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The production of maleic anhydride by ~~the~~ selective catalytic oxidation of n-butane

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The production of maleic anhydride by the selective catalytic oxidation of n-butane

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Place : Delft

SUMMARY

This project is a study case given by Prof. dr. J.A. Moulijn and Dr. ir. A. Cybulski of the section Chemical Process Technology of the Technical University of Delft.
The purpose of this project is the production of 50,000 ton maleic anhydride (MA) per year with a new process technology. The process includes the production of MA by the oxidation of n-butane with lattice oxygen on a vanadium-phosphorous-oxide catalyst in a transport bed reactor. The catalyst contains $(VO)_2P_2O_7$ with about 10 wt% of silica. The new technology is based on recirculating the VPO catalyst with the transport bed reactor (TBR) and a fluidized bed regenerator where the re-oxidation of the VPO catalyst takes place. With this technology, a higher yield of MA can be realized, because the chosen TBR reactor can handle larger feed loads of n-butane then the other reactor types (current fluidized bed and fixed bed reactors), because the oxygen here used is not from an open gas stream, but from the selective VPO catalyst.

The process units operate mostly under ~~on~~ low pressure (atmosferic) and relative high temperature and are based to handle large feed loads and products.

The process technology is generally comprised of:
1. Reactor Design and Heat Removal.
2. Product Recovery.
3. Purification.

The process is designed to produce 50 ktons of MA per year with a production time of 8000 hours per year and a MA purity of over the 99 % (in flakes form), using n-butane (47.425 ktons/yr) and (lattice) oxygen (110.024 ktons/yr) as feed. As inert, a gas mixture of nitrogen (originally inert gas), carbon monoxide, carbon dioxide and water gas is used (75.300 ton/hr).

The calculated investment costs are 204,811,200 gld. The method used is the Taylor method. The proceeds by a price of 2,653 gld/ton for Maleic anhydride is 132,630,000 gld per year. Over a period of 10 years, the Return on Investment (ROI) is 10 % and the Internal Rate of Return (IRR) is 32 %.

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Industr. Katalyse

1. INTRODUCTION

This project is a study case given by Prof. dr. J.A. Moulijn and Dr. ir. A. Cybulski of the section Chemical Process Technology at the Technical University of Delft.
The purpose of this project is the production of 50,000 ton maleic anhydride (MA) per year with a new process ~~technology~~. The process includes the production of MA by the oxidation of n-butane with lattice oxygen on a vanadium-phosphorous-oxide (VPO) catalyst in a transport bed ~~reactor~~. The new technology is based on recirculating the VPO catalyst with the transport bed reactor and a fluidized bed regenerator where the re-oxidation of the VPO catalyst takes place. In chapter 2, this new technology is compared with the current technologies.

Maleic anhydride was first produced some 150 years ago by dehydration of maleic acid (MAC). ~~Today~~, it is a chemical of considerable commercial importance. From only 4.5 million lbs produced in 1940, MA has gained impressively, with a production of 341 million lbs in 1978 [1]. Table 1.1. presents the geographic distribution of the installed capacity in 1988. The present world capacity is in excess of 600,000 tons/year.

?

~2 × 10⁶ kg = 2000 t/a?

~153 × 10⁶ kg = 153000 t/a?

Table 1.1. Maleic anhydride installed capacity [2]

	*1000 metric tons
West Europe	176
North America	185
Japan	86
Asia/Mid East (excl. Japan)	19
South America/Africa	38
East Europe	76
Total	580

MA is an important chemical intermediate. With its two functional groups (double bond and anhydride), it is very versatile and can be used to prepare many derivatives. The end uses (1990) in Europe, USA and Japan are reported in table 1.2.

Table 1.2. End uses of maleic anhydride [2]   in ktons?

	Europe	USA	Japan
Unsaturated Polyester resins	55	57	35
Fumaric and Malic acids	12	10	25
Lube Oil Additives	8	9	10
Agricultural Chemicals	3	10	3
Paper sizing	2	4	5
Others	20	10	22
	100 %	100 %	100 % ?

Σ_{World} = 600000 t/a ?

In chapter 3 of this report, the MA process structure is decribed and in chapter 4, the design and calculation of the chosen process equipments are given. Chapter 5 includes the mass and energy balance of the process. Some short safety aspects are given in chapter 6 and the costing evaluation is described in chapter 7. At last, the conclusions and discussion can be find in chapter 8.

Process

(15)

2. MALEIC ANHYDRIDE ~~PRODUCTION~~ TECHNOLOGIES

Until the early '70's practically all the MA was produced from benzene. In 1974-75, at the conclusion of long research work, first Monsanto in the USA, and a few months later Alusuisse Italia in Italy, converted some commercial reactors using benzene feed to butane feed. In subsequent years, several companies converted existing plants from benzene to butane and others constructed new plants specially for butane feedstock. This happened mostly in the USA where butane was easily available and environmental regulations for benzene emissions became very strict. There is also stoichiometric advantage in using C4 hydrocarbons over benzene since the latter two carbons or one-third of the molecule is wasted. Thus, ideally 100 lb of benzene would yield 125.6 lb of MA whereas 100 lb of butane would give 168.9 lb of MA. At the present time, all the production in the USA is based on butane [2,3].

0.8 + Bene/t M

Worldwide, half of the production is still based on benzene, but this technology is considered obsolete and not of interest for new plants, except for special isolated cases. Some processes, based on benzene, are the 'Scientific Design (SD) Process', the 'Ruhrol-Lurgi Process', the 'Ruhrol-Bayer Process' and the 'SAVA Process'. Some C_4-Based processes are the 'Mitsubishi Process', the 'BASF Process' and the 'ALMA Process' [1,2].

Du Pont developed a Tetrahydrofuran (THF) plant with a production capacity of 100 million lb/yr based on MA from n-butane [3]. This plant is scheduled to start up in 1995 in Asturias, Spain and consists of the new technology which is the basis of this rapport.

The production of MA still increases and the increasing capacity is almost exclusively based on C_4 feedstocks (n-butane, butene-1 and butene-2) [3].

Whether one uses benzene as a starting material or C_4 hydrocarbons, there are some common features in the production tecnology. These are generally comprised of:

1. Reactor Design and Heat Removal.
2. Product Recovery.
3. Purification.

2.1. Reactor Design and Heat Removal

In MA production, reactor design is of paramount importance because the partial oxidation of hydrocarbons to MA is a highly exothermic reaction and a properly designed reactor is needed to maintain the temperature and hence the reactions under control. An uncontrolled reaction may result in severe reduction of yields and loss of catalyst life.
There are 3 types of reactors possible :

1. Fixed Bed
2. Fluidized Bed
3. Riser Reactor (Transport Bed Reactor)

In table 2.1. the three reactors are compared with each other for the selective oxidation of n-butane to MA.

Table 2.1. Relative rating of various reactor types for the selective oxidation of n-butane to maleic anhydride [3].

System parameter	Fixed Bed vl.	Fluidized Bed	Riser Reactor
Heat Removal	(-)	(+)	(+)
Temperature Control	(-)	(+)	(+)
Maximum Feed Conc.,%	1.8 - 2.1	4	> 10
Capital Investment $	(-)	(+)	(++)
Selectivity	(+)	(-)	(++)
Catalyst Attrition	(+)	(-)	(-)

N.B. + = higher coefficient.

Mostly, air is used to carry the hydrocarbon in the Fixed Bed Reactor and in the Fluidized Bed Reactor. In the Riser Reactor, lattice oxygen on the catalyst is used for the oxidation of n-butane. To carry the hydrocarbon in the reactor, pure nitrogen is used, but it is also possible to use a mixture of the (recycle) nitrogen and the inert by-products (carbon monoxide, carbon dioxide and water) of the oxidation step [8].

2.2. Product Recovery

Besides MA, maleic acid, fumaric acid, carbon monoxide, carbon dioxide and water are the major by-products of the oxidation of benzene. The major by-products of the oxidation of n-butane are carbon monoxide, carbon dioxide and water. In either situation (benzene or n-butane), nitrogen, water and the oxides of carbon are vented to the air after the recovery of products and hydrocarbons. If a significant amount of hydrocarbon is unreacted, it may be recycled if practical. If this is not possible, any of the available emission control technologies, especially for benzene-based processes, may be considered [1].

The major difference between various commercial processes is observed in the recovery of MA from the effluent stream of the reactor. Commonly employed methods fall into one of the following categories:

1. Cooling to recover solid MA, (m.p. 56 °C).
2. Cooling to recover liquid MA.
3. Collecting in a solvent.
4. Collecting in H_2O or aqueous maleic acid.

The effluent stream contains (mostly) a low concentration of ~~MA in~~ the gas fase. Part of this is recovered as a solid by cooling the effluent as in the Ruhroll process. The Scientific Design (SD) process, on the other hand, collects MA as a molten liquid by cooling the stream above the dew point of water. This prevents formation of any significant concentration of maleic acid produced by hydrolysis which may potentially isomerize to fumaric acid.

Alternatively, the molten MA can be collected on ceramic supports as claimed by Monsanto [1].

In the solvent-type recovery, MA may be recovered as a solution in dibutyl phthalate, dimethyl phthalate, diphenyl pentachloride, and the like; however, this inert-solvent absorption method is commercially less important because most of these solvents are hazardous to the environment and the 100 percent recovery of the solvents is difficult [1,4,5].

In the aqueous recovery, generally a 40% solution of maleic acid is used in the srubber. Aqueous recovery is ~~a~~ part of most of the processes and is used after a primary collection. The aqueous solution so produced is either used for recovering ~~of~~ MA or may be converted to fumaric acid by thermal isomerization [1].

2.3. Purification

Where water is a part of the recovery system as in maleic acid solution, water is removed by azeotropic distillation or by evaporation and dehydration. Appropriate care is taken to prevent significant isomerization. Commonly employed solvents for azeotropic removal of water are xylene or o-diclorobenzene. Octane, diisobutyl ketone, etc. have also been claimed in the patent literature. Thin-film evaporation technology has also been employed.

The MA so produced and that from the primary recovery are combined at this stage and purified by distillation. The distillation can be performed on the crude product as such in the presence of an additive. The purpose is to obtain a low-color and color-stable MA.

2.4. Choice of the Production Technology and Process Units

For this FVO-project the following production technology is chosen :

I. Reactor Design and Heat Removal

Transport Bed Reactor (TBR) with internal spiral wounded coils with a molten salt as the cooling medium. The energy produced by the exothermic reaction is used for the making of steam. Recycle nitrogen and the inert oxidation products (CO, CO_2, H_2O) is used for carrying the n-butane. The unreacted n-butane is almost completely recycled and re-used for the oxidation step. Lattice oxygen on the VPO catalyst is used. The VPO catalyst is re-oxidized in a regenerator with hot oxygen. Part of this oxygen is used to fluidize the regenerator catbed and to heat the inert recycle stream. The TBR is chosen because this reactor can handle larger feed loads of n-butane then the other reactor types, because the oxygen here used is not from an open gas stream, but from the selective VPO catalyst.

II. Product Recovery

The product gas from the reactor is cooled in a reactive absorber with water. The MA reacts with water to form maleic acid and the inert gasses are removed from the top of the absorber. The maleic acid leaves from the bottom of the absorber. Water is used as absorbent, because no by-products are formed (except maybe fumaric acid) and the costs of using water are low.

only one of the factors!

what, if so?

III. Purification

The maleic acid from the Reactive Absorber goes to a Thin Layer Evaporator/ Dehydrator and the formed MA goes to two serial condensers. A thin layer evaporator/dehydrator is chosen, because the evaporation and dehydration of the maleic acid must be done fast, otherwise part of the liquid maleic acid will isomerize to fumaric acid. The water (gas) is recycled to the Reactive Absorber. The crude MA from the condensers is further purified by vacuum distillation and solidification takes place in a Flakes Drum.

(For more details of the chosen Production Technology: see Chapter 3).

3. THE MA PROCESS STRUCTURE

3.1. Process Description and Conditions

The Flow Scheme of the Process Description can be found in appendix I. Temperature and pressure conditions are also on this scheme. The material properties of the mentioned compounds are in appendix II. The component mass (kg/hr) and energy (kW) flows of the streams are found in appendix III and the overall mass and energy balance is in appendix IV. Only the most important process conditions and streams are mentioned in this paragraph.

The process is designed to produce 50 ktons of MA per year with a production time of 8000 hours per year and a MA purity of over the 99 %, using n-butane and lattice oxygen on a VPO-catalyst as feed.

75883.0 ?

75301.62
581.38
75888.00

I. Feed make-up

From the Storage Tank **V1**, fresh liquid n-butane (5928,16 kg/hr; 0 °C; 1.5 bar) is vaporized in the Vaporiser **H2**. The heated n-butane gas is mixed in a mixer with recycle n-butane (581.38 kg/hr) and a mixture of inert gasses consisting of N_2, CO, CO_2 and H_2O (75301.62 kg/hr) (stream 30). N_2 is the originally inert gas (start up inert gas) and the other gasses are by-products of the oxidation reaction in R4. The feed gas of the reactor (stream 4) must always consists 7.957 wt% of n-butane. The mixture of recycle gas and fresh n-butane is heated in heat exchanger **H3** to a temperature of 370 °C. The feed pressure is 1.5 bar. The pressure of 1.5 bar is raised by the compressor unit **C13**, which consists of two compressors.

5344640
13753
5358393 = str 8 ?

str 11

II. Reaction, heat removal and separation

The oxidation reaction of n-butane and oxygen takes place in the Transport Bed Reactor **R4**. The oxygen (13753 kg/hr) used is lattice oxygen on an VPO catalyst (5344640 kg/hr), which enters the large reactor with ~~from~~ stream 8. Because of the highly exothermic reaction and the relatively large amound of n-butane, special care is taken to remove the excess heat (about 43.15 MW), using five units of spiral wounded coils with molten salt as cooling medium. The heat removed with the coil units, is used to produce steam of 190 °C and 3 bar in the external heat exchanger unit **H5**. The circulating of the molten salt is done by the pumping unit **P6**. The reaction temperature must be hold at about 370 °C and the pressure about 1.5 bar. About 90% of the n-butane converts to MA (6358.08 kg/hr) and CO (2070.50 kg/hr), CO_2 (3253.22 kg/hr) and H_2O (7929.48 kg/hr). As the catalyst also flows with the gas mixture to the top of the reactor (residence times for both solid and gas is 5 seconds), the catalyst is separated from the gas/solid mixture in the external cylone battery **M7** (stream 5 to streams 6 and 7), which consists of four parallel cylones. str 5. ?

III. Regeneration and heat integration

The oxidized VPO catalyst (stream 6) is re-oxidized in regenerator **R8** with pure oxygen. The oxygen used is for the re-oxidation of the catalyst (13753 kg/hr) and for fluidizing the cat-bed. The total amound of oxygen is 31035.47 kg/hr and consists of fresh oxygen (stream 51; 13753 kg/hr) and the recycle oxygen (stream 9) from the regenerator. This oxygen flow first heats the recycle inerts/n-butane gas in heat exchanger **H15**.

The recycle oxygen flow from H15 is mixed up with fresh oxygen (stream 51). Because the regenerator operates at 1.5 bar and 370 °C, the make up oxygen feed is compressed to 1.5 bar and is heated to 370 °C in the heat exchangers H11 and H12. The excess oxygen in the regenerator is purified from cat-solids with a unit of three cylones **M9**.

IV. Absorption and water/gas recovery

The product gas from the cylone battery M7 (stream 7; 95563.89 kg/hr, 370 °C) first heats the recycle inert/n-butane gas in **H14**. After that, the product gas is futher cooled in heat exchanger **H22** to a temperature above the melting point of MA (stream 13). This gas flow is absorbed with liquid water in the Reactive Absorber **T24**. Almost all the MA from the gas reacts with the water to maleic acid (MAC). The water (stream 20; 10026.83 kg/hr) flow separates the other gasses from the formed liquid MAC, which leaves the absorber from the bottom; together with a fraction of liquid water and very small fraction of dissolved N_2, n-butane, CO and CO_2 (stream 14; 8226.52 kg/hr). The gasses leave T24 from the top and are further cooled to a temperature of about 40 °C in the heat exchanger **H20** (stream 16) and part of the gasses, mostly water, are condensed. In vessel **V18**, the condensed mixture and the gasses are separated. Part of the liquid mixture (about 28.5 wt% of the total liquid stream 17) enters the Neutralization Tank **V21**. The water that leaves V21 must have a pH between 6.5 and 8 and a temperature not higher then 30 °C [6]. Neutralization takes place with a NaOH solvent of 20 °C from tank **V19**. Part of the gas mixture which leave **V18** (stream 25), is purged into the air from valve **M17** (about 10.70 wt% of stream 25). Care must be taken of the emission, because of the temperature of the purge gas (low enough ?) and of the CO and CO_2 emission. The part of the gas which is not purged, is used as recycle inert gas for the oxidation reaction. The gas contains about 0.766 wt% n-butane (stream 27; 581.38 kg/hr). The recycle gas is preheated, as was written above, in **H14** and **H15** and pressurized in compressor **C13**. In case something goes wrong with the absorber, vessel **V25** is used for collecting the MAC mixture. V25 can be heated, otherwise the MAC can isomerize to fumaric acid.

V. Dehydration and filtration

The crude MAC flow (stream 14) from the bottom of the Reactive Absorber (with about 2 wt% H_2O) is pumped with liquid pump **P26** to the top of the Evaporation/Dehydration unit **M30**, which consists of two parallel Thin Layer dehydrators. Both dehydrators operate at atmosferic pressure and at a temperature above the melting point of MA, so the crude MAC is evaporised and dehydrated to MA and H_2O. As the dehydrating reaction is endothermic, extra (steam) heat is added for the reaction. About 95% of the MAC is evaporised and dehydrated and the gas mixture of MA and H_2O and the other gasses (traces of N_2, CO, CO_2 and n-butane) leaves M30 from the top (stream 33). Part of the MAC isomerizes to fumaric acid

(FAC) (106 kg/hr) and this part and the unreacted liquid MAC (302.75 kg/hr) leaves M30 from the bottom (stream 34) where it is cooled in heat exchanger **H31** and enters vessel **V32**. V32 has no special function and is only used for in case something goes wrong with the dehydrators or if there are too much by-products in the feed.
The flow from V32 is pumped with **P29** to the filter unit **F27/F28**. Two filters are used because the process is continuoes and the fumaric acid, traces VPO-cat and other high melting point by-products are removed. The liquid MAC is so recycled to the dehydrator feed (stream 40 to stream 32).

VI. Purification and solidification

After the dehydration section, the MA/H_2O gas mixture from the top of M30 enters two serial condensers **M33** and **M34**. Both condensers operate at atmosferic pressure with a condensating temperature above the dew point of H_2O. Part (6.62 wt%) of the MA and all the other gasses leave the condensers and are, after cooled in heat exchanger **H23**, recycled to the feed of the absorber T24. The liquid MA from both condensers are further purified in the Vacuum Distillation Tower **T35**. T35 operates at a pressure of 0.6 bar (with **P38**) and uses the thermosyfon reboiler **H36** for the heating and the vacuum pump **P16** for creating the operating pressure. The purified MA is solidificated to flakes in the Rotary Flakes Drum **M37**. The MA end product is almost 100% pure and has a temperature of about 40 °C (stream 48). The produced MA has a flow of 6261.08 kg/hr. The gas (mostly water and a very small amount of MA) from the vacuum distillation tower goes to the neutralization tank **V21** (stream 47).

3.2. Process Aspects

3.2.1. Thermodynamic aspects

Simulation program used: CHEMCAD.
The K-values are calculated with the PSRK Model.
The PSRK (Predictive Soave-Redlich-Kwong) equation is a group contribution equation-of-state based on the SRK equation. This concept makes use of recent developments and has the main advantage, that vapor-liquid-equilibria (VLE) can be predicted for a large number of systems without introducing new model parameters that must be fitted to experimental VLE-data. The PSRK equation of state can be used for VLE-predictions over a much larger temperature and pressure range than the UNIFAC-γ-Φ- approach and is easily extended to mixtures containing supercritical compounds. Additional PSRK parameters, which allow the calculation of gas/gas and gas/alkane phase equilibria, are provided by the Chemcad program. In addition to those mixtures covered by UNIFAC, phase equilibrum calculations may also include gases like CH_4, C2H6, C3H6, C4H10, CO2, N2, H2 and CO. More details of PSRK can be find in the CHEMCAD III manual [28].

Entalpy: Heat of Vaporization.
Liquid density model: API Lu's method.
Liquid viscosity model: Library.
Vapor viscosity model: Library.

Liquid Thermal Conductivity Model: Library.
Vapor Thermal Conductivity Model: Library.
Liquid Surface Tension Model: Library.

3.2.2. Reactions and kinetics

In R4, 90% of the n-butane feed is converted to MA, water, CO and CO_2. The reaction mechanism and kinetic is given in paragraph (4.1.). In R8, the VPO catalyst is re-oxidized from V^4 to V^5. The kinetic of the re-oxidation reaction is still unknown or confidential. In T24, the MA and part of the water is formed to MAC. Only the value of the reaction rate constant k is found in literature. See paragraph (4.4.) for more details. In M30 the dehydration reaction of MAC to MA and H_2O takes place (95 % coversion) (paragraph 4.5.).

3.2.3. VPO catalyst

According to R.M. Contractor [8,10], the best catalysts for the butane oxidation to maleic anhydride contain $(VO)_2P_2O_7$ which must be prepared from a $(VO)_2H_2O(PO_3OH)_2$ precursor (see the figure in appendix V). By itself, $(VO)_2P_2O_7$ is mechanically too weak to be useful in fluid bed or recirculating solids reactors, but Contractor and others have discovered a novel method of imparting attrition resistance without loss of selectivity to maleic anhydride. The attrition resistance is provided using only small amounts (~10 wt%) of silica. The technique results in a thin layer of silica at the periphery of the spray dried particle (see figure 3.2, appendix V). This layer is very durable, yet it is porous to reactants and products. Higher selectivities to maleic anhydride are observed when the two steps of the redox process are separated. The vanadium phosphate is circulated between two reactors. In one, butane is oxidized by vanadium phosphate (reactor R4); in the other, the vanadium phosphate is re-oxidized by oxygen (regenerator R8). An overall preparation of the VPO catalyst is given by Contractor in [26]. The P/V ratio of the catalyst is usually 0.9 to 1.1 and the S.A. (= surface area by B.E.T method) is about 20 m^2/g. The catalyst form is spherical and the diameter is 200 μm. The catalyst density (inclusive pores) is 800 kg/m^3.

3.2.4. Process Control

In this report, no special care is taken of the process control, but in practice, process control of the reaction- and regeneration section is very important because of the exothermic oxidation reactions in R4 and the oxygen gas stream in R8.

3.2.5. Utilities

Steam: HP steam; 40 bar, 410 °C; Condensation temperature: 250 °C;
MP steam; 10 bar, 220 °C; " " : 180 °C;
LP steam; 3 bar, 190 °C; " " : 133.5 °C.

Electricity: 220 V, cycle electricity.

Water: Cooling water: inlet temperature 20 °C, maximum outlet temperature: 40 °C.
Pressure 3 bar.
Drinking water: 7 bar.

4. DESIGN/CALCULATION OF THE EQUIPMENTS

4.1. Reactor R4 (with heat exchanging equipment)

The reactor must be designed to handle a production of 50 ktons MA per year. The reactor is a transport bed type, so all the feed (gas and VPO cat) enters from the bottom and leaves from the top of the reactor. Because the oxidation reaction is highly exothermic, the heat removal must be sufficient and carefull.

From the reaction kinitics an optimal reactor temperature and pressure is chosen for a certain amount of n-butane. This amount is calculated from the stoichimetric reaction mechanism and the conversion, and the demand of 50 ktons MA per year. The conversion is calculated from the kinitics and checked with literature. Because this process is relatively new, most of the important data of the new VPO catalyst and the reactor is convidential and no more data of Dupont itself was possible.

Reaction mechanism

From literature [3,7,8] the following stoichiometric equations are possible:

58 98 MA.

$C_4H_{10}(g) + 3.5\ O_2(g) \xrightarrow{R1} C_4H_2O_3(g) + 4\ H_2O(g)$ (R.1)

MA $C_4H_2O_3(g) + 2\ O_2(g) \xrightarrow{R2} 2\ CO(g) + 2\ CO_2(g) + H_2O(g)$ (R.2)

$C_4H_{10}(g) + 5.5\ O_2(g) \xrightarrow{R3} 2\ CO(g) + 2\ CO_2(g) + 5\ H_2O(g)$ (R.3)

5 $4CO_2 + 2H_2O$

Reaction kinetics

According to the literature, there are 5 models possible for the above reaction network : (1) First-Order Model; (2) Wohlfahrt Model; (3) Power-Law Model; (4) Sharma Model and (5) Adsorption Model.

Lerou and Mills [3] have studied the above models and came to the conclusion that the Sharma Model and the Adsorption Model were the best suited for calculating the optimal space-time (W/F_{bu0}) for a plug flow reactor. W is the total amount of VPO catalyst (kg) needed for the optimal MA conversion and F_{bu0} is the start amount of n-butane (kmol/hr). Chosen is the **Sharma Model** (for fixed bed reactors) [7], because no data was available for the Adsorption Model in literature.

were

Assuming plug-flow of the gas, a mass balance over a differential element of reactor volume leads to the coupled system of ordinary differential equations given below for the model-predicted yields of MA, CO and CO_2:

$$\frac{d(x_{bu})}{d(W/F_{})} = -(R1 + R3) \qquad (4.1)$$

$$\frac{d(x_{MA})}{d(W/F_{bu0})} = R1 - R2 \tag{4.2}$$

$$\frac{d(x_T)}{d(W/F_{bu0})} = R2 + R3 \tag{4.3}$$

x_T = fraction of the total oxidation by-products.
The Sharma Model and the simulated output can be ~~find~~ in appendix **VI**. The figure of the output shows the total oxidation products (TOP), n-butane and MA (Y-as) versus the space time W/F_{bu0} (X-as). The Sharma Model was first fitted with the experimental output data of Lerou [3] and checked with the experimental data of Contractor [8] and then simulated at the chosen (optimal) temperature and pressure for the process [8, 27].
According to this model at an operating pressure of 1.5 bar, a temperature of 370 °C and P_{bu0}/P_{tot} is 0.04, the optimal conversion for MA is **0.57** (reaction R.1) and ~~for the~~ oxidation by-products **0.33** (Mostly reaction R.3). ~~The simulated~~ optimal spacetime W/F_{bu0} is **47720** (~~kg cat/kmol~~ butane). About **10%** of the n-butane feed did not react. If a ~~higher~~ reactor temperature is chosen, more CO, CO_2 and water will be formed. The pressure is of lesser importance, but the optimal value is at 1 bar. A higher pressure will reduce the n-butane conversion.

The simulation of the Sharma model was done by the computer program Psi/c, with the Runge Kutta 2 option (The same output was ~~find~~ found by RRSTIFF).

Column dimensions

Reactor exit

The typical riser bed porosity lays between 0.90 and 0.98. The chosen porosity is **0.95** (volume basis). With a demand of 63.736 kmol MA/hr (6250 kg/hr), the needed n-butane is : 63.736/0.57 = **112 kmol n-butane per hour**. The amount of catalyst needed is : 112 * W/F_{bu0} = 112 * 47720 = **5344640 kg catalyst per hour**. With a catalyst bulk density of 800 kg/m^3, the total flow (gas + cat) is (5344640/800)/(1-0.95) = 133616 m^3/hr. That is 37.166 m^3/s. With a residence time (τ) of **5 seconds** (both gas and cat) the total reactor volume V is 5 * 37.166 = 185.83 m^3.
The minimal superficial gas velocity is calculated with the Kozeny Carman equation :

$$U_{mf} = \frac{(1-\epsilon_{bed})^3 * (\rho_{cat} - \rho_{gas}) * g}{(5 * (\frac{6}{D_{cat}})^2 * \epsilon_{bed} * \eta_{gas})} \tag{4.4}$$

with ρ_{gas} = 0.5418 kg/m3,
ρ_{cat} = 800 kg/m3,
η_{gas} = 2.884 e-5 Pa.s,
D_{cat} = 0.0002 m. ~ 0.2

The calculated U_{mf} is lower than 0.1 m/s.

The most important gas velocity for the transport bed reactor is the terminal velocity U_t :

$$U_t = \sqrt{\frac{(4 * g * (\rho_{cat} - \rho_{gas}) * D_{cat}}{(3 * 0.43 * \rho_{gas})}} \tag{4.5}$$

The calculated U_t is 3 m/s. If the gas velocity is 5.2 m/s (about 2 x U_t); the column height is then τ * gas velocity = 5 * 5,2 = **26** m. So, the ~~diameter~~ of the reactor is then **3** m (without spiral wounded coils: see further).

$37.166\ m^3/sec = \frac{\pi}{4} D^2 \times$

$185.83\ m^3 = \frac{\pi}{4} D^2 \times 26.$

Pressure drop

The pressure drop dP is calculated with :

$$dP = \rho_{cat} * g * H * (1 - \epsilon_{bed}) \tag{4.6}$$

dP = 800*9.81*26*(1-0.95) = 10202.4 Pa ≈ 0.102 bar.

Inert carrier gas

The start inert carrier gas of the feed is nitrogen, but according to the literature [8], product oxidation gas may be used as carrier inert gas for the butane. So, in this process, a fixed amount of the N_2, CO, CO_2 and H_2O (e.d. part of the gas that is not purged) is recycled to the reactor (see also chapter 3.1).

Heat removal

With the stoichiometric reaction network and the calculated conversions of MA, CO, CO_2 and H_2O, the total heat of reaction is calculated with CHEMCAD, assuming that the total amount of lattice oxygen on the catalyst is well enough to cover the two fast reactions (R.1) and (R.3). It is assumed that the decomposition reaction of MA in the transport bed reactor is too slow to play a major rule.

The two fast reactions are exothermic and a mass balance over the reactor is :

	Flow in (start) [kg/hr]	**Flow out** (stream 5) [kg/hr]
n-Butane	6509.0	650.9
N2	75301.6	75301.6
CO	--	2070.5
CO2	--	3253.2
MA	--	6358.1
H2O	--	7929.5
O2 (in catalyst)	13753.0	--
VPO catalyst	5344640.0	5344640.0
	------------- +	------------- +
Total	5440203.6	5440203.8

With Chemcad, the following heat duties were calculated :

For reaction (R.1) with a 0.57 conversion of n-butane: Q = - 21.73 MW 93.1 (155)

For reaction (R.3) with a 0.33 conversion of n-butane: Q = - 21.42 MW 93.1

should be ≠

Total heat to be removed : - 43.15 MW

This heat has to be removed, otherwise the temperature in the reactor will rise and the conversion of MA will decrease. The temperature in the reactor must be hold at 370 °C, and therefore the excess heat is removed by five units of spiral wounded coils; each unit consists of seven coils with different diameter and length. As cooling medium, molten salt is used. With the heat removed by the molten salt, LP steam is produced with an external heat exchanger unit. This steam is delivered to the steam-net of the total plant.

Same Heat (

Design of a spiral wounded coil unit

One unit consists of seven coils. One unit has to remove about 43.15/5 = 8.63 MW. In the following table a summary is given :

Table 4.1. Design summary of one spiral wound coil unit

	coil 1	coil 2	coil 3	coil 4	coil 5	coil 6	coil 7	Total
d_o	0.05	0.05	0.05	0.05	0.05	0.05	0.05	
d_i	0.045	0.045	0.045	0.045	0.045	0.045	0.045	
L_c	56.55	94.2	132	170	207.35	245	273.3	
D_c m	0.6	1.0	1.4	1.8	2.2	2.6	2.9	
A_c m^2	9	14.8	20.74	26.70	33	38.5	42.93	
V_c m^3	0.111	0.185	0.259	0.334	0.407	0.481	0.537	2.314
U	300	300	300	300	300	300	300	
Q	432	710.4	995.5	1282	1584	1848	2061	8913
F_{salt}	25.13	41.32	57.90	74.57	92.13	107.49	119.9	

d_o = outside tube diameter, m,
d_i = inside tube diameter, m,
L_c = length of the coil = $\pi * D_c * (H/(d_o + d_g))$, m,
d_g = distance between 2 coils = 0.10 m,
D_c = diameter of the (spiral) coil, m,
A_c = heat exchanging surface area, m^2,
V_c = volume of the coil, m^3,
U = overall heat transfer coefficient, $W/m^2.C$,
Q = transfer heat = $U * A_c * (T_r - T_{s,gem})$, kW,
H = heigth of one unit = 4.5 m,
F_{salt} = mass flow salt = $[Q*3600)/(cp_{salt} * (T_{s,out} - T_{s,out}))]/\rho_{salt}$, kg/hr.

With : cp_{salt} = specific heat of the salt = 1.563 kJ/kg.°C,
ρ_{salt} = salt density = 1980 kg/m^3,
$T_{s,in}$ = temperature of the incoming salt = 200 °C
$T_{s,out}$ = temperature of the leaving salt = 220 °C
$T_{s,gem}$ = mean temperature of the salt = 210 °C
T_r = reactor temperature = 370 °C

The total volume of the five units is 5*2.314 = 11.57 m^3
The total volume of the reactor with the five units is 195.35 m^3
So, the new reactor dimensions are :
Diameter D_r of the transport bed reactor is 3.10 m
Height H_r of the reactor is 26 m
The total heat removal capacity of the five units is 5*8.913 = 44.565 MW

The estimated U is recalculated with the following equations [9] :

$$\frac{1}{U} = \frac{1}{h_o} + \frac{(d_w - d_i) * d_o}{(k_w * d_w)} + \frac{d_o}{h_i * d_i} + R_o + \frac{R_i * d_o}{d_i} \tag{4.7}$$

With : d = d_i = 0.045, m,
d_w = $(d_i + d_o)/2$, m,
x = $d_w - d_i$, m,
R_o = scale resistance = 0.0002, (W/m^2.°C)$^{-1}$
R_i = scale resistance = 0.0004, (W/m^2.°C)$^{-1}$
h_o = outside film coefficient, (W/m^2.°C),
h_i = inside film coefficient, (W/m^2.°C),
k_w = thermal conductivity of the material, (W/m.°C).

And :

$$h_o = 0.87 * (\frac{k_o}{D_r}) * (Re_o)^{0.62} * (\frac{(Cp_o * \mu_o)}{k_o})^{0.33} * (\frac{\mu_o}{u_s})^{0.14} \tag{4.8}$$

$$h_i = 0.023 * \frac{k_i}{d} * (Re_i)^{0.8} * (\frac{Cp_i * \mu_i}{k_i})^{0.4} * (1 + 3.5 \frac{d}{D_c}) \tag{4.9}$$

$$Re_o = \frac{\rho_o * v_o * D_r}{\mu_o} \tag{4.10}$$

$$Re_i = \frac{\rho_i * v_i * d}{\mu_i} \tag{4.11}$$

With: Cp_i = specific heat of the salt = 1.563 kJ/kg.°C,
Cp_o = specific heat of the gas = 1.2817 kJ/kg.°C,
μ_i = viscosity of the salt = 1.7 e-3 Pa.s,
μ_o = viscosity of the gas at the reactor inlet = 2.9217 e-5 Pa.s,
μ_i = viscosity of the gas = 2.884 e-5 Pa.s,
k_i = thermal conductivity of the salt = 0.6055 W/m.°C,
k_o = thermal conductivity of the gas = 0.0493 W/m.°C,
D_r = Reactor diameter = 3.1 m,
v_i = velocity of the molten salt in the coil, m/s,
v_o = velocity of the gas outside the coil, m/s.

For all the seven coils the overall heat coefficient is recalculated and the values are between U = 303 and U = 308 W/m^2.°C, so the first estimations of U were good.

Steam production

The heat of the molten salt is transfered in the heat exchanger unit **H5** to make LP steam (3 bar). The incoming temperature of the salt (T_{in}) is 220 °C and the salt leaves the H5 unit at a temperature (T_{out}) of 200 °C and is recirculated to the reactor section.
The incoming medium (tube side) is LP steam of 3 bar at the condensing temperature (t_{in}) of 133.5 °C and the output steam of H5 has a temperature of 190 °C (t_{out}).
The unit H5 consists of 2 parallel identical heat exchangers, each having a total heat exchanging surface of 785 m^2. The equations for calculating the dimensions of both exchangers are written in paragraph (4.13). The equations were taken from Chemical Engineering Vol. 6 [18].

A summary of the calculated dimensions for one heat exchanger of H5 is :

A = 785 m^2,
ΔT_{lm} = logaritmic temperature difference = 45.85 °C
F_t = correction factor = 1
ΔT_m = mean temperature difference = $F_t * \Delta T_{lm}$ = 45.85 °C
U = estimated heat overall coefficient = 600 W/m^2.°C

Type heat exchanger: 1 shell pass; 1 tube pass; 1 shell in serie ;
Shell side: molten salt; Tube side: LP steam ;
Number of tubes N_t = 2557;
Shell side fluid not so clean : use square pitch ;
Bundle diameter D_b = 1405 mm ; Split ring floating head type ;
Bundle diameter clearance = 80 mm : Shell diameter D_s = 1485 mm.

Re-calculating U

h_i = tube-side coefficient = 5735 W/m^2.°C

h_o = shell-side coefficient = 58478 W/m^2.°C

k_w = thermal conductivity of material = 50 W/m.°C

h_{od} , h_{id} = fouling coefficients = 6000 W/m^2.°C

Calculated U = 1527 W/m^2.°C : well above estimated value.

Too bad, Heat of Evap. forgotten!

Total amount of LP steam (3 bar, 190 °C): F,steam

F_{steam} = $Q/(Cp_{steam}*(T_{out} - T_{in}))$ = $155340 \cdot 10^3/(1.9206*(190-133.5)$
= 1431522 kg/hr → 397 kg/s

→ 108 kJ/kg

again 20 x larger v.u. 22 kg/s p.8

Material and type

Reactor : S.S. 18 Cr/8 Ni, Ti stabilised (321)

f = design stress at 370 °C = 120 N/mm^2

e = mimimum plate thickness = 12 mm (incl. corrosion allowance of 2 mm)

Head type : hemispherical

Shell : cylindrical

The stress in the head would be greater than that in the cylindrical section; the optimum thickness ratio is normally taken as 0.6 : e_{head} = 20 mm.

Used material for the coils : AISI 304.

Used material for the heat exchangers: AISI 304.

4.2. Regenerator R8 (with internal cyclones M9)

The regenerator has the function to re-oxidize the oxidized VPO-catalyst.
Recycle and fresh oxygen is used to regenerate the catalyst. The regenerator is a fluidized bed type.
The oxygen-stream goes from bottom to top and the catalyst in reverse direction. The re-oxidized (regenerated) catalyst is then recycled to the reactor section.
The usual bedporosity of a fluid-bed is about 0.3. To obtain a fluidized bed, the velocity of oxygen, U_{O2} , must be greater than the minimum fluidizing velocity, U_{mf} , and smaller than the terminal velocity, U_t . The formulas for the U_{mf} and U_t are given below :

$$U_{mf} = \frac{(1-\epsilon_{bed})^3 * (\rho_{cat}-\rho_{O_2}) * g}{5 * (\frac{6}{d_{cat}})^2 * \epsilon_{bed} * \eta_{O_2}} \tag{4.12}$$

$$U_t = \sqrt{\frac{4 * g * (\rho_{cat}-\rho_{O_2}) * d_{cat}}{3 * 0.43 * \rho_{O_2}}} \tag{4.13}$$

where ε_{bed} = porosity of the bed,
ρ_{cat} = density of the catalyst, kg/m^3,
ρ_{O2} = density of oxygen, kg/m^3,
g = acceleration, 9.81 m/s^2,
d_{cat} = diameter of the catalyst, m ,
η_{O2} = viscosity of oxygen, kg/m.s ,

In U.S. patent 4,668,802 [10], the regenerating process is descibed and the typical conditions for the regenerator are:

- the regeneration zone temperature is maintained at about 300 °C to about 500 °C,
- the catalyst residence time is about 5 seconds to, typically, about 5 minutes, and the oxygen residence time is about 1 to about 30 seconds, factor :
- the oxygen velocity ranges from a few 0.07 m/s to about 2 m/s,
- the catalyst concentration ranges from about 200 kg/m^3 ~~to about~~ 700 kg/m^3 . (800

Because the residence times of the catalyst particles are not the same, the mean catalyst residence time, $\tau_{mean,cat}$, should be calulated. The equation therefore is :

$$\tau_{mean,cat} = \frac{\tau}{\ln(1-F)} \tag{4.14}$$

where τ = minimum residence time of catalyst, s ,
F = the percentage of catalyst particles that have a residence less than τ.

When the $\tau_{mean,cat}$ is known the volume of the catalyst, V_{cat} , the volume and the height of the regenerator, (resp. V_{reg} and H_{reg}) can then be calculated with the following equations :

$$V_{cat} = \phi_{v,cat} * \tau_{mean,cat} \tag{4.15}$$

where $\phi_{v,cat}$ = volume flow of catalyst, m^3/s.

$$V_{reg} = \frac{V_{cat}}{\epsilon_{cat}} \tag{4.16}$$

$$H_{reg} = \frac{V_{reg}}{\cancel{0.25 *}\ \frac{\pi}{4} * d_{reg}^2} \tag{4.17}$$

where d_{reg} = diameter of the regenerator, m.

The constants and chosen parameters are :

$\phi_{v,cat}$ = 1.856 m^3/s
ρ_{O2} = 0.597 kg/m^3,
η_{O2} = $3.2 \cdot 10^{-5}$ kg/m.s,
d_{cat} = 200 μm,
g = 9.81 m/s^2,
τ = 0.7 s,
F = 0.1 (10%),
ε_{cat} = 0.3,
d_{reg} = 3 m.

The pressure drop, $\Delta P = (1 - \varepsilon_{bed}) * \rho_{cat} * g * H_{reg} = 0.7*800*9.81*6 = 32962$ Pa ≈ 0.33 bar.

The results of the calculations are summarized in table 4.2.

Table 4.2. Conditions and designed dimensions of the regenerator.

U_t	2.852 m/s	d_{reg}	3 m
U_{mf}	0.062 m/s	H_{reg}	6 m
U_{O2}	1.5 m/s	V_{reg}	41 m
τ_{O2}	1.2 s	P	1.1 - 1.5 bar
$\tau_{mean,cat}$	6.64 s	T	370 °C
V_{cat}	12.3 m^3	ΔP	0.33 bar
C_{cat}	240 kg/m^3	Material	S.S

At the top of the fluidized bed, a series of 3 cyclones are installed serially for the separation of oxygen and catalyst. The dimensions of the cyclones are tabulated below :

Table 4.3. Dimensions of the cyclones

Cyclone diameter	0.5 m
Inlet height	0.25 m
Inlet weight	0.10 m
Outlet height	0.25 m
Outlet diameter	0.25 m
Cylinder height	0.75 m
Overall height	2.00 m
Dust outlet diameter	0.1875 m
No. of gas turns	5
No. of cyclones	3

P.S. See chapter (4.3.) for the calculations of the dimensions of the cyclones.
The total pressure drop over the 3 cyclones is about 0.3 bar (Chemcad).
So, the gas stream out of the regenerator has a pressure of about 1 bar.

4.3. Cyclone Battery M7

The cyclone battery consists of 4 parallel cyclones, because the feed flow from the reactor R4 is large. The method used is the high efficiency **Koch and Litch method**. The method is described in Perry [11]. The cylones of this project are calculated with Chemcad with the 'Cyclone option'. The feed of the cylone (stream 5) consists of a gas amount of 95563.89 kg/hr and a solid amount of 5344640 kg/hr. The mean diameter of the catalyst is 200 μm and the density is 800 kg/hr.

Calculated summary of one cyclone :

Cylone diameter	D	=	1 m
Inlet height	H_{inlet}	=	0.5 m
Inlet width	B_{inlet}	=	0.2 m
Outlet length	L_{outlet}	=	0.5 m
Outlet diameter	D_{outlet}	=	0.5 m
Cylinder height	H_{cyl}	=	1.5 m
Overall length	L	=	4 m
Dust outlet diameter	D_{dust}	=	0.375 m
Number of gas turns		=	5
Vane constant		=	16

Total pressure drop *dP* of the 4 cyclones = 0.1897 bar.

4.4. Reactive Absorber T24

In the reactive absorber, the MA product is separated from the other gasses with water. But MA reacts quickely with water to liquid maleic acid (MAC), so the bottom product is mostly MAC with some water. The top product consists of the reactor inert gasses and water gas.

Reaction :

$$C_4H_2O_3(l) \quad + \quad H_2O(l) \quad \underset{\longleftarrow}{\longrightarrow} \quad C_4H_4O_4(l) \qquad (R.4)$$

With the Chemcad SCDS option, the absorber is simulated. Because only the reaction rate constant k and no activation energy was found in literature, only the equlibrium option of the SCDS was possible. It is assumed that the dehydration (left) reaction is much slower than the hydration (right) reaction. From literature [12] the k for the right reaction is 41.40 s^{-1}. The reaction is assumed to be in the liquid fase.

The theory of the absorption is mainly based on the distillation theory. The literature used is from Ž. Olujić [13].

Specifications :

Average tray values, calculated with Chemcad :
Mass flow of the gas, M_g = 27.03 kg/s
Mass flow of the liquid, M_L = 2.755 kg/s
Density of the liquid, ρ_L = 1063.6 kg/m^3
Density of the gas, ρ_G = 1.11 kg/m^3
Viscosity of the liquid, η_L = 0.4 mPa.s
Surface tension, σ = 0.064 J/m

- First feed stage (water flow) on tray 1 (stream 20)
  Temperature = 42 °C, pressure 1.19 bar.
  Flow : 10482 kg/hr
- Second feed stage (gas) on tray 5 (stream 13)
  Temperature 214 °C, pressure 1.21 bar.
  Flow : 95564 kg/hr
- Gas output product from the top (stream 15)
  Temperature = 68.3 °C, pressure = 1.19 bar
  Flow: 97820 kg/hr
- Liquid output product from the bottom (stream 14)
  Temperature = 120 °C, pressure = 1.295 bar
  Flow: 8226 kg/hr

Reaction : on liquid phase; reaction volume per stage is about 0.1 m^3
Reaction type : equlibrium
Tray type : sieve trays

The K values were calculated with the PSRK Model (Chemcad).
The relative volatility α_i is calculated with : $\alpha_i = K_i/K_{HK}$
The light key (LK) is water and the heavy key (HK) in this case is MA.
The relative volatility of the light key is :

$$\alpha_{LK} = \alpha_{H2O} = (\alpha_{LK,1} * \alpha_{LK,N})^{0.5} \tag{4.18}$$

where $\alpha_{LK,1}$ = relative volatility of the light key on stage 1
$\alpha_{LK,N}$ = relative volatility of the light key on stage N (N = 5)

The calculated $\alpha_{LK} = 4.747$

The liquid vapour flow parameter F_{LG} is calculated with [13]:

$$F_{LG} = (\frac{M_L}{M_G})(\frac{\rho_G}{\rho_L})^{0.5} \tag{4.19}$$

Calculated $F_{LG} = 3.293 \cdot 10^{-3}$

Assumed tray spacing, $T_s = 0.61$ m

The maximum flooding velocity, $U_{G,max}$, is calculated from the Souders correlation [13] :

$$U_{G,\max} = C_{tr} * (\frac{\sigma}{0.02})^{0.2} \sqrt{\frac{\rho_L - \rho_G}{\rho_G}} \tag{4.20}$$

The capacity (gas load) coefficient C_{tr} is defined by figure 2.45 of [13]
From this figure with a tray spacing of 0.61, $C_{tr} = 0.1$ m/s
$U_{G,max} = 3.904$ m/s

Theoretical number number of trays, N = 5 (CHEMCAD)
Number of trays, $N_{col} = N/E_{col} = 5$
Column efficiency, $E_{col} = 0.95$
The total column pressure drop is 0.1 bar, that is 0.02 bar per tray.

The column height $H_{col} = h_{TB} + h_{top} + h_{bottom} + h_{skirt}$
The height between top and bottom $h_{TB} = (N_{col} - 1)*T_s$
$H_{col} = (5 - 1)*0.61 + 1.5 + 2.5 + 2 = 8.44$ m.
Take $H_{col} = 8.50$ m.

The column diameter is calculated with the following equation :

$$D_{col} = 1.1284 \sqrt{\frac{M_G}{\rho_G * 0.8 * U_{G,\max}}} \tag{4.21}$$

with : $D_{col} = 3.15$ m

The column specifications can be find in appendix **XI**.

4.5. Thin Layer Evaporator/Dehydrator M30

The type of this dehydrator is a thin-layer dehydrator.
There are two processes taken place in the dehydrator, namely: evaporation and dehydration of maleic acid. Thus, the heat of duty required for the dehydrator can be simply defined
as :

$$Q_{dehydrator} = Q_{evaporation} + Q_{dehydration} \tag{4.22}$$

144 kJ

The incoming temperature of the feed is 121 °C and the temperature of the product gas is 204 °C.
The heat of dehydration can be determined with the simulation program CHEMCAD. For this simulation the Stoichiometric Reactor option was used. The calculated value of $Q_{dehydration}$ is 2893 kW. The heat of evaporation is also calculated with CHEMCAD, whereby first the enthalpies of the feed- and product streams are calculated.
The $Q_{evaporation}$ is then equal to :

$$Q_{evporation} = (m{\cdot}H)_{products} - (m{\cdot}H)_{feed} \tag{4.23}$$

where m stands for mass flow. The calculated value of $Q_{evaporation}$ is 2801 kW.

$Q_{dehydrator}$ is then 5694 kW. This heat of duty is served by steam (410 °C, 40 bar), using a jacket around the outside wall of the dehydrator (see appendix VII).
The typical overall heat transfer coefficient U for this type of dehydrator is 1200 W/m². °C [15]. The calculated ΔT_m is 236.3 °C. With $Q = U{*}A{*}\Delta T_m$, a heat-transfer area of 20.08 m² is calculated. The amount of steam required is 497839 kg/hr.

Because the capacity limit of dehydrators, the dehydrator unit is divided into two identical parallel dehydrators.
From A.B. Mutzenburg [14] the range of thickness for a thin-layer is 1.25 - 2.55 mm. The equation for the volume of the layer is :

$$V_{layer} = h * \pi * (R_2^2 - R_1^2) \tag{4.24}$$

Where
h = height of the dehydrator heat exchanging surface, 5.2 m,
R_1 = inside radius of the layer, 0.8 m,
R_2 = outside radius of the layer, 0.8025 m.

The height is fixed at the chosen inside radius. The volume of the layer is then $1.021{\cdot}10^{-3}$ m³. Take a total height of the dehydrator as 1.15*5.2 = 6 m (including: spacing for gasoutlet, electrical motor, etc.). With a feed stream of $8.17{\cdot}10^{-4}$ m³/s, the residence time of the feed in the dehydrator is $(1.021{\cdot}10^{-3}/8.17{\cdot}10^{-4})$ 1.25 seconds. This value is satisfied because the residence time must be lower than 5 minutes, preferably less than 1 minute, because of the danger of isomerization of maleic acid to fumaric acid [16,17].

4.6. Cake Filter F27/F28

To design the cake filter without experimental data is very difficult, however, the filtration theory is clear. The theory to calculate the mean parameters of the filter is taken from the TUD college paper 'Apparaten voor mechanische scheidingen' [24].

If it is assumed that the cake is not compressible, D'Arcy's law is possible:

$$v = \frac{dV}{Adt} = \frac{K}{\eta}\frac{\Delta p_k}{d_k} \tag{4.25}$$

With :

v = linear liquid velocity, m/s;
V = volume of the filtrate, m^2;
A = surface area of the filter, m^2;
t = time, s;
K = D'Arcy constant, m^2;
η = viscosity of the liquid, Ns/m^2;
Δp_k = pressure drop over the cake, N/m^2;
d_k = thickness of the cake, m.

A mass balance over the cake :

$$(1 - \varepsilon_k)*d_k*A*\rho_s = V*\rho*[x/(1-x)] \tag{4.26}$$

With :

ε_k = volume fraction liquid in cake;
x = volume fraction solid in feed;
ρ = density of the filtate, kg/m^3;
ρ_s = density of the solid, kg/m^3.

Assume $x/(1-x) = r$, then equation (4.26) is written as:

$$(1 - \varepsilon_k)*d_k*A*\rho_s = V*\rho*r \tag{4.26a}$$

After substitution:

$$d_k = \frac{V*\rho*r}{(1-\epsilon_k)*A*\rho_s} \tag{4.27}$$

Substitution in the equation of D'Arcy :

$$\frac{dV}{Adt} = \frac{A*(1-\epsilon_k)*\rho_s*K*\Delta p_k}{\mathrm{H}*V*\rho*r} \tag{4.28}$$

For a sudden situation, ε_k, ρ, ρ_s, η, K and r are all constant, so that :

$$\frac{dV}{dt} = \frac{A^2 \Delta P_k}{C_v V} \tag{4.28a}$$

After substitution of V :

$$V = \frac{(1-\epsilon_k) A \rho_s d_k}{\rho r} \tag{4.29}$$

So :

$$\frac{(1-\epsilon_k) A \rho_s}{\rho r} * \frac{d(d_k)}{dt} = \frac{K \Delta P_k}{\eta d_k} \tag{4.30}$$

With also ε_k, ρ, ρ_s, η, K and r are all constant :

$$\frac{d(d_k)}{dt} = \frac{\Delta P_k}{C_k d_k} \tag{4.31}$$

For the total pressure drop, the equations are re-arranged to :

$$\frac{dV}{dt} = \frac{A^2}{C_v} * \frac{\Delta P_{tot}}{(V + V_{eq})} \tag{4.32}$$

With V_{eq} = equivalent filtrate volume, m^3.
After re-arranging of the former equation, the following important equation is assumed :

$$\frac{dt}{dV} = \frac{C_v}{A^2 \Delta P_{tot}} * V + \frac{C_v V_{eq}}{A^2 \Delta P_{tot}} \tag{4.33}$$

With this equation, lab-scale filtration experiments could be taken, in order to design the correct filter dimensions, e.g. the slope of the curve (dt/dV v.s. V) is : $C_v/(A^2\ \Delta P_{tot})$.

Chosen is a centrifugal discharge filter unit M27/28 which can handle a throughput of about 300 - 500 kg/h. See figure 4.1.; this figure is from Perry [11].

The centrifugal pressure is then:
$\Delta P = 0.5\ \rho\omega^2\ (R_2^2 - R_1^2)$
With $R_2 - R_1 = d_k$, the total pressure drop is by approximation :
$\Delta P_{tot} = \rho\omega^2\ d_k\ R_w$.
With R_w = radius of the centrifugal shell.
The same above equations (with lab. experiment data) can be used to design the centrifugal filter in practice.

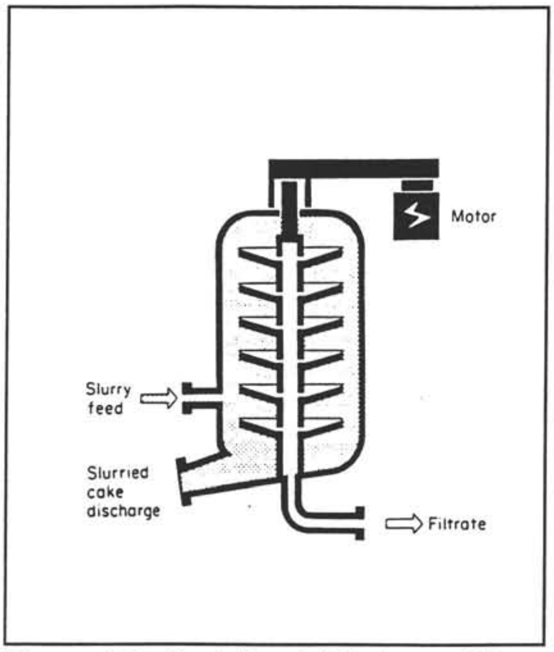


Figure 4.1. Centrifugal Discharge Filter

4.7. Vacuum Distillation Tower T35

The theory of the distillation is already written in chapter 4.4 (Reactive Aborber). The vacuum tower **T35** uses an external thermosyphon reboiler (**H36**) for heating and recirculating the (bottom) feed. Part of the reboiler feed is the final product flow (stream 46). The top product gas (mostly water gas) is return to the neutralization tank **V21** (stream 47). No condenser is used.

Specifications :

Average tray values, calculated with CHEMCAD :

Mass flow of the gas, M_g = 0.1266 [kg/s]

Mass flow of the liquid, M_L = 0.7138 [kg/s]

Density of the liquid, ρ_L = 1208.6 [kg/m^3]

Density of the gas, ρ_G = 0.622 [kg/m^3]

Viscosity of the liquid, η_L = 1.06 [mPa.s]

Surface tension, σ = 0.0554 [J/m^2]

- Feed stage (MA/water gas) on tray 4 (stream 45)
  Temperature = 161 °C, pressure ~~1 bar~~.
  Flow: 6823.56 kg/hr.
- Gas output top product (stream 47)
  Temperature = 86.4 °C, pressure = 0.6 bar
  Flow: 562.48 kg/hr.
- Liquid ~~output~~ product from the bottom (stream 46)
  Temperature = 187 C, pressure = 0.6 bar
  Flow: 6261.08 kg/hr.

Tray type : sieve trays

The K values were calculated with the PSRK Model (CHEMCAD).
The relative volatility α_i is calculated with : $\alpha_i = K_i/K_{HK}$

The light key (LK) is water and the heavy key (HK) in this case is MA.
The relative volatility of the light key is :

$$\alpha_{LK} = \alpha_{H2O} = (\alpha_{LK,1} * \alpha_{LK,N})^{0.5} \quad ; \quad N = 5 \tag{4.18}$$

[redacted]

The calculated $\alpha_{LK} = 4.96$

The liquid vapour flow parameter F_{LG} is calculated with equation (4.19).
Calculated $F_{LG} = 4.0 \cdot 10^{-3}$

Assumed tray spacing, $T_s = 0.40$ m

The maximum flooding velocity, $U_{G,max}$, is calculated with equation (4.20).
The capacity (gas load) coefficient C_{tr} is defined by figure 2.45 of [**13**].

From this figure with a tray spacing of 0.40, $C_{tr} = 0.06$ m/s
$U_{G,max} = 3.229$ m/s

Theoretical number number of trays, N = 5 (CHEMCAD)
Number of trays, $N_{col} = N/E_{col} = 6$. Without the reboiler is $N_{col} = 5$.
Column efficiency, $E_{col} = 0.90$
The total column pressure drop is 0.015 bar, that is 0.003 bar per tray [**13**].

The column height $H_{col} = h_{TB} + h_{top} + h_{bottom} + h_{skirt}$
The height between top and bottom $h_{TB} = (N_{col} - 1)*T_s$
$H_{col} = (5 - 1)*0.40 + 1.5 + 2.5 + 1 = 6.6$ m.

The column diameter is calculated with equation (4.21).
Calculated $D_{col} = 0.35$ m

More specifications of T35 are in appendix XI.

Design of the reboiler H36.
An external thermosyphon reboiler is used for heating and recirculating of the bottom section of T35.
For the design of the reboiler: see appendix X.
Specifications can be find in appendix XI.

4.8 MA Flakes Drum M37

The Rotating Flakes Twin Drum operates at atmosferic pressure. The theory is from Perry [11]. No special design equations were found in the literature. A figure of the equipment is given (figure 4.2.) M37 consists of 2 rotating drums on which the feed is solidificated by indirect cooling of water of 20 °C. The water is sprayed on the internal shell of the drum. The MA molten feed is equally divided over the external shell of both rotating drums and at the end of one rotation, the thin layer of solid product is cut out with a 'doctor knife'. The form of the solid product is like flakes.

On the external shell of the drums :
Feed in: temperature, T_1 = 187 °C
(stream 46) mass (liquid) in = 6261.08 kg/hr
enthalpy in = 7530 kW

Product out: temperature, T_2 = 40 °C
(stream 48) mass (solid) out = 6261.08 kg/hr
enthalpy out = 7952.78 kW

Transfer Heat Duty Q = 422.78 kW.

The equations for calculating the heat transfer surface area is given in paragraph (4.9.).

On the internal shell of the drums :
Sprayed water : temperature, t_1 = 20 °C
t_2 = 40 °C

The ΔT_{lm} is 68.87 °C; without any correction factor : the mean temperature difference, ΔT_m is 68.87 °C.
With an overall heat coefficient U of 400 $W/m^2.°C$ (from Perry), the calculated area is : 15.35 m^2.

The usual thin layer is between 0.4 - 6 mm [11]
The mean feed load density, ρ_{MA} , is 1248.03 kg/m^3.
The feed load is 104.35 kg/min.

Specification of a single drum

$A = 15.35/2 = 7.675\ m^2$.
If the internal diameter of the drum, D_{in} is 1.5 m, then drum width B will be 1.65 m. The internal drum radius R_{in} is 0.75 m. With a mean thin layer of 6 mm, the external radius R_{ex} will be 0.756 m.

The volume of the thin layer will be: $B*\pi*(R_{ex}^2 - R_{in}^2) = 0.046\ m^3$.

The capacity of the drum must be at least 0.042 m^3 MA/min; so one rotation per minute is enough to solidificate the molten MA. It is assumed that other complex transport and heat effects are neglectable.

The amount of water for a single drum is :
$Q/(Cp_{water}*(t_2 - t_1)) = 761004/(4.18*20) = 9102$ kg/hr = 9.1 m^3/hr.

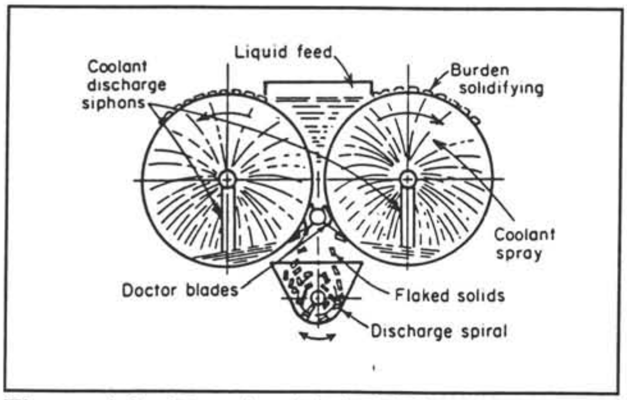


Figure 4.2 Rotating Twin Flakes Drum

4.9 Heat-transfer equipments

The general equation for heat transfer across a surface is :

$$Q = U * A * \Delta T_m \tag{4.34}$$

with :

$$\Delta T_m = F_t * \Delta T_{lm} \quad \text{(for heat-exchangers and condensers)} \tag{4.34a}$$

$$\Delta T_m = T_s - T_b \quad \text{(for vaporisers and reboilers)} \tag{4.34b}$$

where Q = heat transferred per unit time, W,
U = the overall heat transfer coefficient, W/m^2.°C,
A = heat-transfer area, m^2,
ΔT_m = the mean temperature difference, the temperature driving force, °C,
F_t = the temperature correction factor,
ΔT_{lm} = logarithmic mean temperature difference, °C.

The logarithmic mean temperature is given by :

$$\Delta T_{lm} = \frac{(T_1-t_2) - (T_2-t_1)}{\ln\frac{(T_1-t_2)}{(T_2-t_1)}} \tag{4.35}$$

where T_1 = inlet shell-side fluid temperature,
T_2 = outlet shell-side fluid temperature,
t_1 = inlet tube-side temperature,
t_2 = outlet tube-side temperature.

When the heat-transfer area is calculated with equation (**4**.34). This value divided bij the area of one tube(tubelength l and diameter d_o are chosen) is the total number of tubes N_t. The bundle diameter D_b of the tube-sheet can than be calculated with the following equation :

$$D_b = d_o\left(\frac{N_t}{K_1}\right)^{\frac{1}{n_1}} \tag{4.36}$$

where the constants K_1 and n_1 depend on the pitch and the number of tube passes . The shell diameter is equal to the bundle diameter plus the shell-bundle clearance, which is depend on the type of exchanger and the manufacturing tolerances.

The estimated U value is re-calculated with the theory, described in Coulson & Richardson Vol. 6 [18].

Design/calculation of :

Vaporiser H2
Appendix VIII.
Specifications: appendix XI.

Condensers M33 and M34
Design of M33: appendix IX.
The same route is chosen to design M34.
Specifications: appendix XI.

Reboiler H36
Appendix X.
Specifications: appendix XI.

Heat-exchangers
Appendix XI.

4.10. Pumps & Compressors

4.10.1. Pumps

Centrifugal pumps will normally be the first choice for pumping process fluids. The power P_{pump} required for pumping an incompressible fluid is given by :

$$P_{pump} = \frac{\Delta p * \phi_v}{\eta_{pump}} \tag{4.37}$$

where Δp = pressure differential across the pump, N/m^2,
ϕ_v = flow rate, m^3/s,
η_{pump} = pump efficiency.

The efficiency of centrifugal pumps depends on the flow rate. The values in fig. 10.62 of Coulson & Richardson [18] can hereby be used.

The electrical power $P_{electric}$ required is given by :

$$P_{electric} = \frac{P_{pump}}{\eta_{electric}} \tag{4.38}$$

The electrical motor efficiency $\eta_{electic}$ depends on the pump power.

4.10.2. Compressors

The work produced(or required) by polytropic compression W_{pol} is given by :

$$-W_{pol} = Z * \frac{R\ T_1}{M} * \frac{n}{n-1} * [(\frac{P_2}{P_1})^{\frac{n-1}{n}} - 1] \tag{4.39}$$

with :

$$n = \frac{1}{1-m} \tag{4.39a}$$

$$m = \frac{(\frac{C_p}{C_v}) - 1}{(\frac{C_p}{C_v})\eta_{pol}} \tag{4.39b}$$

P,6 :

$1.0 \times \frac{8.314.(86+273)}{18}$

where Z = compressibility factor(1 for an ideal gas),
R = universal gas constant, 8.314 J/mol/K,
T_1 = inlet temperature, K,
$p_{1,2}$ = resp. the inlet and the outlet pressure, bar,
M = molecular mass(weight) of gas, g/mol,
C_p = specific heat at constant pressure, J/g/K
C_v = specific heat at constant volume, J/g/K,
η_{pol} = polytropic efficiency.

The polytropic efficiency depends on the volumetric flow rate. The values in fig. 3.6. of Coulson & Richardson can hereby be used.

The polytropic work divided by the polytropic efficiency gives the actual work that is required :

$$W_{actual} = \frac{W_{pol}}{\eta_{pol}} \tag{4.40}$$

In appendix XI, a summary of the designed pumps and compressors is given.

4.11 Tanks/Vessels

4.11.1. Liquid storage tanks

Vertical cylindrical tanks, with flat bases and conical roofs, are universally used for the bulk storage of liquids at atmospheric pressure.
The main load to be considered in the design of these tanks is the hydrostatic pressure of the liquid, but the tanks must also be designed to withstand wind loading.
The minimum wall thickness required to resist the hydrostatic pressure can be calculated from the equations for the membrane stresses in thin cylinders :

$$e_s = \frac{\rho_L * H_L * g}{2 * f_t * J} * \frac{D_t}{10^3} \qquad (4.41)$$

where e_s = tank thickness required at depth H_L , mm,
H_L = liquid depth, m,
ρ_L = liquid density, kg/m^3
J = joint factor,
g = gravitational acceleration, 9.81 m/s^2
f_t = design stress for tank material, N/mm^2
D_t = tank diameter, m.

4.11.2. Thin-walled vessels under internal pressure

For a cylindrical shell the minimum thickness to resist internal pressure can be determined from the following equation :

$$e = \frac{P_i * D_i}{2*f - P_i} \qquad (4.42)$$

The equation for a spherical shell is given :

$$e = \frac{P_i * D_i}{4*f - 1.2*P_i} \qquad (4.43)$$

where e = the minimum thickness required, mm,
P_i = internal pressure, N/mm^2,
D_i = internal diameter, mm,
f = design stress, N/mm^2.

4.11.3. Minimum practical wall thickness

There will be a minimum wall thickness equired to ensure that any vessel is sufficiently rigid to withstand its own weight, and any incidental loads. As a general guide the wall thickness of any vessel should not be less than the values given below; the values include a corrosion allowance of 2 mm :

Table 4.4. The vessel diameter and the minimum thickness.

Vessel diameter (m)	Minimum thickness (mm)
1	5
1 to 2	7
2 to 2.5	9
2.5 to 3.0	10
3.0 to 3.5	12

The following table gives a summary of the several parameters of the vessels :

Table 4.5. The parameters of the vessels.

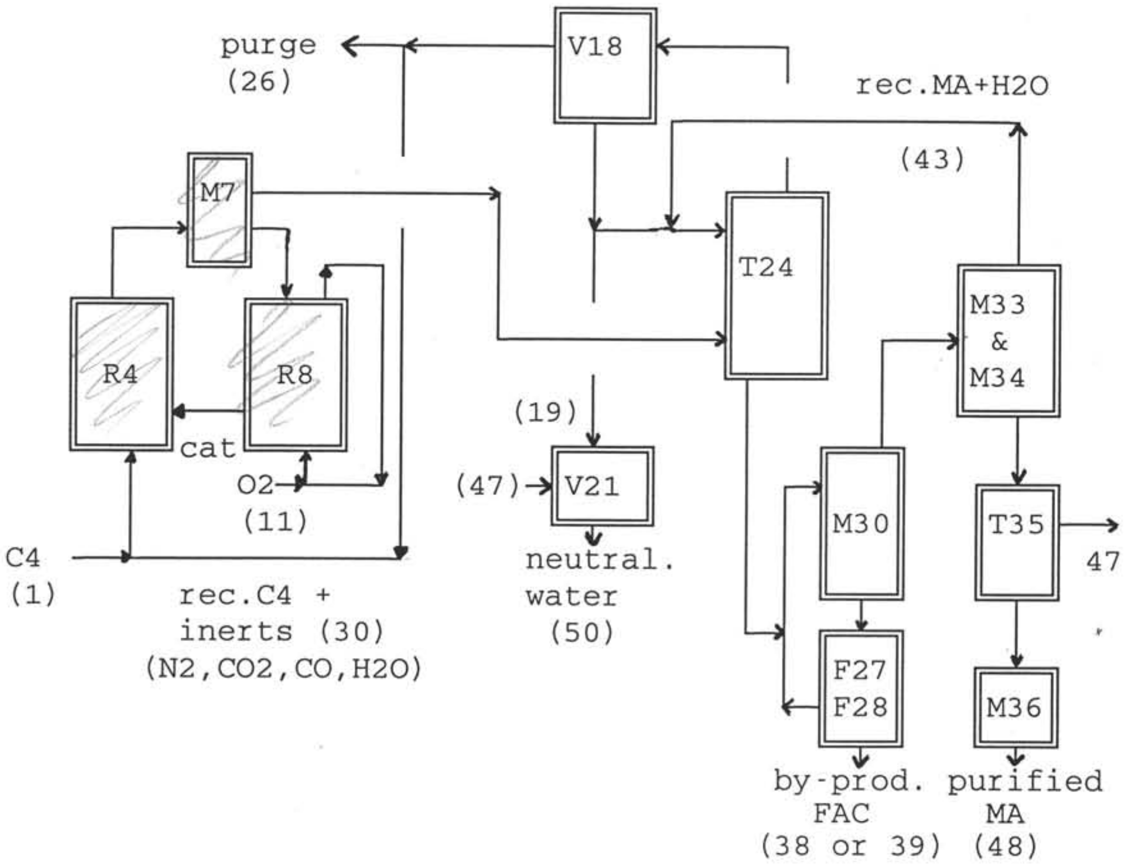
	V1	V18	V19	V21	V25	V32
P_i (bar)	1.5	1.433	1	1	1	1
T (°C)	0	40	23	< 40	130	139
D_i (m)	4.40	3	1	1.5	2	1
H (m)	--	5.66	2.6	3	2.5	2
e_s , e (mm)	12	12	5	7	7	5
shell	sphere	cylinder	cylinder	cylinder	cylinder	cylinder

The material of the vessels are all from stainless steel (18Cr/8Ni, unstabilised (304)).

Literature: Coulson & Richardson Vol. 6 [18].

5. MASS AND ENERGY BALANCE

Simplified Scheme of the Selective Butane Oxidation Process



In above scheme, a simplified flow diagram for the overall mass balance is given.
Overall mass balance:

Table 5.1 Overall mass balance of the process: in = out ?

Stream number	IN (kg/hr)	OUT (kg/hr)
✓ 1 (fresh n-butane)	5928.16	
✓ 11 (fresh oxygen)	13753.0	
✓ 26 (gas purge)		9093.44
✓ 38/39 (by-products)		106.0
✓ 48 (MA product)		6261.08
→ 50 (neutr. water)		4221.73
TOTAL	**19681.16**	**19682.25**

Overall mass balance: IN ≈ OUT

In appendix III, the component mass- and heat balance of all the streams are given.

In appendix IV, the mass- and heat balances of the units (except the pumps and mixer) are given.

Results of appendix IV:

MASS BALANCE (kg/hr)

IN	OUT
3340974	3340977

The mass balance seems to be o.k!

ENERGY BALANCE (kW)

IN	OUT
-330263	-400881

There is a difference in the energy balance, because of the reactions in reactor R4 (-43150 kW) and M30 (-8495 kW). And further, the input of enthalpy to R4 is not equal to the output value ($H_{in} \neq H_{out}$; $H5 \neq H4 + H8$). The input enthalpy is the value of stream 5, calculated with the first inlet feed gas (with only pure nitrogen as the start inert carrier medium; CO_2, CO, H_2O were 0). Also, the energies of the pumping units were not involved in the balance.

6. SAFETY ASPECTS

6.1. Hazard and Operability Study (HAZOP)

The HAZOP is essentially a qualitative procedure in which a small team examines a proposed design by generating questions about it in a systematic manner.
The results of the HAZOP study for the reactor section is summarized in table 6.1.

Table 6.1. The HAZOP study of the reactorsection

Deviation	Possible Causes	Consequences	Action Required
No Flow Where? liquid C_4!	(1) No n-butane available at storage tank	Loss of feed to reaction section and reduced output	(a) Ensure good communication with intermediate storage operator (b) Install low level alarm on tank
	(2) Line fracture	As for (1) n-Butane discharged into area adjacent to public highway	(c) Institute regular patrolling and inspection of transfer line
More Flow	(3) Valve fails open	Excess of n-butane	(d) Check feed rating and install valve-controller
More Temperature	(4) Heat removal defect	Decrease MA production Increase CO, CO_2, H_2O	(e) Continue temperature checking
Less Flow	(5) Leaking flange or valve stub not blanked and leaking	Material loss adjacent to public highway	(f) Covered by (c) and checks in (d)
Less Temperature	(6) Feed not at the reaction temperature	Decrease MA production	(g) Covered by (e) and reduced heat removal
Low Oxygen Concentration in reactor	(7) Oxydizing-capacity of catalyst reduced	Decrease reaction activity	(h) Check the rate of unreact n-butane and put in fresh catalyst

Because the strong exothermic reaction the need of heat removal is very important.
If the heat removal is not good controlled, there is a danger of tank melting or explosion.

Literature: B.H. Bibo, P. Bos, S.M. Lemkowitz [19]

6.2. Safety, Health and Environment

A hazard identification method has developed by The American National Fire Protection Agency (NFPA). This method is based solely on the properties of the materials used. The NFPA method assigns five "rating" (numbers) to materials. These ratings, which range from 0 (no hazard) to 4 (maximum hazard), are based on Flammability, Reactivity (related to explosiveness), and Health (related to toxicity). Application of this method for the reactants and products gives the following results.

Table 6.2. NFPA ratings for the reactants and products

Substance	Flammability (N_f)	Reactivity (N_r)	Health (N_h)
Maleic Anhydride	1	3	2
Maleic Acid	1	2	2
n-Butane	4	4	3
Fumaric Acid	1	3	2
N_2	0	0	1
O_2	0	4	0
CO_2	1	0	1
CO	4	4	2
H_2O	0	0	0
NaOH	0	4	2

**The properties of the materials are tabulated in appendix II

Most of the reactants and products are flammable, so the use of open fire and smoking in the plant are strictly forbidden.

To ensure safe operation if flammability limits and ignition temperatures are simultaneously reached, standard procedures should additionally used. Rupture discs at the top of the reactor are large and quick enough to act to mitigate emergencies, automatic n-butane feed shutt off with nitrogen purge for variation of pressure and temperature outside predefined limits, visual and audible alarm facilities.

Literature: B.H. Bibo, P. Bos, S.M. Lemkowitz [19],
Chemiekaarten [21].

7. COST EVALUATION

7.1. Production Costs

To calculate the cost of production a simplefied model as equation 7.1. can be used :

$$K_T = 1.13K_P + 2.6K_L + K_I \tag{7.1}$$

where K_T = Total production costs
K_P = Variable costs
K_L = Labor costs
K_I = Investments costs

Variable costs K_p

-Materials :
n-Butane 47,425 ton/yr
oxygen 110,024 ton/yr
nitrogen 1,000 ton/yr

-Steam :
In H2, H3, H11, H12, M30, H36 : 7,085,407 ton/yr
In H5 : 11,452,000 ton/yr (production)

-Cooling water :
In H20, H22, H23, H31, M33, M34, M37 : 8,032,683 m^3/yr

-Catalyst :
Lifetime = 1 year
Used = 17 ton

-Electricity :
pumps = 2 kW
Compressors = 1,500 kW
Dehydrators = 0.6 kW
Total : 8,000 * 1,502.6 = 12,020,800 kWh/yr

The following table gives a summary of the total variable costs.

Table 7.1. Calculation of the total variable costs, K_P.

	Stream	Price/unit	Cost (gld/yr)
n-butane	47,425 ton/yr	201.6 gld/ton	9,560,880
oxygen	110,024 ton/yr	70 gld/ton	7,701,680
nitrogen	1000 ton/yr	65 gld/ton	65,000
catalyst	17 ton/yr	37,038 gld/ton	629,646
steam	- ton/yr	30 gld/ton	--
cooling water	8,032,683 m^3/yr	0.10 gld/m^3	803,268
electricity	12,020,800 kWh/yr	0.13 gld/kWh	1,562,704
Total K_P			20,323,178

Labor cost, K_L

For these integrated factory is just one employment needed.
The cost of this is : 350,000 gld/yr

Investment costs, K_I

The investment costs can be calculated by the 'Lang factor method' and by the 'Taylor method'.

The Lang factor method

I_F = 1.45*3.4*Major Equipment Costs (= Ib + Ih)

Table 7.2 Major Equipment Costs

Equiment	number	Cost [*1000 gld]
Reactor	1	1,200
Regenerator	1	300
Absorber	1	250
Dehydrators	2	500
Condensors	2	600
Distillation column	1	200
Vaporiser	1	300
Heat-exhangers	11	5,500
Pumps	4	100
Compressors	3	1,250
Cyclones	7	35
Filters	2	30
Vessels	6	75
Total Major Equipment Costs :		10,340

I_F = 1.45 * 3.4 * 10,340 = 50,976.2 k.gld
I = 100/80 * 50,976.2 = 63,720.3 k.gld

The Taylor method

For the Taylor method, the process is divided in different process unit operations (see scheme 5.1, pag.).

Table 7.3. Calculation of the costliness index for process in scheme 5.1.

Units	Through-put	Constr. mat.	Time	Pres. & T.	Total score = Si	Cost-liness index
Storage/Handling						
n-butane	1	1	0	0	2	1,7
n-butane(recycle)	-3	1	0	0	-2	0,6
inert(recycle)	3.5	1	0	0	4,5	3,3
catalyst	9	1	0	0	10	13,8
water (recycle)	1	1	0	0	2	1,7
oxygen	3	1	0	0	4	2,9
Maleic Anhydride	0	1	0	0	1	1,3
Process						
Reaction	9	1	0	0	10	13,8
Regeneration	9	1	0	0	10	13,8
Absorption	5.3	1	0	0	6,3	5,2
Dehydration	0.5	1	0	0	1,5	1,5
Condensation	0.5	1	0	0	1,5	1,5
Distillation	0.1	1	0	0	1,1	1,3
Total = f						62,3

P = the production capacity = 50 kton/yr

C_I = the EPE index = 790 (year 1990)

$I_b = 93*f*P^m*C_I/300 = 93*62.3*50^{0.39}*820/300 = 72,822$

$I = 100/64 * 72,822 = 113,784$ k\$

m = degression-exponent

Rate of exchange : 1\$ = 1.80 gld

I = 204,811,200 gld

Normally, if both calculated investment costs are close to each other, a mean value is taken as to be the realistic investment cost.

But here, there is a large difference between the calculated values, so a mean value can not be taken.

By doubt between the two methods, mostly the Lang-Factor is chosen. With this method, the costs of all the equipments and the needed amounts of the feeds are estimated. For a good estimation of these costs, a lot of knowledge about the costs of several equipments is needed, but fortunately the authors of this report don't have that experience.

The Taylor method is chosen, because the authors have the feeling that the investment costs of this big project must be greater than 63,720,300 gld.

The costs that related to the investments are 14,9% (Capital Charge) and 13% (other related costs) from I. Thus, $K_I = (0.13+0.149)*I = 0.279*I = 57,142,325$ gld/yr

The total production cost is :

$K_T = 1.13*20,323,178 + 2.6*350,000 + 57,142,325 = \underline{81,017,516}$ gld/yr

The proceeds by a price of 2,150 gld/ton for Maleic anhydride :
50,000 * 2,150= **107,500,000 gld/yr**

7.2. Economic Criterions

The earning-capacity of the investment can be calculated by two types of methods :
1. Statistic method (Return on Investment, ROI).
2. Dynamic method (Internal rate of return, IRR).

7.2.1. Return Of Investment

By this method will the net income divided by the total cost of investments :

Investment, I_F, fixed (80% of I from Taylor method)	163,848,960	gld
, I_W, working capital (6% of I)	12,288,672	+
Total funds committed	176,137,632	gld
Annual receipts from sales	107,500,000	gld
Cost of ~~sales~~	81,017,516	-
Receipts minus cost of ~~sales~~ Manuf.	26,482,484	gld
Depreciation, 10%/yr	16,384,896	-
Net taxable income	10,097,588	gld
Income taxes, at 50%	5,048,794	-
Net income	5,048,794	gld

Return on Investment, ROI : (5,048,794/176,137,632)*100 % = 2.9 %

This value is too low, because by a period of 10 years the ROI must be at least 10%. That means that the minimum proceeds must be : 132,630,000 gld/yr.
The selling-price of Maleic Anhydride will be than : **2,653 gld/ton.**

7.2.2. Internal rate of return

The IRR based on the annual minimum cash flow that defined as the receipts minus the production cost plus the depreciation. The depreciation occured in 10 years and amount to 10% of the fixed investment (I_F).

Cash Flow = 132,630.000 - 81,017,516 + 16,384,896 = 67,997,380 gld/yr

Table 7.4. Calulation of the IRR.

year	Net cash flow		D.C.F. (40%)		D_i
	out	in	out	in	
0	*204,811,200*		*204,811,200*		1.000
1		67,997,380		48,550,129	0.714
2		67,997,380		34,678,664	0.510
3		67,997,380		24,751,046	0.364
4		67,997,380		17,679,319	0.260
5		67,997,380		12,647,513	0.186
6		67,997,380		9,043,652	0.133
7		67,997,380		6,459,751	0.095
8		67,997,380		4,623,822	0.068
9		67,997,380		3,263,874	0.048
10		67,997,380		2,379,908	0.035
11		27,622,000		716,839	0.025
	708,447,368		*164,794,517*		
	In/Out	**3.46**	In/Out	**0.80**	

P.S. In year 12 restitution of :
1. Remain-value ; 10% of I_F = 0.1 * 163,848,960 = 16,384,896 gld
2. Working capital ; 6% of I = 0.06 * 204,811,200 = 12,886,672 gld

With use of figure V.7 of lit. [20] follows that the IRR is about 32%

Literature: [20, 22, 25]

CONCLUSIONS AND DISCUSSION

The MA process is designed to produce 50 ktons of MA per year with a production time of 8000 hours per year and a MA purity of over the 99 % (in flakes form), using n-butane (47.425 ktons/yr) and (lattice) oxygen (110.024 ktons/yr) as feed. As inert, a gas mixture of nitrogen (originally inert gas), carbon monoxide, carbon dioxide and water gas is used (75.300 ton/hr).

The chosen process units operate mostly on low pressure and relative high temperature and are based to handle large feed loads and products.

The process includes the production of MA by the oxidation of n-butane with lattice oxygen on a vanadium-phosphorous-oxide catalyst in a transport bed reactor. The catalyst contains $(VO)_2P_2O_7$ with about 10 wt% of silica. The new technology is based on recirculating the VPO catalyst with the transport bed reactor (TBR) and a fluidized bed regenerator where the re-oxidation of the VPO catalyst takes place. With this technology, a higher yield of MA is realized, because the chosen TBR reactor can handle larger feed loads of n-butane then the other reactor types (current fluidized bed and fixed bed reactors), because the oxygen here used is not from an open gas stream, but from the selective VPO catalyst. Nowadays, the research of this VPO catalyst is still a main item for many scientists and if in future, the selectivity (towards MA) of the catalyst is optimized, a much higher yield of MA can be realized with the same or less amoun~~d~~t of catalyst used in this project.

The calculated investment costs are 204,811,200 gld. The method used is the Taylor method. The current selling price of MA is 2,150 gld/ton. With this value, the ROI was 2.9 %. But because the ROI must be at least 10 % over a period of 10 years, the selling price of MA is assumed to be 2,653 gld/ton. The proceeds by a price of 2,653 gld/ton for MA is 132,630,000 gld per year. Over a period of 10 years, the Return on Investment (ROI) is 10 % and the Internal Rate of Return (IRR) is 32 %.

The reactor technology of this process is found to be complex, especially when there is a lack of certain information, e.g. the value of the specific heat (Cp) of the VPO catalyst was unknown or confidential. The authors of this report spent a lot of time in the design of the transport bed reactor and the reactive absorber.

LIST OF SYMBOLS

Greek symbols

$\tau_{mean,cat}$	residence time of the catalyst in the regenerator	s
ρ_i	density of i	kg/m^3
ρ	density of the filtate	kg/m^3
ρ_s	density of the solid	kg/m^3
τ	residence time	s
η_i	viscosity of i	Pa.s
ϕv_{cat}	volume flow of catalyst	m^3/s
$\in_{bed}$	porosity of the bed	-
ρ_L	density of the liquid	kg/m^3
ρ_G	density of the gas	kg/m^3
η_L	viscosity of the liquid	mPa.s
σ	surface tension	J/m
α_i	relative volatility of i	-
ΔT_{lm}	logaritmic temperature difference	°C
ΔT_m	mean temperature difference	°C
ΔP	pressure drop	bar
Δp_k	pressure drop over the cake	N/m^2
ε_k	volume fraction liquid in cake	-
η	viscosity of the liquid	Ns/m^2
Δp	pressure differential across the pump	N/m^2
ϕ_v	flow rate	m^3/s
η_{pump}	pump efficiency	%
$\eta_{electric}$	electrical motor efficiency	%

Normal Symbols

A	heat exchanging surface area	m^2
A	surface area of the filter	m^2
B_{inlet}	inlet width	m
C_I	the EPE index	
C_{tr}	(gas load) capacity coefficient	m/s
C_{cat}	concentration catalyst in the regenerator	kg/m^3
dP	pressure drop	bar
d_o, o.d.	outside tube diameter	m
d_i, i.d.	inside tube diameter	m
d_g	distance between 2 coils	m
D_{cat}	diameter of catalyst	m
D_c	diameter of the spiral wounded coil	m
D_r	reactor diameter	m
d_w	mean diameter of the tube	m
D_b	bundle diameter	mm
D_s	shell diameter	mm
d_{cat}	diameter of the catalyst	m
d_{reg}	diameter of the regenerator	m
D	cyclone diameter	m
D_{outlet}	outlet diameter	m
D_{dust}	dust outlet diameter	m
D_{col}	column diameter	m
D_t	tank diameter	m
D_{in}	the internal drum diameter	m

d_k	thickness of the cake	m
D_i	internal diameter	mm
e	mimimum plate thickness	mm
e	the minimum thickness required	mm
e_s	tank thickness required at depth H_L	mm
E_{col}	column efficiency	%
F	percentage of catalyst particles with a residence less than τ	%
f	design stress	N/mm^2
F_{salt}	mass flow of the molten salt	kg/hr
F_{bu0}	start amound of catalyst	kmol/hr
F_t	correction factor	-
F_{steam}	steam flow	kg/hr
f	design stress at 370 °C	N/mm^2
f_t	design stress for tank material	N/mm^2
F_{LG}	liquid vapour flow parameter	-
g	acceleration, 9.81	m/s^2
H	height	m
	enthalpy	kJ/hr
h_o	outside film coefficient	$W/m^2.°C$
h_i	inside film coefficient	$W/m^2.°C$
h_{od} , h_{id}	fouling coefficients	$W/m^2.°C$
H_{reg}	height of the regenerator	m
H_{inlet}	inlet height	m
Hr	reactor height	m
h_{TB}	the height between top and bottom	m
h_{top}	the height of the top	m
h_{bottom}	the height of the bottom	m
h_{skirt}	the height of the skirt	m
H_{cyl}	cylinder height	m
H_L	liquid depth	m
h	height of the dehydrator heat exchanging surface	m
H_{col}	column height	m
I	Total investment costs	gld/yr
IRR	Internal Rate of Return	%
J	joint factor	-
K	D'Arcy constant	m^2
k_w	thermal conductivity of the material	W/m.°C
K_T	total production costs	gld/yr
K_P	variable costs	gld/yr
K_L	labor costs	gld/yr
K_I	investments costs	gld/yr
L_{outlet}	outlet length	m
L	overall length	m
L_c	length of the spiral wounded coil	m
m	mass flow	kg/hr
M_g	mass flow of the gas	kg/s
M_L	mass flow of the liquid	kg/s
N_t	number of tubes	-
N	theoretical number of trays	-
N_{col}	number of trays	-
$P_{electric}$	the electrical power	kW
P_{pump}	the electrical power	kW
P_i	partial pressure of i	bar
P_{tot}	total pressure	bar

P_i	internal pressure	N/mm^2
P	the production capacity	kton/yr
Q	heat duty	kJ/hr, kW
R	universal gas constant = 8.314	J/mol.K
R_{in}	the internal drum radius	m
R_{ex}	the external drum radius	m
R_o	outside scale resistance	$(W/m^2.°C)^{-1}$
R_i	inside scale resistance	$(W/m^2.°C)^{-1}$
R_1	inside radius of the layer	m
R_2	outside radius of the layer	m
ROI	Return of Investments	%
S.A.	catalyst surface area by BET method	m^2/g
t	time	s
T	temperature	°C
T_s	temperature of the molten salt	°C
T_s	tray spacing	m
U_{mf}	minimal superficial gas velocity	m/s
U	overall heat coefficient	$W/m^2.°C$
$U_{G,max}$	maximum flooding velocity	m/s
V	volume	m^3
v	linear liquid velocity	m/s
V_f	volume of the filtrate	m^2
v_i	velocity of the molten salt in the coil	m/s
v_o	velocity of the gas outside the coil	m/s
V_{cat}	total volume of catalyst	m^3
V_{reg}	volume of the regenerator	m^3
V_{layer}	volume of the layer	m^3
W	total amound of catalyst	kg
W/F_{bu0}	space time	kg.hr/kmol
W_{pol}	polytropic work of the pump	J/mol
W_{actual}	actual work of the pump	J/mol
x_i	mol fraction of i	-
x	difference between d_w and d_i	m
x	volume fraction solid in feed	-
Z	compressibility factor	-

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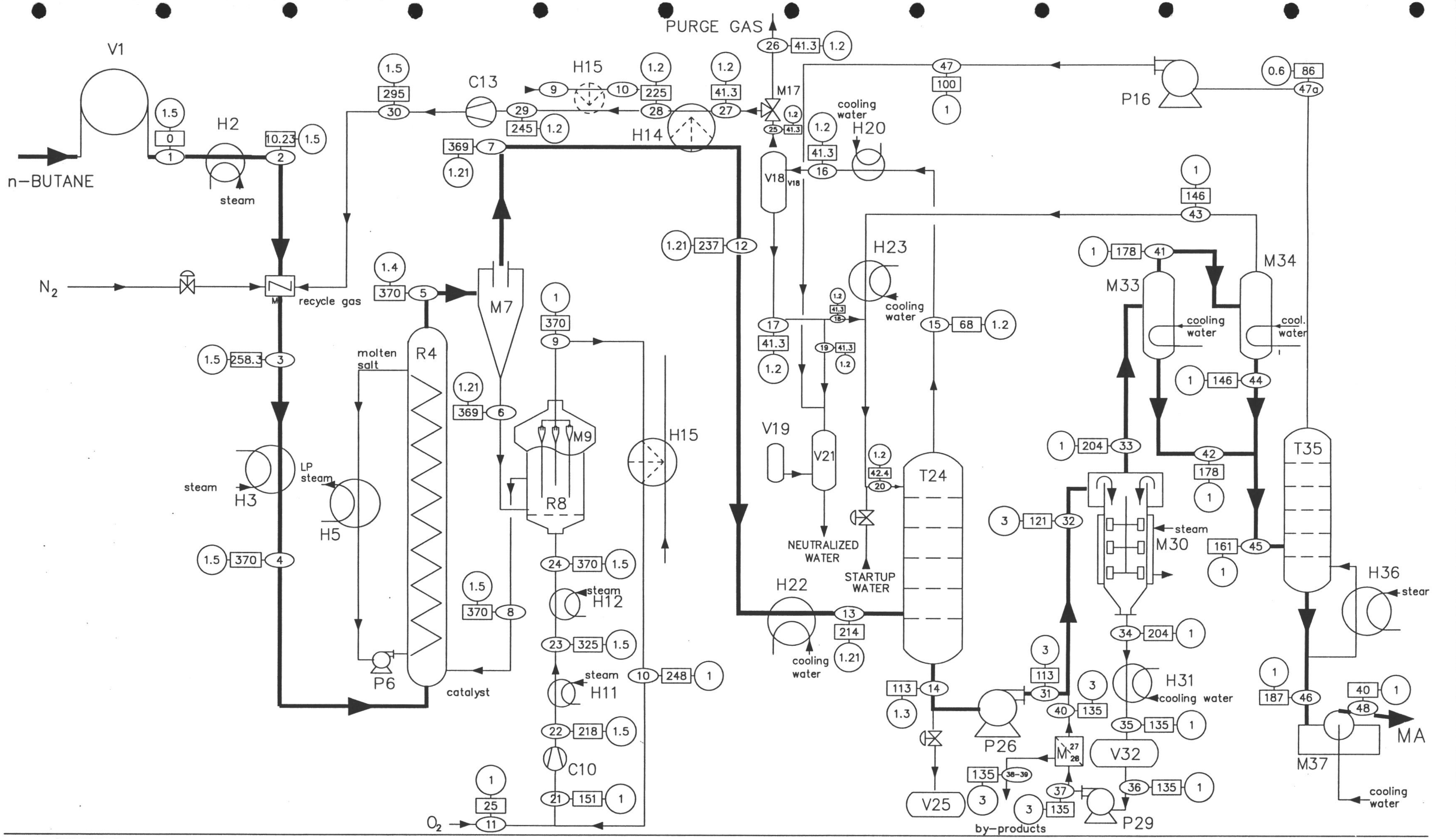
APPENDICES (I - XI)



V1	n-butane storage	M9	Regenerator cyclones (3)	V18	L/G separator vessel	M33	MA condenser
H2	n-butane vaporiser	C10	Oxygen compressor	V19	NaOH solution tank	M34	MA condenser
H3	reactor feed preheater	C13	recycle gas compressor	V21	neutralized water tank	T35	vacuum distillation tower
R4	Transport bed reactor	H14	gas/gas heat exchanger	T24	reactive absorber	H36	external reboiler of T35
H5	reactor heat exchanger unit	H15	gas/gas heat exchanger	P26	MAC pump	M37	rotating twin flakes drum
M7	Cyclone battery (4)	P16	vacuum pump	M27/28	Filtration unit		
R8	Catalyst regenerator	M17	purge valve	M30	thin layer dehydrator unit		

PROCESS SCHEME

Maleic Anhydride production by the selective catalytic oxidation of n-butane

W.S. Lam — F.V.O. Nr. 3058
S.M.L.K. Sjauw Koen Fa — Sept. 1994

⬭ stream number
▭ temperature Deg. C
○ pressure bar

Appendix II

Material properties

Properties of the reactants and products.

Sub-stance	Formula	Molmass (g/mol)	Density (kg/m^3)	$T_{boiling}$ (°C)	T_{smelt} (°C)	Flam-mable	Explo-sion-risk	MAC-value	
Maleic Anhydride	$C_4H_2O_3$	98	1400	202	53	yes	fine par-ticles + air	0.1 ppm	✓
Maleic Acid	$C_4H_4O_4$	116	1600	135	130	yes	no	---	✓
n-Butane	C_4H_{10}	58	580	-0.5	-138	very	gas + air	600 ppm	✓
Fumaric Acid	$C_4H_4O_4$	116	1600	290	287	yes	fine par-ticles + air	---	✓
Nitrogen	N_2	28	0.97	-196	-210	no	no	---	✓
Oxygen	O_2	32	1.1	-183	-218	no	no	---	✓
Carbon Dioxide	CO_2	44	1.5	-79	-57	no	no	5000 ppm	✓
Carbon monoxide	CO	28	0.97	-191	-205	very	gas + air	25 ppm	✓
water	H_2O	18	1000	100	0	no	no	---	✓
Sodium Hydroxide	NaOH	40	2100	1390	318	no	no	2 mg/m^3°c	✓
Molten Salt	$NaNO_2$ $NaNO_3$ KNO_3	92	1980	>593	146	no	no	---	✓

⇒ Catalyst 6 ✓

APPENDIX III Component mass and energy balances

EQUIPMENT STREAM →	1a/1 C4° feed	2 C4° feed	3 R4 feed.	4	5* R4 effl.
COMPONENTS ↓	M	M	M	M	M
N-Butane	5928.16	5928.16	6509.54	6509.54	650.98
Nitrogen			67241.87	67241.87	75301.63
Carbon Monoxide			1849.0	1849.0	2070.50
Carbon Dioxide			2903.50	2903.50	3253.22
Maleic Anhydride					6358.08
Water			3307.25	3307.25	7929.48
Catalyst					5344640
Oxygen					
Maleic Acid					
Fumaric Acid					
TOTAL	5928.16	5928.16	81811.16	81811.16	5440204

75883.00
5928.16
81,811.16

5* = The first product stream, calculated with the first inlet feed gas (with only pure nitrogen as the start inert carrier medium; CO2, CO, H2O are 0).

4 = The last calculated stream with the recycled inert gasses (N2, CO2, CO, H2O) of the first reactor product gasses. The needed O2 is in the catalyst from stream 8.

EQUIPMENT STREAM →	1a/1	2	3	4	5*
COMPONENTS ↓	Q	Q	Q	Q	Q
N-Butane					
Nitrogen					
Carbon Monoxide					
Carbon Dioxide					
Maleic Anhydride					
Water					
VPO catalyst					
Oxygen					
Maleic Acid					
Fumaric Acid					
TOTAL:	-4263.33	-3581.67	-19301.9	-16110.3	-136836.1

STREAM/COMPONENTS

M in kg/hr
Q in kW

13

EQUIPMENT STREAM →	6	7 // Ovhd Cycl R7	8 R4 Cat. feed	9 OVHD vap R8	10 OVHD Vap R8
COMPONENTS ↓	M	M	M	M	M
N-Butane		650.98			
Nitrogen		75301.63			
Carbon Monoxide		2070.50			
Carbon Dioxide		3253.22			
Maleic Anhydride		6358.08			
Water		7929.48			
VPO catalyst	5344640		5358393		
Oxygen				17282.47	17282.47
Maleic Acid					
Fumaric Acid					
TOTAL:	5344640	95563.89	5358393	17282.47	17282.47

EQUIPMENT STREAM →	6	7	8	9	10
COMPONENTS ↓	Q	Q	Q	Q	Q
N-Butane					
Nitrogen					
Carbon Monoxide					
Carbon Dioxide					
Maleic Anhydride					
Water					
VPO catalyst					
Oxygen					
Maleic Acid					
Fumaric Acid					
TOTAL:	-100000	-36836.1	-101266.7	1597.60	1013.5

STREAM/COMPONENTS

M in kg/hr
Q in kW

EQUIPMENT STREAM →	11 O_2 feed	12	13 =7 Abs Feed	14 Btms T24	15 T24 OVHD
COMPONENTS ↓	M	M	M	M	M
N-Butane		650.98	650.98	0.08	651.02
Nitrogen		75301.63	75301.63	2.43	75308.20
Carbon Monoxide		2070.50	2070.50	0.07	2070.77
Carbon Dioxide		3253.22	3253.22	0.41	3254.50
Maleic Anhydride		6358.08	6358.08		
Water		7929.48	7929.48	170.49	16536.24
VPO catalyst					
Oxygen	13753				
Maleic Acid				8053.04	0.03
Fumaric Acid					
TOTAL:	13753	95563.89	95563.89	8226.52	97820.76

EQUIPMENT STREAM →	11	12	13	14	15
COMPONENTS ↓	Q	Q	Q	Q	Q
N-Butane					
Nitrogen					
Carbon Monoxide					
Carbon Dioxide					
Maleic Anhydride					
Water					
VPO catalyst					
Oxygen					
Maleic Acid					
Fumaric Acid					
TOTAL:	0.11	-41052.8	-41761.1	-15230.8	-71075

STREAM/COMPONENTS

M in kg/hr
Q in kW

EQUIPMENT STREAM →	16	17	18	19 Water Bleed	20 To Abs.
COMPONENTS ↓	M	M	M	M	M
N-Butane	651.02	0.06	0.04	0.02	0.12
Nitrogen	75308.2	8.94	6.40	2.54	8.82
Carbon Monoxide	2070.77	0.37	0.27	0.10	0.34
Carbon Dioxide	3254.5	1.78	1.28	0.50	1.69
Maleic Anhydride					444.20
Water	16536,24	12833.14	9177.06	3656.08	10026.83
VPO catalyst					
Oxygen					
Maleic Acid	0.03	0.03	0.02	0.01	0.02
Fumaric Acid					
TOTAL:	97820.76	12844.32	9185.07	3659.25	10482.02

EQUIPMENT STREAM →	16	17	18	19	20
COMPONENTS ↓	Q	Q	Q	Q	Q
N-Butane					
Nitrogen					
Carbon Monoxide					
Carbon Dioxide					
Maleic Anhydride					
Water					
VPO catalyst					
Oxygen					
Maleic Acid					
Fumaric Acid					
TOTAL:	-80441.7	-56302.8	-40263.9	-16040.6	-44544.4

STREAM/COMPONENTS

M in kg/hr
Q in kW

EQUIPMENT STREAM →	R8 21 feed	22	23	R8 24 feed.	OVHD 25 V18
COMPONENTS ↓	M	M	M	M	M
N-Butane					650.96
Nitrogen					75299.26
Carbon Monoxide					2070.40
Carbon Dioxide					3252.72
Maleic Anhydride					
Water					3703.10
VPO catalyst					
Oxygen	31035.47	31035.47	31035.47	31035.47	
Maleic Acid					
Fumaric Acid					
TOTAL:	31035.47	31035.47	31035.47	31035.47	84976.44

stg 9=10.

31035.47
17282.47
13753.00
= O_2

EQUIPMENT STREAM →	21	22	23	24	25
COMPONENTS ↓	Q	Q	Q	Q	Q
N-Butane					
Nitrogen					
Carbon Monoxide					
Carbon Dioxide					
Maleic Anhydride					
Water					
VPO catalyst					
Air					
Maleic Acid					
Fumaric Acid					
TOTAL:	1013.6	1556.3	2466.2	2858.0	-24138.9

STREAM/COMPONENTS

M in kg/hr
Q in kW

EQUIPMENT STREAM →	26 purge gas	27 C_4° recycle.	28	29	30 C_4° recycle
COMPONENTS ↓	M	M	M	M	M
N-Butane	69.58	581.38 ✓	581.38	581.38	581.38
Nitrogen	8057.39	67241.87	67241.87	67241.87	67241.87
Carbon Monoxide	221.4	1489.0	1849.06	1849.06	1849.06
Carbon Dioxide	349.22	2903.50	2903.50	2903.50	2903.50
Maleic Anhydride					
Water	395.85	3307.25	3307.25	3307.25	3307.25
VPO catalyst					
Oxygen					
Maleic Acid					
Fumaric Acid					
TOTAL:	9093.44	75883.0	75883.0	75883.0	75883.0

EQUIPMENT STREAM →	26	27	28	29	30
COMPONENTS ↓	Q	Q	Q	Q	Q
N-Butane					
Nitrogen					
Carbon Monoxide					
Carbon Dioxide					
Maleic Anhydride					
Water					
VPO catalyst					
Oxygen					
Maleic Acid					
Fumaric Acid					
TOTAL:	-2584.5	-21554	-17338	-16754	-15721

STREAM/COMPONENTS

M in kg/hr
Q in kW

EQUIPMENT STREAM →	31	32	33	34	35
COMPONENTS ↓	M	M	M	M	M
N-Butane	0.08	0.08	0.08		
Nitrogen	2.43	2.43	2.43		
Carbon Monoxide	0.07	0.07	0.07		
Carbon Dioxide	0.41	0.41	0.41		
Maleic Anhydride			6705.99		
Water	170.49	170.49	1411.54		
VPO catalyst					
Oxygen					
Maleic Acid	8053.04	8355.79		302.75	302.75
Fumaric Acid				106 ✓	106
TOTAL:	8226.52	8529.27	8120.52	408.75	408.75

EQUIPMENT STREAM →	31	32	33	34	35
COMPONENTS ↓	Q	Q	Q	Q	Q
N-Butane					
Nitrogen					
Carbon Monoxide					
Carbon Dioxide					
Maleic Anhydride					
Water					
VPO catalyst					
Oxygen					
Maleic Acid					
Fumaric Acid					
TOTAL:	-15230.8	-15773.3	-12242.5	-729.6	-747.6

STREAM/COMPONENTS

M in kg/hr
Q in kW

EQUIPMENT STREAM →	36	37	38 or 39 Byprod.	40	41
COMPONENTS ↓	M	M	M	M	M
N-Butane					0.08
Nitrogen					2.43
Carbon Monoxide					0.07
Carbon Dioxide					0.41
Maleic Anhydride					3265.33
Water					1181.42
VPO catalyst					
Oxygen					
Maleic Acid	302.75	302.75		302.75	
Fumaric Acid	106	106	106		
TOTAL:	408.75	408.75	106	302.75	4449.74

EQUIPMENT STREAM →	36	37	38 or 39	40	41
COMPONENTS ↓	Q	Q	Q	Q	Q
N-Butane					
Nitrogen					
Carbon Monoxide					
Carbon Dioxide					
Maleic Anhydride					
Water					
VPO catalyst					
Oxygen					
Maleic Acid					
Fumaric Acid					
TOTAL:	-747.6	-747.6	-205	-542.6	-7836.4

STREAM/COMPONENTS

M in kg/hr
Q in kW

EQUIPMENT STREAM →	42	43	44	45	46
COMPONENTS ↓	M	M	M	M	M
N-Butane		0.08			
Nitrogen		2.43			
Carbon Monoxide		0.07			
Carbon Dioxide		0.41			
Maleic Anhydride	3440.66	444.20	2821.13	6261.79	6261.08
Water	230.12	849.77	331.65	561.77	
VPO catalyst					
Oxygen					
Maleic Acid					
Fumaric Acid					
TOTAL:	3670.78	1296.96	3152.78	6823.56	6261.08

6823.56
6261.08
562.48

EQUIPMENT STREAM →	42	43	44	45	46
COMPONENTS ↓	Q	Q	Q	Q	Q
N-Butane					
Nitrogen					
Carbon Monoxide					
Carbon Dioxide					
Maleic Anhydride					
Water					
VPO catalyst					
Oxygen					
Maleic Acid					
Fumaric Acid					
TOTAL:	-5123.3	-3598.1	-4869.4	-9992.8	-7531.4

STREAM/COMPONENTS

M in kg/hr
Q in kW

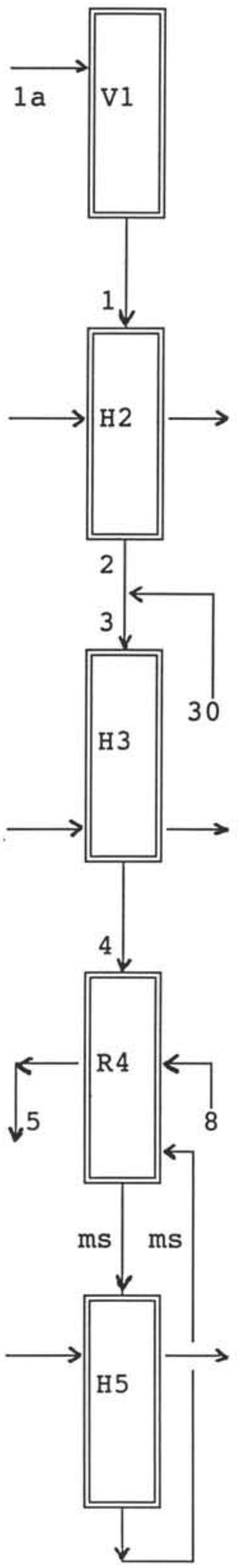
EQUIPMENT STREAM →	47 Vac Pump Disch	48 MA Prod.	49	50 ?	
COMPONENTS ↓	M	M	M	M	M
N-Butane			0.08	0.02	
Nitrogen			2.43	2.54	
Carbon Monoxide			0.07	0.1	
Carbon Dioxide			0.41	0.5	
Maleic Anhydride 98	0.71	6261.08	444.2	0.71	
Water 18	561.77		849.77	4217.85	
VPO catalyst	28				
Oxygen					
Maleic Acid				0.01	
Fumaric Acid					
TOTAL:	562.48	6261.08	1296.96	4221.73	

EQUIPMENT STREAM →	47	48	49	50	
COMPONENTS ↓	Q	Q	Q	Q	Q
N-Butane					
Nitrogen					
Carbon Monoxide					
Carbon Dioxide					
Maleic Anhydride					
Water					
VPO catalyst					
Oxygen					
Maleic Acid					
Fumaric Acid					
TOTAL:	-2076.9	-7952.8	-4280.6	-18117.5	

STREAM/COMPONENTS

M in kg/hr
Q in kW

MASS and ENERGY BALANCE

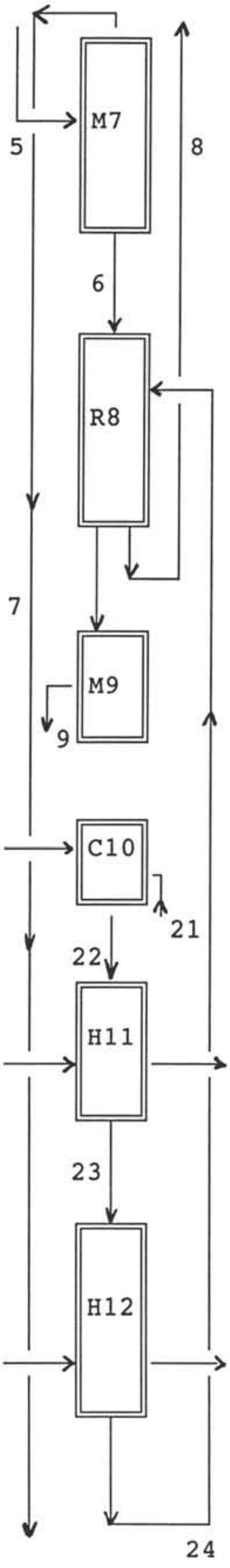


IN		Forward	Return	OUT	
M	Q	M Q	M Q	M	Q
5928.16	-4263.3				
		5928.16			
		-4263.3			
22623.8	-2293.3			22623.8	-1611.3
		5928.16			
		-3581.7			
		81811.2			
		-19302			
			75883		
			-15721		
223399	-52344			223399	-49152
		81811.2			
		-16110			
		5440204	5358393		
		-136836	-101268		
		5132005	5132005		
		-445629	-402479		
1431530	-101957			1431530	-145107

Mass in kg/hr
Energy in kW

MASS and ENERGY BALANCE

IN M	IN Q	Forward M	Forward Q
		5440204	-136836
		5344640	-100000
		95563,9	-36836
		17282.5	1598.3
	542.7	31035.5	1556.3
79548.3	-18653		
		31035.5	2466.2
34247.8	-8031.1		

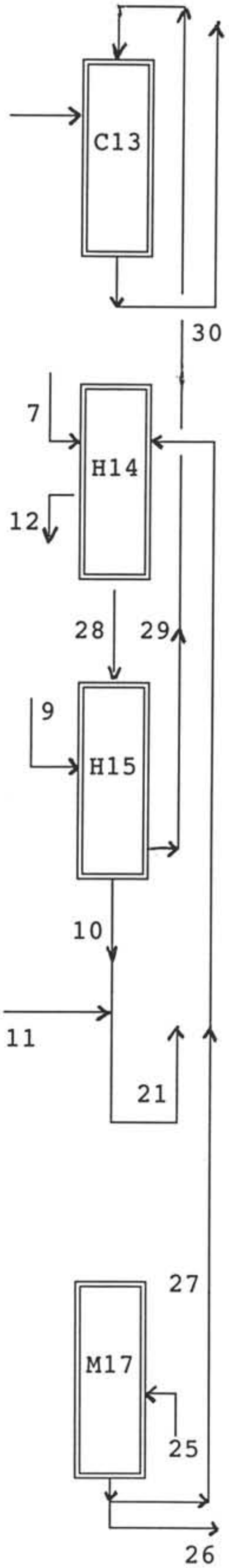


Return M	Return Q	OUT M	OUT Q
5358393	-101267		
31035.5	1013.6		
		79548.3	-17744
		34249.8	-7639.3
31035.5	2858.0		

Mass in kg/hr
Energy in kW

MASS and ENERGY BALANCE

IN M	IN Q	Forward M	Forward Q
	1033.2		
		95563.9	-36836
		95563.9	-41053
		75883	-17338
		17290.5	1597.6
		17290.5	1013.5
13753	0.11		

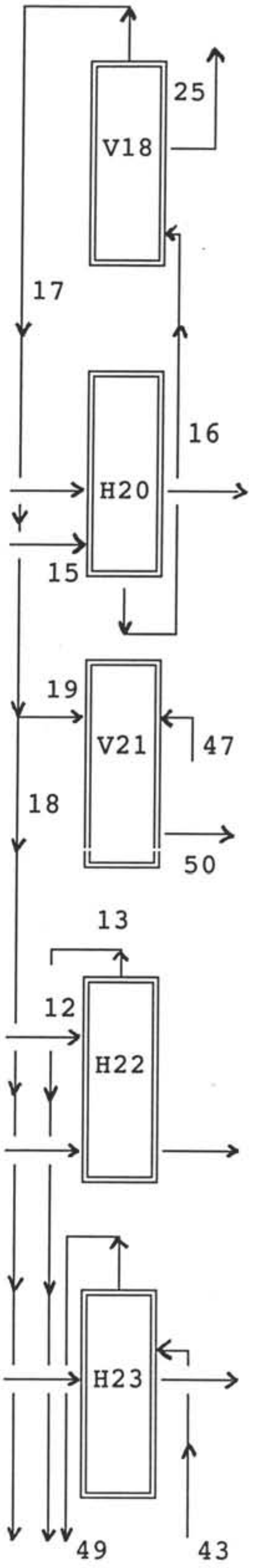


Return M	Return Q	OUT M	OUT Q
75883.0	-15721		
75883	-16754		
31035.5	1013.6		
75883	-21554		
84976.4	-24139		
		9093.44	-2584.5

Mass in kg/hr
Energy in kW

MASS and ENERGY BALANCE

IN		Forward	
M	Q	M	Q
		12844.3	-56303
805990	-18734	97820.8	-71075
		3659.25	-16041
		9185.07	-40264
		95563.9	-41761
		95563.9	-41053
62144.5	-1444.4		
29390.0	-682.6		
		1296.96	-4280.6

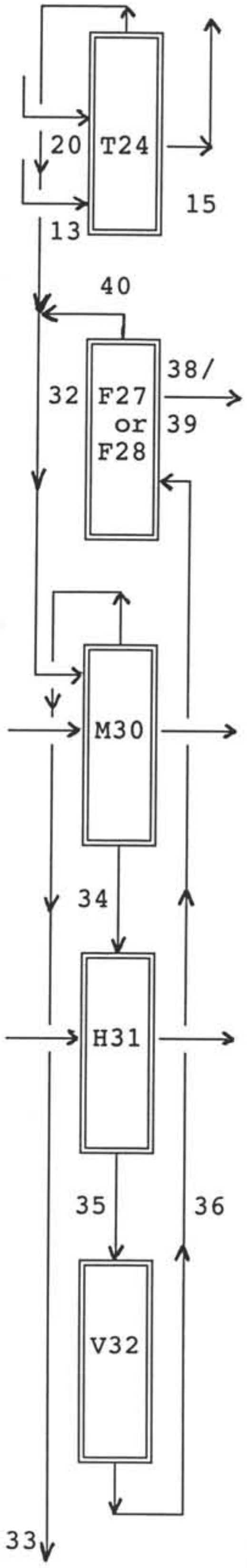


Return		OUT	
M	Q	M	Q
84976.4	-24139		
97820.8	-80442		
		805990	-28101
562.48	-2076.9		
		4221.73	-18118
		62144.5	-2153.8
		29390	-1365.2
1296.96	-3598.1		

Mass in kg/hr
Energy in kW

MASS and ENERGY BALANCE

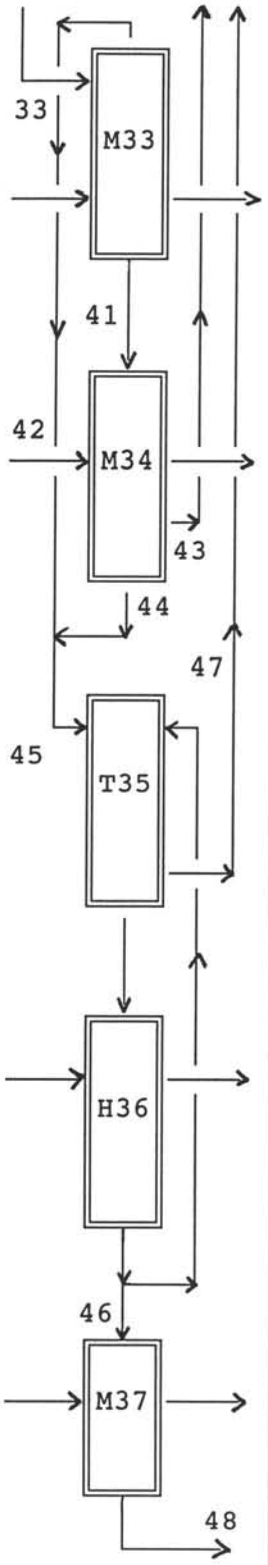
IN M	IN Q	Forward M Q
		10482.0 -44544
		95563.9 -41761
		302.75 -542.6
		8529.27 -15773
497839	-116736	
		408.75 -729.6
3110.05	-72.2	
		408.75 -747.6
		8120.52 -12243



Return M Q	OUT M	OUT Q
97820.8 -71075		
	106	-205
	497839	-111042
	3110.05	-90.3
408.75 -747.6		

Mass in kg/hr
Energy in kW

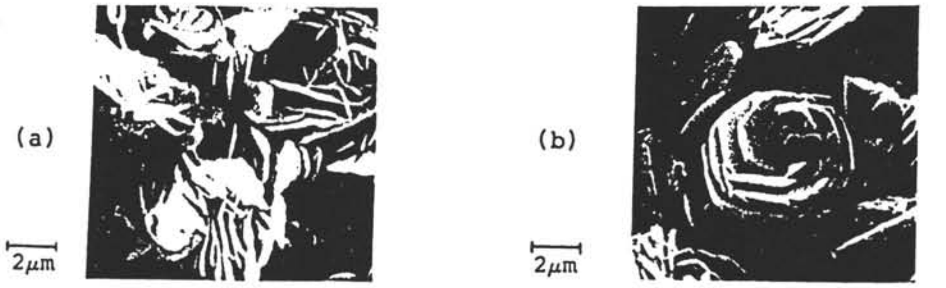
MASS and ENERGY BALANCE



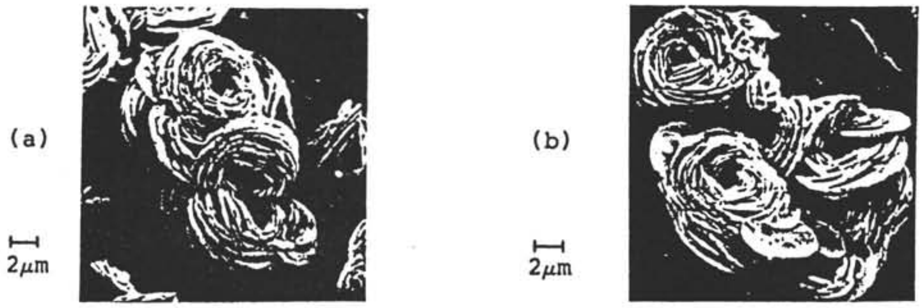
	IN M	IN Q	Forward M	Forward Q	Return M	Return Q	OUT M	OUT Q
			8120.52	-12243				
	30885	-717.2					30885	-1434.4
			4449.74	-7836.4				
	54360	-1262.4	3670.78	-5123.3			54360	-1893.5
					1296.96	-3598.1		
			3152.78	-4869.4	562.48	-2076.9		
			6823.56	-9992.8				
	28019	-4225.9					28019	-3841.7
			6261.08	-7531.4				
	18205.8	-422.8					18205.8	-845.6
							6261.08	-7952.8
TOTAL	3340974	-330263					3340977	-400881

Mass in kg/hr
Energy in kW

APPENDIX V



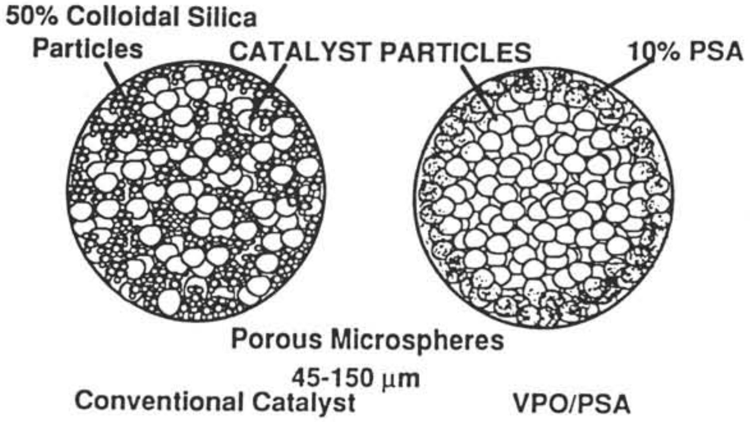
Electron micrographs of $(VO)_2H_2O(PO_3OH)_2$ showing morphology changes with P:V synthesis ratio: (a) SEM for P:V = 1.0 and (b) SEM for P:V = 2.0.



SEM?

Electron micrographs showing lack of morphology change on conversion of $(VO)_2H_2O(PO_3OH)_2$ to $(VO)_2P_2O_7$: (a) SEM for $(VO)_2H_2O(PO_3OH)_2$ and (b) SEM for $(VO)_2P_2O_7$.

Figure 3.1 Sem pictures of the VPO precursor and VPO catalyst



?

PSA

Particle surface area!

Figure 3.2 Conventional catalyst v.s. new VPO catalyst

Appendix VI

Sharma kinetic model for butane oxidation to maleic anhydride

kJ/mol

$C_4H_{10} + 3.5\,O_2 \xrightleftharpoons{k_1} C_4H_2O_3 + 4\,H_2O$ (1) K1 -93.1

$C_4H_2O_3 + 2\,O_2 \xrightleftharpoons{k_2} 2\,CO + 2\,CO_2 + H_2O$ (2) K2 -155.0

$C_4H_{10} + 5.5\,O_2 \xrightleftharpoons{k_3} 2\,CO + 2\,CO_2 + 5\,H_2O$ (3) -93.1

Rate equations:

$$R_1 = \frac{k_1 * p_{BU}^{\alpha 1}}{(1 + K_2 * p_{MA})}$$

$$R_2 = \frac{k_2 * p_{MA}}{(1 + K_2 * p_{MA})^2}$$

$$R_3 = k_3 * p_{BU}^{\alpha 3}$$

The rate constants (k_1, k_2 and k_3 : k_{jT}) were reparameterized as: from where?

$$k_{jT} = c_j \exp\left[\frac{E_j}{673 * R}\left(1 - \frac{673}{T}\right)\right]$$

?

Where c_j is the constant value, fitted at the rate constant k_{j693} of the reference experimental data of **J.J. Lerou** ('Du Pont Oxidation Process', Precision Process Technology, Kluwer Academic Publishers, the Netherlands, 1993, pag. 175-195) at T = 693 K, P = 1 bar and $X_{bu0} = 0.00654$.

$c_1 = 5.7$ e-5 $\quad kmol.kg^{-1}.s^{-1}.atm^{0.54}$

$c_2 = 3.9$ e-4 $\quad kmol.kg^{-1}.s^{-1}.atm^{-1}$

$c_3 = 4.1$ e-6 $\quad kmol.kg^{-1}.s^{-1}.atm^{-0.54}$

? assumption? or Result?

370°C

Process conditions:

T = 643 K

P = 1.5 bar

R = 8.314 kJ/kmol.K

E_1 = 93100 kJ/kmol

E_2 = 155000 kJ/kmol

E_3 = 93100 kJ/kmol

α_1 = 0.54

K_2 = 310 atm^{-1}

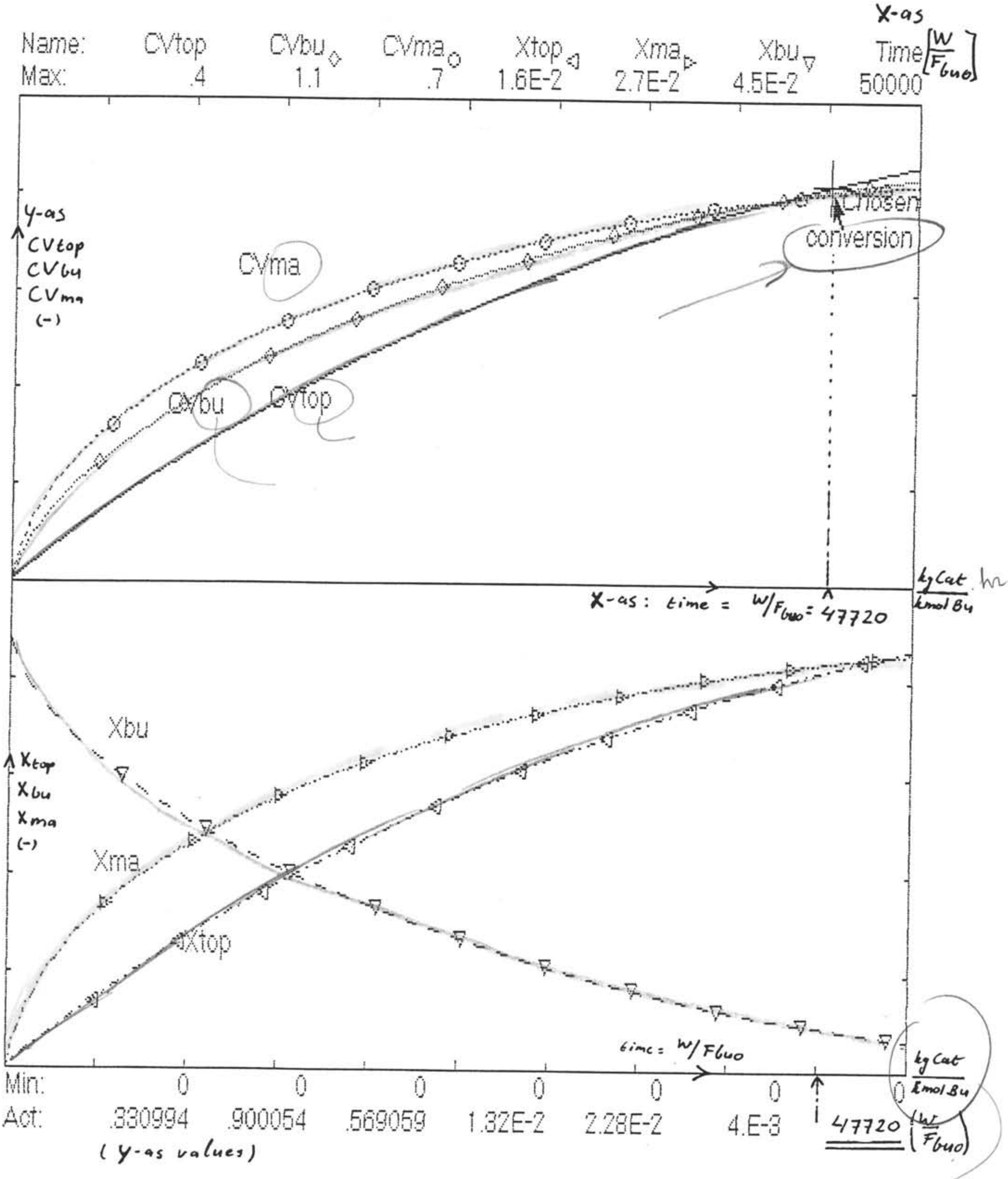
X_{BU0} = 0.04

?

Lit: R.K. Sharma, D.L. Cresswell, 'Kinetics and Fixed-Bed Reactor Modeling of Butane Oxidation to Maleic Anhydride', AIChE Journal, Vol.37, No. 1,Jan.1991, pag. 39-47.

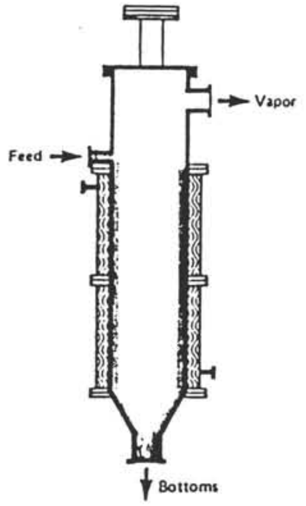
Appendix VI (continued)

Simulated output of the n-butane conversion. Program used: Psi/c

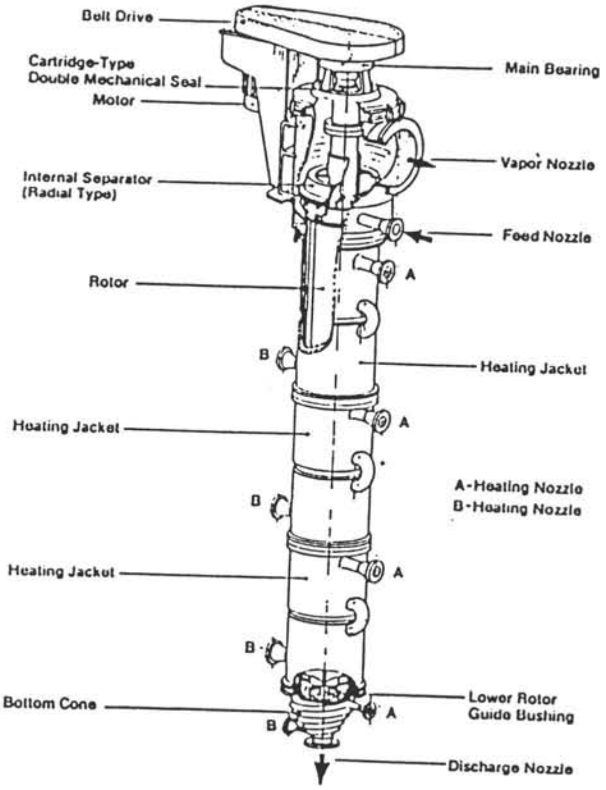


Appendix VII

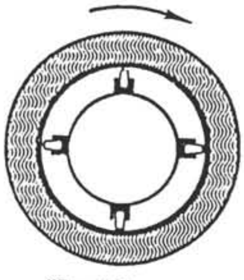
Vertical Thin layer evaporator/Dehydrator with cylindrical thermal zone and different rotor types



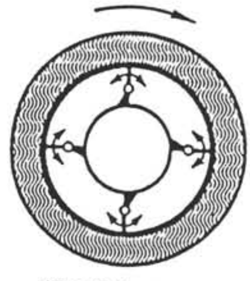
Cylindrical Thermal Zone



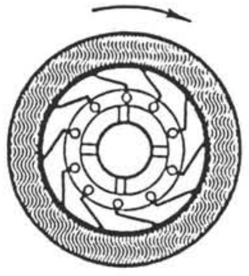
Vertical thin-film evaporator, cylindrical thermal zone.



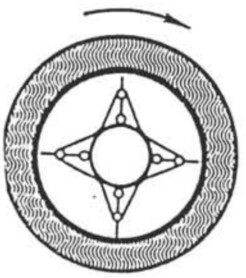
"Zero" Clearance
Carbon or Teflon Wipers



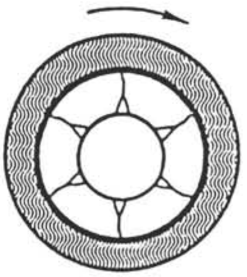
"Zero" Clearance
"Pendulum" Hinged Blades



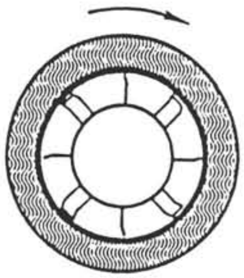
"Zero" Clearance
"Scraping" Hinged Blades



Fixed Clearance
Low Viscosity



Fixed Clearance
Medium Viscosity



Fixed Clearance
High Viscosity

Appendix VIII

Design of the n-butane vaporiser H2

The following design to vaporise 5933.5 kg/h n-butane is based on example 12.9 of Coulson & Richardson. The vaporiser is a **Kettle type.**

Physical properties of n-butane at 1.5 bar:
Boiling point = 10.23 °C
Latent heat = 326 kJ/kg
Mean specific heat, liquid = 2.51 kJ/kg°C

Heat loads:
Sensible heat(maximum) = (10.23-0)*2.51 = 25.68 kJ/kg
Total heat load = (25.68+326)*(5933.74/3600)=579.66 kW,
Add 5% for heat losses: maximum heat load(duty) = 1.05*579.66 = 608.64 kW

Assume $U = 1000\ W/m^2\ °C$.
Mean temperature difference; both sides isothermal, steam saturation temperature at 3 bar = 190 °C, $\Delta T_m = 190-10.23 = 179.77$

Area(outside) required = $607{,}450/(1000*179.77) = 3.38\ m^2$
Select 25 mm i.d., 30 mm 0.d. plain U-tube,
Nominal length 4.8 m (one U-tube)
Number of U-tubes = $3.38/(30*10^{-3})*\pi*4.8 = 7.5$
Use square pitch arrangement, pitch = 1.5*tube o.d. = 1.5*30 = 45 mm
Draw a tube diagram, take minimum bend radius = 3*tube o.d. = 90 mm
Proposed layout gives 9 U-tubes, tube outer limiet diameter 330 mm.

Boiling coefficient
Use Mostinki's equation:
Heat flux, based on estimated area, $q = 607.45/3.38 = 179.7\ kW/m^2$

$$h_{nb} = 0.0104*(38)^{0.69}*(179.7*10^3)^{0.7}*[1.8*(1.5/38)^{0.17}+4*(1.5/38)^{1.2}+10*(1.5/38)^{10}]$$
$$= 6841.96\ W/m^2°C$$

Take steam condensing coefficient as $8000\ W/m^2°C$, fouling coefficient $5000\ W/m^2°C$, butane fouling coefficient, essentially clean, $10{,}000\ W/m^2°C$.
Tube material will be plain carbon steel, $k_w = 55\ W/m°C$

$$1/U_0 = 1/4855 + 1/10{,}000 + (0.30*\ln(30/25))/(2*55) + (30/25)*(1/5000 + 1/8000)$$
$$= 1457.98\ W/m^2°C$$

Close enough to original estimate of $1000\ W/m^2°C$ for the design to stand.

Layout
From tube sheet layout $D_b = 330$ mm.
Take shell diameter as twice bundle diameter, $D_s = 2*330 = 660$ mm.
Take liquid level as 400 mm from base, freeboard(at least 250 mm) = 660-400 = 260 mm, satisfactory.
From sketch, width at liquid level = 70 mm.
Surface area of liquid = $0.7*2.4 = 1.68\ m^2$.
Vapour velocity at surface = (5933.74/3600)*(1/12.6)*(1/1.68) = 0.08 m/s
Maximum allowable velocity, $\hat{u}_v = 0.2*[(550-12.6)/12.6]^{1/2} = 1.3$ m/s
so actual velocity is well below maximum allowable velocity.

APPENDIX IX

Condenser design M33

Tables, figures and equations are taken from Chemical Engineering, Vol.6, Coulson and Richardson.

Heat transferred from vapour = H,in - H,out = $4.4073\cdot10^7$ - ($1.8444\cdot10^7$ + $2.8211.10^7$)= - $2.582\cdot10^6$ kJ/h, i.e. -717.22 kW.

The cooling water is at 20 °C and the temperature rise is assumed to be 20 °C
Cooling water flow = 717.22/(40-20)*4.18 = 8.58 kg/s, i.e. 30885 kg/h.

Assumed overall heat coefficient, U = 800 W/m^2°C

Mean temperature difference : the condensation range is small and the change in saturation temperature will be linear, so the corrected logarithmic mean temperature difference can be used.
ΔT_{lm} = {(204-40) - (178-20)}/ln(164/158) = 160.98 °C
Chosen: 1 shell and 1 tube pass: F_t = 1, then ΔT_m =1*ΔT_{lm} = 160.98 °C

Trial area = $717.22.10^3/800*160.98$ = 5.57 m^2
Choose tubes : 16 mm o.d. ; 14.8 mm i.d. ; 1.83 m length (6 ft.)
Surface area of one tube = $16\cdot10^{-3}*\pi*1.83$ = 0.092 m^2 (ignore tube sheet thickness)
Number of tubes, N_t = 5.57/0.092 = 61.
Use square pitch, P_t = 1.25*16 = 20 mm.
From table 12.4: k_1 = 0.215 ; n_1 = 2.207.
Tube bundle diameter : $D_b = 16*(61/0.215)^{1/2.207}$ = 207 mm
Number of tubes in centre row $N_{cent} = D_b/P_t$ = 207/20 = 10.33 ≈ 10.

The assumed overall coefficient is checked by the following calculations:

Shell-side coefficient

Estimate tube wall temperature, t_w ; assume condensing coefficient of 1500 W/m^2°C,
Mean temperature:
Shell-side = (204-178)/2 = 191 °C
Tube-side = (40+20)/2 = 30 °C
$(191-T_w)1500 = (191-30)900$
T_w = 94.4 °C
Mean temperature condensate = (191+94.4)/2 = 142.7°C

Physical properties at 142.7°C
condensate viscosty μ_L = 0.345 mNs/m^2
condensate density ρ_L = 1141 kg/m^3
condensate thermal conductivity k_L = 0.1576 W/m^2°C
vapour density at mean vapour temperature ρ_v = 2.675 kg/m^3

$\Gamma_h = W_c/LN_t = (3667.97/3600)/(1.83*61) = 9.13\cdot10^{-3}$ kg/sm
W_c = total condensate flow (stream 42).

L = tube length.

$N_r = (2/3) * N_{cent} = 2/3 * 10 = 7$
N_r = average number of tubes in a vertical tube row.

$h_c = 0.95*k_L[\rho_L(\rho_L - \rho_v)g/\rho_L.\Gamma_h]^{1.3}.N_r^{-1/6}$
$= 0.95*0.1576*[1141(1141-2.675)9.81/(0.345\cdot10^{-3}*9.13\cdot10^{-3})]^{1/3}*7^{-1/6}$
$= 1725$ W/m^2°C

Close enough to assumed value of 1500 W/m^2°C, so no correction to T_w needed.

Tube-side coefficient

Tube cross-sectional area $= \pi/4 * (i.d)^2.Nt/(no.tube\ passes)$
$= \pi/4 * (16.8\cdot10^{-3})^2 * 161/2 = 0.0178$ m^2
Density of water, at 30°C = 993 kg/m^3
Tube velocity $u_t = 8.58/993 * 1/0.0105 = 0.82$ m/s
$h_i = 4200(1.35 + 0.02t).u_t^{0.8}/i.d^{0.2}$
$= 4200(1.35 + 0.02*30)0.82^{0.8}/14.8^{0.2}$
$= 4076$ W/m^2°C

Overall coefficient

Fouling factors : as neither fluid is heavily fouling, use 6000 W/m^2°C for each side.
$k_w = 50$ W/m°C

$1/U = 1/h_c + 1/h_{od} + o.d*\ln(o.d/i.d)/2.k_w + o.d/(i.d.*h_{id}) + o.d/(i.d*h_i)$
$= 1/1725 + 1/6000 + 16\cdot10^{-3}\ln(16/14.8)/(2*50) + 16/14.8 * 1/6000$
$+ 16/14.8 * 1/4076.45$
$= 1.204\cdot10^{-3}$
U = <u>830.4 W/m^2°C</u>

Close enough (and above) the assumed value of 830 W/m^2°C ; good estimation.

Condenser M34

The condenser M34 is designed at the same method as the above condenser M33. Summary of the calculated values:

Heat transferred from vapour = 631 kW.
Cooling water flow = 54360 kg/h.
Assumed overal heat coefficient U = 900 $W/m^2.°C$.
Log. mean temperature difference ΔT_{lm} = 160.98 °C
Chosen: 1 shell and 1 tube pass: F_t = 1
ΔT_m = 160.98 °C
Calculated area A = 5.13 m^2

Choose tubes : 16 mm o.d. ; 14.8 mm i.d. ; 1.83 m length (6 ft.)
Surface area of one tube = 0.092 m^2 (ignore tube sheet thickness)
Number of tubes, $N_t = 56$.
Use square pitch, $P_t =$ 20 mm.
From table 12.4: $k_1 = 0.215$; $n_1 = 2.207$.
Tube bundle diameter : $D_b = 199$ mm
Number of tubes in centre row $N_{cent} = 3$.

<u>The assumed overall coefficient is checked by the following calculations</u>:

Shell-side coefficient
Estimate tube wall temperature, t_w ; assume condensing coefficient of 3050 $W/m^2°C$,
Mean temperature:
Shell-side = 162 °C
Tube-side = 25 °C
T_w = 125 °C
Mean temperature condensate = 143.5°C

$\Gamma_h = 8.545 \cdot 10^{-3}$ kg/sm
$N_r = 2$
$h_c = 2718.58$ $W/m^2°C$

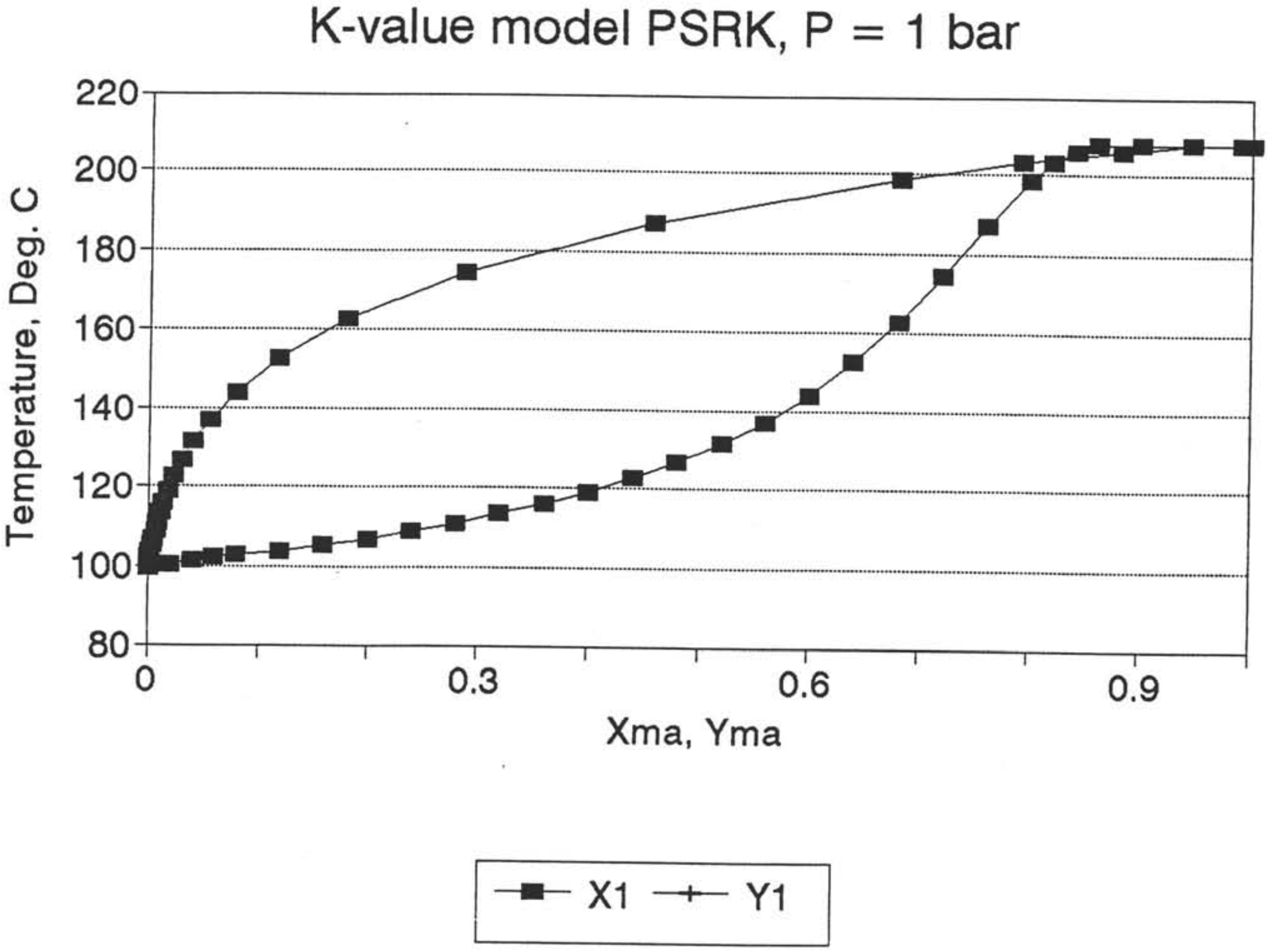
Well above the assumed value of 1500 $W/m^2°C$, so no correction to T_w needed.

Tube-side coefficient
Tube cross-sectional area = 0.00963 m^2
Density of water, at 25°C = 993 kg/m^3
Tube velocity $u_t = 1.58$ m/s
$h_i = 6535.7$ $W/m^2°C$

Overall coefficient
Fouling factors : as neither fluid is heavily fouling, use 6000 $W/m^2°C$ for each side.
$k_w = 50$ W/m°C
U = <u>1120.35 $W/m^2°C$</u>

Well above the assumed value of 830 $W/m^2°C$; good estimation.

XY Data for Maleic Anhydride/Water



APPENDIX X

Design of the reboiler H36 for the vacuum distillation tower

Design based on example 12.8 of Coulson & Richardson (C & R).
The reboiler is of a **vertical thermosyphon type**.
The heat of duty that simulated is with Chemcad is $1.383 \cdot 10^6$ kJ/h, (i.e. 384.17 kW).
The column bottom pressure is taken as 0.6 bar. Boiling point of MA at 0.6 bar is 187 °C.
Steam is using as heating medium. Steam saturation temperature is 200 °C.

Mean overall $\Delta T = (200 - 187) = 13$ °C.
Reduced temperature, $T_r = T/T_c = (187+273)/(447+273) = 0.64$
From fig. 12.59 of C & R, design heat flux = 9000 W/m^2
Area required = $384.17 \cdot 10^3/9000 = 42.69$ m^2.

Use 25 mm i.d., 30 mm o.d., 2.44 m long tubes.
Area of one tube = $\pi * 0.025 * 2.44 = 0.192$ m^2
Number of tubes $N_t = 42.69/0.192 = 222$
Approximate diameter of bundle, for 1.25 square pitch and one pass ; $n_1 = 2.207$, $k_1 = 0.215$

$D_b = 30[222/0.215]^{1/2..207} = 696.2$ mm

A fixed tube sheet will be used for a vertical thermosyphon reboiler.
From fig. 12.10 of C & R, shell diameter clearance = 13 mm,
Shell inside diameter = 696.2 + 13 = 709.2 mm.

Outlet pipe diameter ; take area as equal to total tube cross-sectional area
$= 222(0.025)^2 \pi/4 = 0.109$ m^2

Pipe diameter = $\sqrt{(0.109*4/\pi)} = 0.37$ m.

APPENDIX XI

EQUIPMENT SPECIFICATIONS

Apparatus list for reactors and columns

APPARATUS NO.	R4	R8	T24	M30	T35
Appellation Type	Transport bed reactor	Regenerator	Reactive absorber	Evaporator/ Dehydrator	Vacuum dist. tower
Abs./Eff. prssure [bar]	1.5	1.5	1.2	1	0.6
Temp. [°C]	370	370	top : 68 Feed$_{in}$: 216 Water$_{in}$: 42 bottom : 113	in : 120 out : 204	top : 86 in : 161 bottom : 187
Volume [m^3] **Diameter [m]** **L or H [m]**	195.35 3.10 26	41 3 6	66 3.15 8.5	12 1.6 5.2	0.64 0.35 6.6
Contents : **Trays (+ number)** **Cat. type** **Cat. shape**	Cooling coils Cat. type : Vanadium-Phosphorous-Oxide, VPO, $\{(VO)_2P_2O_7)\}$	Cyclones Reduced VPO-catalyst	5 sieve trays	Rotor : Carbon or Teflon wipers	5 sieve trays
Used material	AISI 304	AISI 304	AISI 304	AISI 304	AISI 304
Number **- serie** **- parallel**	1	1	1	2	1
Others					

Apparatus list for the Reactive Absorber

Equipment number : T24

General qualifications

Function : **Absorption with reaction**

Tower type : **Sieve**

Tray type : **Sieve tray**
Number of trays
- theoretical : **5**
- practical : **5**
Tray distance (HETS) : **0.6 [m]**
Material tray : **AISI 304**
Tower diameter : **3.15 [m]**
Tower heigth : **8.5 [m]**
Material tower : **AISI 304**
Heating : **no heating**

Conditions

	Feed	**Top**	**Bottom**	**Absorption material**	
Temp. [°C]	216	68	113	42	
Pressure [bar]	1.21	1.2	1.3	1.2	
Density [kg/m³]	0.853	1.096	1453.1	848.2	
Mass flow [kg/h]	95564	97821	8226	10482	
	wt%	**wt%**	**wt%**	**wt%**	
Components:					
N-Butane	0.68	0.67	0	0	
Nitrogen	78.8	76.99	0.03	0.08	
Carbon Monox.	2.17	2.12	0	0	
Carbon Diox.	3.40	3.33	0	0.02	
Maleic Anhydr.	6.65	0	0	4.24	
Water	8.30	16.90	2.07	95.66	
Maleic Acid	0	0	97.89	0	

Design

Downcomer dimension:
Width : 0.58 [m]
Length : 2.44 [m]
Clearance : 0.08 [m]
Area : 0.98 [m2]

Avg. weir length: 2.44 [m]
Weir heigth : 0.051 [m]

Tray area : 7.84 [m2]
Tray active area: 5.88 [m2]

Apparatus list for the Vacuum Distillation Tower

Equipment number : T35

General qualifications

Function : **Distillation (vacuum)**

Tower type : **Sieve**

Feed tray nr ?

Tray type : **Sieve tray**
Number of trays
- theoretical : **5**
- practical : **5**

Tray distance (HETS)	**: 0.40 [m]**	**Material tray:**	**: AISI 304**
Tower diameter	**: 0.35 [m]**	**Tower heigth**	**: 6.6 [m]**

Material tower : **AISI 304**
Heating : **reboiler H36 (external)**

Conditions

	Feed	**Top**	**Bottom**	**Absorption material**	
Temp. [°C]	161	86	187		
Pressure [bar]	1.0	0.6	0.6		
Density [kg/m^3]	265.52	0.364	1164.3	no absorption	
Mass flow [kg/h]	6824	562.5	6261		
	wt%	**wt%**	**wt%**	**wt%**	
Components:					
N-Butane	0	0	0		
Nitrogen	0	0	0		
Carbon Monox.	0	0	0		
Carbon Diox.	0	0	0		
Maleic Anhydr. HK	91.77	0.13	100		
Water LK	8.23	99.87	0		
Maleic Acid	0	0	0		

Design

Downcomer dimension:
Width : 0.04 [m]
Length : 0.21 [m]
Clearance : 0.08 [m]
Area : 0.01 [m2]

Avg. weir length : 0.22 [m]
Weir heigth : 0.051 [m]

Tray area : 0.07 [m2]
Tray active area: 0.06 [m2]

APPENDIX XI

Apparatus list for vaporiser,condensers and reboiler

APPARATUS NO.	H2	M33	M34	H36
Appellation Type	kettle vaporiser	pull-through floating head	pull-through floating head	vertical thermosyphon
Medium **- tubes** **- shell side**	- Steam - n-Butane	- Water - MA + water	- water - MA + water	Steam
Capacity Heat-transfer [kW]	608.64	717.22	631.11	384.17
Heat-transfer area [m^2]	3.38	5.57	5.13	43
Number **- serie** **- parallel**	1	1	1	1
Abs./Eff. prssure [bar] **- tubes** **- shell side**	3 1.5	3 1	3 1	0.6 3
Temp. in/out [°C] **- tube side** **- shell side**	190/185 0/10.23	20/40 204/178	20/30 178/146	187/200 220/200
Used material	AISI 304	AISI 304	AISI 304	AISI 304
Others	n-butane vaporiser	MA condenser	MA condenser	MA reboiler of **T35**

APPENDIX XI

Apparatus list for heat exchangers

Equipment number	H3	H11	H12	H14
tube side: T1/T2	258/370	217/324	324/370	42/225
shell side: t1/t2	410/389	410/390	410/390	370/237
shell passes	1	1	1	1
tube passes	1	1	1	1
LMTD (C)	76.32	123.71	51.54	168.21
Ft	1	1	1	1
mean delta T (C)	76.32	123.71	51.54	168.21
U (W/m2.C)	300	49	50	50
A (m2)	142	150	150	501
Q (kW)	3192	910	910	4217
tubes				
outside dia. (mm)	30	30	30	30
inside dia. (mm)	25	25	25	25
sheet thickn. (mm)	50	50	50	50
length (m)	4.88	4.88	4.88	4.88
eff. length (m)	4.83	4.83	4.83	4.83
surf.area 1 tube (m2	0.455	0.455	0.455	0.455
number of tubes	312	330	334	1101
K1	0.215	0.215	0.215	0.215
n1	2.207	2.207	2.207	2.207
bundle diam. (mm)	812	833	838	1438
clearance (mm)	67	72	71	88
shell diam. (mm)	879	905	909	1526
type heat exch.	Fl.Head	Fl.Head	Fl.Head	Fl.Head

APPENDIX XI

Apparatus list for heat exchangers (continued)

Equipment number	H15	H20	H22	H23
tube side: T1/T2	225/2503	20/30	20/30	20/40
shell side: t1/t2	70/248	68/41	237/216	146/48
shell passes	1	1	1	1
tube passes	1	1	1	1
LMTD (C)	58.45	28.86	201.33	58.88
Ft	1	1	1	1
mean delta T (C)	58.45	28.86	201.33	58.88
U (W/m2.C)	50	325	120	148
A (m2)	199	998	29	78
Q (kW)	584	9367	722	683
tubes				
outside dia. (mm)	30	30	30	30
inside dia. (mm)	25	25	25	25
sheet thickn. (mm)	50	50	50	50
length (m)	4.88	4.88	4.88	4.88
eff. length (m)	4.83	4.83	4.83	4.83
surf.area 1 tube (m2	0.455	0.455	0.455	4.55
number of tubes	312	330	66	172
K1	0.215	0.215	0.215	0.215
n1	2.207	2.207	2.207	2.207
bundle diam. (mm)	948	1966	401	620
clearance (mm)	71	89	56	66
shell diam. (mm)	1019	2055	457	686
type heat exch.	Fl.Head	Fl.Head	Fl.Head	FlHead

APPENDIX XI

Apparatus list for heat exchangers (continued)

Equipment number	H31
tube side: T1/T2 shell side: t1/t2	20/25 204/135
shell passes tube passes	1 1
LMTD (C) Ft mean delta T (C)	145 1 145
U (W/m2.C)	25
A (m2)	5
Q (kW)	18
tubes outside dia. (mm) inside dia. (mm) sheet thickn. (mm) length (m) eff. length (m) surf.area 1 tube (m2	 30 25 50 4.88 4.83 0.455
number of tubes	11
K1 n1	0.215 2.207
bundle diam. (mm) clearance (mm) shell diam. (mm)	178 71 249
type heat exch.	Fl.Head

Apparatus list for heat exchangers (continued)

APPARATUS NO.	H3	H5	H11	H12
Appellation Type	Internal Floating head with clamp ring	Internal Floating head with clamp ring	Internal Floating head with clamp ring	Internal Floating head with clamp ring
Medium **- tubes** **- shell side**	- n-Butane (g) + N_2(g) - Steam	- Steam - molten salt	- Oxygen - Steam	- Oxygen - Steam
Capacity Heat-transfer [kW]	3192	21595	910	392
Heat-transfer area [m^2]	142	785	150	151
Number **- serie** **- parallel**	1	2 parallel	1	1
Abs./Eff. pressure [bar] **- tubes** **- shell side**	- 1.5 - 40	- 3 - 3	- 1.5 - 40	- 1.5 - 40
Temp. in/out [°C] **- tube side** **- shell side**	- 258/370 - 410/389	- 133/190 - 220/200	- 217/324 - 410/390	- 324/370 - 410/390
Used material	AISI 304	AISI 304	AISI 304	AISI 304
Others	Reactor feedgas heater	Cooling molten salt and Steam production	1^e Oxygen heater for catalyst regeneration	2^e Oxygen heater for catalyst regeneration

Apparatus list for heat exchangers (continued)

APPARATUS NO.	H14	H15	H20	H22
Appellation Type	Internal Floating head with clamp ring	Internal Floating head with clamp ring	Internal Floating head with clamp ring	Internal Floating head with clamp ring
Medium **- tubes** **- shell side**	- Recylcle inerts gas - product stream (g)	- Reycle inert gas - Oxygen	- Water - Recycle inerts gas	- Water - Product stream (g)
Capacity Heat-transfer [kW]	4217	584	9367	722
Heat-transfer area [m^2]	501	199	998	29
Number **- serie** **- parallel**	1	1	1	1
Abs./Eff. Pressure [bar] **- tubes** **- shell side**	- 1.2 - 1.2	- 1.5 - 1.2	- 7 - 1.2	- 7 - 1.2
Temp. in/out [°C] **- tube side** **- shell side**	- 42/225 - 370/237	- 225/250 - 370/248	- 20/30 - 68/41	- 20/30 - 237/216
Used material	AISI 304	AISI 304	AISI 304	AISI 304
Others	Cooling productgas with recycle inerts gas	Recycle inerts gas heating with hot oxygen from regenerator	Recycle inerts gas cooling	Product stream cooling to reactive absorber

APPENDIX XI

Apparatus list for heat exchangers (continued)

APPARATUS NO.	H23	H31		
Appellation Type	Internal Floating head with clamp ring	Internal Floating head with clamp ring		
Medium **- tubes** **- shell side**	- Water - Recycle water	- Water - Recycle MAC (l)		
Capacity Heat-transfer [kW]	683	18		
Heat-transfer area [m^2]	78	4		
Number **- serie** **- parallel**	1	1		
Abs./Eff. prssure [bar] **- tubes** **- shell side**	- 7 - 1	- 7 - 1.5		
Temp. in/out [°C] **- tube side** **- shell side**	- 20/40 - 146/48	- 20/25 - 204/135		
Used material	AISI 304	AISI 304		
Others	Recycle water cooling	Cooling recycle MAC (l) from dehydrator		

APPENDIX XI

Apparatus list for pumps and compressors

APPARATUS NO.	P6	C10	C13	P26
Appellation Type	Centrifugal pump	Centrifugal compressor	Centrifugal compressor	Centrifugal pump
Medium to be pumped	Molten salt	Oxygen	Recycle inerts gas	MAC (1)
Capacity [kg/hr]	5132005	31035	75883	8227
Density in/out [kg/m^3]	1980	0.908/1.176	0.764/0.884	1450/1349
Suck-/press-pressure (abs./eff.) [bar]		1/1.5	1.2/1.5	1.2/3
Temp. in/out [°C]	200/200	151/218	250/294	68/199
Power [kW] **- theory** **- actual**		- 407 - 543	- 775 - 1034	- 0.27 - 0.36
Number **- serie** **- parallel**	1	1	1	1
Used material	---	---	---	---
Others	Pumping of molten salt to cooling coils in the reactor	Recycle + fresh oxygen compressing	Compressing of recycle inerts gas	Pumping of MAC (1) to dehydrator

Apparatus list for pumps and compressors (continued)

APPARATUS NO.	P29	P38		
Appellation Type	Centrifugal pump	Centrifugal pump		
Medium to be pumped	MAC (1)	recycle water		
Capacity [kg/hr]	418	563		
Density in/out [kg/m^3]	1398/1398	0.364/0.592		
Suck-/press-pressure (abs./eff.) [bar]	1/3	0.6/1		
Temp. in/out [°C]	135/135	86/100		
Power [kW] - theory - actual	 - 0.017 - 0.023	 - 0.0067 - 0.0089		
Number - serie - parallel	1	1		
Used material	---	---		
Others	Pumping of recycle MAC (1) to dehydrator	Recycle water from vavuum distillator to reactive absorber		

APPENDIX XI

Apparatus list for vessels

APPARATUS NO.	V1	V18	V19	V21	V25	V32
Appellation **Type**	n-Butane (1) storage tank	L/G-seperation tank	NaOH (1) storage tank	Water neutra-lisation tank	MAC crude tank	MAC crude tank
Abs./Eff. prssure [bar]	1.5	1.4	1	1	1	1
Temp. [°C]	0	40	23	< 40	130	135
Volume $[m^3]$ **Diameter [m]** **L of H [m]**	44.6 4.40	40 3 5.66	2.04 1 2.6	3.5 1.5 3	3.93 2 2.5	2.36 1 2
Contents : **Shell** **-shape** **-thickness [mm]**	sphere 12	cylinder 12	cylinder 5	Rotor : Carbon wipers cylinder 7	cylinder 7	cylinder 7
Used material	AISI 304	AISI 304	AISI 304	AISI 304	AISI 304	AISI 304
Number **- serie** **- parallel**	1	1	1	1	1	1
Others						

APPENDIX XI

Apparatus list for cyclones

Unit	M7	M9
	Cyclone battery unit	Cyclone unit regenerator
Cyclone diameter	1.0 m	0.5 m
Inlet height	0.5 m	0.25 m
Inlet width	0.2 m	0.10 m
Outlet height	0.5 m	0.25 m
Outlet diameter	0.5 m	0.25 m
Cylinder height	1.5 m	0.75 m
Overall height	4.0 m	2.00 m
Dust outlet diameter	0.375 m	0.1875 m
No. of gas turns	5	5
Temperature	370 °C	370 °C
Pressure (total) in	1.4 bar	1.2 bar
Total pressure drop	0.2 bar	0.3 bar
Material	AISI 304	AISI 304
No. of cyclones series/parallel	4 parallel	3 series

Apparatus list for Dehydrators

Unit	M30
Heigth	8 m
Diameter (inside)	1.6 m
Temperature inside jacket	400 °C
Pressure inside jacket	40 bar
Temperature in/out cylinder	121/204 °C
Pressure	1 bar
Overall heat capacity	1200 W/m^2.°C
Heat exchanging area	10 m^2
Heat Duty	2850 kW
residence time	1 - 5 seconds
Thin layer	1.27 - 2.54 mm
rotor blades	teflon, non-scraping
Blade tip speed	9 - 12 m/s
number of dehydrators series/parallel	2 parallel
motor electrical power	7 kWh
Used material	AISI 304

APPENDIX XI

Apparatus list for the Twin Flakes Drum

Unit	M37
Temperature on drums (feed side)	187/40 °C
Temperature on drums (cooling water side)	20/40 °C
Heat capacity	400 $W/m^2.°C$
Heat exchanging area	15.35 m^2
Heat duty	423 kW
Diameter of the drum (internal)	1.5 m
Drum width	1.65 m
N	1 r.p.m.
Thin layer	0.4 - 6 mm
Spray unit water capacity per 1 drum	9.1 m^3/hr
Used material	AISI 304

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