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Conceptual Process Design

Process Systems Engineering
DelftChemTech - Faculty of Applied Sciences
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Subject

Exergy loss reduction by combining exothermic and endothermic reaction routes

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Summary

The objective of this CPD project is to make a preliminary design of alkenes plant with emphasis in exergy loss reduction by combining exothermic and endothermic reaction. The idea is to combine an endothermic and exothermic reaction in one reactor to reduce energy consumption in reaction section. The endothermic reaction is propane dehydrogenation and the the exothermic reaction is oxidative propane dehydrogenation. Both reactions produce alkenes; ethylene and propylene.

The world demand for alkenes; ethylene and propylene is predicted increasing significantly. Capacity of ethylene derivatives worldwide will increase from 97.0 million ton/a in 1998 (results) to 119 million ton/a in 2004 (annual growth of 3.5%). World capacity for propylene will increase from 36.7 million ton/a in 1998 (results) to 47 million ton/a in 2004 (annual growth of 4.2%). The present industrial capacity of lower olefins is predicted to be insufficient, as the demand grows for these important intermediates of modern petrochemical industry. This plant is built in the standard industrial site and located near by the FT plant because propane as feedstock is obtained from the capacity of designed plant is 202,878 ton/a. The plant is expected to operate in 8040 hours continuously and has 30 day for turn-around for maintenance and cleaning. Ethylene produced is chemical grade with price 518 US$/ton and propylene is also chemical grade which will be sold 408 US$/ton. One of the strengthness of this process is almost no waste in the production. Water and CO_2 as by product can be sold for injection in oil and gas recovery. The light mixtures gas can be sent back to the FT plant as feedstock. In sustainable perspective, this is promising and attractive.

The total investment cost is 37.45 US$ million. The plant will be constructed within 2 years and the life time of the plant is 15 years. The expected cash flow of the plant is 13.82 US$ million. The predicted pay back period or pay ou time (POT) is 6 years. The rate of return is 25.61%. Furthermore, the investor's rate of return (IRR) is 28.44%. The capital cost and production variables determine the the IRR significantly or the process is sensitive to change in capital cost, price of raw material and products.

The coupling of exothermic and endothermic reaction to produce alkenes is a novel process. None of this coupling process is applied in petrochemical industry yet because it is still in early stage of development. The basis of calculation in this CPD is derived from experimental data from laboratory stage. In addition, the heat exchanger reactor (HEx reactor) combining catalytic reactions are also new frontier in reactor engineering. The research should be conducted in those developing areas.

In addition to exergy loss reduction in reaction section, an integrated low energy membrane-based separation processes is proposed to reduce lost work in separation section as main recommendation. It is also recommende to encourage the research direction in propane dehydrogenation with or without oxygen to obtained enough data in reaction kinetic and some design parameters.

As the conclusion, this alkenes producing process is profitable and feasible. Energy can be reduced in 28 kcal/mole propane, compared to the separated process.

Table of Contents

Chapter & Title Pages

Summary **i**

1 Introduction **1**

2 Process Options and Selection **4**

2.1 Process concept chosen *4*

2.2 Process options and option chosen *5*

2.3 Type of process: batch, continuous or combination *7*

3 Basic of Design (BOD) **8**

3.1 Description of the design *8*

3.2 Process definition *8*
- 3.2.1 Process concept chosen 8
- 3.2.2 Block schemes 11
- 3.2.3 Thermodynamics properties 14
- 3.2.4 Pure component properties 16

3.3 Basic Assumptions *17*
- 3.3.1 Plan capacity and location 17
- 3.3.2 Battery limit 18
- 3.3.3 Input/output streams and diagram 19

3.4 Economic Margin *21*

4 Thermodynamics properties and reaction kinetics **24**

4.1 Thermodynamics general concept *24*

4.2 Thermodynamics Model *24*

4.3 Data Validation *26*

5 Process Structure & Description **27**

5.1 Criteria and selections *28*
- 5.1.1 Part 1: Reaction Part Design 28
- 5.1.2 Part2: Pinch technology for heat integration 29
- 5.1.3 Part3: Distillation column 31

5.2 Process Flow Scheme (PFS) *33*

5.3 Utilities *39*

5.4 Process Yields *43*

6 Process Control **45**

6.1 Section 1: The material feed and preheated 45
6.2 Section 2 : The endothermic reaction 46
6.3 Section 3 : The exothermic reaction 46
6.4 Section 4 : Separation section 47
6.5 Section 5 : CO2 Removal unit 47

7 Mass and Heat Balances 48
7.1 Practical Aspects 48
7.2 Balance for Total Streams 48
7.3 Balance for Stream Components 48

8 Process and Equipment Design 52
8.1 Integration by Process Simulation 52
8.1.1 Encountered problems and solution 52
8.1.2 Component and model settings 52
8.1.3 Setting of units 53
8.2 Equipment Selection and Design 56
8.2.1 Reactor 56
8.2.2 Heat Exchanger 57
8.2.3 Separation column (T301, T302, T303) 58
8.2.4 CO_2 Removal 62
8.2.5 Gas liquid separation 63
8.2.6 Buffer tanks 64
8.2.7 Compressor 67
8.2.8 Pump 71
8.3 Special Issues 72
8.3.1 Exergy Theory 72
8.3.2 Work loss 75
8.4 Equipment data sheets 77

9 Wastes 78

10 Process Safety 82
10.1 HAZOP 82
10.2 FEI 87

11 Economy 91
11.1 Investment cost 91
11.2 Economic criteria 93

12 Creativity and Group Process Tools 95

12.1 Group performance 95

12.2 Creativity 96

12.3 Group Process Tools 97

13 Conclusions and Recommendations 100

13.1 Conclusion 100

13.2 Recommendations 101
13.2.1 Reaction and Task integration 101
13.2.2 Optimal Design in Alkenes Separation to Reduce Exergy Loss 102

List of symbols 105

Reference 106

1 Introduction

Chemical reactions at elevated temperatures are usually associated with a latent heat effect caused by the reaction enthalpy. This latent heat is mediated towards lower temperatures using coolants resulting in a loss of exergy. Exergy is explained more detail mathematically in Chapter 8.3.

A fundamental way to reduce this loss is to store this latent heat in the enthalpy of other chemicals. The idea is to combine an endothermic and exothermic reaction in one reactor and choose the reactions in such a way that the net heat effect of the two reactions together is substantially less than that of the separate reactions.

This idea is that both the exothermic and endothermic reactions produce valuable chemicals in the supply chain, which is nowadays; the demand for bulk chemicals like olefins is increasing tremendously. The present industrial capacity for lower alkenes including ethylene, propylene, and butenes is expected to be insufficient. Concerning as an economic state-of-the-art, n-alkenes are proposed to be valuable products, which are produced from alkanes as reactants from this idea.

This report on Conceptual Process Design is focused on design the plant of alkene with the concept of exergy loss reduction by combining exothermic and endothermic reaction routes. In this design, propane dehydrogenation (endothermic reaction) is combined with propane partial oxidative dehydrogenation (exothermic reaction). Feedstock propane from Fischer-Tropsch process consists of 90wt% propane and 10wt% propylene that will not effect reaction kinetics change. For oxidation part, oxygen contains 5wt% nitrogen. Main products after the process are ethylene and propylene, which are both valuable materials. In the world, 53.7% ethylene is used to produce polyethylene, 17.7% for ethylene dichloride, 12.4% for ethylene oxide, 8.5% for alpha-olefins, 5.6 for ethyl-benzene and 2.1% for linear alcohols vinyl acetate; miscellaneous, including vinyl acetate and linear alcohols. And propylene is raw material of polypropylene (39%), acrylonitrile (14%), propylene oxide (11%), cumene (10%), oxo alcohols (8%), isopropanol (7%), oligomers (5%), acrylic acid (3%) and miscellaneous (3%). [*] Each year, the plant is fed 237.15kton propane and 52.92kton oxygen; produces 66.05kton ethylene and 135.82kton propylene and others included light ends, carbon dioxide and water.

Ethylene and propylene, as main products, are produced and sold. Light ends gas is a mixture of methane, carbon monoxide and hydrogen. This mixed gas can be sold as synthesis gas back to Fischer-Tropsch process. After separation, carbon dioxide and water as by product also can be sold. The Block Scheme of whole processes with process conditions is presented in Chapter 3.

This design concerns the exergy loss reduction by combining endothermic and exothermic reactions, that's why a shell and tube reactor is proposed in process. This type of reactor is constructed with the specific catalyst both sides, shell and tube, it is so called a novel type of reactor. In this report, it is proposed the way how to design this type of

reactor by reasonable assumption that can be found in Chapter 8. The two exothermic and endothermic reaction routes can occur at the same phase simultaneously, and exothermic reaction route occurs in tube side can supply heat consumed in endothermic part occur in shell side. It is obvious that if two reaction routes exchange reaction heat each other, the required heating and cooling media for their reactions can be conserved.
In order to reduce more exergy loss, this report discussed two alternatives: without heat integration and with heat integration. The one without heat integration is simulated by Aspen Plus. All relative results are presented in chapters followed. The one with heat integration has the same composition and condition of inputs and outputs; however, some streams are heated or cooled by other streams in this system. Especially, the reactor inlets are partial preheated by products themselves. This process is partially simulated by Aspen Plus simulation and other part is calculated using pinch principles. All calculation of heat integration is shown. See Appendix C.3.

In economic point of view, comparing these two alternatives; the one with heat integration presents that the operating cost, which will be utilized as the heating/cooling media can be reduced, however, since this process heat integration associates with heat exchanging between gasses both sides, it results in high investment of heat transfer equipment. In this report, it presents and compares both alternatives in terms of economic criteria that introduce us to view the difference margin of both alternatives.

Moreover, in separation section, which has three main distillation columns, they are designed with cryogenic itself, for instance in light gas column, it is designed to use H_2 expanded from Fischer-Tropsch process 20 bar to 5 bar. For ethylene column, it is designed to use ethylene product expanded itself. And the last column, separation between propane and propylene, it is designed with heat pump process as well. These designs all are to bring the whole process to the target of exergy loss reduction.

For the conceptual design, after the aspect of process is specified, it is important then to clarify the process control loop and positioned from a process point of view as well as estimates the main unit operations and specifications. They are presented in detail in Chapter 6 and Chapter 8, respectively.

Not only exergy loss reduction process design is presented, but also safety and waste related to the environment, sustainability are described such that the flammable gasses used in the process are taken into account safety aspects from a process design point of view, for instance. The evaluation of Wastes and Process Safety can be found in Chapter 9 and Chapter 10.

The conceptual design cannot be fulfilled for the further evaluation as process feasibility, unless the process economy is estimated. The economic criteria like a value of Pay Out Time (POT), discounted Cash Flow Rate On Return (DCFROR).

At the end of this report, it shows the Creativity and Process Tools that the designers have been cope with this project so far. These tools give the process design being more meticulously and more efficiently. And, conclusion with recommendations for the whole process design is issued.

2 Process Options and Selection

One of the techniques to reduce energy losses is to design a process with better energy utilization such as the combination of exothermic and endothermic reactions. Furthermore, to design the integrated plant it is also necessary to concern about process concepts chosen such as process options, option chosen, the type of process (batch/continuous process), the thermodynamic properties and reaction kinetics, and the catalysts. Additionally, the list of pure component properties is also studied in order to have the correct data of thermodynamic properties and reaction kinetics. After process concepts chosen, the block scheme of the process is built up. According to this block scheme, we present the stream summary, and make the mass balance for the process for further works.

2.1 Process concept chosen

According to the concept of exergy loss reduction and optimum energy utilization, the project is designed by combining endothermic and exothermic reactions to produce the valuable alkenes. There are a lot of options can be used in our project. How to choose the best pair is the priority should be achieved. Firstly, some criteria are established as the tool for selecting the best option for our design. They are defined as follows:

a. Combination of Exothermic & Endothermic
   The process is aimed to combine exothermic and endothermic in order to reduce the exergy losses. The energy, which is generated by exothermic reaction, will be utilized to heat endothermic reaction. The pair of reaction is chosen in such a way the net heat effect of the pair is substantially less than that of the separate reactions.
b. In one equipment
   The coupling of endothermic and exothermic will be applied in equipment as an effort to promote *process intensification.* There is no intermediate utilities medium, which will be used as heat transfer medium.
c. $T_{exothermic}$ higher than $T_{endothermic}$
   According to the concept of heat transfer, the temperature of exothermic reaction must be higher than that of endothermic reaction. Otherwise, the heat cannot be transferred except using other utility like heat pump.
d. Product Alkenes
   Process is aimed to produce highly valuable alkenes such as ethylene and propylene.
e. Both reactions produce valuable products
   In this process, both of the two reactions should produce the valuable products. Consequently we cannot choose combustion reaction, an exothermic reaction, to generate heat for the corresponding endothermic reaction because combustion does not produces valuable products.
f. Economy, environment, safety, sustainability

As one of the general criteria, the process will be assessed by economy evaluation such as margin, Return on investment (ROI), and Discounted Cash Flow Rate of Return (DCFROR). In addition, the pair of reaction should fulfill environment regulation, safety rules and sustainability concept.

2.2 Process options and option chosen

Generally, there are three-process options to produce alkenes presented here, which are thermal cracking, catalytic cracking and dehydrogenation. These process options have been assessed based on the related chemical reaction pairs, not as the individual process.

Afterwards, some alternatives are generated refer to the criteria, which have been defined above. The alternatives are summarized in Table 2.2.1. In addition, the stoichiometry, enthalpy and temperature of reactions are described in Table 2.2.2.

***Table 2.2.1** Selection of alternatives using criteria*

Case	Alternatives	Criteria					
	Endothermic & Exothermic	A	B	C	D	E	F
1	Thermal Cracking & NH_3 Production	√	×	×	√	√	×
2	Thermal Cracking & CH_2O Production	√	×	√	√	√	×
3	Thermal Cracking & 1-Butene Production	√	√	√	√	√	×
4	Thermal Cracking & $C_4H_2O_3$ Production	√	×	×	√	√	×
5	Catalytic Cracking & NH_3 Production	√	×	√	√	√	×
6	Catalytic Cracking & Regeneration (FCC)	√	×	√	√	×	√
7	C_3H_8 Dehydrogenation & CH_4 Oxidation	√	√	√	√	×	×
8	C_3H_8 Dehydrogenation & C_3H_8 Oxidation	√	√	√	√	√	√

Note of above table:

A. Combination of Exothermic & Endothermic
B. In one equipment
C. $T_{exo} > T_{endo}$
D. Product Alkenes
E. Both reactions produce valuable products
F. Economy, environment, safety, sustainability

√ = Advantage
×= Disadvantage

Table 2.2.2 *Stoichiometry, enthalpy, and temperature of Chemical reaction options*

Case	Main Reaction	ΔH_{298} * (kJ/mol)	T (K)
Thermal Cracking	$C_{7+} \rightarrow C_nH_{2n}$	70.1 to 94.9	923-1023
Catalytic Cracking	$C_{7+} \rightarrow C_nH_{2n}$	70.1 to 94.9	753-973
C_3H_8 Catalytic Dehydrogenation	$C_2H_6 \rightarrow C_2H_4 + H_2$	+ 130.2	973
$C_4H_2O_3$ Production	$C_4H_8 + 3O_2 \rightarrow C_4H_2O_3 + 3H_2O$	na*	673-753
NH_3 Production	$N_2 + 3H_2 \rightarrow 2NH_3$	- 91.1	723-773
Catalyst Regeneration	$C + O_2 \rightarrow CO_2 / CO$	- 70.1	973
CH_2O Production	$CH_3OH + \frac{1}{2}O_2 \rightarrow CH_2O + H_2O$	- 159.2	953-1003
1-Butene Production	$C_2H_2 + C_2H_6 \rightarrow C_4H_8$	- 144.1	1203
CH_4 Oxidation	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	- 118.9	1273
C3H8 Oxidative Dehydrogenation	$C_3H_8 + \frac{1}{2}O_2 \rightarrow C_3H_6 + H_2O$ $C_3H_8 \rightarrow C_2H_4 + CH_4$	-118.9 78.5	1123

Note: ΔH_{298} = + is Endothermic; ΔH_{298} = - is Exothermic; and na=Not available

In case 1-4

The most famous process to produce light alkenes is thermal cracking. We start to consider process selection from this conventional process. The disadvantage of thermal cracking as the endothermic reaction is the high operating temperature (about 1023 K). During thermal cracking, coke is deposited. This drawback reduces heat transfer rates, increases pressure drop, lowers yield and reduces selectivity towards alkenes. Thermal cracking and chemicals production have specific reactor design. It is not feasible to couple them in one simple reactor even though both of them produce alkenes and valuable products.

In case 5-6

For fluidized catalytic cracking (FCC), there is also coke formation and the catalysts need to be regenerated by the regenerator. Indeed, the regenerator is necessary in order to provide heat for FCC reactor or preheat the feedstock. However, it increases the capital. The product from regenerator is flue gas and it is not valuable.

In case 7

Although it matches other criteria, we are not going to choose it due to the fact that the methane oxidation (exothermic reaction) only produces carbon dioxide & water and do not produce the highly valuable product such as alkenes.

In case 8
The best option is the combination of propane dehydrogenation and propane partial oxidation. These two reactions can occur simultaneously in the same state. Then it is possible to simplify the process. For reactor design, according to reaction conditions and product composition control, it is easy and better to make two reactions take place at the same time but separately in two parts of one reactor. In addition, both the exothermic and endothermic reactions can produce valuable products: ethylene and propylene respectively. Another advantage is that propane as the raw material can directly and mainly produces ethylene and propylene. Fortunately, there are some experimental data for the catalysts of propane dehydrogenation and oxidation. In such case, related to reaction state and product components, it has higher selectivity than other alternative processes. Also, fewer by-products are what the designer and clients desired. For long-term development, it is a nice alternative to fulfill the criteria of this design.

2.3 Type of process: batch, continuous or combination

To determine whether to choose a batch process or continuous process, there are some rough guidelines [8] that help to find a better solution. The guidelines are production rate, market forces and operational problems. Generally, plants with have capacity of greater than 5 kton/yr, are usually continuous processes, whereas plants having a capacity of less than 0.5 kton/yr are normally batch processes.

In this project, the main products are ethylene and propylene, which are not seasonal demand. It means that a batch process is not an appropriate option. Feedstock and main products are in gas phase under operating. Therefore, the system is difficult to be operated as a batch process. The batch process is not safe for highly exothermic reaction, due to its difficult controlling of temperature and pressure and the runaway might be happened. The advantage of continuous process is that it is easily to pump and pipe the gaseous components during operating.

Due to the utilization of catalyst in this process, the regeneration or the replacement of the catalyst is necessary. This regeneration/replacement is not continuous. However, it can be done excluded in operation time and does not influence the whole process running. Therefore, we propose to use the continuous to cope with this process.

3 Basic of Design (BOD)

3.1 Description of the design

This design is aimed to combine exothermic and endothermic reaction in one reactor in order to reduce the exergy loss. The feedstock should be alkanes from Fischer-Tropsch process, and the plant should have a production capacity of 200kton/year of alkenes. Conclude from the previous chapter, propane is select here to be the feedstock to produce alkenes: ethylene and propylene. Ethylene is one of the most valuable alkenes, so this process will be profitable. Propane Dehydrogenation will act as the endothermic reaction and propane oxidative dehydrogenation is the exothermic reaction.

3.2 Process definition

3.2.1 Process concept chosen

According to the concept for reducing energy utilization, our project is to design a process combining endothermic and exothermic reactions with alkanes to produce the valuable alkenes. There are a lot of options can be used in our project. How to choose the best pair is priority should be achieved. Firstly, some criteria are established for selecting the best option for our design. In this process, both of the two reactions should produce the valuable products. According to the concept of heat transfer, the temperature of exothermic reaction must be higher than that of endothermic reaction; otherwise, the heat cannot be transferred. Finally, the process of oxidative dehydrogenation and dehydrogenation of propane are selected as exothermic and endothermic reaction combination as mentioned in Chapter 2.2.

3.2.1.1 Stoichiometry

By combining some conversion, selectivity and thermodynamic information from experimental data from literature, we make the mass and component balance for the reaction. Afterwards, we obtain the combined reactions for both and exothermic and endothermic reactions as shown in eq. 3.1 and eq. 3.2. The experimental data and the proposed reaction mechanism are explained in detail in Appendix A.1 and selected operating temperature is showed in Appendix C.1.

a) Propane oxidative dehydrogenation, *Exothermic in tube reactor*

Overall reaction is calculated according to the selectivity and conversion data.

$$C_3H_{8(g)} + 0.4759O_{2(g)} \rightarrow 0.6946C_2H_{4(g)} + 0.3053CH_{4(g)} + 0.3607C_3H_{6(g)} + \\ + 0.2236H_{2(g)} + 0.6945H_2O_{(g)} + 0.1894CO_{(g)} + 0.0339CO_{2(g)} \quad (3.1)$$

At $T = 1123K; \Delta H = -84 \ \ kJ/mol$

Catalyst: V_2O_5/CeO_2/SA5205 [1]

Catalyst was selected base on the optimum selectivity and conversion data that we obtained from literature [1]

The exothermic reaction is non-equilibrium reaction, which is composed of series heterogeneous and homogenous reactions.

b) Propane dehydrogenation, *Endothermic in shell reactor*

Overall Reaction is calculated according to the selectivity and conversion data.
This endothermic reaction is non-equilibrium reaction.

$$C_3H_{8(g)} \rightarrow 0.002C_2H_{4(g)} + 0.002CH_{4(g)} + 0.998C_3H_{6(g)} + 0.998H_{2(g)} \quad (3.2)$$

At $T = 813K; \Delta H = +130 \ \ kJ/mol$

Catalyst: Pt, on MFI zeolite [2]

3.2.1.2 Kinetics

The reaction kinetics of oxidative dehydrogenation and propane dehydrogenation obeys a first order reaction [1] as shown in Eq. 3.3 and Eq. 3.4.

$$r = k_{oxi}C_{C_3H_8} \quad (3.3)$$

$$r = k_{endo}C_{C_3H_8} \quad (3.4)$$

The proposed catalyst for this process is V_2O_5, which is the catalyst with the best selectivity and conversion compared to the other candidates. The data of V_2O_5 is assumed having the same order with VMgO because we could find the specific data for V_2O_5. The kinetic data of VMgO catalyst is available in [3].
Figure 3.2.1.2 shows the reaction rate of propane dehydrogenation catalyzed by VMgO.

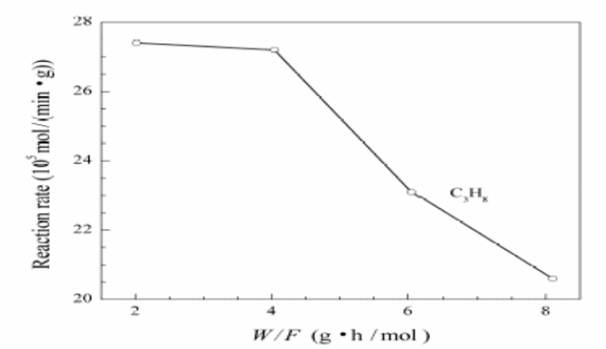


Figure 3.2.1.2. *Reaction rate of propane oxidative dehydrogenation catalyzed by VMgO (Late and Blekkan, 2002)*

The modeling of kinetics is described in Appendix A.1. Some literature works describe the kinetics by modeling oxidative dehydrogenation in exothermic reaction and the dehydrogenation of propane in endothermic reaction. Even though the modeling is still in developing phase, these tentative of reaction models can be used as an outlined method to estimate the reaction rates.

3.2.1.3 Catalyst

The conventional process to produce valuable alkenes has encountered on thermodynamic limitation, high temperature condition such as thermo cracking. So catalytic has been so far introduced to approach the better condition and also selectivity. In this project, there are two catalysts considered. One is for catalytic dehydrogenation of propane and the other is for oxidative dehydrogenation of propane to propylene and ethylene.

a) Catalytic dehydrogenation of propane

Pt on MFI zeolite will be used in this reaction. This catalyst was chosen base on the optimum selectivity and conversion among other catalyst options, which are available for catalytic dehydrogenation of propane such as tabulated in the following Table 3.2.1.3a.

Table 3.2.1.3a *Catalytic dehydrogenation of propane (Baerns et al, 2003)*

Feedstock	Catalyst	T (K)	Press. total (bara)	X_{alkane} (%)	S_{olefin} (%)	Y_{olefin} (%)
C_3H_8	Pt, on MFI zeolite	813	1.05	23	98	22.5
C_3H_8	Pt on Al_2O_3	773-923	1	~55	~90	~50
C_3H_8	Pt (Sn), (K,Cs) on MgO or Al_2O_3	873	1	58	96	55.5
C_3H_8	CrOx on Al_2O_3	873	<1	60	90	54
C_3H_8	Pt, Sn, on Mg(Al)O	873	1	45-58	95-98	45-55

Note: X = Conversion; S = Selectivity; Y = Yield

b) Catalytic for oxidative dehydrogenation of propane to propylene and ethylene

The coupling of exothermic and endothermic reactions mentioned in Chapter 2.2 guarantees the process operating in an energy-efficient and safe manner. The net heat of reaction can be controlled by the reaction temperature and concentration of O_2. V_2O_5 is used as the catalyst on this reaction, containing mixed metal-oxide catalysts showing good activity and selectivity in the oxidative dehydrogenation of propane to propylene. The condition of this reaction showed in Table 3.2.1.3b.

Table 3.2.1.3b. *Catalytic for oxidative dehydrogenation of propane to propylene and ethylene (VH Rane, et al, 2003)*

Feedstock	Catalyst	T (K)	Press. total (bara)	X_{alkane} (%)	S_{olefin} (%)	Y_{olefin} (%)
C_3H_8	V_2O_5	908	1	12	55	22.5

Note: X = Conversion ; S = Selectivity ; Y = Yield Experimental data

The conversion and selectivity will be estimated from available experimental data. Products, which are aimed in this project, are 200 kton/a alkenes (ethylene and propylene). The product distribution of ethylene and propylene is calculated base on the availability of selectivity data. The experimental data (VH Rane, 2003) shows that the conversion of the C_3H_8 increases with temperature increases referring to Figure 3.2.1.3. In addition, effects of temperature on the CO_x, CH_4, C_2H_4, and C_3H_6 selectivity in oxidative conversion of propane is presented in Appendix A.1.

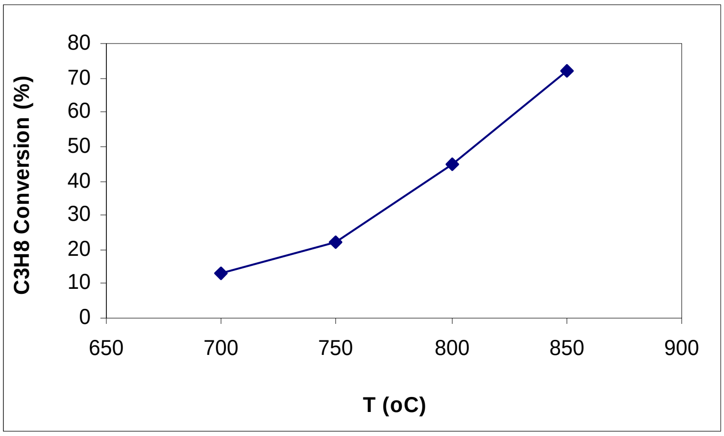


Figure 3.2.1.3. *Effect of temperature on the C_3H_8 conversion in oxidative conversion propane (VH Rane et al, 2003)*

3.2.2 Block schemes

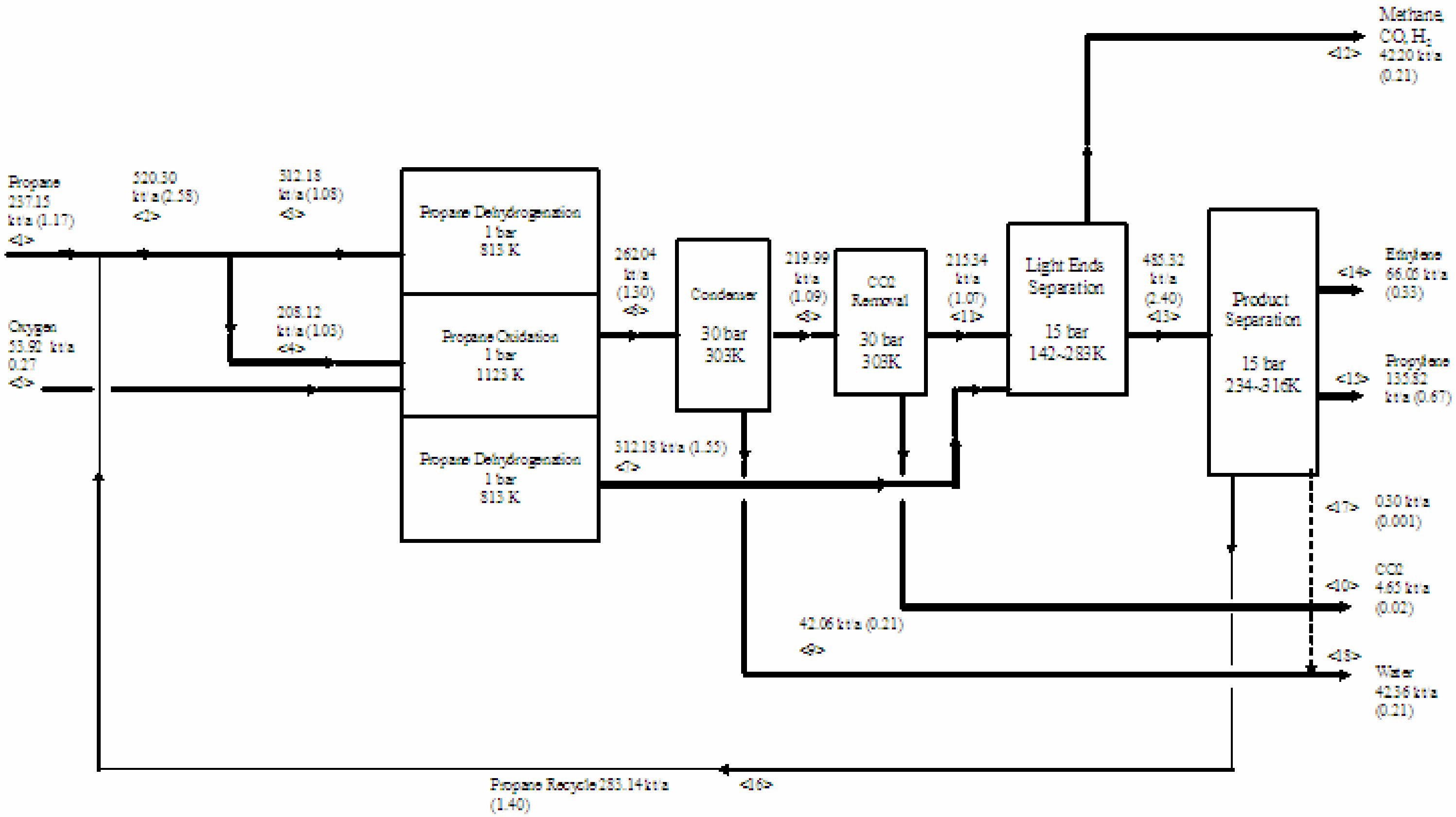
After choosing catalytic propane dehydrogenation as the process, block scheme for this design is proposed as showing in Figure 3.2.2.

In this process, the feedstock is from Fischer-Tropsch process, and after the pretreatment keeps the propane as the main component (90wt%) in it. This feedstock is separated into two streams according to the fraction of propane converted in tube side (exothermic reaction) and shell side (endothermic reaction). During start up the plant, the electricity heater is provided to heat up this two feed streams to the designed operating temperatures of shell side and tube side, and then, enter Shell and Tube reactor where reactions take place. The products from endothermic reaction side are fed into the distillation directly for methane separation. On the other hand, products from exothermic reaction side are condensed first to remove water, and fed into carbon dioxide removal section where carbon dioxide existing in the stream is removed by methyl diethanolamine (MDEA). MDEA can be regenerated by stripper and recycled to carbon dioxide removal section. After carbon dioxide removal, the products are fed into the distillation for methane, carbon monoxide, and hydrogen separation. The carbon monoxide and hydrogen are further separated from methane by membrane and they can be sole as feedstock of Fischer-Tropsch process; on the other side, methane are for sale. The products from the first distillation are further fed to ethylene separation, propylene separation. In the end, the unconverted propane is recycled to feedstock.

As mentioned above, the block scheme can offer some important information, e.g. the battery limit, the tasks taking place in process, and the sequence of the tasks or equipments. In Figure 3.2.2, the reaction condition i.e. the flow rate, temperature, pressure, and phase are also provided in the block scheme. In order to achieve the further design, the block scheme must be very reliable. Therefore, it is necessary to concern some aspects to fulfill the block scheme:

- **Feedstock preheated**. The furnace is necessary, however, design it just required at the beginning of operation and further feedstock preheated is done by heat exchange from product stream instead of continuous electrical utility operation. In this way, reduce the cost of the process and the emission of flue gases.
- **Type of reactor**. For combination of exothermic and endothermic reaction in one reactor, and not mixing together for easy design, shell and tube reactor is chosen.
- **Sequence of separations**. The most interesting products are alkenes i.e. ethylene and propylene. Therefore, the by-product separations are necessary and the sequence is important. By Heuristic rules, the poisonous and plentiful material should be removed as soon as possible, i.e. carbon monoxide and water respectively in this process. In this process, carbon monoxide, methane and hydrogen can be sold together to be the feedstock of Fischer-Tropsch process. Therefore, first separate the water and followed the carbon dioxide removal.
- **Margin**. In order to achieve the best margin, it should reduce the investment and sale more products. In this process, not only ethylene and propylene for sale, but also the carbon monoxide and hydrogen for Fischer-Tropsch process, methane for methanol production, and carbon dioxide for bottle drink factory.

Base on the block scheme, next step is to calculate the mass balance of this process according to the reaction conditions. It will be discussed in detail in Chapter 7.



Total IN:
291.1 kton/a (1.44)

Total OUT:
291.1 kton/a (1.44)

Note: the product stands for both ethylene and propylene and the amount is 201.87 kt/a.

Figure 3.2.2. *Block Scheme*

3.2.3 Thermodynamics properties

Thermodynamics properties are the basis of exergy calculation of the overall process. The heat capacity data and enthalpy of formation data are shown in the Table 3.2.3.a and Table 3.2.3.b. Meanwhile, The Gibbs energy and saturated liquid density data are presented in Appendix A.2.

Table 3.2.3.a.*List of thermodynamics heat data—heat capacity*

Component name			Heat capacity				
Design Systematic	Formula	CAS-Nr.	Cp values (kJ/mol K) $C_P = (A + BT + CT^2 + DT^3 + ET^4) \times 10^{-3}$				
			A	B	C	D	E
Propane	C_3H_8	74-98-6	28.277	1.16E-01	1.96E-04	-2.33E-07	6.87E-11
Propylene	C_3H_6	115-07-1	31.298	7.24E-02	1.95E-04	-2.16E-07	6.30E-11
Ethylene	C_2H_4	74-85-1	32.083	-1.48E-02	2.48E-04	-2.38E-07	6.83E-11
Methane	CH_4	74-82-8	34.942	-4.00E-02	1.92E-04	1.53E-07	3.93E-11
Hydrogen	H_2	1333-74-0	25.399	2.02E-02	-3.85E-05	3.19E-08	-8.76E-12
Oxygen	O_2	7784-44-7	29.526	-8.90E-03	3.81E-05	-3.26E-08	8.86E-12
Water	H_2O	7732-18-5	33.933	-8.42E-03	2.99E-05	1.78E-08	3.69E-12
Carbon dioxide	CO_2	124-38-9	27.437	4.23E-02	-1.96E-05	4.00E-09	-2.99E-13
Carbon monoxide	CO	630-08-0	29.556	-6.58E-03	2.01E-05	-1.22E-08	-1.06E-11

CP of Liquid			$C_P = (A + BT + CT^2) \times 10^{-3}$ (kJ/mol K)			
			A	B	C	Cp @ 25°C
Methyl Diethanolamine	$CH_3N(CH_2CH_2OH)_2$	105-59-9	n/a	n/a	n/a	n/a

Table 3.3.3b.*List of thermodynamics heat data—Enthalpy of formation*

Component			Enthalpy of formation			
Design Systematic	Formula	CAS-Nr.	$H_f = A + BT + CT^2$ (kJ/mol)			
			A	B	C	Hf@298K
Propane	C3H8	74-98-6	-80.697	-0.0905	4.2E-05	-103.85
Propylene	C3H6	115-07-1	37.334	-0.0652	2.8E-05	20.42
Ethylene	C2H4	74-85-1	63.053	-0.0411	1.7E-05	52.30
Methane	CH4	74-82-8	-63.425	-0.0434	1.7E-05	-74.85
Hydrogen	H2	1333-74-0	n/a	n/a	n/a	0
Oxygen	O2	7784-44-7	n/a	n/a	n/a	0

Water	H2O	7732-18-5	n/a	n/a	n/a	-241.80
Carbon dioxide	CO2	124-38-9	-393.42	0.00016	4.2E-05	117.07
Carbon monoxide	CO	630-08-0	-112.19	0.00812	-8E-06	-110.54
Methyl Diethanolamine	$CH_3N(CH_2CH_2OH)_2$	105-59-9	n/a	n/a	n/a	n/a

3.2.4 Pure component properties

In order to design the entire process, it is necessary to list up the pure component properties related to. That we can consider not only for the process separation, but also in safety point of view, will be concerned during the design stage. Table 3.2.4 shows the list of pure component.

Table 3.2.4.*List of Pure Component Properties*

PURE COMPONENT PROPERTIES													
Component name	Technological Data												
Design Systematic	Form.	Mol. Weight G/mol	Phase (S/L/V)	BP (K)	MP (K)	FP (K)	Ign.T (K)	Auto-ign. T (K)	Fl. Lm Vol%	LEL Vol%	UEL Vol%	Liq. Density kg/m^3	Rel. Vap. Density Air=1
Propane	C_3H_8	44.1	V	231	84	24.2	739.11	723	2.1-9.5	2.1	9.5	0.439^{25}	1.6
Propylene	C_3H_6	42.1	V	225	88	-78.4	n/a	733	2.0-11.1	2.0	11.0	0.505^{25}	1.5
Ethylene	C_2H_4	28.05	V	169	103.8	-245.8	136.89	763	2.7-36	2.7	36.0	0.5678^{-104}	0.98
Methane	CH_4	16.042	V	112	90	13.4	810.22	810	5.0-15.0	5.0	15.0	0.4228^{-162}	0.6
Hydrogen	H_2	2	V	20	13.8	n/a	n/a	773-844	4-74	n/a	n/a	0.082	0.07
Oxygen	O_2	32	V	90	54.6	n/a	n/a	n/a	n/a	n/a	n/a	1.308	1.43
Water	H_2O	18.016	L	373	273	n/a	n/a	n/a	n/a	n/a	n/a	0.997	
Carbon dioxide	CO_2	44.01	V	T_{sub} 194	215.5	n/a	n/a	n/a	n/a	n/a	n/a	1.779	1.5
Carbon monoxide	CO	28.01	V	82	68	n/a	881.89	878	12.5-74	12.5	74	1.145	0.97
MDEA	$CH_3N(CH_2CH_2OH)_2$	119.16	L	520.3	n/a	411	n/a	n/a	n/a	n/a	n/a	n/a	n/a

Table 3.2.4.*List of pure component properties (con't)*

	Medical Data			
Component name	MAC (DFG) ppm(vol)	Mg/m^3	LD_{50} Oral g/kg	LC_{50}
Propane	1000	1800	n/a	>12,190 ppm (4-hr., Rat)
Propylene	n/a	n/a	n/a	>7,2000 ppm (4-hr., Rat)
Ethylene	n/a	n/a	n/a	n/a
Methane	n/a	n/a	n/a	n/a
Hydrogen	n/a	n/a	n/a	n/a
Oxygen	n/a	n/a	21.0 - 33.7 (Rat)	5000 mg/L (24-hr, Goldfish)
Water	n/a	n/a	n/a	n/a
Carbon dioxide	5000	9000	n/a	n/a
Carbon monoxide	30	33	n/a	1807 ppm (4-hr, Rat)
MDEA	n/a	n/a	n/a	n/a
CO Removal	n/a	n/a	n/a	n/a

3.3 Basic Assumptions

In this chapter, the basic assumptions are defined for our project, including plant capacity, location, battery limit, performance, operating time and operating conditions (*e.g.* temperature and pressure) of main units and other utilities.

3.3.1 Plan capacity and location

Propane, which is used in this plant, is supplied from refinery. The propane could be produced from Thermal cracking or the Fischer-Tropsch process. The propane in feedstock should be assumed as pure component. The proposed production capacity is 200 kton/annum alkenes (ethylene and propylene) and the assumed operating time is 8040hr/year. The product distribution has been determined according to the selectivity and conversion data from literature. Location of plat is in 'grey area', in which all of standard industrial facilities are available.

Oxygen is one of the main reactant of propane oxidative dehydrogenation. There are impurities CO_x and N_2 in the air, air combustion will results in CO_x and NO_x. CO_x is poisonous for our catalyst and NO_x is harmful to the environment. If use air in the feedstock, we need to invest for extra catalyst regeneration and NO_x removal unit. And with the CO_x presence, the catalyst will be regenerated more often. These will request more capital. Although the fact that pure oxygen is more expensive than air, it is good for the catalyst and no harm to environment. The cost of catalyst regeneration is less than using air.

3.3.2 Battery limit

3.3.2.1 Main Units Description

Battery limit is defined as shown in Block Scheme, Figure 3.2.2. In this figure, seven main units are involved in the battery limits. The main units and their conditions inside battery limits are presented in Table 3.3.2.1.

Table3.3.2.1.*Main units' description*

No	Unit	Pressure [bara]	Temperature [K]	States	Equipment efficiency
1	Furnace	1	>573	V	100%
2	Shell Reactor	1	813	V	N/A
3	Tube Reactor	1	1123	V	N/A
4	CH_4 Separation	5	298	L/V	95%*
5	CO_2 Removal	4.5	298	L/V	95%*
6	Condenser	4.5	298	L/V	95%*
7	Separators	50	313	L/V	95%*

*In BOD report, we make the material balance based on 99-100% equipment efficiency to simplify calculation

3.3.2.2 Facilities

The plant will be built in the industrial park so-called "grey area", where standard facilities are available. The facilities are listed in Table 3.3.2.2. Some specific data were chosen according to CPD Manual.

a) Steam

Superheated steam is considered to be available at the temperatures and absolute pressures given below.

Table 3.3.2.2a.*Stream supplied conditions*

Conditions	Steam Class		
	High Pressure	Medium Pressure	Low Pressure
P [bara]	38	17	4
T (saturated) [^oC]	250	200	150

b) Electricity

Table 3.3.2.2b.*Electricity supplied conditions*

Power	Voltage [V]	Current
Low	110/220	AC
Medium	380	Three-phase AC

High	3000-10000 (3-10 kV)	Three-phase AC

c) Pressurized Air

Pressurised air is intended for instrumentation and other applications, with the exception of process air. Pressurised is available at the following conditions:

Table 3.3.2.2c.*Instrument air conditions*

Conditions	Value
T [^oC]	25
P [bar]	7
Dew point [^oC]	-40 (max)

d) Water

Table 3.3.2.2d.*Water supplied conditions*

Water	T [^oC]		P [bara]
	In	Out	
Portable water	25	*	4
Demineralized (process) water	25	*	7
Cooling water	25	*	4

*: depend on operating conditions

e) Air-cooling

Table 3.3.2.2e.*Air-cooling supplied conditions*

Conditions	Value
Humidity (design) [%]	70
T (design) [^oC]	25
T (max.) [^oC]	40

3.3.3 Input/output streams and diagram

Stream conditions and flow rates are summarized in Table 3.3.3a. The Input/output diagram across the battery limits is presented in Figure 3.3.3.

Table 3.3.3a *.Input/Output and flow rates*

	Stream nr.	Components	Flow rate [kton/a]	Yields [kton/kton product] *
Input	<1>	Propane	237.15	1.17
	<5>	Oxygen	53.92	0.27
Output	<12>	Methane	42.2	0.21
		Hydrogen		
		Carbon monoxide		
	<14>	Ethylene	66.05	0.33
	<15>	Propylene	135.82	0.67
	<10>	Carbon dioxide	4.65	0.02
	<18>	Water	42.36	0.21
* Assume the yield is based on alkenes products.				

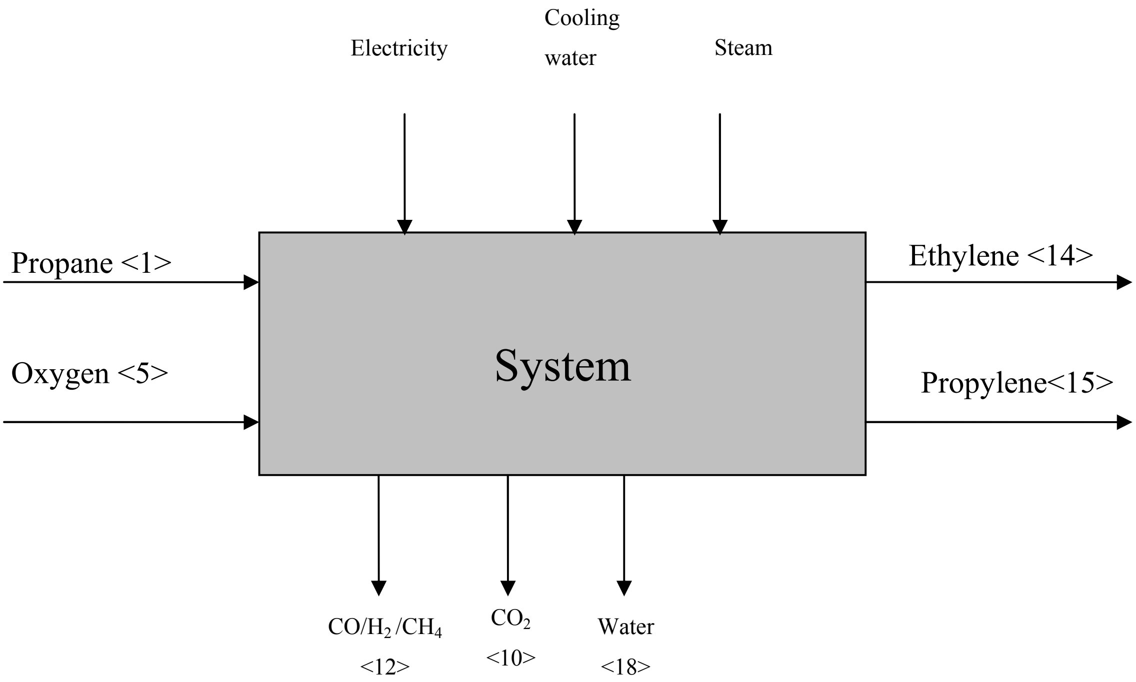


Figure 3.3.3.*Input/Output Diagram*

Table 3.3.3b shows the list of all chemicals participated in this process. The propane and oxygen are fed in as feedstock, and the alkenes product consist of ethylene and propylene.

Besides the main products, some other components are formed in the reaction. Actually they can be sale as by-products after some treatment and separation process. Therefore, although they are includes in waste part, they should be regards as by-products. See Appendix A.3 for the detailed information of feedstock and product.

Table 3.3.3b.*List of chemicals*

	Str. Nr.	Components	Stream Condition	Flow rate [kton/a]	Yield [kton/kton product]
Feedstock	<1>	Propane	298K, 1bara	237.15	1.17
	<5>	Oxygen	298K, 1bara	53.92	0.27
Products	<14>	Ethylene	234~316K, 15bara	66.05	0.33
	<15>	Propylene	234~316K, 15bara	135.82	0.67
Wastes (by-product)	<10>	Carbon dioxide	303K, 30bara	4.65	0.02
	<18>	Water	303K, 30bara	42.36	0.21
	<12>	Methane Hydrogen Carbon monoxide	142~283K, 15bara	42.2	0.21
Utilities	[-]	Hot water	373~423K, 4bara	5957.64	29.51
	[-]	Cooling water	293K, 4bara	4108.44	20.35
	[-]	Electricity	[-]	42612 kWh/a	211.09 kWh/kt/a
Catalysts	[-]	V_2O_5/CeO_2/SA5205	1123K, 1bara	6.8	0.03
	[-]	Pt on MFI zeolite	813K, 1bara	3.3	0.02

3.4 Economic Margin

According to the stream summary and the basic assumptions discussed in previous chapter, combine the information of prices of raw materials and products to estimate the margin and maximum investment of this process.

Margin is defined as following:

$$\text{Margin}=\text{Total Value (Products, Wastes } \mathit{OUT}\text{) - Total Value (Feedstock's, Process Chemicals, } \mathit{IN}\text{)}$$

All the values of these items are summarized in Table 3.4.

Table 3.4.*Material Balances and Economic Evaluation*

Stream hrs/annum = 8040

Raw Materials	***Str.No.***	***ton/a***	***Price US$/ton***	***Cost Million US$/a @2003***
Propane	001	238,341	160	38.194
Oxygen	008	54,194	143	7.771
Catalyst1 (V2O5/CeO2/SA5205)	[-]	6.8	106,549	0.725
Catalyst2 (Pt on MFI zeolite)		3.3	181,939	0.600
Total catalyst cost				1.325
Total Raw Material cost (IN)				47.290

Product	***Str.No.***	***ton/a***	***Price US$/ton***	***Income Million US$/a @2003***
Ethylene	308	66,376	518	34.383
Propylene	313	136,502	408	55.693
Light gas for syngas plant	303	42,414	64	2.719
CO2 for EOR	402	4,670	6.5	0.030
Water for EOR	208-5	42,267	0.01	0.000
Total Income (OUT)				92.825

Margin	**OUT-IN**	45.53

Then margin of this process is calculated as 45.53 million US$/annum. This process has very high margin, therefore, the process would be profitable and feasible. For further economic evaluation and profitability analysis, please refer to chapter 11 and Appendix G.

Discounted cash-flow rate of return (DCFROR): the particular rate is at which the cumulative net present worth at the end of the project is zero.

$$\sum_{n=1}^{n=t} \frac{NFV}{(1+r')^n} = 0 \qquad (3.5)$$

$$\sum_{n=1}^{n=t1} \frac{NFV}{(1+r')^n} + \sum_{n=t1}^{n=t} \frac{NFV}{(1+r')^n} = 0 \qquad (3.6)$$

The maximum investment is $\sum_{n=1}^{n=t1} \frac{NFV}{(1+r')^n}$.

In this process, NFV is just the margin of each year and r' is 10%.

Assume that the total project time $t = 15$ [years], and the construction time $t_1 = 2$ [year], and the savage at the plant life time is 8% of Fixed Capital investment

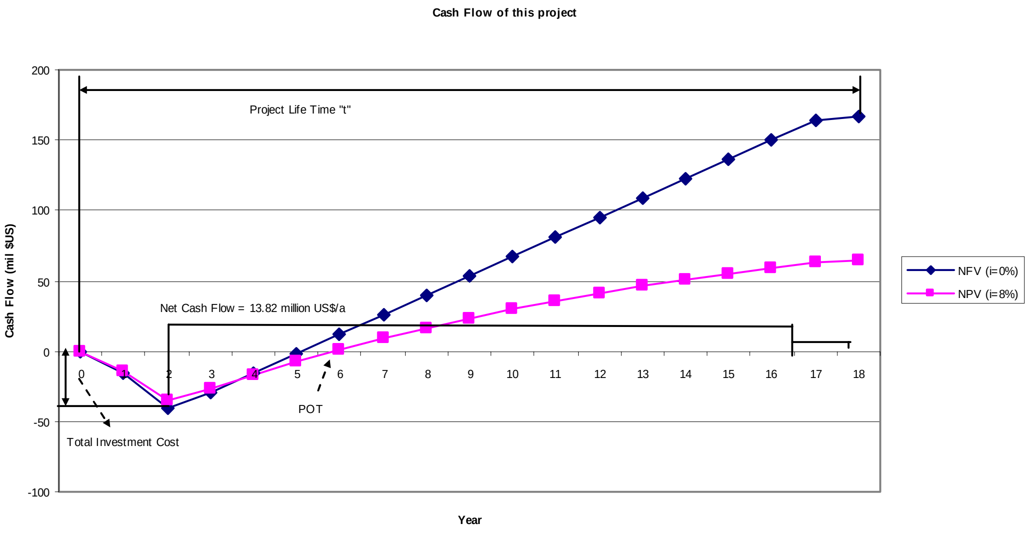


Figure 3.4.*Cash Flow*

From Figure 3.4 we found that the cash flow of this project is 13.82 million US$/ annual and the Rate of Return (ROR) 25.61% with Pay Out Back Time (POT) around 6 years.

4 Thermodynamics properties and reaction kinetics

4.1 Thermodynamics general concept

In this design system, nearly all the components, Propane, Propylene, Ethylene and Methane, etc. exists in vapor phase. Therefore, it is necessary to consider thermodynamics properties for each component, including heat capacity, enthalpy of formation and Gibbs energy.

4.2 Thermodynamics Model

Since there are a lot of VLE model in Aspen Plus for the designers to be chosen, it is important to select the appropriate model*. Most flowsheet simulators distinguish three methods of calculating phase equilibrium, which are *the equation-of-state method, the activity coefficient method and a special application method*. From these three candidates, *the equation-of-state (EOS)* model is used to describe both liquid and vapor phase behavior. This is for most hydrocarbon systems at high pressure and moderate temperature. In this project, most components are hydrocarbon to be separated at high pressure. The model using to cope with this process should be an equation of state model. Typical equations-of-state are RK, SPK and PR. However, the PR equation should not be used for close boilers system such as propane-propylene system. Therefore, both RK and SPK can be used for this project. We choose RK-ASPEN as the thermodynamic model. Moreover, the thermodynamics from simulation results are compared with the thermodynamic data from literature as shown in Chapter 3.2.3.

The VLE equilibria of ethylene-propylene system and propane-propylene system are presented in Figure 4.2a and Figure 4.2b.

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* Reference: M.Hirata, S.OHE, K,Nagahama, *Computer aided data book of Vapor-liquid Equilibria*. Kodansha limited Elsevier scientific publishing company.

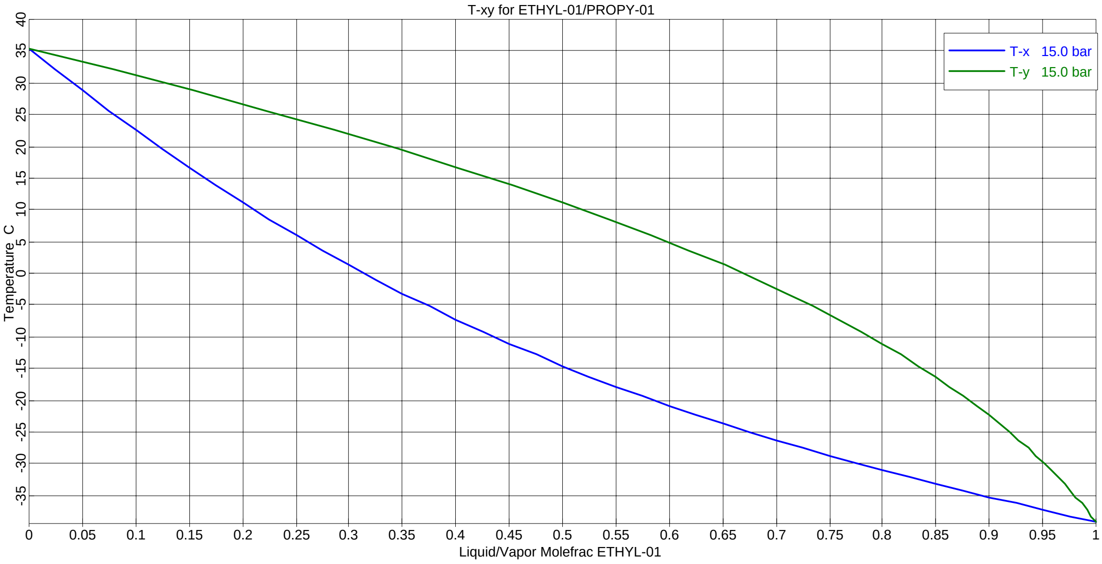

Figure 4.2a.*VLE of Ethylene and propylene system*

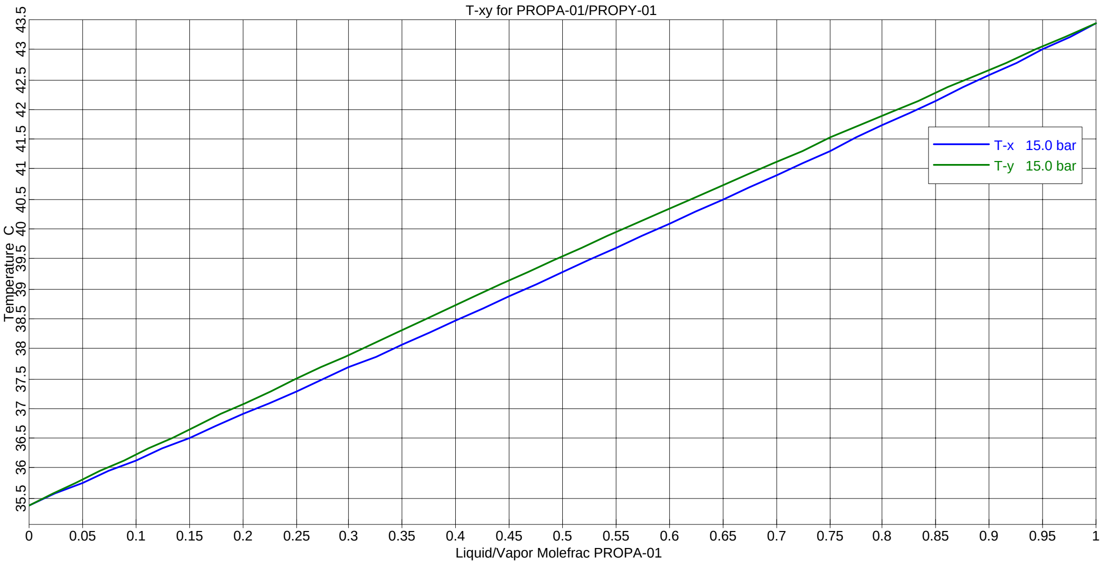

Figure 4.2b.*VLE of Propane and propylene system*

4.3 Data Validation

It is suggested to compare the boiling point of the pure component by Aspen Plus simulation with those of literature. Using Aspen Plus to simulate the boiling points, the results are listed in Table 4.3.

Table 4.3. *Comparison of literature &* Aspen Plus

Component	Literature Boiling point[1] P=1 atm (^oC)	Aspen Plus Boiling point P=1 atm (^oC)	Difference Error [%]
Propane	-42	-41.7	0.5%
Propylene	-48	-47.4	1.1%
Ethylene	-104	-103.5	0.5%
Methane	-161	-160.1	0.06%
Hydrogen	-253	-252.5	0.2%
Oxygen	-183	-182.6	0.2%
Water	100	100.0	0.01%
Carbon dioxide	T_{sub}=-79	N/a	N/a
Carbon monoxide	-191	-191.39880	-0.3%

For the propane-propylene equilibrium, we can simulate the binary system by Aspen Plus using RK-ASPEN. Compare the results from simulation and from literature. See Appendix B.

From the comparison result, it is obvious that all of the boiling points of pure components simulated by Aspen Plus are almost the same with those from literature. Therefore, these results are reliable and the model is suitable.

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[1] Reference: Yaws, C.L., *Chemical Properties Handbook,* McG RAW-HILL

5 Process Structure & Description

For this project, propane is used as the feedstock; the reaction takes place in gaseous phase. Normally, the gaseous reaction is operated in fluidized bed reactor or fixed bed reactor. For this project, it is concerned as the heat transfer between endothermic and exothermic reaction and product conversion. Even though, the fluidized bed reactor is better in view of heat transfer, it is difficult to predict the product distribution and also this project data reference to a novel research literature, hence it will be difficult to scale up because flow characteristic of catalyst in fluidized is quite different in small and large reactor. Therefore, it is proposed to use the fixed bed reactor, which is constructed in *Shell and Tube reactor*[2]. The coupling process (oxidative dehydrogenation) is placed in Tube side, which is equipped with a catalyst, V_2O_5. This catalyst is a novel one used for producing in high selectivity. The net reaction heat of this coupling is exothermic. To prevent heat loss from this exothermic process, we propose to add propane dehydrogenation, which is an endothermic reaction, fed into the shell side, which the supported platinum on MFI zeolite used as the catalyst. The kinetics of both reactions are described in Chapter3. The operating temperature of both reactions selected as in Appendix C.1.

There are two product streams coming out from both of tube and shell sides. The products of oxidative dehydrogenation in tube side, which consist of propylene (C_3H_6), ethylene (C_2H_4), methane (CH_4), hydrogen, CO_x and water respectively, will be firstly condensed the water out. This water will be transferred and then used for the oil-gas separation process. The main products stream will be then treated at CO_2 removal unit, which is an absorption column. MDEA, methyl diethyl amine, will be used as absorbent. The spent MDEA with absorbed CO_2 will be transferred to the stripping column. MDEA will be recycled and CO_2 can be sold out for the oil-gas industry. The purpose of the first separation step is to remove CO, CH_4, and H_2 as vapor phase out from the top of the column. These vapor components including CO, H_2, CH_4, will be sent to Fischer-Tropsch process as recycle stream. At the bottom of the first separation, the compositions of stream are C_2H_4, C_3H_6, and unconverted C_3H_8. They are delivered to the second separation unit in order to separated C_2H_4 as the commercial product at the top of the column. For the heavier, C_3H_6, and unconverted C_3H_8, they are quite difficult to be separated according to the thermodynamic property, closed boiling point. They will be finally separated in C_3H_6 and C_3H_8 separator. C_3H_6 as the commercial product is got at the top, whereas C_3H_8 will be fed back as the feed recycle stream. The other product streams from the shell side are directly transferred to the first product separation unit.

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[2] Shell and Tube reactor is a novel concept in reactor engineering to allow heat exchange between reactions in tube and reactions in shell. Both of shell and tube are equipped with specified catalyst to combine two reactions in one equipment.

After the three separation column, the trace water contained in recycle propane stream will be removed by standard water dryer. This kind of standard dryer can be bought from company as a package, so here it isn't considered in equipment design. See Block Scheme of the whole process as Figure 3.2.2.

To achieve the target of this project, exergy loss reduction, we have designed the process into 3 main parts, which are:

Part 1: Design Reaction by combining the endothermic and exothermic reaction
Part 2: Using pinch technology to make heat integration within the process
Part 3: Design distillation column in separation unit with exergy loss concept

5.1 Criteria and selections

Explanation of unit operation types used, process conditions, and chemicals used in each part will be presented this chapter.

5.1.1 Part 1: Reaction Part Design

For this project, we concern the heat transfer between endothermic and exothermic reaction and product conversion. Even though, the fluidized bed reactor is better in view of heat transfer, it is difficult to predict the product distribution and also this project data reference to a novel research literature, hence it will be difficult to scale up because flow characteristic of catalyst in fluidized is different in small and large reactor. Therefore, it is proposed to use the fixed bed reactor. We design shell and tube reactor in Vertical geometric and co current because this reaction is gas phase and has heat reaction exchange, so co current is better to be applied in order to exchange heat at once when reaction taking place. Moreover, the reactions take place in the high temperature, so the material of reactor is design with stainless steel. The temperature condition design for endothermic reaction is at 540^{o}C and 850^{o}C for exothermic reaction. The reason of choosing operating temperature is presented in Appendix C.1. The detail calculation of reactor design will be presented in Chapter 8.

To obtain the high-required conversion, catalyst used in endothermic reaction is the supported platinum on MFI zeolite, and V_2O_5 used for the exothermic reaction.

After the reaction, shell gas products, which consist of ethylene, propylene, methane, hydrogen and remained propane, are pressured up to 30 bar in order to deliver to the separation unit. So, compressor, C101 is needed for this purpose.

The type of equipment best suited for pumping the gases in pipelines depends on the flow rate, the differential pressure required, and the operating pressure. From the table 10.16 and compressor operating range in Figure 10.60, Coulson Volume 6, use the Centrifugal multi stages, 2 stages, isentropic compressor. Before gas product, the gas needs to be cooled down as well as after compressor. After compressor cooler, the gas products will be separated into gas and liquid product. Gas products will be fed to the light gas distillation column and liquid product will be fed to the propane and propylene distillation column.

For tube gas product, these gases consist of ethylene, propylene, methane, hydrogen, remained propane, water, carbon dioxide, and carbon monoxide. The water will be removed first by cooler after reaction. Then these products will be pressured to 30 bar in order to deliver to the CO_2 removal unit. The compressor here also is design as same as in shell side product, multi stages, 2 stages, isentropic compressor. The CO_2 removal unit is designed with absorption and stripping column. Theoretically, in absorption condition, it should be operated at the low temperature and high pressure. For this design, we design at $30^{o}C$ and 30 bar as usual condition in industry. For the stripping column, basically this column is designed with the low pressure and stripped with heating media. Here, we design the stripper at 1 bar with recycle MDEA and use hot water as the heating media. Both columns are designed with packing column in order to reduce the pressure drop on column.

In CO_2 removal unit, MDEA is used as the absorption liquid. The reason why we design to use MDEA is presented in Appendix C.2. After removing the $CO_{2,}$ the product gases will combine with the gas products from shell side before delivering to the light gas distillation column.

5.1.2 Part2: Pinch technology for heat integration

To reduce the energy used in the process, heat integration is applied. The detail of calculation and result are showed in Appendix C.3. For the economic point of view, even though we can reduce the operating cost of utilities of heating and cooling media, we have to invest the a number of heat transfer equipment. (See also Chapter11 and Appendix H.4.) This is because in this process, the fluid of both side to exchange heat are gases. The heat transfer coefficient is quite low and lead to require huge of heat transfer area. Thereby, at the final decision, we propose the process without heat integration in reaction part. The heat exchangers used in this process are designed with shell and tube heat exchanger. Options and selected reasons can be found in Appendix C.4.

The heat exchangers used in this process can be separated into three parts, first heat exchangers use as cooling such as AE101, AE102, AE202, AE203, and E401. Secondly, reboiler to vaporize a fraction of bottom product of distillation column to be vapor such as E301A, E302A, E303A, and E402. And the last one is group of condensers, which use to condense a fraction of top product stream of distillation column such as E301B, E302B, and E303B.

For this project, we design all of heat exchangers with the exchanger type of shell and tube because shell and tube heat exchanger units is by far the most commonly used of heat transfer equipment in the chemical and allied industries. Shell and tube heat exchanger gives a large surface area in a small volume, good shape for pressure operation. In extreme cases, high pressure may impose limitations by fabrication problems associated with material thickness, and by the weight of the finished unit. Differential thermal expansion under steady conditions can induce severe thermal stresses either in the tube bundle or in the shell.

In shell and tube heat exchanger type, still can be classified into fixed tube plate, U-tube, Internal floating head, and external floating head, Kettle reboiler.

For the first group, cooler heat exchangers, we design with internal floating head because this type is suitable for high-temperature differentials as this process and, as the tubes can be rodded from end to end and the bundle removed, are easier to clean and can be used for fouling fluids.

For the reboiler, Thremosyphon reboilers are the most economical type for most applications, the liquid circulation through the exchanger is maintained by the difference in density between two-phase mixtures of vapor and liquid in the exchanger, so this type gives the higher heat transfer coefficient than the others.

For the condenser, horizontal shell-side and vertical tube-side are the most commonly used types of condenser.

5.1.3 Part3: Distillation column

There are three columns used in this section. They are Light gas separation, ethylene distillation and propane-propylene separation.

The dimensioning (sizing) of columns depends on the type of contacting device used.
Generally, there are three types of contacting devices used in distillation practice: trays, random packings, and structured packings.

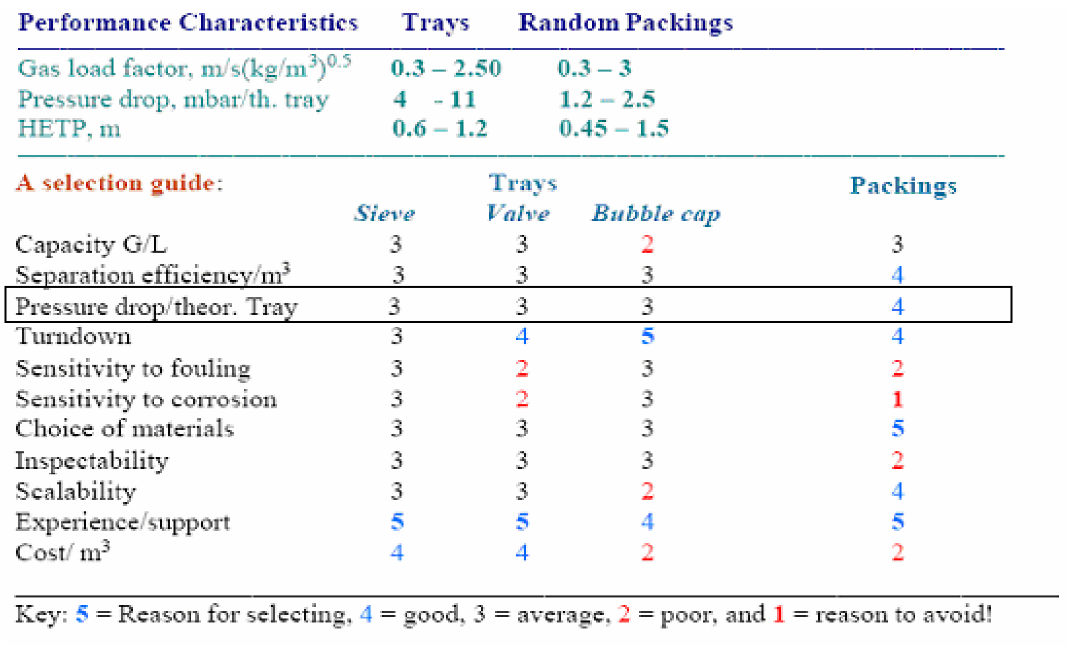
In the distillation design, random packing is applied even though trays are widely used in alkenes plants. Pressure drop is the key design variable why random packing is chosen. The pressure drop in trays is much higher than in packing columns. So, all of them are designed with the packing columns.

In exergy perspective, the pressure drop is considered as loss work which is the obtained main attention in this CPD project. It is a benefit to use packing column which has less pressure drop.

In order to achieve the purpose of exergy loss reduction process and according to the column design, the less pressure drop on the column would be extremely concerned.
Moreover, the last column, which is used for separating propane and propylene, is designed with heat pump process. More alternative designs of propane and propylene separation are presented in Appendix C.5. The detail comparison of tray and packed column properties is presented in Appendix C.6.

The packing material used in the column use metal pall ring because this shape provides good contacted surface between liquid and vapor phase in side the column. The 50 mm of diameter is used with the reason of material cost. The comparison of each column, tray and packing column is presented in Table 5.1.3. The general packing column configuration is showed in Figure 5.1.3.

Table 5.1.3 *Criteria for selecting the column*



Performance Characteristics	Trays	Random Packings
Gas load factor, m/s(kg/m^3)$^{0.5}$	0.3 – 2.50	0.3 – 3
Pressure drop, mbar/th. tray	4 - 11	1.2 – 2.5
HETP, m	0.6 – 1.2	0.45 – 1.5

A selection guide:	Trays			Packings
	Sieve	*Valve*	*Bubble cap*	
Capacity G/L	3	3	2	3
Separation efficiency/m^3	3	3	3	4
Pressure drop/theor. Tray	3	3	3	4
Turndown	3	4	5	4
Sensitivity to fouling	3	2	3	2
Sensitivity to corrosion	3	2	3	1
Choice of materials	3	3	3	5
Inspectability	3	3	3	2
Scalability	3	3	2	4
Experience/support	5	5	4	5
Cost/ m^3	4	4	2	2

Key: 5 = Reason for selecting, 4 = good, 3 = average, 2 = poor, and 1 = reason to avoid!

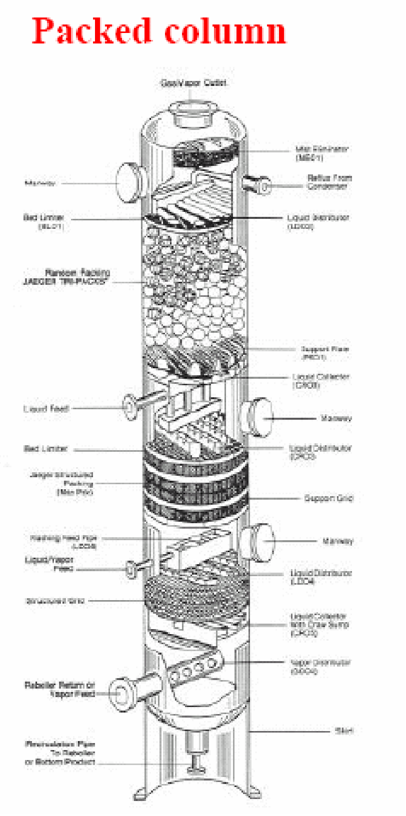


Figure 5.1.3 *General detail of packed column*

However, the drawback of C2 and C3 Splitter is the separation efficiency (NTSM) of a packing (random and structured) is very unpredictible in such high pressure distillations. Experience showed that efficiencies drop down to very low values, due to close densities of liquid and gas[3]. Consequently, the low efficiency of the packings requires a high volume of packing, i.e. height of bed is bigger. As a packing bed requires not more than 10 NTS per bed, C2 and C3 splitter require a few number of beds and it is common to install redistribution of gas and liquid. Liquid collectors and distributors and gas redistributor trays are quite expensive and increase the tower sizes. Therefore, in economic perspective, the cost of internals and vessel increases.

The light gas separation column is aimed to separate hydrogen, methane and carbon monoxide from the process stream. In which, hydrogen and carbon monoxide is the feedstock, syngas, for the Fischer-Tropsch process. There are several alternative ways to deal with the light gas. Here we design to sale the light gas as a whole product to the Fischer-Tropsch process. See Appendix C.7 for the alternative recommendations.

5.2 Process Flow Scheme (PFS)

As mentioned early in this chapter, we have designed in two options regarding to reduce the energy loss by heat integration, first is process with heat integration and the other one is without heat integration. In economic point of view, the process without heat integration is chosen. So, at here the fully equipped Process Flow Scheme is showed in Figure 5.2.1 On the Process Flow Scheme, the equipment and stream number are presented in numbering.

Section 1 : The material feed and preheated , the starting number of equipment and
stream is A0
Section 2 : The endothermic reaction, the starting number of equipment and stream isA1
Section 3 : The exothermic reaction, the starting number of equipment and stream is A2
Section 4 : The separation unit, the starting number of equipment and stream is 3
Section 5 : CO_2 Removal unit, the starting number of equipment and stream is 4

Remark: A in front of the number, just to distinguish between process with heat integration and without heat integration.

See Appendix H.1 for the Process by heat integration design.

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[3] Sulzer Chemtech Ltd, Switzerland, *personal communication*

Section 1: The material feed and preheated

Propane at normal condition gas phase is heated in the furnace combined with propane recycle stream<314> after preheating at the point M001 in PFS. The outlet temperature of propane <A001>, 540 C, is spitted into two parts, feed to tube and shell side, which the ratio of it depends on the reactor temperature. The portion of propane feed to shell is directly fed through the shell side because only propane takes place with dehydrogenation reaction, while the portion of propane to tube side is mixed with limited amount of oxygen <A202> prior to being heated more in furnace to reach the required temperature 850 C and feeding to tube side<A204>.

Section 2: The endothermic reaction

Propane feed to shell reactor takes place with the endothermic reaction. The direction of feed is from the top to downward direction as stream <A101> because feed is gas phase condition. After reaction, the product stream<A102> is cooled down by AE101. In this heat exchanger, we use Boiler Feed Water, BFW, as cooling media to remove heat from process stream. The outlet stream of BFW is steam that can be used as utility or supplied to the other processes. Then, the product stream<A103> is upped pressure to 30 bar by AC101 in order to prepare the suitable condition before delivering to the separation units and also propane and propylene mixture can be primary separated as liquid condense and resulting in less load in the further distillation column as well. Then, because the temperature after compressing gas is quite high, the gas is needed to cool down with after cooler AE102. The stream <A104> is exchanged heat with process water, which is then become the hot water utility. The stream<A105> consists of two phases, they will be separated in gas and liquid in D101.The gas stream<A106> is combined with the gas product from tube side stream<401> in D102, while the liquid product, which are mostly propane and propylene, stream <A107> is reduced the pressure by sizing control valve pressure drop of level control of D101 from 30 bar to 15 bar and then mixed with the bottom product from ethylene separation column to be separated further.

Section 3: The exothermic reaction

Propane feed to tube reactor takes place with the exothermic reaction on the top to downward direction <A204>. The stream is exchanged heat co current with the stream feed in shell side <A101>. The gas product stream<A205> is cooled down by AE202. This heat exchanger also uses BFW to remove heat from product stream. The outlet stream of BFW becomes steam that can be used as utility or supplied to other processes. There is water as by product in stream<A205>. It will be removed out from AE202 after condensing via AP202 to the water storage as stream<A207>. Gas product stream<A206> is compressed by 2-stage compressor (AC201) in order to up the pressure to 30 bar as the required condition of CO_2 removal unit. The compressed gas product as stream<A208> is cooled down with after cooler AE203 resulting in stream<A209>. Some of water, stream<A210> is condensed and discharged to the storage, and then the gas stream is passed through the CO_2 absorption tower T401.

After passing through the CO_2 removal unit, the gas product stream<401> is combined with product from shell side in D102 before going through the separation unit.

Section 4: The Separation unit

Combined gas product as stream <301> is delivered to the light gas column T301. The overhead column consists of methane, hydrogen, and carbon monoxide as stream<302> and condensed in overhead condenser E301B. The coolant used in condenser E301B is hydrogen expanded, which obtain from the F-T process, from 20 bar to 5 bar. This is because the overhead gas temperature is quite low, around –130 C. and expanded H_2 can be used as refrigerant. The temperature of H_2 expanded is around –250 C. The light gas product consists of methane; hydrogen and carbon monoxide will be delivered to further separate and feedback like the circulation feed stock of F-T process. At the bottom of light gas separation column, stream<305> is fed through the ethylene column; T302.This column is used to separate ethylene out from the mixture between propane and propylene. Overhead stream as <306> is condensed by E302B, and reflux stream as stream<307> can be used for purity adjust. The condenser of this column uses part of ethylene product as refrigerant itself, by passing through expansion valve. This is because at the top column, the temperature is around –40 C. Ethylene after expansion valve will be reach to –70 C that can be used to condense the overhead gas. At the bottom of product, stream<309> is the mixture of propane and propylene. This stream is combined with the liquid product from D101 as stream<A109>. Then the total combination flow stream <310> will be fed to the last column, to separate propane and propylene. The last distillation column,T303, normally is quite tall and need more stages because the boiling temperature of propane and propylene are quite near each other. Propane and propylene have similar boiling points,(propane: -42.1 C, propylene, -47.7 C) and as a result separation of these compounds requires highly complicated units. Mixture stream<310> is fed to T303. Overhead gas from T303 is propylene at temperature around 35 C. E303B and E303A re used as condenser and reboiler, respectively. This normal design require more energy and loss work could be happened. In this design, we proposed to use process heat pump as showed in Figure 5.2.2. (See also Appendix C.5).

From Figure 5.2.2, the overhead gas is condensed by E303B, which use part of propylene product as heat pump process referring to Appendix C.5. After heat pump, propylene will be used as the heating media for reboiler, E303A. Propylene product as stream<313> will be transferred to the storage tank as the final product. At the bottom of this column, propane will be recycle to be like a feed stock stream <314> after treating the trace of water remained, stream <314-W>. The standard of water dryer in dash-line in PFS will not be explained in this design.

Section 5: CO_2 Removal unit

As mentioned above, the gas products after condensing the water out in AE204 and AE203, before combining with the gas product from shell side in D102, gas product stream<209> should be treated for removing CO_2 in this section, so this stream<209> is fed to the absorption tower, T401, which is controlled operating pressure at 30 bars by manipulating the gas outlet stream <401>. This operating condition is simple condition in the industry currently. The gas stream<209> is contacted with MDEA solution stream<403>, which is already regenerated from T402. For the regeneration of MDEA, spent MDEA stream<404> is fed to the stripper column, T402, which is operate at 1 bar. Spent MDEA is stripped by E402, which control the stripping temperature condition by hot water. After stripping the CO_2 gas will vaporize to the top of column, T402 as stream<402>. At the bottom of column, treated MDEA temperature is around 100 C is cooled down by E401 before delivering to the MDEA solution buffer drum, D401, and feeding to T401 as the cycle via P403. After operating for some time, MDEA solution need to be topped up and used continuously.

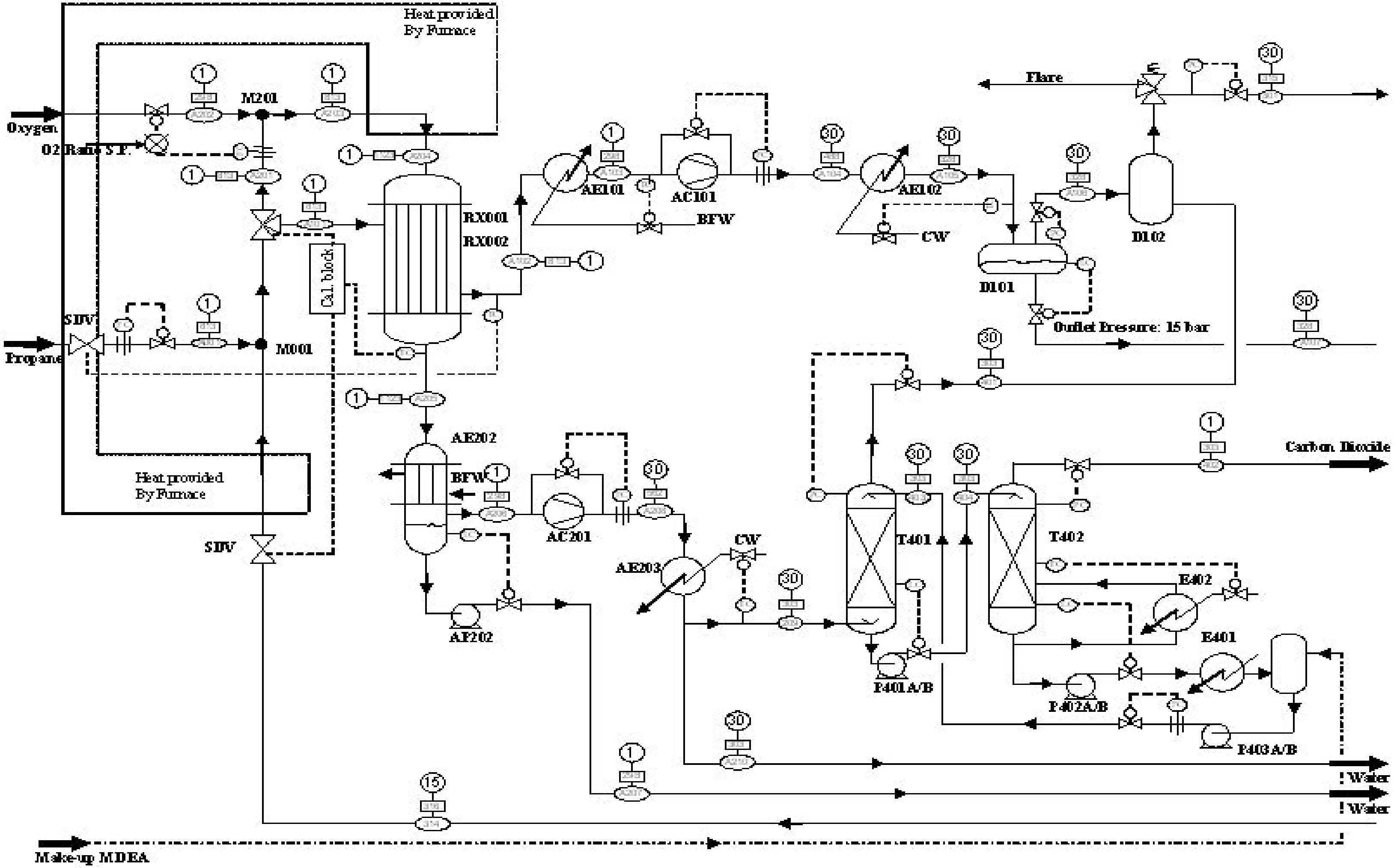

Figure 5.2.1 *Process Flow Schemes*

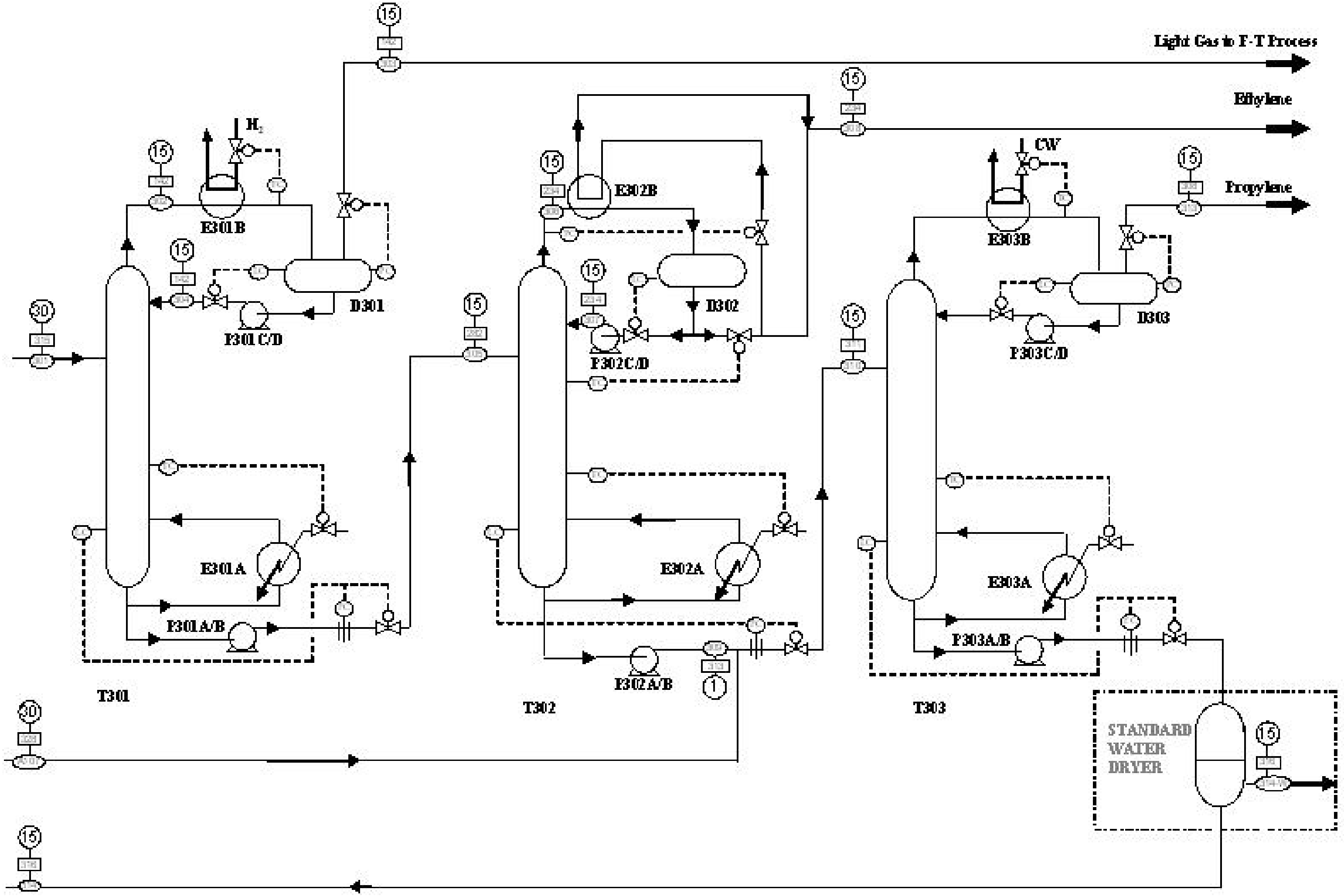

Figure 5.2.1 *Process Flow Schemes (con't)*

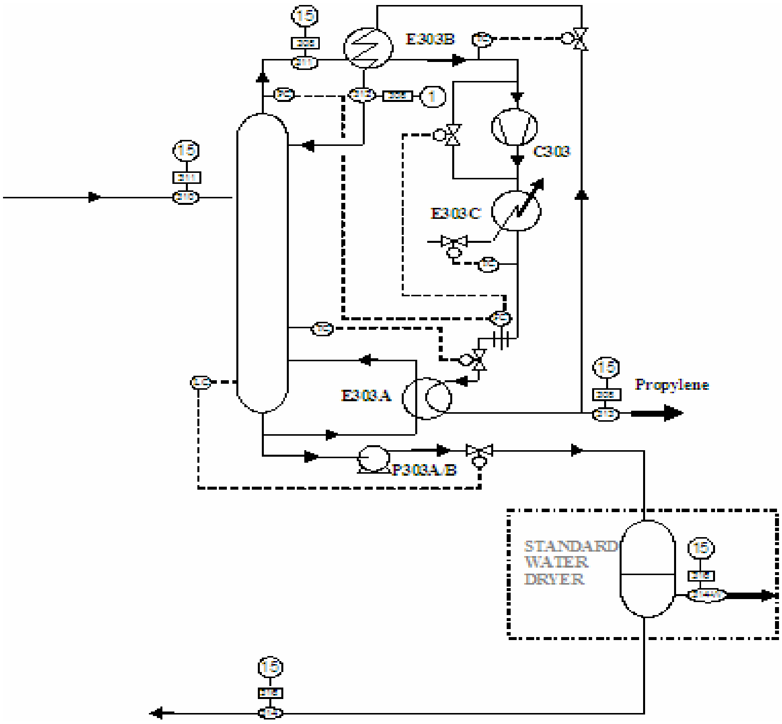

Figure 5.2.2. *Heat pump process for T303*

5.3 *Utilities*

As mentioned before in BOD part, utilities which are required for the alkenes production are cooling water, hot water and electricity. Utilities are one of the most significant factors in production cost. For the economic evaluation, a detail calculation of utilities is needed. The utilities requirement is referred to the process flow scheme Because the process flow scheme is more advanced that the Aspen Plus simulation,. Utilities consumption is summarized in Table 5.3.1. the more detailed utility requirement is presented in Table 5.3.2. The utilities of the process with heat integration can be found in Appendix H.2.

Fortunately, some of utility requirements can be fulfilled by the steams in The alkenes and the FT plant. At E-01B, the H_2 expanded is used as refrigerant.

At 302B. The Ethylene is used as refrigerant. In addition, the big energy requirement in Propylene splitter (T-303) can be solved by application of heat pump.

Table 5.3.1.*Utilities consumption summary*

Utilities	Consumption
Cooling water	387 ton/h
Hot water	1,004 ton/h
Electricity	42,344 kW

Table 5.3.2.*Summary of utilities*

SUMMARY OF UTILITIES															
EQUIPMENT		UTILITIES													REMARKS
Nr.	Name	Heating					Cooling				Power				
		Load	Consumption (t/h)				Load	Consumption (t/h)			Actual	Consumption (t/h, kWh/h)			
			Steam			Hot		Cooling	Air	Refrig.	Load	Steam (t/h)		Electr.	
		kW	LP	MP	HP	Water	kW	Water			kW	HP	MP	kWh/h	
AE202	Gas Product Cooler						20,727	37							[1] At E-301B, the H2 expanded is used as refrigerant [2] At 302B. The Ethylene is used as refrigerant [3] Energy requirement at E303A & E303B is fulfilled by heat pump
AE203	Gas Product Cooler						4,970	19							
AE101	Gas Product Cooler						14,722	55		3.6					
AE102	Gas Product Cooler						4,140	44							
E301A	Light Gas Column Reboiler	1,515				87									
E301B	Light Gas Column Condenser						7,290			[1]					
E302A	C2 Column Reboiler					263	4,601								
E302B	C2 Column Condenser						3,954			[2]					
E303A	C3 Column Reboiler	61								[3]					
E303B	C3 Column Condenser						604			[3]					
E303C	Heat Compresor after cooler						543	93							
E402	Stripper Column	34,377				655									
E401	MDEA cooler						8,132	139							
AE201	Feed Heater (Furnace)	32,912									32,912				

Table 5.3.2.*Summary of utilities (con't)*

SUMMARY OF UTILITIES															
EQUIPMENT		UTILITIES													REMARKS
Nr.	Name	Heating					Cooling				Power				
		Load kW	Consumption (t/h)				Load kW	Consumption (t/h)			Actual Load kW	Consumption (t/h, kWh/h)			
			Steam			Hot Water		Cooling Water	Air	Refrig.		Steam (t/h)		Electr. kWh/h	
			LP	MP	HP							HP	MP		
C101	Shell Product Compressor										4,171				
C201	Tube Product Compressor										4,516				
C303	Propylene heat Compressor										670				
P301 A/B	T301Bottom pump										6.25				
P301C/D	T301Reflux pump										7.31				
P101A/B	Process water pump1										0.25				
P102A/B	Process water pump2										0.25				
P103A/B	Process water pump3										0.25				
P401A/B	T401Bottom pump										4.50				
P402A/B	MDEA recycle pump										4.50				
P302A/B	T302Bottom pump										30.00				
P302C/D	T302Reflux pump										6.00				
P303A/B	T303Bottom pump										7.00				
P401A/B	T401Bottom pump										4.50				
P402A/B	MDEA recycle pump	68,865									4.50				
TOTAL		137,370	0	0	0	1,004	69,683	387	0	0	42,344	0	0	[1]	

5.4 Process Yields

Process yield shows the relation of utilities and amount of product. The stream yields are shown in table 5.4.1, and the utilities yields are shown in table 5.4.2. See Figure 5.4 for the Utilities summary.

Table 5.4.1.*Stream yields*

Process Streams							
Name	Ref. Stream	kg/s		t/h		t/t alkenes	
		IN	OUT	IN	OUT	IN	OUT
Feed							
Propane	<A001>	7.45		26.8			
Propylene	<A001>	0.79		2.8			
Oxygen	<A202>	1.79		6.4			
Nitrogen	<A202>	0.08		0.3			
Subtotal		10.11		36.4		1.44	
Alkenes products							
Ethylene	<308>		2.26		8.136		
	<303>		0.03		0.108		
Propylene	<313>		4.71		16.956		
	<308>		0.01		0.036		
Subtotal			7.01		25.236		1.00
None Alkenes products							
Methane	<303>		0.58		2.088		
Hydrogen	<303>		0.16		0.576		
Carbon monoxide	<303>		0.62		2.232		
Carbon dioxide	<402>		0.16		0.576		
	<308>		0.02		0.072		
Water	<A207>		1.36		4.896		
	<A210>		0.1		0.360		
	<314-W>		0.01		0.036		
Nitrogen	<308>		0.08		0.288		
Subtotal			3.08		11.1		0.44
Wastes	-	-	-	-	-	-	-
Total		10.11	10.11	36.4	36.4	1.44	1.44

Table 5.4.2. *Utilities yield*

Utilities							
Name	Ref. Stream	kg/s	kW	t/h	kWh/h	t/t alkenes	kWh/t alkenes
Hot water	-	279		1004		39.8	
Cooling water	-	108		387		15.4	
Electricity	-		42344		42344		1680

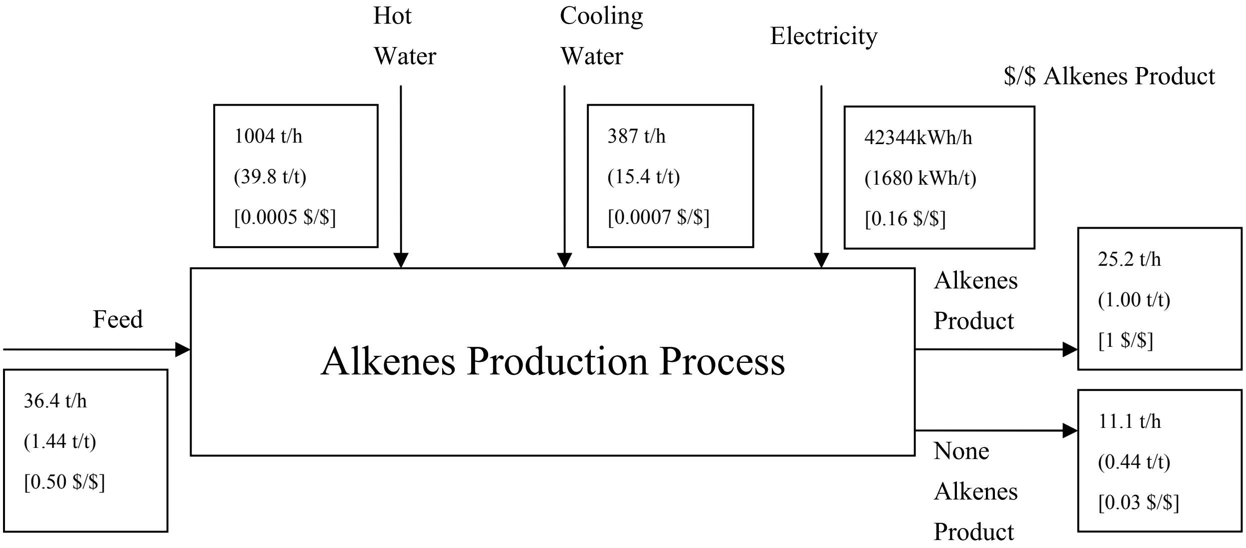

Figure 5.4.*Process yields summary*

6 Process Control

To achieve the controllability of process, control loops are chosen and positioned from a process point of view. For control system design concept of this process, the designers focus on

- Keep the control system as simple as possible like feed forward, feed back controller
- Use feed forward to compensate for large, sequent and measurable disturbances
- Use override control to operate at or to avoid constraints.
- Avoid large time lags and dead time in feedback loops.
- In detail controller, use proportional only level controls where the absolute value is not important
- Eliminate disturbances by using cascade control such as the feed control to distillation column by using level of preceding column as the set point of flow control.
- Avoid control loops interaction.
- Check the control system for problems during abnormal conditions, safety point of view is taken into account, so shut down valves and pressure safety valves are installed such as the feed of propane and pressure of D102.
- Avoid nesting control loops

For this process, we divided the process into five sections.
Section 1 : The material feed and preheated , the starting number of equipment and stream is A0
Section 2 : The endothermic reaction, the starting number of equipment and stream is A1
Section 3 : The exothermic reaction, the starting number of equipment and stream is A2
Section 4 : The separation unit, the starting number of equipment and stream is 3
Section 5 : CO_2 Removal unit, the starting number of equipment and stream is 4

6.1 Section 1: The material feed and preheated

In this section, the flow of material, like propane is controlled by flow feed forward control and additionally, in order to control the reaction temperature, which is influence to feed for material. The control calculation block is provided to estimate the flow ratio between shell and tube because the temperature of both reactions interfere each other and can be controlled only each feed to the reactions. For oxygen flow control, because the reaction is oxygen limited, so oxygen is set by the set point of ratio between propane fed to tube reactor.

6.2 Section 2 : The endothermic reaction

In this section, the most important controller is to control the temperature of reaction, which adjusts the feed of material. If the reaction temperature is out of set point, the temperature transmitter will send the measurement to calculation block and adjust the material ratio between shell and tube. At here, for the flow control, we propose to use the type of micro motion to control the flow because this type gives most accuracy. The gas product from shell will be up the pressure from 1 bar to 30 bar by compressor in order to separate the heavier like propane and propylene out first. Normally, the outlet of pressure driving equipment like compressor is constant, so flow after compressor is controlled by adjusting the by pass of compressor. For the temperature control in the whole process, the concept used here is to control the flow inlet of cooling media like feed back control. The gas product combination between shell and tube in D102 is pressure control, if pressure is to high, the load of separation will be increase by opening the control valve on stream<301>. In case of pressure increasing drastically, in safety point of view, the safety valve is provided on D102 discharged to flare system. In emergency case, temperature of reaction becomes run away, the shut down valves of raw material including recycle stream are provided.

6.3 Section 3 : The exothermic reaction

In this section, The temperature and feed to the tube side reactor are similar to the control in endothermic reaction, but of more by-product produced, then water will be removed from the gas product by the series of heat exchangers that obtain from the heat integration. The water removed from the gas product by controlling the level at the discharge of pump. The gas product is controlled to the pressure 30 bar and 30 ^{o}C in order to deliver further to the CO_2 removal unit. In emergency case, temperature of reaction becomes run away, the shut down valves of raw material including recycle stream are provided.

The temperature control for tube reactor side is meticulously considered, because in fact there would be the profile of temperature inside tube reactor, Selective control is used. The scheme of selective is depicted as the figure 6.3.

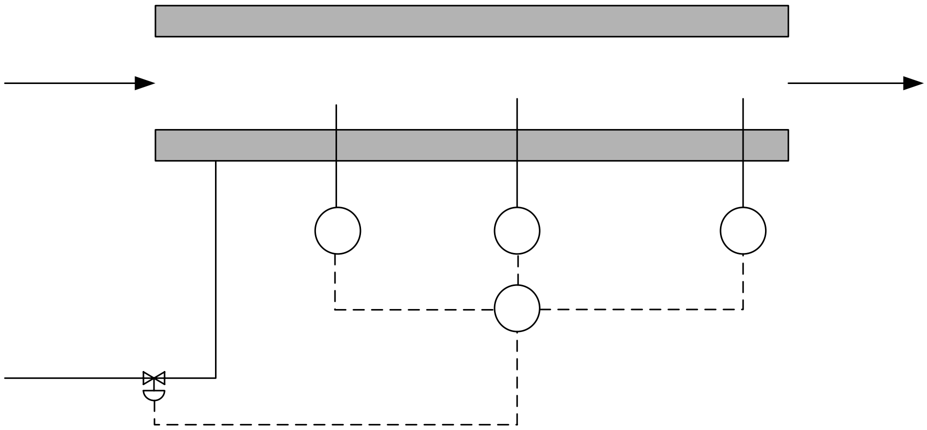

Figure 6.3. *Scheme of temperature control for tubular reactor*

6.4 Section 4 : Separation section

In this section, there are 3 columns in the process, distillation normally control the product specification by reflux ratio. The reflux of distillation columns are controlled by the ratio control The temperature of top column and bottom can be controlled by adjusting flow of cooling and heating media. Especially, for the distillation column of propane and propylene we design with heat compressor and use propylene as the coolant media. Feed to the distillation columns, are controlled by feed forward controlled. Especially in T301, which the feed to this column is vapor, the feed stream is pressure control from D102.

6.5 Section 5 : CO2 Removal unit

From the reaction of exothermic, CO_2 is produced as by-product. There are two columns used in this section, one for absorber and the other for regenerator. MDEA, which is used for absorbed solution, is controlled to the absorption column by feed forward flow control. Both columns are pressure control at the operating condition. The temperature of the stripping column is control as simple way, feed back to adjusting the steam flow.

All sections are controlled and constructed in the Process Flow Scheme, See the Figure 5.2.1 and Figure 5.2.2.

7 Mass and Heat Balances

Mass and Heat Balance, basically are the imperative tools for the process designers, to be a check measure of the design. Mass and Heat Balance are the simulation results of Aspen Plus. In this chapter, the briefly mass and heat balance are presented, while the lengthy table like stream summary will be showed in Appendix D. (Also see Appendix H.3 for the mass and heat balances of the process with Heat integration).

7.1 Practical Aspects

To show the result of practical aspects, the summary of Mass and Heat Balance Total Streams are showed in Table7.1. The result shows the reasonable both mass and heat balance. Special attention is paid for heat balance, as the tendency of imbalance is higher. From Table 7.1, the imbalance of heat could be from the compressor that input energy of its in fact is power supplied and efficiency of compressor is not 100%. The Overall Component Mass Balance & Stream Heat balance and checked table are presented in Table7.2 and Table 7.3.

7.2 Balance for Total Streams

The mass and heat balance of the total streams for individual equipments are presented in Table7.1. In the table, it consists of 4 parts, which are in put of the total plant, input of specific equipment, output of specific equipment and output of total plant.

In Table 7.1, positive heat in to the plant means heating is required while positive out of the plant means cooling is required. At the end of table7.1, we find that total mass is balance and heat is 0.05 % different.

7.3 Balance for Stream Components

For the process, to check design whether it is correct or not, it is also need to balance the components of all used in the process. Stream component balance is showed in Table 7.2. As the reactions are occurred in the process, difference between input and output for every component is not zero depending on conversion. However the difference between the total input streams and total output streams remains zero.

For consistency of heat balance, the difference between stream enthalpy entering and leaving the plant should be equal to the difference between heating and cooling requirements. Heat balance checked is presented in Table7.3.

Table 7.1 *The summary of Mass and Heat Balance Total Streams*

IN					Equipm. Identif.	OUT				
Plant		EQUIPMENT				EQUIPMENT			Plant	
Mass kg/s	Heat kW	Mass kg/s	Heat kW	Stream Nr.		Stream Nr.	Mass kg/s	Heat kW	Mass kg/s	Heat kW
8.23	**-5975**	8.23	-5975	<A001>	**M001**	<A101>	10.84	-7900		
		9.83	-7193	<314>		<A201>	7.23	-5267		
		18.07	-13167		Total		18.07	-13167		
		7.23	-5267	<A201>	**M201**	<A203>	9.10	-4308		
1.87	**959**	1.87	959	<A202>						
		9.10	-4308		Total		9.10	-4308		
		9.10	4957	<A204>	**RX001**	<A205>	9.10	-4243		
								9200		**9200**
		9.10	4957		Total		9.10	4957		
		10.84	-7900	<A101>	**RX002**	<A102>	10.84	-1247		
	6653		6653							
		10.84	-1247		Total		10.84	-1247		
		14.88	-14585	<301>	**T301**	<303>	1.47	-5786	1.47	**-5786**
						<305>	13.42	-14573		
	1515		1515		**E301A**					
					E301B			7290		**7290**
		14.88	-13069		Total		14.88	-13069		
		13.42	-14573	<305>	**T302**	<308>	2.29	2994	2.29	**2994**
						<309>	11.12	-16920		
	4601		4601		**E302A**					
					E302B			3954		**3954**
		13.42	-9972		Total		13.42	-9971		
		14.56	-23305	<310>	**T303**	<313>	4.72	2093	4.72	**2093**
						<314>	9.83	-24058		
	33509		33509		**E303A**					
					E303B			32169		**32169**
		14.56	10204		Total		14.55	10204		
		10.84	-16528	<A103>	**C101**	<A104>	10.84	-12344		
	4170		**4170**							
		10.84	-12357		Total		10.84	-12344		
		10.84	-1247	<102>	**E101**	<103>	10.84	-16528		
								15280		**15280**
		10.84	-1247		Total		10.84	-1247		
		10.84	-12344	<A104>	**E102**	<A105>	10.84	-17475		
								5131		**5131**
		10.84	-12344		Total		10.84	-12344		
		10.84	-17475	<A105>	**D101**	<A106>	7.40	-11090		
						<A107>	3.43	-6385		
		10.84	-17475		Total		18.24	-17475		
		9.10	-4308	<203>	**E201**	<204>	9.10	4957		
	9265		9265							
		9.10	4957		Total		27.34	4957		

***Table7.1** The summary of Mass and Heat Balance Total Streams(con't)*

IN						OUT				
Plant		EQUIPMENT			Equipm. Identif.	EQUIPMENT			Plant	
Mass kg/s	Heat kW	Mass kg/s	Heat kW	Stream Nr.		Stream Nr.	Mass kg/s	Heat kW	Mass kg/s	Heat kW
		9.10	-4243	<A205>	**E202**	<A206>	7.74	-6063		
						<A207>	1.36	-21804	1.36	**-21804**
								23624		**23624**
		9.10	-4243		Total		9.10	-4243		
		7.74	-1533	<A208>	**E203**	<A209>	7.64	-4946		
						<A210>	0.10	-1665	0.10	**-1665**
								5078		**5078**
		7.74	-1533		Total		7.74	-1533		
		7.64	-4946	<A209>	**D201**	<401>	7.48	-3494		
						<402>	0.16	-1451	0.16	**-1451**
		7.64	-4946		Total		7.64	-4946		
		9.84	-24058	<311>	**D302**	<312>	9.83	-20911		
						<313>	0.01	-168	0.01	**-168**
	2979		2979							
		9.84	-21079		Total		9.84	-21079		
		9.83	-20911	<312>	**E301**	<314>	9.83	-7193		
	13718		13718							
		19.67	-7193		Total		19.67	-7193		
10.11	63668								10.11	63638
									0.00	**-30**

***Table7.2.** Overall Component Mass Balance & Stream Heat balance*

Overall Component Mass Balance & Stream Heat balance							
STREAM Nr. :		A001+A202		A207+A210+A212+303+308+313+314W			OUT-IN
Name :		Total Plant	IN	Total Plant	OUT	Total Plant	
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
Propane	44	7.45	0.1692	0.00	0.0001	-7.44	-0.1691
Oxygen	32	1.79	0.0559	0.00	0.0000	-1.79	-0.0559
Ethylene	28	0.00	0.0000	2.29	0.0819	2.29	0.0819
Propylene	42	0.79	0.0188	4.72	0.1125	3.93	0.0937
Carbonmon-oxide	28	0.00	0.0000	0.62	0.0223	0.62	0.0223
Carbondi-oxide	44	0.00	0.0000	0.18	0.0040	0.18	0.0040
Methane	16	0.00	0.0000	0.58	0.0361	0.58	0.0361
Hydrogen	2	0.00	0.0000	0.16	0.0780	0.16	0.0780
Water	18	0.00	0.0000	1.47	0.0817	1.47	0.0817
Nitrogen	28	0.08	0.0029	0.08	0.0029	0.00	0.0000
Total		10.11	0.2439	10.11	0.4165	0.00	
Press.	Bara						
Temp	oC						
Enthalpy	kW	-5015		-25,787			

Table7.3.*Heat Balance Check*

	Input	Output
difference (kw)	-30	
difference (%)	0.108	

8 Process and Equipment Design

8.1 Integration by Process Simulation

8.1.1 Encountered problems and solution

Aspen Plus is the simulation program used as primary tool for this project. The most important thing when using this program to approach the accuracy is selection of model for process simulation. Aspen Plus can provide the different property methods, thus it is necessary to make the right choice. However, during working on this process simulation, the problems were certainly encountered with this tool even choosing the properly model such as availability of physical and chemical properties in some specific condition. The report of component property sometimes is not consistency, that we could not get some information in the same time. And, the tremendous problem of process simulation is that the result of simulation could not get the convergent value during simulating in loop. This problem consumed too much time to achieve the result. Moreover, even we got the convergent result from simulating, and then we would modify something like changing the feed composition or changing the process conditions. The result of simulation could not be kept on the convergent condition.

To achieve the convergent result in loop simulation, we used a way to solve this problem by opening the loop simulation and add one more stream to that object we put for recycle, and manual simulate that stream until getting the same result of real recycle. After that, connect that stream and run again. Another problem like changing some process condition and then could not get the convergent result can be solved by starting the unit one by one. It could save time compared to changing the condition directly.

The status of simulation result showed ‘Result available without warning’ because we set up all of components used in the process for any streams, and the reaction we put in reactor configuration needed oxygen, in fact oxygen was limited or completely reacted in the reaction, so no oxygen left in the process and that’s why the status of simulation still keep warning.

8.1.2 Component and model settings

Before simulation, it is necessary to set up the components used in the process simulation. In this process, the total components are propane, oxygen, nitrogen, ethylene, propylene, methane, hydrogen, water, carbon dioxide, carbon monoxide and MDEA. They all exist in the Aspen Plus databanks.

The properties of these components are compatible with literature that mentioned in Chapter4. And then, the next step to simulate is to set up the model to be used. This process consists of hydrocarbons. So the model used is one of the equations of state method (EOS). The equation of state is used to describe both liquid and vapor phase behavior. One equation relating pressure, volume and temperature (usually explicit in pressure) is used to calculate thermodynamic properties (using the symmetric form of Kj). This method is applicable for systems where the interaction of the components in the liquid phase is assumed to be minimal. This is for most hydrocarbon systems at high and moderate pressure and temperature. In this process, Peng- Robinson model should not be used, since this model may not predict the boiling temperature as precise when components have close boiling point in the system (here are propane and propylene). Thereby, in this process simulation we used Redlich-Kwong model.

8.1.3 Setting of units

This process simulation started with feed setting and the unit operation is set up one by one according to the process description mentioned in Chapter 5. The main equipments were set up step by step. The whole process simulation sheet is presented in Appendix E.1.

8.1.3.1 Reactors

Since the novel type of reactor, Shell and Tube reactor; is proposed, it was not available in the equipment list of Aspen Plus. So, this problem is solved by making it into two reactors separately, one for endothermic reaction and the other one for exothermic reaction. For both reactions, it is known that the result of the reaction which informs the ratio of each product produced and reactants used. Hence, the reactor model selected was RStoic. Configure the specification and reaction to each reactor is necessary. The summary of reactor configuration is presented in Table 8.1.3.1a-b.

***Table 8.1.3.1a**. Setting of reactor RX-ENDO*

Reactor	RX-ENDO
Temperature (^{o}C)	540
Pressure (bar)	1
Fraction conversion	$C_3H_8 \rightarrow 0.002C_2H_4 + 0.002CH_4 + 0.998C_3H_6 + 0.998H_2$

***Table 8.1.3.1b**. Setting of reactor RX-EXO*

Reactor	RX-EXO
Temperature (^{o}C)	850
Pressure (bar)	1
Fraction conversion	$C_3H_8 + 0.4759O_2 \rightarrow 0.6946C_2H_4 + 0.3053CH_4 + 0.3607C_3H_6$ $+0.2236H_2 + 0.6945H_2O + 0.1894CO + 0.0339CO_2$

Furthermore, in this project purpose, to exchange the reaction heat between endothermic and exothermic reaction, the design spec tool should be used. Heat exchange from both reactors could be set as equal each other produced or consumed. The design spec and parameter varied are presented in Table 8.1.3.1c.

***Table 8.1.3.1c.** The design spec for the reactor*

Define	H1 : heat duty of endothermic reaction
	H2 : heat duty of exothermic reaction
Criteria	H1-H2 = 0
Varied parameter	Flow of stream 101, propane to shell reactor

8.1.3.2 Distillation columns

There are three main columns in the process, which are light gas column (T301), ethylene column (T302), and propylene column (T303). They were all started simulation first with the shortcut distillation column to obtain the main parameters like number of tray and reflux ratio. Then, to simulate rigorously, the model of RadFrac would be used further. After that, to achieve the specification of product, design spec would be set as well as the pack column sizing. The summaries of the column configurations are presented in Table 8.1.3.2 and total results of simulations are presented in Appendix E.2.

Table 8.1.3.2. *The summaries of column configuration*

Column	T301		T302		T303	
	Top stage	Bottom stage	Top stage	Bottom stage	Top stage	Bottom stage
Temp. (^{o}C)	-131	9.5	-39	39.9	34.8	42.7
Heat duty (kw)	-7,290	1,515	-3,954	4,601	-32,169	33,508
Reflux ratio	4.1	-	3.8	-	21.13	-
Boil up ratio	-	0.3	-	1.33	-	11.15

8.1.3.3 Heat Exchangers

For cooler, heaters, heat exchangers in the process were set with ‘Heater’ in Aspen Plus. Heater is thermal and phase state changer. The summary of all heat exchanger setting is presented in Table 8.1.3.3.

Table 8.1.3.3. *Heat exchanger setting*

Heat exchanger	Temperature (C)	Pressure (bar)	Heat duty (kw)
AE101	25	1	-
AE102	55	30	-
AE201	850	1	-
AE202	25	1	-
AE203	30	30	-
E301	540	1	-

8.1.3.4 Compressors

For the compressors, some required specifications depend on the compressor type. This stage; we would get the power, BHP, to drive the gas to required discharge. In Aspen Plus, to model an isentropic compressor, it provides either the GPSA, ASME method. However, normally the ASME method is more rigorous than the GPSA method for polytropic or isentropic compressor calculations. So, set the required discharge pressure is set by using model of isentropic using ASME method and estimate the power required as presented in the Table 8.1.3.4.

Table 8.1.3.4. *Summary of compressor results*

Compressor	Suction Pres. (bar)	Discharge Press.(bar)	Brake Horsepower (kw)	Efficiency (%)
C101	1	30	4170	72
C201	1	30	4516	72
C303	15	17	938	72

8.1.3.5 CO_2 Removal unit

For this unit, in fact there are two columns to be set as absorption column and stripping column. Unfortunately, the MDEA, which is used as the absorption solvent, is perhaps not enough information in Databank, and the chemical kinetic of absorption should be known to configure the system, resulting in high flow rate of MDEA solution used and not reasonable result,. Hence, we design this unit in flow sheet simulation with Sep2 [4] by putting the fraction of CO_2 after separation in the block input, instead.

8.2 Equipment Selection and Design

8.2.1 Reactor

In this process, the Shell and Tube Reactor is proposed to apply for combination of endothermic and exothermic reactions. The design of this type of reactor is based on plug flow reaction both sides. The summary of reactor design is presented in Table 8.2.1. For the lengthy calculation of this design, it can be found in Appendix E.3.

Table 8.2.1*. The summary of Reactor design*

Side	Reactor dimension					Operating		Catalyst		
	Height (m)	Dia. (m)	Surf. Area (m^2)	Vol. (m^3)	No.	Temp. (°C)	Press. (bar)	Type	Sphere Shape (mm)	Amount (kg)
Shell	6.41	1.63	121	4.45	1	540	1.0	Pt. On zeolite	5	3,300
Tube	6.41	0.30	121	9.06	20	850	1.0	V_2O_5	5	

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[4] Dr. ir. C. Sorin Bildea , personal communication

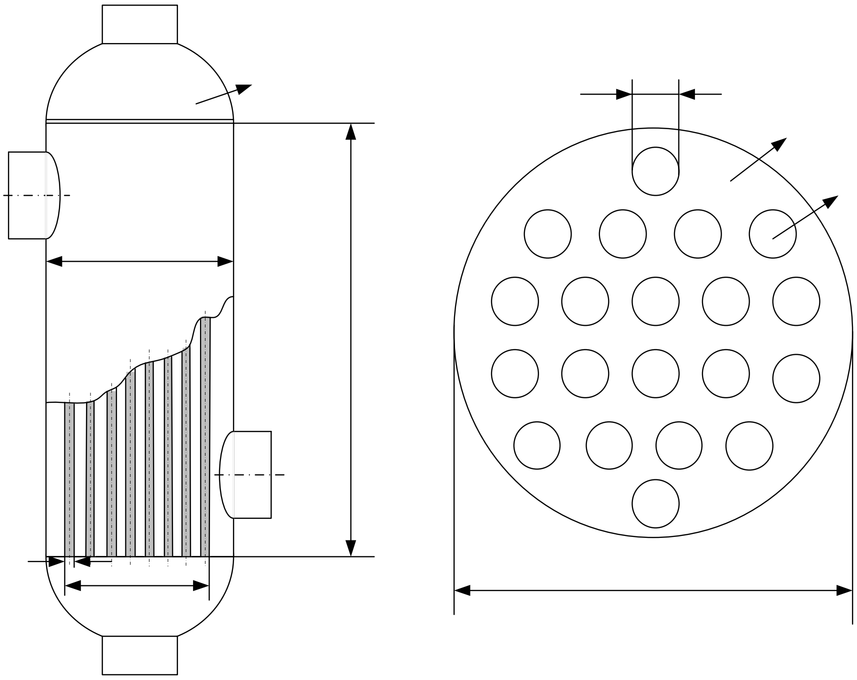


__Figure 8.2.1.__ Scheme of shell and tube reactor

The operation temperature of this reactor is 540°C (shell side) and 850 °C

8.2.2 Heat Exchanger

There are three types of heat exchangers used in this process, which are coolers, condensers, and reboilers. The detail calculation is quite complicated in case of precisely designing. A lot of information needed and also iterative and check back calculation needed. The elaborate design is showed in Appendix E.4 for instance. In this conceptual design stage, the heat exchangers are designed by estimating heat transfer coefficient. Other important parameters like temperature in and out of streams, for shell and tube side the value of logarithm mean of temperature difference can be calculated. For heat duty of each heat exchanger, it is a bit different from the mass and heat balance because this calculation, mass and average of Cp between in and out of stream to the heat exchanger are used to calculate heat duty. The summaries of heat exchanger design are showed in Table 8.2.2.

D=1.6

Table 8.2.2 The summaries of heat exchanger design.

Heat Exchanger	Heat duty (kW)	U ($W/m^2\ ^oC$)	Delta Tlm (^oC)	Area (m^2)
AE101	14,722	450	70	621
AE102	4,140	450	71	172
AE202	20,727	450	81	756
AE203	4,970	450	27	538
E301A	1,515	500	48	85
E301B	7,290	100	92	1,060
E302A	4,601	500	17	733
E302B	3,954	300	33	526
E303A	61	400	0.19	1,073
E303B	604	400	4	503
E303C	543	1,000	5	145
E401	8,132	1,000	23	464
E402	34,377	1,000	44	1,034

8.2.3 Separation column (T301, T302, T303)

T301 and T302 are multi-component systems; however, the presence of the other components does not significantly affect the volatility of the key components. Therefore, the keys can be treated as a pseudo-binary system.

The design procedure of packed columns for given flow rates and properties of gas (vapor) and liquid can be summarized as below,

1. Column diameter is established, based on the type and size of chosen packing.
2. Column height/efficiency is estimated, based on mass transfer as well as fluid mechanics relationships.
3. Pressure drop over the whole bed is calculated/checked.

For random packing a generalized method is available and for structured packing the proprietary correlations provide the best basis. And a fixed pressure drop per unit bed length is taken as outgoing point. Normally the range for distillation is 4-8 mbar/m. we want the pressure drop as small as possible, so at here we set the pressure drop to be 4.1mbar/m.

8.2.3.1 Column diameter estimation

For given flow rates and properties of gas (vapor) and liquid at a given location, the diameter of the column can be calculate by,

$$d_c = \sqrt{\frac{4}{\pi}\frac{M_G}{\rho_G \mu_{G,oper}}} = \sqrt{\frac{4}{\pi}\frac{M_G}{F_{G,oper}\sqrt{\rho_G}}} \qquad (8.2.3.1a)$$

In which M is mass flow rate and ρ is the flow density. The mass flow rates are known and density can be found in Chemical properties handbook.

$F_{G,oper}$ is the operating gas load, it can be calculate by:

$$F_{G,oper} = \sqrt{\frac{C_{rp}(\rho_L - \rho_G)}{13F_{rp}\left(\frac{\mu_L}{\rho_L}\right)^{0.1}}} \qquad (8.2.3.1b)$$

In which, C_{rp} is an empirical capacity factor expressed usually as a function of the flow parameter and the chosen operating pressure drop. μ_L is the viscosity of liquid, which can be found in chemical handbooks.

F_{rp} is characteristic packing factor (constant).

The flow parameter F_{LG} can be calculated by:

$$F_{LG} = \frac{M_L}{M_G}\sqrt{\frac{\rho_G}{\rho_L}} \qquad (8.2.3.1c)$$

With the F_{LG} value, the C_{rp} value can be read in Figure 8.2.3.1, capacity factor correlation.

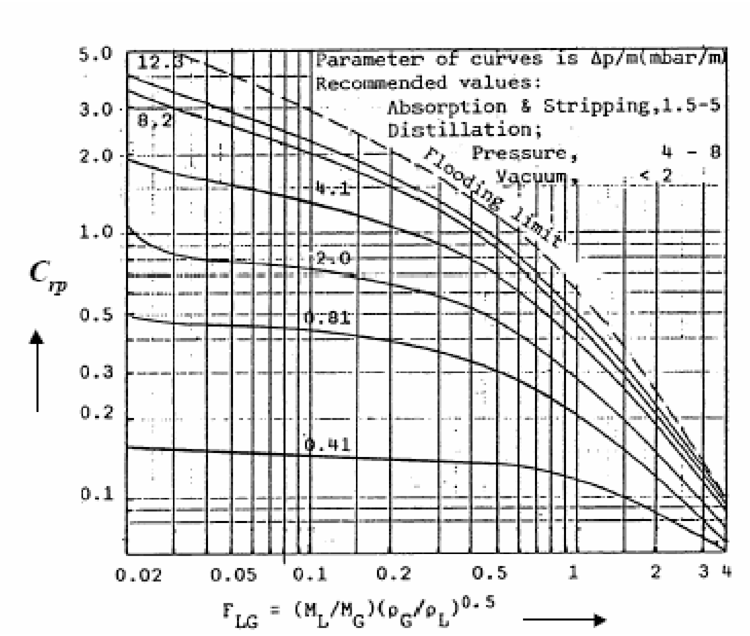
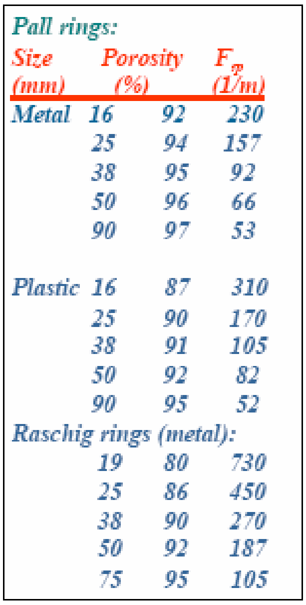


__Figure 8.2.3.1.__ Capacity factor correlation

Select metal pall rings as packing material, packing size 50mm.

Read from Table 8.2.3.1, F_{rp} of 50mm size pall rings is 66m^{-1}.

Table 8.2.3.1. *Characteristic packing factor correlation of pall rings*



Pall rings:	Size (mm)	Porosity (%)	F_{rp} (1/m)
Metal	16	92	230
	25	94	157
	38	95	92
	50	96	66
	90	97	53
Plastic	16	87	310
	25	90	170
	38	91	105
	50	92	82
	90	95	52
Raschig rings (metal):			
	19	80	730
	25	86	450
	38	90	270
	50	92	187
	75	95	105

All the parameters in equation 8.2.3.1b are known till now, and then $F_{G,oper}$ can be calculate by equation 8.2.3.1b.

$$F_{G,oper} = \sqrt{\frac{C_{rp}(\rho_L - \rho_G)}{13F_{rp}\left(\frac{\mu_L}{\rho_L}\right)^{0.1}}}$$

Therefore, the diameter can be derived by equation 8.2.3.1c.

8.2.3.2 Column height estimation

According to the HETP data source and *Rule-of-Thumb* values, when packing size =50mm, HETP=0.85m. See Table 8.2.3.2.

Table 8.2.3.2.*Rule-of-thumb values**

Packing size [mm]	HETP [m]
25	0.50
38	0.65
50	0.85
70	>1.0

*Valid for Raschig and Pall rings in distillation, with moderate values of surface tension, low viscosities, and a pressure drop below 6mbar/m.

$$HETP(m) = \frac{height\ of\ packing}{number\ of\ theoretical\ trays}$$

$$\Rightarrow height\ of\ packing = HETP \times N_T$$

8.2.3.3 Pressure drop

The overall pressure drop can be calculated by:

$$\Delta P = \mathrm{Pr}\,essure\ drop \times height\ of\ packing$$

8.2.3.4 Aspen Plus Sizing

In sizing mode, Aspen Plus determines the column section diameter from:

- The approach to the maximum capacity
- A design capacity factor one specify

One can impose a maximum pressure drop per unit height (of packing or per section) as an additional constraint. Once Aspen Plus has determined the column section diameter, it re-rates the stages in the section with the calculated diameter.

In calculation of the maximum capacity, Aspen Plus provides several methods for maximum capacity calculations. For random packing of pall ring, Eckert method is used at here.

The capacity factor is:

$$CS = VS\sqrt{\frac{\rho_V}{\rho_L - \rho_V}}$$

Where:

CS = Capacity factor
VS = Superficial velocity of vapor to packing
ρ_V = Density of vapor to packing
ρ_L = Density of liquid from packing

See Appendix E.5 for the detailed calculation of column T302. T301 and T303 are calculated by the same method. After calculation and simulation from Aspen Plus, the two sizing results are in the same magnitude. The comparison of results is shown in Table 8.2.3.4. At here, we choose the result from Aspen Plus for further calculation.

Table 8.2.3.4. *Comparison of separation column sizing of T302*

	Data from calculation	Data from Aspen Plus
Diameter	1.6 m	1.9 m
HETP	0.85 m	0.85 m
Ideal stage numbers	24	24
Height of column	24m	19m

8.2.4 CO_2 Removal

Due to the environmental effect of CO_2, a CO_2 removal unit is designed in this project. In CO_2 removal unit, packed column is used. The packed material is metal pall rings. 50wt% MDEA solution is applied here as solvent in CO_2 absorption.

Referring to the complicated theory in *Coulson and Richardson, vol.6*, the parameters of unit T401 are derived. The complete calculation is shown in Appendix E.6. The results are summarized as below:

Equipment number: T401
Column diameter: 1.30m
Column height: 17m
Column volume: 22.6m^3

8.2.5 Gas liquid separation

First, the setting velocity of the liquid droplets should be estimated, for the design of separating vessels.

$$u_t = 0.07\left[\left(\rho_L - \rho_v\right)/\rho_v\right]^{1/2} \qquad (8.2.5)$$

where u_t = Settling velocity, m/s
ρ_L = Liquid density, kg/m^3
ρ_V = Vapor density, kg/m^3

In horizontal separator design, the diameter and length, and the liquid level, must be chosen to give sufficient vapor residence time for the liquid droplets to settle out, and for the required liquid hold-up time to be met.

The most economical length to diameter ratio depends on the operating pressure, and the relation is shown in Table 8.2.5.

Table 8.2.5. *Length to diameter ratio depending on operating pressure*

Operating pressure, bar	Length : diameter, L_V/D_V
0-20	3
20-35	4
>35	5

For preliminary design, set the liquid height at half the vessel diameter,

$h_v = D_v / 2$ and $f_v = 0.5$,

where h_V = Height above the liquid level, m
f_v = Fraction of the total cross-sectional area occupied by the vapor

See Appendix E.7 for detailed calculation. The results are shown as below:

Equipment number: D-101	Equipment number: D-301
Vessel diameter: 1.5m.	Vessel diameter: 2.4m.
Vessel length: 6m.	Vessel length: 7.2m.
Vessel volume: 10.6m^3	Vessel volume: 32.6m^3

8.2.6 Buffer tanks

1. D-102 Gas buffer feed drum

Here, two streams: 108 and 401 mix into one stream 301 piped in T-301. A flow control is necessary on stream301 to keep constant inlet flow rate of T-301. However, if two streams mix directly, flow control cannot work well, i.e. the real flow rate changing range will much big and is not easy to control. In order to reduce the range, a buffer tank, D-102 can be set before the control valve. The scheme is designed as Figure 8.2.6.1.

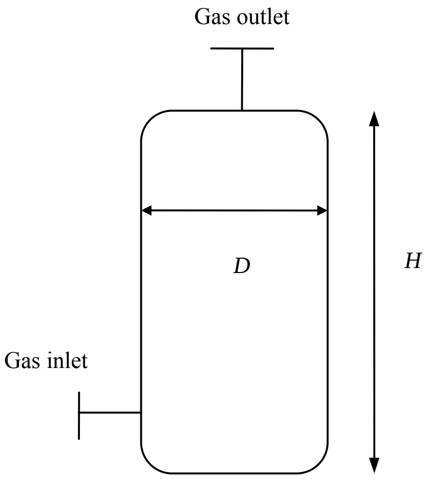


Figure 8.2.6.1 *The scheme of gas buffer tank*

The operating condition of D-102 is at 30bar, 42^{o}C. Carbon steel is applied. The volume of buffer tank mostly depends on the flow rate of streams. In this case, design is based on stream301.

From stream table, the flow rate is 1225.3m^3/hr.

Assume the residence time in vessel is 2 minutes.

The flow volume $V = 1225.3/60*2 = 40.8\ \text{m}^3$

$$V = \pi\frac{D^2}{4}H = \pi\frac{D^2}{4}2D = \pi\frac{D^3}{2} = 40.8\ \text{m}^3$$

Then $D = 2.96\ \text{m}$, round to 3m

$H = 2*3 = 6\ \text{m}$

$$V = \pi \frac{D^2}{4} H = \pi \frac{3^2}{4} 6 = 42.4 \text{ m}^3$$

Result:

Equipment number: D-102
Vessel diameter: 3m.
Vessel length: 6m.
Vessel volume: 42.4m^3

2. D-201 Gas Comp. Suc. Drum

To protect the compressor surged, the suction compressive drum D-201, which is set before compressor, is required. For this capacity, let approximate around 50 m^3.

$$V = \pi \frac{D^2}{4} H = \pi \frac{D^2}{4} 2D = \pi \frac{D^3}{2} = 50 \text{ m}^3$$

Then $D = 3.17 \text{ m}$, round to 3.2m

$$H = 2*3.2 = 6.4 \text{ m}$$

$$V = \pi \frac{D^2}{4} H = \pi \frac{3.2^2}{4} 6.4 = 51.5 \text{ m}^3$$

Result:

Equipment number: D-201
Vessel diameter: 3.2m.
Vessel length: 6.4m.
Vessel volume: 51.5m^3

3. D-302 T302 Reflux Drum

D-302 is used to keep flow rate to be separated into reflux and top stream306 of T302 distillation.

For T-302 distillation, top outlet will be separated as liquid reflux and top product stream306 which go to different destinations. Before separate, a liquid buffer tank will be used, which can make flow control easier and efficient. Figure8.2.6.2 indicates the scheme of this vessel. In distillation process, a horizontal buffer tank is preferred in order to reduce the total height. Assume the length of tank is 2 times of diameter.

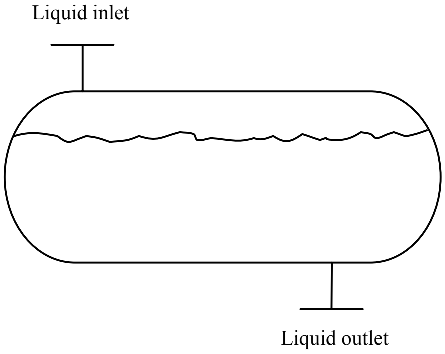


Figure 8.2.6.2 *Scheme of D-302 liquid buffer tank*

The operating condition of D-302 is at 15bar, -39^{o}C. Carbon steel is applied. The design is based on inlet flow.
From Aspen simulation result, the inlet flow rate is 92.255m^3/hr.
Assume the residence time in vessel is 2 minutes.

The flow volume $V = 92.255/60*2 = 3.08\ \mathrm{m}^3$

$$V = \pi\frac{D^2}{4}L = \pi\frac{D^2}{4}2D = \pi\frac{D^3}{2} = 3.08\ \mathrm{m}^3$$

Then $D = 1.24\ \mathrm{m}$, round to 1.3m
$L = 2*1.3 = 2.6\ \mathrm{m}$

$$V = \pi\frac{D^2}{4}H = \pi\frac{1.3^2}{4}2.6 = 3.45\ \mathrm{m}^3$$

Result:

Equipment number: D-302

Tank diameter: 1.3m.

Tank length: 2.6m.

Tank volume: 3.45m^3

4. D-401 MDEA Sol Drum

Stream 403 is recycled into T-401 CO_2 absorber. Owing to MDEA loss in stripper, some make-up MDEA solution should be added before the stream recycled into absorber. And also for the same reason of D-302, a buffer tank is supplied here. See Figure 8.2.6.3.

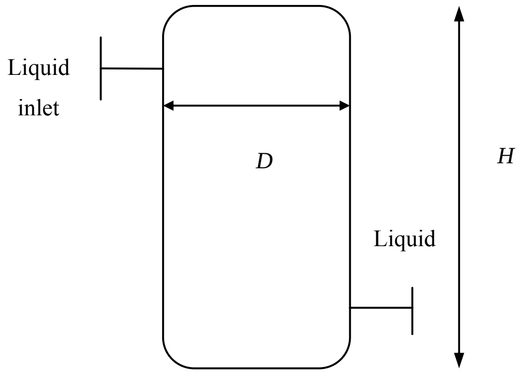


Figure 8.2.6.3 *The scheme of D-401 liquid buffer tank*

The operating condition of D-401 is at 30bar, 30°C. Carbon steel is applied. The design is based on inlet flow.

From Aspen simulation result, the inlet flow rate is 175m^3/hr.
Assume the residence time in vessel is 2 minutes.

The flow volume $V = 175/60*2 = 5.83 \text{ m}^3$

$$V = \pi \frac{D^2}{4} H = \pi \frac{D^2}{4} 2D = \pi \frac{D^3}{2} = 5.83 \text{ m}^3$$

Then $D = 1.22 \text{ m}$, round to 1.3m

$H = 2*1.3 = 2.6 \text{ m}$

$$V = \pi \frac{D^2}{4} H = \pi \frac{1.3^2}{4} 2.6 = 3.45 \text{ m}^3$$

Result:

Equipment number: D-401

Vessel diameter: 1.3m.

Vessel height: 2.6m.

Vessel volume: 3.45m^3

8.2.7 Compressor

In order to up the pressure of vapor to the required pressure, compressor is used as usual. In this design process, there are three main compressors used, which are C-101, Shell gas product compressor, C-201, Tube gas product compressor, and C303, Propylene heat compressor. To design the compressor, many process applications do not require the detailed evaluation of all factors affecting the actual horsepower requirements. A convenient and yet reasonably accurate calculation can be made using graph method.

To determine the compressor, we would estimate the value of “k”, which is the ratio of C_p and C_V [From the Literature “Applied Process Design for Chemical and Petrochemical Plants, Volume3; Ernest E. Ludwig”]. The parameter and condition design of main three compressor in this plant are showed in the Table 8.2.7.1 and Table 8.2.7.2.
The ratio, k, may be calculated from the ideal gas equation:

$$k = \frac{C_p}{C_V} = \frac{M_{cp}}{M_{cp} - 1.987}$$

$$M_{cp} = A + BT$$

where Mcp = heat capacity at the constant pressure, BTU/lb mol (R)
And then estimate the compression ratio for each compressor with T in degrees Rankine at inlet and the constants A and B can be found Table 8.2.7.1

Table 8.2.7.1. *Constant and Molar Heat Capacity*

Gas Composition	A	B	Temp in (C)	Temp in (R)	Mcp (BTU/lbmol)
Hydrogen	6.662	0.000417	25	20	6.670
Methane	4.877	0.006773	25	20	5.012
Propane	3.256	0.026733	25	20	3.791
Propylene	4.234	0.020600	25	20	4.646
Ethylene	3.175	0.013500	25	20	3.445
CO	6.780	0.000327	25	20	6.787
CO2	6.075	0.005230	25	20	6.180
Water	7.521	0.000926	25	20	7.540

The compression ratio across stages can be calculated by:

$$R_n = \sqrt[n]{\frac{P_f}{P_1}}$$

where P_f = final pressure
P_1= inlet pressure
n= number of stage

For this process, the compressors C-101 and C-201, which up the pressure to 30 bars, are designed as two stages compressor with half for each stage and C-303 is design as single stage. From the result of Aspen Plus Simulation, the value of gas compositions and condition are known and depicted as the Table 8.2.7.2

Table8.2.7.2. *Compression ratio and k of Compressors*

Compressor	Component	Flow (cu.ft./min)	Press$_{in}$ (bar)	Press$_{f}$ (bar)	Fraction	Mcp (BTU/lbmol)
C101	Hydrogen				0.17	1.14
	Methane				0.00	0.00
	Propane				0.58	2.18
	Propylene				0.25	1.18
	Ethylene				0.00	0.00
	Total	1.63^{e}4	1	30	1.00	4.50
	k					1.79
	Compression Ratio					3.87
C201	Hydrogen				0.10	0.65
	Methane				0.13	0.67
	Propane				0.12	0.44
	Propylene				0.22	1.01
	Ethylene				0.30	1.05
	CO				0.08	0.56
	CO2				0.02	0.09
	Water				0.02	0.18
	Total	1.47e4	1	30	0.99	4.65
	k					1.75
	Compression Ratio					3.87
C303	Propylene	3.35e2	15	20	1	4.65
	k					1.75
	Compression Ratio					1.33

Horsepower

The work done during the complete compression cycle, the theoretical horsepower is that required to isentropically (adiabatically) compress a gas through a specified pressure range.

Theoretical HP:

$$= \frac{144}{33,000}\left(\frac{k}{k-1}\right)P_1V_1\left[\left(\frac{P_2}{P_1}\right)^{(k-1)/k}-1\right] \qquad (8.2.7.1)$$

Actual Brake Horsepower, BHP:

$$= \frac{144}{33,000}\left(\frac{k}{k-1}\right)P_1V_1\left[\left(\frac{P_2}{P_1}\right)^{(k-1)/k}-1\right](L_o)(F_L)(Z_1) \qquad (8.2.7.2)$$

where:

P_1 : Suction pressure,psia
P_2: Discharge pressure,psia
V_1: Suction volume,cu.ft./min. at suction conditions.
L_o: Loss factor, comprised of losses due to pressure drop through friction of piston rings, valves and manifold
F_L : Frame loss for motor-driven compressors only, value range 1.0 to 1.05
Z_1 : Compressibility factor, based on inlet conditions to cylinder (usually negligible, except at high pressures)

In case of multi stages, the total horsepower is the summation of each stage required. From the parameter and data above, we can estimate theoretical horsepower and actual brake horsepower as showing the results in Table 8.2.7.3

Table 8.2.7.3. *The required Horsepower for compressor used in the process*

Compressor	No. of stage	Theoretical HP (MW)	Actual Brake Horsepower, BHP(MW)
C-101	2	9,419(7.03)	11,491(8.57)
C-201	2	8,442(6.3)	10,299(7.68)
C-303	1	99(0.074)	173(0.13)

Fortunately, the Aspen Plus Simulation can estimate the result of compressor as well, the power required for the compressor are showed in Table 8.2.7.4

Table 8.2.7.4 *The required power for compressor from Aspen Plus Simulation*

Compressor	Theoretical HP (MW)	Actual Brake Horsepower, BHP(MW)
C-101	2.92	4.17
C-201	3.16	4.52
C-303	0.47	0.67

The results of required power from Aspen Plus are quite different from the calculation above. To compromise this difference, the results from Aspen Plus would be used because they could impact the result of heat balance of simulation. The specification of compressors is summarized in Appendix E.8.

8.2.8 Pump

In order to increase pressure of liquid to the required condition, pump will be used. It is necessary to know the liquid to be handled, the total dynamic head, the suction and discharge heads, and in most case, the temperature, viscosity, vapor pressure, and specific gravity. The most widely used in the chemical industry for transferring liquids of all types is a centrifugal pump because the primary advantage of the centrifugal pump is simplicity, low first cost, uniform (no pulsating) flow, small floor space, low maintenance expense, quiet operation and adaptability for use with a motor or a turbine drive.

In this process, there are twelve main pumps used. To estimate the power requirement for pumping liquid, and to transport liquid from one vessel to another through a pipeline, energy has to be supplied to overcome the friction losses in the pipes, miscellaneous, process equipment, difference in elevation from end to end of the pipe and difference in pressure between the vessels. The total energy required can be calculated from the equation

$$g\Delta z + \frac{\Delta p}{\rho} - \frac{\Delta p_f}{\rho} - w = 0 \qquad (8.2.8.1)$$

where : w = work done, J/kg,

Δz = difference in elevations, m,

Δp = differnce in system pressure,N/m^2,

Δp_f =pressure drop due to friction including miscellaneous losses and equipment,N/m^2,

ρ = liquid density,kg/m^3,

g = acceleration due to gravity,m/s^2

If w is negative, a pump is required. The head required from the pump = $\frac{\Delta p_f}{\rho g} - \frac{\Delta p}{\rho g} - \Delta z$

The power is given by:

$Power = (w \times m)/\eta$,for a pump

where: m = mass flow-rate, kg/s,

η = efficiency = power out/power in

To calculate precisely, we should know the pipe sizing and miscellaneous that result in friction loss in the line from

$$\Delta p_f = 8 f (L/d_i) \frac{\rho u^2}{2} \qquad (8.2.8.2)$$

where : Δp_f = pressure drop,N/m^2,

f = friction factor,

L = pipe length,m,

d_i = pipe inside diameter, m,

ρ = fluid density,kg/m^3,

u = fluid velocity, m/s.

At this design stage, we can estimate the power used for the pump by simulating with Aspen Plus simulation. The design efficiency is 70% for the whole pumps. The design result is shown in Appendix E.8.

8.3 Special Issues

8.3.1 Exergy Theory

To perform a thermodynamic analysis of a process, the principles of such an analysis are defined first. From the calculation of the minimum, also called ideal amount of work to perform a certain task, the convenience, not the necessity, of defining the concept of exergy is made plausible. Exergy can have a physical and a chemical component.

In the following, we will deal with a steady state flow process and consider a flow originally at ambient conditions; P_0, T_0, and requiring work at the rate W_{in} to bring its conditions at P and T. In the process heat is transferred to the environment at a rate of Q_{out}.

As is justified for most situations in process technology macroscopic changes are ignored in the kinetic and/or potential energy of the flow in this process. Applying the first law of thermodynamics for flow processes it can be wrote

$$W^{\bullet}_{in} = m^{\bullet}\Delta H + Q^{\bullet}_{out} \qquad (8.3.1.1)$$

The second law for this process reads

$$S^{\bullet}_{gen} = m^{\bullet}\Delta S + S^{\bullet}_{0} \qquad (8.3.1.2)$$

in which $S^{\bullet}_0$ denotes the rate of the change in entropy of the environment

Next, establish the minimum amount of work to accomplish the change in the flow's conditions from P_0, T_0 to P,T to bring about the corresponding changes in the state properties H and S of the flow, ΔH and ΔS, with

$$\Delta H = H_{P,T} - H_{P_0,T_0} \qquad (8.3.1.3)$$

and

$$\Delta S = S_{P,T} - S_{P_0,T_0} \qquad (8.3.1.4)$$

Therefore,

$$W^{\bullet\,min}_{in} = m^{\bullet}\Delta H + Q^{\bullet\,min}_{out} \qquad (8.3.1.5)$$

The heat released to the environment must have no potential to perform work left in order to assess the true minimum for $W^{\bullet}_{in}$. The minimum rate of input of work is associated with the minimum output if the heat as $m^{\bullet}\Delta H$ is fixed by the choice of the mass flow rate and the thermodynamic conditions of the initial and the final state.

Then, by applying the relation

$$Q^{\bullet}_0 = T_0 S^{\bullet}_0 \qquad (8.3.1.6)$$

and find

$$W^{\bullet}_{in} = m^{\bullet}(\Delta H - T_0\Delta S) + T_0 S^{\bullet}_{gen} \qquad (8.3.1.7)$$

The true minimum will of course require that the process is free of driving forces, thus

$$S^{\bullet}_{gen} = 0$$

The minimum amount of work to bring about the required change in conditions appears then to be given by

$$W^{\bullet\,min}_{in} = m^{\bullet}(\Delta H - T_0\Delta S) \qquad (8.3.1.8)$$

We can now define the property exergy, Ex, according to

$$\begin{aligned} Ex &\equiv W^{\bullet\,min}_{in}/m^{\bullet} \qquad (8.3.1.9)\\ &= \left(H_{P,T} - H_{P_0,T_0}\right) - T_0\left(S_{P,T} - S_{P_0,T_0}\right) \end{aligned}$$

As the amount of useful work confined in a unit of mass of the flow at conditions P and T with respect to the conditions of the environment. It is the maximum amount of work that a unit mass of flow can perform if it is brought reversibly to the conditions of the environment. Then eq. 8.3.1.9 can be rewrote as

$$Ex = \left(H - T_0S\right)_{P,T} - \left(H - T_0S\right)_{P_0,T_0} \qquad (8.3.1.10)$$

The purpose of introducing the concept of exergy is to express the amount of work available in an amount of mass, in rest or flowing, to perform work if it prevails at conditions different from those of the environment. The exergy can be distinguished into physical exergy and chemical exergy as

$$Ex = Ex_{phy} + Ex^0_{chem} \qquad (8.3.1.11)$$

The first term of the right-hand side of eq.8.3.1.11 expresses the amount of work that is available due to differences in pressure and temperature with the environment. The second term, the chemical exergy, expresses the amount of work available due to the differences in composition with respect to the environment. The superscript in Ex^0_{chem} expresses the chemical exergy considered at ambient conditions.

The chemical exergy can be simply calculated from the Gibbs energy of formation. The only difference between these two concepts is that their zero values are defined for different reference substances. The standard chemical exergy of its elements can be calculated from

$$Ex^0_{chem,j} = \Delta_f G^0_{i,298} + \sum \nu_i Ex^0_{chem,i} \qquad (8.3.1.12)$$

As exergy has been defined purely in terms of work, an exergy balance around a process, including its interaction with the environment, should result in an exergy loss that is precisely the amount of lost work, thus

$$Ex_{in} + Ex_{out} = W_{lost} \qquad (8.3.1.13)$$

In case of heat exchanger with the adiabatic condition the W_{lost} can be read as

$$W_{lost} = T_0\left(\Delta S_{low} + \Delta S_{high}\right) \qquad (8.3.1.14)$$

$$= T_0\Delta S$$

then,

$$W_{lost} = T_0 Q\left(\frac{1}{T_{low}} - \frac{1}{T_{high}}\right) \qquad (8.3.1.15)$$

And the efficiency of the process in terms of exergy can be estimated by

$$\eta = \frac{\dot{Ex}_{out}}{\dot{Ex}_{in}} \qquad (8.3.1.16)$$

8.3.2 Work loss

Exergy analysis compared between separated reactions and combination of endothermic and exothermic reactions can be considered from work loss as mentioned in Chapter 8.3.1.

8.3.2.1 Separated reaction process

1. Endothermic reaction

For this reaction, we want the heating media to heat up and maintain the reaction condition, traditionally furnace is used and fuel gas is combusted to generate heat and supplied heat to the reaction. The temperature of flue gas from the combustion can be approximate around 110-150 °C. Simplified scheme is showed in Figure8.3.2.1a.

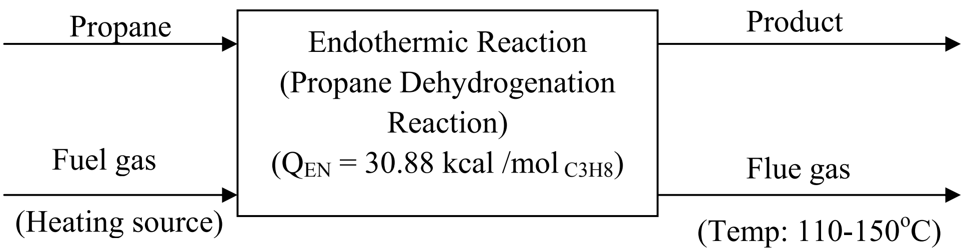


Figure8.3.2.1a *Scheme of Propane dehydrogenation reaction*

2. Exothermic reaction

For this process, the boiler feed water; (BFW) is needed to cool down the reaction and then produced to super high-pressure steam (SHPS) pressure ~100 bar at temperature ~500 °C, which is then used within the process. Simplified scheme is showed in Figure8.3.2.1b.

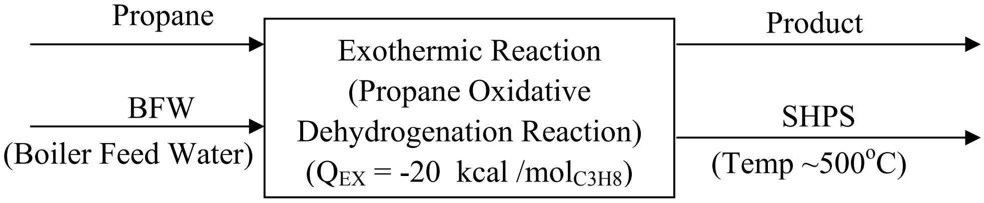


Figure8.3.2.1b *Scheme of Propane oxidative dehydrogenation reaction*

8.3.2.2 Combination reaction process

Since, the heat from exothermic reaction can be exchanged to the endothermic reaction. Based on the same propane feed to both reaction and same conversion the same amount of product is obtained. It is obvious that the combination of exothermic and endothermic reactions can reduce the exergy loss in part of the heating and cooling media more or less. Simplified scheme of combination is shown in Figure8.3.2.2.

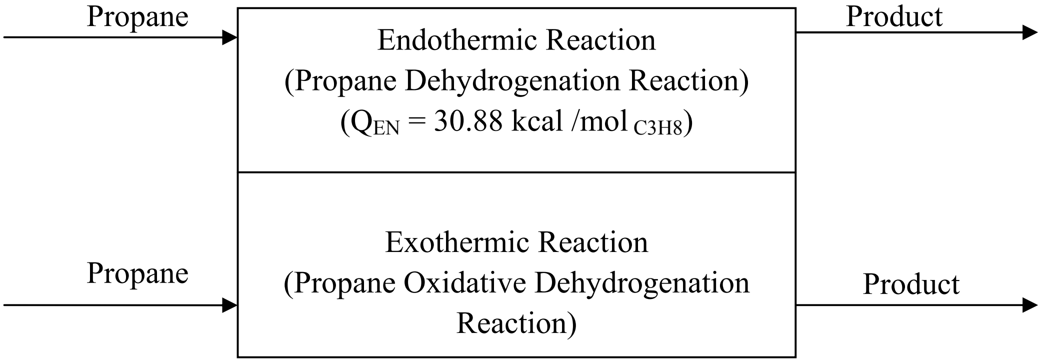


Figure8.3.2.2 *Scheme of combination reactions*

To present how much exergy loss can be reduced, the work loss of these reactions can be representative. Considering each reaction and heat removed compatible with the performance of heat exchanger, eq.8.3.1.15 can be used to determine this question.

For endothermic reaction:

$$W_{lost}^{endo} = T_0 Q_{endo}\left(\frac{1}{T_{low}} - \frac{1}{T_{high}}\right) \qquad (8.3.2.2.1)$$

where: W_{lost}^{endo} = work lost of fluel gas from feed condition to flue gas

Q_{endo} = heat ramoved from endothermic reaction, 30.88 $kcal/mol_{C_3H_8}$

T_0 = temperature of environment, 25 °C

T_{low} = temperatue of fuel gas, 25°C

T_{high} = temperature of flue gas, 130°C

resulting , W_{lost}^{endo} = 8.05 $kcal/mol_{C_3H_8}$

For exothermic reaction:

$$W_{lost}^{exo} = T_0 Q_{exo}\left(\frac{1}{T_{low}} - \frac{1}{T_{high}}\right) \qquad (8.3.2.2.2)$$

where: W_{lost}^{exo} = work lost of BFW from the feed condition to SHPS

T_0 = temperature of environment, 25 °C

T_{low} = temperatue of BFW, 25°C

T_{high} = temperature of SHPS, 500°C

resulting , W_{lost}^{exo} = 19.97 $kcal/mol_{C_3H_8}$

After combination of both reactions, that the total W_{lost} is around 28kcal/molC_3H_8 can be reduced. Be caution, this is what we consider the taking place of reaction, reactor only. In fact, for instance, this work lost from exothermic can be used in preheating or in separation unit. That's why when we make the analysis of the whole process; we should consider the whole process by evaluating unit-by-unit or section-by-section.

8.4 Equipment data sheets

The equipment used in this process is summarized in table and equipment specifications of each are presented in Appendix E.8. In Appendix E.8, the table included both cases heat integration process and without heat integration process.
(See Appendix E.8, also PFS of both cases)

9 Wastes

All processes produce varies of wastes, directly or indirectly. Indirect wastes include all pollution occurring during, *e.g.,* manufacturing of feedstock's and plant equipment or as a result of product usage*, e.g.,* fuels for heating or traction. Direct wastes can be classified as gases, liquids, solids or combinations and originate directly from the designed plant. For CPD only direct wastes are paid attention.

Waste can be released directly or treated before release into the environment. For hazardous wastes, there are five primary methods for management:

1. Recycling materials off-site or to other on-site processes
2. Reuse as fuel
3. Incineration
4. Physical, chemical, and biological treatment of aqueous wastes
5. Land treatment and disposal

Followed paragraphs will describe the wastes' identification and classification.

Items from a. to d. are indicated as by-products in this design because of their valuable use; however, they are still mentioned in this chapter.

a. Stream 402 (Carbon dioxide stream)

The main component in this stream is carbon dioxide. Temperature and pressure of this stream is 101°C, 1bar.

Table 9.1. *Stream 402 component and effect*

Component	Amount (kg/hr)	Effect on environment	Notes
CO_2	576	Greenhouse gas, causes global warming	Gas

This stream is gaseous waste. Carbon dioxide is not toxic and hazardous. However, emission should be controlled because carbon dioxide is greenhouse gas and causes global warming. Carbon dioxide in stream 402 has high concentration.

Carbon dioxide also can be injected into well of oil field to increase oil recovery. CO_2 can, to some extent, replace/supplement injection of natural gas and water for pressure support in oil and condensate reservoirs for improved recovery of oil and condensate. In this CPD project, the alkenes plant obtains raw materials (propane) from a Fischer-Tropsch plant. Some of Fischer-Tropsch plants use natural gas as feedstock. Natural gas is often produced simultaneously with the oil from a reservoir. In this case, the Fischer-

Tropsch plant based natural gas is located nearby oil and gas field, the produced CO_2 can be sold to the oil company for enhancing oil recovery (EOR). Carbon dioxide injection has been already proven to be one of the most efficient EOR methods in oil and gas industry. This scenario offers additional benefit to sequester carbon dioxide gas produced by the alkenes plant for EOR and to prevent CO2 buildup in the atmosphere where it can contribute to the "greenhouse effect". The utilization of CO2 from this plant for EOR, results an additional income for the cash flow and inline with sustainable technology concept.

b. Stream 303 (light gas mixture)

The main components in this stream are carbon monoxide (CO), hydrogen (H_2) and methane (CH_4). The temperature and pressure of stream is –131°C, 15bar.

Table 9.2 *Stream 303 component and effect*

Component	Amount (kg/hr)	Effect on environment	Notes
CO	2232	Toxic	Gas
CH_4	2088	Flammable material	Gas
H_2	540	None	Gas

This stream is gaseous waste. The three components have close and low boiling points, and carbon monoxide and methane is quite difficult to be separated even use membrane. On the other hand, carbon monoxide/hydrogen mixture is synthesis gas, raw material in Fischer-Tropsch process. As principles suggestion, stream 303 (light gas mixture) can be sold to Fischer-Tropsch (FT) plant directly. Fischer-Tropsch plant can further adjust the composition of the stream and use it as synthesis gas (syngas). Also see Appendix C.7 for alternative recommendations for the treatment of light gas.

c. Stream 208 & 314-W (process water); E101, E103, E203, E303C & E401 (cooling water); E301A, E302A & E402 (hot water)

The main component in these streams and utilities is water. The data of them are:

S208 : 25°C, 3bar
S314-W : 43°C, 15bar
E101 : 26 °C
E103 : 27.2 °C
E203 : 121 °C
E303C : 25 °C
E401 : 70 °C
E301A : 50 °C
E302A : 50 °C

E402 : 105 °C

Table 9.3. *Water streams component and effect*

Component	Steam/Equip. number	Amount (kg/hr)	Effect on environment	Notes
Water	S208	5256	None	Liquid
	S314-W	36		
	E101	36000		
	E103	35388		
	E203	41940		
	E303C	93168		
	E401	139320		
	E301A	86580		
	E302A	262944		
	E402	654804		

All of them are liquid wastes. They are not toxic or hazardous and have no effect to environment. It is possible that sell water stream to pure water industry. However, according to the cost, pure water industry will prefer to use environmental water because of its low price and low transport fee.

Corresponding with CO_2 utilization for Enhancing Oil Recovery (EOR) in oil and gas field, the produced water can be used similarly in oil field for water injection to maintain the formation pressure and displacing the crude oil in the reservoir.
Water injection has been used successfully to improve oil recovery from oil wells. This scenario utilization of water is in accordance with environmental regulation. Throughout the world, strict environmental regulations are being introduced to limit the disposal of produced water. In addition to the environmental benefit, produced water injection for EOR in oil field will produce financial benefits by saving on treatment cost.

d. Stream 314 (propane stream)

The main components in this stream are propane and propylene. The temperature and pressure of stream 314 is 43°C, 15bar.

Table 9.4. *Stream 314 component and effect*

Component	Amount (kg/hr)	Effect on environment	Notes
Propane	32076	Flammable material	Gas
Propylene	3312	Flammable material	Gas

The stream is gaseous waste. Propane and propylene are flammable gas. The MAC (DFG) value of propane is 1800mg/m^3. The most important thing is that propane is the raw material of the process and propylene present will not influence reactions. As a result, recycle this stream is a preferred way to improve margin and reduce effects on environment. Hence, in design, stream 314 is heated and recycled to the beginning of process.

e. Spent catalyst: Pt on MFI zeolite

The main components are platinum (Pt) and zeolite. The formula of zeolite can be indicated as $M_{x/n}\left[\left(AlO_2\right)_x\left(SiO_2\right)_y\right]\cdot wH_2O$. M is the cation of valence *n*; *w* is the number of water molecules, *y/x* is the silicon/aluminum ratio for zeolite. Although zeolite has no toxic effects, dust generation is a problem. Clean up and recover are suitable manners to avoid dust. On the other hand, Platinum sponge, powder or black may cause sensitization by skin contact, and may act as an irritant. Tumorigenic effects have been noted in tests with laboratory animals. Many platinum compounds are sensitizers.

As a result, spent catalyst must be regenerated. The normal way in catalyst cracking industry is burning-off of coke deposits. Contact catalyst supplier to sell spent catalyst back at low price is a suitable manner for this process due to fixed bed reactor.

f. Spent catalyst: vanadium pentoxide (V_2O_5)

The main component is vanadium pentoxide, stable material.

V_2O_5 is hazardous in the environment. It is extremely toxic. It may be fatal if swallowed, inhaled or absorbed through skin, may cause reproductive defects and may cause severe irritation or burns on contact. Typical TLV/TWA is 0.05 mg/m3. And detail risk of V_2O_5 lists below:

- Harmful by inhalation
- Harmful if swallowed
- Toxic by inhalation
- Irritating to respiratory system
- Limited evidence of a carcinogenic effect
- Danger of serious damage to health by prolonged exposure
- Toxic to aquatic organisms
- May cause long-term adverse effects in the aquatic environment
- Possible risk of harm to the unborn child
- Possible risk of irreversible effects

Accordingly, releasing this spent catalyst directly is unacceptable and is also a kind of wasting raw materials. In practice, the normal treating way is to return spent catalyst V_2O_5 as low price to the catalyst manufacturer.

10 Process Safety

Process safety is a discipline that focuses on the prevention of fires, explosions and accidental chemical releases at chemical process facilities. Excludes classics worker health and safety issues involving working surfaces, ladders, protective equipment etc.
In quantifying process safety, two tools can assist: a Hazard and Operability study (HAZOP) and the Fire and Explosion Index (F&EI) assessment.

10.1 HAZOP

Hazard is an inherent chemical or physical characteristic that has the potential for causing damage to people, property, or the environment. It can be classified in several special items: toxicity, flammability, corrosiveness, etc.

Hazard and Operability Study (HAZOP) is a systematic, qualitative technique to identify process hazards and potential operating problems using a series of guidewords to generate process deviations. A HAZOP is used to question every part of the process to discover what deviations from the intention of the intention of the design can occur and what their causes and consequences may be. This is done systematically by applying suitable words. This is a systematic detailed review technique for both batch and continuous plants that can be applied to new or existing processes to identify hazards.
Following is the operability study:

- ***RX001+RX002 Tube and shell reactor***

Intention: *To produce all products and supply shell part enough heat for reaction progressing from tube part that form heat*

Shell part (endothermic reaction): at 1 bar, 540^oC
Tube part (exothermic reaction): at 1 bar, 1123^oC

Table 10.1.1. *RX001+RX002 HAZOP analysis*

Guide word*	Deviation	Possible causes	Consequences	Action required
Not, no	Flow	Line fracture	Propane exposure and causing flammable	Institute regular patrolling and inspection of transfer line. Install additional line
More	Flow	Raw material stream valve opened in error	Low conversion Incomplete separation	Install additional storage before reactor

	Pressure	Valve closed in error	Less residence time in the reaction, causes less conversion	Check the flow control on input stream
	Temperature	High temperature of propane input stream	Reactions occurs at high temperature have different thermodynamic and cannot have good couple of heat exchange.	Check the temperature control on input stream
		Endothermic reaction can not absorb whole heat formed from exothermic reaction	Explosion.	Decrease ratio of tubes over shells
		Thermal expansion in an isolated valve section due to fire or strong sunlight	Line fracture or flange leak. High pressure in transfer line and reactor. Product might get pale.	Install thermal expansion relief on valve section
Less	Flow	Leaking flange or valve	Low rate of production	Institute regular patrolling and inspection of transfer line. Install additional line
	Temperature	Low temperature of propane input stream	Reactions occurs at low temperature have different thermodynamic and cannot have good couple of heat exchange.	Check the temperature control on input stream
		Exothermic reaction cannot supply enough heat absorbed by endothermic reaction	Reactor cannot key a constant operation temperature. Low conversion	Increase ratio of tubes over shells
* The meaning of guidewords, explained in 'Chemical risk management', is mentioned in Appendix F				

- ***C101 Compressor***

Intention: *To supply raw product stream from shell part at 30bar, 39384 kg/hr, 215^oC*

Table 10.1.2. *C101 HAZOP analysis*

Guide word	Deviation	Possible causes	Consequences	Action required
Not, no	Flow	Compressor failure	Followed steps cannot progress. Processing stopped	Low flow pressure alarm
Reverse	Flow	Fall in line pass (compressor fails)	Explosion hazard	Fit non-return valve

- ***C201 Compressor***

Intention: *To supply raw product stream from tube part at 30bar, 27864 kg/hr, 289oC*

Table 10.1.3.*C201 HAZOP analysis*

Guide word	Deviation	Possible causes	Consequences	Action required
Not, no	Flow	Compressor failure	Followed steps cannot progress. Processing	Low flow pressure alarm

			stopped	
Reverse	Flow	Fall in line pass (compressor fails)	Explosion hazard	Fit non-return valve

a. D101 Liquid/Vapor separator

Intention: *To separate liquid and vapor phase of stream at 30bar, 39384kg/hr, 55°C*

Table 10.1.4. *D101 HAZOP analysis*

Guide word	Deviation	Possible causes	Consequences	Action required
Not, no	Flow	Line fracture	Stream leakage, causes flammable	Institute regular patrolling

➢ T402 CO2 stripper

Intention: *To separate carbon dioxide from MDEA and regenerate MDEA*

Line OUT

Intention: *Transfer MDEA recycle stream to CO2 absorber*

Table 10.1.5. *L_{out} HAZOP analysis*

Guide word	Deviation	Possible causes	Consequences	Action required
Not, no	Flow	Line fracture	MDEA leaks at the site. Floor will be corroded.	Institute regular patrolling and inspection of transfer line. Install additional line

a. T301 Light ends distillation column

Intention: *To remove light ends (methane, carbon monoxide and hydrogen) from raw product stream*

Line IN

Intention: *Transfer light ends*

Table 10.1.6. *T301 L_{in} HAZOP analysis*

Guide word	Deviation	Possible causes	Consequences	Action required
Not, no	Flow	Line fracture	CO leaks and it is very hazardous for labor	Institute regular patrolling and inspection of transfer line. Install additional line
More	Pressure	Stream input valve opens in error	Higher pressure in column, explosion	Check flow control Install additional storage

Line OUT

Intention: *Transfer product mix stream to ethylene distillation column*

Table 10.1.7.*T301 L_{out} HAZOP analysis*

Guide word	Deviation	Possible causes	Consequences	Action required
Not, no	Flow	LCV fails shut	Pump heats up	Install kickback on pump. Check design of pump strainers
More	Flow	LCV fails open or LCV bypass open in error	Column overfills. Separation efficiency decreases.	Install locking off procedure for LCV bypass when not in use.

b. T302 Ethylene distillation column

Intention: *To separate and purify ethylene from product stream*

Line IN

Intention: *Transfer ethylene*

Table 10.1.8. *T302 L_{in} HAZOP analysis*

Guide word	Deviation	Possible causes	Consequences	Action required
Not, no	Flow	Line fracture	Ethylene leakage is flammable	Institute regular patrolling and inspection of transfer line. Install additional line
More	Flow	Stream input valve opens in error	Poor quality of product ethylene	Check flow control Install additional storage
	Pressure	Stream input valve opens in error	Higher pressure in column, explosion	Check flow control Install additional storage
Less	Flow	Stream input valve closed in error	Low production rate	Check flow control Install additional storage

Line OUT

Intention: *Transfer product mix stream to propylene distillation column*

Table 10.1.9. *T302 L_{out} HAZOP analysis*

Guide word	Deviation	Possible causes	Consequences	Action required
Not, no	Flow	LCV fails shut	Pump heats up	Install kickback on pump. Check design of pump strainers
More	Flow	LCV fails open or LCV bypass open in error	Column overfills. Separation efficiency decreases.	Install locking off procedure for LCV bypass when not in use.

c. T303 Propylene distillation column

Intention: *To separate and purify propylene from product stream*

Line IN

Intention: *transfer propylene*

Table 10.1.10. *T303 L_{in} HAZOP analysis*

Guide word	Deviation	Possible causes	Consequences	Action required
Not, no	Flow	Line fracture	Propylene leakage is flammable	Institute regular patrolling and inspection of transfer line. Install addition line
More	Flow	Stream input valve opens in error	Poor quality of product propylene	Check flow control Install additional storage
	Pressure	Stream input valve opens in error	Higher pressure in column, explosion	Check flow control Install additional storage
Less	Flow	Stream input valve closed in error	Low production rate	Check flow control Install additional storage

Line OUT

Intention: *transfer propane/water mix stream to water dryer*

Table 10.1.11. *T303 L_{out} HAZOP analysis*

Guide word	Deviation	Possible causes	Consequences	Action required
Not, no	Flow	LCV fails shut	Pump heats up	Install kickback on pump. Check design of pump strainers
More	Flow	LCV fails open or LCV bypass open in error	Column overfills. Separation efficiency decreases.	Install locking off procedure for LCV bypass when not in use.

d. D302 Water dryer

Intention: *to remove water exists in propane recycle stream*

Table 10.1.12. *D302 water dryerHAZOP analysis*

Guide word	Deviation	Possible causes	Consequences	Action required
Not, no	Flow	Line fracture	Propane leakage is flammable	Institute regular patrolling and inspection of transfer line. Install additional line
More	Flow	Absorbent has low capacity	Water remains in propane, influence whole process, damage	Change absorbent periodically

e. Heat exchangers

Intention: *transfer heat from higher temperature side to lower temperature side.*

Lines with higher temperature

Intention: *transfer stream to next unit with certain temperature*

Table 10.1.13.*L high T Heat exchangers HAZOP analysis*

Guide word	Deviation	Possible causes	Consequences	Action required
More	Flow	(1)Valve opened in error	Both out-streams have higher temperature than requirement, causes hazard to followed steps	Check flow control
	Temperature	Exothermic reaction occurs too fast	The same as (1)	Decrease ratio of tubes over shells
		Heat exchanger before doesn't work well	The same as (1)	Check the heat exchanger before Install flow control

Lines with lower temperature

Intention: *transfer stream to next unit with certain temperature*

Table 10.1.14.*Llow T Heat exchangers HAZOP analysis*

Guide word	Deviation	Possible causes	Consequences	Action required
Not, no	Flow	(1)Line fracture	Heat exchanger doesn't work, causes big hazard to followed steps	Institute regular patrolling and inspection of transfer line. Install additional line
Less	Flow	Line leakage	Both out-streams have higher temperature than requirement, causes hazard to followed steps	Institute regular patrolling and inspection of transfer line.
	Temperature	Endothermic reaction occurs too fast	Both out-streams have higher temperature than requirement, causes hazard to followed steps	Increase ratio of tubes over shells
		Heat exchanger before doesn't work well	The same as (1)	Check the heat exchanger before Install flow control

10.2 FEI

Dow Fire and Explosion Index (F & EI) is a method (developed by Dow Chemical Company) for ranking the relative fire and explosion risk associated with a process. Analysts calculate various hazard and explosion isentropic flow against a pressure gradient. The procedure for calculating unit hazard factor F & EI is indicated in Figure AF.2.

Follow this procedure; F & EI are given below:

In the plant, shell and tube reactor, light ends distillation column, ethylene distillation column, propylene distillation column would have the great impact on the magnitude of a fire or explosion. Shell and tube reactor is considered pertinent to the process. It is checked by comparing other columns' F&EI mentioned in Appendix F,
From the Guide the relative material factors (MF) are given in Table 10.2.1.

Table 10.2.1. *Relative material factors*

Material	MF	Hc BTU/lb $*10^{-3}$	N_h*	N_f**	N_r***	Flash point ^oC
Propane	21	19.9	1	4	0	Gas
Ethylene	24	20.8	1	4	2	Gas
Propylene	21	19.7	1	4	1	Gas
Methane	21	21.5	1	4	0	Gas
Hydrogen	21	51.6	0	4	0	Gas
Carbon monoxide	16	4.3	2	4	0	Gas

* N_h is the health value.
** N_f is the flammability value.
*** N_r is the reactivity value.

Choose the material that has the biggest MF in the process unit for calculation: Ethylene, **MF=24**.

Shell and tube reactor

1. <u>*General process hazards*</u>

a. Exothermic reaction, oxidation dehydrogenation, occurs in the reactor. Refer to the Guide; it requires a penalty of **1.00**.
b. Endothermic reaction, dehydrogenation, occurs in the reactor. Refer to the Guide; it requires a penalty of **0.20**.
c. Loading and unloading operation involving flammables receives a penalty of **0.50**.
d. The reactor is outdoor process unit. Not applicable in this item.
e. Adequate access provides and then penalty is **0.00**.
f. Adequate drainage provides and then penalty is **0.00**.

2. <u>*Special process hazard*</u>

a. For mixture, use the component with the highest Nh. In the process unit, carbon monoxide has the highest Nh, 2. The penalty is 0.20*Nh=0.40.
b. Not applicable because the penalty is applied only if the absolute pressure is less than 500mm Hg and the reactor operation pressure is 1bar higher than limitation. No penalty.

c. The process is by nature always in the flammable range, a penalty is given as 0.80.
d. No dust explosion and no penalty.
e. The operation pressure is 1bar that the same with atmospheric pressure. No penalty here.
f. No applicable
g. The penalty is based upon the amount of fuel for a fire that can be released within 10 minutes from the Process Unit. From the stream data of the process, the amount of gas-mixture released within 10 minutes is (39022+32755)*10/60 =11963kg =26374lb. Use the highest Hc value (hydrogen has little fraction in process unit and is not considered here): 21.5*103 BTU/lb.
   Potential energy release =26374*21.5*103 =5.67*108BTU
   Refer to Figure 3 [Guide], penalty is 1.00.
h. In the Process Unit, no corrosive material exists. As a result, penalty of this item is 0.00.
i. The gland seals are likely to give some leakage of a minor nature. Accordingly, the penalty is 0.10.
j. No fired heater is used in process. This penalty is not applicable.
k. The Process Unit doesn't use a hot oil exchange system, so no penalty.
l. No rotating equipment is applied in the Process Unit, no penalty.

Table 10.2.2 indicates the result of Dow F & EI analysis.

***Table 10.2.2** Dow Fire and Explosion Index Form of Shell and Tube reactor*

PREPARED BY CPD 3297	APPROVED BY	DATE 16-Dec-03
SITE Shell and Tube reactor	LOCATION Grey area	
MATERIALS IN PROCESS UNIT: Propane, oxygen, nitrogen, ethylene, propylene, methane, hydrogen, water, carbon monoxide, carbon dioxide		
STATE OF OPERATION X_DESIGN __STARTUP _NORMAL OP __SHUTDOWN	BASIC MATERIAL(S) FOR MATERIAL FACTOR	Ethylene
MATERIAL FACTOR (Table I or Appendices A or B) Note requirements when unit temp over 60°C		24
1. GENERAL PROCESS HAZARDS	**Penalty Factor Range**	**Penalty Factor Used**[1]
BASE FACTOR……………………………………………………………………………	1.00	1.00
A. EXOTHERMIC CHEMICAL REACTIONS	0.30 to 1.25	1.00
B. ENDOTHERMIC PROCESSES	0.20 to 0.40	0.20
C. MATERIAL HANDLING AND TRANSFER	0.25 to 1.05	0.50
D. ENCLOSED OR INDOOR PROCESS UNITS	0.25 to 0.90	0.00
E. ACCESS	0.20 to 0.35	0.00
F. DRAINAGE AND SPILL CONTROL		0.00
GENERAL PROCESS HAZARDS FACTOR (F1)………………………………………………		2.70
2. SPECIAL PROCESS HAZARDS		
BASE FACTOR……………………………………………………………………………	1.00	1.00
A. TOXIC MATERIAL(S)	0.20 to 0.80	0.40
B. SUB ATMOSPHERIC PRESSURE (>500 mm Hg)	0.50	0.00
C. OPERATION IN OR NEAR FLAMMABLE RANGE ___ Inerted _X_ Not		

Inerted		
1. TANK FARMS STORAGE FLAMMABLE LIQUIDS	0.50	
2. PROCESS UPSET OR PURGE FAILURE	0.30	
3. ALWAYS IN FLAMMABLE RANGE	0.80	0.80
D. DUST EXPLOSION (See Table 3)	0.25 to 2.00	0.00
E. PRESSURE (See Fig 2) OperatingPressure 14.5 psig		0.00
F. LOW TEMPERATURE	0.20 to 0.30	0.00
G. QUALITY OF FLAMMABLE / UNSTABLE MATERIAL: Quantity 26374 lb / kg H_C =21.5*10^3 BTU/lb		
1. LIQUIDS OR GASES IN PROCESS		1.00
2. LIQUIDS OR GASES IN STORAGE		
3. COMBUSTABLE SOLIDS IN STORAGE, DUST IN PROCESS		
H. CORROSION AND EROSION	0.10 to 0.75	0.00
I. LEAKAGE - JOINTS AND PACKING	0.10 to 1.50	0.10
J. USE OF FIRED EQUIPMENT		0.00
K. HOT OIL EXCHANGE SYSTEMS	0.15 to 1.15	0.00
L. ROTATING EQUIPMENT	0.50	0.00
SPECIAL PROCESS HAZARDS (F2)…………………………………………		3.30
PROCESS UNITS FACTOR HAZARDS (F1 x F2) = F3…………………………		8.91
FIRE AND EXPLOSION INDEX (F3 x MF = F&EI)………………………………		213.84

Table 10.2.3 mentions the relationship between hazard and F & EI.

Table 10.2.3 *Degree of Hazard for F & EI*

Index range	Degree of hazard
1-61	Light
62-96	Moderate
97-127	Intermediate
128-158	Heavy
159-up	Severe

Conclusion

From Table 10.2.2 the index works out at 213.84. Refer to Table 10.2.3, the process has severe hazard. How to reduce so high hazard without changing main process is to do more efficient and timely process control.

11 Economy

Profitability analysis is required to evaluate the economic aspect of a project design. Some crucial measures such as Purchased Equipment (PCE), Total Investment cost, production cost, profit margin, return on investment (ROI), payback period (PBP). The cash flow, net present value (NPV) and the investor's rate of return (IRR) (also know as the discounted cash-flow rate of return (DCFRR) to count the time value of money.

Margin is defined as follows:

$$\text{Margin=Total Value (Products, Wastes } OUT\text{) - Total Value (Feedstock's, Process Chemicals, } IN\text{)}$$

In order to prevent confusion, in this conceptual stage, profitability analysis would not include some local regulation such as, local taxes, depreciation, subsidy, grant etc. Thereby, they will be taken on board in further stage.

In this chapter, it presents the economic indexes such as investment cost, margin, and economic criteria in order to view the feasibility of proposed design.

11.1 Investment cost

Lang method is used in order to estimate the investment of the designed process. Investment is considered in term of direct capital cost, indirect capital cost, fixed capital cost, license cost, and working capital cost.

Some commodity chemicals can be obtained from the Chemical Marketing Reporter and Chemical week magazine.

Direct Capital Cost: The summation of the material costs required to build the complete process that are incurred in the construction of a plan, in addition to the cost of equipment are:

1. Equipment erection, including foundations and minor structural work.
2. Piping, including insulation and painting
3. Electrical, power and lighting.
4. Instruments, local and control room
5. Process building and structures
6. Ancillary buildings, offices, laboratory buildings, workshops.

7. Storages, raw materials and finished products.
8. Utilities, provision of plant for steam, water, air, firefighting services
9. Site and site preparation

Indirect Capital Cost: The costs that are first, for Design and engineering, which cover the cost of design and the cost of engineering, purchasing, procurement and construction supervision. Secondly, for Contractor's fees and for Contingency allowance.

Fixed Capital Cost is the summation of Direction Capital Cost and Indirection Capital Cost. Purchased Equipment Costs (PSE) with Lang method and capital cost can be found in the Appendix G. The summary of the capital investment cost presents in Table11.1.1.

Table 11.1.1. *Capital Investment Cost*

Costs	2003
	US$
1. Direct Capital Cost	26,676,201
2. Indirect Capital Cost	8,002,860
3. Fixed Capital Cost	34,679,062

The total investment cost consists of fixed capital cost and working capital, where working capital is 8% of fixed capital cost. Therefore the total capital cost is summarized in Table11.1.2.

Table 11.1.2 *Total Capital Cost*

Total Investment Costs	Year' 2003 US$ million
1. Fixed Capital Cost 2.Working Capital Cost	34.68 2.77
Total Investment Costs	37.45

Note:

Working Capital Cost means the additional investments for start up until income starts such as initial catalyst charge, raw material & intermediates, finished product inventories.

Table 11.1.3 presents the production cost. The raw material and utilities cost can be found in the Appendix G.

Table 11.1.3 *Production Cost*

Production Cost	**Cost US$/a @2003**	**Cost Million US$/a @2003**	**% of Total Production Cost**
Variable cost			
1. Raw Materials	***47,290,450***	47.290	59.78
2. Miscellaneous materials	173,395	0.173	0.22
3. Utilities	***14,581,679***	14.582	18.43
4. Shipping and Packaging		0.000	0.00
Sub Variable cost A	*62,045,524*	62.046	78.43
Fixed cost			
5. Maintenance	1,733,953	1.734	2.19
6. Operating Labor	1,500,000	1.500	1.90
7. Laboratory costs	300,000	0.300	0.38
8. Supervision	300,000	0.300	0.38
9. Plant Overheads	750,000	0.750	0.95
10. Capital charges	3,467,906	3.468	4.38
11 Insurance	346,791	0.347	0.44
12. Local taxes	693,581	0.694	0.88
13. Royalties	346,791	0.347	0.44
Sub Fixed cost B	*9,439,022*	9.439	11.93
Direct production costs A+B	71,484,545	71.485	90.37
14. Sales Expense	3,574,227	3.574	4.52
15. General overheads	3,574,227	3.574	4.52
16. Research and Development	471,951	0.472	0.60
Sub-total C	*7,620,406*	7.620	9.63
Annual production cost = A+B+C	***79,104,951***	79.105	100.00

11.2 Economic criteria

In order to determine the economic, Process Cash Flow, Rate of Return (ROR) and Pay Out (Back) Time (POT) of the investment are summarized in Table 11.2. Detail calculation of each criterion can be found in Appendix G.

***Table11.2.** Economic Criteria*

Economic Criteria	
Cash Flow M US$	13.72
Rate of Return (ROR) [%]	*25.38*
Pay Out Time yrs	6
DCFROR %	28.44

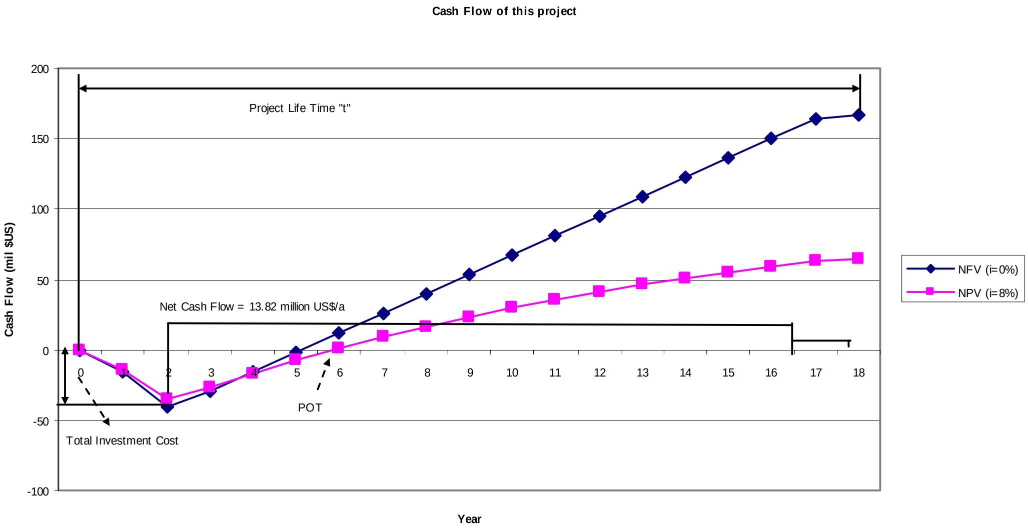


***Figure 11.2.**Discounted Cash Flow (Economic criteria) for i=0% and i=8%*

(Also see Appendix H.4 for the economy for the process with Heat integration)

12 Creativity and Group Process Tools

Creativity and group process tools are imperative methodologies to design a process, even to solve problems. In the group design, every member should have his or her own creativity to solve the problem encountered. Among these creativities, developing the best creativity and process tools for the team is necessary. In this chapter, all activities and results regarding to creativity, or process tools are mentioned.

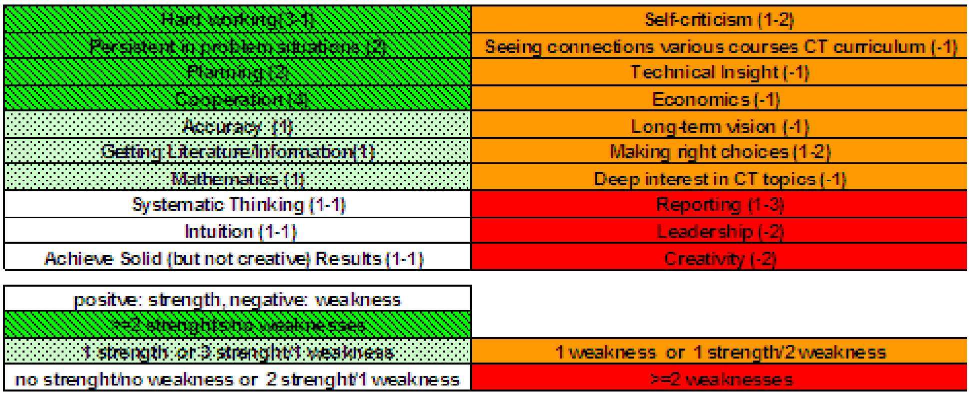
12.1 Group performance

Before starting the project, we had evaluated our group situation by group performance tool, which finds out the strength and weakness of each team member then combines in-group performance. At first, we found that the strengths of our group were Cooperation, Hard working, Persistent in problem situations, and Planning. These strengths we have to keep them on throughout the project. On the other hands, the weaknesses of our group, which should be improved, were Reporting, Leadership and Creativity. From this analysis, we had set up the rule to tackling these weaknesses such as:

Reporting: Planning to check meticulously the final report
Leadership: Setting up the role rotation share and practice the leadership
Creativity: Coach meeting, Internal meeting, Brainstorming, Note diary and Discussion with Specialist, could be improved.

The group performance before and after doing this design project are presented in Table 12.1 and 12.2

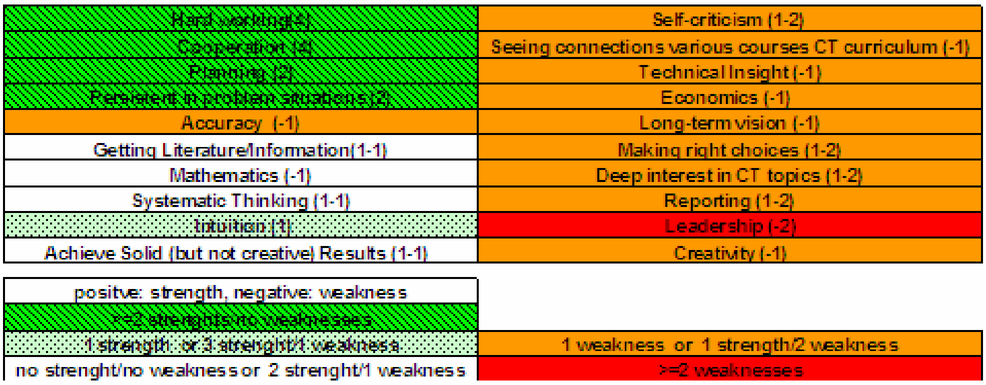
__Table 12.1__ Group performance before doing design project



Hard working(3-1)	Self-criticism (1-2)
Persistent in problem situations (2)	Seeing connections various courses CT curriculum (-1)
Planning (2)	Technical Insight (-1)
Cooperation (4)	Economics (-1)
Accuracy (1)	Long-term vision (-1)
Getting Literature/Information(1)	Making right choices (1-2)
Mathematics (1)	Deep interest in CT topics (-1)
Systematic Thinking (1-1)	Reporting (1-3)
Intuition (1-1)	Leadership (-2)
Achieve Solid (but not creative) Results (1-1)	Creativity (-2)

positve: strength, negative: weakness	
>=2 strenghts/no weaknesses	
1 strength or 3 strenght/1 weakness	1 weakness or 1 strength/2 weakness
no strenght/no weakness or 2 strenght/1 weakness	>=2 weaknesses

Table 12.2.*Group performance after doing design project*



Hard working(4)	Self-criticism (1-2)
Cooperation (4)	Seeing connections various courses CT curriculum (-1)
Planning (2)	Technical Insight (-1)
Persistent in problem situations(2)	Economics (-1)
Accuracy (-1)	Long-term vision (-1)
Getting Literature/Infomation(1-1)	Making right choices (1-2)
Mathematics (-1)	Deep interest in CT topics (1-2)
Systematic Thinking (1-1)	Reporting (1-2)
Intuition (1)	Leadership (-2)
Achieve Solid (but not creative) Results (1-1)	Creativity (-1)

positve: strength, negative: weakness	
>=2 strenghts/no weaknesses	
1 strength or 3 strenght/1 weakness	1 weakness or 1 strength/2 weakness
no strenght/no weakness or 2 strenght/1 weakness	>=2 weaknesses

After doing design stage, the group performance analysis presented that our design group still have problem in leadership. From this weakness, however, we still remain our group strength as hard working, cooperation, planning and persistent in problem situations; moreover we have improved our own creativity more or less. That means our rules set and our responses on tackling the weakness satisfy as well.

12.2 Creativity

Creativity is considered as an important tool in design project especially in chemical plant design. As a designer, one should be able to benefit from enhancing his or her creativity during this CPD project.

In order to be more creative during the CPD project, the following techniques are applied:

1) Formulating and understanding the real problems, which are the heart of the matter (*the state of the art*). The chart of creative method to perform CPD project is presented on Figure 12.1.
2) Generating diverse ideas and solutions by brainstorming
3) Focusing on the problem by analyzing the desired target and the specified criteria. Using drawing as a tool to focus on our problem in a different way.
4) Utilizing the incubation phase (after activities, take an appropriate activity to leave the problem for sometime).
5) After incubation phase, some ideas are expected, sudden brainwave; clear ideas come up, here notebook/note pad needed.
6) Evaluating potential solutions, finding the right solution for the problem. Careful formulation of alternative process combinations during the process selection, for instance are shown in Figure 12.2.
7) During design stage, discussion with specialist in technical in very important, it will make task more confidently.

12.3 Group Process Tools

To optimize group performance, the following approaches have been applied during the CPD project:

1) High and fixed Frequency of meeting, in order to communicate, share new ideas, monitor the progress of work which is done by each member
2) Punctuality, in order to improve the efficiency by penalty
3) Openness, to talk with each other, in order to prevent something going into the wrong direction
4) Good planning, to organize the work in good order
5) Documentation, day by day activities should be recorded in neat files

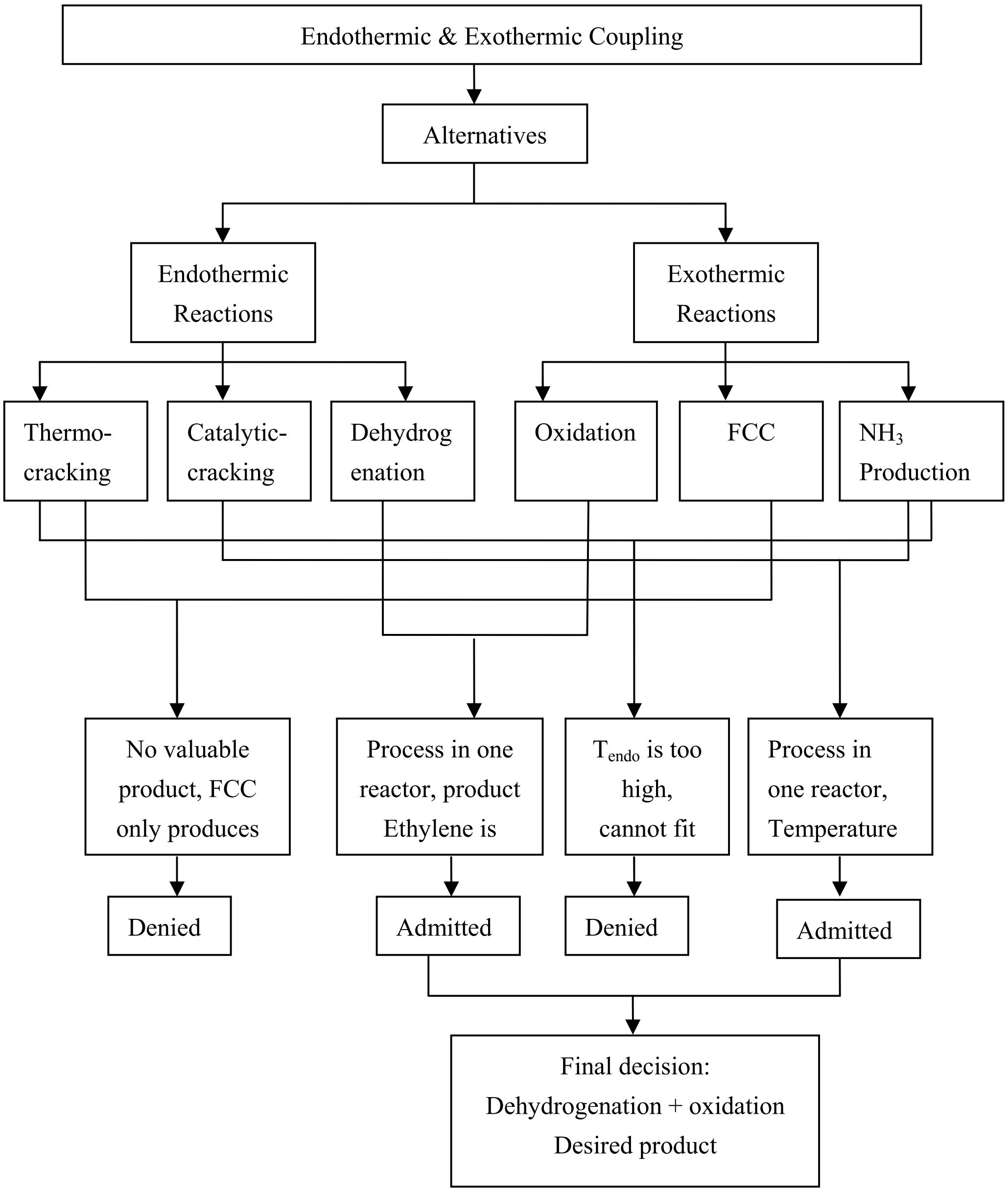


***Figure12.2.** Creativity steps in process selection*

Project design

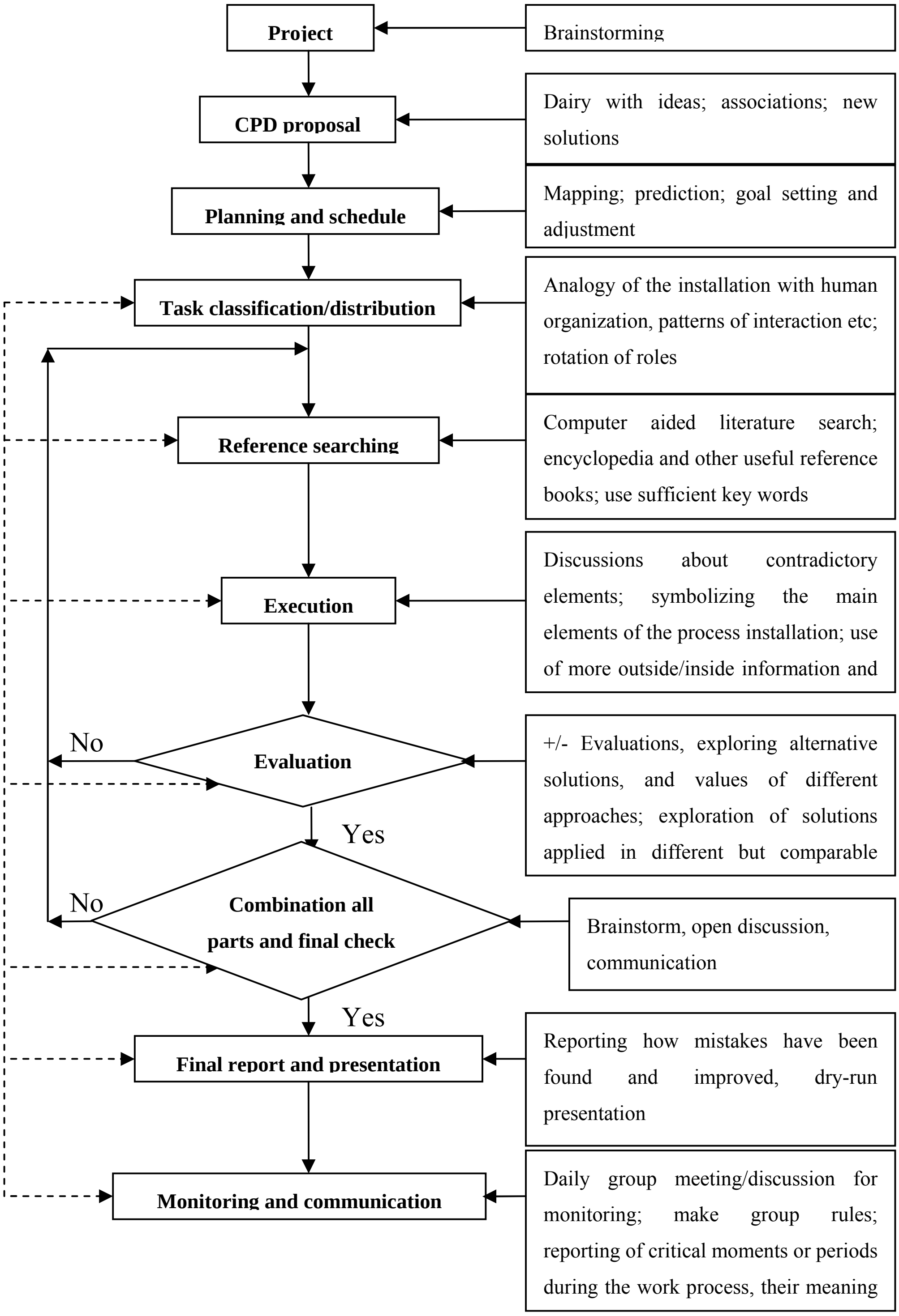


Figure 12.1. *The chart of creative method to perform CPD project*

13 Conclusions and Recommendations

13.1 Conclusion

In order to design an alkenes-producing plant which applied exergy loss reduction concept, this CPD project proposes to combine the endothermic reaction (propane dehydrogenation) and exothermic reaction (propane oxidative dehydrogenation) to exchange reaction heat each other. A coupling of exothermic and endothermic propane conversion reactions, makes the process highly energy efficient with a drastic reduction in the external energy requirement.

The reactor used in this design is a novel reactor so called heat exchanger reactor (HEx reactor). The shell and tube configuration is proposed as HEx reactor which constructed with fixed bed catalyst in both side. Catalysts used in the reactions are V_2O_5 for oxidative propane dehydrogenation in shell side and and Pt on MFI zeolite for propane dehydrogenation in tube side.

Exergy loss is related directly to work loss from the process. The ‘work loss’ term is used here as well. Compared to the separated process of each reaction and this combination route, we found that the work loss that we can conserve the utilities consumption from the reaction is 28kcal/molC_3H_8.(See calculation in Chapter 8.3.). It is obvious that the combination of endothermic and exothermic can be designed and approach to the milestone of this idea.

In this project, the design is not only focused on the coupling of exothermic and endothermic reaction, but also focused on the design of separation section and heat integration within process. It is hard to compare how much this coupled process design can reduce the exergy loss compared to the separated process because the separated processes also are designed with heat integration to reduce energy consumption in industrial scale.

The design of distillation column uses the idea of self-refrigerant and heat pump process to get less work loss and to achieve more energy saving. Some cooling duties are supplied by cold streams in the alkenes plant and FT plant. Two cold streams are utilized as refrigerant for condensers. The light gas column use expanded hydrogen stream which is obtained from the F-T process. The ethylene separation column uses a part of ethylene product passing through expansion valve as refrigerant. Meanwhile, in the propane/propylene column (C3 splitter), the less energy loss consumption is achieved by applying with heat pump process.

Two flowsheets of processes were assessed; process with heat integration and process without heat integration. In process with heat integration, even though the utilities media consumption can be reduced, the total investment is very high. The cost of heat exchanger increases tremendously. The high cost is caused by huge heat transfer area. In this alkenes process, the heat exchange is occurred between gas and gas. The heat transfer coefficient of gas-gas heat exchanger is very low. This low heat transfer coefficient leads to extremely large heat transfer area. The economic evaluation of proposed design with heat integration also can be found in Appendix H.4. From economic point of view, process with heat integration is less attractive compared to the process without heat integration. The economic evaluation for process without heat integration, the more profitable is presented in Chapter 11 and Appendix G. Economic evaluation shows that the proposed process design is profitable and attractive. The ROR is 25.38%, pay back period (PBP) or pay out time (POT) is 6 years and 28.44 % DCFOR.

13.2 Recommendations

13.2.1 Reaction and Task integration

Coupling exothermic reaction and endothermic reaction is an example of Heat Exchanger Reactor (HEx reactor) concept, a novel concept in reactor engineering according to process intensification approach. Process intensification is a novel design approach, which aims to reduce the exergy loss, to substantial save in capital cost and to reduce the environmental impact. Those topics are new frontier in chemical engineering. Consequently, most of them are still in early stage of development and there are lots of researches to be done.

In Reaction section, more research on kinetic and operating condition of specific catalysts are needed. Reactor should be designed a more rigorous and advanced calculation instead of applying some simplified models and assumptions. For distillation design, the condition of distillation column, such as temperature difference between top and bottom column should be considered as operating condition. The column design has been done by using packing column which has lower pressure drop than tray column. However, this type is suffered from the low efficiency at high pressure and mal-distribution phenomena.

Heat integration can be elaborately designed by standard methods. However, the heat integration is difficult to be applied due to most of fluids in the process are in gaseous state. As a note in heat exchanger, if steam used in the process, it should be used in saturated condition because heat transfer coefficient and latent heaof liquid phase are higher than sensible heat of steam vapor.

For control design, theoretical background seems to be not enough; some practical experience is highly appreciated to locate the position and to set the loop control properly.

13.2.2 Optimal Design in Alkenes Separation to Reduce Exergy Loss

In the CPD project, the separation processes, which are applied, are the mature and reliable techniques. Most of separation duties are performed by distillation, which are highly energy consuming. In order to reduce the exergy losses, some novel separation technologies are suggested. In addition to propose some improvements in reaction and design aspect, we also have recommended to optimize alkenes production process by reducing exergy loss in separation section.

In energy loss reduction perspective, membranes gain interest because there is no phase change and high temperatures are not needed for membrane process. Membrane based gas separation, therefore, must compete primarily on the basis of overall economics and convenience. However this technology is still to be developed technology. Some problems remain to be solved before industrial systems will be installed. One of the major problems confronting the use of membrane based gas separation processes in a wide range of applications is the lack of membranes yielding high flux and high selectivity.

13.2.2.1 Alternatives separation technique to remove CO2

Instead of using amine treatment (MDEA treatment), the alternative technique to separate CO2 is by using Zeolite membrane and zeolite filled polymeric membranes. Zeolite is very potential to be applied in gas separation because of their high surface area (up to 1000 m2/g), high void volume (30% of the total volume of zeolite) and uniform pore size distribution [1]. As the result of zeolite membrane process, A permeate consisting carbon dioxide and non permeate contains hydrocarbon are achieved.

13.2.2.2 Light gas mixtures separation by novel inorganic membrane

The largest area for energy reduction is the cryogenic isolation of the product hydrocarbons from the reaction by-products; methane and hydrogen. This separation requires temperatures as low as -140ºC and pressures exceeding 15 bara. The research will focus on developing a capillary condensation process to separate olefin mixtures from light gas byproducts at temperatures that approach ambient conditions and at low pressure [2,3]. This technology breakthrough will result in substantial energy savings.

13.2.2.3 Non-cryogenic Purification Ethylene technology

In the conventional process, ethylene is purified from the product stream by using cryogenic distillation column which is highly energy consumptive. Ethane/ethylene separations (C2 Splitter) are large industrial cryogenic processes. Membrane based separation is a potential alternative method. Facilitated transport membrane is proposed to replace cryogenic process [4]. The facilitated transport membranes have high selectivity for olefins.

13.2.2.4 Propane/ Propylene Separation

Propane/Propylene separation is a very difficult separation. The high cost and intensive energy low temperature distillation are caused by the very similar boiling points of propylene and propane, requiring large distillation columns around 120-180 trays and high reflux ratios. There are some candidates to replace conventional distillation column to separate propane and propylene. Polyimide and composite membranes [5-7], supported liquid membranes [8], and selective adsorption [9-10] is some of the promising techniques. Previous research showed that propylene plasticized the membrane material (polyimide). Heat-treatments is suggested in order to investigate the possibilities to suppress the plasticization. Selective adsorption is based on the interaction between the olefin and chemically modified adsorbents. Chemically modified absorbents provide very attractive olefin/paraffin selectivity. The best sorbents so far were AlPO4-14 and AgNO3/SiO2.

The simplified alkenes production scheme is proposed with membrane-based separation technology. CO2 can be removed by zeolite based membrane or zeolite filled polymeric membranes. Cryogenic light gas separator can be replaced by a novel inorganic membrane. The Light gases may be further processed in inorganic membrane reactor (mixed conducting membrane) to produce syngas. Furthermore, the cryogenic ethane/ethylene column (C2 Splitter) will be replaced by facilitated-transport membrane.

Finally, polyimide membrane is recommended to replace the tall and costly distillation propane /propylene separation column (C3splitter). The recommended process scheme for the future (research to be explored) process is presented in Figure 13.2.

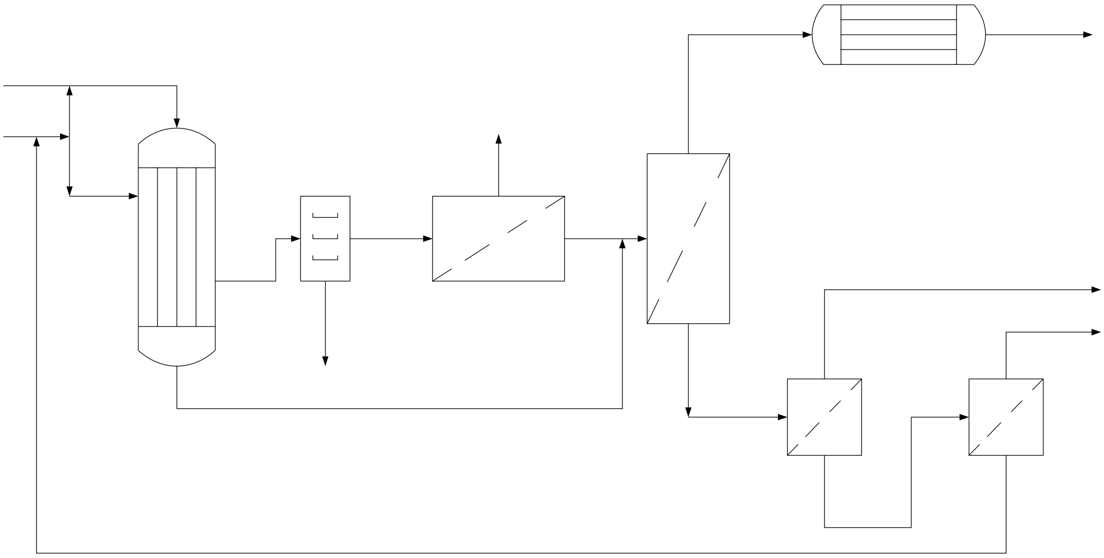


Figure 13.2. *The proposed alkenes production scheme with optimized separation process to reduce exergy losses*

List of symbols

CH_2O : formaldehyde
CH_4 : ethane
CO : carbon monoxide
CO_2 : carbon dioxide
C_2H_4 : ethylene
C_3H_6 : propylene
C_3H_8 : propane
$C_4H_2O_3$: maleic anhydride
CeO_2 : cerium dioxide
H_2O : water
NH_3 : ammonia
O_2 : oxygen
MDEA : methyl diethanolamine
Pt : platinum
V_2O_5 : vanadium pentoxide
SA5205 : aluminum flush cap rings
FCC : fluidized catalytic cracking
Auto-ign. T : auto-ignition temperature [K]
BP : boiling point [K]
Cp : heat capacity under constant pressure [kJ/mol K]
DCFROR : discounted cash-flow rate of return [%]
EOS : equation-of-state
Fl. Lm : flammable limits in air [vol%]
FP : flash point [K]
Ign.T : ignition temperature [K]
LD_{50} : lethal dose of a chemical, which kills 50% of a sample population [g/kg]
LC_{50} : lethal concentration of a chemical, which kills 50% of a sample population
LEL : lower explosive level [vol%]
MAC : maximum allowable concentration
MP : melting point [^oC]
NCF : net cash flow
NFV : net future value
NPV : net present value
PR : Peng Robinson
RK : Redlich-Kwong
SRK : Soave-Redlich-Kwong
VLE : vapour/liquid equilibrium
UEL : upper explosive level [vol%]
Liq. Density : liquid density [kg/m^3]
Rel. Vap. Density : relative vapour density (air=1)
ROR : The rate of return
POT : Pay out back time

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