.	n.a.	n.a.

2.10. The objectives

- Design, simulation and calculations of the production of 100,000 tons/year acetic acid from methanol.
- Calculations and design of the equipment in the process of the production of acetic acid.
- Safety, health and environmental (SHE) analysis and hazard and operability study of the process.
- Economic analysis of the process: calculations of the investments and the earning capacity, by the parameters; return on investment and internal rate of return of the process.

2.11. The assumptions

- The raw materials methanol and carbon monoxide are 100% pure. In practice impurities will occur. The necessity for pure carbon monoxide is not as high, since the rhodium catalyst is insensitive for hydrogen presence (section 2.6).
- The formation of the by-product propionic acid is zero. Consequently the selectivity of methanol towards acetic acid is 100 mol%. (section 2.6)
- The formation of the water-gas shift products has a reaction rate, which is 0.002 times the rate of the carbonylation. Consequently the selectivity of carbon monoxide to acetic acid is 99.8 mol%. (section 2.6)
- Lithium iodide stays always in solution. Lithium iodide has superior solubility characteristics (section 2.5).
- The rhodium complex always stays in solution. (section 2.5)
- The catalyst loss and deactivation are zero.
- In the Chemcad simulation of the process are:
  ⇒ the rhodium catalyst simulated with estimated values,
  ⇒ the solubility of lithium iodide the same as the solubility of sodium chloride,
  ⇒ methyl iodide infinitely soluble in methanol,

⇒ the Wilson interaction parameter between methyl iodide and acetic acid at reactor conditions the same as the Wilson interaction parameter at 1 bar and 20°C.

- The ion exchange resin beds are not included in the Chemcad simulation.
- In the design calculations of the bubble column reactor the gas phase obeys the ideal gas law.
- In the design calculations of the ion exchange resin beds, an amount of metals and iodides given by literature [lit.21] is taken as maximum value (section 4.2.8).
- For the calculation of the heat balance the heat loss to surroundings in the pipes and equipment are zero.
- The simulation is based upon a steady-state process, so start-up and shutdown are not involved in the simulations.
- For the calculations of the economic analysis, a year is taken as 8000 hours, which is standard in process industry.
- The plant is depreciated in 10 years, which is standard in process industry.

3.   *Process structure and process flowsheet*

With the help of the starting criteria from chapter 2 the process structure is determined and therewith also the process flowsheet. The flowsheet is found in appendix B and described in paragraph 3.2. The process structure consists of four sections; the reaction section, the off-gas treatment section, the catalyst recovery section and the purification section.

3.1. The Process Structure

3.1.1. The Reaction Section

The reaction section exists of a reactor (R3), in which methanol is carbonylated with carbon monoxide to acetic acid, a heat exchanger (H7) and a flash drum (V9). The liquid stream of the flash is cooled (H13), pumped (P21) and recycled to the reactor. The vapour stream of the flash is expanded (E12) before it enters the off-gas treatment section.

3.1.1.1. The reactor

In the reactor the two reactants are added in two different phases. The carbon monoxide enters the reactor as a gas. The reaction phase is the liquid phase, consisting of the recycle fluid (mainly acetic acid, additives and catalyst) and the methanol feed.

Parameters which determine the different regimes and influence the choice of the gas-liquid reactor type, are the Hatta number and α.

The first parameter of importance is Hatta. Hatta is a dimensionless number, which is the ratio of the maximum possible conversion in the film of the bubble and the maximum diffusion transport through the film of the bubble. A value of the Hatta-number << 0.2 [lit.26, page 418] indicates that the reaction rate is in the slow regime. In this case the rate of transport of carbon monoxide in the film will be much larger than the rate of reaction. And therefor no concentration gradient of carbon monoxide in the film will be present.

$$Ha = \sqrt{\frac{t_{diffusion}}{t_{reaction}}} = \frac{\sqrt{kD_{co}}}{k_L} \tag{3.1}$$

In equation (3.1) the mass transfer coefficient k_L is dependent on the reactor type. The typical values for the mass transfer coefficient for different reactor types varies between 0.4e-4 m/s and 20e-4 m/s [lit.6, page 639]. With a first estimation of 5e-9 m²/s for the diffusion coefficient, the value of the Hatta number is regardless the reactor type << 0.2. In this case there will be an excess amount of carbon monoxide in the film of the liquid. This amount will be transported from the film into the bulk liquid phase.

The second parameter of importance is α, which is the ratio between the maximum amount of carbon monoxide supplied by absorption to the liquid and the maximum conversion of this reactant in the liquid. A value for α >>1 implies a larger supply of

carbon monoxide through the specific surface area than possible conversion in the bulk of the liquid. The bulk of the liquid will therefore be saturated with carbon monoxide and the volume of the liquid will have an important influence on the capacity of the reactor, while enlargement of the specific surface area will have no influence on the capacity.

$$\alpha = \frac{t_{reaction}}{t_{mass\_transfer}} = \frac{k_L a}{k} \qquad (3.2)$$

The specific surface area will also be dependent on the reactor type and operation of the reactor. With a value of $k_L a$ between 0.5e-2 s^{-1} and 102e-2 s^{-1} [lit.6, page 639], the value of $\alpha \gg 1$ independent of reactor type and operation.
The resistance of the mass transfer is assumed to be completely in the liquid phase. This assumption is validated, since the reaction rate is in the slow regime and therefore the gas phase resistance will be negligible.

From the above results, for Hatta and α could be concluded that any type of gas-liquid reactor could be chosen. The three most widely used industrial gas-liquid reactors are the packed, mechanically agitated and the sparged reactors. Because the reaction is zero order in the reactants, a stirred reactor has no disadvantage in comparison with a tubular flow reactor with respect to the efficient use of reactor volume. A stirred reactor might therefore be preferred to facilitate rapid heat transfer and good gas-liquid contacting for rapid gas-liquid mass transfer (dissolution of CO into the reactant solution). But chosen is a sparged gas-liquid reactor, the vertical bubble column reactor. The reasons for this choice are the characteristics of a large liquid residence time and a relatively high heat transfer rate in the bubble column reactor. The large liquid residence time is necessary since the reaction rate is in the slow regime (Ha $\ll$ 0.2). A relatively high heat transfer coefficient is preferable since the reaction is strong exothermic. Other advantages of the bubble column are the low cost, the ease of construction, the low maintenance and the absence of moving parts. The absence of moving parts eliminates sealing problems which is important since the operating pressure is high and the vapour phase is toxic (contains iodide components).

3.1.1.2. The operation

As mentioned the reaction kinetics are zero-order and the selectivity of methanol to acetic acid is 1. Therefore an excess amount of methanol to increase the concentration in the reactor, is not necessary, the rate is independent of the concentrations of the reactants. The amount of produced acetic acid is only dependent on the amount of reactants in the reaction phase and not dependent on the concentration of the reactants. Therefore operation without a methanol recycle and at a total conversion of methanol is possible. For total conversion of methanol a finite reactor volume will be required.

3.1.1.3. The catalyst

The catalyst, a rhodium iodide complex, which is dissolved in the liquid phase of the reactor, acts as homogeneous catalyst. Mainly acetic acid and water serve as solvent. Assumed is a catalyst deactivation of zero. Some catalyst losses can be observed. These losses are so called seal losses for example pump seal losses. Rhodium losses due to formation of insoluble RhI_3, is prevented by maintaining a reactor composition

within limits on water, addition of lithium iodide and a minimum carbon monoxide partial pressure (chapter 2).

3.1.1.4. The conditions

The operating pressure is 30 bar. The partial carbon monoxide pressure is 13.9 bar, which is also mentioned and explained before in chapter 2. The partial pressure between 3 and 25 bar [lit.20]. At a partial pressure above the 3 bar the kinetics will be zero-order in carbon monoxide. The operating temperature is 192°C. The steps in the catalytic cycle can all occur under mild conditions. Therefore the use of elevated temperatures (>150°C) is related to increasing efficiency by increasing the reaction rate by use of temperature rather than catalyst level. [lit. 15]

3.1.1.5. The heat control

The reaction in the bubble column is an exothermic reaction. The produced heat has to be distracted from the reactor. In literature [lit.12] several methods are described to distract heat from the reactor.
Cooling of the reactor with a jacket is not preferred since the surface area to volume ratio of the reactor is not favourable for efficient cooling. The amount of heat transfer surface area will not be sufficient despite the high heat transfer in the bubble column.
Cooling with an internal heat exchanger has the disadvantage of the corrosive character of the liquid phase of the reactor.
Therefore the heat will be distracted by adiabatic operation of the reactor.
- The heat of reaction is partly distracted by external cooling of the recycle streams. Potential temperature gradients caused by the addition of a cold recycle stream, are essentially broken down as a result of the high heat transfer coefficient in the liquid and the high effective diffusion (dispersion) of heat.
- The heat of reaction is partly distracted by partial vaporisation of the liquid phase of the reactor, mainly acetic acid and methyl iodide, which is recycled to the reactor after partial condensation and separation of the liquid and gas phase.

3.1.1.6. The flash drum

The vapour stream leaving the reactor is at 30 bar and 192°C. This stream contains mainly of carbon monoxide, methyl iodide and actic acid along with carbon dioxide, hydrogen, water and methyl acetate. First of all this stream is cooled in a heat exchanger to 100°C. This heat exchanger generates middle pressure steam, this steam will be used for heating the feed stream of the flash in the catalyst separation section as mentioned below. The cooled stream is fed to a horizontal flash. The bottom stream of the flash contains methyl iodide, methyl acetate and almost all of the acetic acid. This is the part of the liquid phase vaporised in the reactor distracting the heat of reaction as mentioned above.
This stream is cooled a couple of degrees to avoid cavitation in the following pump. In the pump the pressure is increased to 31 bar and is sent to the recycle stream.
The top stream contains of course carbon monoxide and carbon dioxide, methyl iodide and some traces of acetic acid and methyl acetate. This stream is sent to the gas-liquid absorber.

3.1.1.7. The recycle

The recycle stream to the reactor exists of the liquid stream of the flash drum of the reaction section (V9), the liquid stream of the flash drum (V10) and the top stream of the tower (T14), the last two belong of the catalyst recovery section.

3.1.2. The Catalyst Recovery Section

The catalyst recovery section consists of a flasher and a distillation column. In the flasher the catalyst and the lithium iodide are separated from the product stream. The rest of the product stream flows to the distillation tower. In the distillation tower the acetic acid will be partly separated from the product stream.

3.1.2.1. The flasher section

The incoming stream is at operating conditions of the flash. The flash conditions are 160°C and 3.5 bar. These are the conditions where there is enough acetic acid in the liquid phase to dissolve the lithium iodide and the rhodium catalyst and where enough acetic acid is vaporised to get the desired product stream of acetic acid.
To reach these conditions first of all a expander is used. The stream coming out of the reactor is lowered in pressure from 30 to 3.5 bar. With lowering the pressure, the temperature also decreases. To get the temperature at the flash temperature the stream flows through a heat exchanger and is heated from 150 to160°C. This heat exchanger is fed with middle pressure steam. This middle pressure steam is generated in the heat exchanger cooling the top product of the distillation tower.
The bottom product of the flasher contains mainly the catalyst and lithium iodide dissolved in a part of the product, acetic acid. First this stream is cooled a couple of degrees to avoid cavitation in the pump. Then the pressure is increased to 31 bar. This is a recycle stream and is lead to the reactor. The top product of the flasher contains mainly acetic acid, methyl iodide and water. This stream is sent to the distillation tower T14.

3.1.2.2. The distillation tower

The top stream of the flasher is at 3.5 bar and 160°C. These are also the conditions of the feed tray of the distillation column. The azeotrope which normally appears between water and acetic acid is not observed. It appeared that at these conditions the azeotrope does not exist.
The bottom stream is 3.9 bar and 168.2°C. This stream is almost a pure acetic acid stream. This stream is sent to the ion exchange resin beds for the final purification.
The top product is at 3.3 bar and 131.3°C. This stream consist of methyl iodide, water and acetic acid. This stream is compressed to 31 bar. Afterwards this stream is cooled to liquefy this stream totally, then it can be mixed with the bottom stream of the flash V10. This recycle stream can be sent back to the reactor.

3.1.3. The Off-Gas Treatment Section

In this section the gas phase leaving the reactor is treated. First in the flash (described under the reactor section) a great part of the methyl iodide and almost all of the acetic acid is separated. Then in a gas-liquid scrubber (T20) the off-gas is scrubbed with methanol to remove the rest of the methyl iodide leaving the flasher V9. The treated off-gas will be flared in order not to bring carbon monoxide into atmosphere.

Since the separation of gases like carbon monoxide and carbon dioxide is difficult, in this design, it is decided not to recycle the offgas stream, that still contains a considerable amount of raw material. It is recommended to look into the possible recyle of the carbon monoxide in the future. Currently a lot of research is done on the separation of gases with new membrane technologies [lit.18].

3.1.3.1. The gas-liquid absorber

In gas-liquid absorber the off-gas will be scrubbed with methanol. Methyl iodide is infinitely soluble in acetic acid and methanol [lit. 31]. A completely cleaned off-gas will leave the scrubber. The feed stream is lowered in pressure from 30 to 10 bar. Hence the pressure is lowered, the temperature also decreases. At an operating pressure of 10 bar are optimal conditions. At lower pressures the amount of trays needed, will increase quickly.

The fresh methanol and the off-gas flow countercurrently through the scrubber. The bottom product will be methanol with methyl iodide, methyl acetate and acetic acid dissolved in it. This stream will be cooled some degrees in temperature, also to avoid cavitation in the pump. The pressure is increased to 31 bar and then recycled to the reactor.

The top stream is clean off-gas and contains only carbon monoxide, carbon dioxide and hydrogen. This stream will be reduced in pressure and it will be flared.

3.1.4. The Purification Section

It is known that acetic acid produced by methanol carbonylation with a rhodium iodide catalyst , frequently still contains small amounts of iodide impurities, even after distillation. Such impurities cause a problem when the acetic acid is used in further production, where the catalysts are extremely sensitive to iodide.

3.1.4.1. The resin beds

Several methods are known for removing the iodide impurities. It can be performed by anionic exchange resins [lit. 4], strong metal (silver) exchanged cationic resins [lit 21], and newer inventions describe purification by ozone treatment [lit. 40]. In this process, after the distillation column, the acetic acid product is purified by strong metal exchanged cationic resin beds. These resin beds could not be simulated within Chemcad 3.2, therefore they are designed with a program in Mathcad. In this program a certain amount of metal- and iodide impurities (respectively 1 ppmwt and 5 ppmwt, maximum) is assumed, based on the experiments performed by Jones [lit. 21]. First the acetic acid is put through a strong cation exchanger to remove the metal contaminants. If only one strong metal (silver) exchanged cationic resin bed is used, the silver will be displaced by metal contaminants of the acetic acid, which results in a lowering of the capacity/efficiency of the resin. Secondly, the acetic acid is put through a strong metal-exchanged cationic resin bed, where the iodide impurities are removed. Both beds can be regenerated easily by a regeneration liquid. The regeneration takes approximately 24 hours. The calculations of the design of the beds are given in appendix D7.

3.1.5. The heat integration

All the cooling heat exchangers use river water as ingoing stream. This water is pumped back to the river at a temperature of 40 °C at the most. In two heat

exchangers middle pressure steam is generated from cooling water, that is brought to a pressure of 10 bar, part of the steam is used in the only heating heat exchanger. The rest of the steam can be sold, or used in steam generators to generate electricity. The river water is first filtered before being pumped to the plantsite.

3.2. The Flowsheet

The process flowsheet can be found in appendix B.
The methanol flows from a storage tank to pump P4, where the pressure is increased from 1 to 10 bar. The methanol will flow to the scrubber T20, where it will scrub the off-gases. The methanol will leave the scrubber at the bottom and will be reduced in temperature in heat exchanger H24. This stream will be pumped to 31 bar in pump P25 and will be mixed with the other recycle streams and sent back to the reactor R3. The catalyst and the promoter can be added to the reactor via stream 85. During the operation the catalyst and promoter can be added to replace the losses. Via stream 84 acetic acid can be sent back to the reactor, to keep the solvent concentration at the desired level. In the reactor carbon monoxide will be sparged from the bottom. Here methanol and carbon monoxide will react to acetic acid and some carbon monoxide will react with water to carbon monoxide and hydrogen in gas-water shift reaction, a side-reaction. The off-gas will leave the reactor at the top and will be cooled in heat exchanger H7. In this heat exchanger middle pressure steam will be generated. The gas and liquid phase will be separated in flasher V9. The top product will flow to the scrubber T20 but before it will be fed to the gas absorber, the pressure will be reduced in expander E12. The scrubbed off-gas will be flared.
The bottom product of the reactor, the product stream, will be expanded from 30 to 4 bar in expander E6 and heated from 150 to 160°C in heat exchanger H8. This heat exchanger uses middle pressure steam generated in the heat exchanger H22. This stream will be fed to the flasher V10. The bottom stream contains mainly acetic acid, lithium iodide and catalyst and will be cooled in heat exchanger H15 and be pumped to 31 bar in pump P23. This stream will be mixed with the other recycle streams and will be sent back to the reactor. The top product will flow to the distillation tower T14. The top product of the distillation tower contains acetic acid, methyl iodide and methyl acetate. This stream will be compressed to 31 bar in compressor C19 and then cooled in heat exchanger H22 from 232 to 71°C and mixed with the other recycle streams. The bottom stream leaving the distillation tower contains almost pure acetic acid. This stream is cooled in heat exchanger H26 and then sent to the resin beds R28, R29, R30 and R31 for the final purification. There are two pairs of beds, so that when one pair is operating the other pair is regenerating. The first bed of the two pairs is for the iron removal. The second ones are for the removal of the last traces of methyl iodide.

4.   Process flowsheeting and equipment calculations

In this chapter the methods are given how the equipment and the design are calculated. Detailed calculations for each piece of equipment used are given in appendix D.

4.1 The flowsheet

All the process flowsheet calculations are done with the use of the simulation program Chemcad 3.2. Also the equipment calculations are performed both manually and with help of the equipment sizing option of the simulation program.
In the system, especially in the reactor, high concentrations of salt are present. The presence of a dissolved salt in a mixture of solvents can often significantly change the vapour-liquid equilibrium of the system. In the gas liquid reactor this salt effect can have a major influence. A model describing the vapour liquid equilibrium of a mixture of solvents containing a dissolved salt, is the salt-effect model. The salt-effect model contains two groups of parameters, one set is the same as that defined by Wilson or solvent-solvent interaction in salt free systems and the other set describes the salt solvent interaction which can be easily calculated from the bubble points of the individual solvent components containing the given salt at system pressure.
In this case the following assumptions have been made.
First there is assumed that the solubility of lithium iodide is the same as that of sodium chloride. With this assumption the salt effect data of sodium chloride with acetic acid and with water are a good estimation for the salt effect data of lithium iodide with acetic acid and water.
Secondly the Wilson interaction parameters between methyl iodide and acetic acid have been calculated with a computer program available at the department of thermodynamics because they were not available in the data base of Chemcad. This could only be done at 1 bar and 20 °C, where the process conditions are at 30 bar and 200 °C.
For the absorption of the gaseous methyl iodide from the off-gas stream with methanol, the TSRK model is used, with SRK for the enthalpy calculations. This last mentioned model is especially suitable for methanol systems with light gases.
The Chemcad flowsheet can be found in appendix B.

4.1.1. The reactor

The reactor is simulated with an adiabatic stoechiometric 'REAC' unit, where the conversion and side reactions are given based on methanol, simulated with the stoechiometric coefficients. The only side reaction that takes place is the water-gas shift reaction. The coefficients are based on 100% conversion of methanol and given in table 4.1.

The heat of reaction is calculated by Chemcad and amounts -121.4 kJ/mol acetic acid. Chemcad only knows this type of reactor with one entrance for the reactants, and therefore the feed streams methanol and carbon monoxide and the recycle stream is first mixed in a mixer.

Table 4.1 Stoechiometric coefficients of the reactor

Components	Stoechiometric coefficient
Hydrogen	0.002
Carbon monoxide	-1.002
Carbon dioxide	0.002
Methyl iodide	0.000
Methyl acetate	0.000
Methanol	-1.000
Water	-0.002
Acetic acid	1.000
Rhodium complex	0.000
Lithium iodide	0.000

4.1.2. The flashers

The flashers are simulated as a 'FLAS' unit. Two flashers are used, one for the gas stream and one for the liquid stream out of the reactor. Basically, the flashers are used as gas-liquid separators. The streams from the reactor are first brought to the right temperature and pressure where phase separation can take place. The phase separation in the flashers is based on this incoming temperature and pressure.

4.1.3. The distillation column

The distillation column is simulated as a rigorous inside-out distillation 'TOWR'unit. the number of stages is based on a simulation with a shortcut column, 'SHOR' unit, in Chemcad. The specifications that were used in the simulation are presented in table 4.2.

4.1.4. The gas absorber

The absorber column is simulated as a rigorous inside-out distillation 'TOWR'unit. the amount of stages is based on a calculation method given by Coulson [lit.9] and Perry [lit.35]. This calculation is given in appendix D.2.
Feed methanol is fed to the top of the column, countercurrent with the off-gas stream coming from the bottom. In table 4.2 the specifications are given that were used in the simulation.

Table 4.2 Column specifications

Column	Distillation	Absorber
Condenser type	partial	none
Column pressure drop(bar)	0.6	0.2
No. of stages (theoretical)	46	8
Feed stage	6	1
2nd feed stage	-	8
Topspecification:		
-method	reflux ratio (R/D)	
-value	3.6	
Bottomspecification:		
-method	mole flowrate	
-value	208.4	
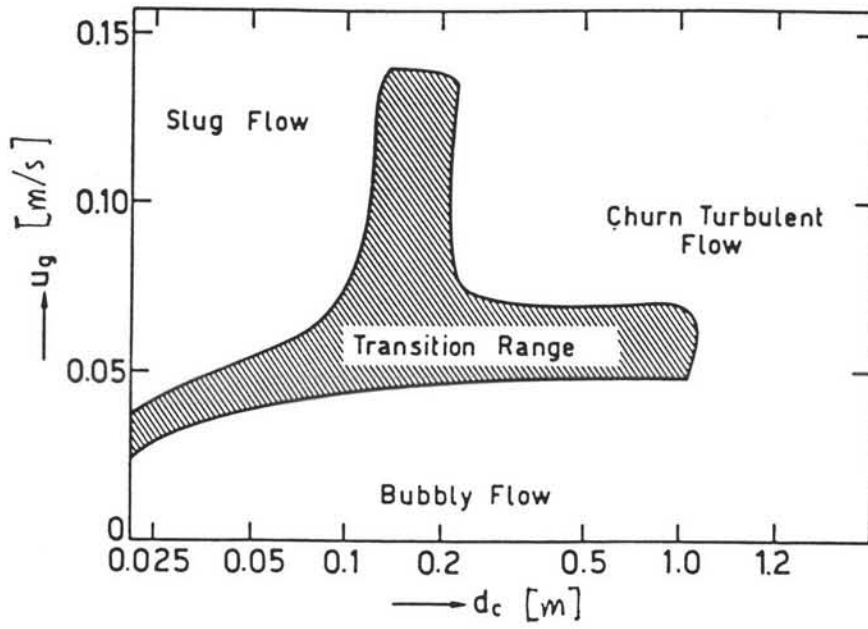
Figure 4.1 Dependency of flow regime on superficial gas velocity and column diameter

4.1.5. The compressors

The compressor is simulated as an adiabatic 'COMP' unit. The outgoing pressure and efficiency (0.75) are specified. The actual power is calculated by Chemcad.

4.1.6. The expanders

The expanders are simulated as adiabatic 'EXPN' units. The outgoing pressure and efficiency (0.75) are specified. The actual power is calculated by Chemcad.

4.1.7. The pumps

The pumps are simulated as adiabatic 'PUMP' units. The outgoing pressure and efficiency (0.75) are specified. The actual power is calculated by Chemcad.

4.1.8. The heat exchangers

The condenser and reboiler from the distillation column are simulated within the 'TOWR' unit. The heat exchangers for cooling and heating the product and recycle streams are simulated as 'HTXR' units. The pressure drop and the outgoing temperature are specified, the heat duty is calculated by Chemcad.

4.2. Equipment calculations

4.2.1. The bubble column reactor

The dimensions of the bubble column reactor are dependent on the gas flow through the column and considerations with regards to the gas hold-up and mass transfer in the bubble column. The gas flow through the column is determined by the amount carbon monoxide required for the acetic acid production and by the desired flow regime in the column.

4.2.1.1. The flow regime

In a bubble column three flow regimes can be distinguished:
- Homogeneous bubble flow regime, characterised by uniform flow of equally sized bubbles; approximately at a superficial gas velocity $U_g < U_{trans}$ (≈ 0.05 m/s).
- Churn turbulent flow, where large and small bubbles are present with different superficial gas velocities leading to an unsteady flow.
- Slug flow, where the bubble occupies the entire column cross section; it occurs with high superficial gas velocities and column diameter $< D_c$ (≈ 0.15 m).

The dependency of the flow regime in the bubble column on the superficial gas velocity, U_g and the column diameter, D, is shown in figure 4.1 [lit.6, page 575].

In the homogeneous bubble flow regime the gas phase behaves as a plug flow and the gas hold-up increases proportionally with the superficial gas velocity. The homogeneous bubble flow will transform to a churn turbulent flow if due to an increase of the superficial gas velocity the gas hold-up increases, so that by coalescence larger bubbles will be formed, which will rise faster through the liquid than the small bubbles. With a further increase of the superficial gas velocity, the volumetric gas fraction in the shape of large, quick rising bubbles will also increase. The difference in shape and

size of the bubbles will lead to an increase of the residence time distribution and back mixing in the gas phase.

Operation of the bubble column on the transition of homogeneous bubble flow and churn turbulent flow is preferred, so the superficial gas velocity will still be small enough to be described as plug flow. The superficial gas velocity will also be high enough to cause good mixing of the liquid phase, and the liquid phase can be described as a continuous stirred tank reactor. The good mixing of the liquid results in a high internal heat transfer coefficient of the liquid phase in the reactor, which will result in the absence of a temperature gradient, so the occurrence of hot-spots in the reactor will be prevented.

For the validations on the description of a plug flow gas phase and the continuous stirred tank reactor model for the liquid phase, the gas and liquid phase Bodenstein numbers are calculated in appendix D.1.4. The Bodenstein number is the ratio between convection and dispersion.
The gas phase Bodenstein number should be > 1 to validate the description of the gas phase flow with plug flow.
The liquid phase Bodenstein number should be ≤ 0.2 to validate the description of the liquid phase as a continuous stirred tank reactor. With liquid phase Bodenstein numbers ≤ 0.2, there is no gradient in concentration or temperature [lit.12, page 332].

4.2.1.2. The superficial gas velocity

For operation on the transition of homogeneous bubble flow and churn turbulent flow, the operating superficial gas velocity is the transition superficial gas velocity. The transition superficial gas velocity is only dependent on physical properties of the gas and liquid phase of the reactor. The gas hold-up for the homogeneous bubble flow increases proportionally to the superficial gas velocity and is also only dependent on physical properties. The physical properties of the gas and liquid phase of the reactor are dependent on the feed and recycle streams and the composition of the reaction mixture. The feed and recycle streams are calculated in appendix D.1.1.

The assumption made on the rate determining step in the bubble column reactor is that the reaction is in the infinitely slow regime compared to diffusion as well as mass transfer. This assumption is validated by the calculation of the Hatta number and α in appendix D.1.4. Hatta and alfa are both dimensionless numbers which give the ratio between the reaction rate and respectively the diffusion and mass transfer rate.

Following is calculated the superficial gas velocity in appendix D.1.2. For the calculation of the superficial gas velocity the gas hold-up has to be determined. A few assumptions are made with regard to the gas hold-up of the bubble column reactor.
First, the gas hold-up is assumed constant through the column, despite the fact that the superficial gas velocity will decrease in the height of the column.
Second, the real gas hold-up will be higher than the calculated gas hold-up due to the presence of electrolytes. The presence of electrolytes will reduce the coalescence rate of the bubbles, which will result in smaller bubbles [lit.47, page 165].
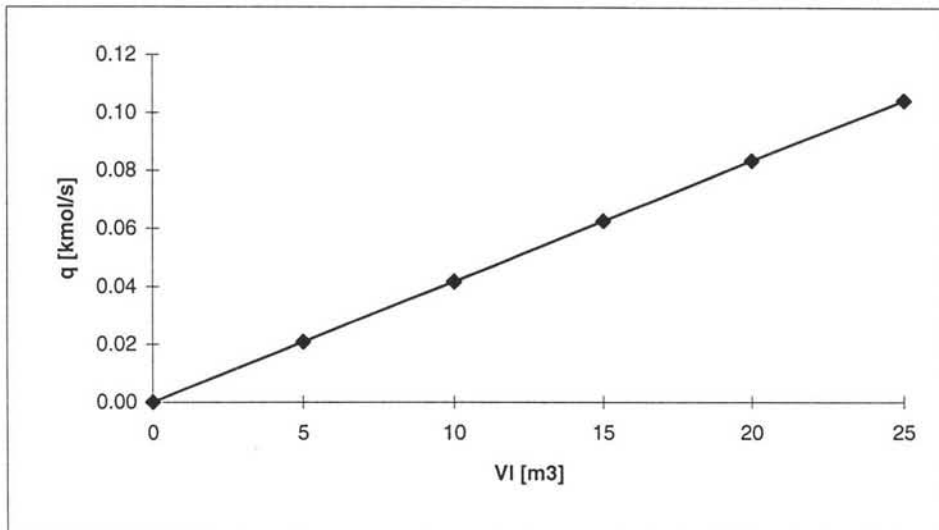
Figure 4.2 The amount of acetic acid produced as a function of the liquid volume of the reactor
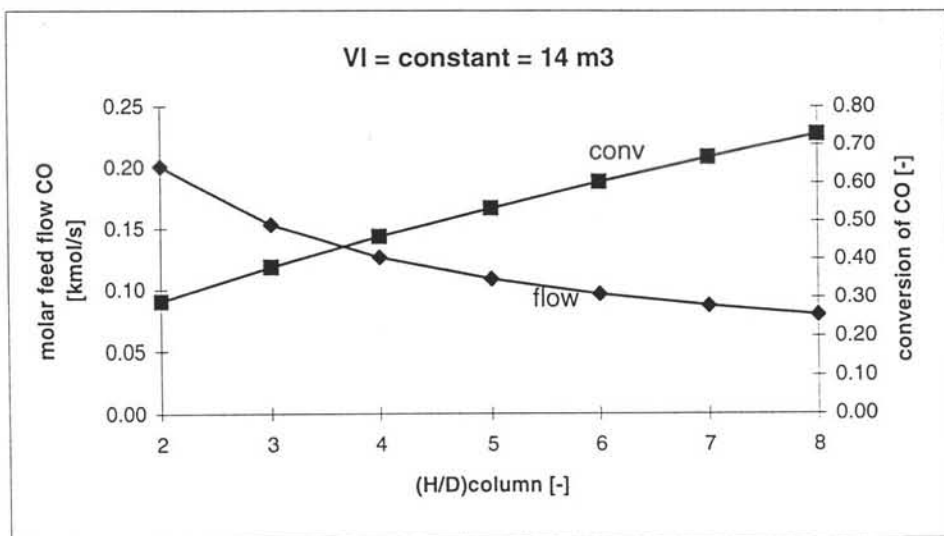
Figure 4.3 The molar feed flow and the conversion of CO as a function of the (H/D)column at a constant liquid volume of the reactor.
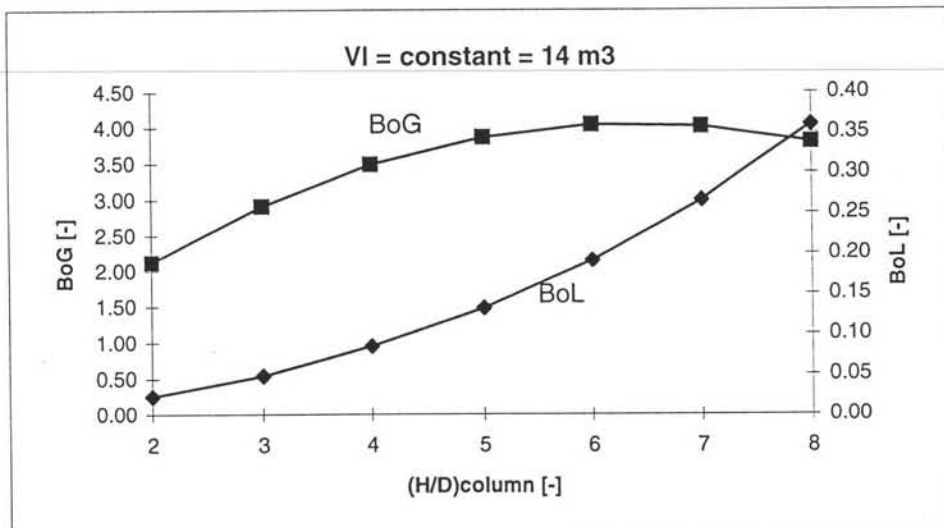
Figure 4.4 The liquid and gas phase Bodenstein number as a function of the (H/D)column at a constant liquid volume of the reactor.

4.2.1.3. The sizing of the bubble column

The size and dimensions of the reactor will be chosen, taking into account the required volume for the production of acetic acid (0.05787 kmol/s) and a few aspects which consider the gas hold-up and the flow regime of the gas and liquid phase in the bubble column.

In figure 4.2 the amount of produced acetic acid, q, is shown as function of the liquid reactor volume, V_l. Figure 4.2 shows that the liquid reactor volume for the production of acetic acid from a total conversion of methanol is within reasonable size. It can be seen that the amount of liquid volume needed for the production of 0.05787 kmol/s acetic acid is around 14 m^3.

The conversion of carbon monoxide and the molar feed flow of carbon monoxide are shown in figure 4.3 as a function of different values of $(H/D)_{column}$, but with a constant liquid volume of 14 m^3. The dependency of the conversion of carbon monoxide and the molar feed flow of carbon monoxide on the $(H/D)_{column}$ is shown in appendix D.1.3. In figure 4.3 the conversion of carbon monoxide to acetic acid increases with an increase of the $(H/D)_{column}$, but the molar feed flow of carbon monoxide decreases with the increase of the $(H/D)_{column}$. Since the liquid volume is constant, the column diameter decreases with increasing $(H/D)_{column}$ ratio. And since the superficial gas velocity is constant, the vapour flow decreases with an increasing $(H/D)_{column}$, which results in a decrease in the column diameter (equation (D.1.6)).
Figure 4.3 shows a preference for a high $(H/D)_{column}$, since an excess molar feed flow of carbon monoxide is preferred to be minimised (high $(H/D)_{column}$ is preferred). But, the excess of carbon monoxide will in practice be necessary to maintain the validation on the flow regime and other considerations for the choice of $(H/D)_{column}$ will have to be taken into account.

The liquid and gas phase Bodenstein numbers are given as a function of the $(H/D)_{column}$ in figure 4.4. The equations for the Bodenstein numbers are given in appendix D.1.4.
As mentioned in section 4.2.1.1, the minimum value of the gas phase Bodenstein number is 1 to validate the description of the gas phase flow with plug flow. Figure 4.4 shows that the gas phase Bodenstein number regardless the chosen $(H/D)_{column}$ validates the description of the gas phase flow with plug flow. As mentioned in section 4.2.1.1, the maximum value of the liquid phase Bodenstein number is 0.2 to validate the description of the liquid phase as a continuous stirred tank reactor. Figure 4.4 shows that the liquid phase Bodenstein number validates the description of the liquid phase flow as CSTR if the $(H/D)_{column}$ is chosen at a value below 6.2.

The other considerations in choice of $(H/D)_{column}$ are [lit.47]:
- The column diameter has to be larger than the critical column diameter, which is usually reported in the literature as close to 0.15 metre, because then the gas hold-up is independent of the column diameter.
- The $(H/D)_{column}$ has to be a minimum of 5 and the height of the column should be at least 3 metres. Otherwise the gas hold-up near the sparger and in the foam region (at top of the column) will influence the overall gas hold-up. Furthermore the gas hold-up could decrease due to a not fully developed liquid circulation pattern. And due to coalescence and bubble break-up, the bubble size distribution will change, which will tend to cause a decrease of the gas hold-up with increasing column diameter. For columns higher than 3 metres and with a $(H/D)_{column}$ above 5 these influences on the gas hold-up will be negligible.

Taking into account the above considerations and the information from figure 4.3 and 4.4 a column with a $(H/D)_{column}$ of 5.8 is chosen. This gives a column diameter, D of 1.75 metre, since the liquid reactor volume is 14 m³. (Appendix D.1.3)

Table 4.3 Bubble column reactor dimensions

D_{column}	[m]	1.75
$(H/D)_{column}$	[-]	5.8
H_{column}	[m]	10.15
V_{column}	[m³]	24.4

4.2.1.4. The heat transfer coefficient

The heat transfer coefficient in the liquid phase of the reactor is given by equation (4.1), [lit.12, page 270]. If for the superficial gas velocity in this equation, the minimal superficial gas velocity is taken, then the calculated coefficient will be the minimal detected heat transfer coefficient in the bubble column, which is at the top of the disperse liquid-gas phase.

$$h = 3.16 \left(\frac{u_g \rho_l g}{\eta_l} \right)^{1/4} \sqrt{\lambda \rho_l c_p} \tag{4.1}$$

The heat transfer coefficient has a high value (1167 W/m²K) conform the characteristics of a bubble column with an ideal mixed liquid phase, which eliminates any temperature gradient in the liquid phase of the reactor.

4.2.1.5. The pressure drop

The pressure drop in the column is given by the following equation [lit.12, page 213]:

$$\Delta P = \rho_l g \varepsilon_l H_{l+g} \tag{4.2}$$

The calculated pressure drop in the bubble column reactor is 0.7 bar.

4.2.1.6. The construction of the bubble column reactor

The material of construction of the bubble column is Hastelloy C, which is part of high alloy group. The high alloys all contain a relatively high percentages of nickel. Hastelloy C is a nickel (54 percent) based alloy containing chromium (15.5 percent), molybdenum (15.5 percent) and iron (5 percent) as major alloying elements. The high chromium content and the addition of molybdenum are responsible for a high corrosion-resistance to oxidising conditions. The molybdenum is also responsible for an improved resistance to pitting. Chromium is the most effective alloying element to give resistance to oxidation.

An approximation on the wall thickness of the reactor is done by the next equation (4.3) [lit.9, page 648]. Equation (4.3) is for the calculation of the minimum thickness, e required for a cylindrical shell to resist internal pressure.

$$e = \frac{P_d D}{2f - P_d}$$

(4.3)

The design pressure, P_d, is taken 10 % above operating pressure, the typical design stress, f, is 120 N/mm^2 at a temperature of 200 °C. With a column diameter of 1.75, the minimum thickness is 23.6 mm. With a corrosion allowance of 2 mm, the wall thickness is taken as a value of 30 mm.

4.2.1.7. The gas distribution

The distribution of the gas feed, carbon monoxide, through the cross section of the reactor is established with a sparger [lit.47].
Porous plate and perforated plate spargers with small hole diameters (<1 mm) lead to the formation of smaller bubbles and thus to a higher gas hold-up and a higher interfacial area. In spite of these advantageous characteristics a sparger with larger hole diameter will be used for a few reasons. First, smaller holes are more sensitive to fouling and give a higher pressure drop over the holes and thus high energy losses. Secondly, the hole diameter of the sparger will only influence the gas hold-up if the bubble column height is < 3 m.
Single nozzle spargers with hole diameters in excess of 2 mm can be used without correction for high pressures on the gas hold-up and will not present the disadvantages mentioned above. Also the sparger design, when the hole diameter is larger than 1-2 mm, has a negligible influence on the gas hold-up.

4.2.2. The flash drums

Appendix D.4 contains the calculation of the flash drums, which is done according to the procedure described in Scheidingsprocessen II [lit.32]. All flash drums are constructed of Hastelloy C, because of the high corrosion resistance.

4.2.2.1. The vertical flash drum

The diameter of the drum is determined by calculation of the maximum gas velocity. The height of the drum consists of three characteristic heights; the height of the liquid level, the distance between the maximum liquid level and the centre of the feed inlet, the height of the drum above the centreline of the feed inlet. The height over diameter ratio should be at least three, with a lower ratio the height is increased arbitrarily to make the ratio 3. If the height over diameter ratio is in excess of 5, then a horizontal flash drum should be used.

4.2.2.2. The horizontal flash drum

Horizontal flash drums are preferred when the feed contains large quantities of liquid. Typical horizontal flash drums are top accumulators. The diameter of the drum is determined by calculation of the maximum gas velocity and the fraction of the drum cross section occupied by the gas phase. The length of the drum is determined by the residence time and the fractional gas cross section. The fraction of the drum cross section occupied by the gas phase is preferred at a value, which will produce a liquid height to diameter ratio of around 0.6, which will give a length to diameter ratio of around 5.

4.2.3. The distillation column

A detailed description of the design of the column can be found in appendix D.2. The distillation column is constructed with Hastelloy C.

4.2.3.1. The trays

The number of trays is determined by using the shortcut column 'SHOR' in Chemcad. Based on this number of trays, calculations have been made. First of all some design calculations have been made with the method mentioned in Coulson & Richardson [lit.9]. This calculation method is for the use for sieve trays. The important criteria for designing trays are flooding, weeping, entrainment and the residence time in the downcomer.

Satisfactory operation will only be achieved over a limited range of vapour and liquid flow rates. The upper limit to vapour flow is set by the condition of flooding. At flooding there is a sharp drop in plate efficiency and increase in pressure drop. Flooding is caused by either the excessive carry-over of liquid to the next plate by entrainment, or by liquid backing-up in the downcomers.
The lower limit of the vapour is set by the condition of weeping. Weeping occurs when the vapour flow is insufficient to maintain a level of liquid on the plate. "Coning" occurs at low liquid rates, and is the term given to the condition where the vapour pushes the liquid back from the holes and jets upward, with poor liquid contact.
In an early stage of the calculation it appeared that weeping would occur when sieve trays would be used. The weeping effect could not be solved by increasing the height of the weir or by changing the hole size.
Another kind of tray had to be used. The decision is made to use valve trays. These kind of trays have the advantage that the valves close at insufficient vapour velocity. In this way weeping cannot occur. The design of these trays is more difficult, so this has been done with the Equipment-Sizing option in chemcad. This design method is described in chemcad III [lit.8].

4.2.3.2. The column height

The column height has been calculated according to a method described in Douglas [lit 13]. The theoretical number of trays, the tray efficiency and the tray spacing are needed to calculate the column height.

4.2.3.3. The shell thickness

The design pressure is taken 10% above operating pressure. A much thicker wall will be needed at the base of the column to withstand the wind and the dead weight. A first trial is to divide the column into three sections. The plate thickness of these sections has been estimated by the thickness of the minimum thickness required for the pressure loading. The design method can be found in Coulson and Richardson [lit 9] and the calculations can be found in appendix D.2.

4.2.4. The gas-absorber column

The number of stages for the column is calculated based on a formula for the vapour-liquid equilibrium K value [lit 32], and on calculations performed by Coulson [lit 9], Perry [lit 35] and Douglas. The gas absorber column is constructed with Hatelloy C.

The valve trays have been used for the absorber column because also here weeping seemed to occur. The gas-absorber column has been calculated in the same way the distillation column is calculated, with the Equipment-Sizing option in chemcad. The calculations and the data of the gas-absorber can be found in appendix D.2.

4.2.5. The compressor

Appendix D.6 contains the calculation of the compressor, which is done according to the procedure described in Perry's [lit.35]. In the design of a centrifugal pump important characteristics are the pumphead, the power of the axis and the energetic efficiency. The compressor is constructed of Hastelloy C, because of the high corrosion resistance.

4.2.6. The pumps

Appendix D.5 contains the calculation of the pumps, which is done according to the procedures described in Pompen en Compressoren [lit.45] and Coulson[lit.9]. In the design of a centrifugal pump important characteristics are the pumphead, the power of the axis and the energetic efficiency. Pumps, P21, P23 and P25 are constructed of Hastelloy C, because of the high corrosion resistance. The other pumps are constructed of mild steel.

4.2.7. The heat exchangers

All heat exchangers are calculated by simulating them with a HTXR-unit within Chemcad. Overall heat transfer coefficients are estimated with fig. 12.1 in Coulson [lit.9]. With the estimated overall heat transfer coefficient , the heat load and temperature difference given by Chemcad, the heat transfer area is calculated. Except for the condenser and reboiler from the distillation tower, the heat exchangers are calculated in appendix D3. The heat exchangers are made of stainless steel, because of the corrosive conditions and streams. The specifications of all the heat exchangers are given in the equipment lists.

The topcondenser and the reboiler from the distillation tower are calculated with the same formula:

$$A = \frac{Q}{U * \Delta T} \tag{4.4}$$

where
A = area   [m^2]
Q = heat load   [J/s]
U = heat transfer coefficient   [W/m^2 K]
ΔT = temperature difference [K]

The heat load is given by Chemcad, the overall heat transfer coefficient is estimated with Coulson [lit.9] and the temperature difference is determined by the condensation and boiling temperature, and the service fluid in the heat exchanger.

In two heat exchangers, H7 and H22, steam is generated. This MP (middle pressure) steam is used as heating fluid for H8. Apart from this one heat exchanger, all other heat exchangers need to be cooled, making heat integration very difficult.

4.2.8. The ion exchange resin beds

The calculations and sizing of the ion exchange resin beds for removing trace amounts of iodide and metals in the acetic acid product is given in appendix D.7. The calculations are based on assumed values of the trace amounts (1 ppmwt metal and 5 ppmwt iodide), given by Jones [lit. 21]. The calculations are based on formulas given by Perry [lit.35] and by Wesselingh [lit. 46] and the capacity of the resin. The resin beds are designed on an operation time of 3000 hours with the above mentioned trace amounts. With given capacity and the number of sites of the resin, the dimensions are calculated. A maximum standard height of a resin bed is 3 metres, which is chosen. The final calculated volume of the two resin beds is 21.2 m^3, with a height and diameter of 3 m.

5. Mass and energy balance

In this chapter the mass and heat streams of the components of the process are described. The overall mass and heat balance is calculated.

5.1 Introduction

With Chemcad the composition and enthalpy of every stream is calculated. Ofcourse this is only done for the streams (1-14, 24-40, 55-82) that are to be found in the Chemcad flowsheet (appendix B). Stream 90 can only be found in the Chemcad flowsheet, it is composed of stream 8 plus stream 35. For stream 15 until 23 the heat load is also calculated by Chemcad, stream 55 is the cooling water before it is pumped to the plantsite, it is taken the same as stream 56. The other streams are the regeneration liquids (41-53) and the catalyst and promoter stream to the reactor (85-86), and the by-pass of acetic acid to the reactor (83-84), for all these streams no mass flow and heat load is given, since they are considered as normally no flow (n.n.f.) streams. The streams are found in appendix E.
The mass and energy balances (appendix E) is only based on the streams calculated by Chemcad. The stream compositions and enthalpies of the streams together with the heat duties of the equipment give the values used for the mass and energy balance. The overall mass and heat balance is calculated and the total in and out streams are equal.

5.2 Methanol and carbon monoxide

Per year 54.4 ktons of methanol is used as a raw material. 100% of this feed is converted into acetic acid. Per year 84.8 ktons of carbon monoxide is used as a raw material.

5.3 Acetic acid

The total production of methanol amounts to 100 ktons per year. The purity is 100%, this is according the specifications of the quality of acetic acid, where the purity should be at least 99.85%

5.4 Catalyst

Since the catalyst used in this process is recycled completely, no catalyst needs to be added. The activity of the catalyst is very high, and does not degrade over the years. There are a few losses of the catalyst over the pumps.

5.5 By-products

Apart from acetic acid there is one side reaction, the water-gas shift reaction. Hydrogen and carbon dioxide are produced, and flared via the offgas stream. The production of hydrogen and carbon dioxide amounts to 5760 kg respectively 146880 kg per year. Also middle pressure steam is generated and 30 ktons is not used and can be sold.

6. Specification of the equipment

After the equipment is designed and calculated in chapter 4, each piece of equipment is specified in equipment lists in appendix F. For each equipment type there is a special equipment list:
- Pumps / Expanders / Compressors
- Heatexchangers
- Reactors / columns / vessels

The codes that are used for the equipment are the same as the codes in the flowsheets in appendix B

Also special specification forms are given in appendix F for reactor R3, pump P21, heat exchanger H15, distillation column T14, and absorber T20.

7.   Process control

7.1. The introduction

The structure of chemical processes has become increasingly complex. As a consequence, the design of control systems for complete plants now constitutes the focal point of engineering interest. The control is made possible by using valves, that are linked to a monitoring system. This monitoring system links the measured variables to the setpoints. By changing the setpoints, it is possible to change the quality and quantity of the product. In designing the control system, the guidelines given by Stephanopoulos are used [lit.44].

7.2. The unit operations

The following units are present in the process:
1. Reactor
2. Horizontal flash
3. Vertical flash
4. Distillation column
5. Absorber
6. Resin beds

For each unit the degrees of freedom are determined, and the control of each unit is looked at.

7.2.1. The reactor R3

There are four degrees of freedom in the reactor. Ofcourse two of these are the temperature and pressure. The temperature is controlled with heat exchanger H24, H22 and H15, they define the temperature of the recycle stream (including the methanol feed). In case the flows to the reactor vary in flow or temperature, there is an extra temperature control on the reactor, that gives the liquid temperature of the reactor. This temperature control is connected to the methanol feed stream, which will be reduced, this will cause a decrease in the heat production. In case of a too high temperature, a shutdown of the process can be performed (see Hazop study of the reactor, appendix G). The pressure is controlled by the incoming recycle stream, and the incoming carbon monoxide stream. The other two degrees of freedom are the flow and the concentration. The flow is controlled by the incoming stream of methanol and carbon monoxide. The concentration is measured in the reactor and is controlled by a valve that is connected to the tanks of catalyst and promoter. In case the concentration of catalyst in the reactor is too low, extra catalyst can be added. The catalyst and the promoter can be added to the reactor via stream 85.
Also there is a bypass, stream 84, of crude acetic acid, leaving the bottom of the distillation column, to the reactor. This is to keep the solvent concentration, acetic acid, in the reactor and especially in the bottom stream of the catalyst recovery flasher V10 at the desired level.

7.2.2. The horizontal flash V9

There are two degrees of freedom for the horizontal flash: the first one is the temperature that is controlled by H7. This heat exchanger also defines second degree

of freedom, the pressure in the horizontal flash. In the flash vessel there is a level controller, regulating the amount of liquid leaving the flash, so a certain amount of liquid in the flash is maintained.

7.2.3. The vertical flash V10

There are two degrees of freedom for the vertical flash: this time the pressure is controlled by expander E6, and heat exchanger H8. The temperature is controlled by heatexchanger H8. Ofcourse this vertical flash also has a level controller.

7.2.4. The distillation column T14

In this column the acetic acid is separated from the recycle stream. In order to get an acetic acid stream that meets the product specifications, the conditions are very strictly controlled. The composition and temperature of the incoming stream are defined by the conditions in flash V10. The temperature of the column is maintained by temperature control in the reboiler. The pressure in the column is controlled by a vlave in the top stream. Two valves will make sure that the liquid level is high enough in the bottom of the column and in top accumulator V18.

7.2.5. The absorber T20

The pressure in the absorber column is controlled by pump P4 of the incoming methanol and expander E12 of the incoming offgas. The temperature is controlled by flash V9. the concentration of the offgas stream is measured, so that in case of emergency immediate actions can be performed.

7.2.6. The resin bed R28, 29, 30, 31

The temperature and the pressure of the crude acetic acid is controlled by heat exchanger H26. Each bed has the same controllers. First of all a level control is present. This is defined by the hazop study (appendix G), to make sure there is no build up of acetic acid in the process. To make sure that the bed is never used too long (this means iron or silver or iodide in the final product), there is a concetration control in the outgoing stream. If the bed is in use, there should be no flow of regeneration liquid and also the valve to the regeneration waste tank should be closed. This is achieved by flow controllers.

7.3. Flare

In case there is an equipment failure, the streams should be led to the flare.

7.4 Start up of the plant

This design is based on a steady-state process. To reach the steady state from the start-up situation, every unit has to be added separately to the process. Until every unit is connected, the "product" should be flared. First the catalyst and other additives together with acetic acid as a solvent are added to the reactor. The carbon monoxide and heated methanol are led to the reactor. Then flash V10 and V9 will be added. the process will first run as a recycle with a purge that is flared. This purge will later be the product. The tower will then be added. Next the gas absorber is installed and there is a product and an offgas stream. The product stream will now be led to the resin beds.

8   Process Safety

In this chapter the process safety is discussed around the central question of risk analysis and management. Risk analysis is used to identify and assess safety, health and environmental risks. Risk refers to a combination of undesired events and effects, and the probability that they occur. Safety risks usually refer to exposures with a high intensity and short exposure times. Environmental risks usually are long-term risks with a low intensity exposure. Health risks usually lie in between. These three terms are discussed below for the production process of acetic acid from methanol.
Risk is a qualitative and a quantative term. Another term this chapter uses is a hazard: an inherent physical or chemical characteristic that has the potential for causing harm to people, property or the environment. This term is essentially a qualitative term. the combination of hazardous material and the operating environment and certain unplanned events can cause an accident.

The following basic factors determine the magnitude of chemical hazards and risks:
- Scale of operations (amounts of materials/size of equipment)
- physical and chemical properties of the materials
- types of operations
- process conditions
- complexity of operations
- age of the plant
- plant layout
- plant siting
- vulnerability of surroundings
- preventive and protective measures taken
- design and operation relative to standards and codes
- special factors (political stability etc.)
- risks of human error
- effectiveness of management in mitigating risk.

8.1 Safety

Safety studies should be undertaken throughout the life of a project. The properties of the materials also need to be considered during the conceptual design. Changes in operating pressures need to be examined, and checked whether they will move into the explosion range. The inventory of any hazardous materials should be minimized, and the operation of special safety systems should be considered.
The total process safety analysis of a process design consists of 5 parts:
1. Identification undesired events
2. Quantification of the results of the undesired events
3. Quantification of the chance on the occurrence of the identified undesired events
4. Quantification of the risk of the industrial activity
5. Risk evaluation

8.1.1 Identification and quantification

Hazard identification is the pinpointing of material, system, process, and plant characteristics that can produce undesirable consequences through the occurrence of

an accident. A few parts of the process need some extra attention, considering the possible occurrence of undesired events:
-the components are very toxic and hazardous (iodides are very toxic)
-the reaction is very exothermic
-the recycle streams are very large, and also contain iodide.
-the components are very explosive in air

In order to identify and quantify the hazards the 'DOW Fire & Explosion Index Hazard Classification' [lit. 14] is used. The results are presented in table 8.1.
Hazards are identified according to a material factor and a process hazard factor. Penalty points are given for certain hazardous aspects of the process and of the materials. Four sections are looked at, and for each the fire and explosion index is calculated. For the calculation of the material factor the average weight composition of the mixture in that section is used. The damage factor and the exposure radius are determined from figure 1 and 2 from appendix G.
A fire & explosion index between 0-20 is light hazardous, 20-60 moderate hazardous, and above 90 extremely hazardous. It is obvious that the reactor section is the most hazardous.

Table 8.1 Factors of the Fire & Explosion index

	reactor	distillation	offgastreatment	purification
material factor	14	12	16	10
unit hazard factor	9.88	5.52	3.28	1.75
F & E index	138.32	66.24	52.48	17.5
damage factor	0.6	0.3	0.41	0.13
exposure radius	35.9 m	17.1 m	13.4 m	4.3 m

8.1.2 Evaluation

Hazard evaluation is the analysis of the significance of hazardous situations associated with a process or activity. A so called HAZOP (hazard and operability) study is a systematic study of all possible occurring undesired events, of the sources and results of these undesired events, and of the necessary actions. This evaluation study [lit. 9 and 5] is done for the reactor system and is presented in appendix G.

8.2 Health

Health risks of a component or process are identified by the toxic properties and the exposure. The total exposure is determined by the exposure level and exposure time.
The basis of toxicity is the interference of a chemical agent with the normal biochemistry of a human. The toxicity is determined by the ability of the agent to penetrate into the organism and the reactivity. To be able to manage toxic risks, there are a few essential concepts:
• Hazard analysis
This comprises of hazard identification, and determination of the exposure-effect relation, which shows the relation between the exposure and the occurring effects.
• Exposure analysis: exploring the location and routes of the emission
• Risk estimation and evaluation
The toxic risk can be evaluated using official norms. A good example of an official norm of the toxicity of components is given by the MAC value. A MAC value is a governmental norm for the maximal acceptable concentration of gases in the air in the

working environment. For the components in this process the MAC values are given in table 8.2.

Table 8.2 MAC-values and explosion limits of the components

component	Explosion lim.(vol% in air)	MAC value (ppm)
hydrogen	4.0-76.0	-
carbon dioxide	n.a.	5000
carbon monoxide	11.0-75.0	25
methylacetate	3.0-16.0	200
methyliodide	n.a.	2
methanol	5.5-36.5	200
water	-	-
acetic acid	4.0-17.0	10
lithium iodide	n.a.	n.a.

As can be seen in the table above, most care should be taken with the components containing iodide and carbon monoxide. Also important are the explosion limits in air. Contact with air should be avoided.

- Risk control
According to the 'ARBOwet'(Dutch law) the following restrictions should be taken to control health risk:
* source restrictions/substitution of components
In this process the most toxic components (the ones containing iodide) cannot be replaced by a catalyst with the same effect. The source of toxic components should therefore be protected well, in a closed system. The equipment is well designed for this.
* ventilation
Although the process system is closed, there should still be a good ventilation.
* exposure limitation
As a third measure the exposure can be limited by keeping distance from the points of emission. This is not an optimal situation, because there will be places where attendance is not always allowed.
* personal protection
This is the last defence line, and is generally used in special situations, e.g. after an accident or while cleaning. In this process employees in these situations should wear skin protection (gloves, safety shoes, glasses etc.) and respiratory protective devices.

8.3. Environment

This process is a closed system and there is no emission during the operation. To be able to look at the implications of the process on the environment, the process outstreams should be monitored. The process flowsheet is given in appendix B. Apart from the pure product stream of acetic acid, there is one gas vent, containing excess carbon monoxide, carbon dioxide, hydrogen and some gaseous methanol. The stream has a temperatur of 20 °C and is at a pressure of 10 bar. The gas should be flared before bringing it out of the process. The most ideal would be to recycle the carbon monoxide to the process, instead of flaring it, since it is raw material of the process. To separate carbon monoxide from carbon dioxide is quite difficult. New technologies are coming up, but at this moment, gas separation is still very expensive. In this project it is recommended that some further research should be put into the recycling of carbon monoxide to the reactor.

9.   Economics

Chemical plants are built to make profit, and an estimate of the investment required and the cost of production are needed before the profitability of a project can be assessed.

9.1. The total investments

The total investment can be subdivided into four groups:

$$I = I_B + I_H + I_L + I_W \tag{9.1}$$

where:

I   = total investments
I_B = investments of the process units
I_H = investment of the side-equipment
I_L = investment of non tangible things
I_w = working capital, stock, cash, ground

The sum of I_B and I_H are called the fixed capital, I_F. The contribution of the four different groups of the total investments are respectively 64, 16, 14, and 6%.[lit.30]

There are two different methods to calculate the investments, one method is the step-method the other one is the factor-method. The investments will be calculated with the Taylor method (step-method) and with the van Lang method (factor-method).

9.1.1. The calculation with the Taylor method

The Taylor method is based on the fact that the investments are a function of the process capacity and the process complexity. This complexity is expressed in a number of important process steps. For every process step a costliness index can be calculated. This index takes into account the extreme temperatures and pressures, kind of construction material, the residence time and the relative conversion of the process step. The sum of these costliness indices give an overall costliness index, which will be used in the following equation:

$$I_B = 93 * P^{0.39} * \frac{C_I}{300} \tag{9.2}$$

where:

I_B = investment of the process units   [$]
f   = overall costliness index   [-]
P   = production capacity   [kton/y]
C_I = cost index (310 in 1978)   [-]

The overall costliness index can be calculated with the next formula:

$$f = \sum_{1}^{N}(1,3)^{S_i} \tag{9.3}$$

where S_i is the score for the complexity of a specific process step. This score can be determined with table III-22 from Montfoort, de Chemische Fabriek, Deel II [lit.30]. Now the investments (I_B) can be calculated in $ for the year 1978. These investments can be converted to the year 1996   by determining the cost-index for the year1996.

Converting to Hfl and to correct for the total investments will give the investment for this process in the year 1996:

I_{Taylor}= 104176.47 kHfl

The calculations with the Taylor method can be found in appendix H

9.1.2. The calculation with the van Lang method

This method is an example of a factor method. This method is based on the fact that the majority (≈2/3) of the investments will be the material investments and the major part (≈1/2) of these investments will be the equipment costs. To calculate the investments the equipment costs have to be determined. By multiplying these costs with the so called "Lang" factor the investments are obtained. The "Lang" factor for gas/liquid processes is 4.74. The investments for this process in 1996 are:

I_{lang}= 66516.42 kHfl

9.2. The costs

The total cost can be subdivided into three groups:

$$K_T = a * K_P + K_I + K_L \qquad (9.4)$$

where:
K_T	= total costs	[Hfl/y]
a	= factor for not calculated production-dependent costs, 1.13	[-]
K_P	= production dependent costs	[Hfl/y]
K_I	= investment related costs	[Hfl/y]
K_L	= labour expense dependent costs	[Hfl/y]

The production dependent costs can be calculated with:

$$K_P = k_p * P \qquad (9.5)$$

where:
k_p	= sum of the raw material and additives costs per ton product	[Hfl/ton]
P	= amount of product per year	[ton/y]

In the calculation of these costs, the utility costs have to be taken into account. (cooling water, electricity and steam)

The investment related costs can be calculated as a fraction of the total investments. The investment calculated with the Taylor method has been taken as the total investment because this method gave the highest investment, and can therefore be seen as a worst case.

$$K_I = f * I \qquad (9.5)$$

where:
f	= Capital Charge	[1/y]
I	= Total investments	[Hfl}

The magnitude of f depends on the depreciation, maintenance and is equal to 0.13.

The labour expense dependent costs can be calculated with the following equation:

$$K_L = d * L \qquad (9.6)$$

where:
d   = factor for not calculated labour expense dependent costs,2.6   [-]
L   = total labour expense   [Hfl/y]

The total labour expense can be calculated with the Wessel relation (lit 16, page II 38).

$$L = 32 * N * C^{0.24} \qquad (9.7)$$

where:
N   = number of steps   [-]
C   = product capacity   [kT/y]

The calculation of the total costs can be found in appendix H. The total income is quite easy to calculate, namely by multiplying the amount of product with its price.

The results of the cost calculation are given in table 9.1.

Table 9.1 Cost calculation of the process

Item	Amount [kHfl/y]
Income	113680.50
K_p	36200.23
K_L	1677.00
K_I	29065.24
K_T	71648.50
Profit	42032.00

9.3. Calculation of the earning-capacity of the process

The earning-capacity of the proces, based on the costs and the income, can be calculated in two ways, namely with the so called Return On Investment (ROI) and the Internal Rate of Return (IRR).

9.3.1. The Return On Investment (ROI)

The ROI can be calculated by dividing the yearly net profit by the investments (I_F and I_W).

$$ROI = \frac{yearly\_net\_profit}{investments} * 100\% \qquad (9.8)$$

De ROI is the expected yearly return on the investments. This method has some disadvantages, because the depreciation of the value of money and the changes of the income and profit in time are not taken into account. To see what the influence of these changes are the ROI is also calculated at a 10% lower income and profit.

Table 9.2 Return on investment calculation

normal situation	47%
profits 10% down	42%
income 10% down	33%

The calculations of the ROI are given in appendix H.

The proces looks very profitable even with a 10% lower income and profit.

9.3.2. The Internal Rate of Return (IRR)

By calculating the net cash flow per year, it is possible to find a interest rate at which the cumulative net present worth at the end of a project is zero. This particular rate is called the Internal Rate of Return (IRR) and is a measure of the maximum rate that the project could pay and still break even by the end of the project life.

$$\sum_{n=0}^{n=t} \frac{NFW}{(1+r)^n} = 0 \qquad\qquad (9.9)$$

where:

r	= Internal Rate of Return	[-]
NFW	= the net cash flow per year	[Hfl]
t	= the life of the project, usually 10 years	[y]

In the year 0 the cash flow is negative and is equal to the amount of investments. In the following years, it is equal to the net profit. In the last year the cash flow is equal to the net profit plus the scrap value (10% of the investments) and the working capital. Usually the life of the project is taken as 10 years.

IRR= 39%

The calculation can be found in appendix H.

The results of the calculations are very positive and this process seems a very profitable one.

10.   Conclusion and Recommendations

In this chapter the objectives of the design made in chapter 2 are evaluated.

10.1   Conclusion

*   The Monsanto process has been the foundation of the design. Some new aspects have been integrated to come to an improved and sustainable process design. The flow diagram presented in chapter 2 has been simulated in ChemCad. The different sections have been split into their individual units. An acetic acid production of 100,000 ton/y has been successfully simulated. ChemCad gave detailed information about the mass and heat flows. And so a good understanding was obtained about the weak and strong sides of the process. The weak sides have been assessed and changed where possible to improve the process design in total.

*   The reactor has been designed and modelled on our own discretion. A bubble column reactor has been chosen and has been designed by minimising the excess amount of carbon monoxide and obey the command of perfect mixing of the liquid. The other equipment have been designed with general design methods. For some of these methods ChemCad has been used but for most of these methods literature like Coulson & Richardson and Douglas have been used. Here some assumptions have been made but the validation of these assumptions have always been checked. In this preliminary design a good inside has been obtained in the sizes and material of construction of the different pieces of equipment.

*   The comprehensive "Safety, Health and Environment" evaluation of the process has been made. The safety has been evaluated with the use of hazard identification according to the "DOW Fire & Explosion Index Hazard Classification". It has been concluded that the reactor is far out the most dangerous unit, because of its high temperature and pressure and its amounts of iodides. A "Hazard and Operability Study (HAZOP)" of the reactor has given the possibility to prevent the occurrence of dangerous situations. From an evaluation of the health aspects it has been showed that methyl iodide is the main concern because of its toxicity. Methyl iodide is present in a closed system, so under normal circumstances there will be no exposure.

*   An economical evaluation of the process has been made. The investments have been calculated with the Taylor method (104.18 MHfl) and with the van Lang method (66.52 MHfl). To calculate the costs the highest investments are used. The total cost has been subdivided in three groups the production dependent costs, the investment related costs and labour expense dependent costs. The total income is the sale of acetic acid and of middle pressure steam. The earning-capacity of the process, based on the costs and the income, has been be calculated in two ways, namely with the so called Return On Investment (ROI) and the Internal Rate of Return (IRR). The ROI and the IRR are respectively 47% and 39 %. The results of the economical evaluation are very positive and the process seems a very healthy and profitable one.

10.2   Recommendations

The excess carbon monoxide is flared in this design. This is not the most ideal situation. Two options should be further investigated to prevent unnecessary flare of the carbon monoxide. In both options the carbon monoxide is recycled. The first option is a situation where the carbon dioxide and hydrogen are separated from the recycle stream. There is a membrane separation technique found, but implementation needs further research. In the second option part of the recycle stream is purged. This option would give a steady-state amount of carbon dioxide and hydrogen in the process. This higher level of hydrogen does not have to influence the reaction selectivity, because of the insensitivity of the catalyst system towards hydrogen. The influence of the higher level of carbon dioxide and the decrease in partial pressure of carbon monoxide has to be further investigated.

For the resin beds, it is recommended that further research is done into the type of regeneration liquid that is needed. Also should be carefully looked at the treatment of the waste streams from the resin beds. Important is the influence of other trace amounts of ions onto the adsorption of the iodide ions. In this design only the influence of iron ions is taken into account.

The British Petroleum Chemicals Hull (GB) manufactures both acetic acid and acetic anhydride in a single reactor, based on the Monsanto process. It offers the flexibility to "swing" the acid-to-anhydride product mix to meet market demand. The flexible acetic acid/anhydride plant (acetyls plant) of BP Chemicals is part of the A5 complex, which includes an carbon monoxide plant, an air separation unit and an ammonia plant. The air separation unit produces oxygen, used by the carbon monoxide plant, and nitrogen used by the ammonia plant. The carbon monoxide plant produces the hydrogen for the ammonia plant and the carbon monoxide for the acetyls plant. Recommended is an evaluation of these concepts for this plant [lit.39].

Symbol	Description	Engineering unit
σ	surface tension	N/m
ζ	contraction factor	-
α	alpha	-
α	relative volatility	-
μ	viscosity	-
ρ	density	kg/m^3
η	efficiency	-
λ	thermal conductivity	W/m K
σ_b	bending stress	N/mm^2
σ_c	critical buckling stress	N/mm^2
ξ_{CO}	conversion of carbon monoxide	-
μ_F	viscosity fluid	cP
ε_g	gas hold-up in column	-
ρ_g	density of gas	kg/m^3
τ_G	residence time of gas phase	s
ρ_G	vapour density	kg/m^3
ϕ_G	fraction drum cross section occupied by gas phase	-
σ_h	pressure stress	N/mm^2
Γ_h	tube loading	kg/m s
η_l	viscosity of liquid	Pas
ρ_l	density of liquid	kg/m^3
ε_l	liquid hold-up	-
τ_L	residence time of liquid phase	s
v_l	kinematic viscosity	m^2/s
σ_L	pressure stress	N/mm^2
μ_l	liquid viscosity	cP
ρ_l	condensate density	kg/m^3
μ_l	condensate viscosity	Ns/m^2
ρ_L	liquid density	kg/m^3
σ_m	maximum compressive stress	N/mm^2
ϕ_m	capacity	kg/s
$\phi_{m, HOAc,out}$	mass flow acetic acid out	kg/s
$\phi_{m,H2O,in}$	mass flow water in	kg/s
$\phi_{m,MeOH,in}$	mass flow methanol in	kg/s
ρ_{MeOH}	density methanol	kg/m^3
ϕ_{mG}	mass flow rate gas phase	kg/s
$\phi_{mol,g}$	gas molar flow	kmol/s
$\phi_{mol,H2O,in}$	molar flow water in	kmol/s
$\phi_{mol,HOAc,out}$	molar flow acetic acid out	kmol/s
$\phi_{mol,MeOH,in}$	molar flow methanol in	kmol/s
ΔP	pressure increase	Pa
ΔP_s	shell side pressure drop	Pa
ΔP_t	pressure drop over tube	Pa
ΔT_{lm}	logarithmic mean temperature difference	°C
ΔT_m	mean temperature difference	°C
ρ_v	vapour density	kg/m^3
ϕ_v	capacity	m^3/s
$\phi_{v, HOAc,out}$	volumetric flow acetic acid out	m^3/s
$\phi_{v,g}$	gas volumetric flow	m^3/s
$\phi_{v,g,in}$	volumetric gas velocity ingoing	m^3/s
$\phi_{v,H2O,in}$	volumetric flow water in	m^3/s
$\phi_{v,l,out}$	volumetric flow liquid out of reactor	m^3/s
$\phi_{v,MeOH,in}$	volumetric flow methanol in	m^3/s
$\phi_{v,recycle,in}$	recycle stream into reactor	m^3/s

Symbol	Description	Units
$\phi_{v,recycle,out,L}$	stream out of the reactor in liquid phase	m^3/s
$\phi_{v,total,in}$	total volumetric flow into reactor	m^3/s
$\phi_{v,total,out,L}$	liquid product flow from reactor	m^3/s
ϕ_{vL}	volumetric liquid flow rate	m^3/s
σ_w	dead weight	N/mm^2
σ_z	resultant longitudinal stress	N/mm^2
a	specific surface area	m^2/m^3
A	antoine constant	-
A	area	m^2
aFe	amount of iron the bed can contain	kg
al	total amount iodide resinbed can contain	kg
AP	acetic acid production	ton/y
APh	acetic acid production	kg/h
as	max. available sites in resin bed	mol
asl	max. amount iodide ions on sites	mol
B	antoine constant	-
Beds	amount of beds /year	-
Bo_G	Bodenstein number gas	-
Bo_L	Bodenstein number liquid	-
BV	bedvolume	m^3
C	antoine constant	-
capvol	capacity per volume	mol/l
capVvol	capacity per bedvolume	mol/l
cp	specific heat	J/kg K
C_{vsep}	capacity coefficient	m/s
D	antoine constant	-
D_c	critical column diameter	m
dcap	dry capacity of resin	mol/kg
D_{CO}	carbon monoxide diffusion coefficent	m^2/s
D_{column}	diameter column	m
d_e	equivalent diameter	m
den	density of liquid	kg/l
d_{hsep}	diameter horizontal flash	m
d_i	inside tube diameter	m
Dia	diameter of the bed	m
d_o	outside tube diameter	m
d_s	sauter mean bubble diameter	m
D_s	diameter shell	m
d_{vsep}	drum diameter	m
E	antoine constat	-
e	minimal thickness	m
E_0	tray efficiency	-
E_{act}	activation energy	kJ/mol
E_g	dispersion coefficient gas	m^2/s
E_l	dispersion coefficient liquid	m^2/s
F	correction factor	-
f	cross sectional area	m^2
f	typical design stress	N/mm^2
Fe	molar weight iron	g/mol
Fe3000	amount of iron bed contains after 3000 hrs	kg
FeH	iron hold up	ppmwt
FeHh	iron hold-up	kg/h
FeHhm	iron hold-up	mol/h
FeIn	iron concentration incoming stream	ppmwt
FeOut	iron concentration outgoing stream	ppmwt
Fes	amount of sites needed	mol
frbed	fraction bedvolume occupied by resin	-
g	gravitational acceleration	m/s^2

G	gas flow	m^3/s
H	pump head	m
H	height resinbed	m
h	heat transfer coefficient	$W/m^2\,K$
Ha	Hatta number	-
H_{ad}	adiabatic head	m
h_c	condensing coefficient	$W/m^2\,°C$
H_{column}	column height	m
h_{extra}	extra height of drum	m
h_{FG}	height of drum above centre of the feed inlet	m
h_i	inside fluid film coefficient	$W/m^2\,°C$
h_{id}	inside dirt coefficient	$W/m^2\,°C$
H_l	column height of liquid mixture	m
h_L	height liquid level	m
H_{l+g}	column height of gas/liquid mixture	m
h_{LF}	distance between max. liq. level and centre of feed inlet	m
h_o	outside fluid film coefficient	$W/m^2\,°C$
h_{od}	ouside dirt coefficient	$W/m^2\,°C$
I	molar weight iodide	g/mol
I2800	amount of iodide after 2800 hours	kg
IH	iodide hold-up	ppmwt
IHh	iodide hold-up	kg/h
IHhm	iodide hold-up	mol/h
Ihk	max. amount iodide	kg/h
Ihm	max amount iodide	mol/h
IIn	iodide conc. incomin stream	ppmwt
IOut	iodide conc. outgoing stream	ppmwt
Is	amount of sites needed	mol
Iwt%	max wt% iodide in acetic acid stream	%wt
j_h	heat transfer factor	-
k	reaction rate constant	$kmol/m^3\,s$
K	distribution coeffcient	-
k	ratio specific heat at constant pressure/constant volume	-
k_0	reaction rate coefficient	l/mol s
K1	equilibrium constant light compound	-
K2	equilibrium constant heavy compound	-
k_{fs}	fluid thermal conductivity	$W/\,m°C$
k_{ft}	fluid thermal conductivity	$w/m^2\,°C$
Ki	vapour liquid equilibrium K value component i	-
k_l	mass transfer coefficient	m^2/s
k_l	condensate thermal conductivity	$W/m\,°C$
k_La	liquid volumetric mass transfer coefficient	1/s
k_w	thermal conductivity tube wall	$W/m\,°C$
L	liquid flow	m^3/s
L	tube length	m
l_b	baffle spacing	m
lcap	capacity of resin	mol/l
l_{hsep}	length horizontal flash	m
l_{vsep}	height flash drum	m
mFe	amount of iron the bed can contain	mol
M_{MeOH}	molar weight methanol	g/mol
N	theoretical number of trays	-
N_p	number of tube side passes	-
NPSH$_{avail,max}$	net positive suction head	m
N_r	average number of tubes in a vertical tube row	
N_t	total number of tubes	-
osFe	resin sites occupied by iron	-

osl	resin sites occupied by one iodide	-
P	pressure	bar
P_{act}	actual work	W
P_{axis}	power for axis	kW
Pc	critical pressure	bar
P_d	design pressure	Pa
Ph	production hours	h/y
Pi	pressure component i	Pa
P_{in}	ingoing pressure	Pa
Pio	pressure component i	bar
por	porosity of resin	l/kg
P_{out}	output pressure	Pa
Pr	Prandtl number	-
Pres	pressure	bar
P_{th}	theoretical work on gas	W
P_{vap}	vapour pressure	Pa
q	amount of acetic acid	kmol/s
Q	heat load	J/s
r	reaction rate	$kmol/m^3\,s$
R	gas constant	kJ/mole K
R	gas constant	J/kg K
Re	reynolds number	-
S	amount of sites in bed	mol
S_{MeOH}	selectivity of methanol to acetic acid	-
Sq	floorsize of the bed	m^2
T	temperature	K
t	storage residence time	s
T	lifetime of the resin bed	h
T_1	inlet temperature hot fluid	°C
t_1	inlet temperature cold fluid	°C
T_2	outlet temperature hot fluid	°C
t_2	outlet temperature cold fluid	°C
Tc	critical temperature	K
TFeHhm	iron hold-up	mol
Tl	min. lifetime bed incase of leakage	h
TlHhm	iodide hold-up	mol
T_{in}	inlet temperature	K
Tr	reduced temperature	-
Tr0	reduced reference temperature	-
TS	tray spacing	m
Tu	time until bed is full	h
U	overall heat transfer coefficient	$W/m^2\,°C$
$U_{g.in}$	superficial gas velocity	m/s
$U_{g.in}$	superficial gas velocity	m/s
U_{gmin}	minimal superficial gas velocity	m/s
u_{hsep}	maximum design vapour velocity horizontal flash	m
U_l	superficial liquid velocity	m/s
u_s	shell side velocity	m/s
U_{sb}	single bell velocity	m/s
u_t	tube side velocity	m/s
U_{trans}	transition superf. gas velocity	m/s
u_{vsep}	maximum design vapour velocity vertical flash	m/s
Vbed	bedvolume	m^3
V_{column}	column volume	m^3
V_l	liquid reaction volume	m^3
V_L	liquid volume	m^3
Vli	liquid volume component i	
Vlio	liquid volume component I at reference temperature	m^3

V_m	molar volume carbon monoxide	m^3/mol
vol	volume of resin plus pores	l/kg
W_c	total condensate flow	kg/s
x	degree of association	-
xin	fraction in liquid in	-
xout	fraction in liquid out	-
yin	fraction in gas in	
yout	fraction in gas out	

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Appendices:

Appendix A   Properties

A.1 Properties of acetic acid

Table A.1. Properties of acetic acid

Property	
Molar weight	60.05300
Critical Temperature, °C	318.800
Critical Pressure, bar	57.8600
Critical volume, m^3/mol	179.7
Melting point, °C	16.6600
Liquid viscosity mPa.s, 25°C	1.1154
Liquid molar volume mol/l	17.3611
Surface tension mN/m, 25°C	27.035
Liquid thermal conductivity W/m-K, 25°C	0.1593
Liquid volume constant cc/mol	7.9681
N. boiling point, °C	117.900
Vapor viscosity mPa.s, 150°C	0.01229
Vapor thermal conductivity W/m-K, 150 °C	0.0203
Vapor pressure bar, 318.8 °C	57.39
Heat of formation kJ/mol	432.8
Gibbs heat of formation kJ/mol, 25°C, ideal gas, atm.pres.	374.6
Heat of vaporization kJ/mol, 16.81 °C	23.412
Solubility parameter	19060 $(J/ m^3)^{0.5}$
Dipole moment C.m	5.8e-30

A.2 Physical properties of the liquid and gas phase of the reactor

general	
temperature [K]	465.36
pressure [bar]	30

liquid phase	
dynamic viscosity [Pa*s]	2.932e-4
molecular weight [kg/kmol]	74.35
surface tension [N/m]	0.0123
specific heat [J/kmol*K]	174715
density [kg/m3]	1108.97
kinematic viscosity [m^2/s]	2.644e-7
thermal condutivity [W/m*K]	0.1216
degree of association [-]	1.7

carbon monoxide	
molair volume [m3/kmol]	0.0013
density [kg/m3]	21.35

concentrations in liquid phase	
Methyl iodide [kmol/m3]	1.84
Rhodium catalyst [kmol/m3]	0.0049

weight percentages in the liquid phase	
Methyl iodide [w%]	23.6
Methyl acetate [w%]	2.7
Water [w%]	1.8
Acetic acid [w%]	55.3
Rhodium catalyst [w%]	0.2
Lithiumiodide [w%]	16.4

Regeneration liquid (iron removal)
Regeneration liquid (iodide removal)

Off gas to flare

Methanol

Water

Cool water

Catalyst and promoter

Carbon Monoxide

Acetic Acid

Acetic Acid

Iodide waste
Iron waste
Water
Water
Water
Water
Water
Water
Steam

P1	PUMP	
P2	PUMP	
R3	BUBBLE REACTOR	
P4	PUMP	
P5	PUMP	
E6	EXPANDER	
H7	COOLER	
H8	HEAT EXCHANGER	
V9	FLASH	

V10	FLASH
E11	CHOKE VALVE
E12	EXPANDER
H13	COOLER
T14	TOWER
H15	COOLER
H16	CONDENSOR
H17	REBOILER
V18	TOP ACCUMULATOR

C19	COMPRESSOR
T20	GAS ABSORBER
P21	PUMP
H22	COOLER
P23	PUMP
H24	COOLER
P25	PUMP
H26	COOLER

R27	RESINBED IRON REMOVAL
R28	2ND BED IRON REMOVAL
R29	RESINBED IODIDE REMOVAL
R30	2ND BED IODIDE REMOVAL
P31	PUMP
P32	PUMP

Production of Acetic Acid from Methanol and Carbon Monoxide

D.J. Lindenbergh

E.C. Smits

M.K. Stegeman

S. van der Waal

FVO nr. 3164

March 1996

stream number   temperature °C   pressure Bar

Regeneration liquid (Iron removal)
Regeneration liquid (Iodide removal)

Methanol

Water

Cool water

Catalyst
and promoter

Carbon Monoxide

Off gas
to flare

Water

Water

Steam

Acetic Acid

Acetic Acid

Iodide waste
Iron waste

Water

Water

Water

Production of Acetic Acid from Methanol and Carbon Monoxide

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FVO nr. 3164

March 1996

P1	PUMP	V10	FLASH	C19 COMPRESSOR
P2	PUMP	E11	CHOKE VALVE	T20 GAS ABSORBER
R3	BUBBLE REACTOR	E12	EXPANDER	P21 PUMP
P4	PUMP	H13	COOLER	H22 COOLER
P5	PUMP	T14	TOWER	P23 PUMP
E6	EXPANDER	H15	COOLER	H24 COOLER
H7	COOLER	H16	CONDENSOR	P25 PUMP
H8	HEAT EXCHANGER	H17	REBOILER	H26 COOLER
V9	FLASH	V18	TOP ACCUMULATOR	

R27 RESINBED IRON REMOVAL
R28 2ND BED IRON REMOVAL
R29 RESINBED IODIDE REMOVAL
R30 2ND BED IODIDE REMOVAL
R31

P31 PUMP
P32 PUMP

stream number   temperature °C   pressure Bar

Production of Acetic Acid

- methanol [1]
- demiwater [38]
- cool water [56]
- CO [8]
- off-gas
- scrubber
- horiz. flas
- water
- water
- steam
- tower
- vert. flash
- reactor
- acetic acid [14]
- water [82]
- water
- water [80]
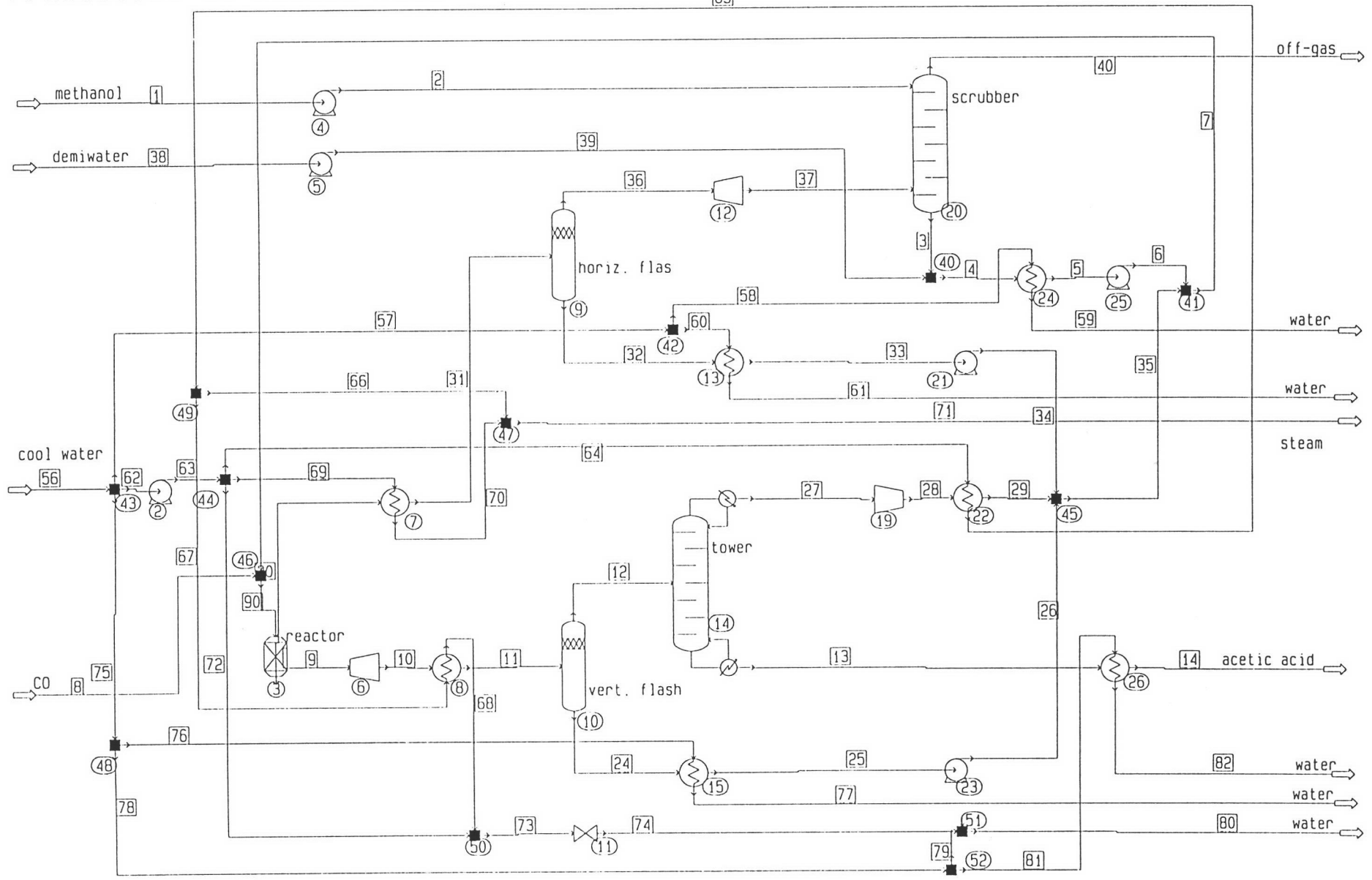
Appendix C   Design guide lines by Douglas

C.1 Conceptual design of chemical processes according to Douglas

The conceptual design and process-flowsheet are being made according to a hierarchical procedure presented by Douglas [lit.13]. The decisions that have to be made are put forward in the following table:

```
1. Batch versus continuous
2. Input-output structure of the flowsheet
3. Recycle structure of the flowsheet
4. General structure of the separation system
        1. Vapour recovery system
        2. Liquid separation system
5. Heat -exchanger network
```

The decisions, made in the process design for the manufacturing of acetic acid from methanol, are explained below, using the table given above.

1. Batch versus continuous
A. Production rates
        100.000 tons/year $\Rightarrow$ continuous
        no multiproduct plant $\Rightarrow$ continuous
B. Market forces
        no seasonal production $\Rightarrow$ continuous
        long product life time $\Rightarrow$ continuous
C. Scale-up problems
        short reaction time (< 0.5 hour) $\Rightarrow$ continuous
        no slurries $\Rightarrow$ continuous
        no rapidly fouling materials $\Rightarrow$ continuous

It is clear that one has to choose for a continuous process for the production of acetic acid from methanol.

2. Input-output structure of the flowsheet
The decisions that have to be made to fix the input-output structure of the flowsheet are discussed below.

1. Purification of the feeds
If the feedstreams have to be purified a pre-process purification system has to be designed. Since the feedstreams in this process contain a negligible amount of impurities no purification step is needed.
2. Recover or recycle reversible by-products
In this process methyl acetate is produced from methanol and acetic acid:

$$CH3OH + CH3COOH \Leftrightarrow CH3COOCH3$$

The methyl acetate is being recycled in order not to lose any valuable product and reactant.

3. *Gas recycle and purge*
Carbon monoxide (CO) in the process is used in excess. The gas is purged, together with the almost negligible amounts of by-products of the water- gas shift reaction. It is recommended to look into possibilities of recycling the carbon monoxide into the process.

4. *Recover and recycle of some reactants*
A design guideline states that 99% of all valuable materials should be recovered. In this process CO is not being recovered.

5. *Number of product streams*
To determine the number of product streams that will leave the process, all components expected to leave the reactor have to be listed as follows:

	Component	Boiling point °C	Destination code
1.	hydrogen	-253	1. vent
2.	carbon monoxide	-191	5. excess vent
3.	carbon dioxide	- 79	1. vent
4.	methyl iodide	42	3. recycle
5.	methyl acetate	57	3. recycle
6.	methanol	65	4. none
7.	water	100	3. recycle
8.	acetic acid	118	7. primary product
9.	lithium salt	-	3. recycle
10.	rhodium catalyst	-	3. recycle

The numbers of the destination codes refer to the numbers used by Douglas for the destinations. The number of the different groups of all but the recycle streams is considered to be the number of product streams.
In this case the following flowsheet is fixed:
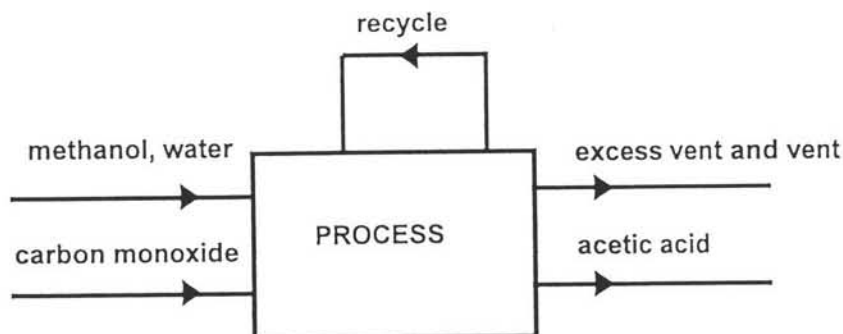
6. *Design variables*
Possible design variables are the reactor conversion, molar ratio of reactants, the amount of reactants not recovered.

3. Recycle structure of the flowsheet
The decisions that fix the recycle structure of the flow sheet are discussed below:
1. *How many reactor systems are required? Is there any separation between the reactor systems?*
One reactor is needed in this process, since the reactions all take place at the same temperature, and the same pressure with the same catalyst.

2. *How many recycle streams are required?*
There is one recycle stream, which recycles the reaction intermediates and reversible products and the catalyst and stabiliser back to the reactor. Gas is not being recycled back to the reactor.
3. *Is an excess of one reactant at the reactor inlet needed?*
An excess of carbon monoxide is supplied to the reactor for mass transfer.
4. *Is a gas compressor required?*
One gas compressor is needed, to bring the gaseous recyclestream containing methyl iodide and methyl acetate, coming from the distillation section, to a pressure of 30 bar.
5. *Should the reactor be operated adiabatically, with direct heating or cooling, or is a diluent or heat carrier required?*
The reactor is operated adiabatically. In order not to make the reactor temperature too high, the incoming feed streams are entered cool, and also the recycle stream is cooled before entering the reactor.
6. *Do we want to shift the equilibrium conversion?*
There is no equilibrium conversion in this process.
7. *How do the reactor costs affect the economic potential?*
The investment costs of the reactor are high, since the reactor should be made out of corrosion resistant material, Hastelloy C.

4. Separation system
To determine the general structure of the separation system, first the phase of the reactor effluent stream must be determined. In this process, there is a gas vent coming out of the reactor, and the main reactor effluent is a liquid. Douglas assumes here that for the main reactor effluent only a liquid separation system is needed, which might include distillation columns. In this process, the liquid effluent is flashed first, after which the vapour, containing the acetic acid, needs to be cooled again, before being brought to the distillation column.
The gas vent is being scrubbed, in order to return any unwanted hazardous materials being vented. This structure is discussed below as the vapour recovery system.

4.1 Vapour recovery system
Two decisions need to be made to synthesise a vapour recovery system.
•What is the best location?
The location to be chosen is on the purge stream, because valuable materials might be lost via that streams (iodide, which is very harmful for the environment).
•What type of vapour recovery system?
An gas absorber needs to be used, which scrubs the gas stream with incoming methanol.

4.2. Liquid recovery system
The decisions that need to be made to synthesise the liquid recovery system are discussed below:
1. *How should light ends be removed if they might contaminate the product?*
There are no light ends in this process. The light ends have already been vented from the reactor and treated with a vapour recovery system.
2. *What should be the destination of the light ends?*
There are no light ends in this process.
3. *Do we recycle components that form azeotropes with the reactants, or do we split the azeotropes?*
Acetic acid forms an azeotrope with water. Therefore a very small amount of water is used in the system, so that distillation is still possible. A large part of the acetic acid will be recycled then, while a smaller part of pure acetic acid will leave the column as the product.

4. *What separations can be made by distillation?*
In general, distillation is the least expensive means of separating mixtures of liquids. However, if the relative volatilities of two components with close boiling points is less than 1.1, distillation will be difficult.
A possible problem in this process is the azeotrope that is formed by water and acetic acid. But since the watercontent is so low (most of the water leaves together with the catalyst, because the iodide salt dissolves best in water), distillation can still be performed to separate acetic acid. Also, the azeotrope is not formed at the pressure and temperature of the colulumn.
5. *What sequence of columns do we use?*
First a flash is used to achieve a phase split, where the heaviest components (catalyst with iodide salt and water) are separated from the rest of the reactor effluent, since they are the most corrosive components. Then a distillation column is used to separate acetic acid from water, methyl acetate and methyl iodide.
6. *How should we accomplish separations if distillation is not feasible?*
After distillation there can still be a trace amount of iodide in the product stream, which is very harmful in further processing of the acetic acid. This trace of iodide is being removed by ion exchange beds.

5. Heat exchanger network
Within the flowsheet the streams to be cooled and the stream to be heated are compared. Heat-integration seems difficult, since far more streams need to be cooled, and only one stream needs to be heated. It seems possible to generate steam in two heat exhangers, that can be used to heat the stream that needs to be heated.

Appendix D.1   Calculation reactor

D.1.1 Feed and product streams of reactor

The required production of acetic acid is 100.000 ton per year, which equals to:

$\phi_{m,HOAc,out}$ $\qquad$ = 3.47 kg/s

The molar and volumetric product flow of acetic acid is equal to:

$\phi_{v,HOAc,out}$ $\qquad$ = 3.31e-3 m³/s

$\phi_{mol,HOAc,out}$ $\qquad$ = 5.78e-2 kmol/s

The amount of acetic acid in the recycle stream is not taken into account. This will be considered separately with the recycle stream. For a total methanol conversion to acetic acid (selectivity, s_{MeOH}, of methanol to acetic acid is 1) is the molar feed flow of methanol to the reactor equal to the molar production flow of acetic acid, $\phi_{mol,HOAc,out}$.

$\phi_{mol,MeOH,in}$ $\qquad$ = s_{MeOH} * $\phi_{mol,HOAc,out}$ = 5.78e-2 kmol/s

The mass and volumetric feed flow of methanol to the reactor are equal to:

$\phi_{m,MeOH,in}$ $\qquad$ = M_{MeOH} * $\phi_{mol,MeOH,in}$ = 1.85 kg/s

$\phi_{v,MeOH,in}$ $\qquad$ = (M_{MeOH} / ρ_{MeOH}) * $\phi_{mol,MeOH,in}$ = 2.37e-3 m³/s

The molar feed flow of water is equal to the amount of water converted due to the water-gas-shift reaction. The amount of water in the recycle stream is not taken into account. This will be considered separately with the recycle stream. As mentioned in chapter 2, the selectivity, s_{CO}, of carbon monoxide for acetic acid is 0.998.

$\phi_{mol,H2O,in}$ $\qquad$ = (1-s_{CO}) * $\phi_{mol,HOAc,uit}$ = 1.157e-4 kmol/s

The mass and volumetric feed flow of water to the reactor are equal to:

$\phi_{m,H2O,in}$ $\qquad$ = M_{H2O} * $\phi_{mol,H2O,in}$ = 2.111e-3 kg/s

$\phi_{v,H2O,in}$ $\qquad$ = (M_{H2O} / ρ_{H2O}) * $\phi_{mol,H2O,in}$ = 2.111e-6 m³/s

The volumetric recycle flow is determined with weight percentages of the different components recommended in chapter 2. The recycle stream exits the reactor in the liquid phase ($\phi_{v,recycle,out,L}$) and in the gas phase.

$\phi_{v,recycle,in}$ $\qquad$ = 1.368e-2 m³/s

$\phi_{v,recycle,out,L}$ $\qquad$ = 1.061e-2 m³/s

The total liquid feed flow to the reactor is given by the following equation:

$\phi_{v,total,in}$ $= \phi_{v,MeOH,in} + \phi_{v,H2O,in} + \phi_{v,recylce,in} = 1.605e\text{-}2 \ m^3/s$

The liquid product flow from the reactor is given by the following equation:

$\phi_{v,total,out,L}$ $= \phi_{v,HOAc,out} + \phi_{v,recylce,out,L} = 1.392e\text{-}2 \ m^3/s$

D.1.2 Calculation of the superficial gas velocity

The calculation of the transient superficial gas velocity, which is chosen as the superficial gas velocity, is done according to the following equations [lit.47 page 184-187].

$$U_{g,in} = \varepsilon_g U_{sb} \tag{D.1.1}$$

In this equation is U_{sb}, the single bell velocity and ε_g, the gas hold-up in the column, which are calculated with the following equations:

$$U_{sb} = 2.25 \frac{\sigma}{\eta_l}\left(\frac{\sigma^3 \rho_l}{g\eta_l}\right)^{-0.273}\left(\frac{\rho_l}{\rho_g}\right)^{0.03} \tag{D.1.2}$$

For the single bell velocity is found 0.149 m/s.

$$\varepsilon_g = 0.5 EXP\left(-193\rho_g^{-0.61}\eta_l^{0.11}\right) \tag{D.1.3}$$

For the gas hold-up, ε_g in the reactor is found a value of 0.365, which gives consequently a liquid hold-up, ε_l of 1 - 0.365 = 0.635. The physical properties of the reactor streams needed for calculations are listed in appendix A.2.
With equation (D.1.1) the inlet superficial gas velocity is calculated at 0.054 m/s.

D.1.3 Sizing of the bubble column

The amount of acetic acid produced is related to the liquid reaction volume and the reaction rate by the following equation:

$$q = rV_l \tag{D.1.4}$$

The reaction rate is a constant value of 4.18e-3 kmol/m³s, which is calculated with equations (2.8) and (2.9) and the data from appendix A.2. This reaction rate gives the straight line in figure 4.2. The minimal required liquid volume, for the production of 0.05787 kmol/s acetic acid, is 14 m³.

The liquid reactor volume will be considered a constant and the (H/D)$_{column}$ will be varied, which results in different column diameters. The column height is chosen an excess of 10% on the column height of the disperse gas and liquid mixture.

$$H_{column} = 1.1 H_{l+g} = 1.1 \frac{H_l}{\varepsilon_l} \tag{D.1.5}$$

This gives for the liquid reactor volume the following equation:

$$V_l = 0.25\pi D^2 H_l = 0.25\pi D^3 \frac{\varepsilon_l}{1.1}\left(\frac{H}{D}\right)_{column} \qquad (D.1.6)$$

The feed flow of carbon monoxide is related with the superficial gas velocity to the column diameter according to the following equation:

$$\phi_{v,g} = 0.25\pi D^2 U_{g,in} \qquad (D.1.7)$$

A $(H/D)_{column}$ gives a certain diameter, which results in a molar feed flow and conversion of carbon monoxide.

$$\phi_{mol,g} = \phi_{v,g}\frac{P}{RT} \qquad (D.1.8)$$

$$\xi_{co} = \frac{1.002q}{\phi_{mol,g}} \qquad (D.1.9)$$

In figure 4.3 are the molar feed flow and conversion of carbon monoxide shown for a constant liquid reactor volume and different values of the $(H/D)_{column}$.

The residence time of the liquid phase is calculated with equation (D.1.10).

$$\tau_L = \frac{V_l}{\phi_{v,l,out}} \qquad (D.1.10)$$

The liquid residence time is calculated with the exiting volumetric liquid flow. The inlet volumetric liquid flow is larger, the real liquid residence time will therefore be longer. The liquid residence time is 16.8 minutes (=1006 s).

The residence time of the gas phase is calculated with equation (D.1.11).

$$\tau_G = \int \frac{H_{l+g}}{U_{g,in}(1+\zeta\xi_{co})}d\xi_{co} = \frac{H_{l+g}}{U_{g,in}}\left[\frac{1}{\zeta}LN(1+\zeta\xi_{co})\right] \qquad (D.1.11)$$

The gas residence time is 2.5 minutes (=150 s).
For the chosen liquid reactor volume, Vl of 14 m3 and a $(H/D)_{column}$ of 5.8, the following dimensions are calculated:

Table D.1 Bubble column dimensions and data

Vl [m3]	14.1
V_{column} [m3]	24.4
$(H/D)_{column}$ [-]	5.8
D_{column} [m]	1.75
H_{column} [m]	10.2
H_{l+g} [m]	9.27
ξ_{co} [-]	0.588
$\phi_{mol,g}$ [kmol/s]	0.0986
τ_L [s]	1006
τ_G [s]	150

D.1.4 Validations of the assumptions on reactor design

In the calculation of the reactor, assumptions are made for the rate determining step, with other words on the values of the Hatta number and α. In this appendix the real values of Hatta and α will be calculated.

The Hatta number is given by the following equation:

$$Ha = \frac{\sqrt{kD_{co}}}{k_L}$$

(D.1.12)

The α is given by the following equation:

$$\alpha = \frac{k_L a}{k}$$

(D.1.13)

Before the α and Hatta could be determined the following calculations should be made. The specific surface area is calculated with equation (D.1.14) [lit.47, page 194], in which ds is the Sauter mean bubble diameter, calculated with equation (D.1.15) [lit.47, page 195].

$$a = \frac{6\varepsilon_g}{d_s}$$

(D.1.14)

$$d_s = \sqrt{8.8 \frac{\sigma}{(\rho_l - \rho_g)g} \left(\frac{U_{g,in}\eta_l}{\sigma}\right)^{-0.04} \left(\frac{\sigma^3 \rho_l}{g\eta_l^4}\right)^{-0.12} \left(\frac{\rho_l}{\rho_g}\right)^{0.22}}$$

(D.1.15)

The specific surface area is 1.652e3 1/m with a Sauter diameter of 1.325 mm. According to equation (D.1.16) the liquid volumetric mass transfer coefficient is calculated.

$$k_L a = 0.6 \frac{D_{co}}{D^2} \sqrt{\frac{\upsilon_l}{D_{co}}} \left(\frac{gD^2\rho_l}{\sigma}\right)^{0.62} \left(\frac{gD^3}{\upsilon_l^2}\right)^{0.31} \varepsilon_g^{1.1}$$

(D.1.16)

The diffusion coefficient is calculated with equation (D.1.17) [lit.12, page 96].

$$D_{co} = \frac{1.8588e-18\sqrt{xM}T}{\eta_l V_m^{0.6}}$$

(D.1.17)

The diffusion coefficient is determined at 1.795e-9 m/s, which gives a $k_L a$ of 0.561 1/s. For k_L is now calculated a value of 3.394e-4 m²/s. For the Hatta number is found a value of 0.008. The value of α is calculated at 134.

In the design of the reactor assumptions are made on the flow of the gas phase (plug flow) and liquid phase (CSTR). The Bodenstein numbers for the liquid and gas phase give an indication of the extend of ideal mixing. Therefore the Bodenstein numbers are calculated to validate these assumptions.

The Bodenstein for the liquid phase is calculated according to equation (D.1.18) [lit.12, page 489].

$$Bo_L = \frac{U_l H_{l+g}}{\varepsilon_l E_l}$$

(D.1.18)

In this equation is the superficial liquid velocity, U_l, calculated with the following equation:

$$U_l = \frac{\phi_{v,l}}{0.25\pi D^2}$$

(D.1.19)

The superficial liquid velocity is 0.006 m/s.
And the dispersion coefficient of the liquid phase is calculated with the following correlation:

$$E_l = 0.678 U_{g\min}^{03} D^{1.4}$$

(D.1.20)

The change in superficial gas velocity is formulated as a function of the conversion level, incorporating a contraction factor, ζ. The minimal superficial gas velocity, U_{gmin} is given by equation (D.1.21).

$$U_{g\min} = U_{g.in}\left(1+\zeta\xi_{co}\right)$$

(D.1.21)

The contraction factor of the vapour flow is given by:

$$\zeta = \frac{\phi_{v,g}(\xi=1)-\phi_{v,g.in}}{\phi_{v,g.in}}$$

(D.1.22)

With contraction factor of -0.996 and a minimal superficial gas velocity of 0.022 m/s, the liquid dispersion coefficient is then 0.475 m²/s. The calculated value of the minimum Bodenstein number is 0.177.
In equation (D.1.20) the minimal superficial gas velocity, U_{gmin} is used, since this will give the minimal liquid dispersion coefficient, E_l. The calculated liquid Bodenstein number will therefore be the maximal present value.

For the gas phase Bodenstein number could be made an analogue calculation, equation (D.1.23). Again the minimal superficial gas velocity is used, which will result in the calculation of the minimal present gad phase Bodenstein number.

$$Bo_G = \frac{U_{g\min} H_{l+g}}{\varepsilon_g E_g}$$

(D.1.23)

In the equation (D.1.24) for the gas dispersion coefficient, E_g, the superficial gas velocity at the inlet can be used, since the (U_g/ε_g) ratio is constant through the column.

$$E_g = 56.4\left(\frac{U_{g.in}}{\varepsilon_g}\right)^{3.56} D^{1.33}$$

(D.1.24)

With a calculated gas dispersion coefficient of 0.134 m²/s, the maximum gas phase Bodenstein number is 4.23.

Appendix D.2   Calculation of the distillation column and absorber

D.2.1 Distillation Column

D2.1.1. Trays
The trays are calculated with the Equipment-sizing option of Chemcad.
All the trays are valve trays.
The input values in Chemcad are:

- The system factor
  This factor is an indicator of the type of foaming action which occurs on the tray. This is the 1 for non-foaming, normal systems.
- Tray spacing
  The default condition is used, 0.6096 m.
- Flood percent
  Flooding is the condition where the pressure drop across a tray is sufficient to cause the dynamic liquid head to be equivalent to the tray spacing plus the weir height. At this point, the liquid backup in the downcomer is just at the point of overflowing the weir on the plate above. When this happens , the column fills with foamy liquid and becomes inoperable.
- The percent flood is the velocity approach to flooding, that is

$$\frac{Actual\_Vapour\_Velocity}{Vapour\_Velocity\_at\_the\_po\operatorname{int}\_of\_flooding} * 100 = percent\_flood$$

  For the most common systems this value is 80%
- Number of passes
  These are basically flow arrangements.
- Hole A/Act A
  This is the area of the holes divided by the total active area of the tray. The default condition is 0.19.
- Weir height
  The weir height affects the total liquid loading on the tray and therefore, the tray pressure drop.
- Downcomer clearance
  The downcomer clearances the distance between the bottom of the downcomer and the floor of the tray below. This clearance affects the downcomer backup and the tray pressure drop. The default is 7.62 cm.
- Type and material of the valve
  The options for the valve type are V1 and V4. The default option,V1, has been set. For the valve material stainless steal has been chosen.
- Valve and deck thickness in gauge
  The valve and deck thickness both affect the tray pressure drop. The defaults are 14 and 12.

First the liquid capacity per tray has been calculated. Now, with table 18.2 from Perry [lit. 35] the flow arrangement can be estimated. The flow arrangement will be crossflow, this means one pass per tray. This number of passes has been set in CHEMCAD. With the default settings the column has been calculated.

Sufficient residence time must be allowed in the downcomer for the entrained vapour to disengage from the liquid stream; to prevent heavily "aerated" liquid being carried under the downcomer. A time of at least 3 seconds is recommended.

By changing the weir height and the down comer clearance, a residence time over 3 seconds is obtained.

The top and bottom diameter are in most cases not the same. The largest diameter has been taken as the column diameter. The tray dimensions are set to the tray dimensions of the tray with the largest column diameter.

Table D.2.1 Column dimensions

Column	
number of passes	1
column diameter, (m)	1.83
tray spacing, (m)	0.61
downcomer dimension, side width, (m) length, (m) area, (m^2)	0.254 1.265 0.221
weir length, (m)	1.265
weir height, (m)	0.090
tray area,(m^2)	2.627
tray active area, (m^2)	2.185
% flood	73.630
hole area,(m^2)	0.415
number of valves	350
pressure drop over column, (bar)	0.462
downcomer clearance, (m)	0.1
downcomer backup, (m)	0.245
downcomer residence time, (s)	4.4

D.2.1.2 Column height

The column height has been calculated with the next equation:

$$H = 1.15 \frac{TS * N}{E_0}$$
(D.2.1)

with:

H	= column height	[m]
TS	= tray spacing	[m]
N	= theoretical number of trays	[-]
E$_0$	= tray efficiency	[-]

The factor 1.15 is the additional space at the ends of the tower as a percentage of the height that contains trays. The space has been set on 15% of the total column height that contains trays.

The plate-efficiency can be calculated with the relation of O'Connell.

$$E_0 = \frac{0.4983}{(\alpha * \mu)^{0.252}}$$
(D.2.2)

with:

α = relative volatility   [-]
μ = viscosity   [-]

The efficiency is dependent on pressure and temperature and therefore differs per tray. The efficiency of the feed tray has been taken as average value for the column. The relative volatility is calculated below:

$$\alpha = \frac{K1}{K2}$$

(D.2.3)

With K1 and K2 as the equilibrium constant for the light and the heavy compound. The viscosity and the equilibrium constants are calculated with Chemcad.

Table D.2.2 Values of the column calculations

Column	
K1	8.38491
K2	0.86052
α	9.74400
μ_F [cP]	0.0144
E_0	0.817
N	41
TS [m]	0.61
H [m]	35.2

D.2.1.3 Plate thickness required for the distillation column

The design pressure is taken 10% above operating pressure. For the construction material stainless steel is taken. A much thicker wall will be needed at the base of the column to withstand the wind and the dead weight. A first trial is to divide the column into three sections. The plate thickness of these sections has been estimated by the thickness of the minimum thickness required for the pressure loading.

Table D.2.3 Design values of the column

Item	quantity
design overpressure [bar]	2.75
design stress of stainless steel at 150°C [N/mm^2]	130
minimum thickness required for pressure loading [mm]	1.94
plate thickness of the first section (11.73m) [mm]	9
plate thickness of the second section (11.73m) [mm]	7
plate thickness of the third section (11.73m) [mm]	5

To check if this estimation has any validation some calculations have been made, shown on the next page.

Table D.2.4. Dead weight of the vessel

Item	quantity
weight (insulation+fittings) [kN]	42.3
weight (plates) [kN]	161
weight (shell) [kN]	167.5
total weight [kN]	370.8

Table D.2.5. Wind loading

Item	quantity
dynamic wind pressure [N/m^2]	1280
mean diameter [m]	1.84
loading per lineair metre [N/m]	2365.44
bending moment at bottom tangent line [Nm}	1485437

Table D.2.6. Analysis of stresses

Item	quantity [N/mm^2]
σ_L (pressure stress)	13.98
σ_h (pressure stress)	27.96
σ_w (dead weight)	7.13
σ_b (bending stress)	62.20 (+/-)
σ_z (resultant longitudinal stress, $\sigma_L+\sigma_w+\sigma_b$)	69.05 (upwind) -55.35 (down wind)

Table D.2.7. The greatest difference between the principal stress will be on the down-wind side.

Item	quantity [N/mm^2]
σ_h-σ_z	83.31

This stress is well below the maximum design stress of stainless steel.

Table D.2.8. Check of the elastic stability (buckling)

Item	quantity [N/mm^2]
σ_c (critical buckling stress)	97.10
σ_m (maximum compressive stress)	69.33

The maximum compressive stress is well below the critical buckling stress. The design is satisfactory.

D.2.2 The gas-absorber column

The gas-absorber column is calculated in the same way the distillation column has been calculated, with the Equipment-Sizing option of Chemcad. All the trays are valve trays. The first calculations are done with the same default settings as done with the distillation column. Also here the weir height and the downcomer clearance has been manipulated the get a somewhat higher residence time in the downcomer. In the gas-absorber it is less urgent to get a residence time over 3 seconds because in a gas-absorber it doesn't influence the performance as much as it does in a distillation column.
For the flow configuration, cross-flow has been chosen. This is a simple construction with good gas-liquid contacting.
The theoretical number of stages has been calculated with Douglas [lit.13]. (see next page)

The gas-absorber column calculation for number of stages

$T = 325$ [K]	$yin = 0.09453$	$xout := 0.0549166$	$G = 131.148$
$Pres = 10$	$yout = 1 \cdot 10^{-10}$	$L = 209.8808$	
$A = 46.608$	$Tc = 528$	$xin = 0$	
$B = -4492$	$Pc = 73.7$	$Tro = \dfrac{298}{Tc}$	
$C = -3.6263$	$Vlio = 0.0627$	$R = 0.08314$	
$D = 2.058 \cdot 10^{-17}$	$Tr = \dfrac{T}{Tc}$	$Tro = 0.564$	
$E = 6$		$Tr = 0.616$	

$$Pi = \exp\left(A - \frac{B}{T} - C \cdot \ln(T) - D \cdot T\right) \qquad\qquad Vli = Vlio \cdot \frac{5.7 - 3 \cdot Tr}{5.7 - 3 \cdot Tro}$$

$$Pi = 1.349 \cdot 10^5 \quad \text{[Pa]} \qquad\qquad\qquad\qquad Vli = 6.4 \cdot 10^{-2}$$

$$Pio = \frac{Pi}{10^5}$$

$$Pio = 1.349$$

Vapour-liquid equilibrium K value (Scheidings Processen II[lit.32])

$$Ki = \frac{Pio \cdot \exp\left[0.4278 \cdot (Pres - Pio) \cdot Pc \cdot Tr^{2.5}{}^{-1}\right] - Vli \cdot \dfrac{(Pres - Pio)}{(R \cdot T)}}{Pres}$$

$$Ki = 0.163$$

Theoretical number of stages (Douglas [lit.13])

$$N = \frac{\ln\left[\left(\dfrac{L}{Ki \cdot G} - 1\right) \cdot \dfrac{yin - Ki \cdot xin}{yout - Ki \cdot xin} - 1\right]}{\ln\dfrac{L}{Ki \cdot G}} - 1$$

$$N = 9.003$$

Table D2.8. Dimensions of the absorber

Gas-absorber column	
number of passes	1
column diameter, [m]	0.457
tray spacing, [m]	0.610
downcomer dimension, side width, [m] length, [m] area, [m²]	0.102 0.380 0.027
weir length, [m]	0.380
weir height, [m]	0.09
tray area,[m²]	0.164
% flood	69.05
hole area, [m²]	0.021
number of valves	36
pressure drop over column, [bar]	0.07
downcomer clearance, [m]	0.059
downcomer backup, [m]	0.224
downcomer residence time, [s]	2.6

D.2.2.1 Column height

The column height has been calculated with the next equation:

$$H = \frac{TS * N}{E_0} \tag{D.2.4}$$

with:

H	= column height	[m]
TS	= tray spacing	[m]
N	= theoretical number of trays	[-]
E_0	= tray efficiency	[-]

The plate-efficiency can be estimated with the diagram of O'Connell in Perry [lit.35]. First the O'Connell gas-absorber parameter has to be calculated:

$$O'\,Connell = \frac{\rho_l}{K * M * \mu_l} \tag{D.2.5}$$

with:

ρ_l	= density of the liquid, [lb/ft³]	
K	= distribution coefficient, [-]	
M	= molecular weight, [kg/kmol]	
μ_l	= viscosity, [cP]	

The distribution coefficient has calculated with Scheidings Processen II [lit.32]. The calculation can be seen in table D.2.9. The density and viscosity are calculated with ChemCad.

Table D.2.9 Calculations of the absorber

Gas-liquid column	
ρ_l [lb/ft^3]	50
K	0.167
M [kg/kmol]	32
μ_l [cP]	0.3
E_0	0.7
TS [m]	0.61
N	9
H [m]	7.9

Appendix D.3   Heat exchanger calculation

The heat exchangers are designed using the typical design procedure presented in Coulson and Richardson [lit. 9]. As the physical layout of the exchanger cannot be determined until the area is known, the design of an exchanger is of necessity a trial and error procedure.
Seven heat exchangers of the production process are designed. The other two heat exchangers in the process are the condenser and reboiler at the distillation column, they are not included in the calculations. For these two, the overall heat transfer coefficient is estimated, and the area is calculated. The nine heat exchangers are shown in table D.3.1.

Table D.3.1. Heat exchangers in the process

Heat exchanger	Shell side	Tube side
H7 (condenser)	offgas from reactor	water → steam
H8 (condenser)	condensing steam	liquid from reactor
H13 (cooler)	cooling water	liquid from gas flash
H15 (cooler)	cooling water	liquid from liquid flash
H16 condensor	cooling water	gas from distillation
H17 reboiler	MP steam	liquid from distillation
H22 (condenser)	recycle to reactor	water → steam
H24 (cooler)	cooling water	methanol from scrubber
H26 (cooler)	acetic acid	cooling water

The condensers involve partial condensation. The heat exchangers generating steam are designed as normal heat exchangers, using average values of steam and water for the calculations.

D.3.1. Heat exchanger H15
In the following description heat exchanger 15 is taken as an example for the calculations. The heat exchanger brings the liquid stream from flashdrum V10 containing mostly acetic acid, methyl iodide, the catalyst and methyl acetate, from 160 °C to 121.5 °C. This is needed because the liquid is at its boiling point and can not be pumped, if the stream is not cooled. The cooling water is at a pressure of 1 bar, while the recycle stream is at a pressure of 3.5 bar. As the recycle stream is the most corrosive, the most fouling, and has the highest pressure, it is assigned to the tube side, while the cooling water is assigned to the shell side.
A U-tube exchanger is chosen, with one shell-pass and two tube passes.
The dimensions chosen are based upon standard dimensions and are shown in table D.3.2.

Table D.3.2. Dimensions of heat exchanger 15

	Symbol	Value
inside tube diameter	d_i	38 mm
outside tube diameter	d_o	34 mm
tube wall thickness		2.0 mm
tube length	L	2.44 m
Baffle spacing+	l_b	$0.3 * D_s$
diameter shell	D_s	393 mm
Baffle cut		25%
pitch		1.25 triangular pitch*

* A triangular pitch is used, since the shell side fluid, water, is clean.
The general equation for heat transfer across a surface is:

$$Q = U * A * \Delta T_m \qquad\qquad (D3.1)$$

Q   = heat load [J/s]
U   = overall heat transfer coefficient [W/ m² °C]
A   = heat transfer area [m²]
ΔT_m = mean temperature difference [°C]

The mean temperature difference can be calculated via the logarithmic mean temperature:

$$\Delta T_{lm} = \frac{(T_1 - t_2) - (T_2 - t_1)}{\ln \dfrac{(T_1 - t_2)}{(T_2 - t_1)}}$$ (D3.2)

ΔT_{lm} = logarithmic mean temperature difference [°C]
T_1 = inlet temperature hot fluid [°C]
T_2 = outlet temperature hot fluid [°C]
t_1 = inlet temperature cold fluid [°C]
t_2 = outlet temperature cold fluid [°C]

The mean temperature difference can be calculated from:

$$\Delta T_m = F * \Delta T_{lm}$$ (D3.3)

F   = correction factor [-]

The correction factor F can only be calculated for U-tube exchangers, for floating head exchangers the factor F should be taken as 1.
An estimation is made from fig. 12.1. [lit. 9] for the overall heat transfer coefficient, as 500 W/m² °C. With the above equation the area A is calculated, the values of the temperatures and heat load are given by Chemcad.
With the following equation the overall heat transfer coefficient is calculated:

$$\frac{1}{U} = \frac{1}{h_o} + \frac{1}{h_{od}} + \frac{d_o * \ln(\dfrac{d_o}{d_i})}{2 * k_w} + \frac{d_o}{d_i} * (\frac{1}{h_{id}} + \frac{1}{h_i})$$ (D3.4)

h_o = outside fluid film coefficient [W/ m² °C]
h_{od} = outside dirt coefficient [W/ m² °C]
k_w = thermal conductivity of the tube wall material [W/m °C]
h_{id} = inside dirt coefficient [W/ m² °C]
h_i = inside fluid film coefficient [W/ m² °C]

using the following equations:

$$h_o = \frac{k_{fs}}{d_e} * j_h * \mathrm{Re} * \mathrm{Pr}^{\frac{1}{3}}$$ (D3.5)

k_{fs} = fluid thermal conductivity [W/ m °C]
d_e = equivalent (hydraulic) diameter [m]
j_h = heat transfer factor [-]
Re   = Reynolds number [-]
Pr   = Prandtl number [-]

$$h_i = \frac{k_{ft}}{d_i} * j_h * \text{Re} * \text{Pr}^{\frac{1}{3}} \qquad\qquad (D3.6)$$

k_{ft} = fluid thermal conductivity [W/ m² °C]

The viscosity term is neglected in the two equations above, because it is almost 1.
The calculated overall heat transfer coefficient amounts to 471 W/m2 °C. This is almost the same as the estimated 500 W/m2 °C.

The pressure drop over the shell side and the tube side is calculated with the following equations:

$$\Delta P_t = N_p * (8 * j_f * (\frac{L}{d_i}) + 2.5) * \frac{\rho * u_t^2}{2} \qquad\qquad (D3.7)$$

ΔP_t = pressure drop over the tube [Pa]
N_p = number of tubeside passes [-]
u_t = tube side velocity [m/s]
ρ = density tubes side fluid [kg/m3]

$$\Delta P_s = 8 * j_f * (\frac{D_s}{d_e}) * (\frac{L}{l_b}) * \frac{\rho * u_s^2}{2} \qquad\qquad (D3.8)$$

ΔP_s = shell-side pressure drop [Pa]
D_s = shell diameter [m]
l_b = baffle spacing [m]
u_s = shellside velocity [m/s]

The calculated values are given in table D.3.4.

D.3.2 Condensers
For condensers approximately the same method is used [lit.9]. The condensing fluid is always assigned to the shell side. An overall heat transfer coefficient is estimated and the heat transfer area is calculated. Dimensions for the exchanger layout are chosen. With the tube wall temperature and an estimation of the condensing coefficient the mean temperature of the condensate is calculated. At that temperature the physical properties of the condensating fluid are taken. With these properties the condensing coefficient is calculated with the following equation:

$$h_c = 0.95 * k_l * \left[\frac{\rho_l * (\rho_l - \rho_v) * g}{\mu_l * \Gamma_h} \right]^{\frac{1}{3}} * N_r^{\frac{-1}{6}} \qquad\qquad (D3.9)$$

$$\Gamma_h = \frac{W_c}{L * N_t}$$

(D3.10)

Γ_h = tube loading, flow per unit length of tube [kg/m s]
k_l = condensate thermal conductivity [W/ m °C]
ρ_l = condensate density [kg/m³]
ρ_v = vapour density [kg/m³]

μ_l = condensate viscosity [N s/m^2]
g   = gravitational acceleration [m/s^2]
N_t = total number of tubes
W_c = total condensate flow
N_r = average number of tubes in a vertical tube row
      (= 2/3 number of tubes in the central row)

The tube side coefficient is calculated the same way as for the normal heat exchanger. From these, the overall heat transfer coefficient is calculated. The pressure drop is calculated with the same equations as above, only for the shell-side temperature drop a factor of 0.5 is introduced, since the real pressure drop is the same as half of the one calculated using the inlet flow.

The values are also given for the other heat exchangers, corresponding with the numbers in the flowsheet. All symbols are explained above or in the symbols list.
The full calculations are given in table D.3.4. and a summary of the results of the calculations is given in table D.3.3.

Table D3.3. Summary of the calculated results of heat exchangers.

	H7	H8	H13	H15	H16	H17	H22	H24	H26
U [W/m^2 °C] estimated	100	100	550	500	500	800	300	500	500
U [W/m^2 °C] calculated	94	97	569	472	-----	-----	290	529	465
Q, heat load [MJ/h]	7235.3	7918.6	211.1	2351.5	30611	25266	13142	230.8	3754.5
ΔTm [°C]	33.9	15.4	64.4	109.6	100.0	10.0	51.4	31.1	60.9
Heat transfer area [m^2]	592.6	1429.9	1.7	11.9	170	877	236.6	4.1	33.5

Table D3.4. Calculations of the heat exchangers.

	H13	H15	H26	H24
	u-tube	u-tube	u-tube	u-tube
Q (J/s)	58637.000	652820.000	1021453.000	63973.000
Thot in	100.000	160.000	168.200	67.600
Thot out	90.000	121.500	50.000	57.000
T cold in	20.000	20.000	20.000	20.000
T cold out	39.800	39.400	39.400	39.700
R	0.505	1.985	6.093	0.538
S	0.248	0.139	0.131	0.414
F correction factor for U-tube	0.992	0.990	0.899	0.965
Logarithmic mean temperature diff. °C	64.977	110.776	67.808	32.236
True log. mean temp. diff. °C	64.465	109.641	60.937	31.121
Overall est. heat transfer coeff. U (W/m2 °C)	550.000	500.000	500.000	500.000
Area m2	1.654	11.908	33.525	4.111
Tube outside diameter, do (m)	0.038	0.038	0.016	0.030
Tube inside diameter, di (m)	0.034	0.034	0.012	0.026
Wall thickness (m)	0.002	0.002	0.002	0.002
L tubelength (m)	1.830	2.440	4.880	2.440
Area one tube (m2)	0.218	0.291	0.245	0.230
Number of tubes, Nt	7.570	40.882	136.672	17.878
Passes (tube)	2.000	2.000	2.000	2.000
Tubes per pass	3.785	20.441	68.336	8.939
Pitch Pt	0.048	0.048	0.020	0.038
	trian	trian	trian	trian
K1	0.319	0.249	0.175	0.249
n1	2.142	2.207	2.285	2.207
Diameter bundle (m)	0.167	0.383	0.295	0.208
Shell bundle clearance (figure 12.10)	0.010	0.010	0.055	0.010
Diameter shell, Ds (m)	0.177	0.393	0.350	0.218
Baffle spacing (factor *Ds) (m)	0.053	0.118	0.175	0.065
Number tubes centre row Nr				
Tube	recycle fluid	recycle fluid	acetic acid	methanol
condensing coeff estimation (W/m2 C)				
Mean temperature tube side (°C)				
Tube wall temperature (°C)				
Tube cross area (m)	0.001	0.001	0.000	0.001
Total flow area per pass (m2)	0.003	0.019	0.008	0.005
mass flow (kg/s)	3.890	9.360	3.470	2.890
fluid mass vel. (kg/s m2)	1131.964	504.349	448.980	608.953
density fluid (kg/m3)	1368.000	1316.000	942.000	957.000
fluid linear vel. (m/s)	0.827	0.383	0.477	0.636
Viscosity (Ns/m2)	0.00038	0.00060	0.00052	0.000
Thermal conductivity (W/m C)	0.118	0.157	0.144	0.169
Cp (J/kg K)	1502.000	1811.000	2531.000	2098.000
Re	100750.744	28819.924	10301.634	44349.534
Pr	4.883	6.859	9.212	4.440
L/di	53.824	71.765	406.667	93.846
heat transfer factor, jh (figure 12.23)	0.004	0.004	0.004	0.004
inside fluid film coeff., hi (W/m2 C)	2056.576	955.299	1026.769	1647.127
Shell	water	water	water	water
Mean shell side temperature (°C)				
mean temp condensate (°C)				
Cross flow area (m2)	0.002	0.009	0.012	0.003
mass vel. (kg/s m2)	378.227	868.361	1019.519	272.764
diam eq. (m)	0.027	0.027	0.011	0.021
mass flow (kg/s)	0.708	8.060	12.500	0.778
density (kg/m3)	995.000	995.000	995.000	995.000
viscosity (Ns/m2)	0.001	0.001	0.001	0.001
thermal conductivity (W/m C)	0.612	0.612	0.612	0.612

Table D3.4. Calculations of the heat exchangers.

Specific heat, Cp (J/kg K)	4200.000	4200.000	4200.000	4200.000
vapor dens. at mean vapor temp(kg/m3)				
tube loading condensate rate per unit tube(kg/s m)				
Nr new				
Re	11806.201	27105.550	13405.727	6721.746
Pr	5.937	5.937	5.934	5.937
baffle cut	0.250	0.250	0.250	0.250
heat transfer factor, jh (figure 12.29)	0.006	0.004	0.006	0.008
shell-side heat transfer coeff, hs (W/ m2 C)	2648.952	4423.026	7142.522	2778.662
condensate coeff., hc (W/m2 C) (12.50)				
1/Uo	0.002	0.002	0.002	0.002
fouling coeff outside, hod	5000.000	5000.000	5000.000	5000.000
fouling coeff, hid	5000.000	5000.000	5000.000	5000.000
therm. cond wall (stainless steel)	16.000	16.000	16.000	16.000
Calc. overall heat tr. coef , Uo (W/m2 C)	569.366	471.876	464.502	528.529
Tube				
Friction factor, jf (figure 12.24)	0.003	0.003	0.003	0.003
pres drop tube (pa)	3551.573	760.647	2623.570	1812.361
Shell				
linear vel (m/s)	0.380	0.873	1.025	0.274
jf (figure 12.30)	0.060	0.045	0.050	0.055
pres drop (pa)	7801.000	41119.364	89744.581	6281.037
new ho (calculated with pres drop)	1521.423	2540.361	4102.302	1595.922

Table D3.4. Calculations of the heat exchangers.

	H8(cond)	H7(cond)	H22 cond	
	float.head	float. head	float. head	
Q (J/s)	2199580.000	2009835.000	3647841.000	
Thot in	180.200	192.200	232.300	
Thot out	161.900	100.000	71.000	
T cold in	150.500	20.300	20.300	
T cold out	160.000	181.900	180.200	
R				
S				
F correction factor for U-tube	1.000	1.000	1.000	
Logarithmic mean temperature diff. °C	15.383	33.918	51.397	
True log. mean temp. diff. °C	15.383	33.918	51.397	
Overall est. heat transfer coeff. U (W/m2 °C)	100.000	100.000	300.000	
Area m2	1429.900	592.561	236.580	
Tube outside diameter, do (m)	0.016	0.016	0.020	
Tube inside diameter, di (m)	0.012	0.012	0.016	
Wall thickness (m)	0.002	0.002	0.002	
L tubelength (m)	4.880	4.880	2.440	
Area one tube (m2)	0.245	0.245	0.153	
Number of tubes, Nt	5829.295	2415.703	1543.152	
Passes (tube)	6.000	8.000	8.000	
Tubes per pass	971.549	301.963	192.894	
Pitch Pt	0.020	0.020	0.025	
	trian	trian	triangular	
K1	0.074	0.037	0.037	
n1	2.499	2.675	2.675	
Diameter bundle (m)	1.455	1.015	1.073	
Shell bundle clearance (figure 12.10)	0.080	0.065	0.075	
Diameter shell, Ds (m)	1.535	1.080	1.148	
Baffle spacing (factor *Ds) (m)	0.767	0.216	0.574	
Number tubes centre row Nr	72.732	50.727	42.902	
Tube	fluid	water/steam	water/steam	
condensing coeff estimation (W/m2 C)	4000.000	8000.000	8000.000	
Mean temperature tube side (°C)	155.250	101.100	100.250	
Tube wall temperature (°C)	170.655	145.538	149.723	
Tube cross area (m)	0.000	0.000	0.000	
Total flow area per pass (m2)	0.110	0.034	0.039	
mass flow (kg/s)	19.640	0.744	1.353	
fluid mass vel. (kg/s m2)	178.741	21.785	34.886	
density fluid (kg/m3)	30.400	501.400	501.400	
fluid linear vel. (m/s)	5.880	0.043	0.070	
Viscosity (Ns/m2)	0.00029	0.00007	0.00007	
Thermal conductivity (W/m C)	0.020	0.316	0.316	
Cp (J/kg K)	1598.000	3062.600	3062.600	
Re	7396.182	4021.933	8587.285	
Pr	23.405	0.630	0.630	
L/di	406.667	406.667	152.500	
heat transfer factor, jh (figure 12.23)	0.004	0.003	0.004	
inside fluid film coeff., hi (W/m2 C)	138.173	272.882	509.804	
Shell	steam/water	reactor gas	recycle	
Mean shell side temperature (°C)	171.050	146.100	151.650	
mean temp condensate (°C)	170.853	145.819	150.686	
Cross flow area (m2)	0.236	0.047	0.132	
mass vel. (kg/s m2)	4.450	134.288	51.713	
diam eq. (m)	0.011	0.011	0.014	
mass flow (kg/s)	1.048	6.260	6.810	at T cond
density (kg/m3) at Tcond	450.000	77.400	1267.000	
viscosity (Ns/m2) at Tcond	0.000	0.000	0.000	
thermal conductivity (W/m C) at Tcond	0.357	0.051	0.100	

Table D3.4. Calculations of the heat exchangers.

Specific heat, Cp (J/kg K) at Tcond	3136.000	559.800	1869.000
vapor dens. at mean vapor temp(kg/m3)	4.940	54.089	72.324
tube loading condensate rate per unit tube(kg/s m)	0.000	0.001	0.002
Nr new	48.488	33.818	28.601
Re	555.543	16582.760	6276.739
Pr	0.799	1.010	2.187
baffle cut	0.250	0.250	0.250
heat transfer factor, jh (figure 12.29)			
shell-side heat transfer coeff, hs (W/ m2 C)			
condensate coeff., hc (W/m2 C) (12.50)	14862.686	192.070	2240.678
1/Uo	0.010	0.011	0.003
fouling coeff outside, hod	6000.000	6000.000	6000.000
fouling coeff, hid	5000.000	5000.000	5000.000
therm. cond wall (stainless steel)	16.000	16.000	16.000
Calc. overall heat tr. coef , Uo (W/m2 C)	97.142	93.723	289.490
Tube			
Friction factor, jf (figure 12.24)	0.004	0.050	0.006
pres drop tube (pa)	46859.009	625.363	89.420
Shell			
linear vel (m/s)	0.010	1.735	0.041
jf (figure 12.30)	0.060	0.060	0.080
pres drop (pa)	9.073	120094.372	232.101

Appendix D.4   Calculation of single stage equilibrium separators

The design of the single stage equilibrium separators is done according to Scheidingsprocessen II [lit.32, page 267-273].

D.4.1 The vertical flash drum

The diameter of the vertical flash drum, is designed with the objective to prevent an excessive carry-over of liquid droplets. Therefore the maximum design vapour velocity is used in the calculation of the vertical flash drum diameter in equation (D.4.2). The maximum design vapour velocity is expressed using the Sounders-Brown empirical equation (D.4.1):

$$u_{vsep} = C_{vdrum} \sqrt{\frac{\rho_L - \rho_G}{\rho_G}} \qquad\qquad (D.4.1)$$

u_{vsep} = maximum design vapour velocity [m/s]
C_{vsep} = capacity coefficient [m/s]
ρ_L = liquid density [kg/m^3]
ρ_G = vapour density [kg/m^3]

The capacity coefficient has for a common wire mesh demister, a value of 0.06 m/s. With the continuity relation, the design vapour velocity is transformed into the drum diameter, d_{vsep}. The drum diameter has a common range of 0.3 to 4 m.

$$d_{vsep} = 1.1284 \sqrt{\frac{\phi_{m.G}}{\rho_G u_{vsep}}} \qquad\qquad (D.4.2)$$

ϕ_{mG} = mass flow rate of the gas phase [kg/s]

The total height or length of the vertical flash drum, l_{vsep}, from top to bottom tangent line, consists of three characteristic heights. The total height has a common range of 1 to 20 m.

$$l_{vsep} = h_L + h_{LF} + h_{FG} \qquad\qquad (D.4.3)$$

h_L = height of the liquid level [m]
h_{LF} = distance between the maximum liquid level and the centre of the feed inlet [m]
h_{FG} = height of the drum above the centre line of the feed inlet [m]

The distance between the maximum liquid level and the centre of the feed inlet, h_{LF}, is at least 0.5 m. The height of the drum above the centreline of the feed inlet, h_{FG}, is usually set to 1 drum diameter, but with a minimum value of 1 m. The height of the liquid level, h_L, depends on the residence time required for smooth operation and control.

$$h_L = \frac{V_L}{f} = \frac{4V_L}{\pi d_{vsep}^2} \qquad\qquad (D.4.4)$$

V_L = liquid volume [m^3]
f = cross sectional area of the drum [m^2]

The liquid volume, in the previous equation (D.4.4), follows from the liquid volume flow rate and the storage residence time.

$$V_L = t\phi_{vL}$$

(D.4.5)

ϕ_{vL} = volumetric liquid flow rate [m³/s]
t = storage residence time [s]

The storage residence is typically 5 to 10 minutes, an exception is a flash drum upstream of a compressor, then the storage residence time is 20 minutes. The storage residence times of flash drum V9 and V10 are chosen at 7.5 minutes.

When the calculated length to diameter ratio is less than 3, the length is increased arbitrarily to make the ratio 3. When the ratio is larger than 5, horizontal flash drum should be used.

Above described calculations give the following results for the vertical flash drums:

Table D.4.1 Dimensions of the vertical flash drums.

	u_{vsep} [m/s]	d_{vsep} [m]	h_L [m]	h_{extra} [m]	l_{vsep} [m]	l_{vsep}/d_{vsep} [-]
V9	0.340	0.464	7.729	0.000	9.229	19.888
V10	0.700	1.414	2.098	0.650	4.248	3.004

Flash drum V9 has a length to diameter ratio larger than 5, which is indication that a horizontal flash drum should be used. The calculations for the horizontal flash drum described in the next section.

Flash drum V10 had a length to diameter ratio smaller than 3, therefore an extra height, h_{extra}, is added to the total length, l_{vsep}, so that the length to diameter ratio is 3.

D.4.2 The horizontal flash drum

The top accumulator, V18 is an example of a horizontal flash drum. Flash drum V9 is designed as a horizontal flash drum, since the previous section showed a length to diameter ratio larger than 5.

The diameter of the horizontal flash drum is based on the allowable gas velocity, which can be taken as:

$$u_{hsep} = 1.25 u_{vsep}$$

(D.4.6)

The corresponding diameter of the horizontal flash drum, d_{hsep}, follows from:

$$d_{hsep} = 1.1284 \sqrt{\frac{\phi_{mG}}{\rho_G u_{hsep} \phi_G}}$$

(D.4.7)

ϕ_G = the fraction of the drum cross section occupied by the gas phase [-]

The length of the horizontal flash drum, l_{hsep}, depends on the residence time and the fractional gas cross section, according to the following equation:

$$l_{hsep} = \frac{4V_L}{\pi(1-\phi_G)d_{hsep}^2}$$

(D.4.8)

The liquid volume is calculated with the equation (D.4.5) from the previous section. The storage residence time for the top accumulator V18 is as chosen 20 minutes, since the top accumulator is upstream of a compressor.

The height of the liquid level corresponding the drum diameter follows from:

$$h_L = d_{hsep}(0.9167 - 0.8333\phi_G)$$

(D.4.9)

The fraction of the drum cross section occupied by the gas phase is chosen so that the liquid height to diameter ratio is between 0.5 and 0.6, which will result in a total length to diameter of around 5.

Above described calculations give the following results for the horizontal flash drums:

Table D.4.2 Dimensions of the horizontal flash drums

	u_{hsep}	ϕ_G	d_{hsep}	h_L	h_L/d_{hsep}	l_{hsep}	l_{hsep}/d_{hsep}
	[m/s]	[-]	[m]	[m]	[-]	[m]	[-]
V9	0.424	0.300	0.758	0.505	0.667	4.141	5.464
V18	0.743	0.275	2.000	1.375	0.688	12.080	6.039

Appendix D.5   Equipment sizing of the pumps

The calculations for the pumps are done according to the equations in Coulson & Richardson [lit.9] and Pompen en Compressoren [lit.45].

The head of the pump is calculated with equation (D.5.1).

$$H = \frac{\Delta P}{\rho_l g}$$
(D.5.1)

ΔP = pressure increase [Pa]
ρ   = density [kg/m³]

The power required for pumping an incompressible fluid is given by:

$$P_{axis} = \frac{\rho g H \phi_v}{\eta}$$
(D.5.2)

ϕ_v = capacity, volumetric flow [m³/s]
η   = efficiency = 0.75 [-]

Table D.5.1 Pump data

	ϕ_v [m³/hr]	ΔP [bar]	T [°C]	P_{vap} [bar]
P2	10.673	9.0	20	0.0235
P4	8.58	9	20	0.1289
P5	0.007576	3.2	20	0.0235
P21	10.452	1.5	90	28
P23	26.274	27.5	121.5	1.4
P25	10.932	20.3	57	8.923

The net positive suction head of a pump, NPSH, is the amount of pressure at the suction point of the pump, expressed as a head of the liquid to be pumped. The NPSH must exceed the vapour pressure of the liquid, otherwise partial vaporisation is liable to occur (cavitation).
As a general guide the NPSH should be above 3 m for pump capacities up to a flow rate of 100 m³/hr [lit.6, page 156]. The NPSH is calculated with equation (D.5.3).

$$NPSH_{avail,max} = \frac{P_{in} - P_{vap}}{\rho g}$$
(D.5.3)

The pump head is usually specified in metre water column. Therefore in table D.5.2 the pump head are also calculated per metre water column, which also gives a NPSH per metre water column.

Table D.5.2 Pump heads, power and NPSH

	H_{H2O} [m]	H_L [m]	P_{axis} [kW]	$NPSH_{avail,max,L}$ [m]	$NPSH_{avail,max,H2O}$ [m]
P2	91.74	91.94	3.56	9.98	9.95
P4	91.74	115.69	2.86	11.20	8.88
P5	32.62	32.69	0.000898	71.27	71.12
P21	15.29	11.27	0.575	11.27	15.29
P23	280.33	218.74	26.76	16.70	21.41
P25	206.93	217.66	8.22	13.69	13.02

Appendix D.6   Equipment sizing of the compressor

Calculation of the adiabatic compressor (C19) is done according to Perry's [lit.35, page 6-17].

The adiabatic head is expressed as follows:

$$H_{ad} = \frac{k}{k-1} \frac{RT_{in}}{g} \left[\left(\frac{P_{out}}{P_{in}} \right)^{k-\frac{1}{k}} - 1 \right]$$ (D.6.1)

H_{ad} = adiabatic head [m]
k = ratio of the specific heat at constant pressure to that at constant volume [-]
R = gas constant [J/(kg*K)] (= 8314 / molecular weight, M)
T_{in} = inlet temperature [K]
g = gravitational acceleration [m/s^2]
P_{in} = input pressure [Pa]
P_{out} = output pressure [Pa]

The thearetical work expended on the gas during compression is calculated with equation (D.6.2).

$$P_{th} = g \phi_m H_{ad}$$ (D.6.2)

P_{th} = theoretical work on gas [W]
ϕ_m = capacity, mass flow [kg/s]

The actual power needed for compression is given with the following equation (D.6.3).

$$P_{act} = \frac{P_{th}}{\eta}$$ (D.6.3)

Pact = actual work [W]
η = efficiency = 0.75 [-]

In table D.6.1 are shown the data of the compressor (C19).

Table D.6.1 Compressor data

	k	P_{in}	P_{out}	ϕ_m	M
	[-]	[bar]	[bar]	[kg/s]	[kg/kmol]
C19	1.11	3.5	31.0	6.79	83.82

In table D.6.2 the results of the calculations of the compressor are shown.

Table D.6.2 Results compressor calculations

	H_{ad}	P_{th}	η	P_{act}
	[m]	[kW]	[-]	[kW]
C19	10035	668.5	0.75	891.3

Appendix: D7
Calculations on resinbeds

Bed to remove traces of iron and other cations

Constants:

$AP := 100000$ Acetic acid production (ton/y)

$Ph := 8000$ Production hours (h/y)

$Fe = 55.845$ Molarweight iron (gr/mol)

Variables:

$FeIn = 1$ Iron concentration incoming stream (ppmwt)

$FeOut := 25$ Iron concentration outgoing stream (ppbwt)

$osFe = 3$ Resin sites occupied by iron (-)

$T = 3000$ Lifetime of the bed, all sites occupied (h)

$dcap = 4.7$ Dry capacity of the resin (mol/kg)

$lcap = 1.8$ Capacity of the resin (mol/l)

$por = 30$ Porosity of the resin (l/kg)

$frbed = 0.6$ Fraction of the bed volume occupied by resin (-)

$H := 3$ Height of the resinbed (m)

Calculations:

Iron hold-up in the bed:

$APh = \dfrac{AP \cdot 1000}{Ph}$ $APh = 1.25 \cdot 10^4$ Acetic acid production (kg/h)

$FeH = FeIn - FeOut \cdot 1 \cdot 10^{-3}$ $FeH = 0.975$ Iron hold-up (ppmwt)

$FeHh = FeH \cdot 1 \cdot 10^{-6} \cdot APh$ $FeHh = 0.012$ Iron hold-up (kg/h)

$FeHhm = \dfrac{FeHh \cdot 1000}{Fe}$ $FeHhm = 0.218$ Iron hold-up (mol/h)

$TFeHhm = FeHhm \cdot T$ $TFeHhm = 654.714$ Iron hold-up (mol)

$Fes = TFeHhm \cdot osFe$ $Fes = 1.964 \cdot 10^3$ Amount of sites needed (mol)

Sites per bedvolume:

$den = \dfrac{lcap}{dcap}$ $den = 0.383$ Density of the liquid (kg/l)

$$vol := por + \frac{1}{den}$$ $vol = 32.611$ Volume of the resin plus pores (l/kg)

$$capvol := \frac{dcap}{vol}$$ $capvol = 0.144$ Capacity per volume (resin plus pores) (mol/l)

$$capVvol := capvol \cdot frbed$$ $capVvol = 0.086$ Capacity per bedvolume (mol/l)

Bedvolume:

$$BV := \frac{Fes}{capVvol \cdot 1000}$$ $BV = 22.714$ Bedvolume (m³)

Size of the bed:

$$Sq := \frac{BV}{H}$$ $Sq = 7.571$ Floorsize of the bed (m²)

$$Dia := \sqrt{\frac{Sq}{3.1415927}} \cdot 2$$ $Dia = 3.105$ Diameter of the bed (m)

The size of the bed is: diameter 3 m and height 3 m.
The volume of this bed is 21.206 m³.

Amount of iron that the bed contains:

$Vbed := 21.206$ Bedvolume (m³)

$S := Vbed \cdot capVvol \cdot 1000$ $S = 1.834 \cdot 10^3$ Amount of sites in the bed (mol)

$$mFe := \frac{S}{osFe}$$ $mFe = 611.253$ Amount of iron the bed can contain (mol)

$$aFe := mFe \cdot \frac{Fe}{1000}$$ $aFe = 34.135$ Amount of iron the bed can contain (kg)

$Fe3000 := FeHh \cdot 3000$ $Fe3000 = 36.563$ Amount of iron that the bed contains after 3000 hours

The amount of iron that the bed would contain after 3000 hours is more the maximum the bed can contain (aFe). The maximum time to use the bed (Tu) has to be calculated.

$$Tu := \frac{aFe}{FeHh}$$ $Tu = 2.801 \cdot 10^3$ Time until the bed is full (h)

Resinbeds a year:

$$Beds := \frac{Ph}{Tu}$$ $Beds = 2.856$ Amount of beds a year (-)

Conclusion:
The bed to remove traces of iron and other cations:
H=3m, D=3m, Volume=21.206 m³, 3 beds (max. 2800 h) a year.

Bed to remove traces of iodide

Constants:

$AP := 100000$ Acetic acid production (ton/y)

$Ph := 8000$ Production hours (h/y)

$I := 126.904$ Molweight iodide (gr/mol)

Variables:

$IIn := 5$ Iodide concentration incoming stream (ppmwt)

$IOut := 0$ Iodide concentration outgoing stream (ppbwt)

$osI := 1$ Resin sites occupied by one iodide (-)

$T := 3000$ Lifetime of the bed, all sites occupied (h)

$dcap = 4.7$ Dry capacity of the resin (mol/kg)

$lcap = 1.8$ Capacity of the resin (mol/l)

$por = 30$ Porosity of the resin (l/kg)

$frbed := 0.6$ Fraction of the bed volume occupied by resin (-)

$H := 3$ Height of the resinbed (m)

Calculations:

Iodide hold-up in the bed:

$APh := \dfrac{AP \cdot 1000}{Ph}$ $APh = 1.25 \cdot 10^{4}$ Acetic acid production (kg/h)

$IH := IIn - IOut \cdot 1 \cdot 10^{-3}$ $IH = 5$ Iodide hold-up (ppmwt)

$IHh := IH \cdot 1 \cdot 10^{-6} \cdot APh$ $IHh = 0.062$ Iodide hold-up (kg/h)

$IHhm := \dfrac{IHh \cdot 1000}{I}$ $IHhm = 0.492$ Iodide hold-up (mol/h)

$TIHhm := IHhm \cdot T$ $TIHhm = 1.477 \cdot 10^{3}$ Iodide hold-up (mol)

$Is := TIHhm \cdot osI$ $Is = 1.477 \cdot 10^{3}$ Amount of sites needed (mol)

Sites per bedvolume:

$den := \dfrac{lcap}{dcap}$ $den = 0.383$ Density of the liquid (kg/l)

$$vol := por + \frac{1}{den}$$ $vol = 32.611$ Volume of the resin plus pores (l/kg)

$$capvol := \frac{dcap}{vol}$$ $capvol = 0.144$ Capacity per volume (resin plus pores) (mol/l)

$$capVvol := capvol \cdot frbed$$ $capVvol = 0.086$ Capacity per bedvolume (mol/l)

Bedvolume:

$$BV := \frac{Is}{capVvol \cdot 1000}$$ $BV = 17.086$ Bedvolume (m^3)

Size of the bed:

$$Sq := \frac{BV}{H}$$ $Sq = 5.695$ Floorsize of the bed (m^2)

$$Dia := \sqrt{\frac{Sq}{3.1415927}} \cdot 2$$ $Dia = 2.693$ Diameter of the bed (m)

The size of the bed is: diameter 3 m and height 3 m, to have the same size as the
resinbed for the removal of iron and other cations.
The volume of this bed is 21.206 m^3.

Lifetime of the bed incase of iodide leakage in the process:
The following calculations are for the 21.206 m^3 bed. The time to regenerate a resinbed is 1 day,
so if there are two beds, one bed has to last at least one day.

Used constants:

$Vbed := 21.206$ Volume of the resin bed (m^3)

$Tl := 24$ Minimum lifetime incase of leakage (h)

$capVvol = 0.086$ Capacity of the bed (mol/l)

$osI = 1$ Resin sites occupied by one iodide (-)

$I = 126.904$ Molarweight iodide (gr/mol)

$APh = 1.25 \cdot 10^4$ Acetic acid production (kg/h)

$IOut = 0$ Iodide outgoing stream (ppbwt)

Calculation:

$$as := Vbed \cdot capVvol \cdot 1000$$ $as = 1.834 \cdot 10^3$ Maximum available sites in the resinbed (mol)

$$asI := \frac{as}{osI}$$ $asI = 1.834 \cdot 10^3$ Maximum amount of iodide ions on sites (mol)

$$Ihm := \frac{asI}{Tl}$$ $Ihm = 76.407$ Maximum amount of iodide (mol/h)

$Ihk := Ihm \cdot \dfrac{I}{1000}$ $Ihm = 76.407$ Maximum amount of iodide (kg/h)

$Iwt\% := \dfrac{Ihm}{APh - Ihm}$ $Iwt\% = 0.006$ Maximum weight percent of iodide in the acetic acid stream going to the resinbed (% wt)

Amount of iodide that the bed contains:

$aI := Ihm \cdot Tl \cdot \dfrac{I}{1000}$ $aI = 232.711$ Total amount of iodide that the resinbed can contain (kg)

$I2800 := IHh \cdot 2800$ $I2800 = 175$ Total amount of iodide in the resinbed after 3000 hours (kg)

$Tu := \dfrac{aI}{IHh}$ $Tu = 3.723 \cdot 10^{3}$ Time until the bed is full (h)

$Beds := \dfrac{Ph}{Tu}$ $Beds = 2.149$ Amount of beds a year (-)

Conclusion:

The bed to remove traces of iodide:

H=3m, D=3m, Volume=21.206 m³, 2.5 beds (max. 3700h) a year.

This bed gives an acetic acid production that meets the product specifications, even if there is a leakage of maximum 0.006 wt% iodide, during 24 hours.

STREAM/COMPONENTS

M : kg/s   Q : kW

STREAM NO.: STREAM NAME: TO EQUIPMENT NO.:	1 methanol P4	2 methanol T20	3 liquid H24	4 liquid + water H24	5 cooled liquid P25
Temperature [°C]	20.0	20.6	67.6	67.6	57.0
Pressure [bar]	1.0	10.0	10.2	10.2	10.2
COMPONENTS:	(M)	(M)	(M)	(M)	(M)
Hydrogen	0.0000	0.0000	0.0000	0.0000	0.0000
Carbon monoxide	0.0000	0.0000	0.0002	0.0002	0.0002
Carbon dioxide	0.0000	0.0000	0.0000	0.0000	0.0000
Methyl iodide	0.0000	0.0000	0.9191	0.9191	0.9191
Methyl acetate	0.0000	0.0000	0.0258	0.0258	0.0258
Methanol	1.8900	1.8900	1.8515	1.8515	1.8515
Water	0.0000	0.0000	0.0037	0.0058	0.0058
Acetic acid	0.0000	0.0000	0.0849	0.0849	0.0849
Rhodium cat.	0.0000	0.0000	0.0000	0.0000	0.0000
Lithium iodide	0.0000	0.0000	0.0000	0.0000	0.0000
TOTAL M-FLOW:	1.8900	1.8900	2.8852	2.8873	2.8873
TOTAL Q-FLOW:	-14119	-14116	-14511	-14544	-14608

STREAM NO.: STREAM NAME: TO EQUIPMENT NO.:	6 recycle liquid R3	7 total recycle R3	8 CO R3	9 liquid product E6	10 product H8
Temperature [°C]	58.4	93.6	20.0	192.2	150.5
Pressure [bar]	30.5	30.5	30.5	30.0	4.0
COMPONENTS:	(M)	(M)	(M)	(M)	(M)
Hydrogen	0.0000	0.0000	0.0000	0.0000	0.0000
Carbon monoxide	0.0002	0.0029	2.9439	0.0013	0.0013
Carbon dioxide	0.0000	0.0000	0.0000	0.0000	0.0000
Methyl iodide	0.9191	7.7821	0.0000	4.6327	4.6327
Methyl acetate	0.0258	0.6950	0.0000	0.5347	0.5347
Methanol	1.8515	1.8515	0.0000	0.0000	0.0000
Water	0.0058	0.4174	0.0000	0.3461	0.3461
Acetic acid	0.0849	8.9060	0.0000	10.8065	10.8065
Rhodium cat.	0.0000	0.0417	0.0000	0.0417	0.0417
Lithium iodide	0.0000	3.2222	0.0000	3.2222	3.2222
TOTAL M-FLOW:	2.8873	22.9188	2.9439	19.5852	19.5852
TOTAL Q-FLOW:	-14600	-97996	-11942	-92625	-92843

STREAM/COMPONENTS

M : kg/s   Q : kW

STREAM NO.: STREAM NAME: TO EQUIPMENT NO.:	11 product V10	12 product T14	13 product H26	14 product R27/R28
Temperature [°C]	160.0	160.0	168.2	50.0
Pressure [bar]	3.5	3.5	3.9	3.4
COMPONENTS:	(M)	(M)	(M)	(M)
Hydrogen	0.0000	0.0000	0.0000	0.0000
Carbon monoxide	0.0013	0.0013	0.0000	0.0000
Carbon dioxide	0.0000	0.0000	0.0000	0.0000
Methyl iodide	4.6327	4.1389	0.0000	0.0000
Methyl acetate	0.5347	0.4103	0.0000	0.0000
Methanol	0.0000	0.0000	0.0000	0.0000
Water	0.3461	0.2301	0.0000	0.0000
Acetic acid	10.8065	5.4654	3.4717	3.4717
Rhodium cat.	0.0417	0.0000	0.0000	0.0000
Lithium iodide	3.2222	0.0000	0.0000	0.0000
TOTAL M-FLOW:	19.5852	10.2460	3.4717	3.4717
TOTAL Q-FLOW:	-90653	-42181	-25171	-26191

STREAM/COMPONENTS

M : kg/s　　Q : kW

STREAM NO.: STREAM NAME: TO EQUIPMENT NO.:	15 product R27	16* product R28	17 product R30/R31	18* product R30/R31	19 product R30/R31
Temperature [°C]	50.0	50.0	40.0	40.0	40.0
Pressure [bar]	3.4	3.4	2.2	2.2	2.2
COMPONENTS:	(M)	(M)	(M)	(M)	(M)
Acetic acid	3.4747	3.4747	3.4747	3.4747	3.4747
Iron ion	trace	trace	none	none	none
Iodide ion	trace	trace	trace	trace	trace
TOTAL M-FLOW:	3.4747	3.4747	3.4747	3.4747	3.4747
TOTAL Q-FLOW:	-26214	-26214	-26289	-26289	-26289

STREAM NO.: STREAM NAME: TO EQUIPMENT NO.:	20 product R30	21* product R31	22 acetic acid product	23* acetic acid product
Temperature [°C]	40.0	40.0	30.0	30.0
Pressure [bar]	2.2	2.2	1.0	1.0
COMPONENTS:	(M)	(M)	(M)	(M)
Acetic acid	3.4747	3.4747	3.4747	3.4747
Iron ion	none	none	none	none
Iodide ion	trace	trace	none	none
TOTAL M-FLOW:	3.4747	3.4747	3.4747	3.4747
TOTAL Q-FLOW:	-26289	-26289	-26362	-26362

* Streams without flow in the situation given in the Autocad flowsheet (appendix B)

Stream 15 to 23 are not calculated by Chemcad (except for the heat load), but are based on the calculations done on the resinbeds (appendix D7).

The values of the indications trace and none are as follows:
Iron ion trace:　　1 ppmwt maximum
Iron ion none:　　25 ppbwt maximum
Iodide ion trace:　5 ppmwt maximum
Iodide ion trace:　0 ppmwt maximum

STREAM/COMPONENTS

M : kg/s   Q : kW

STREAM NO.: STREAM NAME : TO EQUIPMENT NO. :	24 bottom flash H15	25 bottom flash P23	26 recycle R3	27 top tower C19	28 top tower H22
Temperature [°C]	160.0	121.5	123.1	131.3	232.3
Pressure [bar]	3.5	3.5	31	3.3	31
COMPONENTS:	(M)	(M)	(M)	(M)	(M)
Hydrogen	0.0000	0.0000	0.0000	0.0000	0.0000
Carbon monoxide	0.0000	0.0000	0.0000	0.0013	0.0013
Carbon dioxide	0.0000	0.0000	0.0000	0.0000	0.0000
Methyl iodide	0.4938	0.4938	0.4939	4.1389	4.1389
Methyl acetate	0.1244	0.1244	0.1244	0.4103	0.4103
Methanol	0.0000	0.0000	0.0000	0.0000	0.0000
Water	0.1160	0.1160	0.1160	0.2301	0.2301
Acetic acid	5.3411	5.3411	5.3411	1.9937	1.9937
Rhodium cat.	0.0417	0.0417	0.0417	0.0000	0.0000
Lithium iodide	3.2222	3.2222	3.2222	0.0000	0.0000
TOTAL M-FLOW:	9.3392	9.3592	9.3592	6.7743	6.7743
TOTAL Q-FLOW:	-48472	-49126	-49101	-18502	-17651

STREAM NO.: STREAM NAME: TO EQUIPMENT NO.:	29 recycle R3	30 top reactor H7	31 top reactor V9	32 bottom flash H13	33 bottom flash P21
Temperature [°C]	71	192.2	100.0	100.0	90.0
Pressure [bar]	30.5	30.5	29.5	29.5	29.5
COMPONENTS:	(M)	(M)	(M)	(M)	(M)
Hydrogen	0.0000	0.0002	0.0002	0.0000	0.0000
Carbon monoxide	0.0013	1.3221	1.3221	0.0014	0.0014
Carbon dioxide	0.0000	0.0051	0.0051	0.0000	0.0000
Methyl iodide	4.1389	3.1494	3.1494	2.2303	2.2303
Methyl acetate	0.4103	0.1603	0.1603	0.1345	0.1345
Methanol	0.0000	0.0000	0.0000	0.0000	0.0000
Water	0.2301	0.0692	0.0692	0.0655	0.0655
Acetic acid	1.9937	1.5712	1.5712	1.4863	1.4863
Rhodium cat.	0.0000	0.0000	0.0000	0.0000	0.0000
Lithium iodide	0.0000	0.0000	0.0000	0.0000	0.0000
TOTAL M-FLOW:	6.7743	6.2775	6.2775	3.9180	3.9180
TOTAL Q-FLOW:	-21281	-16856	-18873	-12956	-13014

STREAM/COMPONENTS

M : kg/s   Q : kW

STREAM NO.: STREAM NAME: TO EQUIPMENT NO.:	34 recycle R3	35 total recycle R3	36 top flash E12	37 top flash T20	38 demiwater P5
Temperature [°C]	90.1	100.8	100.0	66.5	20.0
Pressure [bar]	31.0	30.5	29.5	10.0	7.0
COMPONENTS:	(M)	(M)	(M)	(M)	(M)
Hydrogen	0.0000	0.0000	0.0002	0.0002	0.0000
Carbon monoxide	0.0014	0.0027	1.3207	1.3207	0.0000
Carbon dioxide	0.0000	0.0000	0.0051	0.0051	0.0000
Methyl iodide	2.2303	6.8630	0.9191	0.9191	0.0000
Methyl acetate	0.1345	0.6692	0.0258	0.0258	0.0000
Methanol	0.0000	0.0000	0.0000	0.0000	0.0000
Water	0.0655	0.4116	0.0037	0.0037	0.0021
Acetic acid	1.4863	8.8811	0.0849	0.0849	0.0000
Rhodium cat.	0.0000	0.0417	0.0000	0.0000	0.0000
Lithium iodide	0.0000	3.2222	0.0000	0.0000	0.0000
TOTAL M-FLOW:	3.9180	20.0315	2.3595	2.3595	0.0021
TOTAL Q-FLOW:	-13014	-83396	-5917	-6046	-33

STREAM NO.: STREAM NAME: TO EQUIPMENT NO.:	39 demiwater T20	40 offgas flare
Temperature [°C]	66.5	30.7
Pressure [bar]	10.2	10.0
COMPONENTS:	(M)	(M)
Hydrogen	0.0000	0.0002
Carbon monoxide	0.0000	1.3205
Carbon dioxide	0.0000	0.0051
Methyl iodide	0.0000	0.0000
Methyl acetate	0.0000	0.0000
Methanol	0.0000	0.0385
Water	0.0021	0.0000
Acetic acid	0.0000	0.0000
Rhodium cat.	0.0000	0.0000
Lithium iodide	0.0000	0.0000
TOTAL M-FLOW:	0.0021	1.3643
TOTAL Q-FLOW:	-33	-5651

STREAM/COMPONENTS
M : kg/s   Q : kW

STREAM NO.: STREAM NAME: TO EQUIPMENT NO.:	41 regener. liq. P31	42 regener. liq. R28/R29	43 regener. liq. R28	44 regener. liq. R29	45 reg.liq.+ iron waste tank
Temperature [°C]	N.N.F.	N.N.F.	N.N.F.	N.N.F.	N.N.F.
Pressure [bar]					
COMPONENTS:	(M)	(M)	(M)	(M)	(M)
Regeneration liquid					
Acetic acid					
Iron ion					
Iodide ion					
TOTAL M-FLOW:					
TOTAL Q-FLOW:					

STREAM NO.: STREAM NAME: TO EQUIPMENT NO.:	46 reg.liq. + iron waste tank	47 reg.liq. + iron waste tank	48 regener. liq. P32	49 regener. liq. R30/R31	50 regener. liq. R30
Temperature [°C]	N.N.F.	N.N.F.	N.N.F.	N.N.F.	N.N.F.
Pressure [bar]					
COMPONENTS:	(M)	(M)	(M)	(M)	(M)
Regeneration liquid					
Water					
Acetic acid					
Iron ion					
Iodide ion					
TOTAL M-FLOW:					
TOTAL Q-FLOW:					

STREAM NO.: STREAM NAME: TO EQUIPMENT NO.:	51 regener. liq. R31	52 regliq+iodide waste tank	53 regliq+iodide waste tank	54 regliq+iodide waste tank
Temperature [°C]	N.N.F.	N.N.F.	N.N.F.	N.N.F.
Pressure [bar]				
COMPONENTS:	(M)	(M)	(M)	(M)
Regeneration liquid				
Acetic acid				
Iron ion				
Iodide ion				
TOTAL M-FLOW:				
TOTAL Q-FLOW:				

STREAM/COMPONENTS
M : kg/s   Q : kW

STREAM NO.: STREAM NAME: TO EQUIPMENT NO.:	55 cool water P1	56 cool water P2/coolers	57 cool water H13/H24	58 cool water H24	59 cool water river
COMPONENTS:	(M)	(M)	(M)	(M)	(M)
Temperature [°C]	20.0	20.0	20.0	20.0	39.7
Pressure [bar]	1.0	1.0	1.0	1.0	1.0
COMPONENTS:	(M)	(M)	(M)	(M)	(M)
Water	31.6667	31.6667	1.4861	0.7778	0.7778
TOTAL M-FLOW:	31.6667	31.6667	1.4861	0.7778	0.7778
TOTAL Q-FLOW:	-502860	-502860	-23599	-12364	-12127

STREAM NO.: STREAM NAME: TO EQUIPMENT NO.:	60 cool water H13	61 cool water river	62 cool water P2	63 cool water H22/H7/E11	64 cool water H22
Temperature [°C]	20.0	39.8	20.0	20.3	20.3
Pressure [bar]	1.0	1.0	1.0	10.0	10.0
COMPONENTS:	(M)	(M)	(M)	(M)	(M)
Water	0.7083	0.7083	2.9583	2.9583	1.3528
TOTAL M-FLOW:	0.7083	0.7083	2.9583	2.9583	1.3528
TOTAL Q-FLOW:	-11268	-11083	-47017	-46974	-21480

STREAM NO.: STREAM NAME: TO EQUIPMENT NO.:	65 MP steam H8/by-prod.	66 MP steam by-product	67 MP steam H8	68 MP cond. E11	69 cool water river
Temperature [°C]	180.2	180.2	180.2	162.0	20.3
Pressure [bar]	10.0	10.0	10.0	10.0	10.0
COMPONENTS:	(M)	(M)	(M)	(M)	(M)
Water	1.3528	0.3044	1.0484	1.0484	0.7444
TOTAL M-FLOW:	1.3528	0.3044	1.0484	1.0484	0.7444
TOTAL Q-FLOW:	-17850	-4016.3	-13834	-16024	-11821

STREAM NO.: STREAM NAME : TO EQUIPMENT NO.:	70 MP steam by-product	71 MP steam by-product	72 cool water E11	73 cool water E11	74 cool water stream 79
Temperature [°C]	181.9	181.4	20.3	98.6	98.8
Pressure [bar]	10.0	10.0	10.0	10.0	1.0
COMPONENTS:	(M)	(M)	(M)	(M)	(M)
Water	0.7444	1.0488	0.8611	1.9095	1.9095
TOTAL M-FLOW:	0.7444	1.0488	0.8611	1.9095	1.9095
TOTAL Q-FLOW:	-9803.9	-13820	-13673	-29697	-29697

STREAM NO.: STREAM NAME: TO EQUIPMENT NO.:	75 cool water H15/H26	76 cool water H15	77 cool water river	78 cool water H26	79 cool water stream 74
Temperature [°C]	20.0	20.0	39.4	20.0	20.0
Pressure [bar]	1.0	1.0	1.0	1.0	1.0
COMPONENTS:	(M)	(M)	(M)	(M)	(M)
Water	27.2222	8.0556	8.0556	19.1667	6.2935
TOTAL M-FLOW:	27.2222	8.0556	8.0556	19.1667	6.2935
TOTAL Q-FLOW:	-432280	-128040	-127130	-304360	-99993

STREAM NO.: STREAM NAME: TO EQUIPMENT NO.:	80 cool water river	81 cool water H26	82 cool water river
Temperature [°C]	38.4	20.0	39.0
Pressure [bar]	1.0	1.0	1.0
COMPONENTS:	(M)	(M)	(M)
Water	8.2030	12.8731	12.8731
TOTAL M-FLOW:	8.2030	12.8731	12.8731
TOTAL Q-FLOW:	-129510	-204540	-203260

STREAM/COMPONENTS

M : kg/s   Q : kW

STREAM NO.: STREAM NAME: TO EQUIPMENT NO.:	83* acetic acid pump	84* acetic acid R3	85* cat+promoter pump	86* cat+promoter R3	90** recycle+CO R3
Temperature [°C]	168.2		20.0		82.3
Pressure [bar]	3.9	30.5	1.0	30.5	30.5
COMPONENTS:	(M)	(M)	(M)	(M)	(M)
Hydrogen	N.N.F.	N.N.F.	N.N.F.	N.N.F.	
Carbon monoxide					
Carbon dioxide					
Methyl iodide					
Methyl acetate					
Methanol					
Water					
Acetic acid					
Rhodium cat.					
Lithium iodide					
TOTAL M-FLOW:					
TOTAL Q-FLOW:					

*   Only in the Autocad flowsheet, not in Chemcad.
**   Only in the Chamcad flowsheet, summation of stream 35 and 8.

Mass and energy balance

IN		Forward		Back	OUT	
M	Q	M		M	M	Q
		Q		Q		
1.8900	-14119		**1**			
	3					
		1.8900				
		-14116				
			2		1.3643	-5651
			40			
		2.8852				
		-14511				
		2.8873	**4**		0.0021	
		-14544			-33	
0.0021	-33		**38**			
	0					
0.7778	-12364		**58**		0.7778	-12127
		2.8873				
		-14608				
	8					
		2.8873				
		-14600				
		6.2775	**30**			
		-16856				
		22.9193	**7**			
		-97996				
2.9439	-11942	19.5852	**8**			
		-92625				

Stream labels on diagram: 1, 2, 40, 3, 37, 4, 39, 38, 4, 58, 59, 5, 6, 35, 30, 7, 8, 9, 30, 35, 37

Units: P 4, T 20, P 5, H 24, P 25, R 3

Mass and energy balance continued

IN		Forward	Back	OUT	
M	Q	M / Q	M / Q	M	Q
		−218			
		19.5852 / −92843			
		1.0484 / −16024			
		19.5852 / −90653			
			0.8611 / −13673		
		1.9095 / −29697			
		1.9095 / −29697			
6.2935	−99993			8.2030	−129510
		10.2460 / −42181			
		9.3392 / −48472			
		6.7743 / −18502			
		3.4717 / −25171			
12.8731	−204540			12.8731	−203260
				3.4717	−26191

Diagram units and streams: E 6, H 8, E 11, V 10, T 14, H 26

Stream labels: 30, 9, 35, 37, 10, 67, 68, 11, 72, 73, 74, 79, 80, 12, 24, 27, 13, 81, 82, 14

Bottom arrows: 30 27 24   67 72 35 37

Mass and energy balance continued

IN		Forward				Back	OUT	
M	Q	M / Q				M / Q	M	Q
8.0556	-128040		76 → H 15 → 77				8.0556	-127130
		9.3392						
		-49126						
	25		25 ↓					
			P 23					
	850		26 →	35		20.0315		
						-83396		
			27 → C 19			9.3392		
						-49101		
		6.7743	28 ↓	67		1.0484		
		-17651				-13834		
			64 →			1.3528		
		1.3528	H 22 → 65			-21480		
		-17850		66 ↓				
		0.3044						
		-4016.3	29 →			6.7743		
			30			-21281		
			69 →			0.7444		
		0.7444	H 7 → 70			-11821		
		-9803.9		71 →			1.0488	-13820
		6.2775	31 ↓					
		-18873						
2.9583	-47017		62 → P 2 → 63			2.9583		
	4					-46974		
			31 ↓	34 37				

Mass and energy balance continued

IN		Forward
M	Q	M
		Q
		2.3595
		-5917.4
		3.9180
		-12956
0.7083	-11268	
		3.9180
		-13014
	1	
	-129	
36.5026	-528772	Total

Back	OUT	
M	M	Q
Q		
	0.7083	-11083
3.9180		
-13014		
2.3595		
-6046.3		
Total	36.5026	-528772

Diagram elements: 31, V 9, 36, 32, 60, H 13, 61, 33, P 21, 34, 36, E 12, 37, 34 37

Equipmentlist for reactors, columns and vessels

Equipment NO.	R3	T14	T20	V9	V10
Name : Type :	Reactor Bubble column	Tower Distillation column	Gasabsorber Absorber	Flash Gas flash horizontal	Flash Liq. flash vertical
Abs.pressure [bar] :	30	3.3/3.9	10.0/10.2	29.5	3.5
Temp. [°C] :	192.2	133.5/ 168.2	30.7/67.6	100	160
Volume [m³]: Diameter [m] : L or H [m] :	24.4 1.75 10.2	1.83 35.2	0.46 7.9	1.87 0.76 4.2	6.67 1.41 4.2
Filling : Trays (+ theor.number): Packing : Cat. type : Cat. form :		Valve trays 41	Valve trays, 9		
Special construction- materials	Hastelloy C	Hastelloy C	Hastelloy C	Hastelloy C	Hastelloy C
Number in - series : - parallel :					
Other :					

Equipmentlist for reactors, columns and vessels

Equipment NO.	V18
Name : Type :	Topaccumulator horizontal
Abs.pressure [bar] :	3.3
Temp. [°C] :	131.3
Volume [m^3]: Diameter [m] : L or H [m] :	37.96 2.00 12.1
filling : Trays (+ theor.number): Packing : Cat. type : Cat. form :	
Special construction- materials	Hastelloy C
Number in - series : - parallel :	
Other :	

Equipment list for heat exchangers

Equipment NO.	H7	H8	H13	H15	H16
Name : Type :	Heat exchanger Float.head condenser	Heat exchanger Float.head condenser	Heat exchanger U-tube cooler	Heat exchanger U-tube cooler	Condenser
Medium - tubes : - shell :	water/ steam gas from reactor	steam liquid from reactor	fluid from gas flash water	fluid from liquid flash water	fluid from column top water
Capacity transferred heat [kW]:	2009.8	2199.6	58.7	652.8	8503.0
Heat transfer area [m^2]:	592.6	1429.9	1.7	11.9	170
Number - series : - parallel :	1 1	1 1	1 1	1 1	1 1
Pressure [bar]: - tubes : - shell :	10 30	10 4	29.5 1	3.5 1	3.3 1
Temp. in/out [°C] - tubes : - shell :	20.3/181.9 192.2/100	180.2/161.9 150.5/160	100/90 20/39.8	160/121.5 20/39.4	131.3/131.3 20/40
Special construction-materials	Hastelloy C	Hastelloy C	Hastelloy C	Hastelloy C	
Other :					

Equipment list for heat exchangers

Equipment NO.	H17	H22	H24	H26
Name : Type :	Reboiler	Heat exchanger Float.head cooler	Heat exchanger U-tube cooler	Heat exchanger U-tube horizontal
Medium - tubes : - shell :	acetic acid + methyliodide MP steam	recycle to reactor water/steam	methanol from absorber water	water acetic acid
Capacity transferred heat [kW]:	7018.4	3647.8	64.0	1021.5
Heat transfer area [m²]:	877	236.6	4.1	33.5
Number - series : - parallel :	1 1	1 1	1 1	1 1
Pressure [bar]: - tubes : - shell :	3.9 10	31 10	10.2 1	1 3.9
Temp. in/out [°C] - tubes : - shell :	168.2/168.2 180/180	232.3/71 20.3/180.2	67.6/57 20/39.7	20/39.0 168.2/50
Special construction-materials		Hastelloy C	Hastelloy C	Hastelloy C
Other :				

Equipmentlist for pumps, blowers and compressors

Equipment NO.	P1	P2	P4	P5	P21
Name : Type :	Pump Centrifugal	Pump Centrifugal	Pump Centrifugal	Pump Centrifugal	Pump Centrifugal
Fluid to be pumped :	cooling water	cooling water	methanol	process water	process fluid
Capacity : [kg/s]	16.03	2.96	1.89	0.0021	3.90
Density [kg/m^3]:	998	998	793	998	1357
Suction-/work pres. (abs.) [bar] :		1/10	1/10	7/10.2	29.5/31
Temp. In/out [°C] :	20/20	20/20.3	20/20.6	20/20.1	90/90.1
Power [kW] - eff. : - pract. :		0.75 3.56	0.75 2.86	0.75 0.000898	0.75 0.575
Number - series : - parallel :	1 1	1 1	1 1	1 1	1 1
Special construction-materials					Hastelloy C
Other :					

Equipmentlist for pumps, blowers and compressors

Equipment NO.	P23	P25	P31	P32	C19
Name : Type :	Pump Centrifugal	Pump Centrifugal	Pump Centrifugal	Pump Centrifugal	Compressor Axial
Fluid to be pumped :	process recycle	methanol from T23	regeneration for resin bed	regeneration for resin bed	recycle gas
Capacity : [kg/s]	9.35	2.89	n.n.f.	n.n.f.	6.79
Density [kg/m^3] :	1282	950.7			
Suction-/work pres. (abs.) [bar] :	3.5/31	10.2/30.5			3.5/31
Temp. In/out [°C] :	121.5/123	57/58			131/232
Power [kW] efficiency : - actual :	0.75 26.76	0.75 8.22			0.75 891.3
Number - series : - parallel :	1 1	1 1	1 1	1 1	1 1
Special construction-materials	Hastelloy C	Hasteloy C			
Other :					

Equipmentlist for pumps, blowers and compressors

Equipment NO.	E6	E12
Name : Type :	Expander Axial	Expander Axial
Fluid to be pumped :	fluid from reactor	offgas from V9
Capacity : [kg/s]*	19.65	2.36
Density [kg/m³]:		
Suction-/work pres. (abs.) [bar] :	30/4	29.5/10
Temp. In/out [°C] :	192/150.5	100/66.5
Power [kW] efficiency : - pract. :	0.75 -290.89	0.75 -171.83
Number - series : - parallel :	1 1	1 1
Special construction- materials		
Other :		

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Specification form Reactor

Equipmentnumber: R-3			
General properties			
Function	:	Carbonylation of methanol with carbon monoxide	
Type of reactor	:	Bubble column	
Type of reaction	:	Exotherm	
Cooling	:	Adiabatic operation	
Diameter	:	1.75	[m]
Height/Diameter	:	5.8	[-]
Volume	:	25.4	[m^3]
Gas distribution	:	Single nozzle sparger	
Materials of construction	:	Hastelloy C	
Wall thickness	:	30	[mm]
Operational conditions			
Temperature	:	192	[°C]
Pressure in/out	:	30.5 / 30	[bar]
Heat of reaction	:	-121.4	[kJ/mol]
Residence time liquid	:	1006	[s]
Residence time gas	:	150	[s]
Conversion MeOH to HOAc	:	100 %	
Conversion CO to HOAc	:	58.7 %	
Overall conversion CO	:	58.8 %	
Catalyst			
Type	:	Homogeneous catalyst	
Catalyst phase	:	Liquid	
Catalyst	:	$Rh(CO)_2I_2$	
Catalyst stabiliser	:	LiI	
Solvent	:	HOAc	
Amount in reactor:			
$Rh(CO)_2I_2$	:	42	[kg]
LiI	:	3222.2	[kg]

Specification form tower

Equipment number T14

General properties

Function = distillation
Type of tower = trays
Type of tray = valve
Number of trays
- theoretic = 41
- actual = 51
- Feed tray(act) = 6
Tray spacing(HETS) = 0.61 [m] Material trays :high alloy stainless steel
Diameter tower = 1.83 [m] Tower height :35.2 [m]
Material tower = high alloy stainless steel Hastelloy C
Heating = reboiler

Process conditions				
	Feed	Top	Bottoms	Reflux ratio
Temp. [°C]	160	133.5	168.2	3.54
Pres. [bar]	3.5	3.3	3.9	
Density [kg/m^3]				
Mass stream [kg/s]	10.29	6.82	3.47	
	wt%	wt%	wt%	wt%
Composition				
Hydrogen	0.000	0.000	0.000	
Carbon monoxide	0.010	0.019	0.000	
Carbon dioxide	0.000	0.000	0.000	
Methyl iodide	40.314	60.845	0.000	
Methyl acetate	3.994	6.028	0.000	
Methanol	0.000	0.000	0.000	
Water	2.238	3.378	0.000	
Acetic Acid	53.444	29.730	100.000	
Rhodium	0.000	0.000	0.000	
Lithium iodide	0.000	0.000	0.000	

Design	
Number of valves :350	
Tray area : 2.6 [m]	
Weir height : 0.09 [mm]	
Diameter downcomer	
side width: 0.254 [mm]	

Specification form tower

Equipment number T20					
General properties					

Function = absorption
Type of tower = trays
Type of tray = valve
Number of trays
- theoretic = 9
- pract. = 13
- Feed tray(pract) = 1/13
Tray spacing(HETS) =0.61 [m] ----- Material trays :high alloy stainless steel
Diameter tower = 0.457 [m] -----Tower height :7.9 [m]
Material tower = high alloy stainless steel, Hastelloy C
Heating = none

Process conditions

	Feed	Feed	Top	Bottoms	Reflux ratio
Temp. [°C]	20.6	66.5	30.7	67.6	
Pres. [bar]	10.0	10.2	10.0	10.2	
Demsity [kg/m^3]					
Massstream [kg/s]	1.89	2.36	1.37	3.47	
	wt%		wt%	wt%	wt%
Composition					
Hydrogen	0.000	0.010	0.017	0.000	
Carbon monoxid	0.000	55.990	96.800	0.007	
Carbon dioxide	0.000	0.216	0.373	0.000	
Methyl iodide	0.000	38.925	0.000	31.851	
Methyl acetate	0.000	1.088	0.000	0.891	
Methanol	100.000	0.000	2.810	64.164	
Water	0.000	0.157	0.000	0.128	
Acetic Acid	0.000	3.615	0.000	2.958	
Rhodium	0.000	0.000	0.000	0.000	
Lithium iodide	0.000	0.000	0.000	0.000	

Design

Number ofvalves :36
Tray area : 0.164 [m]
Weir height   : 0.09 [mm]
Diameter downcomer
side width: 0.102   [mm]

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Specification form heat exchanger

Equipment number: H15	Number series:1 Number parallel :1

General properties

Type	: cooler
Design	: U-tube
Position	: horizontal

Capacity   :652.8   [kW]   (calculated)
Heat transfer area   :11.9   [m^2]   (calculated)
Overall heat transfer coefficient   :471.6   [W/m^2.K] (global)
Logarithmic temperature diff. (LMTD)   :110.7   [°C]

Number of passes tube side   :2
Number of passses shell side   :1

Correction factor LMTD (min. 0.75)   :0.99
True LMTD   :109.6   [°C]

Operating conditions

		Shell side	Tube side
Fluid		water	recycle (acetic acid, cat., Mel)
Mass stream	[kg/s]	8.06	9.36
Mean specific heat	[kJ/kg.°C]	4.2	1.89
Temperature IN Temperature OUT	[°C] [°C]	20.0 39.4	160.0 121.5
Pressure	[bar]	1	3.5
Material		Hastelloy C	Hastelloy C

Specification form centrifugal pump

Equipment number :P23	

Duty :recycle acetic acid and catalyst to reactor
Type :single stage centrifugal pump
Number :1

Physical properties of the fluid

Fluid   :acetic acid and catalyst
Temperature (T)   :121.5   [°C]
Density (ρ) :1281.6 [kg/m^3]
Viscosity (μ) :5.45*10^{-4} [N.s/m^2]
Vapor pressure (p_d) :1.4   [bar] at temperature (T) : 121.5[°C]

Power

Capacity   (F_v)   :7.32*10^{-3} [m^3/s]
Suction pressure(p_z) :3.5   [bar]
Work pressure (p_p) :31   [bar]

Theoretical power :20.12   [kW] { $= F_v.(p_p - p_z).10^2$ }

Efficiency   :0.75   [ ]
Actual power   :26.76   [kW]

Appendix G   Process safety

G1: DOW Fire & Explosion index classifications

1. Reactor
2. Catalyst recovery/distillation
3. Offgas treatment
4. Purification

The sections are made according to figure 2.2.

G2: Hazop analysis of the reactor

FIRE AND EXPLOSION INDEX ◆ Dow

Exhibit "A"

LOCATION		DATE

PLANT	UNIT	CHARGE
Acetic Acid from methanol	Reactor	

MATERIALS AND PROCESS

MATERIALS

Methanol / Carbon Monoxide   Water / Carbon dioxide / Hydrogen

CATALYSTS   **SOLVENTS**

Rhodium iodide   Acetic acid / Methyl iodide / Methyl acetate / Lithium i.

	PENALTY	PENALTY USED	
MATERIAL FACTOR (SEE TABLE I APPENDIX A) ⟶			14
1. GENERAL PROCESS HAZARDS (SEE TABLE II)			
BASE FACTOR ⟶	1.00	1.00	
A. EXOTHERMIC REACTIONS (FACTOR .30 to 1.25)		0.50	
B. ENDOTHERMIC REACTIONS (FACTOR .20 to .40)		—	
C. MATERIAL HANDLING & TRANSFER (FACTOR .25 to .85)		0.50	
D. ENCLOSED PROCESS UNITS (FACTOR .30 to .90)		0.60	
E. ACCESS	.35	—	
F. DRAINAGE (FACTOR .25 to .50)		—	
GENERAL PROCESS HAZARD FACTOR (F_1) ⟶		2.60	
2. SPECIAL PROCESS HAZARDS			
BASE FACTOR ⟶	1.00	1.00	
A. PROCESS TEMPERATURE (USE ONLY ONE)			
1. ABOVE FLASH POINT	.30	0.30	
2. ABOVE BOILING POINT	.60	0.60	
3. ABOVE AUTOIGNITION	.75	—	
B. LOW PRESSURE (SUB-ATMOSPHERIC)	.50	—	
C. OPERATION IN OR NEAR FLAMMABLE RANGE		—	
1. TANK FARM STORAGE FLAMMABLE LIQUIDS	50	—	
2. PROCESS UPSET OR PURGE FAILURE	.30	—	
3. ALWAYS IN FLAMMABLE RANGE	.80	—	
D. DUST EXPLOSION (FACTOR .25 to 2.00)(SEE TABLE III)		—	
E. PRESSURE (SEE FIGURE 2)		0.60	
F. LOW TEMPERATURE (FACTOR .20 to .50)		—	
G. QUANTITY OF FLAMMABLE MATERIAL		—	
1. LIQUIDS OR GASES IN PROCESS (SEE FIG. 3)		—	
2. LIQUIDS OR GASES IN STORAGE (SEE FIG. 4)		—	
3. COMBUSTIBLE SOLIDS IN STORAGE (SEE FIG. 5)		—	
H. CORROSION AND EROSION (FACTOR .10 to .75)		0.50	
J. LEAKAGE — JOINTS AND PACKING (FACTOR .10 to 1.50)		0.30	
K. USE OF FIRED HEATERS (SEE FIG. 6)		—	
L. HOT OIL HEAT EXCHANGE SYSTEM (FACTOR .15 to 1.15)(SEE TABLE IV)		—	
M. ROTATING EQUIPMENT. PUMPS. COMPRESSORS	.50	0.50	
SPECIAL PROCESS HAZARD FACTOR (F_2) ⟶		3.80	
UNIT HAZARD FACTOR ($F_1 \times F_2$ F_3) ⟶		9.88	
FIRE AND EXPLOSION INDEX ($F_3 \times MF$) F & EI) ⟶			138.32

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FIRE AND EXPLOSION INDEX   ◆DOW◆

Exhibit "A"

LOCATION		DATE

PLANT	UNIT	CHARGE
Acetic acid from methanol	cat. recovery /distillation	

MATERIALS AND PROCESS

MATERIALS
methyl iodide / methyl acetate / lithium iodide.

CATALYSTS	SOLVENTS
Rhodium iodide	acetic acid

MATERIAL FACTOR (SEE TABLE I APPENDIX A) ————————————————————→			12

1. GENERAL PROCESS HAZARDS (SEE TABLE II)	PENALTY	PENALTY USED	
BASE FACTOR ————————————————————→	1.00	1.00	
A. EXOTHERMIC REACTIONS (FACTOR .30 to 1.25)		—	
B. ENDOTHERMIC REACTIONS (FACTOR .20 to .40)		—	
C. MATERIAL HANDLING & TRANSFER (FACTOR .25 to .85)		—	
D. ENCLOSED PROCESS UNITS (FACTOR .30 to .90)		0.60	
E. ACCESS	.35	—	
F. DRAINAGE (FACTOR .25 to .50)		—	
GENERAL PROCESS HAZARD FACTOR (F_1) ————————————→		1.60	

2. SPECIAL PROCESS HAZARDS			
BASE FACTOR ————————————————————→	1.00	1.00	
A. PROCESS TEMPERATURE (USE ONLY ONE)			
1. ABOVE FLASH POINT	.30	0.30	
2. ABOVE BOILING POINT	.60	0.60	
3. ABOVE AUTOIGNITION	.75	—	
B. LOW PRESSURE (SUB-ATMOSPHERIC)	.50	—	
C. OPERATION IN OR NEAR FLAMMABLE RANGE		—	
1. TANK FARM STORAGE FLAMMABLE LIQUIDS	50	—	
2. PROCESS UPSET OR PURGE FAILURE	.30	—	
3. ALWAYS IN FLAMMABLE RANGE	.80	—	
D. DUST EXPLOSION (FACTOR .25 to 2.00)(SEE TABLE III)		—	
E. PRESSURE (SEE FIGURE 2)		0.25	
F. LOW TEMPERATURE (FACTOR .20 to .50)		—	
G. QUANTITY OF FLAMMABLE MATERIAL		.	
1. LIQUIDS OR GASES IN PROCESS (SEE FIG. 3)		—	
2. LIQUIDS OR GASES IN STORAGE (SEE FIG. 4)		—	
3. COMBUSTIBLE SOLIDS IN STORAGE (SEE FIG. 5)		—	
H. CORROSION AND EROSION (FACTOR .10 to .75)		0.50	
J. LEAKAGE – JOINTS AND PACKING (FACTOR .10 to 1.50)		0.30	
K. USE OF FIRED HEATERS (SEE FIG. 6)		—	
L. HOT OIL HEAT EXCHANGE SYSTEM (FACTOR .15 to 1.15)(SEE TABLE IV)		.	
M. ROTATING EQUIPMENT, PUMPS, COMPRESSORS	.50	0.50	
SPECIAL PROCESS HAZARD FACTOR (F_2) ————————————→		2.45	
UNIT HAZARD FACTOR ($F_1 \times F_2$ F_3) ————————————→		5.52.	
FIRE AND EXPLOSION INDEX ($F_3 \times MF$) F & EI) ————————————→			66.24
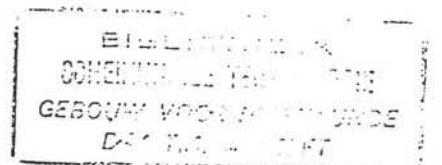
7

FIRE AND EXPLOSION INDEX ◆DOW◆

Exhibit "A"

LOCATION		DATE

PLANT	UNIT	CHARGE
Acetic acid from methanol	off gas treatment	

MATERIALS AND PROCESS

MATERIALS

carbon monoxide / carbon dioxide / hydrogen / methanol / methyl iodide

CATALYSTS ___

SOLVENTS methanol

		PENALTY	PENALTY USED	
MATERIAL FACTOR (SEE TABLE I APPENDIX A) ———————→				16
1. GENERAL PROCESS HAZARDS (SEE TABLE II)				
BASE FACTOR ————————→		1.00	1.00	
A. EXOTHERMIC REACTIONS (FACTOR .30 to 1.25)			—	
B. ENDOTHERMIC REACTIONS (FACTOR .20 to .40)			—	
C. MATERIAL HANDLING & TRANSFER (FACTOR .25 to .85)			—	
D. ENCLOSED PROCESS UNITS (FACTOR .30 to .90)			0.60	
E. ACCESS		.35	—	
F. DRAINAGE (FACTOR .25 to .50)			—	
GENERAL PROCESS HAZARD FACTOR (F_1) ————————→			1.60	
2. SPECIAL PROCESS HAZARDS				
BASE FACTOR ————————→		1.00	1.00	
A. PROCESS TEMPERATURE (USE ONLY ONE)			—	
1. ABOVE FLASH POINT		.30	0.30	
2. ABOVE BOILING POINT		.60	—	
3. ABOVE AUTOIGNITION		.75		
B. LOW PRESSURE (SUB-ATMOSPHERIC)		.50	—	
C. OPERATION IN OR NEAR FLAMMABLE RANGE			—	
1. TANK FARM STORAGE FLAMMABLE LIQUIDS		.50	—	
2. PROCESS UPSET OR PURGE FAILURE		.30	—	
3. ALWAYS IN FLAMMABLE RANGE		.80	—	
D. DUST EXPLOSION (FACTOR .25 to 2.00)(SEE TABLE III)			—	
E. PRESSURE (SEE FIGURE 2)			0.35	
F. LOW TEMPERATURE (FACTOR .20 to .50)				
G. QUANTITY OF FLAMMABLE MATERIAL				
1. LIQUIDS OR GASES IN PROCESS (SEE FIG. 3)				
2. LIQUIDS OR GASES IN STORAGE (SEE FIG. 4)				
3. COMBUSTIBLE SOLIDS IN STORAGE (SEE FIG. 5)				
H. CORROSION AND EROSION (FACTOR .10 to .75)			0.1	
J. LEAKAGE – JOINTS AND PACKING (FACTOR .10 to 1.50)			0.3	
K. USE OF FIRED HEATERS (SEE FIG. 6)			—	
L. HOT OIL HEAT EXCHANGE SYSTEM (FACTOR .15 to 1.15)(SEE TABLE IV)			—	
M. ROTATING EQUIPMENT, PUMPS, COMPRESSORS		.50	—	
SPECIAL PROCESS HAZARD FACTOR (F_2) ————————→			2.05	
UNIT HAZARD FACTOR ($F_1 \times F_2 \quad F_3$) ————————→			3.28	
FIRE AND EXPLOSION INDEX ($F_3 \times MF$) F & EI ————————→				52.48

FORM C-22380 PRINTED R-10-80 (471-036)

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FIRE AND EXPLOSION INDEX ◆DOW◆

Exhibit "A"

LOCATION	DATE

PLANT	UNIT	CHARGE
Acetic Acid from methanol	Purification / resin bed.	

MATERIALS AND PROCESS

MATERIALS
acetic acid / iodies / metals

CATALYSTS	SOLVENTS

MATERIAL FACTOR (SEE TABLE I APPENDIX A) ⟶		10

1. GENERAL PROCESS HAZARDS (SEE TABLE II)	PENALTY	PENALTY USED	
BASE FACTOR ⟶	1.00	1.00	
A. EXOTHERMIC REACTIONS (FACTOR .30 to 1.25)		/	
B. ENDOTHERMIC REACTIONS (FACTOR .20 to .40)		/	
C. MATERIAL HANDLING & TRANSFER (FACTOR .25 to .85)		/	
D. ENCLOSED PROCESS UNITS (FACTOR .30 to .90)		/	
E. ACCESS	.35	/	
F. DRAINAGE (FACTOR .25 to .50)		/	
GENERAL PROCESS HAZARD FACTOR (F₁) ⟶		1.00	

2. SPECIAL PROCESS HAZARDS			
BASE FACTOR ⟶	1.00	1.00	
A. PROCESS TEMPERATURE (USE ONLY ONE)		—	
1. ABOVE FLASH POINT	.30	0.30	
2. ABOVE BOILING POINT	.60	/	
3. ABOVE AUTOIGNITION	.75	/	
B. LOW PRESSURE (SUB-ATOMOSPHERIC)	.50	/	
C. OPERATION IN OR NEAR FLAMMABLE RANGE		/	
1. TANK FARM STORAGE FLAMMABLE LIQUIDS	50	/	
2. PROCESS UPSET OR PURGE FAILURE	.30	/	
3. ALWAYS IN FLAMMABLE RANGE	.80	/	
D. DUST EXPLOSION (FACTOR .25 to 2.00)(SEE TABLE III)		/	
E. PRESSURE (SEE FIGURE 2)		0.15	
F. LOW TEMPERATURE (FACTOR .20 to .50)		·	
G. QUANTITY OF FLAMMABLE MATERIAL		/	
1. LIQUIDS OR GASES IN PROCESS (SEE FIG. 3)		·	
2. LIQUIDS OR GASES IN STORAGE (SEE FIG. 4)		/	
3. COMBUSTIBLE SOLIDS IN STORAGE (SEE FIG. 5)		·	
H. CORROSION AND EROSION (FACTOR .10 to .75)		/	
J. LEAKAGE – JOINTS AND PACKING (FACTOR .10 to 1.50)		0.3	
K. USE OF FIRED HEATERS (SEE FIG. 6)		—	
L. HOT OIL HEAT EXCHANGE SYSTEM (FACTOR .15 to 1.15)(SEE TABLE IV)		/	
M. ROTATING EQUIPMENT, PUMPS, COMPRESSORS	.50	/	
SPECIAL PROCESS HAZARD FACTOR (F₂) ⟶		1.75	
UNIT HAZARD FACTOR (F₁ x F₂ F₃) ⟶		1.75	
FIRE AND EXPLOSION INDEX (F₃ x MF) F & EI) ⟶			17.5

Figure 1 — Unit Hazard (F₃)

Figure 1 — Unit Hazard (F₃)

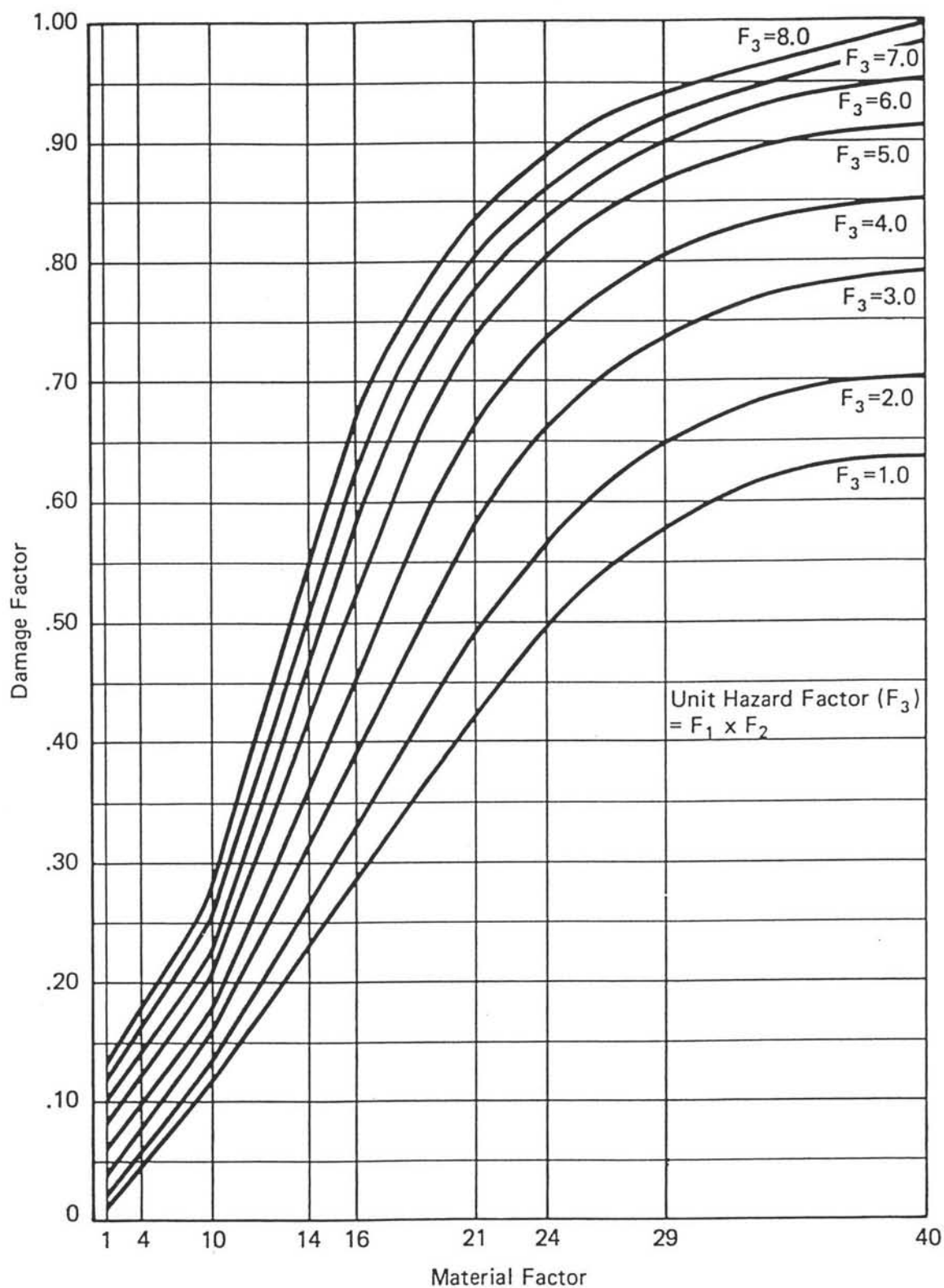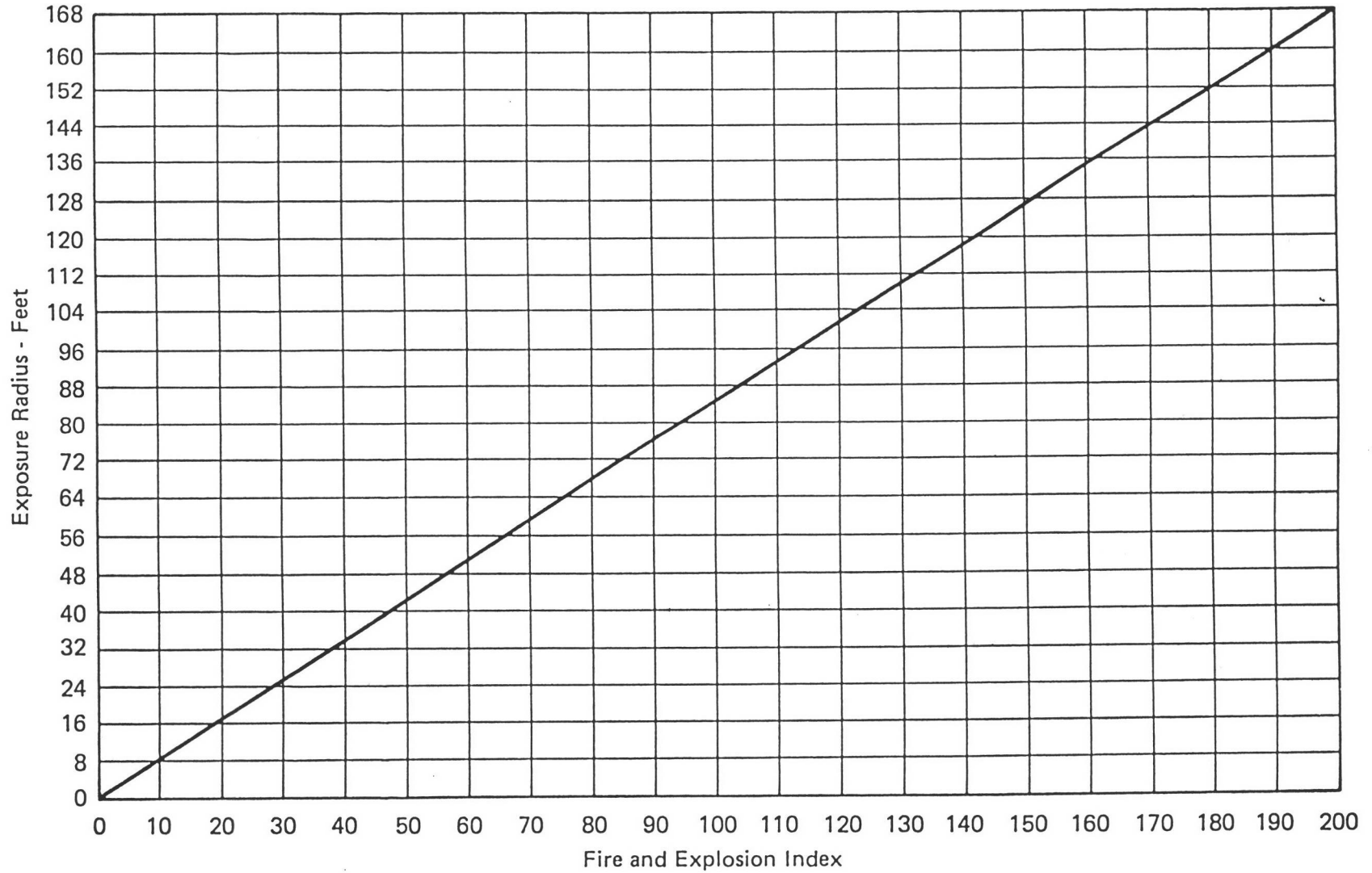Unit Hazard Factor (F_3) = $F_1 \times F_2$
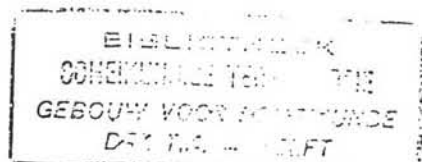
Figure 8 — Area of Exposure

Fig 2. Area of exposure

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G.2 Hazop analysis of the reactor

Deviation	Cause	Consequences	Immediate actions	Preventive actions
NO methanol feed flow	1. pipeline leakage	explosion hazard low temperature methanol in surroundings	repair leakage	(a)flowcontrol reactor alarm (b)inspection equipment (c)temperature control, alarm, reactor (d)establish link between storage and product flow (a,c) (e)offgas measurement (a,b)
	2. empty storagetank	methyl iodide in offgas	contact supplier	
	3. pump failure	methyl iodode in offgas	repair pump	
NO CO feed flow	4. pipeline leakage	explosion hazard toxic hazard no conversion of methanol, low temp.	shut down, immediate evacuation of employees repair leakage	(a,c,e)
NO Acetic acid product	5. valves of both resinbeds of one or both types closed	build up of product in resinbed or proces	open valves	(f)levelcontrol in resin beds
NO Offgas	6. pipeline blockage	build up of gas in process, pressure increase	pressure release	(g)pressure control in reactor
NO Cooling water	7. low water level in river	only gasfase, temperature increase, run away explosion hazard	pressure release,stop methanol feed	(c,g)
MORE methanol flow	8. flow control failure	more conversion, temperature increase	more cooling.	(c)
MORE CO feed flow	9. flow control failure	more CO recycle, and more CO in offgas, pressure increase, offgas increase	pressure release valve	(e,g)
LESS feed flow	10. pipeline leakage methanol	as 1.	as 1.	(a,b,c)
	11. pipeline leakage recycle	high methanol concentration, no catalyst, no conv.	repair leakage	(a,b,c)
LESS offgas	12. reactor leakage	explosion hazard	repair leakage, shut down	(a,b,c)
	13. pipeline blockage	as 12, pressure increase	pressure release	(a,b,c,g)
LESS product	14. reactor leakage	explosion, toxic hazard	repair leakage, shut down	(a,b,c)
	15. pipeline blockage	explosion hazard, pressure increase	as 12	(a,b,c,g)
acetic acid AS WELL as propionic acid	16. catalyst not active	distillation not possible, product not sellable	shut down, replace catalyst	(h)product measurement

No hazards are observed regarding the guide words *part of*, *reverse* and *other than*.

Calculation of the costliness index

	Throughput	Material of construction	Reaction time	Min max pressure	Min max temperature	Other	Total score	Costliness index
Storage/handling								
methanol	-1	0	0	1.5	0	0	0.5	1.5
carbon monoxide	0	0	0	1.5	0	0	1.5	1.5
recycle	3.5	1	0	1.5	0	1	7	6.3
Proces								
reactor	3.5	1	0	1.5	0	1	7	6.3
scrubber	0	1	0	1	0	1	3	2.2
separator	3	1	0	0	0	1	5	3.7
purification	0	1	0	0	0	0	1	1.3
Total								22.8

CI-index (1978)	310
Investments Ib (1978 k$)	13202.56
CI-index 1996	1010
Investments Ib (1996 k$)	43014.80
$/hfl ratio 1996	1.55
Investments Ib (1996 kHfl)	66672.94
Total investments I (1996 kHfl)	104176.47

Calculation of the investments with Lang

calculation of the equipment costs

Heat exchanger	H7	791000	
	H8	791000	
	H13	50000	
	H15	50000	
	H24	50000	
	H25	595000	
	H26	56000	
Pump	P1	30000	
	P2	22000	
	P4	16000	
	P5	22000	
	P21	16000	
	P23	64000	
	P25	32000	
	P31	11000	
	P32	11000	
Reactor	R3	1000000	
Expander	E6	750000	
	E11	650000	
	E12	650000	
Flasher	V9	950000	
	V10	1100000	
Scrubber	T20	550000	
Distillation column	T14	1200000	
Compressor	C19	300000	
Resin bed	R28	750000	
	R29	750000	
	R31	750000	
	R32	750000	
Condenser	H16	235000	
	V18	250000	
Reboiler	H17	791000	
Total equipment costs		14033000	Hfl
Total Investments		66516420	Hfl

Appendix H: Calculation of the economics

Cost calculations

Production costs	A	c$/A	$/kg	kg/y	$/y	kHfl/y
methanol	gal	53.8	0.177675	54432000	9671207	14990.37
carbon monoxide	scf	0.348	0.098375	84768000	8339015	12925.47
methylacetate	gal	2.78	0.177675	115999	20610.13	31.95
Iodide and iron waste (estimation)						250.00

Cooling water	A	fl/A	kW	kg/y	fl/y	
H7	ton	0.1	2018	6.92E+08	69188.57	69.19
H25	ton	0.1	4262	1.46E+09	146125.7	146.13
H15	ton	0.1	106.3	36445714	3644.571	3.64
H13	ton	0.1	23.82	8166857	816.6857	0.82
H24	ton	0.1	21.7	7440000	744	0.74
H26	ton	0.1	1030.3	3.53E+08	35324.57	35.32

Proces water	A	fl/A		kg/y	fl/y	
total	m3	0.15		60000	9000	9.00

Katalyst	A	c$/A	$/kg	kg/y	fl/y	
Rhodium complex	mg	2.75	27.5	300	8250	12.79
Methyl Iodide	lb	50	1.101322	56058	61737.89	95.69
Lithium Iodide	lb	800	17.62115	116000	2044053	3168.28

Electricity		fl/A	kW	kWh/y	fl/y	
pump P3	kWh	0.13	2.862	22896	2976.48	2.98
pump P5		0.13	2.882	23056	2997.28	3.00
pump P20		0.13	0.581	4648	604.24	0.60
pump P27		0.13	8.225	65800	8554	8.55
pump P4		0.13	0.002	16	2.08	0.00
pump P22		0.13	28.84	230720	29993.6	29.99
compressor C21		0.13	830.68	6645440	863907.2	863.91

Steam		fl/A	MJ/h	ton/y	fl/y	
reboiler	ton	35	25370	101480	3551800	3551.80
Total						36200.23

Labour costs Kl

Calculation with the Wessel-relation	1677

Investment related costs Ki   Itot= 104176

Capital charge (0.13* Itot)	13542.94
General related costs	15522.29
Total	29065.24

Total Production Costs (Ktot=1.13*Kp+Kl+Ki)	71648.5

Income		c$/A	$/kg	ton/y	$/y	kHfl/y
steam	ton			30200		981.5
Acetic acid	lb	33	0.726872	100030	72709031	112699
Total						113680.5

Appendix H: Calculation of the economics

Return On Investment

Total investments (If+Iw)	89592	kHfl
	42032	kHfl
ROI	47%	
Profits 10% down		
Total investments (If+Iw)	89592	kHfl
Total profit	37828.8	kHfl
ROI	42%	
Income 10% down		
Total investments (If+Iw)	89592	kHfl
Total profit	29780.6	kHfl
ROI	33%	

Pay-Out Time (POT)

Vast kapitaal (0.8*Itot)	83341.18	kHfl
Eploitatie overs(opbr-Kp-2.6*KI)	72138.57	kHfl
POT (year)	1.155293	

Investor's Rate of Return

cash flow	49384.62	kHfl
rest waarde	8334.118	kHfl
werk kapitaal	6250.588	kHfl

		i=40%			
Year	Cash Flow	Di		Di*cash flow	
0	-104176	1	-104176	-104176
1	42032	0.714	30010.85	30226.51
2	42032	0.510	21436.32	21736.81
3	42032	0.364	15299.65	15631.61
4	42032	0.260	10928.32	11241.17
5	42032	0.186	7817.952	8083.872
6	42032	0.133	5590.256	5813.361
7	42032	0.095	3993.04	4180.567
8	42032	0.068	2858.176	3006.374
9	42032	0.048	2017.536	2161.976
10	56617	0.035	1981.585	2094.225
	434905		101933.7	0
in/out ratio	-4.17469		-0.97847	

IRR	39%