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FVO Nr. **3140**

Fabrieksvoorontwerp
Vakgroep Chemische Procestechnologie

Onderwerp

Palladium catalysed hydrogenation of aqueous bicarbonate salts in formic acid production

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S.M.W. Berkemeijer	070-3995270
H.C. de Lange	015-132619
E.J.J. Ramaker	015-125578
S.F. Woo	015-146026

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Formic Acid

Datum opdracht:20 February 1995

Datum verslag: 1 June 1995

TU Delft
Technische Universiteit Delft

Faculteit der Scheikundige Technologie en der Materiaalkunde

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SUMMARY

In this design the formation of formic acid via carbondioxide and hydrogen is simulated. The main reaction that takes place is a hydrogenation reaction catalysed by a palladium catalyst. The flowsheet of the process is shown in Appendix VIII. This process route is based on a thesis of D. Engel.

While the ideas of D. Engel where based on a new invention (regarding to the extraction column) , there where some problems with simulating the process. Also there were no possible computer programs who could simulate the electrolyte model that was necessary.

The designed process has a yearly capacity of 100,000 metric tons a year. The rendement of the process is 99 %
The formic acid price is $ 904,8 per ton. With this price the process has a loss of $ -9,387,000 a year.
The process isn't economically feasable due to the huge consumption of catalyst, wich on yearly base costs $44,593,000.

When there can be found a new catalyst, wich has less loss of acivity, there might be a possibility of a profitable process.

CONTENTS

1. INTRODUCTION

Formid acid, sometimes called methanoic acid, is a colorless, odourous acid. It is used in the textile souring, leather preparation, cattle-fodder preservation and chemical manufacture.
Several new concepts of industrial formic acid production are based on carbon dioxide and water as raw materials. Hereby an aqueous formate salt intermediate, either directly available as a byproduct in the production of polyhydric alcohols or formed by the reduction of the corresoponding bicarbonate salt with hydrogen, is used. This factory design discuss the formic acid production by palladium catalysed hydrogenation of ammonium bicarbonate salt.
Nowadays industrial formic acid production is primilary based on two processes, which use carbon monoxide and water as raw materials. One process employs the formation and subsequent hydrolysis of methyl formate. The world-wide largest formic acid production factory from BASF in Ludwigshaven, with a capacity of 100,000 metric tons per year, is based on this process. The other proces, but on a smaller scale, employs the carbonylation of sodium hydoxide. Disadvantages of these processes are the large consumption of a strong mineral acid and the simultaneous production of a low value inorganic salt. In former times the low value inorganic salt, e.g. Na_2SO_4 or $Ca(NO_3)_2$, could be applied as fertilizer, but today this kind of fertilizers are replaced by NH_4NO_3, which has a higher nitrogen content (Zapp et al.; Weston). As a result, the obtained inorganic salts have to be disposed, which is currently unacceptable for environmental reasons. Moreover, the demand for fertilizers has decreased during recent years and the general expectation is a continued decline in the future (DSM).
By using a process with an aqueous formate salt intermediate, which uses carbon dioxide and water as raw materials, the classical disadvantages, as described above, can be avoided. Other advantages compared to the classical processes are; an increased conversion per pass, resulting in smaller recycle streams; a better reaction selectivity, an easier catalyst recovery and reduced corrosion problems.
At present an overcapacity for the production of formic acid currently exists. In 1988 the formic acid production was about 330,000 metric tons per year. As the demand for formic acid has shown hardly any growth, the introduction of a new process will logically imply a partial substitution of one of the traditional processes based on the expectation of more favourable process economics, rather than having the purpose to provide additional production capacity.

2. STARTING POINTS

2.1 SELECTION OF THE PROCESS ROUTE

2.1.1 Options for formic acid production

The production routes of formic acid out of base chemicals is possible using either carbon monooxide and water, or carbon dioxide and hydrogen. As carbon dioxide and water are inexpensive, and energy requirements of both routes are comparable, the economics of the two routes are mainly determined by the costs of the carbon monooxide and hydrogen. Most traditional processes are based on the carbon monooxide route. The advantage is that carbon monooxide is more reactive at mild conditions. An advantage of the carbon dioxide route is, that hydrogen is frequently available in higher purity than carbon monooxide and pre-concentration is not necessary. Environmentally, the carbon dioxide route is also favourable, due to the essentially clean combustion of purge gases (Engel) .

Present preliminary process design is concerned with the preparation of formic acid using the base chemicals carbon dioxide and hydrogen as reactants. Formic acid production routes that use carbon dioxide and hydrogen as raw materials are:

1. Catalysed hydrogenation of carbon dioxide with a nitrogenous base
2. Electrodialytic water dissociation
3. Catalysed hydrogenation of bicarbonate salts

Disadvantages of the first process are the high hydrogen pressure needed for a detectable conversion, e.g. 200-400 bar in a heterogeneous Raney nickel process and 50-100 bar in homogeneous transition metal catalysts, and the diffultness of the recovery of formic acid from the formate. Beside the high pressure needed for a homogeneous catalysed process, separation of the catalyst is difficult.
In the second process dissociation of water is achieved with bipolar membranes. As there will always be a leakage of formic acid across the membranes, production of formic acid with a high purity can not be achieved. Another disadvantage is that the long term resistence of the membranes towards strong bases like NaOH is still unsatisfactory (Tholen).
In the third process a heterogeneous catalyst like palladium is used. Separation of the catalyst is therefore simple. Another advantage is the that the whole process is carried out in the same solvent.

2.1.2 Objective

The goal of present design is the continous production of formic acid using carbon dioxide and hydrogen as reactants. The process route of the catalysed hydrogenation of bicarbonate salts is selected. The design is partly based on an invention described by D.C. Engel (Engel). The main features are described in the next paragraph. Important advantages compared to traditional formic acid production methodes are: better reaction selectivity, easier catalyst recovery and reduced corrosion problems.

The worldwide installed formic acid production capacity was about 330,000 metric tons per year in 1988. This capacity has shown hardly any growth in recent years. The largest production facility is owned by the BASF company, with a maximum capacity of 100.000 metric tons per year (Engel). Present design should equal the BASF capacity, and produce 100.000 metric tons of formic acid/year. The total of on-stream operation time will be 8000 hours per year.

2.2 REACTION INFORMATION

The main features of the process are the hydrogenation of bicarbonate to its corresponding formate, and the decomposition of formate giving formic acid.

The conversion of bicarbonate to the corresponding formate compound and water is one of the few reactions where an electrolyte can be reduced with hydrogen. In presence of a heterogeneous catalyst the reaction takes place already at mild temperatures (20-80°C) with a favourable equilibrium conversion at relatively low partial pressure of hydrogen (1-20 bar). The reaction is represented by:

$$MHCO_3\ (aq)\ + H_2\ (g) \square MOOCH\ (aq)\ +\ H_2O\ (l) \qquad \textbf{(2.2.1)}$$

in which M, the counterion, preferably is an amino compound. Requirements for the amino compound are: soluble in water, its formate salt should be decomposible at a temperature lower than the boiling point of the aqueous aminoformate solution, higher volatility than the formic acid in the aqueous solution of aminoformate and formic acid, and stability under process conditions. According to Engel et al (Engel et al.), a particular attractive cation for the process is ammonium. The phases present in the process are: aqueous solutions of electrolytes, gasses and solids (the catalyst particles). The concentration of the solid particles is very low, so this stream can be seen as one phase.

Using ammonia, the methode can be summarized in the following three sequences:

1) Gasabsorption
Reaction of ammonia with carbon dioxide and water, producing an aqueous ammonium bicarbonate solution:

$$NH_3\ (g)\ + CO_2\ (g)\ +\ H_2O\ (l) \square NH_4HCO_3\ (aq) \qquad \textbf{(2.2.2)}$$

2) Hydrogenation
Reaction of ammonium bicarbonate with hydrogen to ammonium formate salt and water:

b) Decomposition of the ammonium formate into formic acid and ammonia with the method according to the invention of D.C. Engel:

$$NH_4OOCH(aq) \square NH_3\ (g) + HCOOH\ (l) \qquad \Delta H^0{}_r = 87.2\ kJ/mol \qquad \textbf{(2.2.4)}$$

A simplified flowsheet of the process as described above is represented in appendix X.

A few problems rise when formic acid is produced according to the methode described above, being:
I) A side-reaction may take place in the first step. Carbamate ($NH_4CO_2NH_2$) can be formed by reaction of bicarbonate with free ammonia. According to D.C. Engel, this can be avoided by using an excess of carbon dioxide. The reacton of this side reaction would be:

$$NH_3\ (g) + NH_4HCO_3\ (aq) \square NH_4CO_2NH_2\ (aq) + H_2O\ (l) \qquad \textbf{(2.2.5)}$$

This reaction can only take place when there is an excess of ammonia in the second absorber.

II) When reaction (2.2.4) is carried out under a temperature of 100°C the equilibrum conversion will be very low. On the other hand when the reaction is carried out above a temperature of 100°C the ammonium formate will be dehydrated into formamide. D.C. Engel found a solution of last named problem. He suggests that the ammonium formate can be heated in the presence of a suitable organic agent. The volatile ammonia will evaporate and the formic acid will be extracted in the organic agent. This will shift the reaction towards the desired products and, in principle, a complete recovery of the formic acid can be achieved.

2.3 SUPPLEMENTARY INPUT-INFORMATION

2.3.1 Product specifications

Typical specifications for commercial grades of formic acid are shown in table 2.3.1 (Kirk Othmer, volume 10). Also see appendix XI.

Table 2.3.1: Specifications for commercial grades of formic acid.

Assay	90%	Technical	Pharmaceutical
Formic acid, wt %, min	89-91	98.0	99.5
Acetic acid, wt %, max		0.8	0.4
Water, wt %, max			0.5
Toluene, ppm, max			5
Chlorides, ppm, max	20	20	5
Heavy metals, ppm, max	5	5	5
Iron, ppm, max	3	3	3
Sulfates, ppm, max	10	10	10
Color, Pt-Co units, max	20	20	15

For this preliminary design, the purpose is to produce technical grade formic acid. Impurities of ammonium formate in the formic acid product are permitted for the use as silage aids.

2.3.2 Feedstock requirements and plant location

The feedstock required in formic acid production are usually obtained from synthesis gas, for which the two main production methodes are steam reforming and partial oxidation of hydrocarbons. Synthesis gas is primarily used in the production of basic chemicals such as methanol and ammonia. The amount of gas consumed in these plants is extremely large in comparison to that of a formic acid plant. The available hydrogen and carbon dioxide gas streams in the ammoinia synthesis satisfy the feedstock purity requirements for formic acid synthesis. Therefore, a production location adjacent to a large ammonia plant is particulary convenient, so gas streams can be withdrawn from the ammonia plant.

Carbon dioxide, can then easily be withdrawn from the gas stream coming out of the CO_2-removal column of the ammonia plant. This carbon dioxide stream is very pure. Required is about 23% of the totally purged out stream of a ammonia plant with a capacity of 300,000 ton per year. The carbon dioxide is provided at 298 K and atmospheric pressure.

The hydrogen used for the bicarbonate reduction has to be essentially free of CO, as it appears to be a severe catalyst poison. Components like CH_4 and N_2 proved to be inert (Engel). Presence of O_2 will yield no problems. Hydrogen is used in very large amounts to synthesize ammonia (Topham). In tabel 2.3.2 the typical composition of the hydrogen stream as used for the ammonia production is shown. It is clear that the required hydrogen can be obtained from the ammonia plant. This will be about 5% of the stream coming off from the ammonia plant. This stream has a pressure of 2.5 MPa and a temperature of 308 K.

Tabel 2.3.2: Composition of the inlet hydrogen stream

composition	**vol%**
H_2	74.23
CO	5 ppm
CO_2	-
N_2	24.78
CH_4	0.72
Ar	0.25
H_2O	-

Another advantage of locating a formic acid plant near an ammonia plant, is the presence of large amounts of ammonia. The withdrawal of a small ammonia make-up stream will present no difficulties.

For component specifications see appendix XI.

2.3.3 Utilities

The following services are available:

1) Saturated steam at 40 bar 410°C (condensation temperature 250°C), at 10 bar 220°C (condensation temperature 180°C) and at 3 bar 190°C (condensation temperature 133°C). Fouling-factor: 0.1 m^2°C/kW

2) Cooling water: inlet temperature 20°C, maximum allowed outlet temperature 40°C. Fouling-factor: 0.5 m^2°C/kW

3) Electricity at 220 V, at 380 V three phase AC and at, 10000 V three phase AC

3 UNIT OPERATIONS

3.1. ABSORBERS (A1 and A4)

3.1.1. Selection of type of column

For absorption of gas into liquid any of the general types of towers may be used: plate towers, packed columns, spray towers.
The ultimate choice between the different types for a particular application can only be made with complete assurance by costing each design. However, this will not be necessary within the frame of this preliminary design, and the choice is made by considering the main economical and technological advantages and disadvantages of each type.

Spray towers are profitable when very corrosive gases or solutions, or dust and other fine particles are present. Their main disadvantages are: high cost for power to press the absorption liquid through the spray nozzles, the necessity of installing entrainment suppressors or mist eliminators, and the substantial height necessary to achieve a theoretical stage of absorption as the tower volume is used less effectively (Zenz). Only moderate success has been obtained for the absorption of ammonia in water (Coulson and Richardson). A spray tower would be a too expensive and is therefore not suitable for the ammonia absorption column.

The advantages of packed towers include simple, and, as long as the tower is not too large, usually relatively cheaper construction (Kirk-Othmer Vol. 1). Packing support and liquid distributor are only every 10 feet along it's height required (Zenz). The versatility of packed towers allows for the dept of the tower to be easily changed, if the efficiency is less than anticipated, or if the flow conditions are changed (Zenz). In packed towers the hold up is relatively small.

Advantages of plate towers include: less channelling and maldistribution in tall towers, easy cleaning and easy cooling. As no polluting substances are present, and there is no need for cooling, the last mentioned advantages do not seem important for the choice between a plate and a packed tower in the present design.

The main selection criterion seems to be the size of the column. A rule of thumb is that for large diameter columns, plates are cheaper than packings. For diameters less than 2 meter, packed columns are more economical and more often used than plate towers (Coulson and Richardson).

Based on the above described properties of the different types of columns, the packed column seems the most suitable choice for the ammonia and the carbon dioxide absorption columns. Besides, packed columns for gas liquid contacting are used extensively for absorption operations in chemical plants. The packed column is characteristically operated with counterflow of the phases (Perry).

3.1.2 Selection of the type of packing

In order to obtain a good rate of transfer per unit volume of the tower, a packing is to be selected

which will promote a high interfacial area between the gas and the liquid phase, and a high degree of turbulence in the fluids. Usually increased area and turbulence are achieved at expense of increased capital cost, so a balance must be made between these factors.
Other requirements are: uniform liquid distribution on the packing surface and uniform vapour gas flow across the column section. In order to achieve this the packing particles should be of as uniform size as possible. A low resistance to gas flow is obtained by an open structure.

Packing can be divided into four main classes: Broken solids, shaped packings, grids, and structured packings. The first type is the cheapest, but is not very satisfactory in regard to liquid flow or to effective surface offered for transfer. The main problem with grid packings is that of obtaining good liquid distribution since, at high liquid rates, the liquid tends to cascade without being broken up into fine droplets which are desirable for a high interfacial surface. Structured packings have a very high capacity and efficiency, but this is achieved at higher initial costs than with the other packings (Perry).
Chosen is for the use of random packing of shaped particles, as they have a large interfacial surface area, cause a small pressure drop and have favourable economics (Perry).

A lot of different types of shaped particles are available for appliance in packed columns. For new columns the choice will normally be between Pall rings, Berl or Intalox saddles, because of their good liquid distribution and favourable economics (Coulson and Richardson Vol. 6). Most of the packings are available in a wide range of materials such as ceramics, metals, glass, plastic and carbon. Ceramic packings are comparatively cheap (Coulson and Richardson Vol. 2). For a column with a diameter of about 1 meter, particles with a size of 1½ -2 inch (38-50 mm) give good results (Coulson and Richardson Vol. 2). To obtain high and uniform voidage and to prevent breakage of the ceramic material, the package will be dumped into a tower full of liquid.

For the preliminary design of the column for the ammonia absorption ceramic 1½ inch Berl saddles are selected, as satisfactory data for this type of packing is available in literature. For detailed design it is advisable to consult packings manufactures' technical literature for detailed data of the many special types, in order to make an ultimate selection.

3.1.3. Vapour-liquid equilibria

In the absorbers carbon dioxide and ammonia occur significantly in the vapour phase. Since these gas mixtures only contains low molecular components, the deviation from ideal behaviour is negligible at the proces conditions applied. Hence the vapour phase can adequately be described according to the ideal gas law. In addition the influence of the total pressure on the Henry coeffients is very small at the system pressures exerted, so the Poynting factor may safely be omitted. The general expression for the vapour-liquid equilibrium of carbon dioxide and ammonia in the solvent, e.g. water or electrolyte solution then simplifies to:

$$P_i = C_i^* H_i \qquad \textbf{(3.1.1)}$$

As in the ammonia absorber the ammonia is absorbed by a liquid flow, that nearly consists of pure

water, the Henry coefficient of ammonia in pure water is used.
In contrast to the second absorber, in which carbon dioxide is absorbed by a electrolyte solution. Danckwerts has developped an expression that relates the Henry coefficient of carbon dioxide in pure water to the Henry coefficient of carbon dioxide in an electrolyte solution. The Henry coefficient of carbon dioxide in pure water is given by the following expression according to Danckwerts:

$$Log_{10}H_w = \frac{1140}{T} - 5.30 \qquad \textbf{(3.1.2)}$$

Then the Henry coefficient of carbon dioxide in a no-reaction electrolyte solution can be estimated to within 10% by the expression:

$$\log_{10}\left(\frac{H}{H_w}\right) = -K_s[NH_4OH] - K_s[NH_4HCO_3] \qquad \textbf{(3.1.3)}$$

As the gas in the two absorbers exists mainly of ammonia or carbon dioxide, the partial pressure is equal to the total pressure.

3.1.4. Process conditions for the Ammonia Absorber (A1)

In the first absorber, that is packed with 38 mm Berl-saddles, a vapour flow that consists mainly of ammonia is contacted countercurrently with a water flow. As ammonia dissolves easily in water it is operated at atmospheric pressure and at a temperature of 293 K. The dissolvation of ammonia in water is exotherm, but as the temperature rise is 70 ° C, it is not necessary to use internal cooling. The liquid flow that comes from the absorber is an aqueous NH_4OH-solution.

3.1.5. Process conditions for the Carbon dioxide Absorber (A4)

In the second absorber, that is packed with 38 mm Berl-saddles, a vapour flow that consists of ammonia and carbon dioxide is contacted with the aqueous NH_4OH-solution coming from the first absorber at a temperature of 293 K to form a saturated aqueous ammonium bicarbonate solution.. As carbon dioxide doesn't dissolve as well as ammonia in water the absorber will be operated at a pressure of 7 bar. As the reaction of carbondioxide with the hydroxyl ions is exothermic, there is a temperature rise of about 125 K. Intern cooling is not necessary as the boiling point of water at 7 bar is 497 K.

3.2. CATALYST

3.2.1. Catalyst selection

It has become clear that production of formic acid with hydrogenation of carbon dioxide with a nitrogenous base, separation of the homogeneous catalysts based on transition metals, e.g.

ruthenium and palladium, has considerable difficulties. Therefore men have done research for a suitable heterogeneously catalysed reaction.
D.C. Engel has demonstrated in his thesis that aqueous solutions of an alkali metal or ammonium bicarbonate can be converted with hydrogen to the corresponding formate salt in the presence of a heterogeneous palladium catalyst. As difficulties of catalyst separation can be avoided, in this preliminary design the choice is made to use palladium on activated carbon.
The size of the catalyst particles used in the thesis of D.C. Engel is 21μm. Although the particle sizes is very small, the same size is used in our plant design. The decision is based on the availability and quantity of the information about the catalysed hydrogenation reaction and catalyst deactivation.
Difficulties could arise to separate these particles from the slurry stream coming out from the reactor. For a more detailed design a decision has to be made wether this problem is solved by using large catalyst particles causing a lower catalyst efficiency or by using smal catalyst particles and applying a more expensive separation system. More research should be done for the final selection of the catalyst size.

3.3. HYDROGENATION REACTOR (R11)

3.3.1. Reactor selection

Two types of reactors exist: 1) a fixed bed reactor 2) suspended bed reactor
As the catalyst deactivates very fast, the removal of the catalyst particles has to be very flexibel. So the fixed bed reactor is no good option.
Three types of suspended bed reactors exist: 1) a bubble collumn 2) an agitated tank 3) a three phase fluidized bed.
The activated carbon support is too weak to apply in a fluidized bed. For a continuous three phase production process at high pressure, usualy bubble collumn suspended bed reactors are preferred, since the construction costs and the energy requirements are low in comparison with a mechanically agitated tank reactor. (Henkel, Zehner and Kraume)

3.3.2. Thermodynamic model for aqueous systems of electrolytes

In general the prediction of an aqueous electrolyte solution is normally based on a suitable model for the solvent activity and the ionic activity coefficients of the solutes. These models are either too complex or have not been tested for application in engineering calculations. Therefore, semi-empirical methods are usually preferred when equilibria in aqueous systems of electrolytes is considered.

The semi-empirical model formulated by Pitzer (1973), that is used as thermodynamic model in the hydrogenation reactor, gives one of the best representations of the experimental data in pure as ell as in mixed strong 1:1 and 2:1 electrolytes up to an ionic strength of 6 molal (Renon et al., Ananth and Ramachandran, Lu and Maurer). In Pitzer's model the osmotic coefficient and the mean activity coefficients are represented by a virial expansion of terms in concentration.

In the modified Pitzer equation the ion-ion binary interaction function B and ternary interaction function C are characteristic for each aqueous single strong electrolyte and are determined by the properties of the respective pure electrolytes. These functions incorporate the pure electrolyte ion interaction parameters $\beta^{(0)}$, $\beta^{(1)}$ and C^{Φ}, which have been tabulated for many electrolytes by Pitzer (1973, 1987)

The ion difference parameters θ and Ψ, which are characteristic for aqueous mixed electrolyte systems, are ignored. As a result, the following equations give the osmotic coefficient of the mixed electrolyte solution and the activity coefficient of cation M and anion X respectively:

$$\Phi = 1 + \frac{2}{\Sigma_i m_i}[-A_\Phi \sqrt{I^3}/(1+1.2\sqrt{I}) + \Sigma_c \Sigma_a m_c m_a (B^{\Phi_{ca}} + ZC_{ca}) + \Sigma_n \Sigma_c m_n m_c \lambda_{nc} + \Sigma_n \Sigma_a m_n m_a \lambda_{na} \qquad \textbf{(3.3.1)}$$

$$\ln \gamma_M = z_M^2 F + \Sigma_a m_a (2B_{Ma} + ZC_{Ma}) + z_M \Sigma\Sigma_c \Sigma_a m_c m_a C_{ca} + 2\Sigma_n m_n \lambda_{nM} \qquad \textbf{(3.3.2)}$$

$$\ln \gamma_X = z_X^2 F + \Sigma_c m_c (2B_{cX} + ZC_{cX}) + z_X \Sigma\Sigma_c \Sigma_a m_c m_a C_{ca} + 2\Sigma_n m_n \lambda_{nX} \qquad \textbf{(3.3.3)}$$

The expression for F, Z, B^{Φ}, B and C are given completely by Pitzer (1987).

The parameter λ represents the binary neutral-ion interaction, I the ionic strength and A_ϕ is the Pitzer-Debye-Hückel limiting slope of the osmotic coefficient.

According to several authors, it appeared to be unnecessary to take the H^+-X^- interactions in to account for the bicarbonate/carbonate system. In addition it is stated that the NH_3-NH_4^+, CO_2-NH_4^+,

CO_2-HCO_3^- and CO_2-CO_3^{2-} are negligible small. Also the interaction between CO_2 and HCOO : The temperature dependence of the interaction parameters is ignored. An overview of the known parameter values for all significant species interactions are given in table 3.3.1.

Table 3.3.1: Estimated Pitzer parameter values at 25 °C of the binary and ternary species interaction for the osmotic and activity coefficient calculation.

Interaction	**10^2*($\beta^{(0)}$, λ) (kg/mol)**	**10*$\beta^{(1)}$ (kg/mol)**	**10^3*C^{ϕ} (kg/mol)**	**Ref.**
NH_3-HCO_3^-	1.47	-	-	Pawlikowski et al.
NH_3-CO_3^{2-}	18.0	-	-	Clegg and Brimblecombe
NH_3-$HCOO^-$	4.8	-	-	Clegg and Brimblecombe
NH_4^+-HCO_3^-	-3.80	0.70	0	Roy et al.
NH_4^+-CO_3^{2-}	12.88	14.33	0.5	Roy et al.
NH_4^+-$HCOO^-$	5.40	4.66	-2.99	Present study

3.3.3. Process conditions for the reactor (R11)

In the reactor, the palladium catalysed hydrogenation of the ammonium bicarbonate into ammonium formate takes place according to the following reaction:

$$NH_4HCO_3\ (aq) + H_2\ (g) \square NH_4OOCH\ (aq) + H_2O\ (l) \qquad \Delta H^0_r = -19.4 kJ/mol \quad \textbf{(3.3.4)}$$

The use of high partial pressures of hydrogen is desirable, because the reaction rate and yield of the formate salt increase with increasing partial pressure. Since the hydrogen will be obtained from a product stream of an ammonia production plant, the reactor will be operated at a pressure 25 MPa. The optimum reaction temperature was determined to be 80 °C. Cooling is needed, to keep the reaction temperature constant for an as large as possible conversion..

3.4. REGENERATION REACTOR (R8)

3.4.1. Reactor selection

As this reactor is comparable to the hydrogenation reactor (R11), a bubble column has been chosen for the same reason as mentioned in paragraph 3.2.1..

3.4.2. Proces conditions for the reactor (R8)

As there is few information available about the regeneration, many data have to be estimated. It is estimated that the regeneration is optimal at a operating pressure fo about 25 bar and at a temperature of 354 K.
The reversed reaction of formate to bicarbonate is calculated to be endothermic. As the heat needed for this reaction is much larger than the heat used for of the regeneration of the catalyst, heat has to be added via steam. This is in contrast with our expectations.

3.5 SOLID/LIQUID SEPARATION (M7, M9 and M13)

3.5.1 Catalyst separation

The catalyst activity is reduced to about 60% of its initial value after 7 minutes in the reactor. As the required minimum value of the mean liquid phase residence time will be about 140 minutes, very frequent catalyst refreshment will be necessary to maintain a sufficient bicarbonate conversion rate (Perry). There will be a very large external recycle of the slurry phase, along with a large catalyst regeneration unit.
The stream leaving the reactor contains 5 kg dry catalyst per m^3. These catalyst particles have to be separated from the liquid phase. The catalyst, with a small amount of the liquid, will go to the regenaration unit (described in § 3.4). The liquid phase is split, with 95% being returned to the reactor and 5% going through to the purification of formic acid.

3.5.2 Selection of the separation unit

The main techniques used to separate solid and liquid phases are: thickeners, clarifiers, hydrocyclones, filtration, centrifuges, pressing and drying. Pressing and drying are not suitable in dilute slurries, because they would consume exteem amounts of energy.

The problem with this separation are the large quantity of the recycle stream, and the small size and low concentration of the solid particles. Very large units would be necessary, and large surfaces required, which is relatively expensive. Two options are availible to handle this problem in an economically favourable way. The first one is to process the slurry as it leaves the reactor (2 volume % solids) by applying a multicyclone, which combines a considerable throughput with a large efficiency even for small particles and diluted slurries (Deeltjes I). The other option is to pre-concentrate the slurry in one unit, and then processing it to the desired solid concentration in a

second unit.

Again the final choice can be made only by determining detailed economics for the two options. For this preliminary design the decision will be based on advantages and disadvantages. Apart from the engineering principle saying that separation processes that have multiple steps are inherently always more effective than single step processes (Deeltjes I), it can also be concluded on practical grounds, that the two step process is the best option for this application. For down stream processing it is important to have a solid free liquid flow, in order to prevent fouling. This requirement can not be met completely by applying a multicyclone. There will always be some particles present in the overflow.

The first step in the solid-liquid separation will thus be pre-concentration. Thickners and clarifiers are frequently used for concentrating diluted slurries. These processes are relatively cheap, due to the relatively low horse power, low maintainance and low operating labour. However, the apparatus would have to be exteemly large and there would be problems maintaining the high pressure.
Another option is cross flow filtration. The advantages are: high flux, sharp selectivity, resistance to fouling, acceptance of abnormal operating conditions, low maintenance costs and ease of operation. Maintenance of high pressure is possible. A disadvantage could be the high investment costs. Catalyst recovery is a typical application of cross flow filtration.

A cross flow filter is selected for the pre-concentration. The liquid stream going through the membrane will contain no solids, and can be processed down stream without any problems. The concantrated slurry will have a solid volume concentration of approximately 10 %.

For the second unit of the solid liquid separation, a choice between the different techniques is made, using the relationship between particle size and solids concentration for several kinds of equipment, given by Dahlstrom and Cornell (Dahlstrom). The catalyst particle size is 21 μm and the concentration catalyst in the feed is now 10%. According to the graph by Dahlstrom and Cornell, suitable separation equipment is: thickeners, filters, centrifuges and cyclones.

Thickeners are not suitable because they are not easily appliable at high pressure. As a general rule filters or filter centrifuges are used when it is required to produce a pure, dry solid (Coulson and Richardson, vol. 6). This is not the case at this stage in the plant. Commercial sedimentation centrifuges with continuous liquid and solids discharge, are peripheral nozzle disc- and screw conveyor centrifuges (Coulson and Richardson, vol. 6). Disc centrifuges have a very low efficiency (approximately 45%)(Morris), and the problem with the screw conveyors is the breakage of the fragile catalyst particles.

For above described reasons, a hydroclyclone is selected as the separation unit to concentrate the concentrated slurry further.

Assumed is that we deal with a fine suspension. No segregration of the particles and liquid occurs. The particles are reasonably uniformly distributed in the liquid.
In addition it is assumed that the suspension is disperse, or deflocculated. Disperse suspensions tend to exhibit Newtonian behaviour. High volumetric concentrations (0.4-0.5) are achievable and pressure drop for pipeline flow are comparatively low and correspond closely with those calculated

for homogenous fluids of the same density as the suspension (Coulson and Richardson, vol. 6).

3.6 FLASH VESSEL (V15)

For the separation of the cleared product stream (ammonium bicarbonate and ammonium formiate) from the reaction section into an ammonia formate solution and a vapour stream, containing CO_2 , NH_3 and H_2O (former ammonium bicarbonate), different types of equipment can be used:

- Multi stage distillation column
- Flash vessel

In Chem Cad a simple flash vessel operated perfectly, and because this is more economical favourable it seemed to be the right choice.

The flash is operated at a pressure drop of 24 bar (25 to 1 bar) and a feed stream temperature of 97 °C and a product temperature of 96 °C. This is calculated with Chem Cad using for the K-model "Sour Water" and for the thermodynamical model "SRK". It should be Pitzer but in Chem Cad no flash calculations (using pitzer) would converge. The split factors for the components were calculated by Chem Cad . See chapter 4.

3.7 EXTRACTION COLUMN (T21)

To obtain the formic acid from the mixture from the reactor, a decent seperation is needed. The proces stream contains a molefraction amoniumformate of 0.11. After this seperation a purity of formic acid need to be 0.96 at least for a comercial grade product.

Possible seperations are:

i. Distillation
ii. Extractive distillation
iii. Azeotropic distillation
iv. Reactive distillation
v. Liquid/liquid Extraction
vi. Crystallization
vii. Adsorption/absorption
viii. Reaction
ix. Chromatografic separation
x. Membrane seperation

Some advantages and disadvantages are:

1. Distillation of the given mixture means a large energy requirement because the light key component is water that need to be evaporated.. A simple distillation would give a mixture of at most 77 %(weight) formic acid because of the existance of a high boiling azeotrope at

107.3 °C at atmosferic pressure. So a distillation needs to be a two column pressure swing distillation. But here also a large energy is required (Perry,Engel).

2. Extractive distillation is used to enlarge α, the relative volatility by adding a high boiling component but at the given temperature range of 100-101°C a phase seperation occurs. This because of the strong polar nature of the aqueous amoniumformate solution and the apolar nature of the generally used basic organic extractants. Also here the light component, the water need to be evaporated so again a large energy consumption(Coulson and Richardson, Engel,Kirk Othmer)
3. Azeotropic distillation is also used to enlarge α, but now a low boiling component is added, wich forms a new azeotropic mixture with the light end. This still means the evaporation of the water (Kirk Othmer).
4. Reactive distillation is only economically favourable if the amoniumformate can be reacted to a lower boiling component than water. This means decomposition of the formic acid or reaction towards a low boiling ester. Decomposition of the desired product is out of the question and an esterification in a polar aqueuos environment wont work satisfactory either (Engel).
5. Liquid/liquid extraction is a good alternative if the used extractant has a high capacity and a high selectivity. Also the solubility of the extractant in the aqueous phase need to be smal. Rather well described extractive agents of high extraction capacity are N,N-dibutylformamide and trioctylamine (Engel). The required energy consumption of such processes in considerably smaller.
6. Crystallisation of the formic acid is not a described route to produce pure formic acid from aqueous solutions. Problems are the little differance in melt temperatures, 0 and 8.3 °C for respectively water and formic acid. Because of the infinite solubility at room temperature there would be if any a large metastable zone. In the ammonium formate solution the first component to be cristallised is probably ammoniumformate, because its lower solubility.(Hand out Scheidingstechnieken II)
7. Absorption/adsorption is not a common technique in the bulk or semibulk production (diktaat scheidingstechnieken I)
8. Reaction is not applicable because the same reasons of point 4
9. Chromatografy is also merely a laboratory scale purification (diktaat scheidingstechnieken I)
10. Membrane technology is an expansive seperation not only because of breakage and fouling of the membranes but also would it need further rechearch for optimal use. Though liquid dispersion membranes for purification becomes in the near future a promising technique(Engel,research at API).

The least expansive purification is yet considered to be Liquid/liquid adsorption which is succesfully used by BASF in Ludwichshafen). According to Engel better result are obtained with a combination of extractive distillation and liquid/liquid extraction. This because of the gain in extractive capacity of the extractant if the amoniumformate is decomposed in ammonia and formic acid (Engel).
This invention is not described in literature and its equipment design thereby is a bit speculative.

Different types of extraction equipment are tabulated in appendix IX, from wich a clear

choise is made for the sieve plate column.

Possible extractive agents are high boiling linear alkylamines and di-alkyl formamides. A neat description of the distribution coefficient is given by Engel for tri-octylamine and di-butyl formamide. In the industry (BASF) the latter is historically used but the former has a higher distribution coefficient with a higher capacity. In this design is chosen for TOA (tri-octyl amine)
although its vavourable equilibrium it has higher recovery costs. But the size of the extractor is considerably smaller.
Modelling of this column in Chem Cad was an absolute dissaster, because the three phase separation that took place.

3.8 DISTILLATION COLUMN (T27)

For the seperation of the top liquid process stream from the extractor (containing TOA and formic acid) a simple distillation is required. This choice of equipment is justified by the large difference in boiling temperature of the two components. Because of the considerable desintegration of the formic acid at higher temperatures a reduced pressure is needed.
The calculations for the separation, wich are used in the mass balance, are made by Chem Cad without the electrolyte model. The thermodynamical model was SRK and the K-value was also calculated with SRK.

3.9 HEAT-EXCHANGERS

3.9.1 . Heat-transfer equipment selection

The most commonly used type of heat-transfer is the shell and tube heat exchanger. They are being used for all kinds of applications. The advantages of this type are: the configuration gives a large surface in a small volume, good shape for pressure operation, well-established fabrication techniques and design procedures, and easy cleaning.

Essentially, a shell and tube exchanger consists of a bundle of tubes enclosed in a cylindrical shell. The ends of the tubes are fitted into tube sheets, which separate the shellside and tub-side fluids. Baffles are provided in the shell to direct the fluid flow and support the tubes. The assembly of baffles and tubes is held together by support rods and spacers.

The simplest and cheapest type of shell and tube exchanger is the fixed tube exchanger. This type is not suitable for fouling fluids, since the tube bundle can not be removed for cleaning. Another disadvantage is that there is no provision for differential expansion of the shell and tubes, so this type is limited to temperature differences up to about 80°C. Some provision for expansion can be made by including an expansion loop in the shell, but their use is limited to low shell pressure, up to about 8 bar. In other types, only one end of the tubes is fixed, and the bundle can expand freely.

The U-tube type is cheaper than the floating-head types, but it is limited to relatively clean fluids.

Exchangers with an internal floating head are more versatile than fixed and U-tube exchangers. They are suitable for high temperature differentials and are easier to clean, so they can be used for fouling liquids. An advantage is that the clearance between the tubes and the shell has to be larger, allowing fluid in the shell bypassing the tubes. In external floating head designs there is a chance of leakage through the slidding gland, so the shell side pressure is limited to about 20 bar.

Wherever possible the cheap, simple fixed tube exchanger will be applied for this preliminary design. When the difference between the temperature of the cooling water and the process stream is more than 80 K or for pressures above 8 bar, exchangers with an internal floating head is applied. For convenience, single pass exchangers are chosen for all.

Fixed tube exchangers are used for: H3, H22 and H24.
Internal floating head exchangers are used, for example: H6, H14, H18 and H25.

3.9.2. Fluid allocation: shell or tubes

Where no phase changes occur, the below mentioned factors will determine the allocation of the fluid streams to the shell or tubes.
Through the tubes should flow: the most corrosive fluid (to reduce the cost of expensive alloy or clay components), the fluid that has the greatest tendency to foul (the tubes are easier to clean and better control over the velocity in tubes than in shell), hottest fluid, fluid with highest pressure (high pressure tube is cheaper than high pressure shell), fluid with lowest allowable pressure drop, less viscous fluid (if flow is turbulent). Allocating the fluids with the lowest flow rate to the shell side will normally give the most economical design.

For all heating processes steam is used, for cooling water is used. As all process streams are corrosive, all the process stream will be led through the tubes, and the cooling water or steam through the shell.

3.10 DESCRIPTION OF PROCESS FLOW SHEET

The process flowsheet of the process is shown in appendix VIII.

According to this flowsheet a water stream is contacted with an ammonia gas stream (both at 20 °C) in the first absorber (A1). A waste stream containing little NH_3 and CO_2 comes out of the top of the absorber and the liquid process stream (12) containing ammoniumhydroxide comes out of the bottom.

This process stream is brought to 7 bar by a centrifugal pump (P2) and cooled to 20 °C by a heat exchanger (H3) so it is on the right temperature for the second absorber (A2) where it is brought in contact with a CO_2 stream (58). In this absorber the formation of ammonium bicarbonate takes place. At the top of the second absorber a small CO_2 waste stream comes out. And at the bottom the process stream comes out.

In a centrifugal pump (P5) the pressure of this process stream is brought to the right pressure for the reactor section and in a heatexchanger (H6) the temperature of the process stream is cooled to the right reactor temperature.

The process stream is being mixed with a catalyst recycle stream (21) (also containing reaction medium) and brought into a cyclone (M7) to separate the catalyst for the regenaration reactor (R8). Out of the top of the cyclone (M7) the process stream goes to the formiate forming reactor (R11).

Out of the bottom of the regeneration reactor (R8) comes the fresh catalyst (26) wich goes via a cyclone (M9) (this cyclone separates a recycle stream of aqeous bicarbonate to stop the the reformation of formiate into bicarbonate in the regenaraion reactor) to the formiate forming reactor (R11).

Out of the regeneration reactor comes a small stream of O_2 wich in fact can be recycled.

At the bottom of the formiate forming reactor (R11) a feed of H_2 comes in. Wich is nessecary to convert the bicarbonate into formiate. This formiate stream (containing still a little bicarbonate) comoe out of the bottom of the reactor.
Out of the top af the formiate forming reactor comes a small stream of H_2 wich contains to much inerts to be recycled and therefore has to be purged.

Between the two reactors there are two centrifugal pumps (p10 & p12) to keep the right pressure in the reactor section.

A filter (M13) separates the formiate stream from the deactivated catalyst. The catalyst stream out of the filter mixes up with the process stream out of absorber 2.
The formiate stream out of the filter is splitted into a process stream (37) and a recycle stream (30). This to ensure the right residence time in reactor (R11).

The filtered process stream enters at high pressure a flash vessel (V15) where the remaining bicarbonate is converted in CO_2,NH_3 en water by flashing to atmospheric pressure.
The CO_2 and NH_3 and a bit water come out of the top of the vessel and after compressing in compressor (C17) and cooling in condensor vessel (V19) they are recycled right bach to absorber 2.

The process stream (44) now containing mostly formate comes out of the bottom of the flash vessel (V15) and enters the extraction column (T21) where at high temperature and use of an extractive agent (stream 56) the formiate becomes formic acid and NH_3 wich leaves (stream 45) at the top of the extractor wich after condensing (V23) is recycled right back to the first absorber.
The formic acid stream (46) with the extractive agent also leaves at the top of the extractor and goes right to the destillation column (T27).

At the bottom of the extractor a water stream (48) comes and is after cooling (H24) recycled right back to absorber 1.

In destillation column (T27) the extrective agent is separated from the formic acid under less then

atmospheric pressure (see P31). The extractive agent is after repressuring again (P29) recycled to the extractor.

The liquid formic acid stream out of the distillation column is te product stream that is wanted.

4 PROCESS FLOW SHEET AND UNIT CALCULATIONS

4.1. ABSORBERS (A1 and A4)

4.1.1. Ammonia Absorber

The diameter of the column is calculated with the correlation of Sherwood et al. and is 1.2 m. The height of the column is calculated to be 4 m.
As the introduction of a temperature gradient over the height of the column would make the calculations much more complicated, a logarithmic mean temperature is used. It is assumed that the column is processed isothermally.
The pressure drop is calculated based on the method given by Wesselingh and Kleizen. The pressure drop over the column is 7392 Pa.
The accurate calculation and further details of the ammonia absorber is given in Appendix V-1.

4.1.2. Carbon dioxide Absorber

The diameter of the column is calculated with the same method as used for the ammonia absorber. This is calculated to be 1.4 m.
The height of the column is calculated with a method given by Danckwerts and is 33 m.
In the carbon dioxide absorber, is is assumed that the column is processed isothermally at the logarithmic temperature. Otherwise the calculation would become much complicate.
The pressure drop is also calculated with the method of Wesselingh and Kleizen and is 38451 Pa.
The accurate calculation and further details of the carbon dioxide absorber are given in Appendix V-2.

4.2. HYDROGENATION REACTOR (R11)

The dimensions of the reactor will be determined by the rate controlling process.
It is determined that the slowest process, that determines the overall rate of hydrogen consumption, is the reaction of hydrogen on the catalyst surface. The reaction rate is calculated with an expression given by D.C. Engel. The production rate of formate is calculated to be 0.0.9 mol/(kg cat·s). Then the minimum residence time is 8300 seconds and the minimum reactor volume is 168 m^3. As the superficial gas flowrate is assumed to be 0.01 m/s, the diameter of the bubble column will be 4.5 m and the height 11 m. The pressure drop over the column is 1.1 bar.
The accurate calculation and further details of the hydrogenation reactor are given in appendices V-3A and V-3B..

4.3. REGENERATION REACTOR (R8)

The calculation of the dimension of the regeneration reactor is based on the fact that the residence time should be 15 minutes (D.C. Engel). With the volume liquid flow-rate the volume of the

reactor is calculated to be about 32.2 m. As the superficial gas flowrate is assumed to be 0.01 m/s, the diameter of the bubble column is 1.6 m and the height is 16 m. The pressure drop over the column is 1.6 bar.
The accurate calculation and further details of the hydrogenation reactor are given in appendix V-4.

4.4 SOLID/LIQUID SEPARATION (M7,M9 and M13)

The cyclone dimensions are calculated with the nomograms from Coulson and Richardson. Assumptions made for this design are:

1) The D_{50}, the particle diameter wich is removed from the liquid stream with an efficiency of 50 % is chosen to be 10 µm.. With this an efficiency of 99.9 of catalysator particles is reached.
2) The viscosity (at 84 °C) is 354 (Janssen and Warmoeskerken)
3) The pressure drop is calculated with Stairmand, wich is a rough estimate (Coulson and Richardson)
4) The surface of friction is taken as a vertical cylinder with diameter $D_{cyclone}$ and height $5*D_{cyclone}$

The diameter of cyclone (M7) is calculated to be 0.35 m and the height is 1.75 m.
The diameter of cyclone (M9) is calculated to be 0.40 m and the height is 2.00 m.
The calculations are shown in Appendix V-5.

The size of the filter is estimated with a total turbulent flow in the filter pipes. So the filter consists of a bundle of 18000 pipes of semipermeable ceramics wich has a lenght of 3 meter. The pressure drop over the filter walls is estimated to be 4 bar, the pressure drop over the feed-filtate is estimated to be 2.5 bar. The total size then becomes 7*7 meter.

For further specification see equipment lists in appendix VI.

4.5 FLASH VESSEL (V15)

Calculation of the dimensions of the flash vessel (appendix VI) are made by Chem Cad. Without use of the electrolyte model.
The calculated split factors, that are used in the mass balance, are shown in table 4.5.1

Tabel 4.5.1 splitfactors

component	splitfactor (V out / L in)
H_2O	0.03412
NH_4OH	1.00000
bicarbonate	0.86321
formiate	0.00054

4.6 EXTRACTION COLUMN (T21)

Assumption made for the extractor design are:

1. The extractor operates with the worst case extractive capacity; this means all amonia is dissolved so only two phases are considered.
2. The extraction is modelled in two seperated units; one reactor in which reaction 1 took place and one simple two fase countercurrent extraction column. This because the Liquid-liquid-vapour extractor would not work, simply due to the fact that the forming of a vapour fase in an extractor column would disturb any formation of equilibrium. It woud sort of mix the two fases and make it a single stage mixer-settler. In the flow sheet only the tower is drawn with a vapour outlet on top.
3. If the amonia is in the vapour fase the distribution coëfficiënt wil be a factor 3 bigger so the column is rather overdimensioned.
4. The distribution coëfficiënt is higly temperature dependend. It is also dependend to the ammoniumformate and formic acid concentration. So it is chosen for the highest temperature and lowest formic acid concentration, at 100 °C and $x_{af} = 0.01$ it is 12 on a molfraction ratio base. On a mass ratio base it becomes 0.60 (kg formic acid/kg TOA)/(kg formic acid/kg water)
5. The volume fluxes are considered constant this gives an error of 10% at most.
6. The viscosities and densities are considered not temperature dependend, this gives an error of 5 % at most
7. For the disperse fase the organic fase is chosen. This because its lower surfacial tension compaired with water so it easier forms smal droplets.

For the optimum design the methode of diktaat scheidingstechnieken II is used.
The column is optimized with respect to:

1. number of stages
2. column diameter
3. column hight
4. drop size
5. massfluxratio

The calculations are made with MathCad 5.0 by microsoft.
See appendix V-6.

4.7 DISTILLATION COLUMN (T27)

The calculations on the distillation column are made by Chem Cad, without use of the electrolyte (pitzer) modell. The dimension and sizes are shown in Appendix VI.
The seperation that takes place and wich is used in the mass balance is that almost all TOA leaves at the bottom of the column and the formic acid (with little water) leaves at the top.

4.8 PUMPS

The calculations of the pump are shown in Appendix V-7. And the specifications of the pumps are shown in Appendices VI and VII.

4.9 HEAT-EXCHANGERS

The coolers and the condensors are calculated with methods described in Coulson and Richardson. The overall heat transfer coefficient of cooling water is estimated from the nomograph given by Frank and is 635 W/m^2K. The overall heat transfer coefficient of steam is taken to be 8000 W/m^2K. Examples of these calculations are given in appendix V-8. the bottom and all water and formic acid leaves at the top of the column.

4.10. DEACTIVATION AND RECYCLE STREAMS

D.C. Engel has observed that the Pd/C-catalyst deactivates very fast.
Probably the deactivation of 5 wt% Pd/C is caused by the exposure of hydrogen. According to D.C. Engel this decrease in catalytic activity might be induced by the transformation of the metal into its hydride:

$$2Pd(s)+\frac{1}{2}H_2(g) \square Pd_2H(s) \qquad \Delta H^0_r = -40.214 kJ/mol$$

A deactivation rate for the catalyst is given by D.C. Engel:

$D(t)=1-1.4658E^{-3}*t+9.5728E^{-7}*t^2$ $\qquad t \leq 400$ s

It appears that the catalyst is reduced to about 60% of its initial value already after 350 s of reaction time. In this preliminary design the maximum residence time of the catalyst is taken to be 420 s.

To maintain a sufficient bicarbonate conversion rate a very frequent catalyst refreshment will be necessary. This implies the requirement of a very large external recycle stream of the slurry phase, along with a large catalyst separation and regeneration unit.
It is already determined that the hydrogenation will take place at a temperature of 353 K. The choice is made to produce formic acid with a conversion of bicarbonate of 0.55, as the residence time seems reasonably. The residence time needed is then 8300 s. As the recycle ratio is defined as the recylce stream divided with the total stream, the recycle ratio is then about 95 %.

5 MASS AND HEAT BALANCE

5.1 mass balance

For the manufacture of the mass balance and the heat balance the following assumptions are being made:

1) The balances are based on a yearly procuction of 100,000 metric tons of formic acid. One production year has 8000 working hours.

2) Loss of production during the start up of the factory isn't taken into account. The balances are based on a steady-state production process.

3) In the second absorber there has to be excess of carbon dioxide, so there won't be any formation of carbamate.

4) The refreshment 2% of catalyst, that dies during the regeneration process, is simulated very simply; just a stream of old catalyst is taken out of the process and a stream of fresh catalyst is put in the process again. The way this happens is not taken into acount. So the loss of fluid wich would accompany the out-take of catalyst isn't mentioned in the mass balance.

5) The conversion of bicarbonate to formiate was taken 55 %. This conversion had the best combination of residence time and formic acid production rate.

6) The whole process couldn't be simulated by Aspen or Chem Cad, because of the problems these programms had with the calculation of the electrolyte models. Especially the reactor section gave a lot of problems.
So therefore some of the necessary split factors where calculated by Chem Cad without the electrolyte model, some with the electrolyte model and some where just calculated by hand.

For the results of the mass and heat balances see appendix II.

5.2 ASSUMPTIONS FOR THE ENERGY BALANCE

In appendix II-2 the total heat balance for the formic acid plant is given.
The principles of the energy balance calculations used for the design are summed up below:

Energy balance
The general equation for the conservation of energy is given by:

ENERGY OUT = ENERGY IN + GENERATION - CONSUMPTION - ACCUMULATION

For steady state the accumulation is zero. Potential and kinetic energy will be small, and are

neglected. As basis for the energy content is chosen 298 K.

Liquid streams
For the calculation of the relative energy content of a liquid stream at temperature T the following equation is used:

$$Q = \Phi[H(T)-H(298)] = \Phi C_p(T-298) \qquad \textbf{(5.2.1)}$$

In this design all liquid process stream exist of aqueuos solutions of electolytes, some containing catalyst particles as well. No information was available about the specific heat of electrolyte solutions. The influence of taking into account the specific heat of the small concentration of solids proved to be very small. Therefore, the specific heat of all process streams was estimated to be 4.2 kJ/(kgK), the value of the specific heat of pure water. The specific heat of TOA is 1.008 kJ/(kgK).

Vapor streams
The relative energy content of the vapor streams is calculated using the simulation program ChemCAD.

Heat of Mixing
Calculation of the heat of mixing for some streams showed that simplification of neglecting this heat effect did not have a great influence, both for the liquid and on the vapor streams.

Heats of Reaction, Heat of Vaporisation

$NH_3(g) + H_2O(l) \rightarrow NH_4OH(aq)$	$\Delta H^0_r =$ -34.4 kJ/mol
$NH_3(g) + CO_2(g) + H_2(g) \rightarrow NH_4HCO_3(aq)$	$\Delta H^0_r =$ -99.0 kJ/mol
$NH_4HCO_3(aq) + H_2(g) \rightarrow NH_4OOCH(aq) + H_2O(l)$	$\Delta H^0_r =$ -19.4 kJ/mol
$NH_4OOCH(aq) \rightarrow NH_3(g) + HCOOH(l)$	$\Delta H^0_r =$ +87.2 kJ/mol
$H_2O(g) \rightarrow H_2O(l)$	$\Delta H^0_r =$ -4.401 kJ/mol
$\frac{1}{2}H_2(g) + 2Pd(s) \rightarrow Pd_2H(s)$	$\Delta H^0_r =$-187.97 kJ/kg Pd_2H
$Pd_2H(s) + O_2(g) \rightarrow 2\ Pd(s) + 1/2\ H_2O(l)$	$\Delta H^0_r =$ 39 kJ/mol
$NH_4HCOO(aq) + O_2(g) \rightarrow NH_4HCO_3\ (aq)$	$\Delta H^0_r =$ 245.95 kJ/mol

Use of steam for heating
Complete condensation of the steam is assumed. The heat that is supplied by the steam is than:

$$Q = Q_1 + Q_2 + Q_3 \qquad \textbf{(5.2.2)}$$

where:
Q_1 = heat needed for cooling the steam to its saturation temperature
= $\Phi_{steam} * C_{p,steam} * (T-T_{sat})$
Q_2 = heat needed for condensation of steam to liquid
= $\Phi_{steam} * \Delta H_v$
Q_3 = heat needed for cooling the liquid to its outlet temperature
= $\Phi_{steam} * C_{p,H2O(l)} * \Delta T$

The ammount of steam required is calculated by dividing the heat duty required for the heating operation by the total Q calculated.

Values of the quantities are:

C_p (steam, 3 bar)	= 2.221kJ/(kgK)
C_p (steam, 40 bar)	= 3.7 kJ/(kgK)
ΔH (steam, 3 bar)	= 2730 kJ/kg
ΔH (steam, 40 bar)	= 2800 kJ/kg

Destillation

The reboiler duty and the condenser duty of the destillation column were calculated with the help of ChemCAD.

Heat exchanger integration

There are not much possibilities for heat integration in this plant, because: cooling takes place with water and the maximum temperature of this cooling water is about 40°C, the stream that are to be heated all have to be heated from 80°C and up so steam or gas heaters are required.

6 PROCESS CONTROL

Process control is a necassary part of a process to guarantee de safety and economical points. So per unit there is looked at the kind of controlers that are necessary and overall there is tried not to let the different controlers interfere with each other (Stephanopoulos).

The both absorbers are provided with a level controler. This to make sure that the liquid level doesn't get to high, for example when there is less gas forming. When the level gets to high the tab will open a little more and when the level gets to low the opposite takes places.

Both the feed lines of the first absorber and the gas feed line of the second absorber are profided with flow ratio controlers, this because of the fact that these lines are connected with process feed streams.

In both the reactors there need to be a constant temperature to ensure a good conversion. Therefor both are profided with heat exchangers (r8 heater, r11 cooler). The temperature is controled by temperature-ratio-controlers. These controle the amount of steam cq.cooling water that are used.

Both reactors have also level-control-systems for the same reasons as with the absorbers. Only the level is controled here with the gas outlet.The reactors also have a flow-ratio-controler on their gas inlet streams for the same reasons as the flow controlers on the absorber feed streams.

The flash-vessel is profided with a pressure controler on the gasoutlet, the to ensure a good separation. When the pressure gets to high the valve opens a little and the opposite takes place when the pressure get below a certain point.The vessel is also profided with a level controler.

The extraction column has two level controlers because a three phase separation takes place here. The first level controler is watching over the liquid(water)/ liquid(TOA) level and the second controler looks at the liquid(TOA)/vapour level.

The destillation column is very important for a proper product stream. So it is also very important to keep the column on the right temperature to attain the right separation. Also fluctuations in the feed streams are dangerous for the product stream. A right formic acid production is attained by the use of an on-line-component-control-system, wich contols the reflux ratio. A temperature-ratio-controler is installed on the reboiler section to control the steam flow. A level controler is also installed at the bottom of the column.

Furthermore do all heaters and coolers have to be profided with a temperature controler and all kick backs over the pumps & compressors must have a pressure controler.

All vessel are profided with level controlers.

For a general view of the control systems there is refered to the flow sheet of the process (appendix VIII)

7 SAFETY, HEALTH AND ENVIRONMENT

To run this formic acid process safely, all safety, health and environmental risks are looked at. All properties and safety measures wich should be taken into accound of the different materials that are used are shown in appendix I, wich shows the chemical chards.

The two reactors, and the big recycle stream that connects both are the most dangerous parts of the process. This because of the high pressure at wich these parts opperate. Esspecially the catalyst regeneration reactor and the formate forming reactor have some critical points, because in the first a reaction with oxigen takes place and in the latter hydrogen is used and all this at about 25 bar. So here the risk of an explosion is the biggest. Therefore a HAZOP study (Coulson and Richardson) is made of the reactor section (appendix III).
The next most dangerous part is the second absorber. This piece of equipment is also working at a higher pressure (about 7 bar). Here also a HAZOP study is made.

Appart from the safety measures that are mentioned in the HAZOP analysis there are some extra measures that could be taken to minimize the damage if something unexpected occurs:

- to minimize the explosion damage there is the possibility to install blast and barrier walls
- the can be installed explosion relief-ventings and bursting disks on the reactors
- minimize the number of operators (no more then necassary) working on the process.

The materials that are being used in this FVO are:

- Water
- Oxygen
- Formic acid
- Hydrogen
- Carbon dioxide
- Ammonia
- Tri-octylamine
- Palladium (supported by active coal) catalyst

8 ECONOMIC ASPECTS OF THE PRODUCITON PLANT

8.1 CAPITAL COST ESTIMATION:

The investment costs are estimated at various described methodes to get a clear view of the total pure investment: Used methodes are of Zevnik-Buchanan, Wilson, Taylor and Lang. With these methodes a calculation for inflation and interest is used. This calculation uses two indices for investment costs; the Process engineering index and the CPE plant cost index. The investments are calculated to the most recent CPE indices of 1994, this because no index is yet available for 1995.
The PE index of 1994 is extrapolated from table in the handout Chemische fabriek because no actual values were available. Its value became 461, based on a index value of 45 in 1969. For the rates of exchange values are used for 14 may 1995 at noon.

The different cost estimations are containing different parts of the total costs so the factors of table 8.1.1 are used to get the same total investment cost estimates. In table 8.1.2 an overview of fixed capital investment and total investment costs is given for all used calculated estimations.

Table 8.1.1; overview of the investments

sort of investment	containing	part of total investment	
Fixed Capital	I_F	0.80	
	I_B		0.64
	equipment & installation		
	piping, instrumentation		
	control		
	indirect costs		
	I_H		0.16
	buildings and structures		
	auxiliary facilities		
	utilities, land, civil		
Miscelleneous costs	I_L		0.14
	licencies, know how		
	pre-operational expenses		
	startup (ex.workingcapital)		
Working capital	I_W		0.06
	start-up		
	initial catalyst load		
	raw materials		
	intermediates		
	finished product		
	inventories		

Table 8.1.2; an overview of the used calculations for the total investment costs

methode	fixed capital investment [10^6 US $]	total investment costs [10^6 US $]
Zevnik-Buchanan	13.85	17.31
Wilson	3.99	4.92
Taylor	18.15	22.34
Lang	6.82	8.5

8.1.1 Investment cost estimation according to Zevnik-Buchanan

The formula used by Zevnik and Buchanan:

$I_B + I_H = N*I_E*1.33*C_I/219$ [10^6 US $]

Where:
I_B = fixed capital costs for equipment.See table 8.1.
I_H = fixed capital costs for Buildings structures etc. See table 8.1
N = number of functional units in the procesflowsheet Pumps and seperator are excluded.
I_E = Cost per funktional unit
C_0 = 219 CPE plant cost index,1978
C_I = 368 CPE plant cost index,1994

I_E is a function of the complexity factor wich is calculated with:

$C_F = 2*10^{Ft+Fp+Fm}$

with
Ft = temperature factor
Fp = pressure factor
Fm = 0.2 material factor all equipment are made of stainless steel

The calculated values for the different factors, the complexity factor (obtained from the graph in the handout Chemische Fabriek) and the total costs are given in table 8.1.3 Values for I_E are obtained from The graphs in the college handouts.

Table 8.1.3; calculated factors for cost estimation according to Zevnik-Buchanan.

functional unit	Ft	Fp	Fm	C_F	I_E	I_B+I_H	number	total
absorber	0.001	0	0.2	3.177093	1.01	2.25674	2	4.513488
reactor	0.02	0.14	0.2	4.581735	1.06	2.36846	2	4.736928
extractor	0.001	0	0.2	3.177093	1.01	2.25674	1	2.256744
distillator	0.001	0.1	0.2	3.999724	1.05	2.34612	1	2.34612
total								13.85328

The fixed capital inverstment (I_B+I_H) is 13.85 $*10^6$ US $(1994)
The total investment $1/0.8*(I_B+I_H) = 17.31 *10^6$ US $

8.1.2 Investment cost estimation according to Wilson

The formula used by Wilson for calculation of the investments costs:

$I_B = f*N*F_p*F_t*F_m*AUC*C_I/C_0*ROE$ $/_{,1995}$ [US $]

with:
f = investment factor from graph, handout college chemische fabriek.
N = number of equipments (pumps, heat exchangers flashes are excluded
$F_{P,T,M}$ = factors for pressure, Temperature and material of construction
AUC = $21*P^{0.675}$ [,]
P = Plant capacity [tons/a]
C_0 = 115 Process engineering index UK, 1971, based on 1969
C_I = 125/45*166 = 461 Process engineering index UK, 1994, based on 1969, extrapolated value
ROE = 0.62 Rate of exchange from UK pounds to US dollars (1995)

The values for the different factors and the total coosts are given in table 8.1.4

Table 8.1.4; factors for capital investment calculation according to Wilson.

f	n	F_p	F_t	F_m	P	auc	ci/115	roe(1995)	total c
1.7	6	1.2	1.4	1.5	100000	49798.8	4.0087	0.62	3181374.4
fixed investments costs IB [10^6 US dollar]								3.19	

The fixed capital investment is $0.8/0.64*I_B = 3.99 *10^6$ US $
The total investment costs are $1/0.64*I_B = 4.97 *10^6$ US $

8.1.3 Cost estimation according to Taylor:

The formula used by Taylor is:

$I_B = 45*f*P^{0.39}*C_I/300*$ ROE $\$/_{1995}$ [US $]

with:
f = costlyness index $\Sigma^n (1.3)^{Si}$
Si = Σ complexity scores for n units (only main production units are considered)scores are given in handout.
P = 100 Plant capacity [kton/a]
C_0 = 300 Process engineering index (UK 1978), based on 1969
C_I = 461 Process engineering index (UK 1994), based on 1969, extrapolated value.
ROE = 0.62

The scores for the methode of Taylor are given in table 8.1.5. The are obtained from the handout

Table 8.1.5; scores and costlyness index for the methode of Taylor.

Taylor	Absorber1	Absorber2	Reactor1	Reactor2	Extractor	disltillation
	Score					
relative throughput	0	1	6	0	1	0
reaction time	0	0	0	0	0	0
storage time	0	0	0	0	0	0
T min	0	0	0	0	0	0
Tmax	1	1	1	1	1	1
Pmin	0	0	0	0	0	2
Pmax	0	1	2	1	0	0
materials of construct.	3	3	3	3	3	3
multistreaming	1	1	1	1	2	0
Si	5	7	13	6	7	6
1.3^Si	3.71293	6.274852	30.2875	4.82680	6.27485	4.826809
f	56.20376					
IB	14519.42					

The total fixed capital investment is 0.8/0.64*14.52 = 18.15 $*10^6$ US $
The total investment costs are 1/0.64*14.52 = 22.34 $*10^6$ US $

8.1.4 Cost estimation according to Lang:

The formula used by Lang :

$I_B+I_H = L^* I_E^*C_I/C_0^* ROE \$/_{,1995}$

With:
I_E = Sum of the major production costs
L = F1*F2
F1 = 1 + Σ9= 3.46 factors direct costs from table in the handout
F2 = 1 + Σ3 = 1.45 factors indirect costs from table in the handout
CI = 461 Process engineering index UK (1994), extrapolated value.
C0 = 163 Process engineering index UK (1979).
ROE = 0.62 Rate of exchange from UK pounds to US dollars

The major production costs are obtained from Coulson & Richardson, and are given in table 8.1.6

table 8.1.6; the equipment costs for the calculation of the investment according to Lang

equipment	cost	matfact.	pressure factor	total costs	total cost 1995
reactor 1	45000	2	1.4	126000	356355
reactor 2	1500	2	1.4	4200	11878
absorber 1	8500	2	1	17000	48079
absorber 2	9400	2	1.1	20680	58487
extractor					
cost per plate	250	2	1	500	1414
33 plates	8250	2	1	13200	46665
vessel	23000	2	1	46000	130098
total extrac	28750	2	1	57500	162622
dist (7 plates)	4000	2	1.4	11200	31676
cyclones (1995)	6300	2	1.4	17640	17640
filter (1995)	80000	2	1.4	224000	224000
11 pumps (1995)	159700	2	1.2	383280	383280
total					1472198.19
IB+IH=					6819535.341

The fixed capital investment is 6.80 $*10^6$ US $
The total investment costs are 8.50 $*10^6$ US $

8.2 OPERATION (PRODUCTION) COSTS

An estimate of the operating costs is needed to judge the viability of this process. These costs can be estimated form the flow-sheet (wich gives the raw materials and sercvice requirements) and the capital cost estimate (calculated in the prior paragraph). The

calculations are done according to a Handout (Example - st451 - Procduction costs & economic criteria)
The production costs can be divided into two different groups: fixed costs and variable costs.

The following assumptions for the calculation of these costs are made:

- There are 8000 production hours in a year.
- The plant life time is taken to be 15 years.
- The rest value of the plant is 10 % of the capital investment.
- The construction time of the plant will be estimated on 2 years.

Variable costs

The most important variable costs are the raw materials, catalyst and the utilitity (service) costs. Table 8.2.1 shows the costs per unit. From the flow-sheet the magnitude of the feed and product (and waste) streams are taken. By combinding this with table 8.2.1 the production costs are calculated. This calculations are shown in appendix IV. The raw material costs come to k$ 11164.218 and the utility costs come to k$ 20858.390 a year.

Table 8.2.1 Utility & raw material costs

UTILITY COSTS PER UNIT ($)		
Utility	**Unit**	**Costs per unit ($)**
Electricity	MWh	64.516 (Handout)
Steam p<	Ton	19.355 (Handleiding fabrieksvoorontwerp)
Steam p>	Ton	22.581 (Handleiding fabrieksvoorontwerp)
Cooling Water	Ton	00.065 (Handout)
RAW MATERIAL COASTS PER UNIT ($)		
Raw material	**Unit**	**Costs per unit ($)**
Ammonia	Ton	120.000 (Chemical marketing reporter (febr.12,1993))
Carbon dioxide	Ton	39.2 (Kirk Othmer, volume 4)
Hydrogen	Ton	209.032 (Kirk Othmer, volume 8)
Oxygen	Ton	100.840 (Kirk Othmer, volume 10)
Proces water	Ton	0.968 (Handout)
Catalist (fresh)	Ton	38709.677 (Engel)
Catalist (used)	Ton	0.000(Engel)
Formic Acid	Ton	904.839 (Coulson and Richardson)

Extra variable production costs have to be taken into acount due to the catalyst. 2% of the catalyst dies during the regenaration of it, so there have to be a continues refreshment of catalyst during the process. In the calculations of appendix IV the catalyst is taken into acount. The annual catalyst costs come to k$ 44593.546.

Some other variable costs that have to be calculated are the labour costs (See appendix IV). The total annual labour costs come to k$ 516.129.

Fixed annual production costs

The fixed production costs, such as maintenance, taxes, insurance etc, are estimated by using the fixed capital costs and the labour costs. To calculate a certain fixed cost most of the time a percentage of the fixed costs is taken. For the right precentages for the induvidual fixed costs see table 8.2.2.

Summary of the production costs

The total annual production costs calculation is shown in table 8.2.2 and they come to k$ 102300.360 a year.

Table 8.2.2 Summary of production costs

PRODUCTION COST ITEM	VAR. COSTS	FIXED COSTS	DIRECT COSTS	SALES R & D OVERH.	REMARKS
1 Raw Materials	11164.21		11164.21		Assessed
2 Miscell. Materials					Maint.: 1.0%
3 Utililties	20858.39		20858.39		Assessed
4 Waste Materials					Assessed
Catalist	44593.55		44593.55		
13 Royalties	178.74		178.74		Fixed Cap: 1.0%
5 Maintenance		1429.92	1429.92		Fixed Cap: 8.0%
7 Laboratory Supp.		3574.8	3574.8		Fixed Cap: 20.0%
6 Oper.Labour		516.129	516.129		Assessed
10 Capital Charges		2681.1	2681.1		Fixed Cap: 15.0%
11 Insurance		178.74	178.74		Fixed Cap. 1.0%
13 Licencies					
12 Local Taxes		3574.8	3574.8		Fixed Cap: 2.0%
8 Supervision		103.2258	103.2258		Oper.Lab: 20.0%
9 Personal Fac.					
9 Fire Dept, Secur.					
9 Laborat. Facil.					
4 Packaging					
Storage					
9 Peronnel Dept					[Oper.Lab: 20.0%
9 Techn.Serv.		103.2258	103.2258		[for all items (9).
Marketing R & D					x
Cust.Techn.Serv.					x
14 Sales					x
4 Shipping					
9 Admin.					x
16 R & D					x
	76646.59 (A)	12161.94 (B)	**88808.53** (A)+(B)	**13321.2798** (C)	[Dir.Costs 15.0% [for x's + Overhead.
ANNUAL PRODUCTION COST (A+B+C),			K$	102**300.360**	FIXED CAP. COSTS
					ASSESSED (k$):
PRODUCTION COSTS			$/Ton	**994.593912**	**17874**

8.3 GROSS INCOME, NET CASH FLOW AND ECONOMIC CRITERIA

The annual gross income is calculated on the annual production of formic acid. The production is multiplied by its price. The income comes to k$ 92913.33 a year. See appendix IV.

To calculate the net cash flow the difference between the earnings and the expenditure should be calculated. Unfortunately the net cash flow of this process is negative and therefor the factory is not commercially feasable. The net cash flow is: k$ -9387.030.

Because of the fact that the net cash flow is negative the pay out time can't be calculated. The pay out time is the amount of years in wich the investment costs are earned back.

The rate of return, wich is the ratio of annual profit to investment, can't also be calculated because of the same reason. Even so as the earning power, wich is the maximum rate that the project could pay and even break eve nby the end of the project life. All last three calculations show negative values in appendix IV.

Conclusion

Due to the non stop nessecary refreshment of catalyst during process (costs k$ 44000.0 a year) and the very high utility steam costs for the distillation (costs k$ 17000.0) the process is not economical feasable. When there could be found an other catalyst for the process and an other way to separate formic acid from TOA, maybe there could be made some profit.

9 CONCLUSION AND DISCUSSION

As shown in the economical evaluation (chapter 8 and Apendix IV) that the process isn't profitable. This comes mostly due to the following points:

- The use of catalyst is much and much to high (This due to some permanent demage done in the regeneration reactor).

- The use of high pressured steam in the distillation process is much to high.

Some other weak points in this formic acid making process are:

- The extraction column, wich is a new invention (D.Engel), is simulated in the best possible manner.

- The high recycle stream in the reactor section, due to the difference in residence time of the catalyst and the reacting raw matterials.

Therefore the follwing recomendations are made to improve the process:

1) The best way to improve the process is by finding a new catalyst, wich doesn't deactivates as fast as the palladium. This solves two problems: the high costs of catalyst and the huge recycle stream.

2) To use less steam, there could be made some heat integrations to make the process more profitable.

3) The steam used in the reboiler in the destillation column is not used in ist condensation traject, so a differt type of heating is advised.

The highest priority, goes to the firtst improvement, because here the highest costs are made.

10. LIST OF TEXT SYMBOLS

A_Φ	Debye-Hückel limiting slope for the osmotic coefficient	$[kg^{1/2}/mol^{1/2}]$
AUC	$21*P^{0.675}$	[-]
B	binary interaction function or second virial coefficient	[kg/mol]
C	ternary interaction function or third virial coefficient	[kg/mol]
C_0	CPE plant cost index (1978) = 219	
C0	Process engineering index (UK 1979) = 163	
C_0	Process engineering index (UK 1978) (1969) = 300	
C_0	Process engineering index (UK 1971) (1969) = 115	
C_1	Process engineering index (UK 1994) (1969) = 25/45*166 = 461	
CI	Process engineering index (UK 1994) = 461	
C_I	plant cost index,1994 = 368 CPE	
C_I	Process engineering index (UK 1994) = 461 based on 1969, extrapolated value.	
C_i^*	concentration of component i at the liquid side	$[mol/m^3]$
f	recovery	[-]
f	investment factor	
f	costlyness index $\Sigma^n (1.3)^{Si}$	
F	collection of terms for the activity coefficient	
F1	1 + Σ9= 3.46 factors direct costs from table in the handout	
F2	1 + Σ3 = 1.45 factors indirect costs from table in the handout	
Fm	0.2 material factor all equipment are made of stainless steel	
Fp	pressure factor	
$F_{P,T,M}$	factors for pressure, Temperature and material of constructionI	I
	ionic strength	[mol/kg]
I_B	fixed capital costs for equipment	
I_E	Cost per funktional unit	
I_E	Sum of the major production costs	
I_H	fixed capital costs for Buildings structures etc.	
L	= F1*F2	
m	molality	[kg/mol]
N	number of equipments (pumps, heat exchangers flashes are excluded)	
N	number of functional units (Pumps and seperator are excluded)	
P	Plant capacity	[tons/a]
P	100 Plant capacity	[kton/a]
P_i	partial pressure of component i	[Pa]
ROE	rate of exchange from UK pounds to US dollars = 0.62	
Si	Σ complexity scores for n units	
T	temperature	[K]
Z	total charge molality	[mol/kg]
z	valency	
γ	activity coefficient	
λ	binary neutral-ion interaction parameter	[kg/mol]

Indices and Abbreviations

i	component i
c	carbon dioxide or cation
a	ammonia or anion
n	neutral
M	cation of electrolyte, MX
X	anion of electrolyte, MX

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APPENDIX I:
SAFETY LISTS OF RAW MATERIALS

CAS-nr.: [1336-21-6]

NH_4OH

AMMONIA

(25% oplossing van ammoniak in water)

FYSISCHE EIGENSCHAPPEN		BELANGRIJKE GEGEVENS
Smeltpunt, °C	– 55	**KLEURLOZE VLOEISTOF, MET STEKENDE GEUR** De damp is zwaarder dan lucht. De stof is een matig sterke base en is corrosief ten opzichte van aluminium en zink. Reageert heftig met zuren. Vormt met halogenen, kwik- en zilveroxide slagge-voelige verbindingen.
Zelfontbrandingstemperatuur, °C	zie opm.	
Relatieve dichtheid (water = 1)	0,9	
Relatieve dampdichtheid (lucht = 1)	1,2	
Relatieve dichtheid bij 20 °C van verzadigd damp/luchtmengsel (lucht = 1)	1,1	MAC-waarde(als NH_3) 25 ppm 18 mg/m^3
Dampspanning, mbar bij 21 °C	440	
Oplosbaarheid in water	volledig	**Wijze van opname:** De stof kan worden opgenomen in het lichaam door inademing en inslikken. Een voor de gezondheid gevaarlijke concentratie in de lucht kan door verdamping van deze stof bij 20 °C zeer snel worden bereikt. **Directe gevolgen:** De stof werkt bijtend op de ogen, de huid en de ademhalingsorganen. Inademing van damp en/of nevel kan ademnood veroorzaken (longoedeem).
Explosiegrenzen, volume% in lucht	zie opm.	
Minimum ontstekingsenergie, mJ	zie opm.	
Relatieve molecuulmassa	35,1	
Log P octanol/water (berekend)	– 1,3	
Brutoformule:	H_5NO	

DIRECTE GEVAREN / SYMPTOMEN	PREVENTIE	BLUSSTOFFEN / EERSTE HULP
Brand: zie opmerkingen.	geen open vuur en niet roken.	bij brand in directe omgeving: alle blusstoffen toegestaan.
Inademen: *bijtend*, keelpijn, hoesten, ademnood.	ruimtelijke afzuiging, plaatselijke afzuiging, ademhalingsbescherming (filtertype K).	frisse lucht, rust, halfzittende houding, en naar ziekenhuis vervoeren.
Huid: *bijtend*, roodheid, pijn, ernstige brandwonden.	handschoenen.	verontreinigde kleding uittrekken, huid spoelen met veel water of douchen, en naar arts verwijzen.
Ogen: *bijtend*, roodheid, pijn, slecht zien.	gelaatsscherm, of oogbescherming in combinatie met ademhalingsbescherming.	eerst langdurig spoelen met veel water (contactlenzen verwijderen mits makkelijk mogelijk), dan naar arts brengen.
Inslikken: *bijtend*, keelpijn, buikpijn, misselijkheid.		mond laten spoelen, en onmiddellijk naar ziekenhuis vervoeren.

OPRUIMING / OPSLAG	ETIKETTERING
Opruimen gemorst produkt: Deskundige waarschuwen! Draag chemicaliën-pak uitrusting en verse luchtkap/persluchtmasker. Bij meer dan 50 liter gevarenzone ontruimen. Extra ventilatie. *Gemorst produkt* indammen en onschadelijk maken met 5% zwavelzuuroplossing (pas op voor reactie). *Reactieprodukt* verwijderen met water. *Spoelwater* afvoeren naar riool. Etiketteren en afvoeren volgens BAGA/KCA regels. **Opslag:** gescheiden van zuren, koel, ventilatie.	**Afleveringsetiket:**  Corrosief R: 34-37 S: 7-26 Nota B **BAGA:** C 1 **KCA :** II

OPMERKINGEN

De verschijnselen van longoedeem openbaren zich veelal pas na enkele uren en worden versterkt door lichamelijke inspanning; rust en opname in een ziekenhuis is daarom noodzakelijk.
De stof kan onder bepaalde omstandigheden brandbare damp/luchtmengsels vormen (15-29 Vol.%), die moeilijk te ontsteken zijn. Indien tanks of vaten, die ammonia bevat hebben, gespoeld worden met water, dienen deze in ruime mate belucht te worden (implosie-gevaar).
Zie voor opslag, vervoer en toepassingen ook PUBLIKATIEBLAD CPR 13 van de Arbeidsinspectie. Luchtdichte verpakking toepassen.

Transport Emergency Card TEC(R)-219 **GEVI: 80; UN-nummer: 2672**

CAS-nr.: [7664-41-7] NH_3

AMMONIAK

(drukhouder)

FYSISCHE EIGENSCHAPPEN		BELANGRIJKE GEGEVENS
Kookpunt, °C	– 33	**ONDER DRUK TOT VLOEISTOF VERDICHT GAS, MET STEKENDE GEUR**
Smeltpunt, °C	– 78	Het gas is lichter dan lucht. Het gas lost op in water onder warmte-ontwikkeling. Vormt met kwik- en zilveroxide slaggevoelige verbindingen. Reageert heftig met halogenen, oxidatiemiddelen en zuren. Tast koper, zink, aluminium en hun legeringen aan.
Vlampunt, °C	brandbaar gas	
Zelfontbrandingstemperatuur, °C	630	
Relatieve dichtheid (water = 1)	0,77	
Relatieve dampdichtheid (lucht = 1)	0,6	
Dampspanning, bar bij 20 °C	8,5	
Oplosbaarheid in water, g/100 ml bij 20 °C	53	
Explosiegrenzen, volume% in lucht	15-29	
Minimum ontstekingsenergie, mJ	680	
Soortelijke geleiding, pS/m	$\approx 1{,}9 \times 10^7$	
Relatieve molecuulmassa	17,0	
Log P octanol/water (berekend)	– 1,3	
		MAC-waarde 25 ppm 18 mg/m³
		Wijze van opname: De stof kan worden opgenomen in het lichaam door inademing. Een voor de gezondheid gevaarlijke concentratie in de lucht kan bij vrijkomen van dit gas zeer snel worden bereikt.
		Directe gevolgen: De stof werkt bijtend op de ogen, de huid en de ademhalingsorganen. Door snel verdampen kan de vloeistof bevriezing veroorzaken. Inademing van damp en/of nevel kan ademnood veroorzaken (longoedeem). In ernstige gevallen kans op dodelijke afloop.
Brutoformule:	H_3N	

DIRECTE GEVAREN / SYMPTOMEN	PREVENTIE	BLUSSTOFFEN / EERSTE HULP
Brand: brandbaar.	geen open vuur, geen vonken en niet roken.	toevoer afsluiten, indien niet mogelijk en geen gevaar voor omgeving, laten uitbranden, anders blussen met poeder, koolzuur, (halonen).
Explosie: gas met lucht explosief.	gesloten apparatuur, ventilatie, explosieveilige elektrische apparatuur en verlichting.	bij brand: drukhouder koel houden door spuiten met water.
Inademen: *bijtend*, keelpijn, hoesten, kortademigheid, ademnood.	ruimtelijke afzuiging, plaatselijke afzuiging, ademhalingsbescherming (filtertype K).	frisse lucht, rust, halfzittende houding, en arts waarschuwen.
Huid: *bijtend, bij bevriezing:* roodheid, pijn, ernstige brandwonden.	koude-isolerende handschoenen, beschermende kleding.	*bij bevriezing:* GEEN kleding uittrekken, huid spoelen met veel water of douchen, en naar arts verwijzen.
Ogen: *bijtend*, roodheid, pijn, slecht zien.	gelaatsscherm, of oogbescherming in combinatie met ademhalingsbescherming.	eerst langdurig spoelen met veel water (contactlenzen verwijderen mits makkelijk mogelijk), dan naar arts brengen.

OPRUIMING / OPSLAG	ETIKETTERING
Opruimen gemorst produkt: Deskundige waarschuwen! Draag chemicaliën-pak uitrusting en verse luchtkap/persluchtmasker. Gevarenzone ontruimen. Explosiegevaar. Extra ventilatie. *Gaswolk* bestrijden met watergordijn. *Neerslag* afvoeren naar riool. Etiketteren en afvoeren volgens BAGA/KCA regels. **Opslag:** brandveilig, indien binnen een gebouw, gescheiden van oxidatiemiddelen, zuren en halogenen.	**Afleveringsetiket:**  Vergiftig R: 10-23 S: 7/9-16-38 **BAGA:** C 1 **KCA :** VI **NFPA:** 

OPMERKINGEN

De verschijnselen van longoedeem openbaren zich veelal pas na enkele uren en worden versterkt door lichamelijke inspanning; rust en opname in een ziekenhuis is daarom noodzakelijk. De geur waarschuwt onvoldoende bij overschrijding van de MAC-waarde.
Het gas is moeilijk brandbaar en moeilijk tot ontsteking te brengen. De opgegeven waarde voor oplosbaarheid geldt voor het gas bij een druk van 1 Bar. Lekkende drukhouder met lek naar boven draaien anders ontsnapt vloeibaar ammoniak.
Zie voor opslag, vervoer en toepassingen ook PUBLIKATIEBLAD CPR 13 van de Arbeidsinspectie. Drukhouder met speciale appendages toepassen.

Transport Emergency Card TEC(R)-1 **GEVI: 268; UN-nummer: 1005**

CAS-nr.: [124-38-9]
koolzuurgas

CO_2

KOOLDIOXIDE

(drukhouder)

FYSISCHE EIGENSCHAPPEN		BELANGRIJKE GEGEVENS
Kookpunt, °C	− 79	**KLEURLOOS EN REUKLOOS ONDER DRUK TOT VLOEISTOF VERDICHT GAS**
Relatieve dichtheid (water = 1)	0,8	De damp is zwaarder dan lucht en kan zich op laaggelegen plaatsen ophopen met aldaar kans op zuurstofgebrek (bewusteloosheid). Bij snel uitstromen van kooldioxide uit drukhouder ontstaat statische elektriciteit waardoor een (reeds aanwezig) explosief mengsel kan worden ontstoken. Vrij uitstromende vloeistof verdicht zich tot *droogijs* (zie aldaar). Reageert bij hogere temperatuur heftig met ammoniak en diverse aminen.
Relatieve dampdichtheid (lucht = 1)	1,5	
Dampspanning, bar bij 20 °C	57,6	
Oplosbaarheid in water, g/100 ml bij 25 °C	0,16	
Relatieve molecuulmassa	44,0	
		MAC-waarde 5000 ppm 9000 mg/m³
		Wijze van opname: De stof kan worden opgenomen in het lichaam door inademing. Dit gas kan bij vrijkomen door verdringing van de lucht verstikkend werken. **Directe gevolgen:** Door snel verdampen kan de vloeistof bevriezing veroorzaken. Inademing van de stof kan ademnood veroorzaken. In ernstige gevallen kans op bewusteloosheid.
Brutoformule:	CO_2	

DIRECTE GEVAREN / SYMPTOMEN	PREVENTIE	BLUSSTOFFEN / EERSTE HULP
Brand: niet brandbaar.		bij brand in directe omgeving: alle blusstoffen toegestaan.
Explosie:		bij brand: drukhouder koel houden door spuiten met water.
Inademen: diep ademen, transpireren, ademnood, hoofdpijn, duizeligheid.	ventilatie, ruimtelijke afzuiging, plaatselijke afzuiging, onder geen beding filtermaskers.	frisse lucht, rust, zonodig beademing, en arts waarschuwen, of naar ziekenhuis vervoeren.
Huid: *bij bevriezing:* roodheid, pijn, ernstige brandwonden.	koude-isolerende handschoenen.	*bij bevriezing:* GEEN kleding uittrekken, huid spoelen met veel water of douchen, en arts waarschuwen.
Ogen: *bij bevriezing:* roodheid, pijn, slecht zien.	zuurbril.	eerst langdurig spoelen met veel water (contactlenzen verwijderen mits makkelijk mogelijk), dan naar arts brengen.

OPRUIMING / OPSLAG	ETIKETTERING
Opruimen gemorst produkt: Deskundige waarschuwen! Draag handschoenen en laarzen (koude-isolerend) en verse luchtkap/persluchtmasker. Bij meer dan 50 liter gevarenzone ontruimen. Extra ventilatie. Etiketteren en afvoeren volgens BAGA/KCA regels. **Opslag:** brandveilig indien binnen een gebouw, koel.	**Afleveringsetiket:** vraag leverancier **KCA : VI**

OPMERKINGEN

Bij hoge concentraties in de lucht, bijvoorbeeld in een slecht geventileerde ruimte, ontstaat zuurstofgebrek met kans op bewusteloosheid. Boven 10% kooldioxide in de lucht: bewusteloosheid en dodelijke afloop; kooldioxide komt vrij bij vele gistingsprocessen (in gistingskelders) en is een belangrijk bestanddeel van rookgas.
In PUBLIKATIEBLAD P 134-5 van de Arbeidsinspectie worden uitvoerige instructies gegeven voor het veilig werken met kooldioxide. Zie ook PUBLIKATIEBLAD P 153 van de Arbeidsinspectie: 'Veiligheid in ruimten bewaakt door automatische kooldioxide brandblusinstallaties'.

Transport Emergency Card TEC(R)-11 **GEVI: 20; UN-nummer: 1013**

CAS-nr.: [64-18-6]
hydrogeencarbonzuur
methaanzuur

HCOOH

MIEREZUUR

FYSISCHE EIGENSCHAPPEN		BELANGRIJKE GEGEVENS
Kookpunt, °C	101	**KLEURLOZE, LICHTROKENDE VLOEISTOF, MET STEKENDE GEUR**
Smeltpunt, °C	8	De damp mengt zich goed met lucht. De stof ontleedt bij verhitting onder vorming van giftig en brandbaar gas (*waterstof*, zie aldaar). Zuren bevorderen de ontleding. De stof is een sterk reductiemiddel en reageert heftig met oxidatiemiddelen. Reageert heftig met basen en is corrosief.
Vlampunt, °C	48	
Zelfontbrandingstemperatuur, °C	480	
Relatieve dichtheid (water = 1)	1,2	
Relatieve dampdichtheid (lucht = 1)	1,6	
Relatieve dichtheid bij 20 °C van verzadigd damp/luchtmengsel (lucht = 1)	1,03	MAC-waarde 5 ppm 9 mg/m^3
Dampspanning, mbar bij 20 °C	42,5	**Wijze van opname:** De stof kan worden opgenomen in het lichaam door inademing en inslikken. Een voor de gezondheid gevaarlijke concentratie in de lucht kan door verdamping van deze stof bij ca. 20 °C vrij snel worden bereikt; bij vernevelen nog sneller.
Oplosbaarheid in water	volledig	**Directe gevolgen:** De stof werkt bijtend op de ogen, de huid en de ademhalingsorganen. Inademing van de stof kan longoedeem veroorzaken. In ernstige gevallen kans op dodelijke afloop.
Explosiegrenzen, volume% in lucht	12-33	
Soortelijke geleiding, pS/m	5,8 x 10^9	
Relatieve molecuulmassa	46,0	
Log P octanol/water	– 0,5	
Brutoformule:	CH_2O_2	

DIRECTE GEVAREN / SYMPTOMEN	PREVENTIE	BLUSSTOFFEN / EERSTE HULP
Brand: brandbaar.	geen open vuur en niet roken.	poeder, alcoholbestendig schuim, sproeistraal water, koolzuur, (halonen).
Explosie: boven 69 °C: damp met lucht explosief.	boven 69 °C gesloten apparatuur, ventilatie.	
Inademen: *bijtend*, keelpijn, hoesten, kortademigheid, ademnood.	ruimtelijke afzuiging, plaatselijke afzuiging, ademhalingsbescherming (filtertype BE).	frisse lucht, rust, halfzittende houding, en naar ziekenhuis vervoeren.
Huid: *bijtend*, roodheid, pijn, brandwonden.	handschoenen, beschermende kleding.	verontreinigde kleding uittrekken, huid spoelen met veel water of douchen, en zonodig naar arts verwijzen.
Ogen: *bijtend*, roodheid, pijn, slecht zien.	gelaatsscherm.	eerst langdurig spoelen met veel water (contactlenzen verwijderen mits makkelijk mogelijk), dan naar arts brengen.
Inslikken: *bijtend*, keelpijn, buikpijn, diarree.		mond laten spoelen, en onmiddellijk naar ziekenhuis vervoeren.

OPRUIMING / OPSLAG	ETIKETTERING
Opruimen gemorst produkt: Deskundige waarschuwen! Draag chemicaliën-pak uitrusting en verse luchtkap/persluchtmasker. Bij meer dan 50 liter gevarenzone ontruimen. Extra ventilatie. *Gemorst produkt* indammen en zorgvuldig opzuigen en eventueel hergebruiken. *Restant* verwijderen met water. *Spoelwater* afvoeren naar riool. Etiketteren en afvoeren volgens BAGA/KCA regels. **Opslag:** gescheiden van oxidatiemiddelen en sterke basen, ventilatie langs de vloer.	**Afleveringsetiket:**  Corrosief R: 35 S: 2-23-26 Nota B **BAGA:** D 6 **KCA** : III **NFPA:** 

OPMERKINGEN

De verschijnselen van longoedeem openbaren zich veelal pas na enkele uren en worden versterkt door lichamelijke inspanning; rust en opname in een ziekenhuis is daarom noodzakelijk. De geur waarschuwt onvoldoende bij overschrijding van de MAC-waarde.
Explosiegrenzen van 90%-ige oplossing in water: 18-57 vol. %.

Transport Emergency Card TEC(R)-89

GEVI: 80; UN-nummer: 1779

CAS-nr.: [1333-74-0]

H_2

WATERSTOF

(drukhouder)

FYSISCHE EIGENSCHAPPEN		BELANGRIJKE GEGEVENS
Kookpunt, °C	– 253	**KLEURLOOS REUKLOOS SAMENGEPERST GAS**
Vlampunt, °C	brandbaar gas	Het gas is lichter dan lucht. Vormt met chloor zgn. chloorknalgas dat o.a. door UV licht ontstoken kan worden. Reageert heftig met acetyleen, distikstofoxide, stikstofoxide, fluor met kans op brand en explosie. Vormt met zuurstof of lucht het zgn. knalgas.
Relatieve dampdichtheid (lucht = 1)	0,07	
Oplosbaarheid in water	niet	MAC-waarde niet vastgesteld
Explosiegrenzen, volume% in lucht	4-76	
Minimum ontstekingsenergie, mJ	0,01	**Wijze van opname:** Dit gas kan bij vrijkomen door verdringing van de lucht verstikkend werken.
Relatieve molecuulmassa	2,0	
Brutoformule:	H_2	

DIRECTE GEVAREN / SYMPTOMEN	PREVENTIE	BLUSSTOFFEN / EERSTE HULP
Brand: zeer brandgevaarlijk.	geen open vuur, geen vonken en niet roken.	toevoer afsluiten, indien niet mogelijk en geen gevaar voor omgeving, laten uitbranden, anders blussen met poeder, koolzuur, (halonen).
Explosie: gas met lucht explosief.	gesloten apparatuur, ventilatie, explosieveilige elektrische apparatuur en verlichting, vonkarm handgereedschap.	bij brand: drukhouder koel houden door spuiten met water.
Inademen: ademnood, hoofdpijn, duizeligheid, bewusteloosheid.		frisse lucht, rust, zo nodig beademing, en naar ziekenhuis vervoeren.

OPRUIMING / OPSLAG	ETIKETTERING
Opruimen gemorst produkt: Deskundige waarschuwen! Draag verse luchtkap/persluchtmasker. Gevarenzone ontruimen. Explosiegevaar. Extra ventilatie. Etiketteren en afvoeren volgens BAGA/KCA regels. **Opslag:** brandveilig indien binnen een gebouw, ventilatie langs het plafond.	**Afleveringsetiket:**  Zeer licht ontvlambaar R: 12 S: 9-16-33 **NFPA:**  **KCA** : VI

OPMERKINGEN

Bij hoge concentraties in de lucht, bijvoorbeeld in een slecht geventileerde ruimte, ontstaat zuurstofgebrek met kans op bewusteloosheid.
Bij krachtig uitstromen van waterstof uit gasfles of in geval van gaslek kan in de lucht zelfontbranding optreden. Waterstof aantonen met geschikte explosiemeter. De gewone explosiemeter niet gebruiken. Bij opslag ventilatie op het hoogste punt.

Transport Emergency Card TEC(R)-20G04

GEVI: 23; UN-nummer: 1049

CAS-nr.: [7782-44-7]

O_2

ZUURSTOF

(drukhouder)

FYSISCHE EIGENSCHAPPEN		BELANGRIJKE GEGEVENS
Kookpunt, °C	– 183	**KLEURLOOS REUKLOOS SAMENGEPERST GAS**
Smeltpunt, °C	– 218	Reageert heftig met brandbare en reducerende stoffen. Speciale aandacht voor (smeer)olie en vet, die door zuurstof tot zelfontbranding kunnen komen.
Relatieve dampdichtheid (lucht = 1)	1,1	
Oplosbaarheid in water mg/l bij 20 °C	ca. 10	
Relatieve molecuulmassa	32,0	MAC-waarde niet vastgesteld
Brutoformule:	O_2	

DIRECTE GEVAREN / SYMPTOMEN	PREVENTIE	BLUSSTOFFEN / EERSTE HULP
Brand: niet brandbaar, doch bevordert brand van andere stoffen en kleding.	geen open vuur, geen vonken en niet roken, geen contact met kleding, smeerolièn en vetten.	
Explosie:	APPARATUUR EN LEIDINGEN OLIE- EN VETVRIJ HOUDEN, nooit tanks, vaten e.d. 'beluchten' met zuurstof.	bij brand: drukhouder koel houden door spuiten met water.
Inademen:	ruimtelijke afzuiging, plaatselijke afzuiging, onder geen beding filtermaskers.	
Huid:		eerst kleding spoelen met veel water, dan de met ZUURSTOF VERONTREINIGDE KLEDING UITREKKEN (BRANDGEVAAR).

OPRUIMING / OPSLAG	ETIKETTERING
Opruimen gemorst produkt: Draag veiligheidsbril. Extra ventilatie. Etiketteren en afvoeren volgens BAGA/KCA regels. **Opslag:** brandveilig indien binnen een gebouw, gescheiden van brandbare stoffen en reductiemiddelen, koel, ventilatie.	**Afleveringsetiket:**  Oxiderend R: 8-34 S: 21 **KCA** : VI

OPMERKINGEN

In zuivere zuurstof branden veel stoffen, die in de lucht niet branden (zoals trichloorethyleen, staal enz.). Reeds bij geringe stijging van het zuurstofgehalte in de atmosfeer neemt de brandbaarheid van alle stoffen sterk toe. Na gebruik als lasgas afsluiter dichtdraaien; slangen en leidingen regelmatig controleren; aansluitingen afzepen.
Verontreinigde kleding uitspoelen met veel water (brandgevaar). Zie voor opstelling en gebruik van zuurstoflessen ook PUBLIKATIEBLAD P 14 van de Arbeidsinspectie. Drukhouder met speciale appendages toepassen.

GEVI: 2; UN-nummer: 1072

APPENDIX II:
MASS AND HEAT BALANCES

APPENDIX II:
MASS AND HEAT BALANCE [KG/S] AND [KJ/S]

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
	M	M	M	M	M	M	M	M	M	M	M	M	M	M
H2O	0.10694	0.00000	0.00000	0.00000	0.00000	0.00000	9.72597	9.41871	0.00514	0.00514	0.00000	8.28247	8.28247	8.28247
NH3	0.00000	0.00540	0.00000	0.00000	0.00000	0.00000	0.14000	0.00000	1.24205	1.23665	0.00138	0.00000	0.00000	0.00000
CO2	0.00000	0.00000	3.41172	0.00000	0.00000	0.00000	0.36200	0.00000	0.00870	0.00870	0.00741	0.00000	0.00000	0.00000
H2	0.00000	0.00000	0.00000	0.00000	0.21704	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
HCOOH	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.03141	0.03141	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
NH4OH	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.14095	0.14095	0.00000	0.00000	0.00000	2.66931	2.66931	2.66931
NH4HCO3	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.65261	0.65261	0.65261
NH4COOH	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00226	0.00226	0.00000	0.00000	0.00000	0.04529	0.04529	0.04529
extr.ag.	0.00000	0.00000	0.00000	0.00000	0.00000	0.00001	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
kat.	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
N2	0.00000	0.00000	0.00000	0.00000	0.72239	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
Ar	0.00000	0.00000	0.00000	0.00000	0.01039	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
CH4	0.00000	0.00000	0.00000	0.00000	0.01202	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
O2	0.00000	0.00000	0.00000	0.51667	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
TOTAL M	0.10694	0.00540	3.41172	0.51667	0.96184	0.00001	10.40260	9.59334	1.25588	1.25048	0.00880	11.64968	11.64968	11.64968
TOTAL Q	-2.23	-0.06	-15.50	-2.61	-131.10	33.26	-257.20	-234.78	-36.73	-36.67	0.50	2748.18	2807.20	-258.80

	15	16	17	18	19	20	21	22	23	24	25	26	27	28
	M	M	M	M	M	M	M	M	M	M	M	M	M	M
H2O	10.12740	1.84492	9.18812	9.18812	9.18812	31.10253	21.91441	24.88202	6.22051	8.78335	15.00385	15.00555	0.00000	8.78335
NH3	0.72400	0.72400	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
CO2	1.87120	1.87120	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
H2	0.00000	0.00000	0.00000	0.00000	0.00000	0.00019	0.00019	0.00000	0.00019	0.00000	0.00019	0.00000	0.00000	0.00000
HCOOH	0.00189	0.00189	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
NH4OH	2.66931	0.00000	0.02525	0.02525	0.02525	0.07516	0.04990	0.06013	0.01503	0.02122	0.03625	0.03625	0.00000	0.02122
NH4HCO3	0.65261	0.00000	10.81936	10.81936	10.81936	20.43993	9.62057	16.35195	4.08799	9.14078	13.22877	15.61619	0.00000	9.14078
NH4COOH	0.04529	0.00000	0.04788	0.04788	0.04788	9.52131	9.47343	7.61705	1.90426	0.00000	1.90426	0.00000	0.00000	0.00000
extr.ag.	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
kat.	0.00000	0.00000	0.00000	0.00000	0.00000	2.00000	2.00000	0.00000	2.00000	0.00000	2.00000	2.00000	0.00000	0.00000
N2	0.00000	0.00000	0.00001	0.00001	0.00001	0.00143	0.00143	0.00115	0.00029	0.00041	0.00069	0.00069	0.00000	0.00041
Ar	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
CH4	0.00000	0.00000	0.00000	0.00000	0.00000	0.00002	0.00002	0.00002	0.00000	0.00001	0.00001	0.00001	0.00000	0.00001
O2	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.03200	0.00000
TOTAL M	16.09170	4.44201	20.08062	20.08062	20.08062	63.14058	43.05996	48.91231	14.22827	17.94576	32.17403	32.65869	0.03200	17.94576
TOTAL Q	-298.76	-39.97	7148.48	7148.48	4628.48	14595.60	9967.11	11676.48	2919.12	4091.16	7000.87	7737.15	-0.15	4091.16

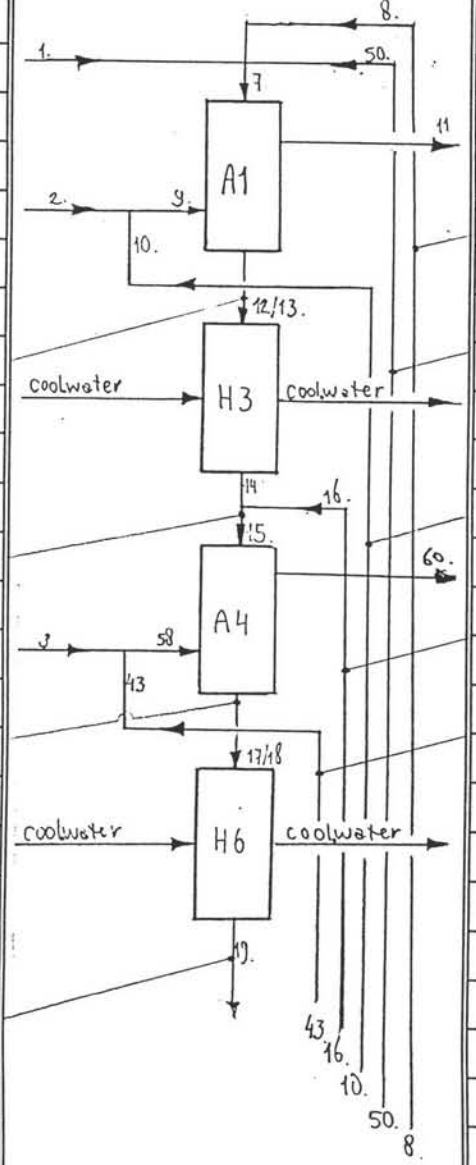
	29	30	31	32	33	34	35	36	37	38	39	40	41	42
	M	M	M	M	M	M	M	M	M	M	M	M	M	M
H2O	6.22220	186.13943	186.13943	217.24365	0.00000	219.14413	219.14413	197.22972	11.09029	11.09029	1.86356	10.18465	1.86356	1.86356
NH3	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.90599	0.00000	0.90599	0.90599
CO2	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	2.33951	0.00000	2.33951	2.33951
H2	0.00000	0.00000	0.00000	0.00000	0.00381	0.00019	0.00019	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
HCOOH	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00189	0.00000	0.00189	0.00189
NH4OH	0.01503	0.42387	0.42387	0.49902	0.00000	0.49902	0.49902	0.44912	0.02525	0.02525	0.00000	0.02525	0.00000	0.00000
NH4HCO3	6.47541	81.71645	81.71645	104.54380	0.00000	96.20573	96.20573	86.58516	4.86871	4.86871	0.00000	0.66599	0.00000	0.00000
NH4COOH	0.00000	80.46665	80.46665	88.08370	0.00000	94.73433	94.73433	85.26090	4.79425	4.79425	0.00000	4.79166	0.00000	0.00000
extr.ag.	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
kat.	2.00000	0.00000	0.00000	2.00000	0.00000	2.00000	2.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
N2	0.00029	0.01212	0.01212	0.01356	0.72167	0.01427	0.01427	0.01285	0.00072	0.00072	0.00072	0.00000	0.00072	0.00072
Ar	0.00000	0.00000	0.00000	0.00000	0.01039	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
CH4	0.00000	0.00020	0.00020	0.00023	0.01201	0.00024	0.00024	0.00021	0.00001	0.00001	0.00001	0.00000	0.00001	0.00001
O2	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
TOTAL M	14.71293	348.75872	348.75872	412.38397	0.74788	412.59793	412.59793	369.53796	20.77924	20.77924	5.11169	15.66755	5.11169	5.11169
TOTAL Q	3646.00	80562.12	92238.60	95055.34	47.80	95330.44	95330.44	85363.32	4801.20	6257.30	5030.00	4585.42	7551.00	-46.00

	43 M	44 M	45 M	46 M	47 M	48 M	49 M	50 M	51 M	52 M	53 M	54 M	55 M	56 M
H2O	0.01864	10.18465	0.20545	0.10273	0.00000	9.96457	0.20545	0.20032	0.54585	9.41871	9.41871	0.00000	0.00000	0.00000
NH3	0.18199	0.00000	1.37665	0.00000	0.00000	0.00000	1.37665	0.14000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
CO2	0.46831	0.00000	0.37070	0.00000	0.00000	0.00000	0.37070	0.36200	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
H2	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
HCOOH	0.00000	0.00000	0.00000	3.46265	0.00000	0.03323	0.00000	0.00000	0.00182	0.03141	0.03141	0.00000	0.00000	0.00000
NH4OH	0.00000	0.02525	0.00000	0.00000	0.00000	0.14912	0.00000	0.00000	0.00817	0.14095	0.14095	0.00000	0.00000	0.00000
NH4HCO3	0.00000	0.66599	0.00000	0.00007	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
NH4COOH	0.00000	4.79166	0.00000	0.00000	0.00000	0.00240	0.00000	0.00000	0.00013	0.00226	0.00226	0.00000	0.00000	0.00000
extr.ag.	0.00000	0.00000	0.00000	19.99988	19.99988	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	19.99987	19.99987	19.99987
kat.	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
N2	0.00072	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
Ar	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
CH4	0.00001	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
O2	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
TOTAL M	0.66967	15.66755	1.95280	23.56532	19.99988	10.14931	1.95280	0.70232	0.55598	9.59334	9.59334	19.99987	19.99987	19.99987
TOTAL Q	-6.03	4585.42	1133.82	1888.81	1915.2	2595.72	-57.16	-20.49	142.19	2453.52	2453.52	4720.46	1948.46	1948.46

	57 M	58 M	59 M	60 M	61 M	62 M
H2O	0.10273	0.01864	0.00000	0.00000	0.00000	0.10273
NH3	0.00000	0.18199	0.00000	0.00000	0.00000	0.00000
CO2	0.00000	3.88003	0.00000	0.09175	0.00000	0.00000
H2	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
HCOOH	3.46265	0.00000	0.00000	0.00000	0.00000	3.46265
NH4OH	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
NH4HCO3	0.00007	0.00000	0.00000	0.00000	0.00000	0.00007
NH4COOH	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
extr.ag.	0.00001	0.00000	0.00000	0.00000	0.00000	0.00001
kat.	0.00000	0.00000	0.04000	0.00000	0.04000	0.00000
N2	0.00000	0.00072	0.00000	0.00072	0.00000	0.00000
Ar	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
CH4	0.00000	0.00001	0.00000	0.00001	0.00000	0.00000
O2	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
TOTAL M	3.56545	4.08139	0.04000	0.09248	0.04000	3.56545
TOTAL Q	98.11	-24.9	0.84	10	9.408	98.11

MASSA- EN WARMTE- BALANS.

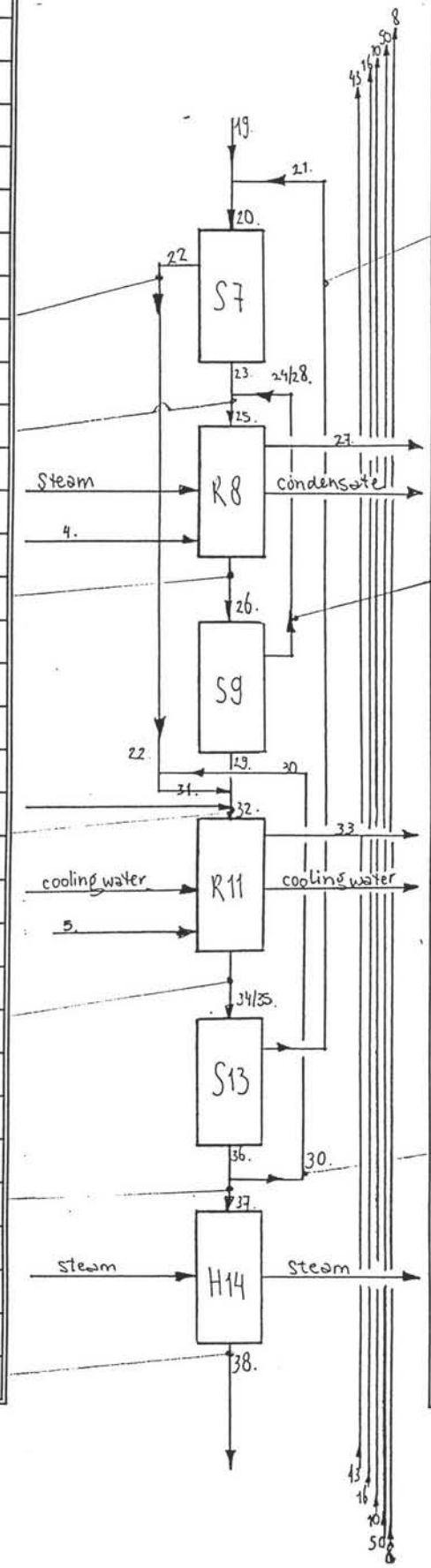
IN		Voor-waarts
M	Q	M
		Q
0.107	-2.23	
0.005	-0.06	
		11.65
		2807.20
36.0	-756	
		16.09
		-298.76
3.41	-15.5	
		20.08
		7148.48
30.0	-630	
		20.08
		4628.48



Retour	UIT	
M	M	Q
Q		
	0.01	0.5
9.59		
-234.48		
0.70		
-20.49		
	36.0	2268
1.25	0.09	10
-36.73		
4.44		
-39.97		
0.67		
-6.03		
	30.0	1890

VERVOLG

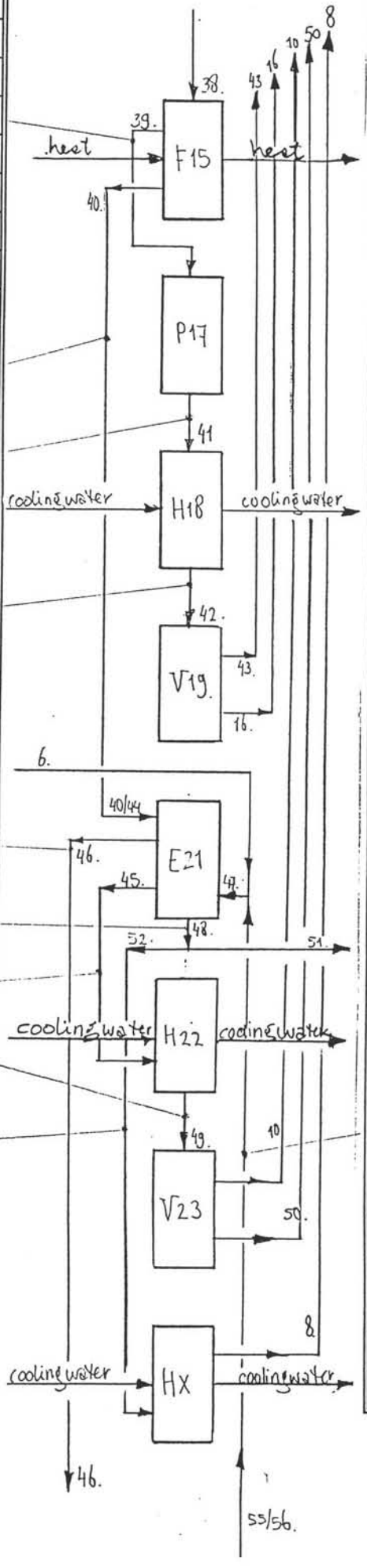
IN		Voor-waarts
M	Q	M
		Q
		48.91
		11676.5
		32.17
		7000.87
2.68	8945.71	
0.517	-2.61	32.66
		7737.15
0.04	0.84	412.38
		95885
27.0	-567	
0.962	-131.1	412.60
		95330.4
		20.78
		4801.2
0.5	1666.09	
		20.78
		6257.30



Retour	UIT	
M	M	Q
Q		
43.06		
9967.11		
	0.032	-0.15
	2.68	754.15
17.95		
4091.16		
	0.748	47.8
	27.0	1701
348.76		
80562.1		
	0.5	210

IN		Voor-waarts
M	Q	M
		Q
168.0	10584	5.11
		5030
		15.67
		4585.42
		5.11
		7551
144.0	-3024	
		5.11
		-46.0
0.00001	33.26	
		23.57
		1888.81
		10.15
		2593.72
		1.95
		1133.82
20.0	-420	1.95
		-57.16
		9.59
		2453.52
32.0	-672	

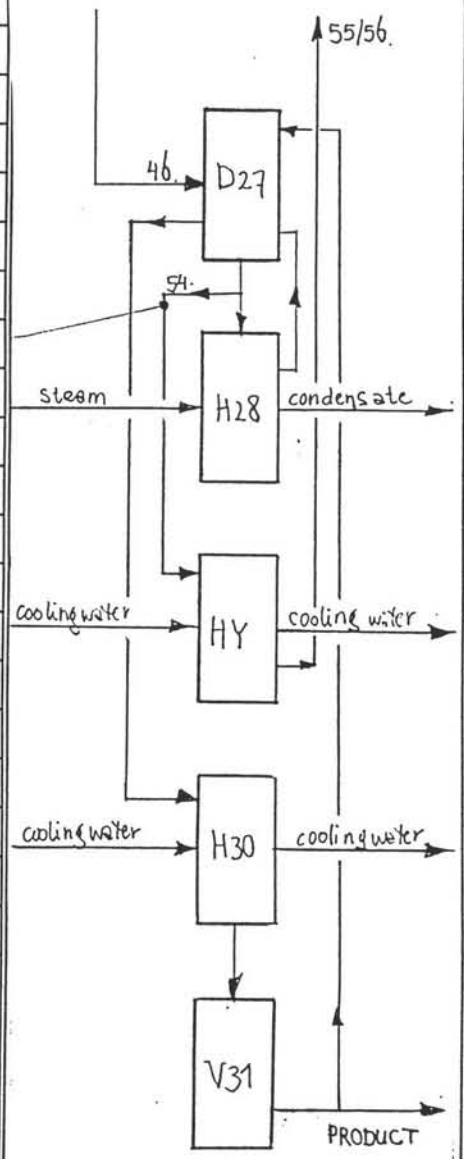
VERVOLG



Retour		UIT	
M	Q	M	Q
		168.0	-3528
		144.0	9072
		0.556	142.19
		20	1260
20.0			
1948.46			
		32.0	2016

VERVOLG

IN		Voor-waarts
M	Q	M
		Q
		20.0
		4720.46
27.45	39108.99	
33.0	-693	
56.72	-1191.12	



Retour		UIT	
M	Q	M	Q
		27.45	30637.6
		33.0	2079
		56.72	3576.06
		3.565	98.11

582.39	52234.7	<---------- TOTAAL ---------->	582.35	52234.3

MASSA IN KG/S
WARMTE IN kW

FABRIEKSVOORONTWERP NO.

3140

APPENDIX III:
HAZOP ANALYSE

Absorber 2

Intentions: Absorption of carbondioxide by an ammonium solution to form ammonium-bicarbonate. Pressure 7 bar, temperature around 90 °C.

Deviation	Possible causes	Consequences	Action required
No flow	(1) One of the pumps of the feed (p2, p20) fails.	(1) No feed to column	(1) Low level alarm in reactors, install spare pumps
	(2) Line fracture	(2) As for (1) and leakage of ammonium-hydroxide	(2) Regular inspection of pipe lines
	(3) Line blockage	(3) As for (1), pumps overheat	(3) Kick-backs over all pumps
	(4) Blockage of column	(4) As for (3)	(4) As for (3)
More pressure	(5) Gas outlet is closed	(5) Less conversion, explosion danger	(5) Install pressure alarm on column
More flow	(6) Liquid outflow fails	(6) Liquid in gas outlet	(6) Install high level alarm on column
More temperature	(7) Coolers (h3, h18) fails, cooling of column fails	(7) Less absorption, formation of carbamate	(7) Temperature controler on column.
Less flow	(8) See (1),(2),(3),(4)	(8) See (1),(2),(3),(4)	(8) See (1),(2),(3),(4)
Less pressure	(9) Pump (p2,p20) failure	(9) Less absorption	(9) Pressure controler
Less carbondioxide in feed	(10) Feed failure	(10) Less absorption, carbamate formation	(10) Flow controler on feed stream

Ammonium formate forming reactor

Intention: formation of ammonium formate out of ammonium bicarbonate and hydrogen. The pressure is 25 bar. Temperature is 80 °C.

Deviation	Possible causes	Consequences	Action required
No flow	(1) Pump failure (p10, p12, p5)	(1) Loss of feed to reactor	(1) Low level alarm in reactor, backup pumps
	(2) Line blockage by catalyst	(2) As for (1), pumps overheat	(2) Kick-backs on all pumps
	(3) Line fracture	(3) As for (1), leakage of bicarbonate solution	(3) Regular inspection of pipe lines
	(4) Blockage of one of the prior units due to catalyst	(4) As for (1), pumps overheat	(4) As for (2)
More pressure	(5) Gas outlet fails	(5) Less conversion, explosion danger	(5) Pressure alarm in reactor
More flow	(6) Liquit outflow fails	(6) Less conversion	(6) High level controler in reactor
More temperature	(7) Cooling system fails	(7) Less conversion because of side reaction, formamide formation	(7) Temperature controler in reactor
Less flow	See (1),(2),(3)and (4)	See (1),(2),(3)and (4)	See (1),(2),(3)and (4)
Less pressure	(8) Pump failure (p5)	(8) Less conversion	(8) Pressure controler reactor
Less temperature	(9) Cooling failure	(9) Less conversion	(9) Temperature controler
Presence of oxigen	(10) Gas outlet regenarator fails	(10) Explosion, less conversion	(10) High pressure alarm on regenarator

Regenaration reactor

Intention: regeneration of the palladium catalyst with oxygen. The pressure is about 25 bar and the temperature is 80 °C.

Deviation	Possible causes	Consequences	Actions required
No flow	(1) Pump failure (p5, p10,p12)	(1) Loss of feed , loss of fresh catalyst	(1) Back-up pumps
	(2) Line blockage	(2) As for (1) pumps overheat	(2) By-passes on all pumps
	(3) Line fracture	(3) Loss of expensive catalyst	(3) Regular inspection of pipe lines
	(4) Blockage of one of the prior unit due to catalyst	(4) As for (1), pumps overheat	(4) As for (2)
More pressure	(5) Gas outlet fails	(5) Explosion danger	(5) Pressure controler on reactor
More flow	(6) Liquid outlet fails, cyclone failure	(6) Less conversion, less fresh catalyst to reactor	(6) High level controler on reactor
Less flow	See (1), (2), (3), (4)	See (1), (2), (3), (4)	See (1), (2), (3), (4)
Less temperature	(7) Heater fails	(7) Less catalyst recovery	(7) Temperature controler in reactor
Hydrogen in reactor	(8) Gas oulet formiate reactor fails	(8) Explosion	(8) Pressure alarm in reactor

APPENDIX IV:
ECONOMICAL CALCULATIONS

Calculation of production costs, income, cash flow and economic criteria

Table IV.1. Annual mass flow

IN OUT	Name	Str.No	kg/s	t/h	t/a	t/t Form/Acid.
IN	Ammonia	2	0.005	0.019	155.548	0.002
	Carbon dioxide	3	3.412	12.282	98257.559	0.957
	Hydrogen +	5	0.962	3.463	27701.012	0.270
	Oxygen	4	0.517	1.860	14879.710	0.145
	Proces water	1	0.107	0.385	3079.943	0.030
	TOA		0.000	0.000	0.236	0.000
	Total IN				144074	1.403
OUT						
	Purge 1 (nh3)	11	0.009	0.032	253.325	0.002
	Purge 2 (co2)	60	0.092	0.333	2663.281	0.026
	Purge 3 (h2)	33	0.748	2.692	21539.068	0.210
	Purge 4 (o2)	27	0.032	0.115	921.600	0.009
	Purge 5 (h20)	51	0.556	2.002	16012.087	0.156
	Formic Acid (product)	57	3.565	12.836	102684.93	1.000
	Total OUT				144074	1.403

Table IV 2 Mass flow of catalyst

IN OUT	Name	Str. No	kg/s	t/h	t/a
IN	Catalist		0.040	0.144	1152.000
	Total IN				1152.000
OUT	Catalist		0.040	0.144	1152.000
	Total OUT				1152.000

Table IV 3.Raw material costs

RAW MATERIALS FROM PFS-MAT.BAL.					
IN/OUT	Name	t/a	Prices $/t	Gross k$/a	Net k$/a
IN	Ammonia	155.548	120.000	18.666	18.666
	Carbon dioxide	98257.559	39.200	3851.696	3851.696
	Hydrogen +	27701.012	209.032	5790.405	5790.405
	Oxygen	14879.710	100.840	1500.470	1500.470
	Proces water	3079.943	0.968	2.981	2.981
	TOA	0.236			
	Total IN	144073.772		11164.218	11164.218
OUT	Purge 1	253.325		0.000	0.000
	Purge 2	2663.281		0.000	0.000
	Purge 3	21539.068		0.000	0.000
	Purge 4	921.600		0.000	0.000
	Formic Acid (product)	102684.935		0.000	0.000
	Total OUT	128062.208		0.000	0.000
IN - OUT =	RAW MATERIALS COST :			11164.218	11164.218

UTILITIES FROM PFS (EARLIER CALCULATED)					
IN/OUT	Name	Unit	Unit/a	$/Unit	k$/a
IN	Steam p<	Tons	86400.000	19.355	1672.258
	Steam p>	Tons	792000.000	22.58064516	17883.871
	Cooling water	Tons	11908800.000	0.065	768.310
	Electricity (prod. !)	mWh	6899.262	64.516	445.114
TOTAL =	UTILITIES				20858.390

Table IV 4. Catalyst costs

IN OUT	Name	t/a	Prices $/t	Gross k$/a	Net k$/a
IN	Catalist (fresh)	1152.000	38709.677	44593.546	44593.546
OUT	Catalist (used)	1152.000	0.000	0.000	
IN - UIT =	CATALIST COST :			44593.546	44593.546

Table IV 5.. Labour costs

COST DATA	RESULTS	REMARKS
Number of Operators/shift:	2	(Maximal !)
Cost per Operator @ 1995, k$ @1995:	51.61290323	
Costs per shift k$ @ 1995:	**103.2258065**	
Number of shifts:	5	
Total operating labour k$ @ 1995:	**516.1290323**	

Table IV 6 GROSS INCOME, NET CASH FLOW, ECONOMIC CRITERIA

ITEM	Unit	RESULT	REMARKS
Formic acid production	t/a	102684.9	
Sales Price	$/t	904.839	
Gross Income	k$/a	92913.33	
Production Costs		102300.36	
NET CASH FLOW			
-Before TAX	k$/a	-9387.03	= (A)
-After Tax @ 45%	k$/a	-4224.16	
CAPITAL INVESTMENT	k$	22342.5	= (B)
PAY OUT TIME (POT)	Years	-2.38015	= (B)/(A)
RATE OF RETURN (ROR)		-42.0142	= (A)/(B)*100%

Table IV Earning power

7

EARNING POWER						
YEARS	CAPIT. COSTS $ mill	NET ANNUAL CASH FLOW (Before TAX) $ mill	DISC. FACTOR @ EARNING POWER 0.000%	DISC. ACCUM CAPIT. $ mill	CASH FLOW $ mill	REMARKS
0	11.17125		1.000	11.171		
1	11.17125		1.000	22.343		
TOTAL	22.3425			22.343		
2		-9.387	1.000		-9.387	
3		-9.387	1.000		-18.774	
4		-9.387	1.000		-28.161	
5		-9.387	1.000		-37.548	
6		-9.387	1.000		-46.935	
7		-9.387	1.000		-56.322	
8		-9.387	1.000		-65.709	
9		-9.387	1.000		-75.096	
10		-9.387	1.000		-84.483	
11		-9.387	1.000		-93.870	
12		-9.387	1.000		-103.257	
13		-9.387	1.000		-112.644	
14		-9.387	1.000		-122.031	
15		-9.387	1.000		-131.418	Rest Value =
TOTAL		-131.418				
16	Rest value	2.234	1.000		-129.184	10.00%
TOTAL				22.34	-129.18	
RATIO : [Cash Flow / Capital] @ Disc.					-5.78	
NET PRESENT VALUE: [Cash Flow - Capital] @ Disc.					-151.53	

APPENDIX V-1:
ABSORPTION OF AMMONIA (A1)

In the ammonia absorber, a gas flow of 81.2 mole/s ammonia is contacted countercurrently with 539.7 mole/s of water at a temperature of 293 °K. The impurities of formic acid, aqeous NH_4OH and NH_4COOH in the liquid phase and carbon dioxide and water in the vapor phase are assumed to be negligble. It takes place in a packed column filled with 38 mm ceramic Berl saddles. The gas is at a pressure of $1 \cdot 10^5$ Pa and all ammonia is to be absorbed into the water. The concentration of dissolved ammonia will be zero and 0.15 mole NH_3/ mole H_2O at the top and the bottom of the column respectively.

A first estimation of the temperature rise in the absorber can be calculated with the heat of solution of ammonia in water. The heat of solution at infinite dilution of ammonia in water at 303 °K and 1 atm, is found by using data given by Beggerow et al.:

$$-\Delta H^{\circ}_{sol} \approx 34.4 \ kJ/mol \ NH_3$$

As the solution rate of ammonia in the water is 81.2 mole NH_3/s, the heat released is:

$$Q \approx 2793.3 \ kJ/s$$

If heat losses are neglected, and all the heat released is absorbed by the water, the temperature rise can be calculated with the following formula:

$$\Delta T = \frac{Q}{L_{m,w} c_{p,w}}$$

The heat capacity of water at 303 K is 4.2 kJ/kg K. The water feed rate is 9.7 kg/s.
Thus, the rise of the water temperature will be about:

$$\Delta T \approx 68.6 \ ^{\circ}K$$

The introduction of a temperature gradient over the height of the column would make the calculations much more complicated, because the overall mass transfer coefficient, diffusion coefficients, densities and viscosities depend on the temperature. By using a logarithmic mean temperature and assuming that the column is processed isothermally, the calculation will be simplificated.

The inlet temperature of the liquid phase is 293 K. The logarithmic mean temperature is then:

$$T_{lm} = \frac{T_{z=0} - T_{z=Z}}{\ln \frac{T_{z=0}}{T_{z=Z}}} = 326\ K$$

The diameter of the column is determined by the gas velocity which gives rise to flooding at the bottom. The empirical correlation of Sherwood, Shipley and Holloway is used to determine this. The density of the gas at the bottom will be 0.63 kg/m^3 (calculated from the perfect gas law). The density of the liquid is 1000 kg/m^3. The gas flow rate at the bottom of the column is 1.8 kg/s and the liquid flow 11.6 kg/s. Thus:

$$\frac{L_m}{G_m}\sqrt{\frac{\rho_G}{\rho_L}} = 0.16$$

From the graph of the generalized correlation of flood points in packed columns by Sherwood et al., found in Perry's Handbook, it is determined:

$$\frac{(G_f')^2(\frac{a_p}{\varepsilon^3})(\mu_L)^{0.2}}{g\rho_G\rho_L} = 0.08$$

Characteristic values for the ceramic Berl saddles are: $a_p = 150\ m^{-1}$ and $\varepsilon = 0.71$. The viscosity of water at 303 K and 1 atm is $8.5 \cdot 10^{-4}$ Pa·s. The calculated mass flow-rate of gas per cross-section leading to flooding is then $G_f' = 2.2$ kg/m^{2}s. Using a factor of 0.7 to determine the operating rate from this flooding rate, we get $G' = 1.5$ kg/m^{2}s. For convenience the diameter of the column is taken to be 1.2 m, giving the gas flow rate per unit cross-section $G' = 1.6$ kg/m^{2}s and the liquid flow rate per unit cross-section is
$L' = 10.3$ kg/m^{2}s. The following equation is obtained from a mass balance for ammonia in the liquid phase, over a small slice of the packed column:

$$C_{NH_3}L_v|_{z+dz} - C_{NH_3}L_v|_z + IK_L a(C^*_{NH_3} - C_{NH_3})A\,dz = 0$$

with:

$$C_{NH_3}{}^* = \frac{P_{NH_3}}{H_{NH_3}} = \frac{P}{H_{NH_3}}$$

As the gas phase exists of mainly ammonia, the assumption that the partial pressure of NH_3 is equal to the total pressure everywhere in the column, is justified. The liquid volume rate is assumed to be constant. The concentration of ammonia in the liquid bulk varies from zero at the top to 0.15 mole NH_3/mole H_2O at the bottum of the column. The Henry coefficient

for ammonia is estimated to be 4 Pa/(mol/m^3) and L_v is 0.01 m^3/s.
The mass balance can then be written as:

$$\frac{dC_{NH_3}}{(C_{NH_3}-\frac{P}{H_{NH_3}})}=\frac{IK_L aA}{L_v}dz$$

with: at the bottom (z=0) : C_a= 7382 mol/m^3
at the top (z=L) : C_a= 0 mol/m^3

The total column height L can be calculated with the equation above after integration.

The overall liquid phase mass transfer coefficient can be expressed as follows:

$$\frac{1}{IK_L a}=\frac{1}{k_L a}+\frac{1}{Hk_G a}$$

As the vapour phase exists of pure ammonia, there is no resistance for the mass transfer at the gas side. The absorption of ammonia in water is expected to be liquid film limited e.g. the mass transfer resistance is mainly situated in the liquid film. Then the overall liquid phase mass transfer coefficient is equal to the liquid film transfer coefficient:

$$\frac{1}{IK_{L,a}a}=\frac{1}{k_{L,a}a}$$

The liquid film transfer coefficient of ammonia, $k_{L,a}$, will be determined using the formula found in Coulson&Richardson given by Semmelbauer:

$$Sh_{L,a}=\frac{k_{L,a}d_p}{ID_{L,a}}=\beta' Re_L^{0.59} Sc_L^{0.5}$$

with:

$$Re_L=\frac{L' d_p}{\mu_L}$$

$$Sc_L=\frac{\mu_L}{\rho_L ID_{L,a}}$$

The diameter of the Berl saddles is 38 mm. The constant β' for Berl saddles is 0.25. The diffusion coefficient in water of ammonia is $2.0\cdot10^{-9}$ m^2/s [3]. The values of other variables are mentioned above. So: Re_L=460, and Sc_L= 425. This results in: $k_{L,NH3}$= $1.01\cdot10^{-5}$ m/s.

In order to estimate the effective interfacial area, it is necessary to know the experimental data of the effective interfacial area. Because these data are not available for 38 mm Berl

saddles at present flow conditions, the ratio of the effective interfacial area and the total surface area of 25 mm Berl saddles are used:

$$Ratio=\frac{a}{a_p}=\frac{131}{250}\frac{m^2/m^3}{m^2/m^3}=0.524$$

It is assumed that this ratio is also constistent for the 38 mm Berl saddles. The total surface area is estimated to be 150 m^2/m^3. The effective surface area determined in this way is: a ≈ 80 m^2/m^3.
Thus $k_{L,NH3}a = 8.1 \cdot 10^{-4}\ s^{-1}$.

It must be emphasised that values of the film transfer coefficients obtained from these equations must be used with caution in designing a large scale tower and an appropriately large safety factor should be incorporated. The value of IK_La depends on the process conditions and the type of packing of the tower.

After integration of the differential, the length of the column is 3.8 m. For convenience the length is taken 4 m.

Wesselingh and Kleizen provide a methode to determine the pressure drop over a packed absorption column. First the volume fraction liquid in the column is calculated using the following equation:

$$\varepsilon=1.2\ (\frac{v_L^2}{gd})^{\frac{1}{3}}$$

With v_L=0.009 m/s, the volume fraction liquid is 0.06.
Then the dry pressure drop is calculated according to:

$$\Delta P_d=0.80\rho_G F_d L v_G^2$$

With v_G=2.9 m/s the dry pressure drop is calculated to be equal to 3645 Pa.
Finally the pressure drop over the column can be calculated using the following equation:

$$\Delta P=\Delta P_d(1-3.5\varepsilon)^{-3}$$

The pressure drop over the column is thus: ΔP = 7392 Pa

Notation

A	= cross section area of column	$[m^2]$
a	= effective interfacial area	$[m^2/m^3]$
a_p	= total surface area of the packing	$[m^2/m^3]$
C^*	= concentration at liquid film	$[kmol/m^3]$
C	= bulk concentration in the liquid phase	$[mol/m^3]$
c_p	= heat capacity	[kJ/kgK]
D_L	= diffusion coefficient in liquid phase	$[m^2/s^2]$
d_p	= packing size particles	[m]
F_d	= packing factor	[-]
g	= gravity constant	$[m/s^2]$
G'	= mass flow-rate of gas per unit cross-section	$[kg/m^2s]$
G_f'	= mass flow-rate of gas per unit cross-section leading to flooding	$[kg/m^2s]$
G_m	= gas mass flow-rate	[kg/s]
H	= Henry's law constant	$[Pa/mol.m^3]$
k_G	= gas film transfer coefficient	[s/m]
K_L	= overall liquid phase mass transfer coefficient	[m/s]
k_L	= liquid film transfer coefficient	[m/s]
L	= height of the packing	[m]
L'	= mass flow-rate of liquid per unit cross-section	$[kg/m^2s]$
L_m	= liquid mass-flow rate	[kg/s]
L_v	= volumetric liquid-flow rate	$[m^3/s]$
P	= total pressure	[Pa]
Q	= total generated heat	[kJ/s]
Re_L	= Reynolds number of the liquid phase	[-]
Sc_L	= Schmidt number of the liquid phase	[-]
Sh_L	= Sherwood number of the liquid phase	[-]
v_G	= superficial gas flow rate	[m/s]
v_L	= superficial liquid flow rate	[m/s]
z	= height	[m]
β'	= packing constant	[-]
$\Delta H°_{sol}$	= heat of solution at infinite dilution	[kJ/mol]
ΔP	= pressure drop	[Pa]
ΔP_d	= dry pressure drop	[Pa]
ΔT	= temperature rise	[K]
ε	= volume fraction liquid in the column	[-]
ε	= fractional voids in dry packing	[-]
μ_L	= liquid viscosity	[Pa·s]
ρ_G	= density of the gas phase	$[kg/m^3]$
ρ_L	= density of the liquid	$[kg/m^3]$

Indices and Abbreviations

a = ammonia
w = water

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APPENDIX V-2:
ABSORPTION OF CARBON DIOXIDE AND AMMONIA

In the second absorber, a gasmixture of 184 mol/s with 29 mole% ammonia and 71 mole% carbon dioxide at a temperature of 293 K is treated with a water flow of 562 mol/s and 76 mol/s ammoniahydroxide coming from the first absorber at a temperature of 293 K. It takes place in a packed collumn. The collumn is operated at a pressure of $7 \cdot 10^5$ Pa and the concentration of the carbondioxide and the ammonia is to be reduced to zero.

As the absorption of ammonia is many times faster than the absorption of carbondioxide and as the carbondioxide flow is greater than the ammonia flow, the calculation of the absorber is totally based on the magnitude and the behaviour of the carbondioxide flow.

In contrast with the first absorber the calculation of the absorber dimensions is based on the reaction of carbondioxide with the hydroxyl-ions in the second absorber.

The reaction that takes place in the second absorber is:

$$NH_4OH\ (aq) + CO_2\ (v) \rightarrow NH_4HCO_3\ (aq) \qquad \Delta H_r^0 = -64.6\ kJ/mol$$

There is a possibility that parallel with the bicarbonate formed carbamate will be formed:

$$CO_2\ (v) + NH_3\ (v) \rightarrow NH_2COOH\ (s)$$

By adding an excess of carbon dioxide this can be avoided.

Adiabatic operation would cause a temperature difference of 121 K. As the boiling point of water at a pressure of $7 \cdot 10^5$ Pa is much higher, cooling will not be needed.
The logarithmic mean temperature, T_{lm}, is then:

$$T_{lm} = \frac{T_{z=0} - T_{z=L}}{\ln \frac{T_{z=0}}{T_{z=L}}} = 350K$$

The calculation of the diameter and gas flowrate will be calculated in the same way as in the first absorber.
The flooding rate is 6.5 kg/m^{2}s. The operating gasflow is then 4.4 kg/m^{2}s and the liquid flow is 13.1 kg/m^{2}s. The calculated diameter of the column is 1.4 m.
The following equation is obtained from a mass balance for bicarbonate in the liquid phase over a small slice of the packed column:

$$L_v * C_b|_{z+dz} - L_v * C_b|_z + RaAdz = 0$$

This can be written as a differential equation:

$$v_L \frac{dC_b}{dz} = -Ra$$

or:

$$h = L \int_{C_b}^{C_0} \frac{dC_b}{Ra}$$

Danckwerts proposed absorption rates for several conditions. As it is assumed that there is no gas film resistance, the absorption rate is:

$$R = k_L C^* \gamma = k_L H_c P \gamma$$

where $\gamma = R/k_L C^*$ is found from a figure found in Danckwerts' article:

For the use of this figure two parameters have to be calculated:
1)

$$\frac{[NH_4OH]}{C^*} \sqrt{\left(\frac{D_{L,OH^-}}{D_{L,c}}\right)}$$

and:

2)

$$\frac{\sqrt{D_{L,c} k_{OH^-} [NH_4OH]}}{k_L} = \frac{\sqrt{1.96 \cdot 10^{-9} * 15 \cdot 10^6 * [NH_4OH]}}{7.21 \cdot 10^{-5}}$$

When the absorption rate for various concentrations of bicarbonate is calculated, the height of the packed collumn is then easily determined.

Calculations of various coefficients needed for determining the height of the collumn are given below.

Calculation of the solubility of carbon dioxide in the electrolyte solution: The solubility of carbon dioxide in pure water, H_w, is given by the expression according to Danckwert et. al.[1]:

$$Log_{10} H_w = \frac{1140}{T} - 5.30$$

It has been found that the solubility of carbon dioxide in non-reacting electrolyte solutions

can be estimated to within 10% by the expression:

$$\log_{10}(\frac{H}{H_w})=-K_S[NH_4OH]-K_S[NH_4HCO_3]$$

where: $K_S = i_+ + i_- + i_G$

The values of i for carbon dioxide and for various ions at 15 and 25 C° are given in table V-2-1. The effect of the temperature on K_S is negligible.

Species	i (l./g ion)
Na^+	0.094
K^+	0.071
NH^+	0.031
CO_3^-	0.021
SO_4^{2-}	0.021
OH^-	0.061
HCO_3^-	0.021
CO_2	-0.017

Table V-2-1: Data for the Computation of K_s

Calculation of the effective value of $D_{L,CO2}/D_{L,OH-}$: The effective value of $D_{L,CO2}/D_{L,OH-}$ has been measured for several solutions of sodium chloride and may be taken as 0.59. As there are no measurements done for NH_4OH solutions this value will be considered accurately enough.

Calculation of the reaction rate constant k_{OH-}: The actual reaction is assumed to be a second-order reaction with hydroxyl-ions. The reaction rate constant k_{OH-} for this reaction for infinite dilutions according to Pinsent, Pearson and Roughton is:

$$\log_{10}k_{OH^-}=13.635-\frac{2895}{T}$$

Calculation of the actual rate of reaction of carbon doxide in concentrated electrolyte solutions is complicated by the effects of ionic strength and composition on the rate constant k_{OH-} and on the equilibrium constants which govern the concentration of hydroxyl ions in solutions containing mixtures of carbonate an bicarbonate. Dankwerts' article shows a figure with the effect of ionic strength on k_{OH-} due to sodium chloride. It will be assumed that this figure is efficiently accurate for carbon dioxide absorption in NH_4OH-solutions. The ionic strength I of the NH_4OH-solution is assumed to be constant and is 14.9 g ion/l. The rate constant k_{OH-} is then determined to be 15000 l/mol·s.

Calculation of the diffusivity for carbon dioxide in NH_4OH-solutions: The diffusivity for carbon dioxide in NH_4OH solution has been estimated with the diffusivity for CO_2 in 2.07 M NaCl solution at 293 K according to Nijsing, Hendriksz and Kramers. So the diffusivity is $1.14 \cdot 10^{-9}$ m^2/s.

Calculation of the liquid film mass transfer coefficient: With the correlation of Semmelbauer (see also absorber 1) an estimation of k_L is used. k_L is calculated to be $0.88 \cdot 10^{-5}$ m/s. As there is no data avaiable for the effective interfacial area, it is estimated to be 80 1/m.
Results of the calculation of the absorption rate for various concentrations are represented in table V-2-2.

C_b [mol/cm^3]	1/(Ra) [cm^{3}s/mol]
0	179
3	139
6	156
9	156
12	156
14	417
14.9	417

Table V-2-1: Reaction rates calculated for various concentrations

As 1/(Ra) is plotted against C_b, then the area under the curve will be 2534.
Then it follows that the height of the column is:

$$L = v_L \int_0^c \frac{dC_{HCO_3^-}}{Ra} = 1.3 \cdot 2534 = 3294 \ cm$$

The height of the column is about 33 m.
The pressure drop over the column is calculated using the method from Wesselingh and Kleizen as described in appendix V-1. The pressure drop is then calculated to be:

$$\Delta P = 38451 \text{ Pa}$$

Notation

a	= effective interfacial area per unit volume of packing	[m^{-1}]
A	= cross-section area of the column	[m^2]
C	= bulk concentration	[mol/m^3]
C*	= gas film equilibrium concentration = H_c*P	[mol/m^3]
D_L	= diffusivity in the liquid phase	[m^2/s]
H	= solubility in given electrolyte solution	[mol/m^3Pa]
H_w	= solubility in water	[mol/m^3Pa]

i_+, i_-, i_G	= respectively contributions due to cation, anion and gas	
k_L	= liquid film transfer coefficient	[m/s]
k_{OH^-}	= reaction rate constant	[m^3/mol.s]
L	= height of the column	[cm]
L_v	= volumetric liquid flow rate	[m^3/s]
P	= total pressure	[Pa]
R	= absorption rate	[mol/m^2s]
R	= absorption rate of carbon dioxide per unit interfacial area	[mol/m^2s]
v_L	= superficial liquid flow rate	[m/s]
ΔP	= pressure drop over the column	[Pa]

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APPENDIX V-3A:
HYDROGENATION REACTOR (S11)

There are three processes involved in the hydrogen mass transfer from the gas phase to the liquid phase:

1) transfer of hydrogen to the bulk liquid; $\varphi_{1,h}$
2) transfer of hydrogen from liquid bulk to the catalyst surface; $\varphi_{2,h}$
3) reaction of hydrogen on the catalyst surface; $\varphi_{3,h}$

1) Transfer of hydrogen to the bulk liquid
The maximum attainable hydrogen flux through the gas-liquid interface depends on the gassolubility of hydrogen in the electrolyte solution as:

$$\varphi_{1,h}=k_L a C^*_{L,h} \qquad \textbf{(V-3A-1)}$$

The hydrogen gassolubility is determined by the hydrogen pressure and by the electrolyte concentration.
The physical solubility of hydrogen in electrolyte solution is less than in pure water. It is caused by the greater attraction between ions and water than between nonpolar or slightly polar gases, as hydrogen, and water. This phenomen is called the salting-out effect and can be described by the equation of Sechenov:

$$\ln[\frac{C^*_{w,i}}{C^*_{es,i}}]=k_S C_e \qquad \textbf{(V-3A-2)}$$

It can be assumed that hydrogen at temperatures ranging from 20 to 70 °C has an ideal gas behaviour. Henry's law is applicable for aqueous solutions of hydrogen:

$$(\gamma_h m^*_h)_{es}=(\gamma_h m^*_h)_w=\frac{P_h}{H_{w,h}} \qquad \textbf{(V-1A-3)}$$

As the activity coefficient of hydrogen in water is assumed to be equal to 1, equation (V-3A-3) becomes:

$$\frac{m^*_{w,h}}{m^*_{es,h}}=\gamma_{es,h} \qquad \textbf{(V-1A-4)}$$

Combining equation (V-3A-3) and equation (V-3A-4), this will lead to:

$$\ln\gamma_{es,h}=k_S C_e=k_S m_e \qquad \textbf{(V-1A-5)}$$

The solubility of hydrogen in the electrolyte solution can be found by combining equations (V-3A-1) and (V-3A-5).
The electrolyte concentration is derived from the mole fraction of formic acid in aqueous solution in the reactor. The electrolyte concentration is then at least 6.7 molal. As the hydrogen is withdrawn from an ammonia plant, the hydrogen pressure is 25 bar.
$\gamma_{es,h}$ is found in a figure given by D.C. Engel by extrapolation, then the hydrogen solubility in the electrolyte solution is estimated to be about 5 mol/m^3.

Engel estimated that k_La is 0.2 1/s by experimental results.
The maximum attainable hydrogen flow, $\varphi_{1,h,}$ is then about 1 mol/(m^3.s).

2) Transfer of hydrogen from liquid bulk to the catalyst surface
The hydrogen flux from the liquid bulk to the catalyst surface can be written as:

$$\varphi_{2,h}=k_S a_p C^*_{L,h} \qquad \textbf{(V-1A-6)}$$

The mass transfer coefficient from liquid bulk to solid surface, k_S, is calculated using a correlation by Sano:

$$Sh=\frac{k_S d_p}{D_h}=[2+0.4(\frac{Ed_p}{\nu^3})^{1/4}Sc^{1/3}]\phi_c \qquad \textbf{(V-1A-7)}$$

As $E=981\cdot10^4$ m^2/s^3, $d_p=21\cdot10^{-6}$ m, φ_c is assumed to be equal to one, $\nu=4.2\cdot10^{-6}$ m/s, $\rho=1000$ kg/m^3 and $D_h=5.24\cdot10^{-6}$ m/s, the solid volumetric mass transfer coefficient is then $0.16\cdot10^{-2}$ m/s.

The interfacial catalyst surface a_p is calculated as follows:

$$a_p=\frac{6w}{\rho_c d_p}=5100\ m^2/m^3 \qquad \textbf{(V-1A-8)}$$

The catalyst loading is 5 kg/m^3 and the density is 280 kg/m^3.
The $\varphi_{2,h}$ calculated is 40.8 mol/m^{3}s.

3) Reaction of hydrogen on the catalyst surface

According to kinetic study by D.C. Engel the general reaction rate expression is:

$$-r_h=r_f=\frac{A_r(0)\exp[-E_a/(RT)]K_h[p_h a_b-\frac{a_f a_w}{K}]}{1+K_h p_h+K_f a_f} \qquad \textbf{(V-1A-9)}$$

Engel assumes that the reaction rate is about zero order in hydrogen at a pressure of 25 bar. As a consequence the reaction rate simplifies to:

$$-r_h = r_f = A_r(0)\exp[-E_a/(RT)]a_b[1-\frac{a_f a_w}{a_b p_h K}] \qquad \textbf{(V-1A-10)}$$

By excerting a significant carbon dioxide pressure ($p_c > 1$bar) and introduction of the conversion ξ and some rearrangement gives:

$$-r_h = r_f = k_r(0)\gamma_b m_M[1-(K_C+1)\xi] \qquad \textbf{(V-1A-11)}$$

With:

$$K_C = \frac{1}{K_A p_h} \qquad \textbf{(V-1A-13)}$$

K_C is only a function of temperature at a given combination of hydrogen pressure and total electrolyte concentration.

In figure 4.10.1 the reaction rate of bicarbonate as a function of the temperature is shown at a

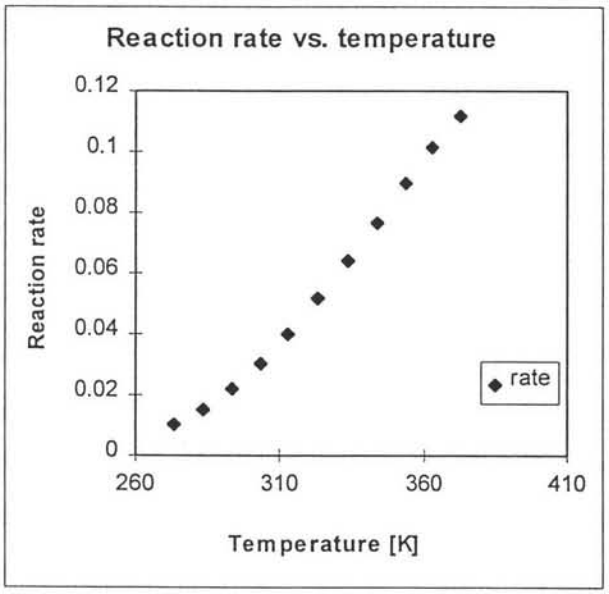


figure 4.10.1: Reaction versus temperature

constant conversion.
It is observed that the reaction rate increases as the temperature increases. As the temperature

should be below 373 K, to avoid dehydration of ammonium formate into formamide, the hydrogenation reactor will be operated at a temperature of 353 K.
In figure 4.10.2 the conversion of bicarbonate is given as a function of the reaction rate.

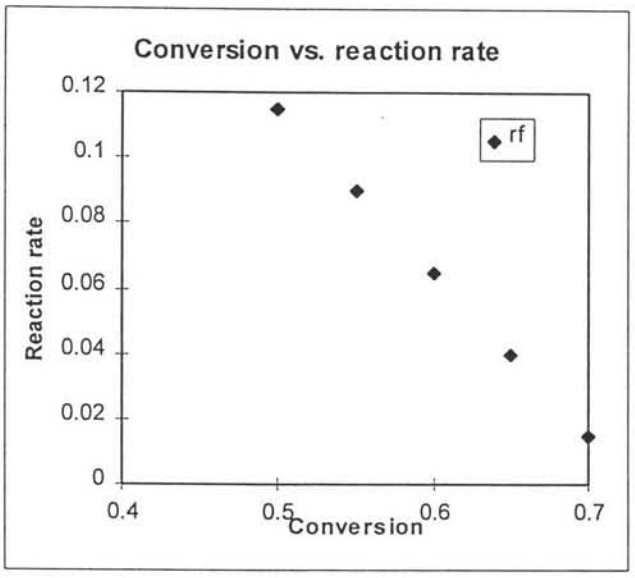


Figure 4.10.2: Conversion versus reaction rate

To choose the conversion, one should take into account the time that the catalyst deactivates. If a high conversion is chosen the recycle stream will be too large and the residence time of the proces fluid will be too long. As a residence time of 8300 s seems reasonably, this will be the residence time of the hydrogenation reactor in this preliminary design. The conversion is then 0.55 and the recycle ratio is 0.95.

Equation (4.3.11) combined with the experimental information on the reaction kinetics according to Engel and the chemical equilibrium of the ammonia system the reaction rate is then:

$$-r_h = r_f = 0.089653 \text{ mol/(kg cat·s)} \qquad \textbf{(V-3A-14)}$$

The precise reaction calculations are done in EXCEL and the spreadsheet is given in APPENDIX V-3B. As the catalyst loading is 5 kg/m^3, the hydrogen flux will be $\varphi_{3,h}$ is 0.44 mol/m^{3}s.

The slowest process, that determines the overall rate of hydrogen consumption, is thus the reaction of hydrogen on the catalyst surface. So the minimum residence time and minimum reactor volume should be determined with $\varphi_{3,h}$.

For a CSTR operating at steady state conditions it can be derived that the residence time is:

$$\tau = \frac{\rho V_L}{\phi_{m,total}} = \frac{\rho \phi_f}{\phi_{m,total} r_f w} = 8300\ s \qquad \textbf{(V-1A-15)}$$

The minimum reactor volume calculated is then determined to be 168 m^3.

The superficial gasflow is assumed to be equal to 0.01 m/s. With a volumetric gasflow of 0.16 m^3/s, the diameter of the bubble column will be 4.5 m. The height of the column is then about 11 m.

The pressure drop in a bubble column is estimated with:

$$\Delta P = \rho g L \qquad \textbf{(V-1A-16)}$$

The pressure drop is then 1.1 bar.

Notation

a	= activity	[-]
a_p	= effective interfacial surface of the catalyst	[m^2/m^3]
$A_r(0)$	= pre-exponential factor	[-]
C	= concentration	[mol/m^3]
$C^*_{es,i}$	= gassolubility in electrolyte solution	[mol/m^3]
C^*_L	= gassolubility in the liquid phase	[mol/m^3]
C^*_w	= gassolubility in pure water	[mol/m^3]
C_e	= electrolyte concentration	[mol/m^3]
D_h	= diffusivity of hydrogen in the liquid	[m/s]
d_p	= diameter of catalyst particle	[m]
E	= $V_g g$=rate of energy dissipation per unit mass of liquid	[m^2/s^3]
E_a	= activation energy	[J/mol]
g	= gravity	[m^2/s]
H_w	= Henry's coefficient of hydrogen in water	[Pa]
K	= chemical equilibrium constant	
k'_S	= salting-out parameter	[kg/mol]
K_A	= equilibrium constant	
K_C	= apparent equilibrium constant	
k_La	= liquid-side mass transfer coefficient	[1/s]
k_S	= mass transfer coefficient from liquid bulk to solid surface	[m/s]
k_S	= Sechenov parameter	[m^3/mol]
L	= height of the column	[m]
m	= molality	[mol/kg]
p	= partial pressure	[Pa]
P_h	= hydrogen pressure	[Pa]
r	= reaction rate	[mol/(kg cat.s)]

R	= universal gas constant	[J/(mol.K)]
r_f	= production rate of formate	[mol/(kg cat.s)]
Sc	= Schmidt number = $\nu/(\rho D_h)$	[-]
T	= temperature	[K]
V_g	= superficial gasflow	[m/s]
V_L	= volume of liquid phase	[m^3]
w	= catalyst loading	[kg/m^3]
γ	= activity coefficient	[-]
ΔP	= pressure drop	[Pa]
ν	= kinematic viscosity	[m^2/s]
ξ	= conversion of bicarbonate	[-]
ρ	= density of liquid	[kg/m^3]
ρ_c	= catalyst density	[kg/m^3]
τ	= residence time	[s]
$\Phi_{m,total}$	= total mass-flow rate	[kg/s]
$\varphi_{1,h}$	= hydrogen flux from gas to liquid	[mol/(m^3s)]
$\varphi_{2,h}$	= hydrogen flux from the liquid bulk to the catalyst surface	[mol/m^3.s]
φ_c	= shape factor	[-]
φ_f	= required formate production	[mol/s]

Indices and abbreviations

a	= ammonia
b	= bicarbonate
aq	= aqueous
c	= carbon dioxide
CSTR	= continuous ideally mixed stirred tank reactor
f	= formate
G	= gas phase
h	= hydrogen
L	= liquid phase
M	= cation
p	= particle
w	= water
X	= anion
*	= pure species

Literature

Engel, D.C.,' Palladium Catalysed hydrogenation of aqueous bicarbonate salt in formic acid production' Ph.d thesis, University of Twente (1994).

Sano, Y., Yamaguchi, N., Adachi, T., 'Mass Transfer Coefficient for Suspended Particles in Agitated Vessels and Bubble Columns', J. Chem. Eng. Jpn, 7, 255 (1974)

Sechenov, M., 'Überdie Konstitution der Salzlösungen auf Grund ihres Verhaltens zu

Kohlensäure', Z. Phys. Chem. **4**, 117-125 (1889)

APPENDIX V-3B:
Calculation of the reaction rate

Constanten:

conversie =	0.55	-	*Ea* =	23000.00	<J/mol>	*mol co2*	0.00E+00
temperatuur =	353.15	<K>	*Ar(0)* =	600.00	<1/kgcat/s>	*mol co3- -*	0
gasconstante =	8.31	<J/mol/K>	*Na* =	6.02E+23		*mol hco3-*	6.17E+01
		<m^3.Pa/mol/K	*Rho water* =	958.34		*mol hco2-*	7.54E+01
ph =	2500000.00	<Pa>	*e* =	1.602E-19		*mol nh4+*	1.37E+02
produktie hcooh =	75.43	<mol/s>	*Epsilon (0)* =	8.854E-12		*mol nh3*	0.00E+00
hoeveelheid water =	51.63	<kg>	*D* =	80.00			
oplos verm.factor =	4.76	-	*k* =	1.38E-23			
massastroom 5 =	20.88	<kg/s>	*w* =	5	<kg cat/m^3>		
molmassa nh4hco3 =	79.06	<g>	*rho overall* =	1000			
molmassa H2O =	1.80E-02	<kg>					

Henry constanten:

	A	B	C	D	
Hh =	-6993.54	187.56	0.02	-26.31	132604975.84

Chemische evenwicht constante:

Kh = 537.1517362

kr(0) (verg. 3.22)

kr(0) = 0.23772991

Molalities:

	molality	valentie (zi)	mi.|zi|	(mi.zi^2)
(NH4+)	6.568151341	1	6.568151341	6.568151341
(HCO3-)	2.95545977	-1	2.95545977	2.95545977
(HCO2-)	3.612691571	-1	3.612691571	3.612691571
(CO3- -)	0	-2	0	0
(NH3)	0	0	0	0
Som m(i)=	13.13630268		13.13630268 =Z	6.568151341 Ii
			6.568151341 = Z(pos)	3.28407567 I(pos)
			6.568151341 = Z(neg)	3.28407567 I(neg)

Derde viriaal coefficient:

C (phi)(nh4+,hco3-)	0	<kg^2/mol^2>
C (phi)(nh4+,hco2-)	-0.00299	<kg^2/mol^2>
C (phi)(nh4+,co3- -)	5.00E-04	<kg^2/mol^2>

C (nh4+,hco3-)	0
C (nh4+,hco2-)	-0.001495
C (nh4+,co3- -)	0.000176777

(x):	5.125680966
g(x):	0.073353986

g'(x):	-0.06741182

Tweede viriaal coefficient:

B (0)(nh4+,hco3-)	-0.038	<kg/mol>
B (0)(nh4+,hco2-)	0.054	<kg/mol>
B (0)(nh4+,co3- -)	0.1288	<kg/mol>
B (1)(nh4+,hco3-)	0.07	<kg/mol>
B (1)(nh4+,hco2-)	0.466	<kg/mol>
B (1)(nh4+,co3- -)	1.433	<kg/mol>

B (nh4+,hco3-)	-0.03286522
B (nh4+,hco2-)	0.088182958
B (nh4+,co3- -)	0.233916262
B (phi)(nh4+,hco3-)	-0.03758405
B (phi)(nh4+,hco2-)	0.056769051
B (phi)(nh4+,co3- -)	0.137315129
B'(nh4+,hco3-)	-0.00071844
B'(nh4+,hco2-)	-0.00478276
B'(nh4+,co3- -)	-0.01470751

Pitzer-Debye-Huckel limiting slope:

A (phi)	0.288786311

Extended Debye-Huckel function:

F	-0.98526706

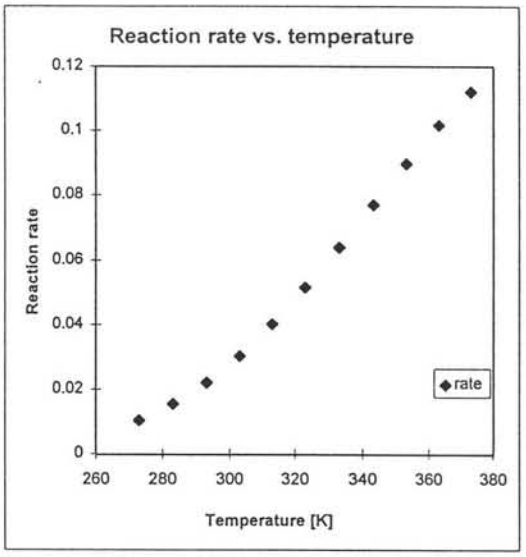
Activiteits coefficienten:

labda (nh3,hco3-)	0.0147
labda (nh3,hco2-)	0.048
labda (nh3,co3- -)	0.18
LN gamma (hco3-)	-1.45246896
gamma (hco3-)	0.233991857
LN gamma (hco2-)	0.073161335
gamma (hco2-)	1.075904104

Osmotic coefficient:

phi	0.841457427

Activity:



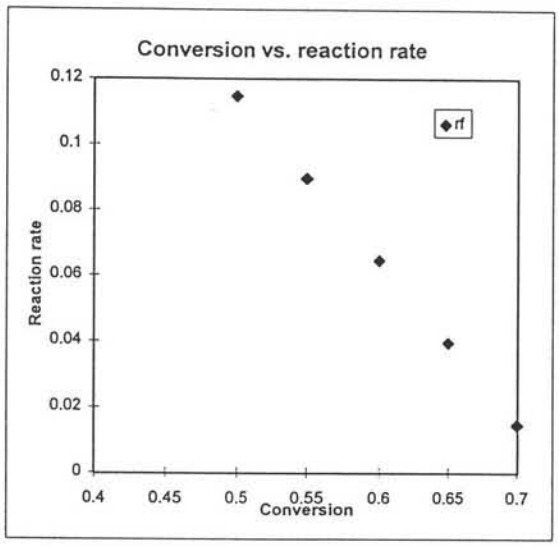
T	rate
273.15	0.0104385
283.15	0.0154804
293.15	0.022074
303.15	0.0303239
313.15	0.0402026
323.15	0.0515195
333.15	0.0639085
343.15	0.0768391
353.15	0.0896526
363.15	0.1016203
373.15	0.112019

aw	0.819396994
Ka	1.07515E-06

Uiteindelijke rate:	
-rh=rf	0.089653

Apparent equilibrium constant:

Kc	0.372040324



conv	rf
0.5	0.114717
0.55	0.089653
0.6	0.064588
0.65	0.039523
0.7	0.014458

APPENDIX V-4:
REGENERATION REACTOR

To regenerate the catalyst, a treatment with oxygen appeared to be suitable.
Probably the reaction that will take place in the regenerator is as follows:

$$Pd_2H + 1/2\,O_2 \rightleftharpoons Pd + H_2O \qquad \Delta H^0{}_r = -142.915\ kJ/mol$$

The reaction enthalpy is found with the formation enthalpy of palladium hydride and the formation enthalpy of water. The reaction is exotherm. In addition with the regeneration, the formate produced during the reaction with hydrogen was completely reverted back to bicarbonate. This is in accordance with the known ability of the platinum group metals to oxidize certain components catalytically at mild conditions (Andersson and Boudart, Nieuwenhuys):

$$HCOO^-\ (aq) + 1/2\ O_2\ (v) \rightleftharpoons HCO_3^- \qquad \Delta H_r^0 = 245.95\ kJ/mol$$

The reaction enthalpy is based on the formation enthalpy and the dissolvation enthalpy of solid ammonium formate and the formation enthalpy of aqeous ammonium bicarbonate.
In contrast to our expectations, this reaction seems to be endothermic.

According to D.C. Engel a treatment with oxygen of the catalyst during 15 minutes is satisfactory. As there is no further information available, it is assumed that this is correct.
As the volumetric liquid flowrate is 0.033 m^3, the volume of the bubble column is 29.7 m^3.
If the superficial gas flowrate is 0.01 m/s, the diameter of the bubble column is about 1.6 m by a volumetric gas flowrate of 0.019 m^3/s. The height of the column is then 16 m.
The pressure drop is at the same wise calculated as the hydrogenation reactor and is 1.6 bar.

Literature

Andersson, J.R., Boudart, M., Catalysis-Science and Technology **1**, Springer-Verlag, Berlin (1981)

Nieuwenhuys, B.E.,"Adsorption and Reactions fo CO, NO, H_2 and O_2 on Group VIII Metal Surfaces" in Joyner, R.W., van santen, R.A. (eds), Elementary Reaction Steps in Heterogeneous Catalysis, NATO ASI Series C: Mathematical and Physical Sciences **398**, Kluwer Academic Publishers, Dordrecht, 155-177 (1993)

Ghmelin

Engel, D.C.; "Palladium catalysed hydrogenation of aqueous bicarbonate salts in formic acid production"Ph.d thesis D.C. Engel.

APPENDIX V-6:
CALCULATION OF THE DIMENSIONS OF THE EXTRACTION COLUMN

Calculation of the extraction column were made from the hand out Scheidingsprocessen II
List of symbols

σ	surface tension	[Pa]
μ_c	viscosity of disperse fase	[Pas]
μ_d	viscosity continue fase	[Pas]
g	gravitation constant	[m/s^2]
ρ_c	density of continue fase	[kg/m^3]
ρ_d	density of disperse fase	[kg/m^3]
$\Delta\rho$	difference in density	[kg/m^3]
M_d	molmass disperse fase	[kg/mol]
M_c	momass continue fase	[kg/mol]
D_c	diffusioncoëfficiënt in continue fase	[m^2/s]
H_t	distance between plates	[m]
H_{bottom}	Height of the bottom stage	[m]
H_{top}	Height of the top stage	[m]
H_{dr}	Height of transport in one stage	[m]
Q_c	volumeflow continue fase	[m^3/s]
Q_d	volumeflow disperse fase	[m^3/s]
Φ_{dmol}	moleflow disperse fase	[mol/s]
Φ_{cmol}	moleflow continue fase	[mol/s]
Eö	Number of Eötvös	[-]
We	Number of Weber	[-]
Fr	Number of Froude	[-]
h	hold up	[-]
d_{min}	minimum dropdiameter	[m]
d_h	diameter of the holes	[m]
d_p	diameter of the drop	[m]
p	pitch	[m]
a	specific area	[m^2/m^3]
A_h	holes area	[m^2]
A_b	plate area	[m^2]
A_d	downcomer area	[m^2]
A_t	column area	[m^2]
U_{CDmax}	maximum velosity in downcomer	[m/s]
U_s	slipvelosity	[m/s]
U_d	velosity disperse fase	[m/s]
U_c	velosity continue fase	[m/s]
U_h	liquid velosity through holes	[m/s]
k_c	tranfercoëfficiënt continue fase	[mol/sm^2]
k_d	transfercoëfficiënt disperse fase	[mol/sm^2]
K_{odr}	overall transfercoëfficiënt	[mol/sm^2]
NTU_{Odr}	number of tranfer units	[-]
E_{md}	Murphree platerendement	[-]
E_o	columnrendement	[-]
λ	extractionfactor	[-]
m	distributioncoëfficiënt	[-]
f	recovery	[-]
$N_{theoretisch}$	Number of theoretical transfer units	[-]

The diameter of the holes was calculated with:

$$d_{hmax} := \pi \cdot \left(\frac{\sigma}{\Delta\rho \cdot g}\right)^{\frac{1}{2}} \qquad d_{hmin} := \frac{1}{2} \cdot \left(\frac{\sigma}{\Delta\rho \cdot g}\right)^{\frac{1}{2}}$$

$$d_{hmin} = 2.765 \cdot 10^{-3} \qquad d_{hmax} = 1.7373 \cdot 10^{-2}$$

And in general as a rule of the thumb

$$3 \cdot 10^{-3} < d_h < 8 \cdot 10^{-3}$$

The velosity trhough the holes was calculated with:

$$Eö := \frac{\Delta\rho \cdot g \cdot (d_h)^2}{\sigma} \qquad We := 4.33 \cdot Eö^{-0.26}$$

$$Eö = 0.2943 \qquad We = 5.9512$$

And

$$u_h := \sqrt{\frac{\sigma}{\rho_d \cdot d_h}} \cdot We \qquad u_h = 0.2517$$

The drop diameter was found with:

$$d_p := if\left[Eö < 0.4, d_h \cdot Eö^{-0.4} \cdot \left[2.13 \cdot \left(\frac{\Delta\rho}{\rho_d}\right)^{0.67} + e^{(-0.13Fr)}\right], d_h \cdot Eö^{-0.42} \cdot \left[1.24 + e^{\left(-Fr^{0.42}\right)}\right]\right] \qquad d_p = 1.764 \cdot 10^{-3}$$

The active surface was calculated:

$$A_h := \frac{Q_d}{u_h} \qquad A_b := 1.103 \cdot A_h \cdot \left(\frac{p}{d_h}\right)^2$$

$$A_h = 0.123 \qquad A_b = 6.028$$

The maximum velocity in the downcomer was calculated:

$$U_{CDmax} := 0.249 \cdot d_{min} \cdot \left(\frac{g^2 \cdot \Delta\rho^2}{\rho_c \cdot \mu_c}\right)^{\frac{1}{3}} \qquad U_{CDmax} = 0.022$$

The area of the downcomer was:

$$A_d := \frac{Q_c}{U_{CDmax}} \qquad A_d = 0.555$$

So the total area became:

$$A_T := A_b + 2 \cdot A_d \qquad A_T = 7.138$$

So the column diameter became:

$$D_T := \sqrt{\frac{4}{\pi} \cdot A_T} \qquad D_T = 3.015$$

The velosity of the disperse fase then became:

$$U_d := \frac{Q_d}{A_b + A_d} \qquad U_d = 0.004$$

The hold-up was obtained from figure 32 of the diktaat scheidingstechnieken II:

$h := 0.70$

the height of one tranferunit became:

$$H_{dr} := H_t - 0.1 \qquad H_{dr} = 0.3$$

The specific surface was calculated:

$$a := 6 \cdot \frac{h}{d_p} \qquad a = 2.38 \cdot 10^3$$

The number of tranferunits in one stage is:

$$NTU_{Odr} := \frac{K_{Odr} \cdot a \cdot H_{dr}}{U_d} \qquad NTU_{Odr} = 0.384$$

In which for the total tranfer coefficient:

$$K_{Odr} := \left(\frac{1}{k_d} + \frac{m}{k_c} \right)^{-1} \qquad K_{Odr} = 2.162 \cdot 10^{-6}$$

with:

$$k_d := U_s \cdot \frac{0.00375}{\left(1 + \frac{\mu_d}{\mu_c}\right)} \qquad k_c := U_s \cdot 0.725 \cdot \left(\frac{d_p \cdot U_s \cdot \rho_c}{\mu_c} \right)^{-0.43} \cdot \left(\frac{\mu_c}{\rho_c \cdot D_c} \right)^{-0.58} \cdot (1 - h)$$

$$k_d = 6.077 \cdot 10^{-5} \qquad k_c = 2.69 \cdot 10^{-5}$$

So the column rendement is:

$$E_o := \frac{\ln\left[1 + E_{Md} \cdot (\lambda - 1)\right]}{\ln(\lambda)} \qquad E_o = 0.673$$

In wich the extraction factor is:

$$\lambda := m \cdot \frac{Q_d}{Q_c} \qquad \lambda = 25.685$$

The number of theoretical stages is given by Kremser formula:

$$N_{theoretisch} := \frac{\log\left(\frac{\lambda - 1}{f} + 1\right)}{\log(1.4)} - 1 \qquad N_{theoretisch} = 22.217$$

the total number of stages than is:

$$N_{praktisch} := \frac{N_{theoretisch}}{E_o} \qquad N_{praktisch} = 33.028$$

So the total column height becomes:

$$H_{kolom} := N_{praktisch} \cdot H_t + H_{top} + H_{bottom} \qquad H_{kolom} = 14.711$$

APPENDIX V-7:
PUMP CALCULATIONS

The required power for the different pumps are calculated with formula 4.8.1 (de Graauw & Touber):

$$P = (\Delta p + \rho * g * h) * \phi_V / (\eta_m * \eta_H) \qquad \text{(V-7.1)}$$

with:
P = power [W]
Δp = needed pressure rise [Pa]
ρ = density [kg/m^3]
h = height of liquid column in the pipeline after the pump [m]
ϕ_V = volume flow [m^3/s]
η_m = mechanical rendement [-]
η_H = hydrolic rendement [-]

The hydrolic rendement is estimated 0.9 according to an example calculation (de Graauw).The mecanical rendements are obtained from Coulson and Richardson.The densities are calculated with Chem Cad and if possible verified with density tables from Perry.

Coulson and Richardson figure 10.62
Perry page 6-7
Touber, S, de Graauw, J, diktaat pompen en compressoren, Onderdeel van het college st42,Vakgroep Proces en Energie, TU Delft, (1993), 6-21

APPENDIX V-8A:
HEAT EXCHANGER CALCULATIONS-Cooling

The cooler needed for cooling in reactor (R11) is choosen to be a helical coil. From the heat balance it is calculated that the capacity should be 2268 kJ/s.
The general equation for heat transfer across a surface is given by:

$$Q = UA\Delta T_m$$

When the heat exchange of a helical coil is assumed to be totally counter current flow, then the temperature driving force is equal to the logarithmic mean temperature and is given by:

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

When a heat exchanger is not totally counter current, a correction factor, F_t, will be taken in to account for the log mean temperature difference.
As the cool water will flow through the tube-side t_1 and t_2 are respectively 293 K and 313 K. The temperature in the reactor should be kept constant at 354 K, so $T_1=T_2=354$ K. The log mean temperature is then 302 K.
The overall heat-transfer coefficient is estimated with a nomograph given by Frank. As the cooling water has a heat-transfer coefficient of about 1500 J/s.m^2.K and the dilute aqueous solution has a heat-tranfer coefficient of about 1400 J/s.m^2.K, the overall heat-transfer coefficient is estimated to be 635 J/s.m^2.K.
Then the heat transfer area is calculated to be 72.4 m^2.

Notations

A	= heat transfer area	[m^2]
Q	= heat transferred per unit time	[J/s]
t_1	= inlet tube-side temperature	[K]
T_1	= inlet shell-side fluid temperature	[K]
t_2	= outlet tube-side temperature	[K]
T_2	= outlet shell-side fluid temperature	[K]
U	= overall heat transfer coefficient	[J/s m^2 K]
ΔT_{lm}	= log mean temperature difference	[K]

APPENDIX V-8B:
HEAT EXCHANGER CALCULATIONS - Condensation

As the heat released during the condensation of steam is by far the largest influence on the total amount of heat transferred and condensation takes place at fixed temperature, it is assumed that the pure, saturated steam has a constant temperature. For steam at 3 bar this saturation temperature is 133.5 °C, and for steam at 40 bar this is 250°C.
For this isothermal process the logarithmic mean temperature difference between the process stream and the heating medium is:

$$\Delta T_{lm} = \frac{t_2 - t_1}{\ln\left(\frac{T_{sat} - t_1}{T_{sat} - t_2}\right)}$$

In which t_1 and t_2 are the inlet and the outlet temperature respectively of the medium that is to be heated.
When the heat duty of the condenser is known (calculated according to the methode described in §5.2), the required area for sufficient heat transfer is calculeted by:

$$A = \frac{Q}{U \Delta T_{lm}}$$

Example 1: calculation of exchange area of heater
Temperature of process stream at inlet: 354 K
Temperature of process stream at outlet: 370 K
The steam is at a pressure of 3 bar, so the T_{sat} is 406.5 K
The logarithmic mean temperature difference is then: 43.5 K
From the heat balance we have: Q = 1456.1 kJ/s
Heat transfer coefficient of air-free steam: U= 8000 W/m^2°C (Coulson and Richardson, 1991).
The required transfer area is then: A=4.18 m^2

Example 2: calculation of exchange area of heating spiral in Regenaration reactor
The temperature of process stream is to be kept constant, at 354 K. The saturation temperature of the steam (at 3 bar) is 406.5 K. The temperature difference is then: 52.5 K.
From the heat balance we have: Q = 8191.586 kJ/s
Heat transfer coefficient of air-free steam: U= 8000 W/m^2°C (Coulson and Richardson, 1991).
The required transfer area is then: A=19.5 m^2

Notations

A	= heat transfer area	[m^2]
Q	= heat transferred per unit time	[J/s]
t_1	= inlet tube-side temperature	[K]
T_1	= inlet shell-side fluid temperature	[K]
t_2	= outlet tube-side temperature	[K]
T_2	= outlet shell-side fluid temperature	[K]
U	= overall heat transfer coefficient	[J/s m^2 K]
ΔT_{lm}	= log mean temperature difference	[K]

APPENDIX VI

Apparatenlijst voor pompen, blowers en compressoren FVO Nr.3140

APPARAAT NO.	P2	P5	P10	P12	P16
Benaming : Type :	feedpump centrifugal	feedpump centrifugal	recyclepump centrifugal	recyclepump centrifugal	extractor feedpump centrifugal
Te verpompen medium :	ammonia solution	ammonium carbonate solution	ammonium carbonate solution	ammonium carbonate solution/ catalysator	ammonium formate solution
Capaciteit : [kg/s][1]	11.65	20.08	17.95	412.60	15.6
Dichtheid [kg/m^3]:	970	858	918	918	1010
Zuig-/pers-druk (abs.) [bar]:	1.0 7.5	7.5 30.4	25 28	23.9 33.0	1.0 2.5
Temp. In/Uit [°C]:	83/83	142/142	84/84	72/72	95/95
Vermogen [kW] - theorie : - praktijk :	14.0	83.3	6.0	538.3	2.9
Aantal - serie : - parallel :					
Speciale constructie-materialen					
Overig :					

[1]Aangeven wat van toepassing is.

APPENDIX VI

Apparatenlijst voor pompen, blowers en compressoren **FVO Nr.3140**

APPARAAT NO.	P17	P20	P26	P29	P32
Benaming : Type :	compressor	feed pump centrifugal	recyclepump centrifugal	recyclepump centrifugal	refluxpeump centrifugal
Te verpompen medium :	vapour $H_2O/NH_3/CO_2$	ammonium carbonate solution	water	Trioctyl ammine	formic acid
Capaciteit : [kg/s][1]	5.11	4.44	9.59	20.0	4.5
Dichtheid [kg/m^3] :	8.22	990	995	756	1220
Zuig-/pers-druk (abs.) [bar] :	1.0 7.0	1.0 2.4	1.0 1.5	0.2 1.0	0.2 1.0
Temp. In/Uit [°C] :	96/394	23/23	87/87	122/122	38/38
Vermogen [kW] - theorie : - praktijk :	487	1.0	7.5	2.9	0.5
Aantal - serie : - parallel :					
Speciale constructie-materialen					
Overig :					

[1]Aangeven wat van toepassing is.

APPENDIX VI

Apparatenlijst voor pompen, blowers en compressoren FVO Nr.3140

APPARAAT NO.	P33				
Benaming : Type :	vacuum pump centrifugal				
Te verpompen medium :	formic acid				
Capaciteit : [kg/s][1]	3.56				
Dichtheid [kg/m^3] :	1220				
Zuig-/pers-druk (abs.)* [bar] :	0.2 1.4				
Temp. In/Uit [°C] :	38/38				
Vermogen [kW] - theorie : - praktijk :	0.8				
Aantal - serie : - parallel :					
Speciale constructie-materialen					
Overig :					

[1]Aangeven wat van toepassing is.

APPENDIX VI

Apparatenlijst voor pompen, blowers en compressoren FVO Nr.3140

APPARAAT NO.	P2	P5	P10	P12	P16
Benaming : Type :	feedpump centrifugal	feedpump centrifugal	recyclepump centrifugal	recyclepump centrifugal	extractor feedpump centrifugal
Te verpompen medium :	ammonia solution	ammonium carbonate solution	ammonium carbonate solution	ammonium carbonate solution/ catalysator	ammonium formate solution
Capaciteit : [kg/s][1]	11.65	20.08	17.95	412.60	15.6
Dichtheid [kg/m^3]:	970	858	918	918	1010
Zuig-/pers-druk (abs.) [bar]:	1.0 7.5	7.5 30.4	25 28	23.9 33.0	1.0 2.5
Temp. In/Uit [°C]:	83/83	142/142	84/84	72/72	95/95
Vermogen [kW] - theorie : - praktijk :	14.0	83.3	6.0	538.3	2.9
Aantal - serie : - parallel :					
Speciale constructie-materialen					
Overig :					

[1]Aangeven wat van toepassing is.

Apparatenlijst voor warmtewisselaars en fornuizen **FVO Nr.** 3140

APPARAAT NO.	H3	H6	R8	R11	
Benaming : Type :	koeler fixed tube	koeler floating head	heater spiraal	koeler spiraal	
Medium - pijpen : - mantel :	proces stroom koelwater	proces stroom koelwater	stoom proces stroom	koelwater proces stroom	
Capaciteit Uitgewisselde warmte [kW]:	3024	2520	8192	2268	
Warmtewisse- lend opper- vlak [m^2]:	294	61.2	19.5	72.4	
Aantal - serie : - parallel :					
Abs./Eff. druk [bar]: - pijpen : - mantel :	7 bar eff. 1 bar abs.	25 bar eff. 1 bar abs.	27 bar eff. 3 bar eff.	1 bar abs. 25 bar eff.	
Temp. in/uit [°C] pijpen : mantel :	81/19 15/40	110/80 20/40	133/133 80/80	20/40 80/80	
Speciale constructie- materialen					
Overig :					

Apparatenlijst voor warmtewisselaars en fornuizen **FVO Nr.** 3140

APPARAAT NO.	H14	F15	H18	H22	H24
Benaming : **Type :**	heater floating head	koeler spiraal	koeler floating head	koeler fixed tube	koeler fixed tube
Medium **- pijpen :** **- mantel :**	proces stroom stoom	koelwater proces stroom	proces stroom koelwater	proces stroom koelwater	proces stroom koelwater
Capaciteit Uitgewisselde warmte [kW]:	1456	4112	12096	1680	2688
Warmtewisselend oppervlak [m^2]:	4	340	259	167	246
Aantal **- serie :** **- parallel :**					
Abs./Eff.* druk [bar]: **- pijpen :** **- mantel :**	25 bar eff. 3 bar eff.	1 bar abs. 1 bar eff.	7 bar eff. 1 bar abs.	1 bar eff. 1 bar abs.	1 bar eff. 1 bar abs.
Temp. in/uit [°C] **pijpen :** **mantel :**	80/97 133/133	20/40 97/95	393/23 20/40	86/18 20/40	86/19 20/40
Speciale constructiematerialen					
Overig :					

*Aangeven wat van toepassing is.

APPARAAT NO.	H25	H28	H30		
Benaming : **Type :**	heater floating head	heater fixed tube	koeler floating head		
Medium **- pijpen :** **- mantel :**	proces stroom koelwater	proces stroom stoom	proces stroom koelwater		
Capaciteit Uitgewisselde warmte [kW]:	2772	8471	4767		
Warmtewisse-lend opper-vlak [m^2]:	29	12	341		
Aantal **- serie :** **- parallel :**					
Abs./Eff.* **druk [bar]:** **- pijpen :** **- mantel :**	 0.2 bar eff. 1 bar abs.	 0.1 bar eff. 40 bar eff.	 0.1 bar abs. 1 bar abs.		
Temp. in/uit [°C] **pijpen :** **mantel :**	 20/40 259/122	 300/259 410/600	 70/38 20/40		
Speciale constructie-materialen					
Overig :					

***Aangeven wat van toepassing is.**

APPARAAT NO.	A1	A4	R8	R11	F15
Benaming : Type :	absorber packed	absorber packed	Reactor three fase buble column	Reactor three fase buble column	Flash vessel
Abs./Eff. druk[1] [bar]:	1 abs.	7 abs.	26 abs.	25 abs.	25/1 abs.
Temp. [K] :	293	415	354	354	369
Inhoud [m^3]: Diameter [m] : L of H [m] :	4.5 1.2 4.0	51 1.4 33	11 1.6 16	168 4.5 11	3.3 1.1 3.4
Vulling * : Schotels (+ aantal) : Vaste pakking: Kat. type : Kat. vorm : _____ _____ _____	berlsadles	berlsadles	-	-	-
Speciale constructie-materialen					
Aantal in - serie : - parallel :					
Overig :					

[1] Aangeven, wat van toepassing is

APPARAAT NO.	V19	E21	V23	V24	D27
Benaming : Type :	l/v seperator	extractor	l/v seperator	l/v seperator	Distillation column
Abs./Eff. druk[1] [bar] :	7 bar abs.	1 bar abs.	1 bar abs.	0.2 bar abs	0.2 bar abs.
Temp. [°C] :	296	370	291	311	T top 311 T bottom
Inhoud [m^3]: Diameter [m] : L of H [m] :	0.6 0.8 1.2	33.4 3.0 14.7	0.2 0.6 0.7	0.4 0.7 1.0	2.7 0.9 3.8
Vulling * : Schotels (+ aantal) : Vaste pakking: Kat. type : Kat. vorm : _____ _____ _____		sieve plates 33			sieve plates 6
Speciale constructie-materialen					
Aantal in - serie : - parallel :					
Overig :					

[1] Aangeven, wat van toepassing is

Technische Universiteit Delft
Vakgroep Chemische Procestechnologie

Datum:31/5/95
Ontwerpers:
S.M.W. Berkemeijer
S.F. Woo

SPECIFICATIEFORMULIER HYDROGENERINGS REACTOR

APPARAATNUMMER : S11

Algemene eigenschappen

Functie : - ~~destillatie~~ / ~~extractie~~ / ~~absorptie~~ / reactie

Type toren : - ~~gepakt~~ / ~~schotel~~ / ~~sproeier~~ / bellenkolom

Type schotel : - klokje / zeefplaat / valve / _____

Aantal schotels
- theoretisch :
- practisch :

Schotelafstand (HETS) : [m] ----- Materiaal schotel :

Diameter toren : 4.5 [m] Hoogte toren : 11 [m]

Materiaal toren :

Koeling : - ~~geen~~ / ~~open stoom~~ / ~~reboiler~~ / spiraal koeler

Bedrijfscondities

	Voeding (L)		Voeding (V)		Top (V)		Bodem (L)		Extractie-middel
Temp. [°C]	80		20		80		80		
Druk [bar]	25		25		23.9		23.9		
Dichtheid [kg/m³]	1000		7.2		16.6		1000		
Massastroom [kg/s]	412.4		1		0.8		412.6		
	mol%	wt%	mol%	wt%	mol%	wt%	mol%	wt%	
Samenstelling									
water		53						53	
NH_4HCO_3		26						23	
NH_4COOH		21						24	
H_2				23		4			
N_2				77		96			

Ontwerp

Aantal klokjes / zeefgaten / _____* :

Actief schoteloppervlak : [m]

Lengte overlooprand : [mm]

Diameter valpijp / gat / _____ : [mm]

Type pakking :
Materiaal pakking :
Afmetingen pakking
- inhoud : [m³]
- lengte : [m]
- breedte : [m]
- hoogte : [m]

FABRIEKSVOORONTWERP NO. 3140

*Indien een toren schotels van verschillend ontwerp bevat, moet dit vermeld worden !

Technische Universiteit Delft
Vakgroep Chemische Procestechnologie

Datum:31/5/95
Ontwerpers:
S.M.W. Berkemeijer
S.F. Woo

SPECIFICATIEFORMULIER REGENERATOR

APPARAATNUMMER : S8

Algemene eigenschappen

Functie : - ~~destillatie~~ / ~~extractie~~ / ~~absorptie~~ / reactie

Type toren : - ~~gepakt~~ / ~~schotel~~ / ~~sproeier~~ / bellenkolom

Type schotel : - klokje / zeefplaat / valve / _____

Aantal schotels
- theoretisch :
- practisch :

Schotelafstand (HETS) : [m] Materiaal schotel :

Diameter toren : 1.6 [m] Hoogte toren : 16 [m]

Materiaal toren :

Verwarming : - ~~geen~~ / open stoom / ~~reboiler~~ /

Bedrijfscondities

	Voeding (L)		Voeding (V)		Top (V)		Bodem (L)		Extractie-middel
Temp. [°C]	81		20		81		81		
Druk [bar]	27.9		27.9		26.3		26.3		
Dichtheid [kg/m^3]	1000		36.7				1000		
Massastroom [kg/s]	32		1		0		33		
	mol %	wt %	mol %	wt %	mol %	wt %	mol %	wt %	
water		50						49	
NH_4HCO_3		44						51	
NH_4COOH		6							
O_2				100					

Ontwerp

Aantal klokjes / zeefgaten / _____* :

Actief schoteloppervlak : [m]

Lengte overlooprand : [mm]

Diameter valpijp / gat / _____ : [mm]

Type pakking :
Materiaal pakking :
Afmetingen pakking
- inhoud : [m^3]
- lengte : [m]
- breedte : [m]
- hoogte : [m]

FABRIEKSVOORONTWERP NO. 3140

*Indien een toren schotels van verschillend ontwerp bevat, moet dit vermeld worden !

APPENDIX VII:

Technische Universiteit Delft
Vakgroep Chemische Procestechnologie

Datum:31/05/95
Ontwerpers:
H.C.de Lange
E.J.J. Ramaker

SPECIFICATIEFORMULIER CENTRIFUGAALPOMP

Dienst : 8000 hours
Type : recessive blades centrifugal
Aantal : 1

Fysische gegevens pompvloeistof

Fluïdum : Aqueous solution of Ammonium formate and ammonium bicarbonate containing 21 μm cat particles,0.5 % mass

Temperatuur (T)	:	81	[°C]			
Dichtheid (r)	:	918	[kg/m^3]			
Viscositeit (h)	:	$1.1*10^{-3}$	[N.s/m^2]			
Dampspanning (p_d)	:	0.8	[bar]	**bij temperatuur (T) :**	81	[°C]
				Vermogen	538.3	[kW]

Capaciteit (F_v)	:	0.450	[m^3/s]
Zuigdruk (p_z)	:	23.9	[bar]
Persdruk (p_p)	:	33.0	[bar]
Theoretisch vermogen	:	419.9	[kW] { = $F_v.(p_p - p_z).10^2$ }
Nuttig effect	:	0.78	[-]
Asvermogen	:	538.3	[kW]

Constructieve gegevens

Aantal omw. per min. :	**Nominale diameter zuigaansluiting :** [ ]
Aandrijving :	**Nominale diameter persaansluiting :** [ ]
Type electromotor :	**Lagerkoeling : ja/nee**
Spanning : [V]	**Pakkingsbuskoeling : ja/nee**
Draairichting :	**Smothering gland : ja/nee**
Fundatieplaat : gecombineerd/ tweedelig	**indien ja :**
Elastische koppeling : ja/nee	**- sluitvloeistof : ja/nee**
Manometer zuigzijde : ja/nee	**- spatringen : ja/nee**
Manometer perszijde : ja/nee	**- pakking, type :**
Min. overdruk boven p_d/p_m : [bar]	**- sleepring-afdichting : ja/nee**
	- N.P.S.H. : [m] { = $p_m.r.g$ }

Materiaal

Pomp-huis :	**Slijtringen :**
Waaier :	**Asbus :**
As :	
Bijzondere voor-zieningen :	
Werkdruk : [bar]	**Persdruk :** [bar]

FABRIEKSVOORONTWERP NO. 3140

Technische Universiteit Delft
Vakgroep Chemische Procestechnologie

Datum:31/5/95
Ontwerpers:
S.M.W. Berkemeijer
S.F. Woo

SPECIFICATIEFORMULIER AMMONIAK ABSORPTIE TOREN

APPARAATNUMMER : A1

Algemene eigenschappen

Functie : - ~~destillatie~~ / ~~extractie~~ / absorptie / _____

Type toren : - gepakt / ~~schotel~~ / ~~sproeier~~ / _____

Type schotel : - klokje / zeefplaat / valve / _____
Aantal schotels
- theoretisch :
- practisch :
Schotelafstand (HETS) : [m] ----- Materiaal schotel :
Diameter toren : 1.2 [m] Hoogte toren : 4 [m]
Materiaal toren :
Verwarming : - geen / ~~open stoom~~ / ~~reboiler~~ / _____

Bedrijfscondities

	Voeding (L)	Voeding (V)	Top (V)	Bodem (L)	Extractie-middel
Temp. [°C]	20	20	81	81	
Druk [bar]	1	1	1	1	
Dichtheid [kg/m^3]	1000	0.7	1.81	1000	
Massastroom [kg/s]	10.4	1.26	0.01	11.65	

	mol%	wt%	mol%	wt%	mol%	wt%	mol%	wt%	
Samenstelling									
water	97						87		
carbondioxide	2		1		100		2		
ammonia	1		99				11		

Ontwerp

Aantal klokjes / zeefgaten / _____* :

Actief schoteloppervlak : 80 [m]

Lengte overlooprand : [mm]

Diameter valpijp / gat / _____ : [mm]

Type pakking :1.5 inch Berl saddles
Materiaal
pakking :ceramic
Afmetingen
pakking
- inhoud : [m^3]
- lengte : [m]
- breedte : [m]
- hoogte : [m]

*Indien een toren schotels van verschillend ontwerp bevat, moet dit vermeld worden !

Technische Universiteit Delft
Vakgroep Chemische Procestechnologie

Datum:31/5/95
Ontwerpers:
S.M.W. Berkemeijer
S.F. Woo

SPECIFICATIEFORMULIER CARBON DIOXIDE ABSORPTIE TOREN

APPARAATNUMMER : A4

Algemene eigenschappen

Functie : - ~~destillatie~~ / ~~extractie~~ / absorptie / _____

Type toren : - gepakt / ~~schotel~~ / ~~sproeier~~ / _____

Type schotel : - klokje / zeefplaat / valve / _____

Aantal schotels
- theoretisch :
- practisch :

Schotelafstand (HETS) : [m] ----- Materiaal schotel :

Diameter toren : 1.4 [m] Hoogte toren : 33 [m]

Materiaal toren :

Verwarming : - geen / ~~open stoom~~ / ~~reboiler~~ / _____

Bedrijfscondities

	Voeding (L)		Voeding (V)		Top (V)		Bodem (L)		Extractie-middel
Temp. [°C]	20		20		81		81		
Druk [bar]	7		7		6.6		6.6		
Dichtheid [kg/m^3]	1000		5.7		12.5		1000		
Massastroom [kg/s]	16.1		4.1		0.1		20.1		
	mol%	wt%	mol%	wt%	mol%	wt%	mol%	wt%	
Samenstelling									
water	87		1				66		
carbondioxide	7		11		100		17		
ammonia	6		88				17		

Ontwerp

Aantal klokjes / zeefgaten / _____* :

Actief schoteloppervlak : 80 [m]

Lengte overlooprand : [mm]

Diameter valpijp / gat / _____ : [mm]

Type pakking :1.5 inch Berl saddles
Materiaal pakking :ceramic
Afmetingen pakking
- inhoud : [m^3]
- lengte : [m]
- breedte : [m]
- hoogte : [m]

*Indien een toren schotels van verschillend ontwerp bevat, moet dit vermeld worden !

Technische Universiteit Delft
Vakgroep Chemische Procestechnologie

Datum: 01/06/1995
Ontwerpers:
S.Berkemeijer
S.F. Woo

SPECIFICATIEFORMULIER KOELER

APPARAATNUMMER: H6

Aantal serie : _____
Aantal parallel : _____

Algemene eigenschappen

Type :
- ~~warmtewisselaar~~
- koeler
- ~~condensor~~
- ~~verdamper~~

Uitvoering :
- ~~met vaste pijpplaten~~
- floating head
- ~~haarspeld~~
- ~~dubbele pijp~~
- ~~platenwarmtewisselaar~~

Positie :
- horizontaal
- verticaal

Capaciteit	:	2520 [kW]	(berekend)
Warmtewisselend oppervlak	:	61.2 [m^2]	(berekend)
Overall warmteoverdrachts-coëfficiënt	:	635 [$W/m^2.K$]	(globaal)
Logaritmisch temperatuursverschil (LMTD)	:	64.9 [°C]	
Aantal passages pijpzijde	:	1	
Aantal passages mantelzijde	:	1	
Correctiefactor LMTD (min. 0.75)	:	1	
Gecorrigeerde LMTD	:	[°C]	

Bedrijfscondities

		Mantelzijde	Pijpzijde
Soort fluïdum		koelwater	proces stroom
Massastroom	[kg/s]	30.0	20.08
Gemiddelde soortelijke warmte	[kJ/kg.°C]	4.2	4.2
Verdampingswarmte	[kJ/kg]		
Temperatuur IN	[°C]	20	110
Temperatuur UIT	[°C]	40	80
Druk	[bar]	1	25

FABRIEKSVOORONTWERP NO. 3140

Technische Universiteit Delft
Vakgroep Chemische Procestechnologie

Datum:01/06/1995
Ontwerpers:
S.Berkemeijer
S.F.Woo

SPECIFICATIEFORMULIER HEATER

APPARAATNUMMER: H_14___

Aantal serie : _____
Aantal parallel : _____

Algemene eigenschappen

Type : - warmtewisselaar
- ~~koeler~~
- ~~condensor~~
- ~~verdamper~~

Uitvoering : - ~~met vaste pijpplaten~~
- floating head
- ~~haarspeld~~
- ~~dubbele pijp~~
- ~~platenwarmtewisselaar~~

Positie : - horizontaal
- verticaal

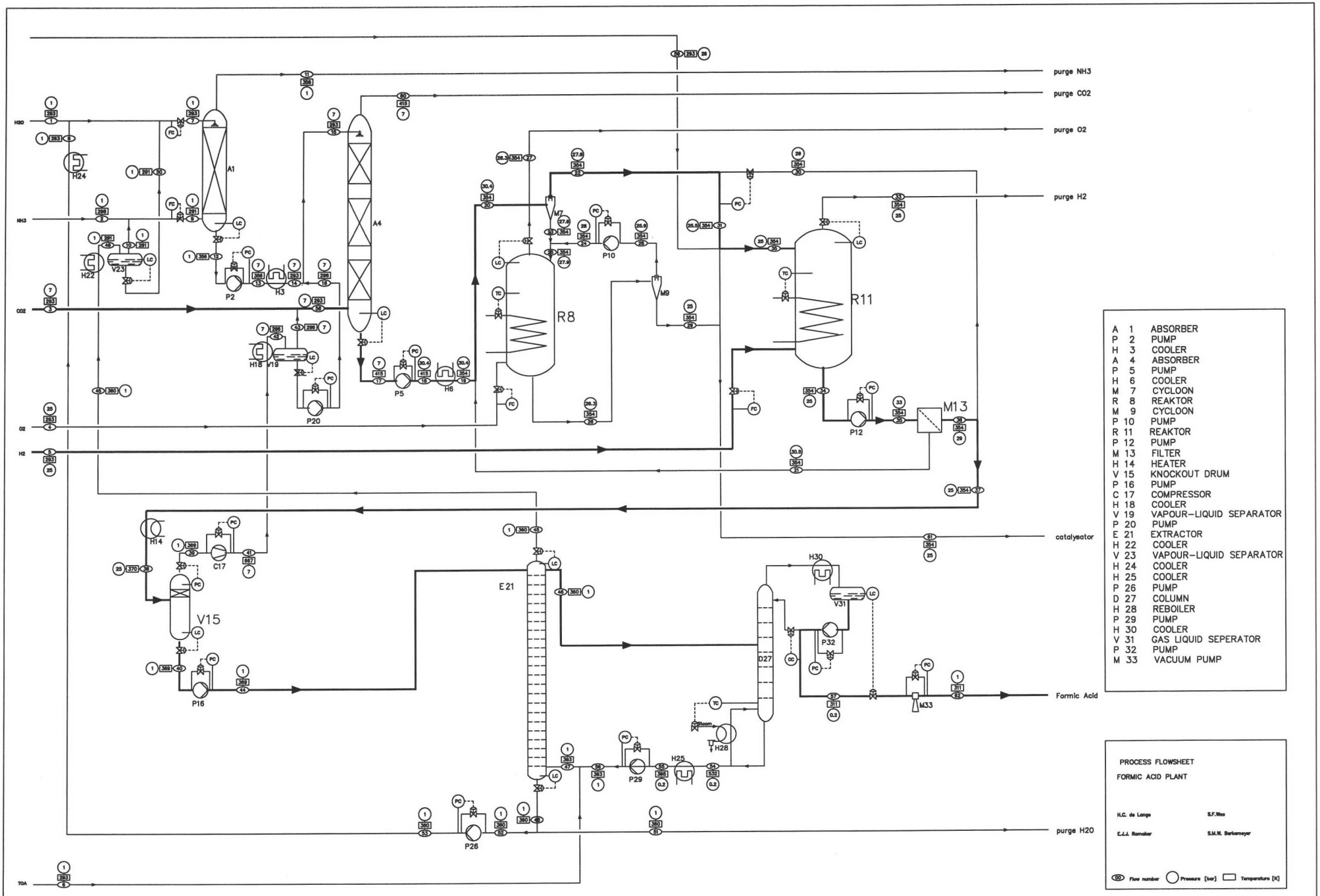
Capaciteit	: 1456	[kW] (berekend)
Warmtewisselend oppervlak	: 4	[m^2] (berekend)
Overall warmteoverdrachts-coëfficiënt	: 8000	[$W/m^2.K$] (globaal)
Logaritmisch temperatuursverschil (LMTD)	: 43.5	[°C]
Aantal passages pijpzijde	: 1	
Aantal passages mantelzijde	: 1	
Correctiefactor LMTD (min. 0.75)	: 1	
Gecorrigeerde LMTD	: 43.5	[°C]

Bedrijfscondities

	Mantelzijde	Pijpzijde
Soort fluïdum	stoom	proces stroom
Massastroom		20.78
- te condenseren [kg/s]	0.5	
Gemiddelde soortelijke warmte [kJ/kg.°C]	2.2	4.2
Temperatuur IN [°C]	190	80
Temperatuur UIT [°C]	120	97
Druk [bar]	3	1

FABRIEKSVOORONTWERP NO. 3140

APPENDIX VIII:
FLOWSHEET



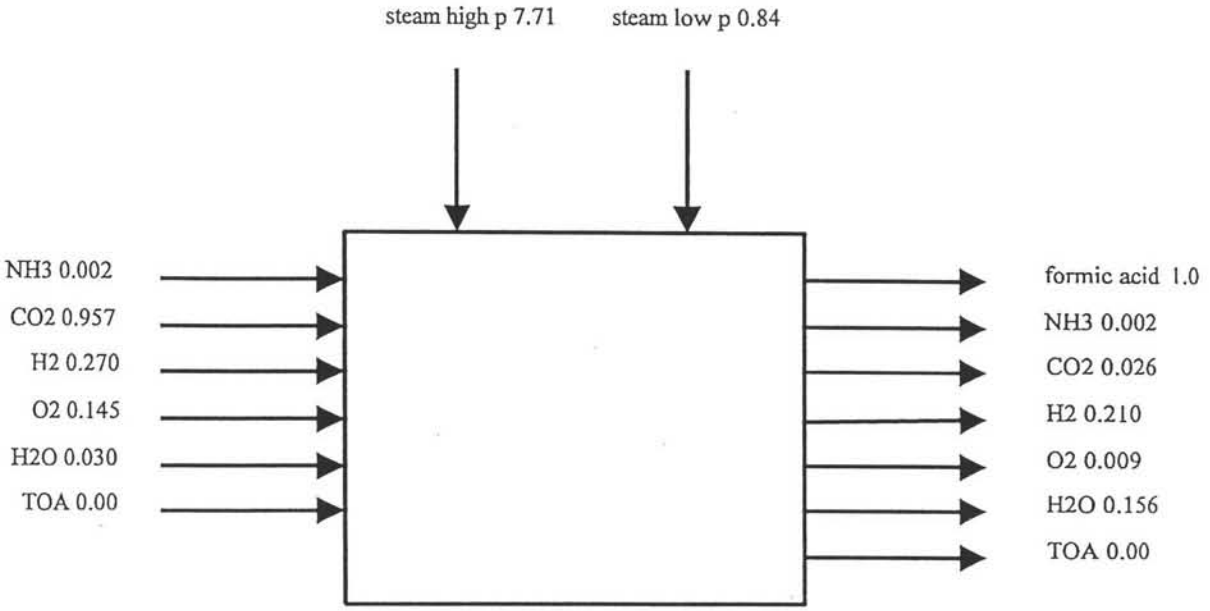
A	1	ABSORBER
P	2	PUMP
H	3	COOLER
A	4	ABSORBER
P	5	PUMP
H	6	COOLER
M	7	CYCLOON
R	8	REAKTOR
M	9	CYCLOON
P	10	PUMP
R	11	REAKTOR
P	12	PUMP
M	13	FILTER
H	14	HEATER
V	15	KNOCKOUT DRUM
P	16	PUMP
C	17	COMPRESSOR
H	18	COOLER
V	19	VAPOUR–LIQUID SEPARATOR
P	20	PUMP
E	21	EXTRACTOR
H	22	COOLER
V	23	VAPOUR–LIQUID SEPARATOR
H	24	COOLER
H	25	COOLER
P	26	PUMP
D	27	COLUMN
H	28	REBOILER
P	29	PUMP
H	30	COOLER
V	31	GAS LIQUID SEPERATOR
P	32	PUMP
M	33	VACUUM PUMP

PROCESS FLOWSHEET
FORMIC ACID PLANT

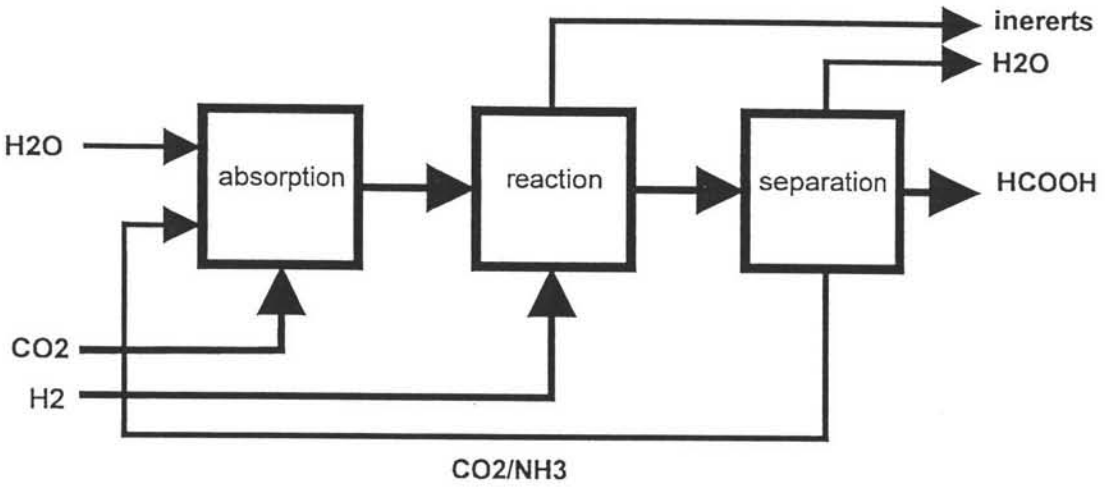
H.C. de Lange — S.F.Woo
E.J.J. Ramaker — S.M.W. Berkemeyer

(00) Flow number ◯ Pressure [bar] ▭ Temperature [K]

APPENDIX IX:
IN AND OUTPUT RENDEMENT

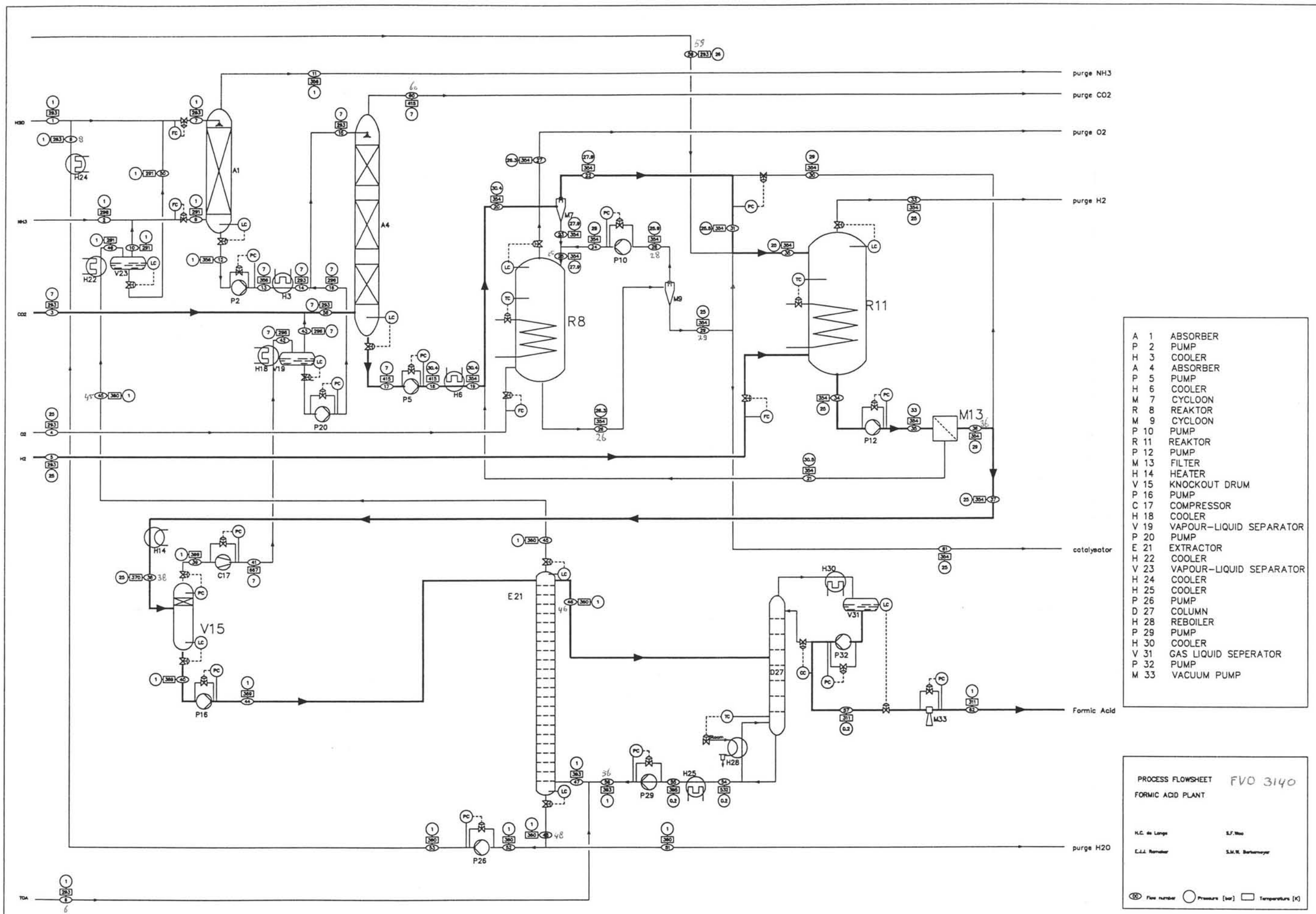


APPENDIX X:
SIMPLEFIED FLOWSHEET



APPENDIX XI:
PROPERTIES OF MAIN COMPONENTS

name	formula	M[g/mol]	T_b [°C]	ρ [kg/m^3]	η [Pa s]
Carbon dioxide	CO_2	44.01	-78.5	1.97	$0.15*10^{-4}$
ammonia	NH_3	17.03	-33.4	0.77	$0.102*10^{-4}$
hydrogen	H_2	2.016	-273.2	0.09	$0.027*10^{-4}$
water	H_2O	18.02	0.0	1000	$1.0*10^{-3}$
ammonium formate	NH_4HCOO	63.06	-	1281	-
ammonium bicarbonate	NH_4HCO_3	79.06	-	1586	-
formic acid	HCOOH	46.03	100.8	1220	$1.47*10^{-3}$
trioctyl ammine	$(C_8H_{17})_2N$	353.41	365	756(80°C)	$2.3*10^{-4}$



A	1	ABSORBER
P	2	PUMP
H	3	COOLER
A	4	ABSORBER
P	5	PUMP
H	6	COOLER
M	7	CYCLOON
R	8	REAKTOR
M	9	CYCLOON
P	10	PUMP
R	11	REAKTOR
P	12	PUMP
M	13	FILTER
H	14	HEATER
V	15	KNOCKOUT DRUM
P	16	PUMP
C	17	COMPRESSOR
H	18	COOLER
V	19	VAPOUR–LIQUID SEPARATOR
P	20	PUMP
E	21	EXTRACTOR
H	22	COOLER
V	23	VAPOUR–LIQUID SEPARATOR
H	24	COOLER
H	25	COOLER
P	26	PUMP
D	27	COLUMN
H	28	REBOILER
P	29	PUMP
H	30	COOLER
V	31	GAS LIQUID SEPERATOR
P	32	PUMP
M	33	VACUUM PUMP

PROCESS FLOWSHEET FVO 3140
FORMIC ACID PLANT

H.C. de Lange — S.F. Was
E.J.J. Ramaker — S.M.W. Berkemeyer

Flow number ○ Pressure [bar] □ Temperature [K]