



National Taiwan University of Science and
Technology

Dept. of Chemical Engineering

Process Design Final Report

**Conceptual Design and Techno-
Economic Analysis of Carbon
Monoxide and Methyl Nitrite to
Produce Ethylene Glycol**

	Name	Student ID
Leader	Cindy Suyitno	B10806211
Member	Jeane Angelica Yulianadi Susanto	B10806212
Member	Philemon Sugiarta	B10806203

June 25th, 2021



JOINT DEGREE PROGRAM
NATIONAL TAIWAN UNIVERSITY OF SCIENCE AND TECHNOLOGY &
WIDYA MANDALA CATHOLIC UNIVERSITY SURABAYA
DEPARTMENT OF CHEMICAL ENGINEERING



APPROVAL LETTER

Student name : Philemon Sugiarta

Student number in NTUST : **B10806203**

Student number in WMCUS : 5503017012

has finished a Plant Design Project in NTUST, which is also acknowledged as “Tugas Akhir Prarencana Pabrik” in WMCUS. The title of Plant Design Project is

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Supervisor WMSCU

(Felycia Edi Soetaredjo)

Taipei, June 25th, 2021

Supervisor NTUST

(Ardilla Hayu Tiwikrama)



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WIDYA MANDALA CATHOLIC UNIVERSITY SURABAYA
DEPARTMENT OF CHEMICAL ENGINEERING



APPROVAL LETTER

Student name : Cindy Suyitno
Student number in NTUST : **B10806211**
Student number in WMCUS : 5503017008

has finished a Plant Design Project in NTUST, which is also acknowledged as “Tugas Akhir Prarencana Pabrik” in WMCUS. The title of Plant Design Project is

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Supervisor WMSCU

(Felycia Edi Soetaredjo)

Taipei, June 25th, 2021

Supervisor NTUST

A handwritten signature in black ink, appearing to read "Ardilla Hayu Tiwikrama", followed by a solid horizontal line underneath.

(Ardilla Hayu Tiwikrama)



APPROVAL LETTER

Student name : Jeane Angelica Yulianadi Susanto
Student number in NTUST : **B10806212**
Student number in WMCUS : 5503017007

has finished a Plant Design Project in NTUST, which is also acknowledged as “Tugas Akhir Prarencana Pabrik” in WMCUS. The title of Plant Design Project is

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Taipei, June 25th, 2021

Supervisor NTUST

(Ardilla Hayu Tiwikrama)

Grading



ABSTRACT

Ethylene glycol is an odorless, colorless, sweet-tasting, sticky liquid that is extremely toxic. It can be used as an antifreeze and coolant, as well as in the industrial sector such as compressors, air-conditioning systems, heating, and ventilation. To make ethylene glycol, we use a coal-based technology. This technology was chosen since it is less expensive than the petroleum-based method. Aspen Plus software is used to design and simulate the production process of 6,800-ton Ethylene Glycol annually with mass purity of 99 wt%. The raw material used are Carbon Monoxide, Methyl Nitrite, Nitric Oxide, and Hydrogen gas. Two process flowsheet diagrams are being assembled. Both are designed with the following steps: reaction 1, separation 1, reaction 2, and separation 2. The main difference will be in the first separation process when the first flowsheet uses a distillation column and recycling some of the reactants, while the second flowsheet uses a flash tank and no recycling at all. The two processes undergo reaction in the presence of catalysts, which are Pd/Al₂O₃ and Cu/SiO₂. Both are amazing catalysts due to the catalysts having great surface conditions, which improves the catalyst's stability and increases the reaction selectivity.

On the other hand, as an engineer, it is also very important to keep the design as profitable as possible. To estimate and compare the profitability of the two flowsheets, calculations of the economic analysis were computed. In the first flowsheet, the total capital investment is NTD 19,780,308 and in the second flowsheet, the total capital investment is NTD 8,138,619,778. And the total production cost (TPC) in the first flowsheet cost NTD 1,939,724,218 and the second flowsheet cost NTD 2,199,755,608 per year. From the profitability analysis, we can conclude that the first flowsheet is more profitable. We can get the interest rate and payout time is better in flowsheet one, which is 0.0894 for the interest rate and 4 years for payout time. While in the second flowsheet the interest is 0.0319 and the payout time is 6 years.

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CHAPTER 1

CONCEPTUAL DESIGN

1.1. Background Introduction

The engineering design process is a series of steps that guides and emphasizes engineers to open-ended problem-solving. It is iterative, meaning that we repeat the steps as many times as needed, making improvements along the way as we learn from failure and uncover new design possibilities to arrive at a great solution. Process simulation is the art of modeling chemical and physical processes in the computer. It is not only drawing equipment alone but is mostly focused on how the unit operation will work.

Being candidate engineers, it is important to take the project of process design into serious consideration, not only to exercise and getting the requirement to graduate, but also to prepare ourselves for a future career by applying what we have learned in reaction engineering, thermodynamics, unit operation, etc., into concrete work. Ethylene Glycol production was chosen to be the topic of this project due to its wide application, potential market, and challenging production process. Focusing on the aim and objectives of the project, works of literature were reviewed, then concept flowsheets were built and simulation was done to evaluate the economic costs and analysis.

1.2. Project Aim and Objective

The goal of this project is to design the Ethylene Glycol (EG) production line to obtain at least 6,800-ton annual production from the raw material of Carbon Monoxide (CO), Methyl Nitrite (MN), and Nitric Oxide (NO) by using a simulation program of Aspen Plus while applying the fundamental knowledges and theories of chemical engineering that we have already learned.

The objectives of the project:

- Achieving purity at least 99 wt% of Ethylene Glycol
- Optimizing, quantifying, and establishing the major equipment design, including the reactor, distillation column, and flash tank.
- Estimating the total cost, interest rate (i), payout time, and revenue including the cost analysis and profitability calculation.

1.3. Literature Review

1.3.1. Introduction of Ethylene Glycol

Ethylene Glycol or ethane-1,2-diol is an odorless, colorless, sweet-tasting, viscous liquid, and very poisonous [1]. There are many applications of ethylene glycol, the first application is for antifreeze and coolant to help car engines not to freeze in winter and cooling the engine in summer. The second application is as a heat transfer agent liquid that is often used in the industrial for compressor, air-conditioning system, heating, and ventilating, etc. The third application of ethylene glycol is for raw material to produce polyester fibers for clothes, and other many polyester products like PET bottles [2].

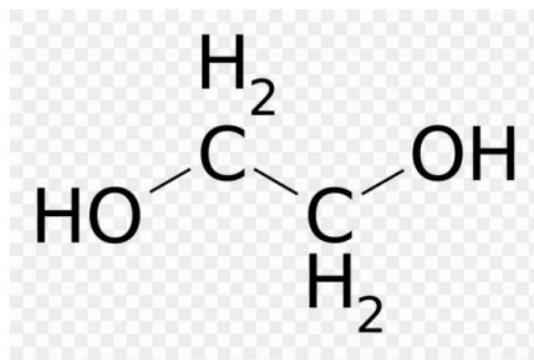


Figure 1.3.1. Molecular Structure of Ethylene Glycol

Ethylene Glycol can be produced in many ways, first way can be produced by oxidation of ethylene. The second way, ethylene glycol can be produced by hydrolysis of ethylene oxide which via ethylene chlorohydrin, and this method proceeds by direct oxidation route to produce ethylene glycol [3]. In our process production, we use coal-based to produce ethylene glycol. We choose this method because it is less costly than using the petroleum-based process. It can save 39.5% compared to petroleum-based ethylene production under the same product amount because the cost of coal is much cheaper than the cost of petroleum. On the other hand, by using a coal-based process we also can make using the coal effectively [4].

1.3.2. Palladium/Alumina Catalyst

Pd/Al₂O₃ is a metal catalyst in a form of a black powder. Pd/Al₂O₃ is an excellent catalyst because of its surface condition that improves the catalyst's stability and increases the reaction's selectivity. Pd/Al₂O₃ has a life span of around 8000h. Palladium surfaces are

effective catalysts for hydrogen and oxygen-based chemical processes, such as the hydrogenation of unsaturated organic molecules. Palladium is a more reactive platinum metal than the others. Acids attack it more rapidly than any of the other platinum metals, for example [5].

The reaction mechanism of the Pd/Al₂O₃ catalyst is the coupling reaction. The coupling reaction is a reaction mechanism that refers to a group of organic reactions in which two chemical species are joined, usually with the help of a metal catalyst. The main aim of both couplings is to transmit power while accommodating misalignment and adjusting for axial or end shaft movement [6].

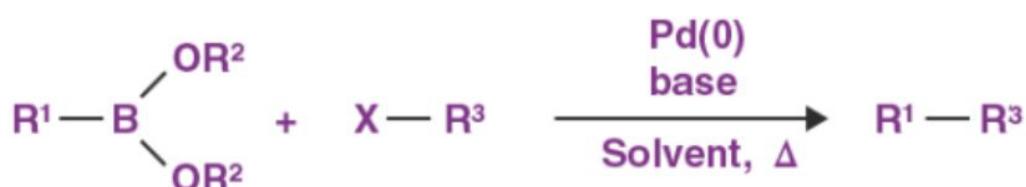


Figure 1.3.2. Reaction Mechanism of Coupling Reaction

Pd/Al₂O₃ catalyst can be relatively simple to regenerate, it can be dissolved in hydrochloric solution with an appropriate oxidant present under a suitable condition. There are 3 steps to this regeneration process. First, the catalyst needs to undergo pretreatment which the catalyst will be roasted under a certain temperature for a certain time. Then, the catalyst will undergo a process called the leaching process, where the catalyst will be leached with HCl and an oxidant. Several oxidants can be used such as H₂O₂, NaClO₃, NaClO₄. Finally, a reduction agent needs to be added to the catalyst, and the reduction agent that can be used are HCOOH, HCOOH + HCl, and N₂H₄.H₂O [7-10].

1.3.3. Copper/Silica Catalyst

Cu/SiO₂ is a metal catalyst in a form of a black powder. It is an amazing catalyst due to its surface modification that improves the catalyst's stability and also increases selectivity. Cu/SiO₂ has a life span of 3080 h. The reaction mechanism of this catalyst is by the covering of the silane coupling agent. The textural features of catalysts, such as pore structure, copper particle size, and morphology, were maintained with surface modification, while the surface areas of copper species were somewhat reduced due to the covering with silane coupling agents. Due to the promotion effects on MG desorption, the stability of catalysts was considerably increased following surface modification. Covering

the hydroxyl groups with silane coupling agents could improve catalytic stability and reduce by-product selectivity [11-18].

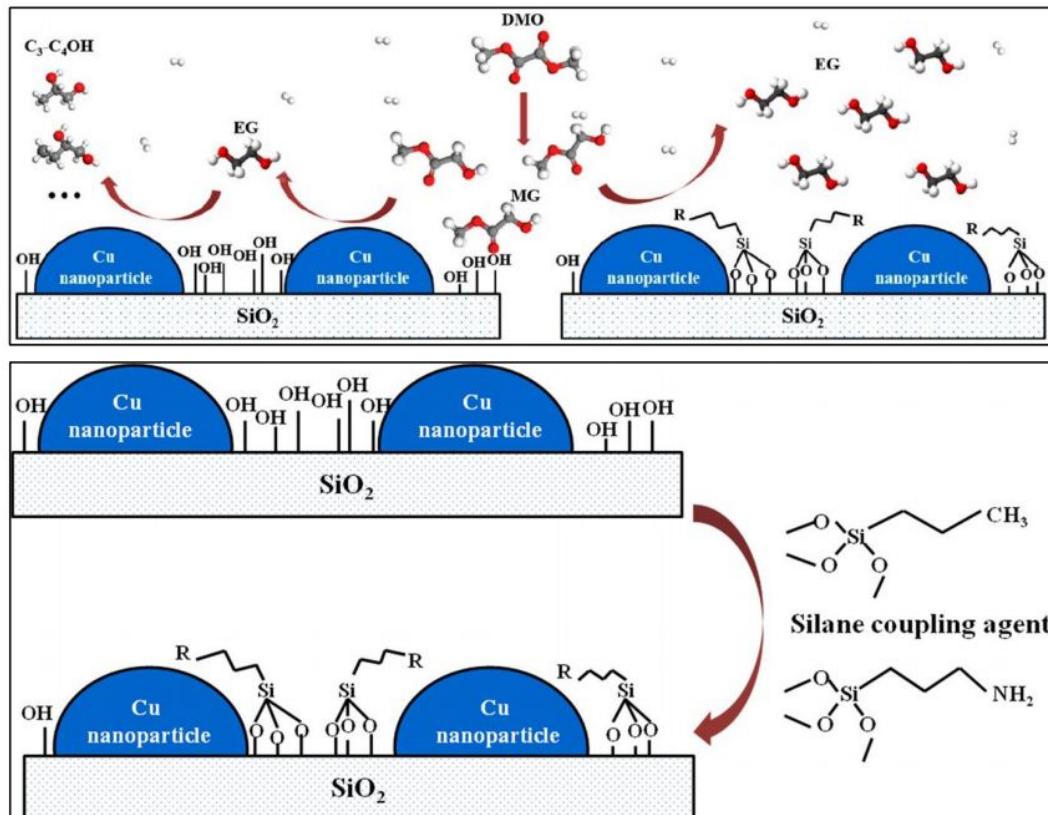


Figure 1.3.3. Reaction Mechanism for Cu/SiO₂ Reaction Mechanism

1.3.4. Marketing

For the target market, nowadays ethylene glycol is in high demand from the consumer because there are still few companies that produce ethylene glycol while the demand for the products is varied. The product demand is varied by the type cover and by the application. By the cover, we can divide into 3 categories which are fiberglass mono-ethylene glycol, industrial-grade mono-ethylene glycol, antifreeze grade mono-ethylene glycol. By the application, we can divide into 4 categories such as polyester resin, antifreeze, and coolant, chemical intermediates, heat transfer fluids. The CAGR of ethylene glycol in 2019 will grow almost 4%, with incremental growth of about 6,548.34 thousand tons. The year-over-year growth rate for 2019 is estimated at 3.5%. The highest growth of ethylene glycol is 80% from the Asia Pacific Region [19]. Newest data showed that from

2021 to 2026 the market of mono-ethylene glycol will increase by 3.2% and it will reach the US \$25,290 million by 2026, from the US \$20,930 million in 2021 [20].



Figure 1.3.4. Global Ethylene Glycol Market

1.4. Concept Design

The provided design should fulfill the goal of 6,500 ton/year and 99 wt% EG as well as low capital and operational cost. The EG production process was taken based on syngas in an indirect way (**Figure 1.4.1.**). In our design, it was decided to drop the esterification reaction as this just add more cost to produce methyl nitrite (MN) from methanol, nitrogen, and oxygen. We have got producer of methyl nitrite with low raw material cost hence it is considered ineffective to build another plant consist of reactor and distillation columns.

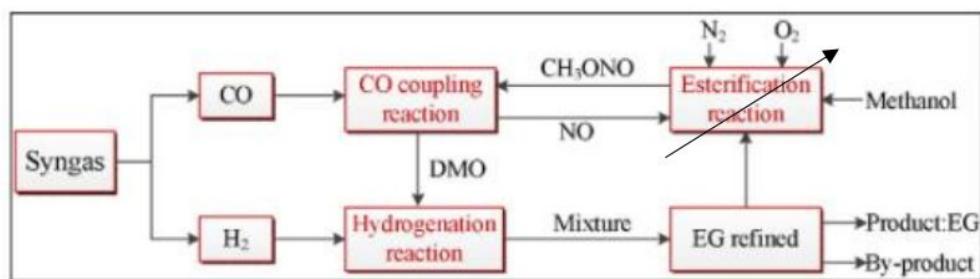


Figure 1.4.1. An overview of the EG production based on syngas in an indirect way [21]

In the making, there will be two reactions occur in different batches (CO coupling reaction in reactor 1 and hydrogenation reaction in reactor 2) therefore two reactors should be provided. Between the reactor, we also should provide a separation process to minimize impurities for further reaction. Hence several operating conditions and design requirements

were set, selectivity was done in every reactor for the temperature, pressure, and concentration ratio with the basis from reference. The reactants that are involved are carbon monoxide (CO), methyl nitrite (MN), nitric oxide (NO), and hydrogen (H₂), which all will be in the gas state. Two designs are provided, both were varied in the first separation process, to check which one is better and more cost-effective. The former utilizes two distillation columns; the first one is to recycle the CO reactant and the second one is to separate the desired product (DMO). The latter utilizes a flash tank to separate DMO (without any reflux). The basic flowchart block can be seen in the figure below.

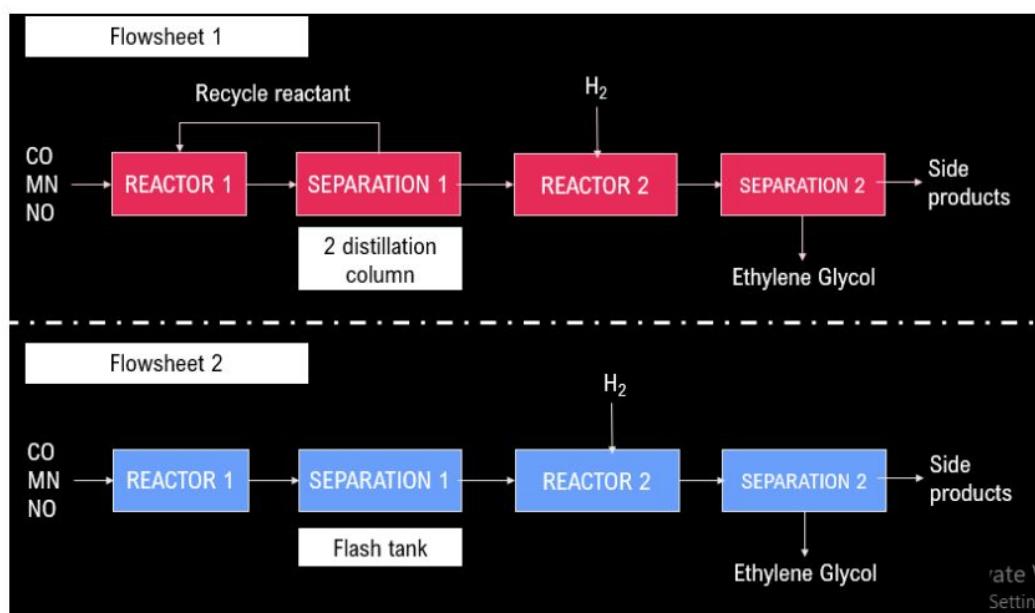


Figure 1.4.2. Process Flow Block Diagram of Flowsheet 1 and 2

The main concern of this design would be in the second reactor part. Based on the objective of achieving as much EG as possible, we have tried lots of reactor configuration, with PFRs and CSTRs and sensitivity tests based on the 4 factors mentioned before. Due to the complexity of the kinetics, the best results we got so far have to use 2 PFRs in parallel with 2 PFRs in series for every parallel line. The temperature has to be above 200°C and the pressure has to be above 15 bar due to the kinetic data. Sensitivity was done in order to get optimized operating parameters. This specific configuration will be furtherly discussed in the reactor section. Another consideration is the reactor size, due to the utility cost, which is the main difference, aside from the duty, for the first reactor in the flowsheet that we designed. The strategy was to increase the reaction rate and reaction conversion of the first

reaction due to more reactant recycled, but this will result in similar results with the limiting reactant in the second flowsheet; the further explanation is also discussed in the reactor section. No azeotrope point was obtained, but the separation of the final product is considerably hard due to the close boiling point of two of the heaviest components in the system, which is DMO and EG. Therefore, reactive distillation was implanted in both designs as we want a highly purified product. The product that is obtained is only EG, as the side product like MeOH is in the middle key of the system. To obtain purified MeOH, a minimum of 2 separation stages is needed and it is considered too costly.

1.5. The Resource of Key Reference and Parameter

1.5.1. Target Production

Goal: 6,800 tons/year, 99 w% purity

$$F_{EG} = 6800 \frac{\text{ton}}{\text{year}} \frac{1000 \text{ kg}}{1 \text{ ton}} \frac{1 \text{ year}}{345 \text{ working days}} \frac{1 \text{ day}}{24 \text{ hours}} \frac{1 \text{ kmol}}{62.07 \text{ kg}} = 13.23 \text{ kmol/hr}$$

1.5.2. Thermodynamics Parameters

A non-random two-liquid model-Redlich Kwong (NRTL-RK) is used. NRTL is applied widely in process design simulation as it is considered one of the most flexible and accurate models for real chemicals. The equation was firstly designed by Renon and Prausnitz [22] as an empirical model that would improve the Wilson equation for the simultaneous heat of mixing, liquid-liquid equilibria (LLE), and activity coefficient in binary and multicomponent systems. Mathematically, the model uses the parameter of the non-randomness (α , generally between 0.2 to 0.47) into Scott's two-liquid model theory, making it empirical based on the local composition representation of the excess Gibbs free energy of the mixtures [23]. For binary system, the NRTL equation is expressed as:

$$\frac{G^E}{RT} = x_1 x_2 \left(\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right)$$

$$G_{12} = \exp(-\alpha_{12} \tau_{12}); \quad \tau_{12} = \frac{\alpha_{12}}{T}; \quad G_{21} = \exp(-\alpha_{12} \tau_{21}); \quad \tau_{21} = \frac{\alpha_{21}}{T}$$

NRTL provides no advantages over simpler equations like van Laar and three-suffix Margules equation when it is faced with a moderately non-ideal system. However, for a strongly non-ideal system, especially in immiscible systems, NRTL provides a good

representation of experimental data [23]. It is superior to the Wilson equation in that it can present LLE, VLE, as well as VLLE, and still simpler in form than the UNIQUAC equation [24] hence is incorporated in this project.

The addition of the Redlich Kwong equation of state was used instead of the other such as the van der Waals equation or the ideal gas equation as it is more accurate above the critical point. The EOS was derived by Otto Redlich and Joseph Neng Shun Kwong back in 1949, which used a two-parameter of the cubic equation of state. It is formulated as follow:

$$p = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T} V_m (V_m + b)}$$

The equation relies heavily on temperature, pressure, and volume of gases [25]. It is also applicable to a mixture of gases. As our process was done in high temperature and pressure, with non-polar substances in gaseous phase takes place in the reactions, the NRTL-RK model was considered excellent modeling this system. The thermodynamics diagram and all binary parameters in the simulation can be seen below. The binary data were obtained from Wei et al. [26] To make it easier, the thermodynamics diagrams that are presented was divided based on the diagram process.

Component i	Component j	Source	Temperature units	Aij	Aji	Bij	Bji
METHANOL	H2O	APV110 VLE-IG	C	-0.693	2.7322	172.987	-617.269
METHANOL	EG	APV110 VLE-IG	C	33.3298	0.1753	-10000	-322.924
H2O	DMO	APV110 LLE-AS...	C	-456.474	-232.384	22864.9	12859.7
H2O	EG	APV110 VLE-IG	C	0.3479	-0.0567	34.8234	-147.137
H2	CO	USER	C	0	0	-271.58	331.71
H2	NO	USER	C	0	0	204.13	-125.36
H2	METHANOL	USER	C	0	0	-605.95	996.38
H2	DMC	USER	C	0	0	-1371.91	5079.03
H2	H2O	USER	C	0	0	-449.67	638.35
H2	DMO	USER	C	0	0	-2213.92	-891.73
H2	EG	USER	C	0	0	-891.73	196.28
CO	NO	USER	C	0	0	-4.47	52.01
CO	METHANOL	USER	C	0	0	-363.11	478.22
CO	DMC	USER	C	0	0	-992.17	2390.07
CO	H2O	USER	C	0	0	191.33	-188.65
CO	DMO	USER	C	0	0	-1445.73	5769.02
CO	EG	USER	C	0	0	-624.71	1045.78
NO	METHANOL	USER	C	0	0	-367.78	465.14
NO	DMC	USER	C	0	0	-1071.35	2841.93
NO	H2O	USER	C	0	0	347.71	-74.81
NO	DMO	USER	C	0	0	-1641.14	8137.29
NO	EG	USER	C	0	0	-690.54	1233.87
METHANOL	DMC	USER	C	0	0	221.04	-1534.97
METHANOL	DMO	USER	C	0	0	426.19	-86.29
DMC	H2O	USER	C	0	0	-571.11	1528.88
DMC	DMO	USER	C	0	0	80.11	-118.42
DMC	EG	USER	C	0	0	-273.39	351.79
DMO	EG	USER	C	0	0	23.72	-131.14
METHANOL	ETHANOL	APV110 VLE-IG	C	4.7119	-2.3127	-1162.29	483.844
H2O	ETHANOL	APV110 VLE-IG	C	3.4578	-0.8009	-586.081	246.18
EG	ETHANOL	APV110 VLE-IG	C	-0.1115	14.8422	157.594	-4664.41
H2	ETHANOL	USER	C	0	0	-1223.64	3829.61
CO	ETHANOL	USER	C	0	0	-946.87	2151.71
NO	ETHANOL	USER	C	0	0	-943.64	2168.32
DMC	ETHANOL	USER	C	0	0	28.78	414.19
DMO	ETHANOL	USER	C	0	0	-108.76	564.84
H2	MG	USER	C	0	0	-1689.14	8822.81
CO	MG	USER	C	0	0	-1157.83	3361.33
NO	MG	USER	C	0	0	-1191.03	3617.66
METHANOL	MG	USER	C	0	0	-85.79	59.31
DMC	MG	USER	C	0	0	-1.78	118.47
H2O	MG	USER	C	0	0	893.61	-275.02
DMO	MG	USER	C	0	0	-225.51	384.71
EG	MG	USER	C	0	0	-734.54	1349.79
ETHANOL	MG	USER	C	0	0	251.82	-116.02

Figure 1.5.2.1. Binary Parameter in Aspen

These are Txy diagrams for the first separation process. The system includes a mixture of CO-NO-MN-DMO, where the main objective is to separate DMO from other components. In the first flowsheet, this separation consists of two processes with a different distillation

column. The first column was used to recycle CO (Fig. 1.3.2.2.-Fig. 1.3.2.3.) while the second column was to separate DMO (Fig. 1.3.2.4.-Fig. 1.3.2.5.). While in the second flowsheet, there is only a flash tank to separate DMO (Fig. 1.3.2.4.-Fig. 1.3.2.5.). There are lines to represent the system temperature, which were obtained from the aspen simulation.

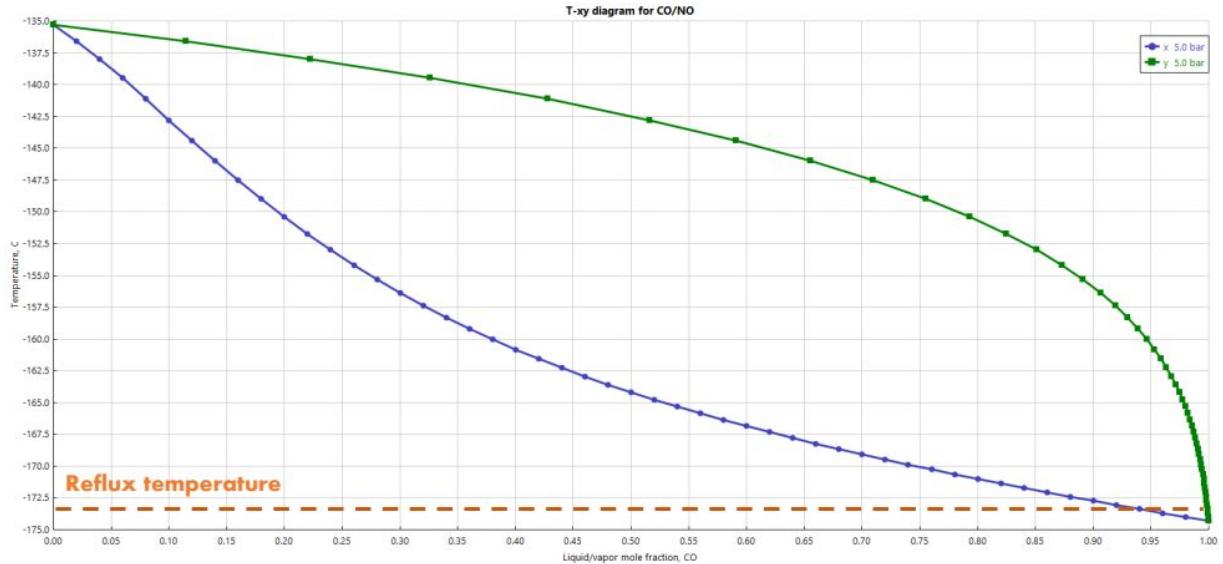


Figure 1.5.2.2. Txy diagram for CO-NO at 5 bar

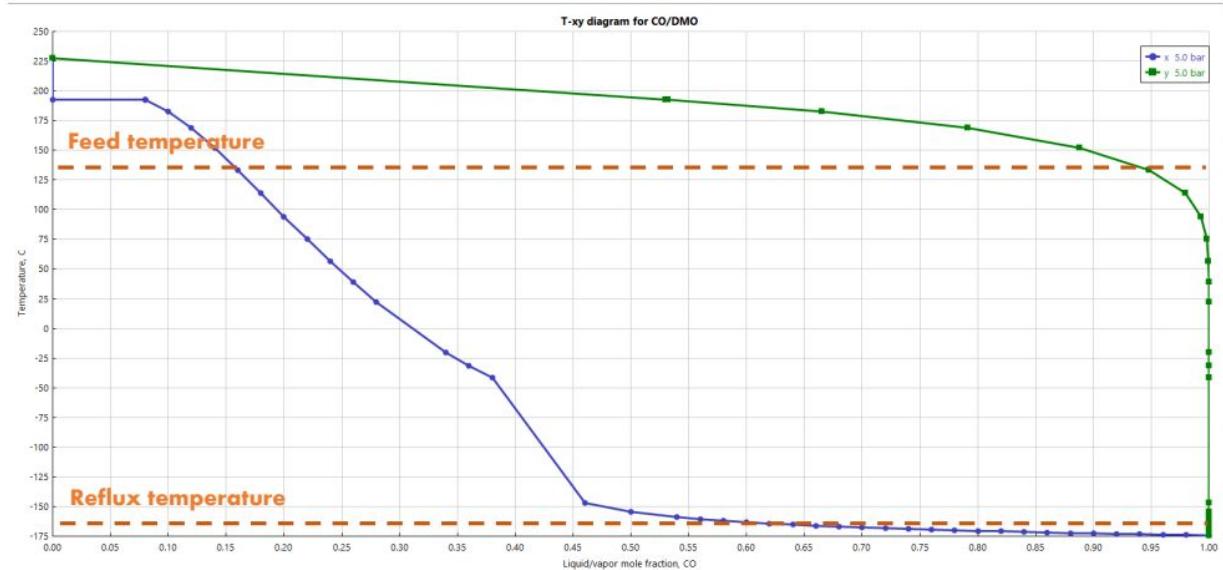


Figure 1.5.2.3. Txy diagram for CO-DMO at 5 bar

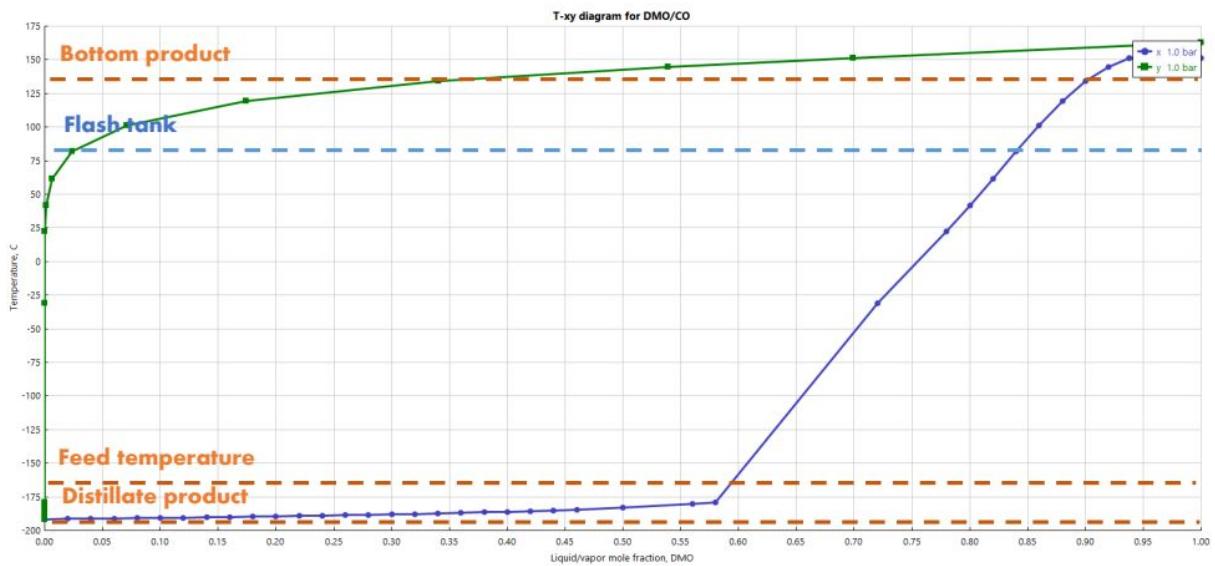


Figure 1.5.2.4. Txy diagram for CO-DMO at 1 bar

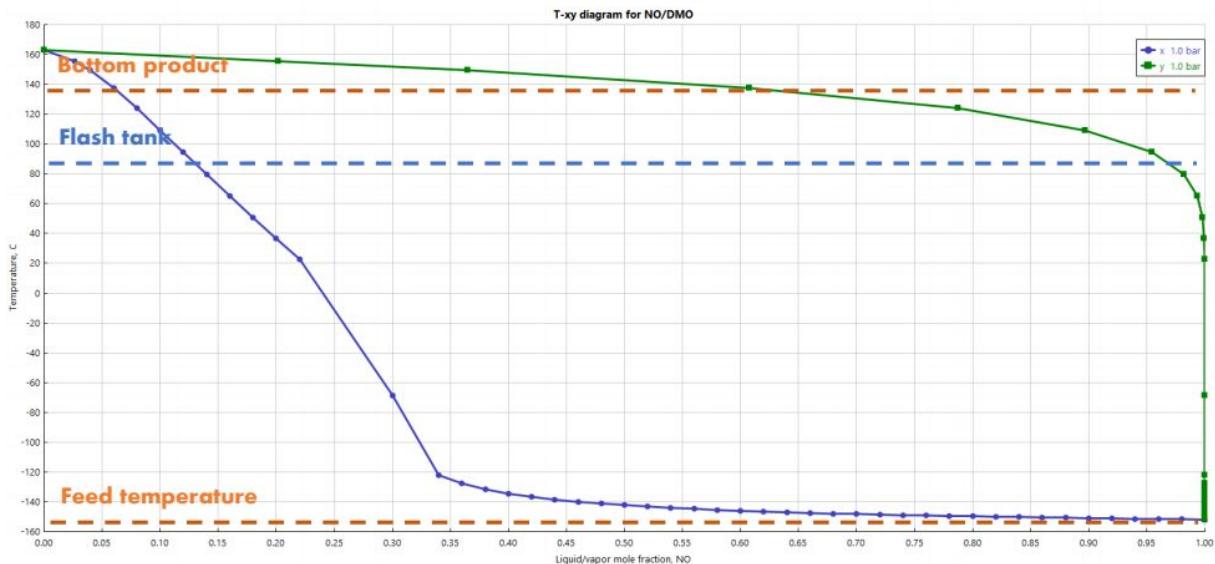


Figure 1.5.2.4. Txy diagram for CO-DMO at 1 bar

The second separation process consists of a mixture of EG-DMO-H₂-MeOH-MG-NO-MN, where the main goal is to separate EG. To give detailed information, the lines in the diagram represent bottom and distillate temperature in the first and second flowsheet, with the legend as follow: green for the bottom product in the first flowsheet, blue for the distillate product in the first flowsheet, yellow for the bottom product in the second flowsheet, and grey for the distillate product in the second flowsheet.

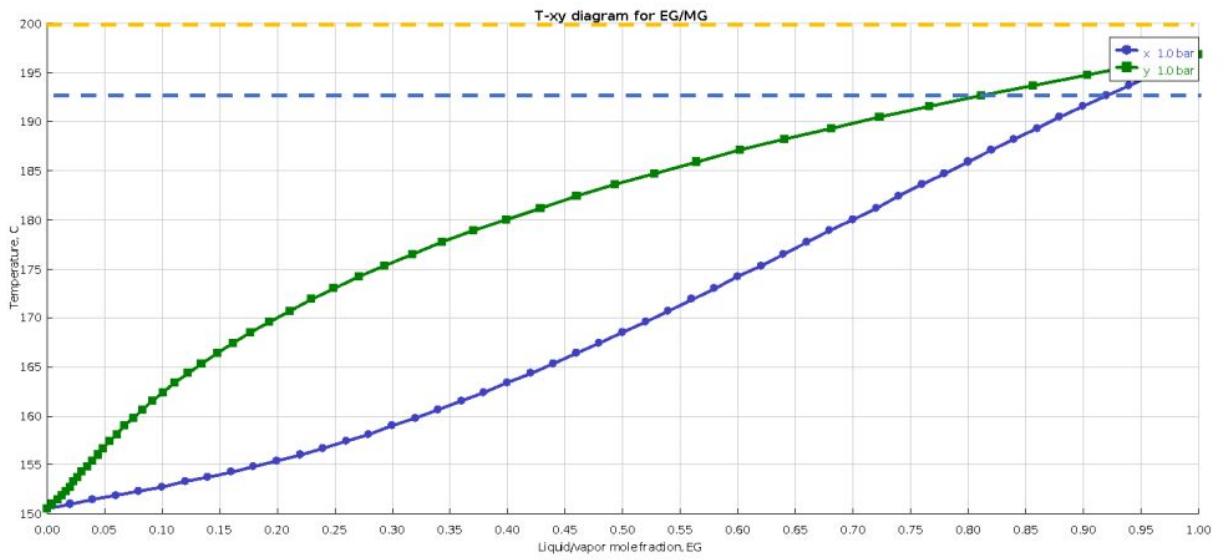


Figure 1.5.2.5. Txy diagram for EG-MG at 1 bar

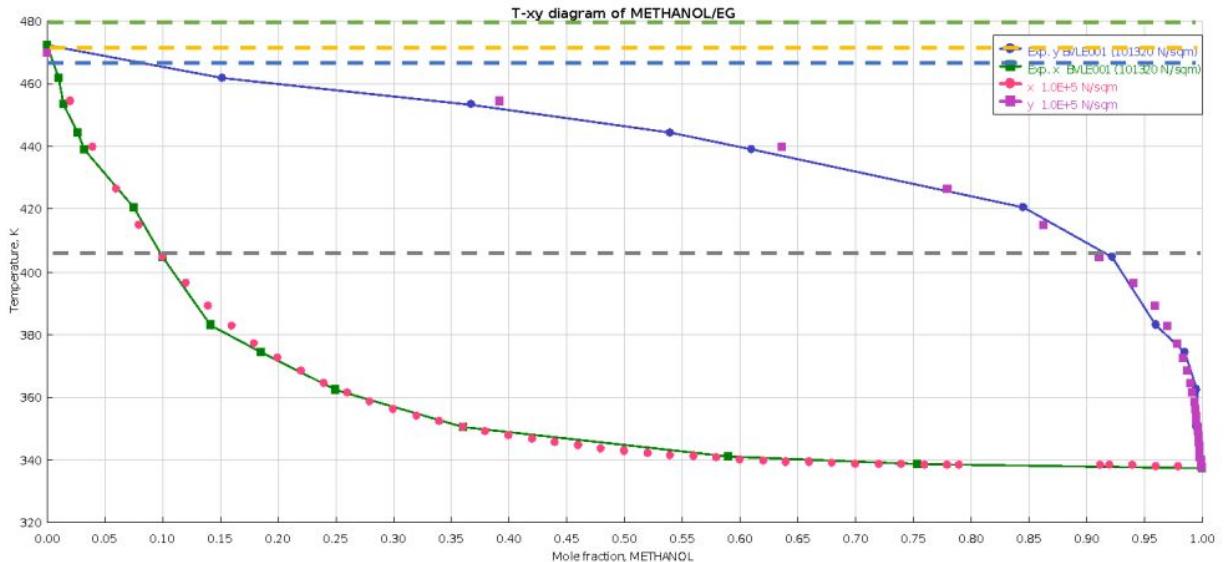


Figure 1.5.2.6. Txy diagram for MeOH-EG at 1 bar

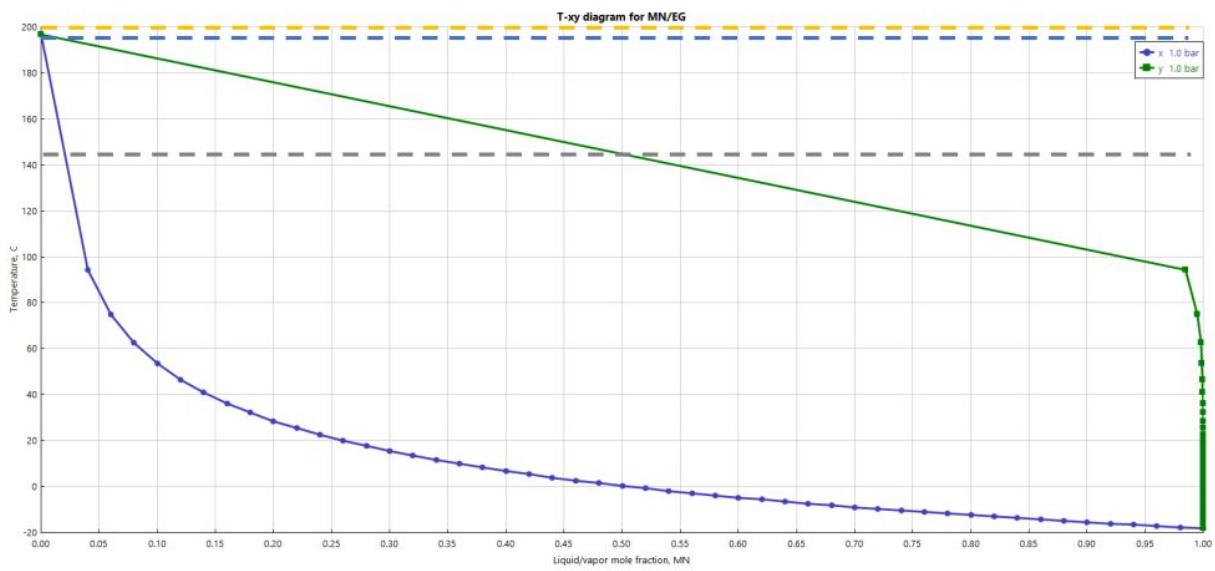


Figure 1.5.2.7. Txy diagram for MN-EG at 1 bar

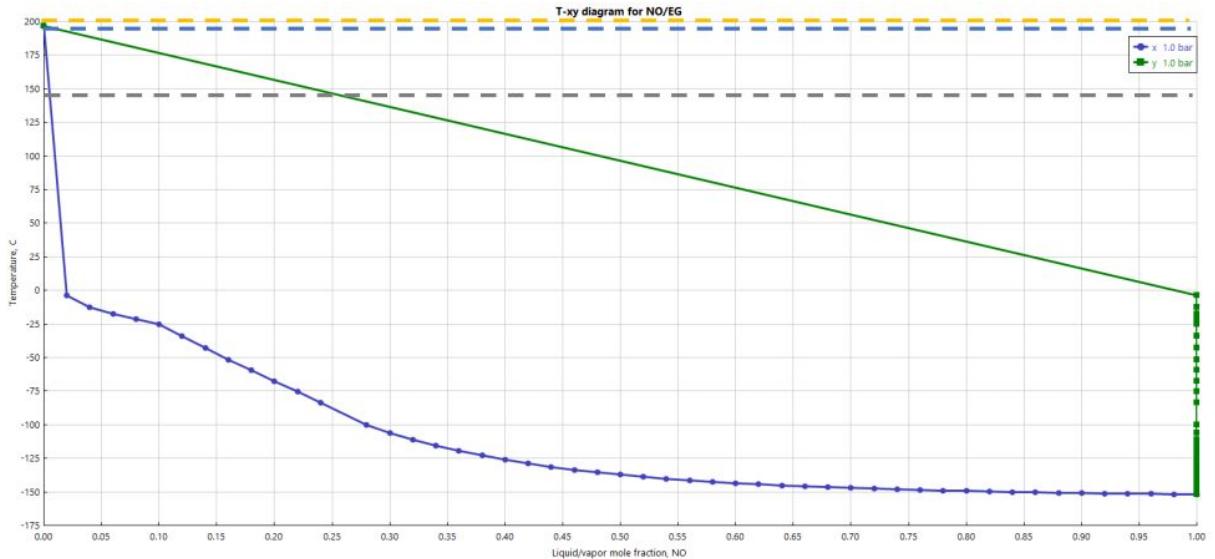


Figure 1.5.2.8. Txy diagram for NO-EG at 1 bar

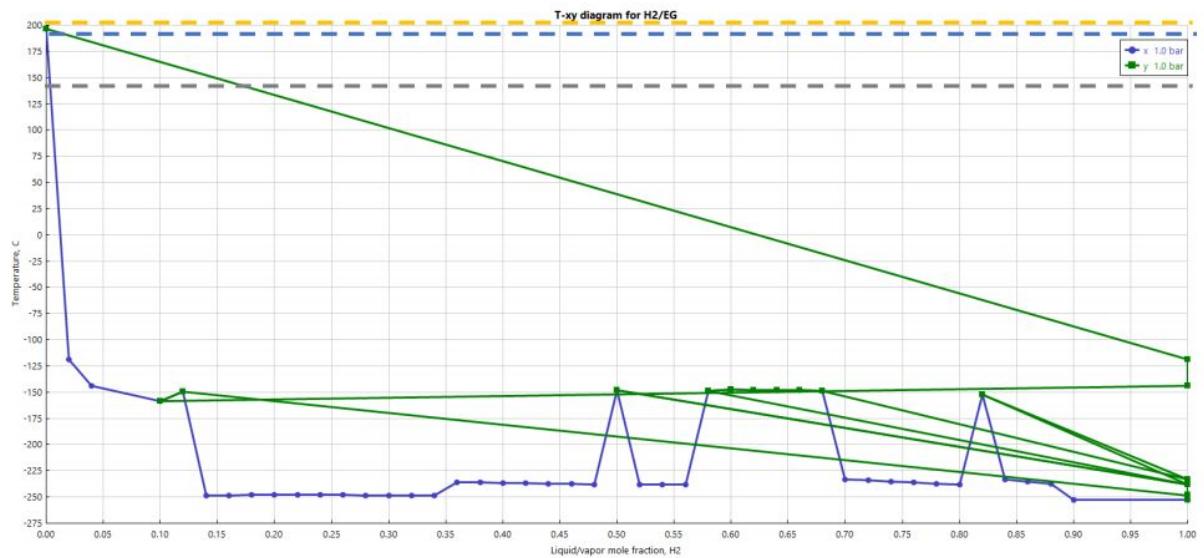


Figure 1.5.2.9. Txy diagram for H₂-EG at 1 bar

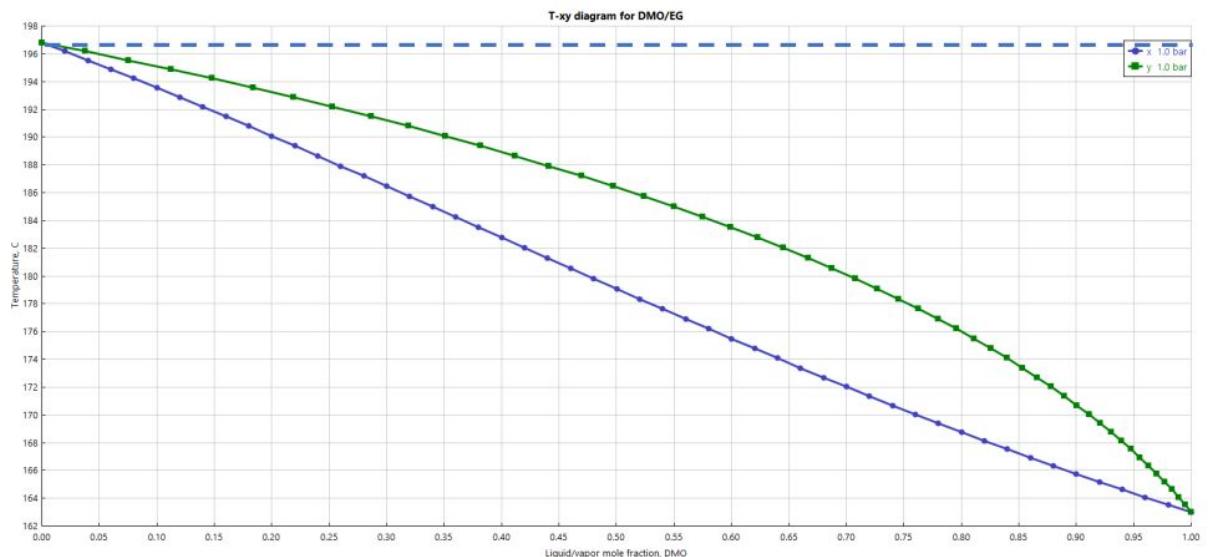


Figure 1.5.2.10. Txy diagram for DMO-EG at 1 bar

1.5.3. Kinetic Model

1.5.3.1. CO Coupling Reaction

In the EG production approach based on the coal-based syngas, there will be two reactions in series: the CO coupling reaction and the hydrogenation reaction. The CO coupling reaction has the objective to produce DMO from CO, but in this process, there

would be a side reaction of dimethyl carbonate (DMC) formation. The reaction equations are shown below:



In this reaction we incorporate Pd/Al₂O₃ catalyst based on the superior selectivity and activity [15]; Al₂O₃ acts as the carrier and the Pd atom dispersed on the alumina acts as an active center. The specification of the catalyst can be seen in **Table 1.5.3.1.1.** The kinetic expression of CO coupling reaction used is in Langmuir-Hinshelwood (LHHW) form [20] with kinetic parameter in **Table 1.5.3.1.2.** and the side reaction kinetic expression was using power law [27]:

$$r_{\text{DMO}} = \frac{\frac{K_4 K_1^2 K_2^2 K_3^2}{K_6^2} \frac{P_{\text{CO}} P_{\text{MN}}}{P_{\text{NO}}}}{\left(1 + K_1 P_{\text{CO}} + K_2 P_{\text{MN}} + \frac{K_2 K_3 P_{\text{MN}}}{K_6 P_{\text{NO}}} + K_5 P_{\text{DMO}} + K_6 P_{\text{NO}}\right)^4}$$

$$r_{\text{DMC}} = 4.68 \exp\left(-\frac{0.179 \times 10^5}{RT}\right) P_{\text{CO}}^{0.88} P_{\text{MN}}^{0.93} P_{\text{NO}}^{-0.35}$$

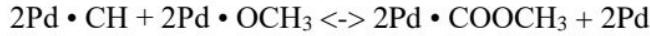
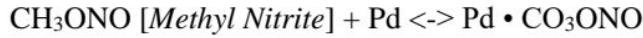
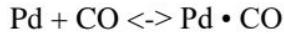
Table 1.5.3.1.1. Catalyst Specification of Pd/Al₂O₃

Specific surface area (m ² /g)	Pore capacity (cm ³ /g)	Diameter (mm)	Bulk density (g/cm ³)
350-400	0.36-0.4	4	0.23

Table 1.5.3.1.2. Kinetic Parameters in CO coupling reaction

K ₁	K ₂	K ₃	K ₄	K ₅	K ₆
10.5677	11.4604	0.5122	2.1910	5.2294	0.2062

Based on studies on this topic [28-31], the reaction goes optimum at 5 bar and temperature range of 125-135°C. The reaction is exothermic hence the temperature of the reactor is one of the main component keys. In the reaction mechanism with the catalyst, the pathway can be seen below [28]:



1.5.3.2. DMO Hydrogenation Reaction

The DMO hydrogenation reaction is a two-step, exothermic, vapor-phase reaction. Cu/SiO₂ is used as the catalyst due to the cheaper price yet high selectivity and activity [32-35]. Overall reactions are shown below [36]:



As it is shown, there will be a side product of ethanol if the reaction is not carefully controlled. Hence aside from the catalyst selection, the temperature, pressure, and reactant ratio play important roles. This would be discussed in more detail in the equipment design. In this work, the catalyst specification (980 kg/m³ density, bed void inside reactor of 0.5) and the kinetic expression that are used are based on Yu, et al. (2017) work. With this complex kinetics, the reaction was put in a custom mode in the aspen simulation. The parameters can be seen in **Table 1.5.3.2.1**.

$$r_{\text{MG}} = \frac{k_1 \left(P_{\text{DMO}} - \frac{P_{\text{MG}} P_{\text{ME}}}{K_{\text{P1}} P_{\text{H}}^2} \right)}{1 + K_{\text{EG}} P_{\text{EG}} + K_{\text{ME}} P_{\text{ME}} + \frac{K_{\text{DMO}} P_{\text{MG}} P_{\text{ME}}}{K_{\text{P1}} P_{\text{H}}^2} + \frac{K_{\text{MG}} P_{\text{EG}} P_{\text{ME}}}{K_{\text{P2}} P_{\text{H}}^2} + K_{\text{H}} P_{\text{H}}}$$

$$r_{EG} = \frac{k_2 \left(P_{MG} - \frac{P_{EG} P_{ME}}{K_{P2} P_H^2} \right)}{1 + K_{EG} P_{EG} + K_{ME} P_{ME} + \frac{K_{DMO} P_{MG} P_{ME}}{K_{P1} P_H^2} + \frac{K_{MG} P_{EG} P_{ME}}{K_{P2} P_H^2} + K_H P_H}$$

$$r_{EtOH} = \frac{k_3 P_{EG}}{1 + K_{EG} P_{EG} + K_{ME} P_{ME} + \frac{K_{DMO} P_{MG} P_{ME}}{K_{P1} P_H^2} + \frac{K_{MG} P_{EG} P_{ME}}{K_{P2} P_H^2} + K_H P_H}$$

Table 1.5.3.2.1. Kinetic Parameters in DMO hydrogenation reaction

k ₁	k ₂	k ₃	K _{ME}	K _{EG}	K _{MG}	K _{DMO}	K _H	K _{P1}	K _{P2}
3.87x10 ⁷	1.75x10 ⁶	8.78x10 ¹³	5.49x10 ⁻¹²	1.85x10 ⁻⁴	2.65x10 ⁻²	7.92x10 ⁻⁵	1.2x10 ⁻³	163.4161	0.2873

The literature suggests the optimal range of reaction temperature to be above 190°C and the pressure to be 15-30 bar [37-39]. Notice that with the given reaction rate equation, we got paradoxical parameters to be maintained. The denominator is all the same for all of the rates, hence it is the nominator that should be manipulated. If the EG supposed to be maximized, the P_{MG}, P_H should be high, the P_{EG}, P_{ME} should be in a low amount. It is trouble already because as more EG is produced, the rate of EG production is decreasing and the rate of EtOH is increasing. To increase the selectivity of the second reaction (r_{EG}), the r_{MG} and r_{EtOH} -should be small, hence the P_{DMO}, P_H, P_{EG} should be small, and the P_{MG}, P_{ME} should be high. In the end, we came up with a conclusion to use parallel and series of PFRs, because CSTR did not work in the simulation and there was no paper use CSTR for this process. 2 parallel lines were designed so that the DMO and H₂ are limited, and 2 PFRs of series were design in every parallel line so that 2 series of hydrogenation reaction can happen. The ethylene glycol cannot be 100% in the reactor yield as it will convert to the side product of ethanol.

1.6. Mass Balance

This whole section is to make sure that everything in the simulation is in mass balance and no error occurred in the system. To make it more systematic, every mass balance will be shown in each of the sections (reaction 1, separation 1, reaction 2, and separation 2) with every significant component in each of the section areas.

1.6.1. CO Coupling Reaction (Reaction 1)

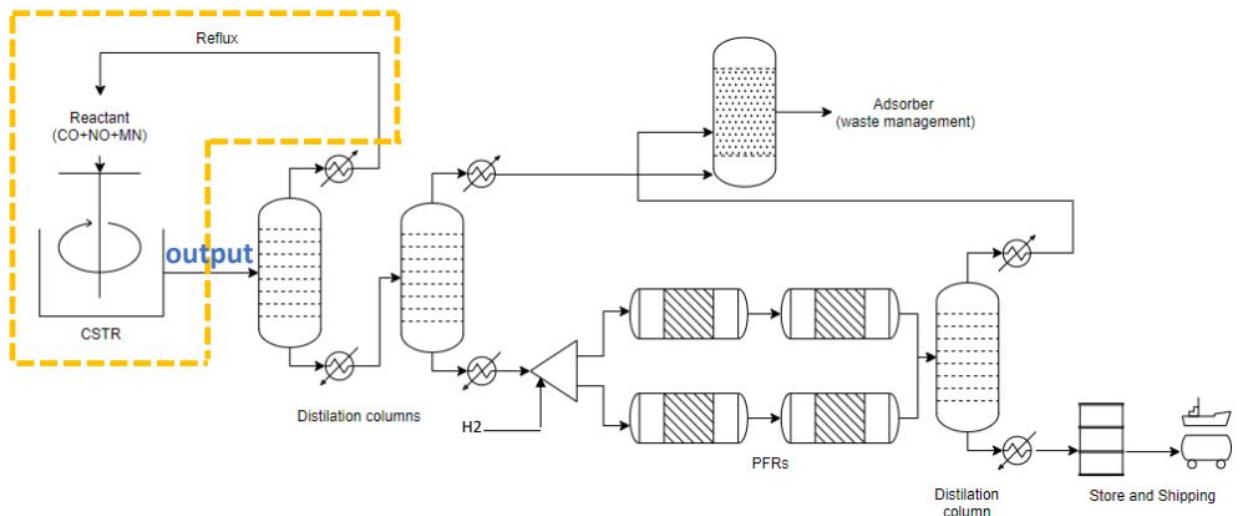


Figure 1.6.1.1. Boundary condition of CO Coupling Reaction in Flowsheet 1

The first boundary consists of the CSTR as the first reactor. The reactor selection is due to the simplicity and agitation it provides as gas reactants need to be mixed well to form more products. Moreover, CSTR provides more control over the temperature and hot spots can be avoided as an agitator is included. The inlet feed would be CO, MN, and NO gases and the main output is DMO. The NO gas is needed to initiate the reaction as it is one of the kinetic parameters, as well as increasing the selectivity towards the main reaction instead of DMC formation. The mass balance can be seen in **Table 1.4.1.1.** It can be seen that almost all of the MN, which is the limiting reactant, is consumed and converted while the CO gas is in excess. The concept of recycling CO was due to the kinetic parameter as well. It was assumed that in excess, the reaction would be faster and convert higher, but the MN should not be too high to avoid side product (as more MN appears in the denominator of the CO coupling reaction rate equation).

Table 1.6.1.1. Mass balance of CO coupling reaction in Flowsheet 1

	F _{CO} (Feed CO)	F _{MN} (Feed MN)	F _{NO} (Feed NO)	R-CO (Recycle CO)	O-DMO (Output DMO)
Mole flow (kmol/hr)	214.206	131.061	33.3265	581.731	894.962
X _{CO}	1	-	-	1	0.7432

X _{MN}	-	1	-	-	0.0004
X _{NO}	-	-	1	-	0.1833
X _{DMO}	-	-	-	-	0.0730

- Mass balance: Carbon Monoxide (CO)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = O_{DMO} - (F_{CO} + F_{MN} + F_{NO} + R_{CO})$$

$$\text{Accumulation} = 0.7432x894.962 - (1x214.206 + 0 + 0 + 1x581.731)$$

$$\text{Accumulation} = -130.595 \frac{\text{kmol}}{\text{hour}}$$

The negative value means that 130.595 kmol/hour of CO was lost due to the formation of DMO.

- Mass balance: Methyl Nitrite (MN)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = O_{DMO} - (F_{CO} + F_{MN} + F_{NO} + R_{CO})$$

$$\text{Accumulation} = 0.0004x894.962 - (0 + 1x131.061 + 0 + 0)$$

$$\text{Accumulation} = -130.703 \frac{\text{kmol}}{\text{hour}}$$

The negative value means that 130.703 kmol/hour of MN was lost due to the formation of DMO.

- Mass balance: Nitric Oxide (NO)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = O_{DMO} - (F_{CO} + F_{MN} + F_{NO} + R_{CO})$$

$$\text{Accumulation} = 0.1833x894.962 - (0 + 0 + 1x33.3265 + 0)$$

$$\text{Accumulation} = 130.720 \frac{\text{kmol}}{\text{hour}}$$

The positive value means that 130.720 kmol/hour of NO was obtained as it is the side product alongside DMO in the reaction.

- Mass balance: Dimethyl Oxalate (DMO)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = O_{DMO} - (F_{CO} + F_{MN} + F_{NO} + R_{CO})$$

$$\text{Accumulation} = 0.0730x894.962 - (0 + 0 + 0 + 0)$$

$$\text{Accumulation} = 65.3322 \frac{\text{kmol}}{\text{hour}}$$

The positive value means that 65.3322 kmol/hour of DMO was obtained.

The overall accumulation was due to the reaction, and it is fitted with the mole balance of the reaction (mole CO: MN: NO: DMO = -2: -2: 2: 1, as in $2\text{CO} + 2\text{MN} \rightarrow 2\text{NO} + \text{DMO}$). All of the MN is reacted hence the conversion is 1, the selectivity is 0.5, and the reactor yield is 1.

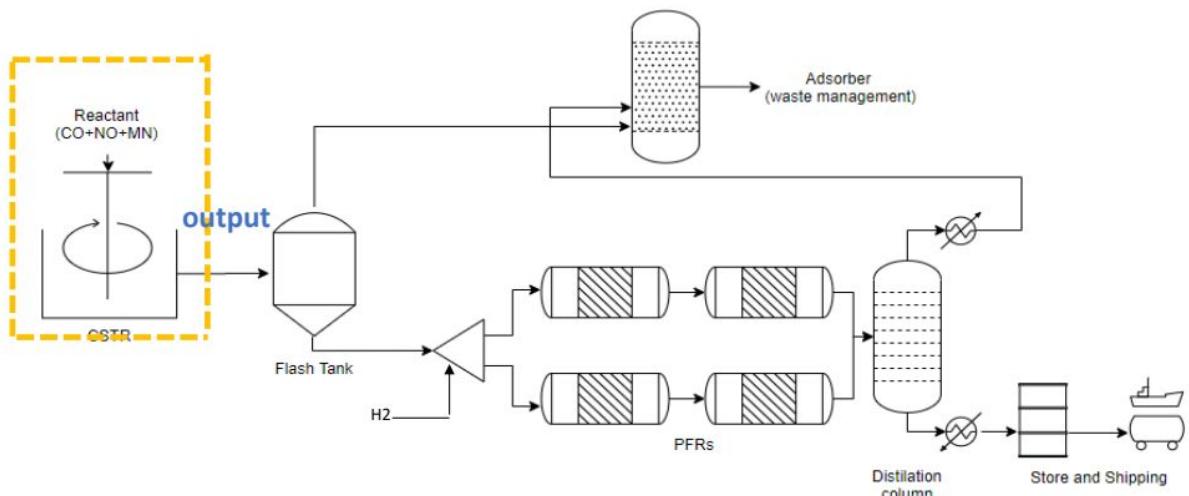


Figure 1.6.1.2. Boundary condition of CO Coupling Reaction in Flowsheet 2

Similar goes to the second flowsheet, just without the recycle stream. Here we tried to use a limited reactant of CO and MN and see whether the conversion is still as high as with the recycled stream. There is still NO gas stream to initiate the reaction and increasing the selectivity. The mass balance can be seen in **Table 1.6.1.2**.

Table 1.6.1.2. Mass balance of CO coupling reaction in Flowsheet 2

	F _{CO} (Feed CO)	F _{MN} (Feed MN)	F _{NO} (Feed NO)	O-DMO (Output DMO)
Mole flow (kmol/hr)	133.522	133.588	3.333	204.064
X _{CO}	1	-	-	0.0044
X _{MN}	-	1	-	0.0044
X _{NO}	-	-	1	0.6662
X _{DMO}	-	-	-	0.3249

- Mass balance: Carbon Monoxide (CO)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = O_{DMO} - (F_{CO} + F_{MN} + F_{NO})$$

$$\text{Accumulation} = 0.0044 \times 204.064 - (1 \times 133.522 + 0 + 0)$$

$$\text{Accumulation} = -132.624 \frac{\text{kmol}}{\text{hour}}$$

The negative value means that 132.624 kmol/hour of CO was lost due to the formation of DMO.

- Mass balance: Methyl Nitrite (MN)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = O_{DMO} - (F_{CO} + F_{MN} + F_{NO})$$

$$\text{Accumulation} = 0.0044 \times 204.064 - (0 + 1 \times 133.588 + 0)$$

$$\text{Accumulation} = -132.690 \frac{\text{kmol}}{\text{hour}}$$

The negative value means that 132.690 kmol/hour of MN was lost due to the formation of DMO.

- Mass balance: Nitric Oxide (NO)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = O_{DMO} - (F_{CO} + F_{MN} + F_{NO})$$

$$\text{Accumulation} = 0.6662x204.064 - (0 + 0 + 1x3.333)$$

$$\text{Accumulation} = 132.614 \frac{\text{kmol}}{\text{hour}}$$

The positive value means that 132.614 kmol/hour of NO was obtained as it is the side product alongside DMO in the reaction.

- Mass balance: Dimethyl Oxalate (DMO)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = O_{DMO} - (F_{CO} + F_{MN} + F_{NO})$$

$$\text{Accumulation} = 0.3249x894.962 - (0 + 0 + 0)$$

$$\text{Accumulation} = 66.300 \frac{\text{kmol}}{\text{hour}}$$

The positive value means that 66.300 kmol/hour of DMO was obtained.

There is also overall accumulation due to the reaction, and it is fitted with the mole balance of the reaction (mole CO: MN: NO: DMO = -2: -2: 2: 1, as in $2\text{CO} + 2\text{MN} \rightarrow 2\text{NO} + \text{DMO}$). Compared to the prior flowsheet, the second flowsheet provides advantages of more DMO fraction in the output, hence the separation is easier. Moreover, because the overall mole flow is not as big as the first flowsheet, hence the volume flow and the reactor size decrease as well. The conversion of MN is also 0.99~1, which is similar to the first flowsheet, with the same 0.5 selectivity and 1 reactor yield.

1.6.2. Distillation and Flash Tank (Separation 1)

As the product of DMO is mixed with other unreacted reactants and side products, separation must be done prior to the following reaction. There will be no reaction in this area and only separation, hence, accumulation should be 0. The inlet feed would be the output from the CO coupling reaction, while the output feed would be the bottom product containing high purity of DMO. Other than the product will be vapor phases that will go to the waste management.

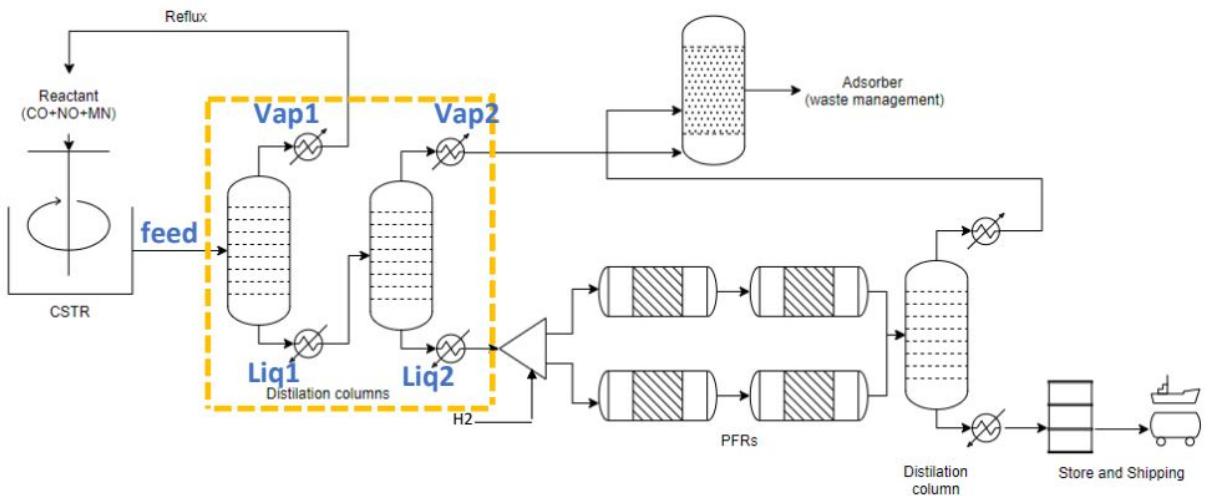


Figure 1.6.2.1. Boundary condition of 2 distillation column in Flowsheet 1

The first flowsheet utilizes 2 distillation columns, where the bottom product is derived for further process. This is due to the boiling point difference. The CO gas is the lightest component with the lowest boiling point hence it is easy to evaporate, making it the perfect choice for a recycled stream which is obtained from the first vapor stream (distillate stream). While the first liquid stream will go to the second distillation column, where the heaviest component with the highest boiling point, the DMO, will be taken in the bottom product.

Table 1.6.2.1. Mass balance of Separation 1 in Flowsheet 1

	Feed	Vap1	Liq1	Vap2	Liq2
Mole flow (kmol/hr)	894.962	581.731	313.24	244.327	68.913
X _{CO}	0.7433	1	0.2665	0.3417	-
X _{MN}	0.0004	-	0.0011	-	0.0049
X _{NO}	0.1833	-	0.5237	0.6583	0.0466
X _{DMO}	0.0730	-	0.2087	-	0.9485

- Mass balance: Carbon Monoxide (CO)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = (\text{Vap1} + \text{Vap2} + \text{Liq2}) - \text{Feed}$$

$$Accumulation = (1x581.731 + 0.3417x244.327 + 0) - 0.7433x894.962$$

$$Accumulation = -0.008 \frac{kmol}{hour} \sim 0$$

- Mass balance: Methyl Nitrite (MN)

$$Accumulation = Output - Input$$

$$Accumulation = (Vap1 + Vap2 + Liq2) - Feed$$

$$Accumulation = (0 + 0 + 0.0049x68.913) - 0.0004x894.962$$

$$Accumulation = -0.02 \frac{kmol}{hour} \sim 0$$

- Mass balance: Nitric Oxide (NO)

$$Accumulation = Output - Input$$

$$Accumulation = (Vap1 + Vap2 + Liq2) - Feed$$

$$Accumulation = (0 + 0.6583x244.327 + 0.0466x68.913) - 0.1833x894.962$$

$$Accumulation = 0.005 \frac{kmol}{hour} \sim 0$$

- Mass balance: Dimethyl Oxalate (DMO)

$$Accumulation = Output - Input$$

$$Accumulation = (Vap1 + Vap2 + Liq2) - Feed$$

$$Accumulation = (0 + 0 + 0.9485x68.913) - 0.0730x894.962$$

$$Accumulation = 0.03 \frac{kmol}{hour} \sim 0$$

Some non 0 value may be due to some tolerance issue, where some of the very small value is ignored. Since the accumulation is very small, it is insignificant, hence the area is in mass balance and no reaction occurs. There is no DMO found in the vapor product, indicating that 100% of the DMO is recovered in the liquid phase.

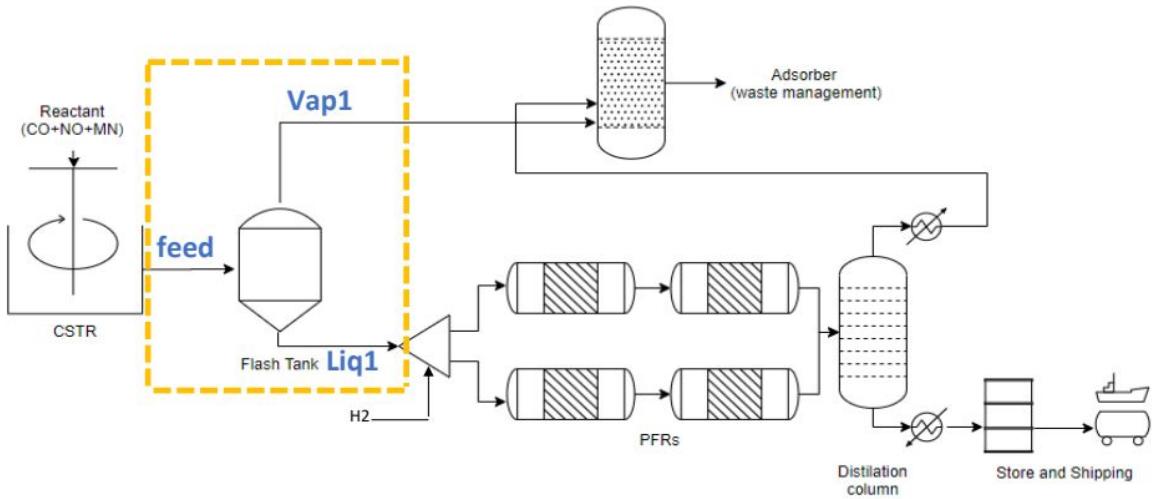


Figure 1.6.2.2. Boundary condition of flash tank in Flowsheet 2

Most of the feed consist of NO and DMO. Since the DMO in the feed is not so low, a flash tank is considered enough to separate the DMO from other chemicals. Same with the prior flowsheet, the product will be in the liquid phase, since DMO is the heaviest key in the system.

Table 1.6.2.2. Mass balance of Separation 1 in Flowsheet 2

	Feed	Vap1	Liq1
Mole flow (kmol/hr)	204.064	130.601	73.463
X _{CO}	0.0044	0.0067	0.0004
X _{MN}	0.0044	0.0068	0.0002
X _{NO}	0.6662	0.9650	0.1351
X _{DMO}	0.3249	0.0215	0.8644

- Mass balance: Carbon Monoxide (CO)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = (\text{Vap1} + \text{Liq1}) - \text{Feed}$$

$$\text{Accumulation} = (0.0067 \times 130.601 + 0.0004 \times 73.463) - 0.0044 \times 204.064$$

$$\text{Accumulation} = 0.006 \frac{\text{kmol}}{\text{hour}} \sim 0$$

- Mass balance: Methyl Nitrite (MN)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = (\text{Vap1} + \text{Liq1}) - \text{Feed}$$

$$\text{Accumulation} = (0.0068x130.601 + 0.0002x73.463) - 0.0044x204.064$$

$$\text{Accumulation} = 0.005 \frac{\text{kmol}}{\text{hour}} \sim 0$$

- Mass balance: Nitric Oxide (NO)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = (\text{Vap1} + \text{Liq1}) - \text{Feed}$$

$$\text{Accumulation} = (0.9650x130.601 + 0.1351x73.463) - 0.6662x204.064$$

$$\text{Accumulation} = 0.007 \frac{\text{kmol}}{\text{hour}} \sim 0$$

- Mass balance: Dimethyl Oxalate (DMO)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = (\text{Vap1} + \text{Liq1}) - \text{Feed}$$

$$\text{Accumulation} = (0.0215x130.601 + 0.8644x73.463) - 0.3249x204.064$$

$$\text{Accumulation} = 0.009 \frac{\text{kmol}}{\text{hour}} \sim 0$$

The accumulation value is so small hence insignificant. The flash tank area is in mass balance with no reaction inside. The DMO recovered is 95.76%, which is slightly lower than the first flowsheet.

1.6.3. DMO Hydrogenation Reaction (Reaction 2)

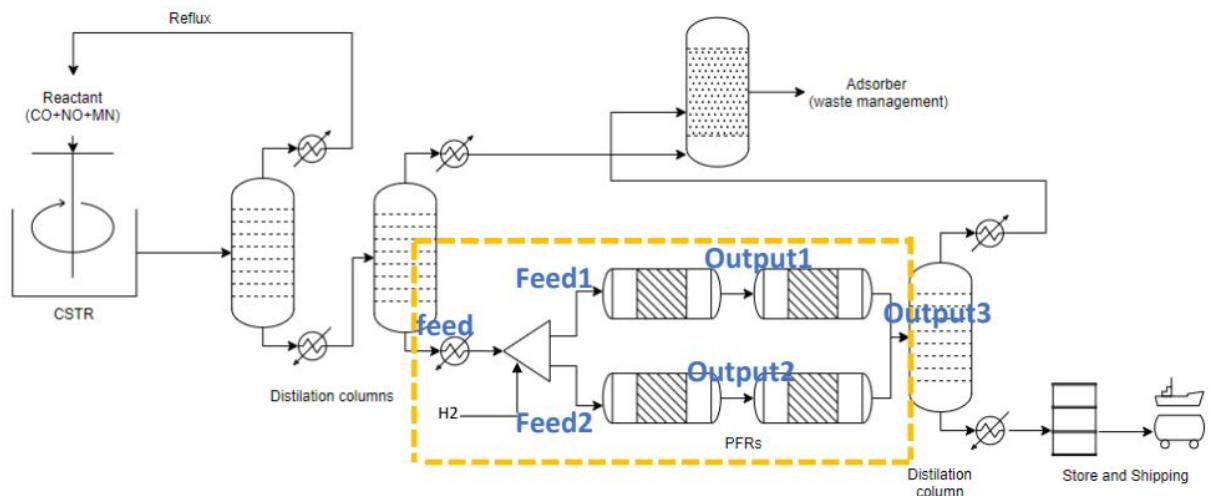


Figure 1.6.3.1. Boundary condition of DMO Hydrogenation Reaction in Flowsheet 1

In the hydrogenation reaction, 4 PFRs are utilized with the reason stated in the kinetic model. The feed is separated by a splitter into two lines with the same composition and flowrate, then each of these feeds will react with H₂ gas inside the 2 PFRs in series. The output will be combined into the further separation process. In the mass balance, CO and MN is neglected as the amount have been so small and out of interest in this area.

Table 1.6.3.1. Mass balance of DMO hydrogenation reaction in Flowsheet 1

	Feed	H2	Feed1	Feed2	Output1	Output2	Output3
Mole flow (kmol/hr)	68.913	281	131.061	131.061	174.639	174.639	306.864
X _{NO}	0.0466	-	0.0092	0.0092	0.0092	0.0092	0.0105
X _{DMO}	0.9485	-	0.1868	0.1868	0.1853	0.1853	0.1163
X _{H2}	-	1	0.8031	0.8031	0.8009	0.8009	0.6352
X _{EG}	-	-	-	-	-	-	0.0436
X _{MG}	-	-	-	-	0.0018	0.0018	0.0530
X _{MeOH}	-	-	-	-	0.0018	0.0018	0.1403

- Mass balance: Nitric Oxide (NO)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = \text{Output}_3 - (\text{Feed} + \text{H}_2)$$

$$\text{Accumulation} = 0.0105x306.864 - (0.0466x68.913 + 0)$$

$$\text{Accumulation} = 0.0107 \frac{\text{kmol}}{\text{hour}} \sim 0$$

The value is considered small, hence insignificant, as some other component like CO and MN is ignored. NO is not reacted in this area.

- Mass balance: Dimethyl Oxalate (DMO)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = \text{Output}_3 - (\text{Feed} + \text{H}_2)$$

$$\text{Accumulation} = 0.1163x306.864 - (0.9485x68.913 + 0)$$

$$\text{Accumulation} = -29.6757 \frac{\text{kmol}}{\text{hour}}$$

The negative value means that 29.6757 kmol/hour of DMO was lost due to the hydrogenation reaction.

- Mass balance: Hydrogen (H_2)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = \text{Output}_3 - (\text{Feed} + \text{H}_2)$$

$$\text{Accumulation} = 0.6352x306.864 - (0 + 1x281)$$

$$\text{Accumulation} = -86.080 \frac{\text{kmol}}{\text{hour}}$$

The negative value means that 86.080 kmol/hour of H_2 was lost due to the hydrogenation reaction.

- Mass balance: Ethylene Glycol (EG)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = \text{Output}_3 - (\text{Feed} + \text{H}_2)$$

$$\text{Accumulation} = 0.0436 \times 306.864 - (0 + 0)$$

$$\text{Accumulation} = 13.379 \frac{\text{kmol}}{\text{hour}}$$

The positive value means that 13.379 kmol/hour of EG was obtained after the hydrogenation reaction.

- Mass balance: Methylene Glycol (MG)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = \text{Output}_3 - (\text{Feed} + \text{H}_2)$$

$$\text{Accumulation} = 0.0530 \times 306.864 - (0 + 0)$$

$$\text{Accumulation} = 16.264 \frac{\text{kmol}}{\text{hour}}$$

The positive value means that 16.264 kmol/hour of MG was obtained after the hydrogenation reaction.

- Mass balance: Methanol (MeOH)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = \text{Output}_3 - (\text{Feed} + \text{H}_2)$$

$$\text{Accumulation} = 0.1403 \times 306.864 - (0 + 0)$$

$$\text{Accumulation} = 43.053 \frac{\text{kmol}}{\text{hour}}$$

The positive value means that 43.053 kmol/hour of EG was obtained after the hydrogenation reaction.

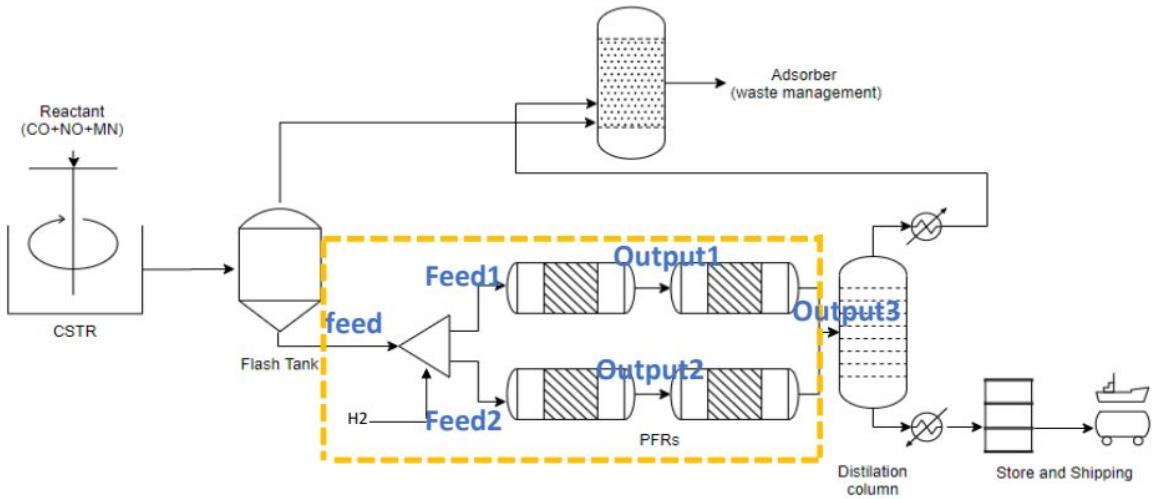


Figure 1.6.3.2. Boundary condition of DMO Hydrogenation Reaction in Flowsheet 1

Similarly, in the second flowsheet, the feed is mixed with hydrogen gas, split into 2 parallel lines, and undergoes 2 tubular reactors. Mass balance can be seen in **Table 1.4.3.2**. The overall accumulation was due to the reaction, and the conversion, selectivity, and reactor yield of EG can be seen in **Table 1.4.3.3**.

Table 1.6.3.2. Mass balance of DMO hydrogenation reaction in Flowsheet 1

	Feed	H2	Feed1	Feed2	Output1	Output2	Output3
Mole flow (kmol/hr)	73.463	284	178.731	178.731	178.414	178.414	307.074
X _{NO}	0.1351	-	0.0278	0.0278	0.0092	0.0092	0.0323
X _{DMO}	0.8644	-	0.1776	0.1776	0.1762	0.1762	0.0889
X _{H2}	-	1	0.7945	0.7945	0.7923	0.7923	0.5967
X _{EG}	-	-	-	-	-	-	0.0462
X _{MG}	-	-	-	-	0.0018	0.0018	0.0717
X _{MeOH}	-	-	-	-	0.0018	0.0018	0.1641

- Mass balance: Nitric Oxide (NO)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = \text{Output3} - (\text{Feed} + \text{H2})$$

$$Accumulation = 0.0323x307.074 - (0.1351x73.463 + 0)$$

$$Accumulation = -0.0063 \frac{kmol}{hour} \sim 0$$

The value is considered small, hence insignificant, as some other component like CO and MN is ignored. NO is not reacted in this area.

- Mass balance: Dimethyl Oxalate (DMO)

$$Accumulation = Output - Input$$

$$Accumulation = Output3 - (Feed + H2)$$

$$Accumulation = 0.0889x307.074 - (0.8644x73.463 + 0)$$

$$Accumulation = -36.2025 \frac{kmol}{hour}$$

The negative value means that 36.2025 kmol/hour of DMO was lost due to the hydrogenation reaction.

- Mass balance: Hydrogen (H₂)

$$Accumulation = Output - Input$$

$$Accumulation = Output3 - (Feed + H2)$$

$$Accumulation = 0.5967x307.074 - (0 + 1x284)$$

$$Accumulation = -100.7689 \frac{kmol}{hour}$$

The negative value means that 100.7689 kmol/hour of H₂ was lost due to the hydrogenation reaction.

- Mass balance: Ethylene Glycol (EG)

$$Accumulation = Output - Input$$

$$Accumulation = Output3 - (Feed + H2)$$

$$Accumulation = 0.0462x307.074 - (0 + 0)$$

$$Accumulation = 14.1868 \frac{kmol}{hour}$$

The positive value means that 14.1868 kmol/hour of EG was obtained after the hydrogenation reaction.

- Mass balance: Methylene Glycol (MG)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = \text{Output}_3 - (\text{Feed} + \text{H}_2)$$

$$\text{Accumulation} = 0.0717x307.074 - (0 + 0)$$

$$\text{Accumulation} = 50.3908 \frac{\text{kmol}}{\text{hour}}$$

The positive value means that 50.3908 kmol/hour of MG was obtained after the hydrogenation reaction.

- Mass balance: Methanol (MeOH)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = \text{Output}_3 - (\text{Feed} + \text{H}_2)$$

$$\text{Accumulation} = 0.0462x307.074 - (0 + 0)$$

$$\text{Accumulation} = 43.053 \frac{\text{kmol}}{\text{hour}}$$

The positive value means that 43.053 kmol/hour of EG was obtained after the hydrogenation reaction.

Table 1.6.3.3. Comparison of EG results in Flowsheet 1 and 2

		Flowsheet 1	Flowsheet 2
Based on DMO	Conversion	0.45	0.57
	Selectivity	0.45	0.39
	Yield	0.45	0.39
Based on H ₂	Conversion	0.31	0.35
	Selectivity	0.16	0.14
	Yield	0.31	0.28
EG produced (kg/hr)		830.96	880.19

The overall result is better in the second flowsheet, as the conversion is better in this flowsheet.

1.6.4. Distillation Column (Separation 2)

The final treatment is to separate EG and purified it. To reach high purity, reactive distillation (RD) column is used. There will be no reaction in this area, hence the accumulation should be 0 in any component mass balance. The inlet feed would be the overall output from the PFRs and the outlet that is kept will be in the bottom product because EG is the heaviest component in the system. The vapor from this section area will be treated in the waste management.

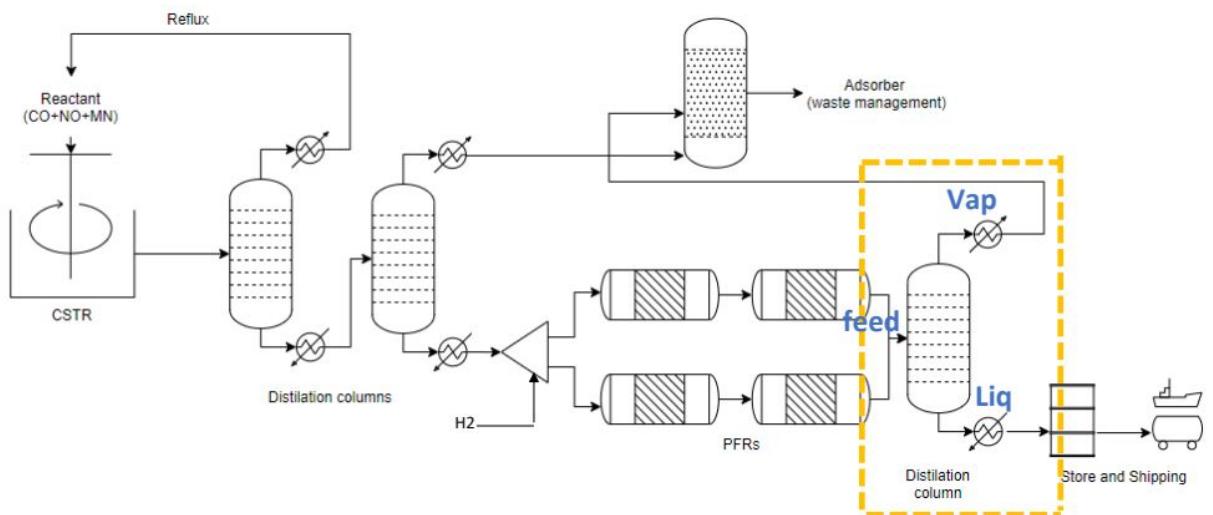


Figure 1.6.4.1. Boundary condition of RD column in Flowsheet 1

Table 1.6.4.1. Mass balance of Separation 2 in Flowsheet 1

	Feed	Vap	Liq
Mole flow (kmol/hr)	306.864	293.5	13.3683
X_{NO}	0.0105	0.0109	-
X_{DMO}	0.1163	0.1216	0.0002
X_{H2}	0.6352	0.6641	-
X_{EG}	0.0436	-	0.9995
X_{MG}	0.0530	0.0554	0.0003

X _{MeOH}	0.1403	0.1467	-
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- Mass balance: Nitric Oxide (NO)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = (\text{Vap} + \text{Liq}) - \text{Feed}$$

$$\text{Accumulation} = (0.0109x293.5 + 0) - 0.0105x306.864$$

$$\text{Accumulation} = -0.02 \frac{\text{kmol}}{\text{hour}} \sim 0$$

- Mass balance: Dimethyl Oxalate (DMO)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = (\text{Vap} + \text{Liq}) - \text{Feed}$$

$$\text{Accumulation} = (0.1216x293.5 + 0.0002x13.3683) - 0.1163x306.864$$

$$\text{Accumulation} = 0.004 \frac{\text{kmol}}{\text{hour}} \sim 0$$

- Mass balance: Hydrogen (H₂)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = (\text{Vap} + \text{Liq}) - \text{Feed}$$

$$\text{Accumulation} = (0.6641x293.5 + 0) - 0.6352x306.864$$

$$\text{Accumulation} = -0.007 \frac{\text{kmol}}{\text{hour}} \sim 0$$

- Mass balance: Ethylene Glycol (EG)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = (\text{Vap} + \text{Liq}) - \text{Feed}$$

$$\text{Accumulation} = (0 + 0.9995x13.3683) - 0.0436x306.864$$

$$\text{Accumulation} = -0.018 \frac{\text{kmol}}{\text{hour}} \sim 0$$

- Mass balance: Methylene Glycol (MG)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = (\text{Vap} + \text{Liq}) - \text{Feed}$$

$$\text{Accumulation} = (0.0554x293.5 + 0.0003x13.3683) - 0.0530x306.864$$

$$\text{Accumulation} = 0.0001 \frac{\text{kmol}}{\text{hour}} \sim 0$$

- Mass balance: Methanol (MeOH)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = (\text{Vap} + \text{Liq}) - \text{Feed}$$

$$\text{Accumulation} = (0.1467x293.5 + 0) - 0.1403x306.864$$

$$\text{Accumulation} = 0.003 \frac{\text{kmol}}{\text{hour}} \sim 0$$

Some non 0 value may be due to some tolerance issue, where some of the very small value is ignored. The accumulation is indeed small, proofing that the area is in mass balance and there is no reaction. The goal of highly purified EG product is also achieved, and all of the EG in the feed stream is 100% recovered in the bottom product.

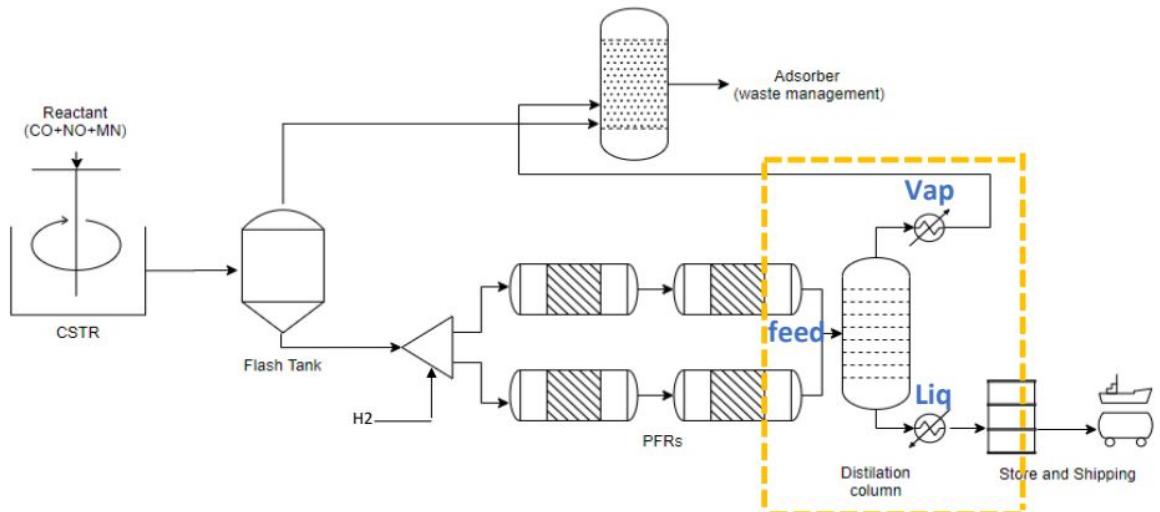


Figure 1.6.4.2. Boundary condition of RD column in Flowsheet 2

Same with the prior flowsheet, the product will be in the bottom liquid, since EG is the heaviest component key in the system. The mass balance summary can be seen in **Table 1.6.4.2.**

Table 1.6.4.2. Mass balance of Separation 2 in Flowsheet 2

	Feed	Vap	Liq
Mole flow (kmol/hr)	307.074	292.994	14.079
X _{NO}	0.0323	0.0339	-
X _{DMO}	0.0889	0.0928	0.0078
X _{H₂}	0.5967	0.6253	-
X _{EG}	0.0462	0.0007	0.9922
X _{MG}	0.0717	0.0752	-
X _{MeOH}	0.1641	0.1720	-

- Mass balance: Nitric Oxide (NO)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = (\text{Vap} + \text{Liq}) - \text{Feed}$$

$$\text{Accumulation} = (0.0339 \times 292.994 + 0) - 0.0323 \times 307.074$$

$$\text{Accumulation} = 0.01 \frac{\text{kmol}}{\text{hour}} \sim 0$$

- Mass balance: Dimethyl Oxalate (DMO)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = (\text{Vap} + \text{Liq}) - \text{Feed}$$

$$\text{Accumulation} = (0.0928 \times 292.994 + 0.0078 \times 14.079) - 0.0889 \times 307.074$$

$$\text{Accumulation} = 0.0008 \frac{\text{kmol}}{\text{hour}} \sim 0$$

- Mass balance: Hydrogen (H₂)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = (\text{Vap} + \text{Liq}) - \text{Feed}$$

$$\text{Accumulation} = (0.6253 \times 292.994 + 0) - 0.5967 \times 307.074$$

$$\text{Accumulation} = -0.02 \frac{\text{kmol}}{\text{hour}} \sim 0$$

- Mass balance: Ethylene Glycol (EG)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = (\text{Vap} + \text{Liq}) - \text{Feed}$$

$$\text{Accumulation} = (0.0007x292.994 + 0.9922x14.079) - 0.0462x307.074$$

$$\text{Accumulation} = -0.012 \frac{\text{kmol}}{\text{hour}} \sim 0$$

- Mass balance: Methylene Glycol (MG)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = (\text{Vap} + \text{Liq}) - \text{Feed}$$

$$\text{Accumulation} = (0.0752x292.994 + 0) - 0.0717x307.074$$

$$\text{Accumulation} = 0.016 \frac{\text{kmol}}{\text{hour}} \sim 0$$

- Mass balance: Methanol (MeOH)

$$\text{Accumulation} = \text{Output} - \text{Input}$$

$$\text{Accumulation} = (\text{Vap} + \text{Liq}) - \text{Feed}$$

$$\text{Accumulation} = (0.1720x292.994 + 0) - 0.1641x307.074$$

$$\text{Accumulation} = 0.004 \frac{\text{kmol}}{\text{hour}} \sim 0$$

The accumulation is insignificant hence it is proven that the area is in mass balance and no reaction occurred. The EG was produced more in the second flowsheet, as more EG is produced in the prior reaction 2 areas. But in purity comparison, although still is considered high to be in the market, flowsheet 1 has a slightly better number.

1.7. Process Flowsheet Diagram

1.7.1. First Flowsheet

1.7.1.1. Simulated Flowsheet Design

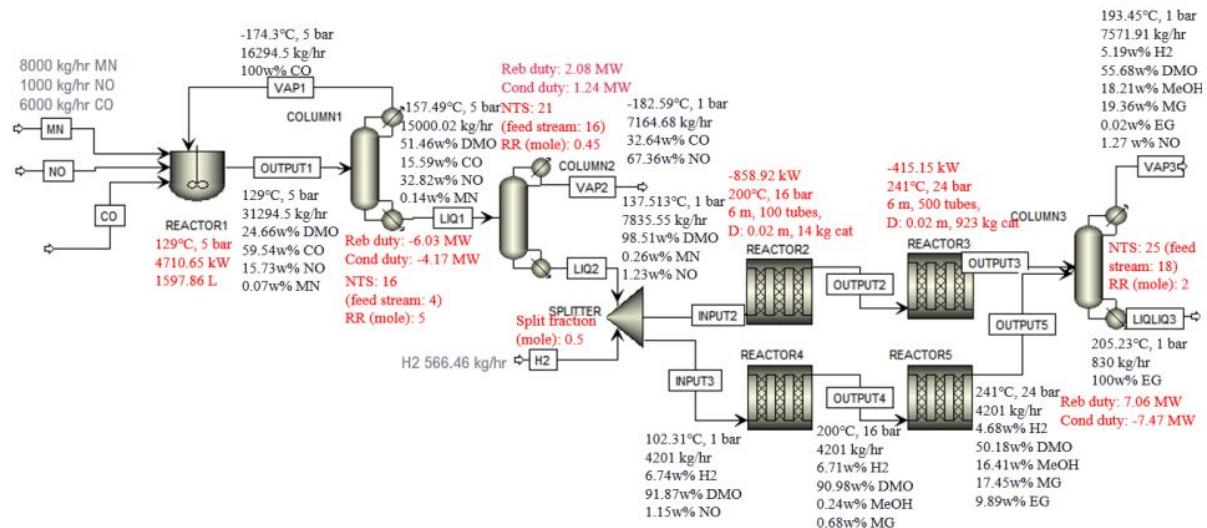


Figure 1.7.1.1. Aspen Simulation Process Flow Diagram for Flowsheet 1

Combining all of the parameters and objectives that are found and decided, this is the successfully simulated aspen flowsheet for the first flowsheet (**Fig. 1.7.1.1.**). It consists of 4 main processes: reaction 1, separation 1, reaction 2, separation 2. The reactor used for the first reaction is the continuous stirred-tank reactor (CSTR) with Palladium/alumina (Pd/Al₂O₃) as the catalyst. Excess CO gas is used as the reactant instead of MN due to the kinetic equation that gives worse selectivity over more MN, and the MN is more costly than CO. Hence the feed for reactor 1 is MN, CO, NO, and recycled CO. Maximizing the operating temperature, pressure, and reactant concentration gives the best results of DMO production without significant DMC side product formation. After it is reacted, the product will go to the separation stage, which consists of 2 distillation columns. The first one is to separate and recycle the CO, while the second is to recover DMO. The DMO in the bottom product will go to a splitter, that divides the stream into 2 lines. Each of the streamlines are mixed with H₂ gas and will undergo hydrogenation reaction to 2 tubular reactors in series. Even though the intermediate product is still existing and the reactant conversion is not 100%, this configuration has been giving the best of EG production for all of the simulations that have been done, and there is no EtOH formed nor no side reaction from impurities (like NO and MN) found in the simulation. In addition, some

PFRs configuration that has been done includes 2 PFRs in series, 3 PFRs in series, 2 PFR with a recycled stream, and 4 PFRs in parallel. None of this configuration provides better performance than the one that we have established, even though the optimal operating conditions are chosen from the sensitivity test. After getting the EG, the production line will go further to the separation 2 processes using the RD column, where ~100wt% EG is obtained in the bottom product.

1.7.1.2. Stream Table

Table 1.7.1.2. Stream Table of Flowsheet 1

Stream	T (°C)	P (bar)	m (kg/hr)	Mass fraction										
				H ₂	MeOH	EtOH	DMO	DMC	EG	CO	NO	MN	H ₂ O	MG
MN	25	1	8000	-	-	-	-	-	-	-	-	1	-	-
NO	25	1	1000	-	-	-	-	-	-	-	1	-	-	-
CO	25	5.17	6000	-	-	-	-	-	-	1	-	-	-	-
Output1	129	5	31294.5	-	-	-	0.2466	-	-	0.5954	0.1573	0.0007	-	-
Vap1	-174.308	5	16294.5	-	-	-	-	-	-	1	-	-	-	-
Liq1	-157.487	5	15000.2	-	-	-	0.5146	-	-	0.1559	0.3282	0.0014	-	-
Vap2	-182.585	1	7164.68	-	-	-	-	-	-	-	0.6736	-	-	-
Liq2	137.514	1	7835.55	-	-	-	0.9851	-	-	-	0.0123	0.0026	-	-
H ₂	20	25.5	566.462	1	-	-	-	-	-	-	-	-	-	-
Input2	102.312	1	4200.99	0.0674	-	-	0.9187	-	-	-	0.0115	0.0024	-	-
Input3	102.312	1	4200.99	0.0674	-	-	0.9187	-	-	-	0.0115	0.0024	-	-
Output2	200	16	4200.99	0.0671	0.0024	-	0.9098	-	-	-	0.0115	0.0024	-	0.0068
Output3	241	24	4200.99	0.0468	0.1641	-	0.5018	-	0.0989	-	0.0115	0.0024	-	0.1745
Output4	200	16	4200.99	0.0671	0.0024	-	0.9098	-	-	-	0.0115	0.0024	-	0.0068
Output5	241	24	4200.99	0.0468	0.1641	-	0.5018	-	0.0989	-	0.0115	0.0024	-	0.1745
Vap3	193.455	1	7571.97	0.0519	0.1821	-	0.5568	-	0.0002	-	0.0127	0.0027	-	0.1936
Liqliq3	205.235	1	830	-	-	-	0.0003	-	0.9992	-	-	-	-	0.0005

1.7.1.3. Utility

The utility cost is adjusted to current Taiwan cost [40-41].

Table 1.7.1.3. Utility Cost of Flowsheet 1

Cooling Water	
Rate (gal/yr)	188,127,763
Cost per hour (NTD/gal)	0.0348
Cost per year (NTD/year)	6,546,847
Steam	
Rate (gal/yr)	768,850,286
Cost per hour (NTD/gal)	0.97
Cost per year (NTD/year)	745,784,778
Electricity	
Rate (kW)	119.46
Cost per hour (NTD/kWh)	3.827
Cost per year (NTD/year)	3,785,396
Total Utility Cost: 756,117,021/year	

1.7.2. Second Flowsheet

1.7.2.1. Simulated Flowsheet Design

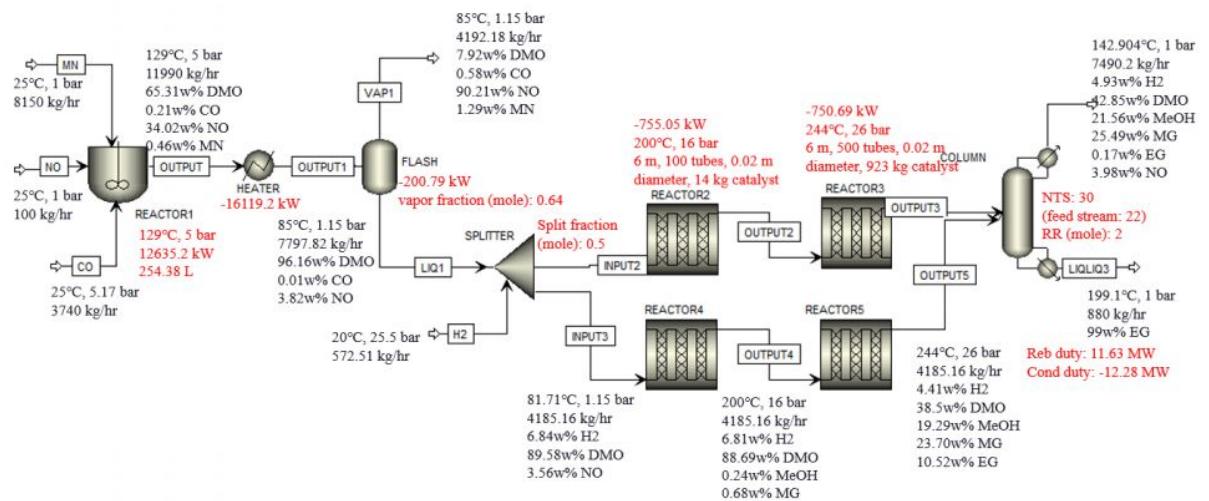


Figure 1.7.2.1. Aspen Simulation Process Flow Diagram for Flowsheet 2

Using a similar flowsheet, we tried to modify some devices to get a more effective yet low-cost production design of EG. In the simulated second flowsheet in aspen (**Fig. 1.7.2.1.**), the main processes are the same: reaction 1, separation 1, reaction 2, and separation 2. Looking at the highly recycled stream of CO resulting in 2 stages of the separation process and a big volume of the reactor, another alternative is simulated, which is using limiting reactant of both CO and MN. With this limited reactant, the NO gas needed to initiate reaction is also limited. CSTR with the same operating temperature and pressure is used, with the same catalyst of Pd/Al₂O₃. The conversion is as high as the first flowsheet, and no significant DMC amount is found in the product. The DMO resulted is slightly higher than the first flowsheet, and the reactor volume is significantly decreased due to the limited flow rate. The duty, however, is much higher than the first flowsheet. This might be due to the recycled stream temperature that can help with the energy balance by supplying some heat. In the separation process, a flash tank is used instead of a distillation column as it is simpler and the DMO mixture contains enough DMO to be separated by its flashpoint. Before entering the flash tank, a heater (cooler) is used to minimizing the flash tank duty by lowering the feed temperature. The first separation recovers DMO up to 95 wt% in the liquid process. Then it goes to the next stage which is reaction 2. The production line is the same as the first flowsheet, with 2 PFRs parallel lines consist of 2 PFRs in series for each line. The operating temperature and pressure are managed to provide maximum production and selectivity of EG. There are still some impurities due to the unreacted reactant and intermediate product of MG, but as is stated before, this has been the best simulation design. In addition, no further reaction of impurities like CO and NO is found in the simulation, nor the side product EtOH is formed. After EG formation, the mixture will go to the last stage, which is separation 2, using the RD column. The recovered ~99 wt% EG product is obtained in the bottom product. Compared to the first flowsheet, this EG production has more amount and only slightly lower purity.

1.7.2.2. Stream Table

Table 1.7.2.2. Stream Table of Flowsheet 2

Stream	T (°C)	P (bar)	m (kg/hr)	Mass fraction										
				H ₂	MeOH	EtOH	DMO	DMC	EG	CO	NO	MN	H ₂ O	MG
MN	25	1	8150	-	-	-	-	-	-	-	-	1	-	-
NO	25	1	100	-	-	-	-	-	-	-	1	-	-	-
CO	25	5.17	3740	-	-	-	-	-	-	1	-	-	-	-
Output	129	5	11990	-	-	-	0.6531	-	-	0.0021	0.3402	0.0046	-	-
Output1	85	1.15	11990	-	-	-	0.6531	-	-	0.0021	0.3402	0.0046	-	-
Vap1	85	1.15	4192.18	-	-	-	0.0792	-	-	0.0058	0.9021	0.0129	-	-
Liq1	85	1.15	7797.82	-	-	-	0.9616	-	-	0.0001	0.0382	-	-	-
H ₂	20	25.5	572.51	1	-	-	-	-	-	-	-	-	-	-
Input2	81.709	1.15	4185.16	0.0684	-	-	0.8958	-	-	-	0.0356	-	-	-
Input3	81.709	1.15	4185.16	0.0684	-	-	0.8958	-	-	-	0.0356	-	-	-
Output2	200	16	4185.16	0.0681	0.0024	-	0.8869	-	-	-	0.0356	-	-	0.0068
Output3	244	26	4185.16	0.0441	0.1929	-	0.3850	-	0.1052	-	0.0356	-	-	0.2370
Output4	200	16	4185.16	0.0681	0.0024	-	0.8869	-	-	-	0.0356	-	-	0.0068
Output5	244	26	4185.16	0.0441	0.1929	-	0.3850	-	0.1052	-	0.0356	-	-	0.2370
Vap3	142.904	1	7490.2	0.0493	0.2156	-	0.4285	-	0.0017	0.0001	0.0398	-	-	0.2649
Liqliq3	199.097	1	880	-	-	-	0.0147	-	0.99	-	-	-	-	-

1.7.2.3. Utility

The utility cost is adjusted to current Taiwan cost [40-41].

Table 1.7.2.3. Utility Cost of Flowsheet 2

Cooling Water	
Rate (gal/yr)	316,116,464
Cost per hour (NTD/gal)	0.0348
Cost per year (NTD/year)	11,627,253
Steam	
Rate (gal/yr)	1,247,376,572

Cost per hour (NTD/gal)	0.97
Cost per year (NTD/year)	1,209,955,275
Electricity	
Rate (kW)	76.565
Cost per hour (NTD/kWh)	3.827
Cost per year (NTD/year)	2,426,158
Total Utility Cost: 1,224,008,686/year	

1.8. P&ID Diagram for Valves and Controller

Table 1.8. P&ID Symbols

Symbols	Meaning	Symbols	Meaning
AC	Analyzer Controller	PT	Pressure Transmitter
AT	Analyzer Transmitter	PR	Pressure recorder
FC	Flow controller	TIC	Temperature indicating controller
FFC	Flow Ratio Controller	TR	Temperature recorder
FT	Flow transmitter	TT	Temperature transmitter
FY	Flow transducer	TY	Temperature relay/transducer
LC	Level controller	—	Main process flow line
LT	Level transmitter	-----	Electrical signal line
PC	Pressure Controller	~ ~ ~	Bluetooth/wireless signal line
PIR	Pressure Indicating Recorder	☒	Control Valve
○	Primary location accessible to operator	○	Field mounted

1.8.1. First Flowsheet

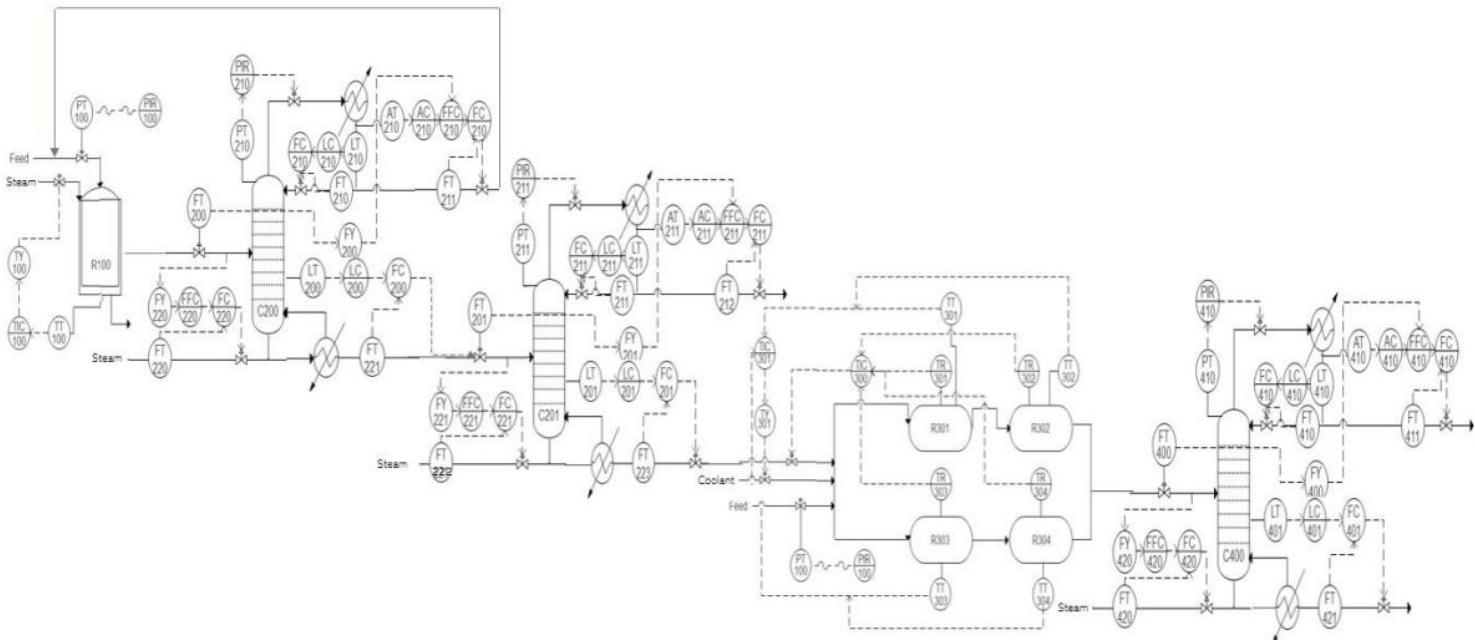


Figure 1.8.1. P&ID Diagram for Flowsheet 1

Piping and Instrumentation Diagram (P&ID) represents the pipelines, equipment, instrumentation, and control system of the designed process. It is important as the design provides the basis for the development of system control schemes. Here will be discussed mainly about the control system, as the key production line has been discussed before and the instrument detail will be covered in chapter 2.

In every line of the process, controllers would be assigned due to safety and operational maintenance reasons. In the feed stream to the first reactor, a pressure controller would be applied, as the feed consists of vapor phase gases. There would be steam to provide the reactor duty, hence the temperature controller would be applied in this stream, as the reaction is sensitive with temperature we want to make it as constant as possible. The product will go to distillation columns. In every distillation column, the bottom flow rate is controlled by the inlet flow rate fluctuation, while the distillate flow is controlled according to the pressure of the column and the feed flow. The steam for the reboiler will be controlled according to the feed flow rate. There will also be a flow controller for the recycled distillate from the partial condenser. In the second reaction, where 4 PFRs are located, the temperature is crucial in the kinetic model hence in every

reactor, a temperature controller would be placed. The Hydrogen gas feed would also be controlled in certain inlet pressure as it is in a vapor phase. The explanation for each abbreviation of the controller can be seen in **Table 1.8**.

1.8.2. Second Flowsheet

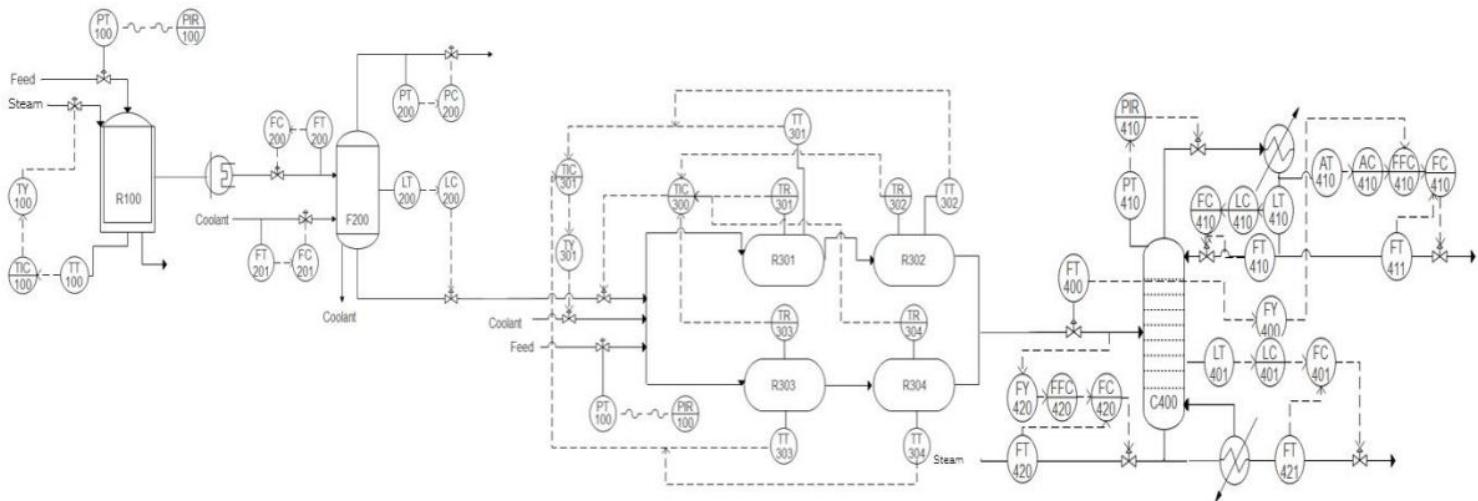


Figure 1.8.2. P&ID Diagram for Flowsheet 2

Similar to the first flowsheet, the first reactor utilizes the pressure controller for the gas feed stream and the temperature controller for the steam. The cooling process would happen in the flash tank, hence there will be a coolant that goes inside that has a flowrate controller. The feed of the flash tank is also maintained using a flow controller. The bottom product flow rate will be controlled by the level of the fluid inside the tank. The vapor product will be controlled by a pressure controller. The next phase would be reaction 2 and separation 2, which utilize the same control system as Flowsheet 1 since every device and production line in the design is the same.

1.9. Floor Plan

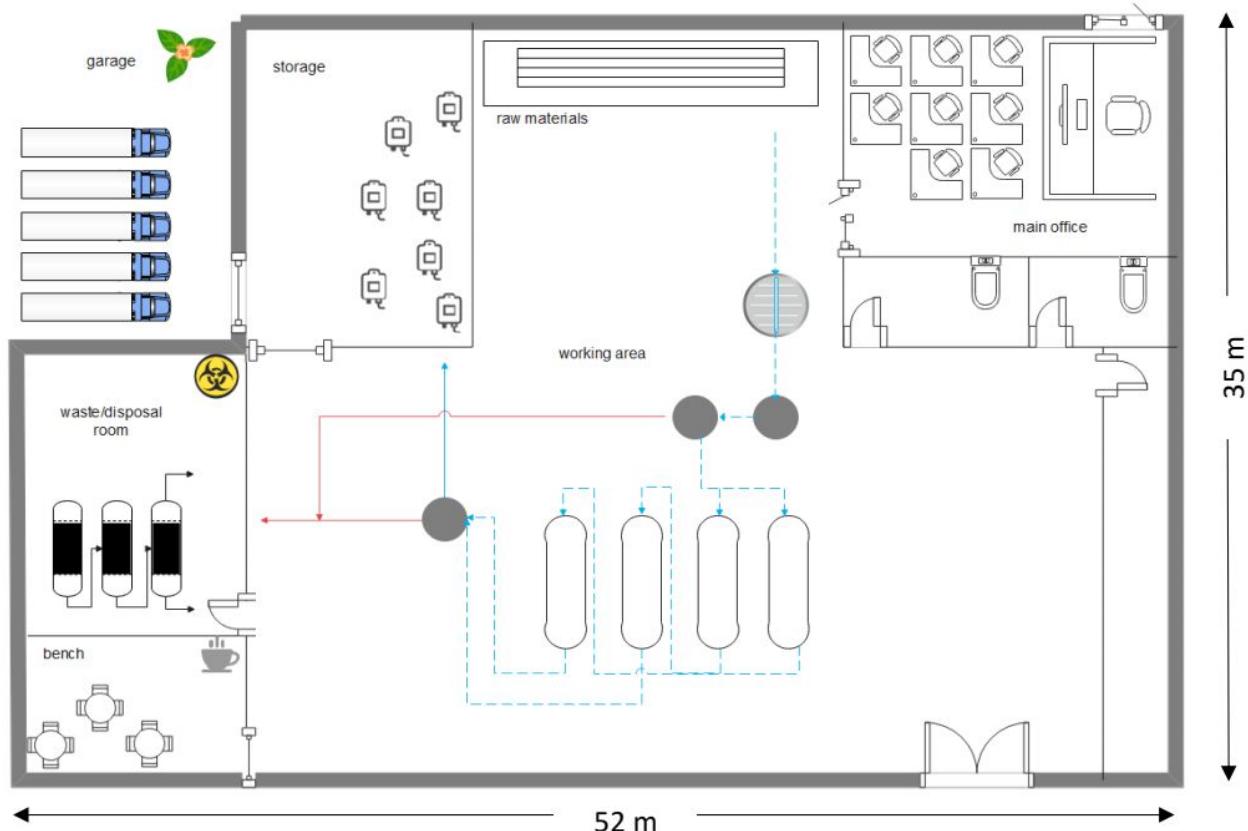


Figure 1.9. Floor Plan Design

The floor plan was made according to the concept and simulated design. There will be a main working area, where every device and instrument would be placed. The red line represents the waste pipeline while the blue line depicts the production line. The output would be stored in a storage tank inside the storage room, which also will be the wrapping and packing area that is connected to the garage outside. The waste disposal room is also separated from the main area to minimize contamination. The disposal room is also next to the bench so that the kitchen liquid waste can be dumped easily with the mixture of treated industrial waste. There will be an empty room (right below corner) to store some extra devices and instruments in case there is some malfunction in the production line, the worker can replace the new instrument quickly. The main office would connect to the front yard, where the customer can discuss freely with the head of the office or going to the factory tour inside. The marketing department can also work in this office. The other

consideration of the floor plan is the height of the building. Since the distillation column varied from 10 to 20 m height, there will be some towers inside the building for Flowsheet 1 and one big tower for Flowsheet 2. In this case, we decided to place the factory in the Taoyuan area. The reasons for our choice are because the labor and utility are relatively low in this area. There are lots of customers and clients in Taiwan, including Formosa Plastic Corporation. Other than the marketing and budgeting reasons, the place is perfect for our building where a tower of distillation should not be a problem since it is an industrial area.

CHAPTER 2

EQUIPMENT DESIGN

2.1. First Flowsheet

2.1.1. Reactor

2.1.1.1. Reactor 1

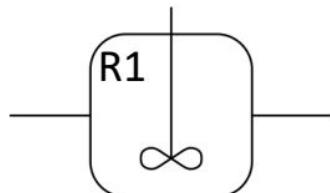


Figure 2.1.1.1.1. CSTR used and its configuration

The first reactor is for the first reaction, which reacts both CO and NO to form DMO for the main product and NO as the side reaction. In the flowsheet design, all the output streams will be flown out to the separation system.

Table 2.1.1.1. CSTR specification of Flowsheet 1

Parameters	Value	Parameters	Value
Reactor Type	CSTR	Volume (m ³)	1.5979
Material	Stainless Steel	Amount of catalyst (kg)	100
Duty (kW)	4710.65	Particle density (g/cm ³)	0.23

The reaction is purposefully done in the presence of excess carbon monoxide, to minimize the side product of DMC and lowering the duty due to the incorporation of recycle stream. The consideration for this reactor specification would be the temperature, pressure, reactant concentration, and residence time (which are directly related to the volume). The temperature and pressure, according to the literature [28-31], should be in the range of 125-135°C and 5 bar. The residence time used is 1 second, as too much time will result in higher volume. The sensitivity test can be seen in **Fig. 2.1.1.2.**

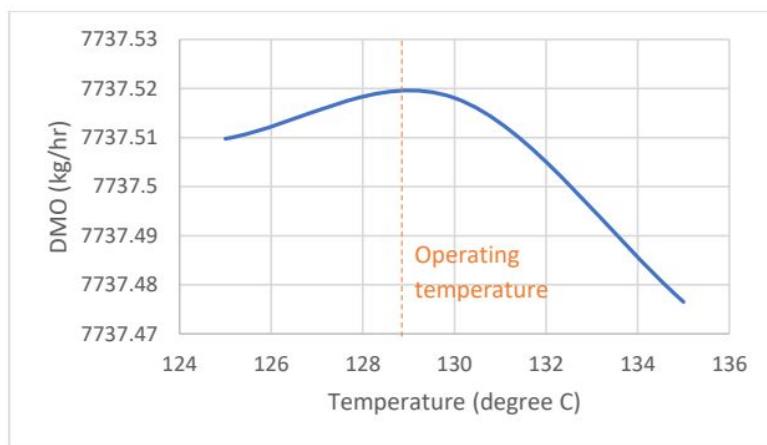


Figure 2.1.1.1.2. Sensitivity results of CSTR temperature

Based on the stream results, the conversion of MN is 100% while the CO is 16.42%. Based on MN as the reactant, the selectivity of DMO is 50% as the rest is for NO% because the DMO formation will give NO as the side product, and the reactor yield is 100% DMO. While based on CO as the reactant, the selectivity of DMO is 15% and the reactor yield is 30%. The conversion is high in terms of MN, hence it is considered effective. Furthermore, there is no significant formation of DMC side product.

2.1.1.2. Reactor 2



Figure 2.1.1.2.1. PFRs used and their configurations

Here, 4 PFRs are utilized with 2 PFRs in series and there are 2 series lines in parallel. Hence, there are two different configurations of PFR, which are the first and the second reactor in each line. For further discussion, this will be referred to R2 for the first PFR and R3 for the second PFR. The input stream will be half of the recovered DMO from the separation process, mixed with Hydrogen gas. After going out from the PFRs, the product will also go through a further separation process.

Table 2.1.1.2.1. PFR (R2) specification of Flowsheet 1

Parameters	Value	Parameters	Value
Reactor Type	PFR	Bed void	0.5
Material	Stainless Steel	Length (m)	6
Number of tubes	100 (D: 0.02 m)	Amount of catalyst (kg)	14
Duty (kW)	-858.92 kW	Particle density (g/cm ³)	0.98

There will be 100 tubes inside with a 0.02 m inner diameter for each tube. Hence, assuming the thickness of each pipe is 0.5 cm, the inner diameter for the R2 is 29 cm and the outer diameter is 29.5 cm; there will be one extra pipe if we run this in the illustrated figure. The configuration illustration can be seen in **Fig. 2.1.1.2.2.**

Maximum number of smaller pipes or circles inside the larger one: **101**

Area large Circle (in², mm², m²): **661**

Area small Circle (in², mm², m²): **4.91**

Area all Circles (in², mm², m²): **496**

Small Circles to Large Circle Area Ratio (%): **75.1**

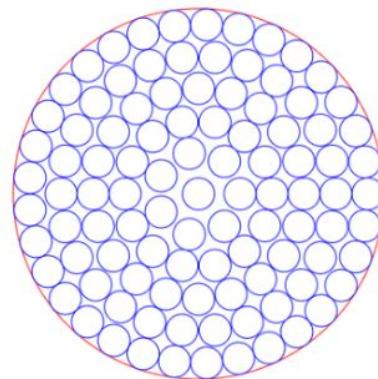


Figure 2.1.1.2.2. R2 illustration

The conversion and comparison for this reactor can be seen in **Table 1.6.1.1.** After being reacted inside this pipe, the DMO will be converted to EG and MG, with a side product of MeOH. There is no side product of EtOH found in the simulated design. The factors considered for this configuration are temperature, pressure, residence time (hence, the length), and reactant concentration. The temperature and pressure are the most crucial parameters since the complicated kinetics are based on these two. The sensitivity results can be seen below, alongside the temperature, pressure, and composition profile. The

literature suggests a temperature range of 190°C [23-25], but in the simulated version, the EG can be formed after 200°C and decreasing with the rising temperature, hence the 200°C operating temperature was chosen (**Figure 2.1.1.2.3.**). The pressure was advised to be 15-30 bar, but considering the higher cost with higher pressure, while the EG was fluctuating only around 0.01 kg/hr from 16-30 bar (**Fig. 2.1.1.2.4.**), the lowest pressure which is 16 bar was adopted. From the length and number of tubes aspect, the EG resulted was constant after 6 m length and 100 tubes (**Fig. 2.1.1.2.5. and 2.1.1.2.6.**) hence it was chosen to be the operating length.

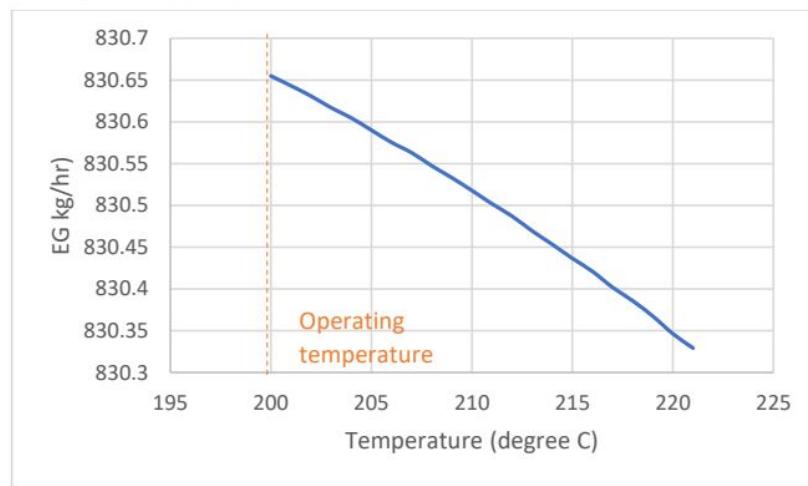


Figure 2.1.1.2.3. Sensitivity results of PFR R2 temperature

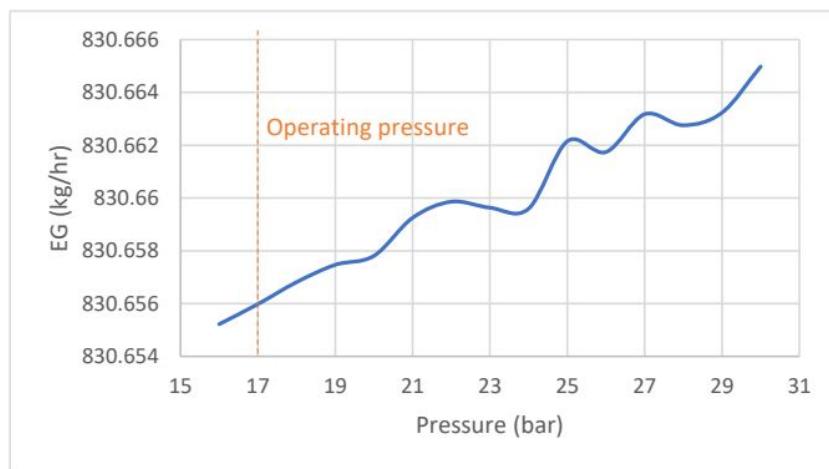


Figure 2.1.1.2.4. Sensitivity results of PFR R2 pressure

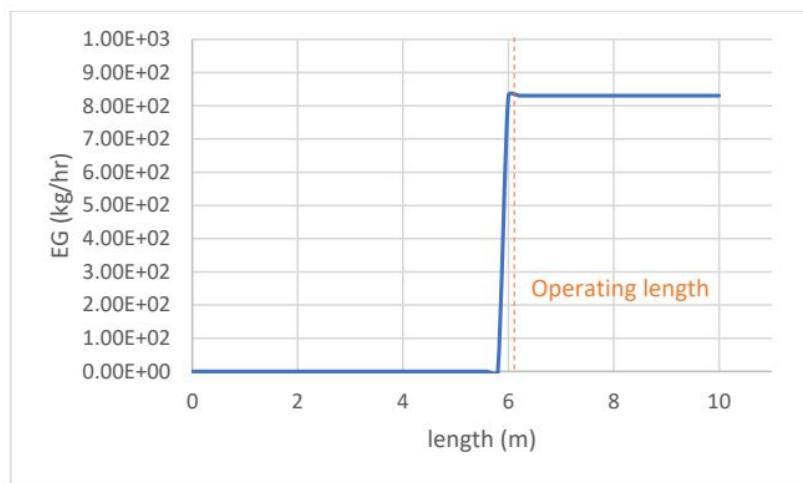


Figure 2.1.1.2.5. Sensitivity results of PFR R2 reactor length

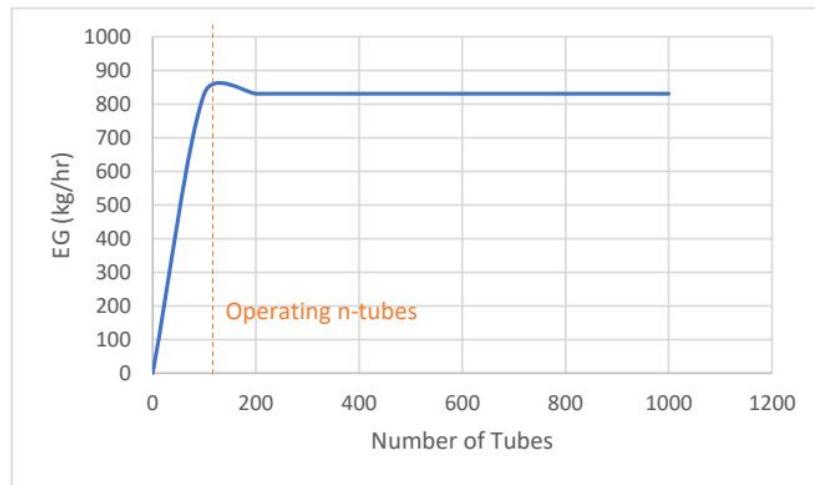


Figure 2.1.1.2.6. Sensitivity results of PFR R2 number of tubes

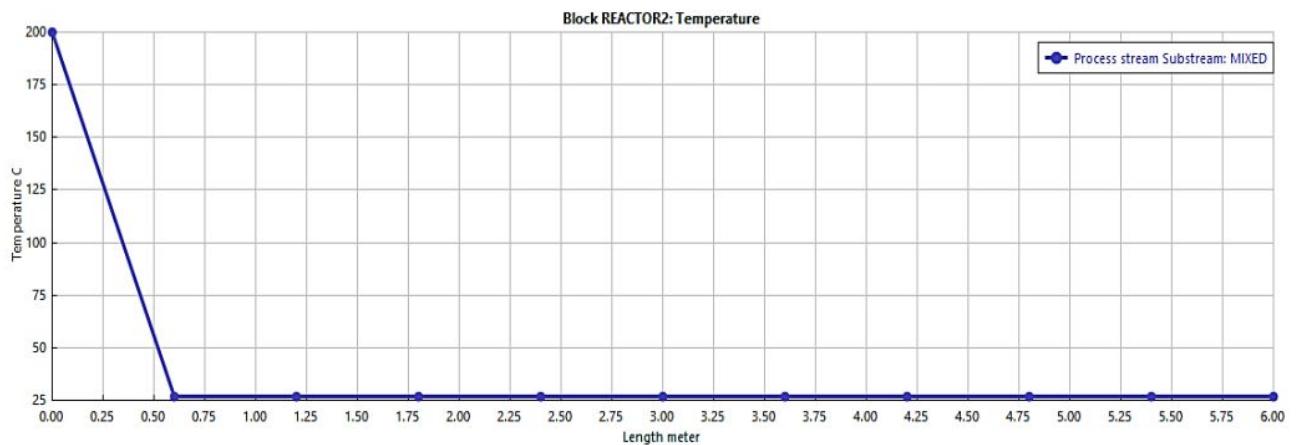


Figure 2.1.1.2.7. Temperature Profile of PFR R2

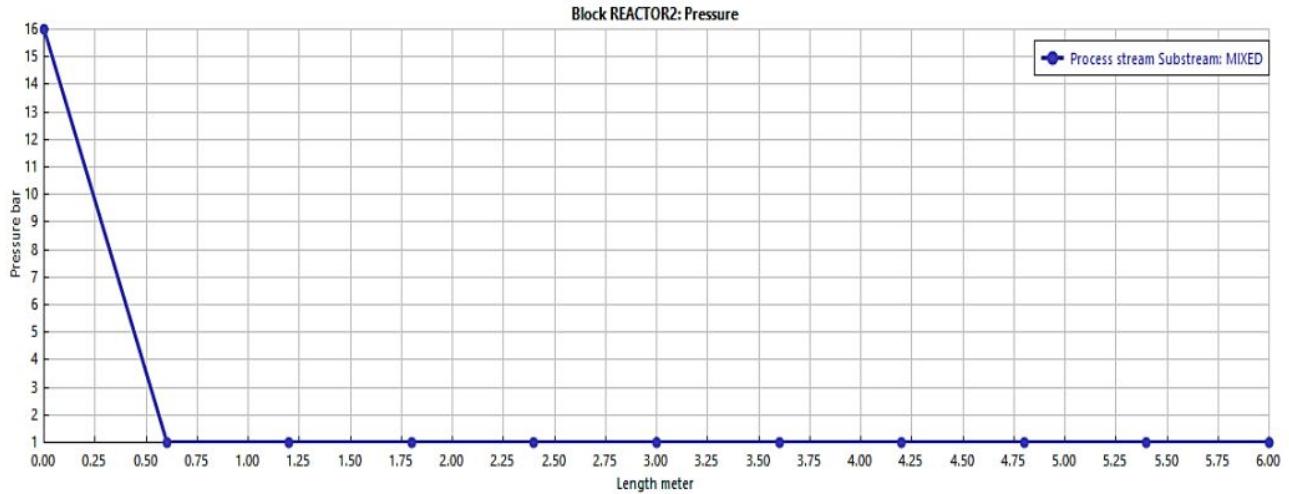


Figure 2.1.1.2.8. Pressure Profile of PFR R2

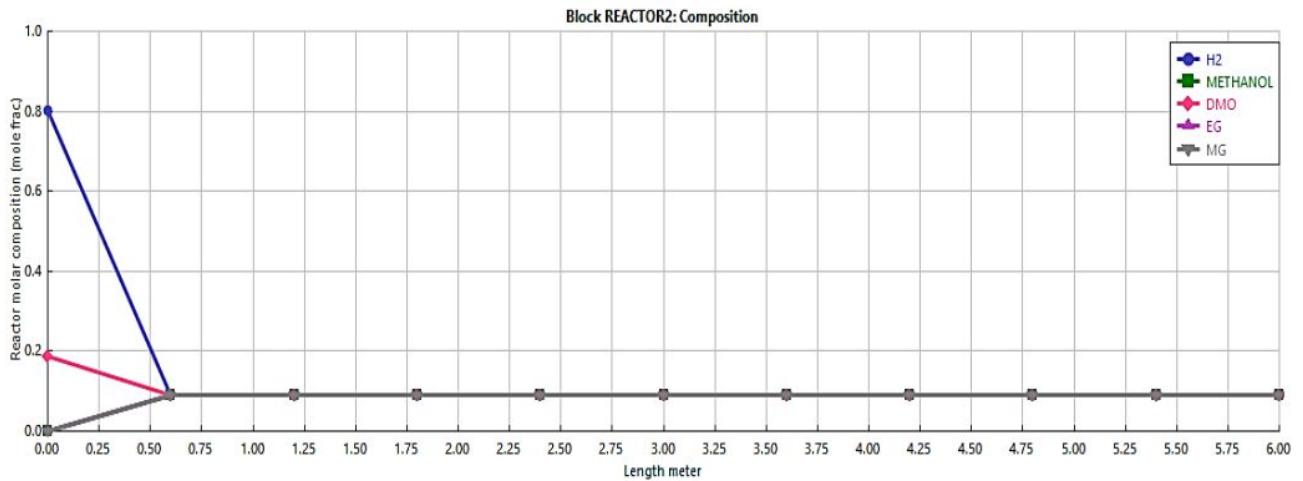


Figure 2.1.1.2.9. Composition Profile of PFR R2

Table 2.1.1.2.2. PFR (R3) specification of Flowsheet 1

Parameters	Value	Parameters	Value
Reactor Type	PFR	Bed void	0.5
Material	Stainless Steel	Length (m)	6
Number of tubes	500 (D: 0.02 m)	Amount of catalyst (kg)	923
Duty (kW)	-419.15 kW	Particle density (g/cm ³)	0.98

A similar simulation and sensitivity test goes to the PFR R3. There will be 500 tubes inside with a 0.02 m inner diameter for each tube. Hence, assuming the thickness of each

pipe is 0.5 cm, the inner diameter for the R3 is 63.5 cm and the outer diameter is 64 cm. The configuration illustration can be seen in **Fig. 2.1.1.2.10.**

Maximum number of smaller pipes or circles innside the larger one: **500**

Area large Circle (in², mm², m²): **3167**

Area small Circle (in², mm², m²): **4.91**

Area all Circles (in², mm², m²): **2454**

Small Circles to Large Circle Area Ratio (%): **77.5**

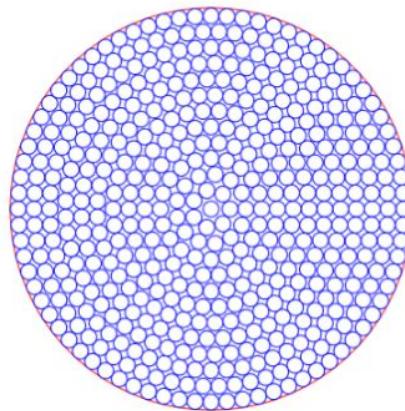


Figure 2.1.1.2.10. R3 illustration

The sensitivity results, the temperature, and pressure profile can be seen from **Fig. 2.1.1.2.11** to **2.1.1.2.17**. The more drastic change of EG amount is resulted from changing the temperature and pressure compared to R2. The chosen parameters are 241°C, 24 bar, 6 m, and 500 tubes due to their maximized performance.

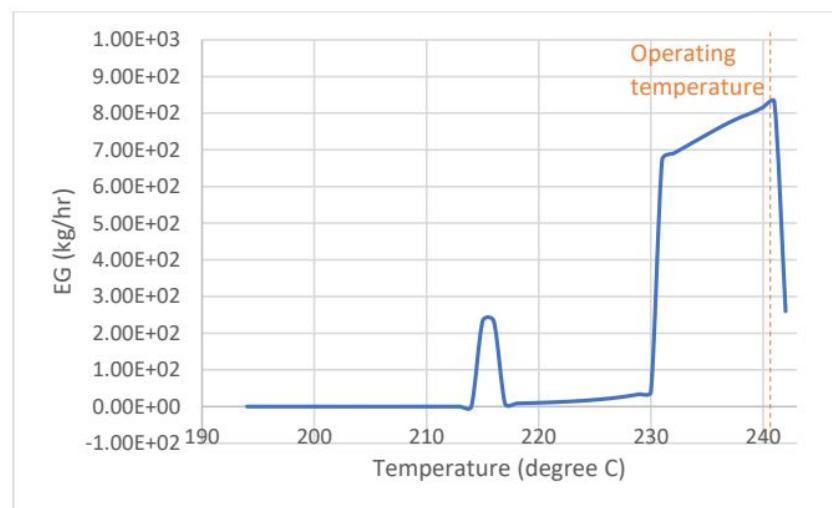


Figure 2.1.1.2.11. Sensitivity results of PFR R3 temperature

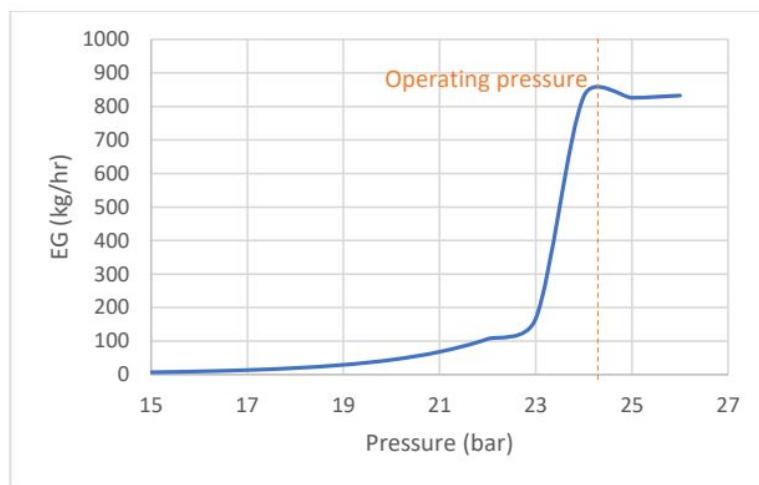


Figure 2.1.1.2.12. Sensitivity results of PFR R3 pressure

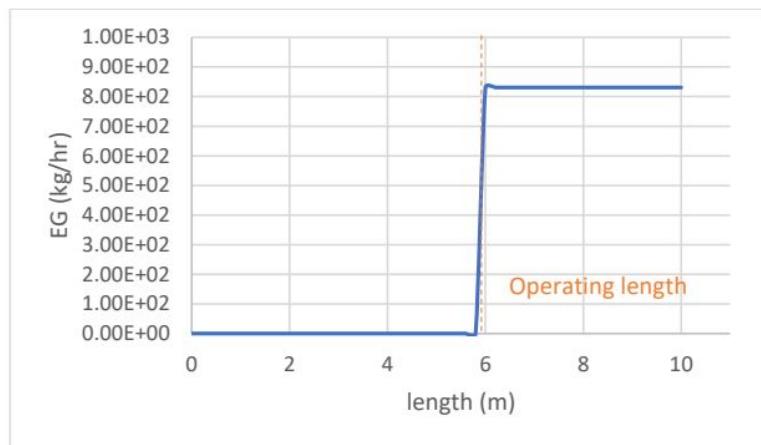


Figure 2.1.1.2.13. Sensitivity results of PFR R3 reactor length

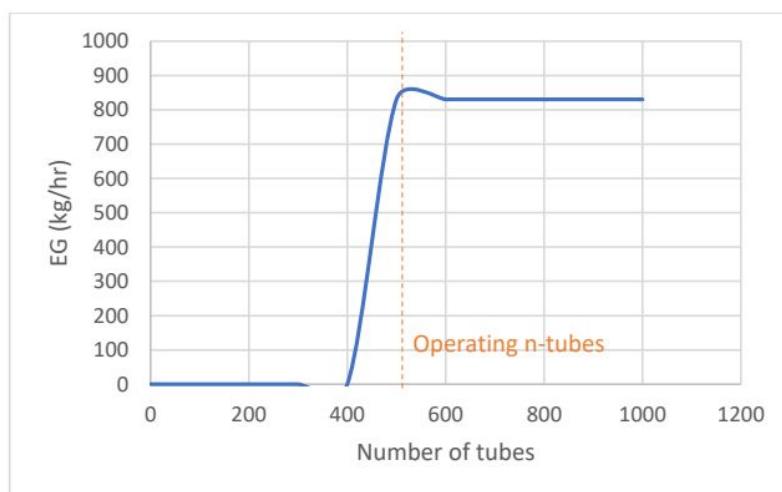


Figure 2.1.1.2.14. Sensitivity results of PFR R3 number of tubes

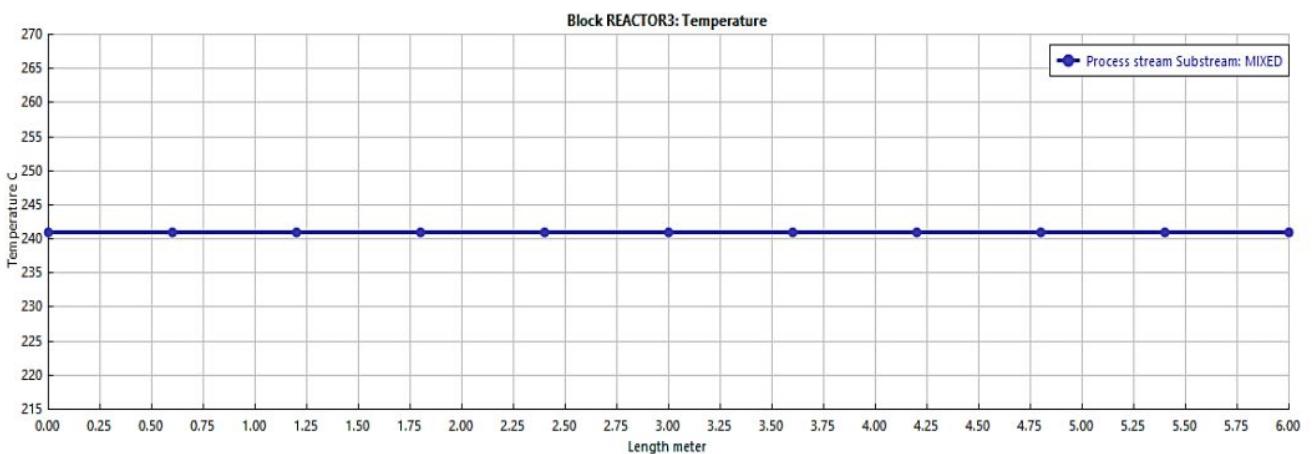


Figure 2.1.1.2.15. Temperature Profile of PFR R3

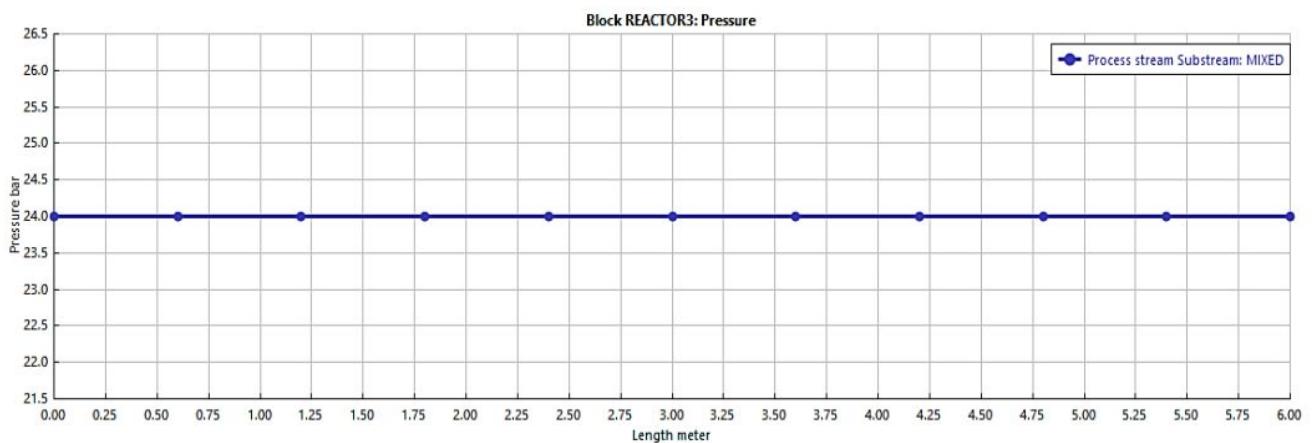


Figure 2.1.1.2.16. Pressure Profile of PFR R3

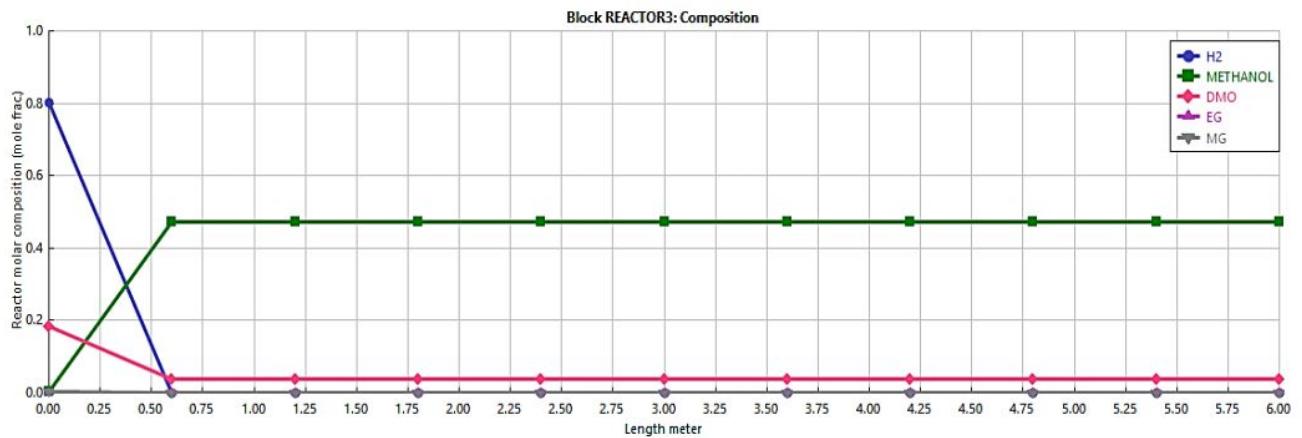


Figure 2.1.1.2.17. Composition Profile of PFR R3

2.1.2. Distillation Column

2.1.2.1. Column 1&2

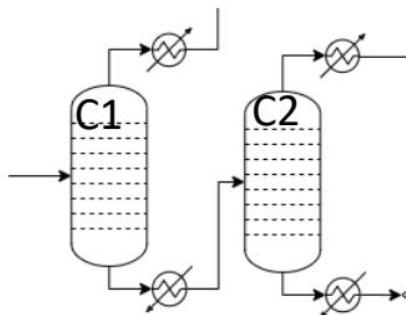


Figure 2.1.2.1.1. Columns used and their configurations

This section covers 2 distillation columns (which next will be referred to as C1 and C2) in separation 1 area. This separation will affect the purities of both the product and recycle stream to the R1. The sensitivity test was made for C1 to obtain pure CO in the vapor stream, hence a sensitivity test was done to determine the maximum amount of CO in the vapor phase (**Fig. 2.1.2.1.3.**). In the ternary diagram (**Fig. 2.1.2.1.2.**) CO-NO-DMO is within the distillation range, and the CO boiling point is far from the other two hence it is relatively easy to get pure CO in the distillate product. The C2 was used to obtain recovered DMO in the bottom product. The sensitivity analysis was also done to determine the number of stages, feed stage, reflux ratio, and distillate to feed mole ratio (**Fig. 2.1.2.1.6. to 2.1.2.1.9.**) that has the best DMO amount in the bottom product. The overall results can be seen in **Table 2.1.2.1.** We also provide the temperature and compositional profiles for C1; while in C2 using a simple distillation column, Aspen does not provide this profile.

Table 2.1.2.1. Specifications of C1 and C2 of Flowsheet 1

Parameters	C1	C2
Materials	Carbon Steel	
Reflux Ratio (moles)	5	0.45
Distillate to Feed Ratio (moles)	0.65	0.78
Number of Stages	16	21
Feed Stages	4	16

Diameter (m)	0.73	0.46
Pressure (bar)	5	1
Condenser Duty (kW)	-4175.38 kW	1236.95 kW
Reboiler Duty (kW)	-6031.5 kW	2076.19 kW

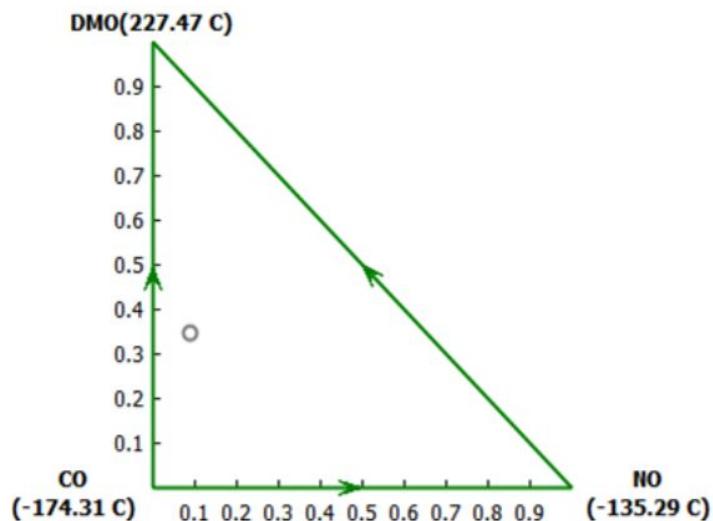


Figure 2.1.2.1.2. Ternary diagram for CO-NO-DMO

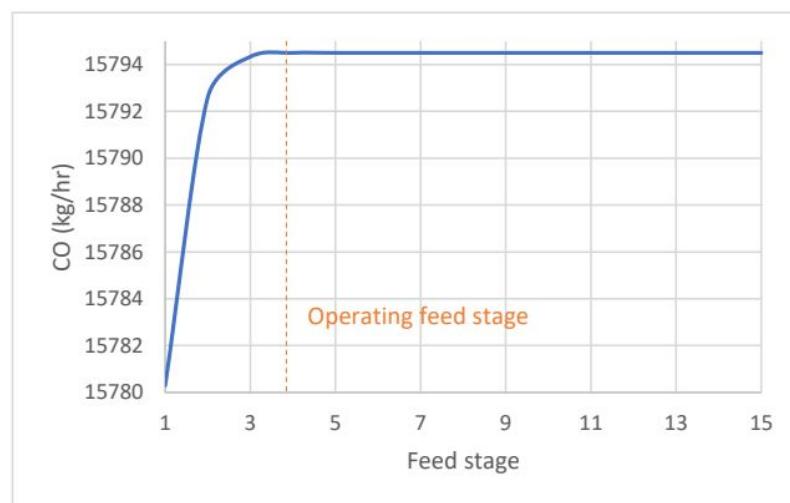


Figure 2.1.2.1.3. Sensitivity results of C1 feed stage

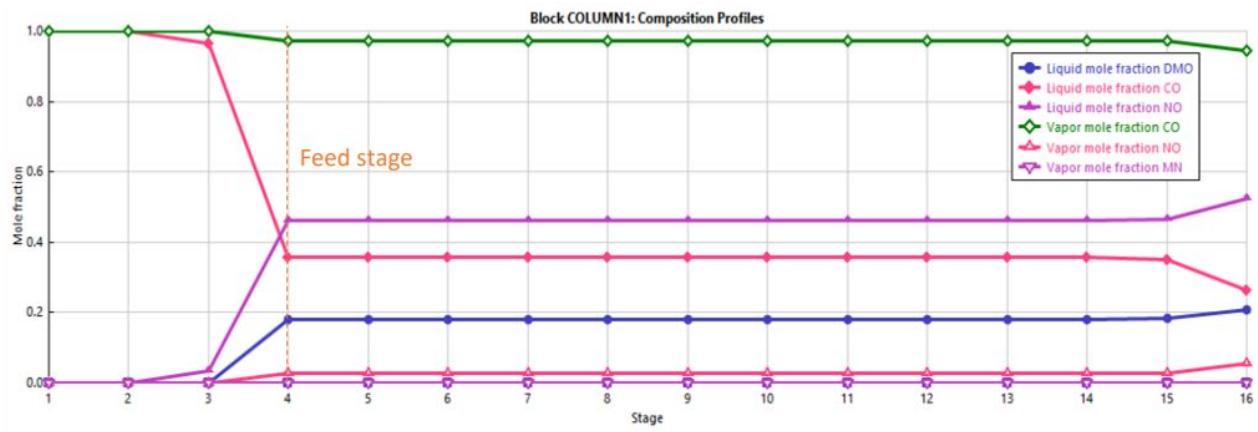


Figure 2.1.2.1.4. Composition profile of C1

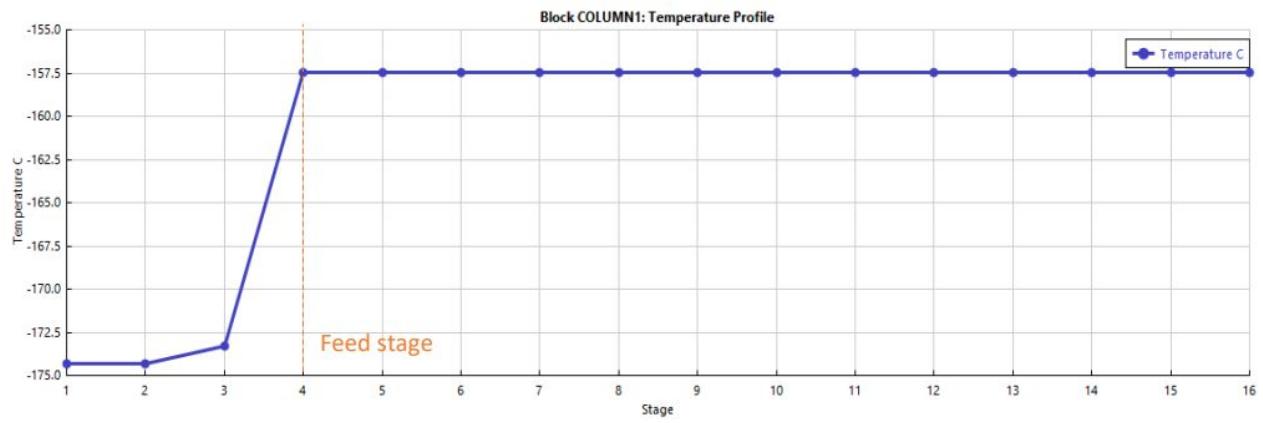


Figure 2.1.2.1.5. Temperature profile of C1

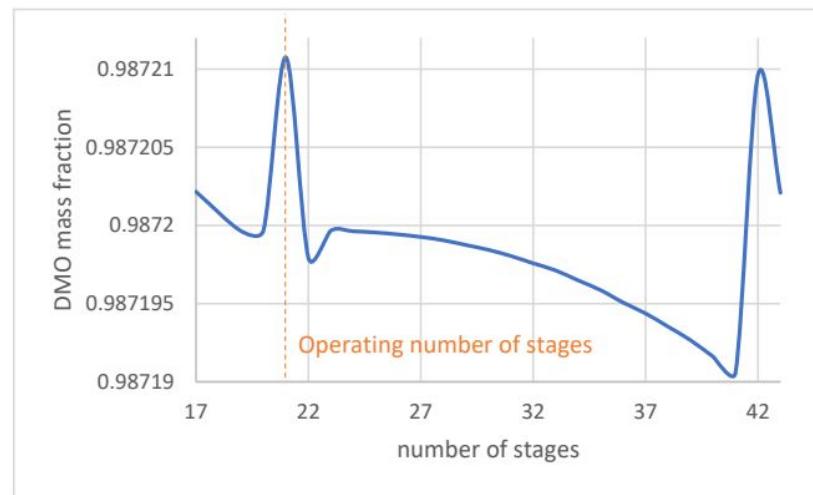


Figure 2.1.2.1.6. Sensitivity results of C2 number of stages

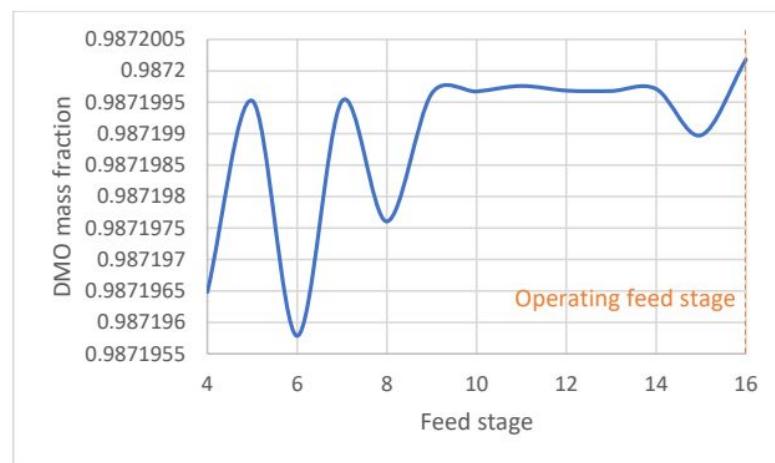


Figure 2.1.2.1.7. Sensitivity results of C2 feed stages

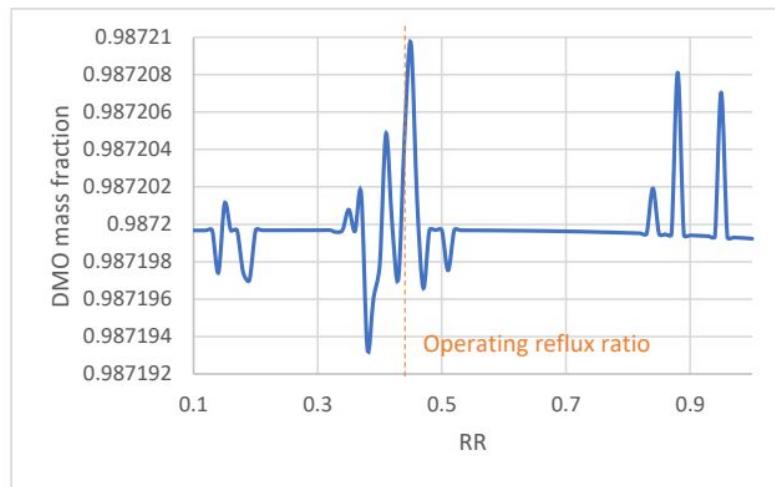


Figure 2.1.2.1.8. Sensitivity results of C2 reflux ratio

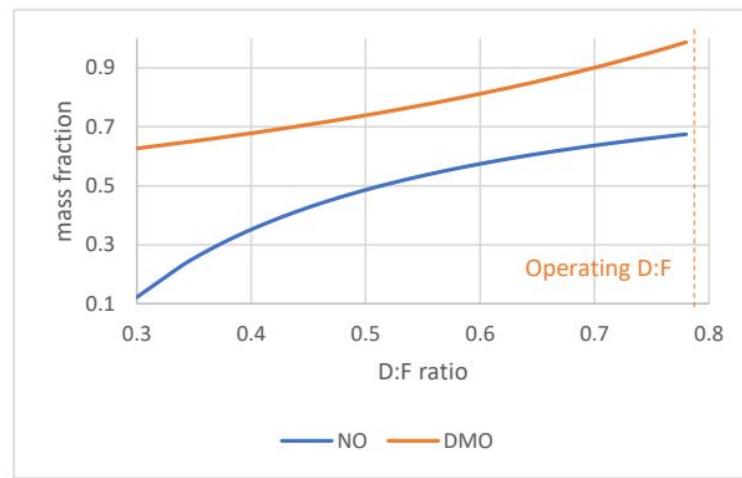


Figure 2.1.2.1.9. Sensitivity results of C2 D:F mole ratio

2.1.2.2. Column 3

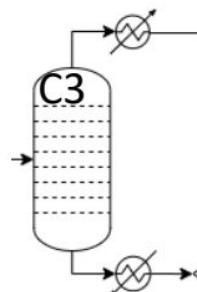


Figure 2.1.2.2.1. Column used and its configuration

Table 2.1.2.2. Specifications of C3 of Flowsheet 1

Parameters	C1
Materials	Carbon Steel
Reflux Ratio (moles)	2
Bottom product (kg/hr)	830
Number of Stages	25
Feed Stages	18
Diameter (m)	0.97
Pressure (bar)	1
Condenser Duty (kW)	-7470 kW
Reboiler Duty (kW)	7060 kW

After reacted, the RD column is used to separate EG from other impurities. Other than EG, the main impurities are MeOH, DMO, and H₂. The ternary diagram can be seen in **Fig. 2.1.2.2.2.**, where the feed location (white circle) is still separable within the distillation range. In the C3 simulation, the bottom product was set to the certain amount (which is 830 kg/hr, the maximum amount of EG that can be obtained). Then the feed stage and reflux ratio were determined using trial and error. The resulted specification can be seen in **Table 2.1.2.2.**, while the composition and temperature profiles can be seen in **Fig. 2.1.2.2.3.**

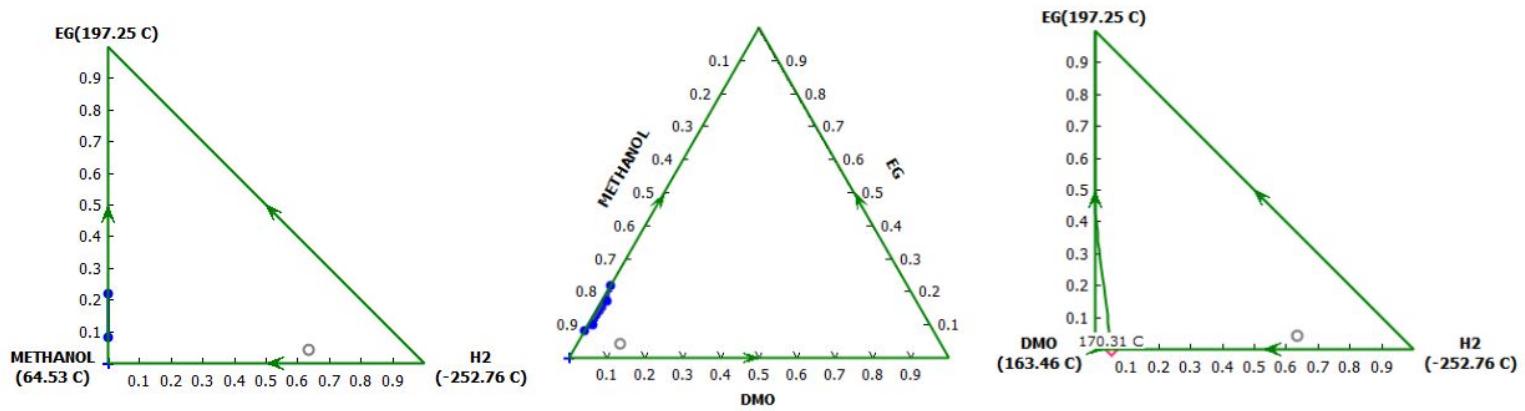


Figure 2.1.2.2.2. Ternary diagrams

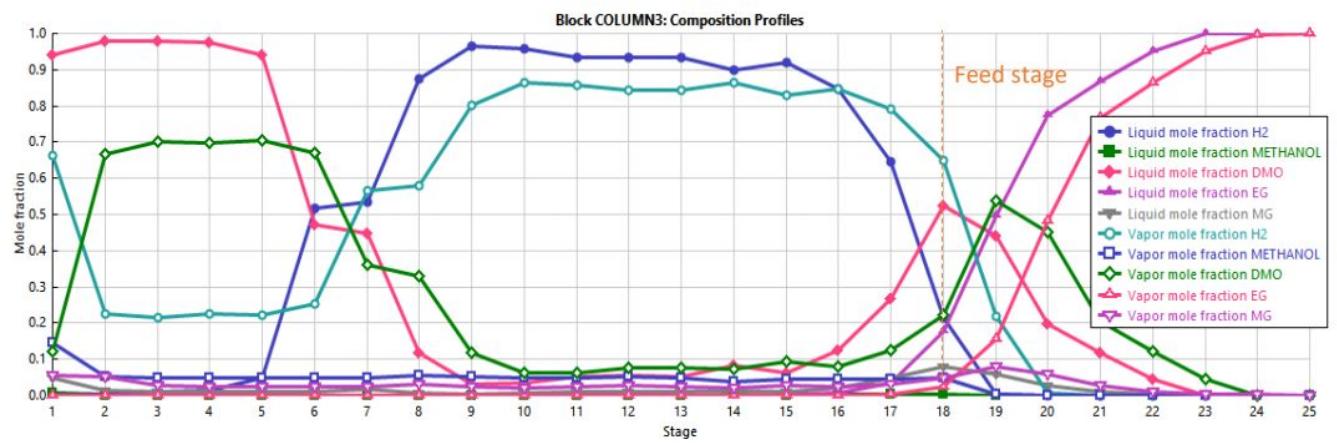


Figure 2.1.2.2.3. Composition profile of C3

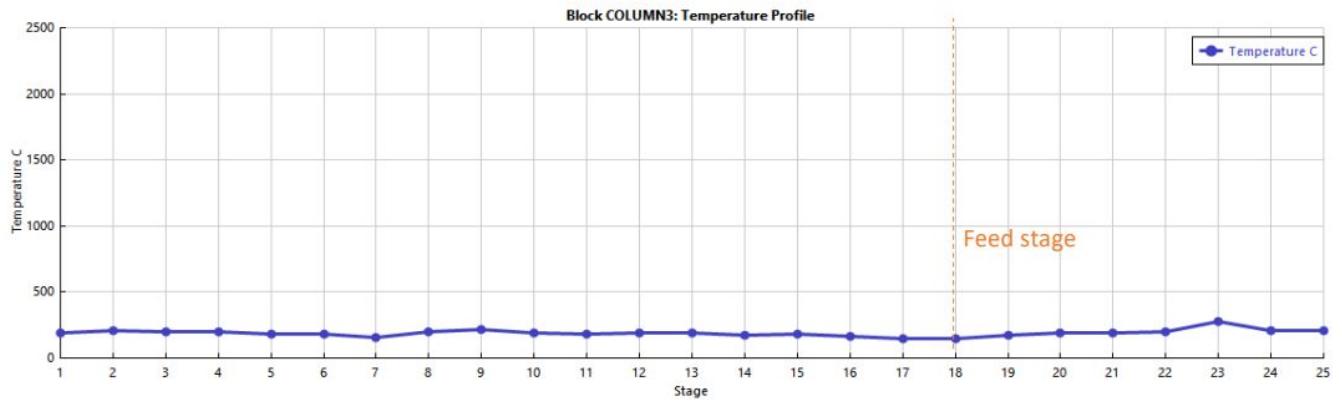


Figure 2.1.2.2.4. Temperature profile of C3

2.2. Second Flowsheet

2.2.1. Reactor

2.2.1.1. Reactor 1

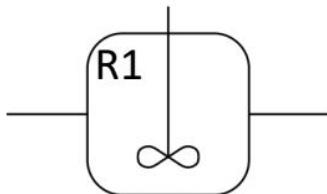


Figure 2.2.1.1.1. CSTR used and its configuration

The purpose of this reactor is the same as the one in the first flowsheet. All of the input specifications are the same as the first flowsheet, the only difference is that both the CO and MN reactant was fed in a limited amount. Based on the results, the conversion of CO and MN is $\sim 100\%$, hence impurities in the product are minimized. No DMC is found, the selectivity and reactor yield of DMO is the same as the first flowsheet, which is 0.5 and 1, respectively. However, since there is no reflux from CO, the duty of this reactor is increased more than twice the amount from the first flowsheet. In terms of size, the volume decreases greatly to only about 0.2 m^3 (which is one-seventh of the first flowsheet) due to the limited flowrate of the reactant. The same amount of catalyst and residence time was used, hence the advantage of the utility size over the utility cost will be further examined in the economic evaluation.

Table 2.2.1.1. CSTR specification of Flowsheet 2

Parameters	Value	Parameters	Value
Reactor Type	CSTR	Volume (m^3)	0.2544
Material	Stainless Steel	Amount of catalyst (kg)	100
Duty (kW)	12635.2	Particle density (g/cm^3)	0.23

2.2.1.2. Reactor 2

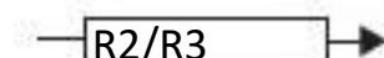


Figure 2.2.1.2.1. PFRs used and their configurations

Same as before, 2 PFRs in series and 2 series lines in parallel were simulated for the second reaction. The input would still be the recovered DMO with H₂ gas. After reacted in the tube, the result would go to the distillation column for the separation process. Since before we know that the R3 tube causes a significant effect of EG resulted, a sensitivity test was done again to examine the optimal properties of R3. Overall specification, sensitivity test, and profiles can be seen below. The diameter, number of tubes, and configuration of the tubes are all the same as the first flowsheet (Section 2.1.1.2.). The specification of R2 is the same, but the R3 operating temperature and pressure are changed to 244°C and 26 bar due to the sensitivity results (**Fig. 2.2.1.2.5.** and **2.2.1.2.6.**). The result is better in terms of net EG product compared to the first flowsheet, but the overall duty is a little bit higher, hence further economic analysis is needed. A further calculation can be seen in **Table 1.6.1.1.** No EtOH was found in the product.

Table 2.2.1.2.1. PFR (R2) specification of Flowsheet 2

Parameters	Value	Parameters	Value
Reactor Type	PFR	Bed void	0.5
Material	Stainless Steel	Length (m)	6
Number of tubes	100 (D: 0.02 m)	Amount of catalyst (kg)	14
Duty (kW)	-755.05 kW	Particle density (g/cm ³)	0.98

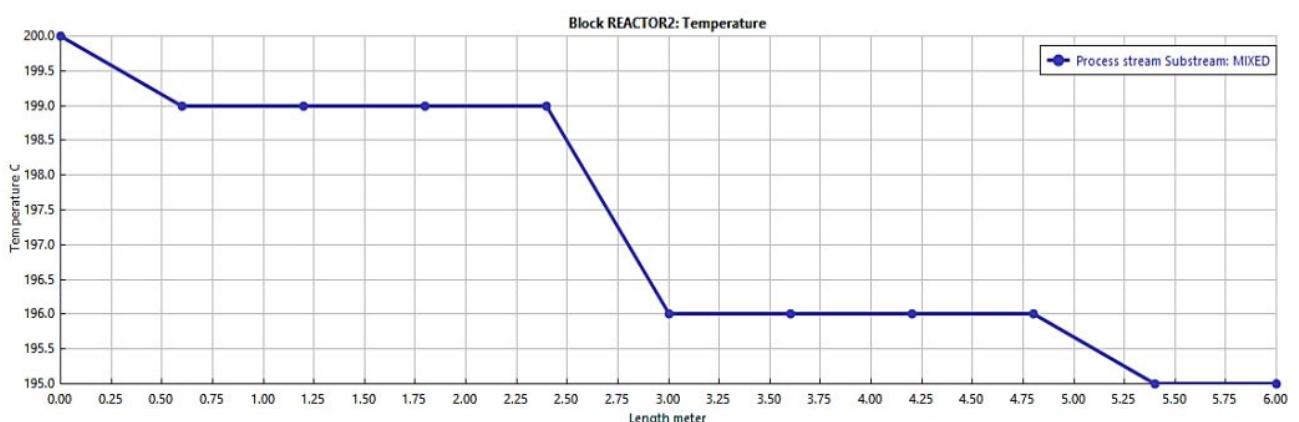


Figure 2.2.1.2.2. Temperature Profile of PFR R2

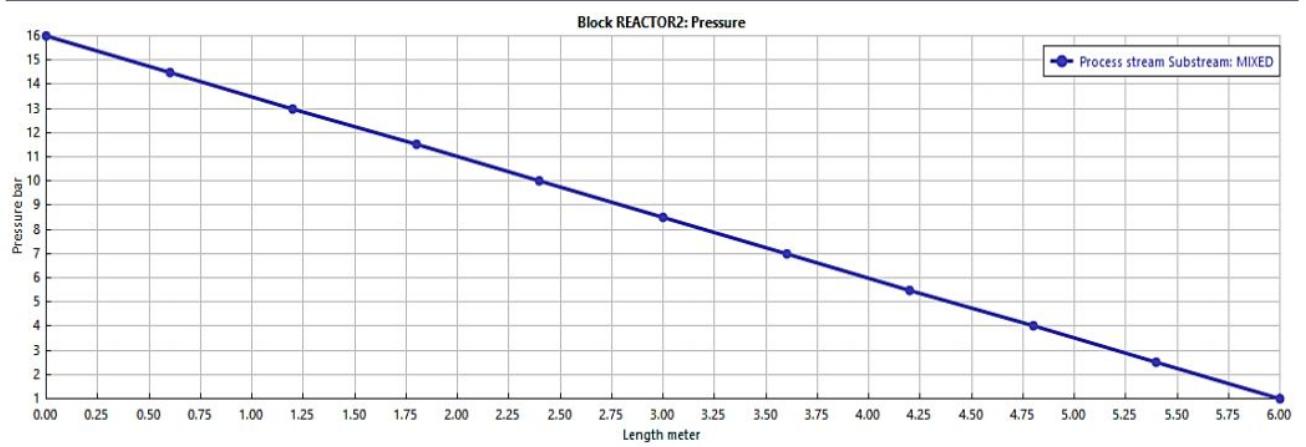


Figure 2.2.1.2.3. Pressure Profile of PFR R2

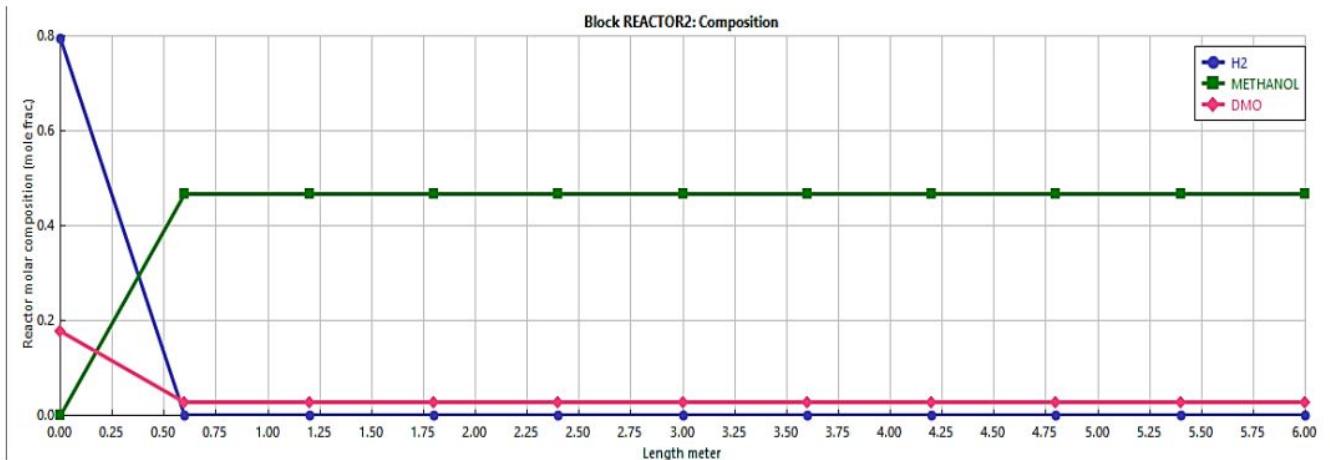


Figure 2.2.1.2.4. Composition Profile of PFR R2

Table 2.2.1.2.2. PFR (R3) specification of Flowsheet 2

Parameters	Value	Parameters	Value
Reactor Type	PFR	Bed void	0.5
Material	Stainless Steel	Length (m)	6
Number of tubes	500 (D: 0.02 m)	Amount of catalyst (kg)	923
Duty (kW)	-750.69 kW	Particle density (g/cm ³)	0.98

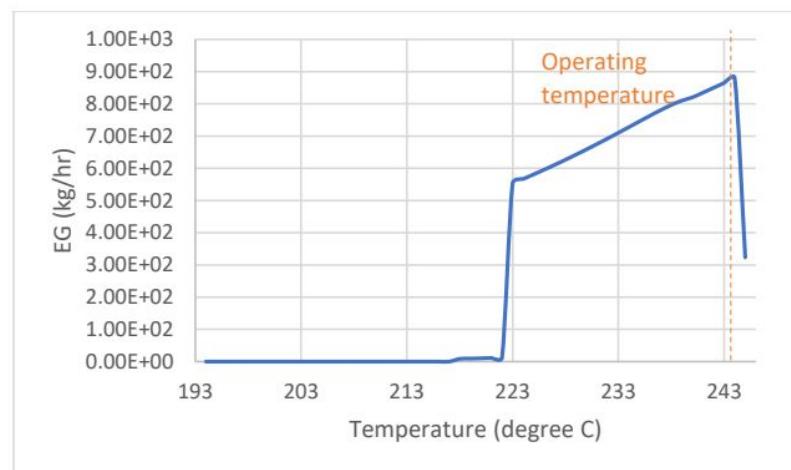


Figure 2.2.1.2.5. Sensitivity results of PFR R3 temperature

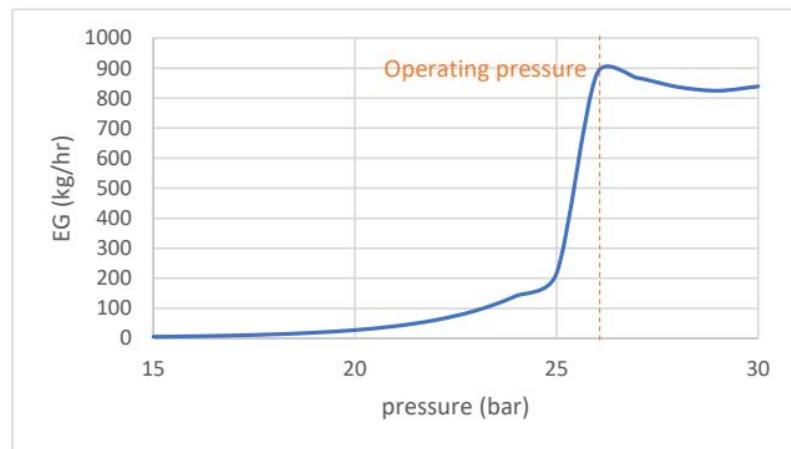


Figure 2.2.1.2.6. Sensitivity results of PFR R3 pressure

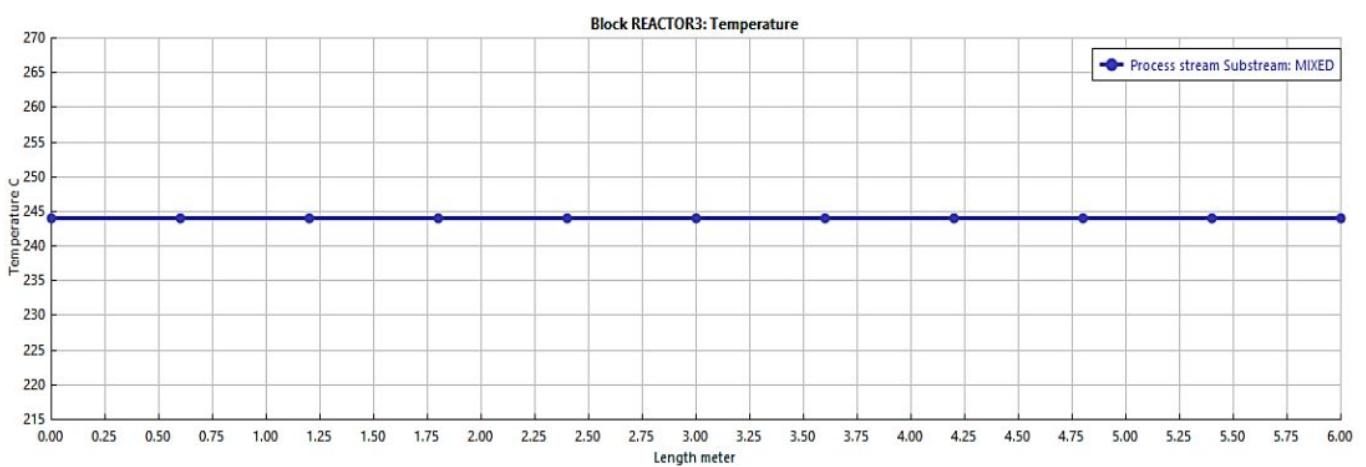


Figure 2.2.1.2.7. Temperature Profile of PFR R3

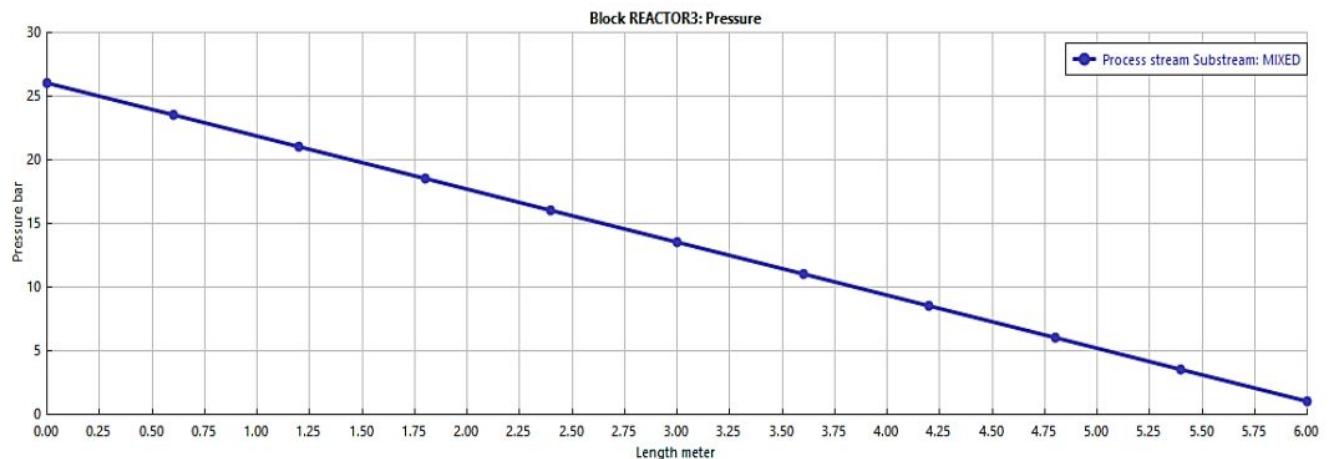


Figure 2.2.1.2.8. Pressure Profile of PFR R3

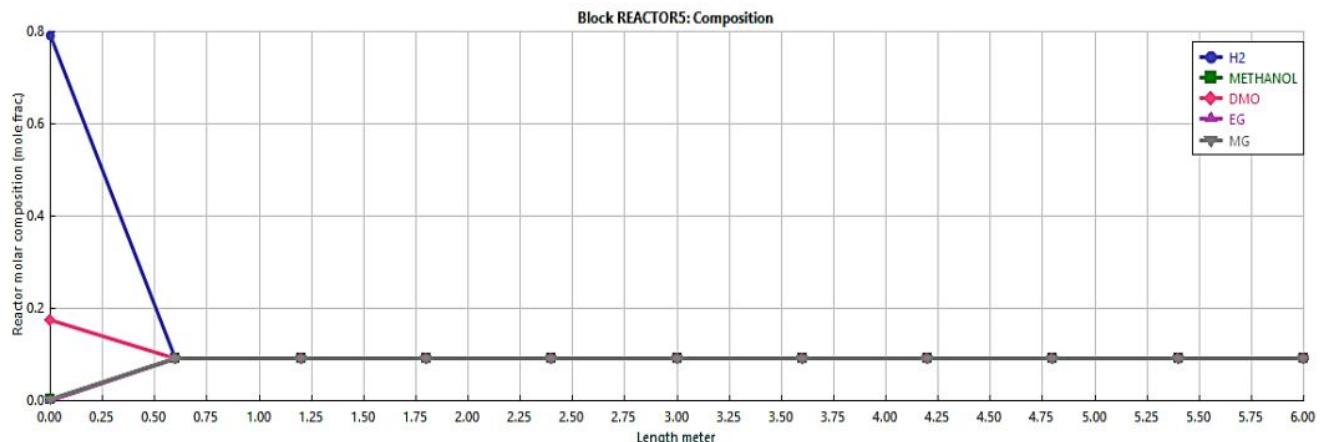


Figure 2.2.1.2.9. Composition Profile of PFR R3

2.2.2. Cooler

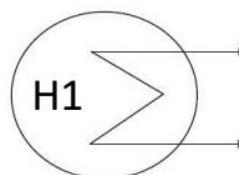


Figure 2.2.2. Cooler used and its configuration

There is one cooler used to reduce the duty of the flash tank in the separation process. It is placed between the CSTR (R1) and the flash tank (F1). Since the output stream of CSTR is in high temperature and pressure (129°C and 5 bar), pretreatment is done by this device to lower the parameter to suit flash tank operating temperature and pressure of 85°C and 1.15 bar. The duty obtained is -16119.2 kW.

2.2.3. Flash Tank



Figure 2.2.3. Flash tank used and its configuration

Flash tank is used to separate DMO from CO-NO-DMO mixture as much as possible. Although the DMO is not fully recovered in the liquid bottom product, it is considerably high (95.76%) and in a similar amount as the first flowsheet. The configuration is summarized in the table below.

Table 2.2.3. F1 configuration of Flowsheet 2

Parameter	Value
Material	Stainless Steel
Duty (kW)	-200.79
Pressure (bar)	1.15
Temperature (°C)	85
Vapor fraction (mole)	0.64

2.2.4. Distillation Column

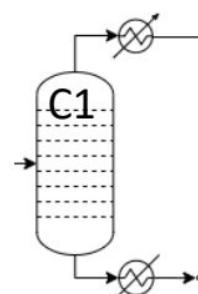


Figure 2.2.4.1. Column used and its configuration

Table 2.2.4. Specifications of C1 of Flowsheet 2

Parameters	Value
Materials	Carbon Steel
Reflux Ratio (moles)	2
Bottom product (kg/hr)	880

Number of Stages	30
Feed Stages	22
Diameter (m)	0.97
Pressure (bar)	1
Condenser Duty (kW)	-12280 kW
Reboiler Duty (kW)	11630 kW

The RD column is used to recover EG from mixtures mainly of MeOH, DMO, and H₂. The feed position is in distillation boundary, it can be seen in the ternary diagram (**Fig. 2.2.4.2.**). In the simulation, the bottom product was set to 880 kg/hr, then the feed stage and reflux ratio were obtained from trial and error. The configuration can be seen in **Table 2.1.2.2.** and the profiles are also shown below. Compared to the first flowsheet, the EG amount is higher. The purity is slightly lower (0.99 wt%), but still within our goal.

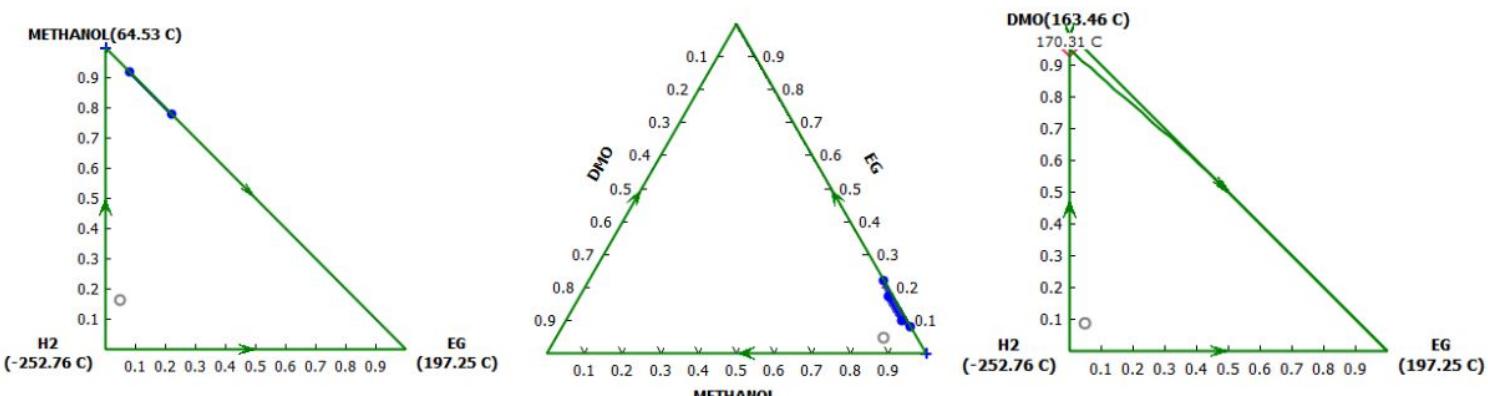


Figure 2.2.4.2. Ternary diagrams

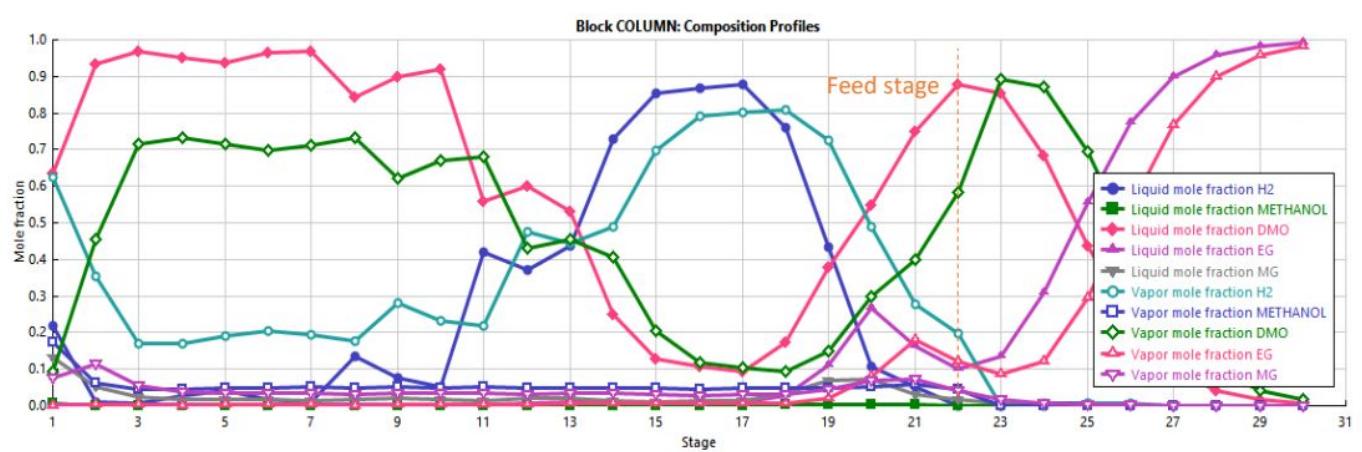


Figure 2.2.4.3. Composition profile of C1

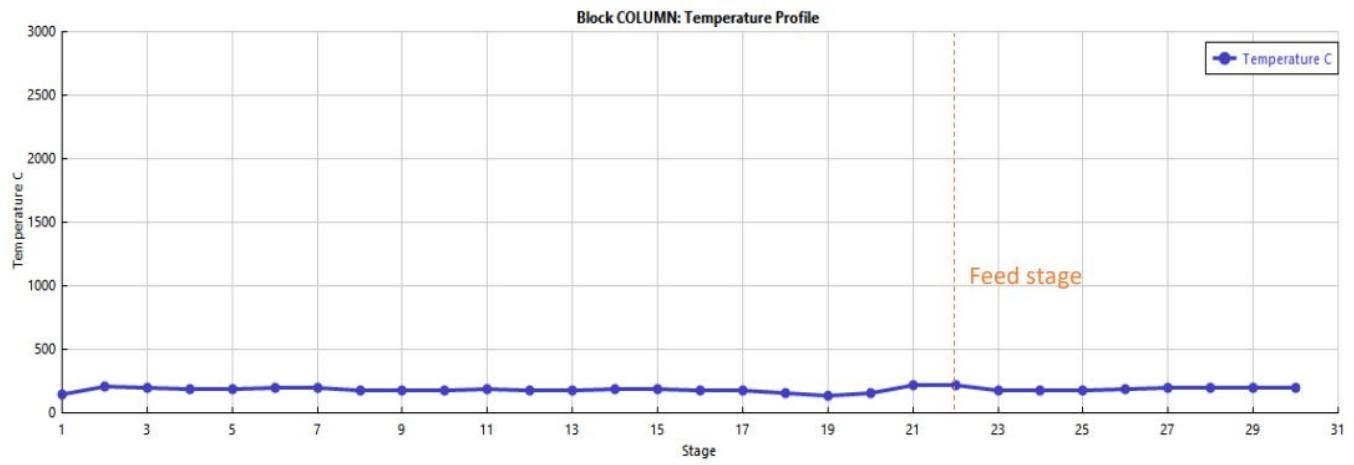


Figure 2.2.4.4. Temperature profile of C1

CHAPTER 3

ECONOMIC ESTIMATION

3.1 Economical Analysis

To build the industrial plan it is important to estimate the economic analysis, where profits are always mandatory. Many calculations have to be done to make sure the economic analysis is correct and bring some profit in the industrial process. In this process, the economic potential is USD 388.5061 or NTD 10,871. The detailed calculation of economic potential can be calculated as below:

Table 3.1.1. Raw Material Price [42-44]

Compound	Price (USD/kg)
Ethylene Glycol	20
Methanol	0.375
Hydrogen	0.45
Carbon Monoxide	0.007
Methyl Nitrite	0.012
Nitrite Oxide	1.63
Methylene Glycol	60

$$\begin{aligned} EP = & (1 \text{ kmol EG} \times \text{Price EG} + 2 \text{ kmol NO} \times \text{Price NO} + 2 \text{ kmol MeOH} \times \text{Price MeOH}) - \\ & (2 \text{ kmol CO} \times \text{Price CO} + 2 \text{ kmol MN} \times \text{Price MN} + 2 \text{ kmol Hydrogen} \times \text{Price hydrogen}) \end{aligned}$$

$$EP = [322.2169 + 48.9163 + 24.03] - [0.39214 + 1.46496 + 1.8] = \mathbf{\text{USD 388.5061}}$$

3.1.1. Flowsheet 1

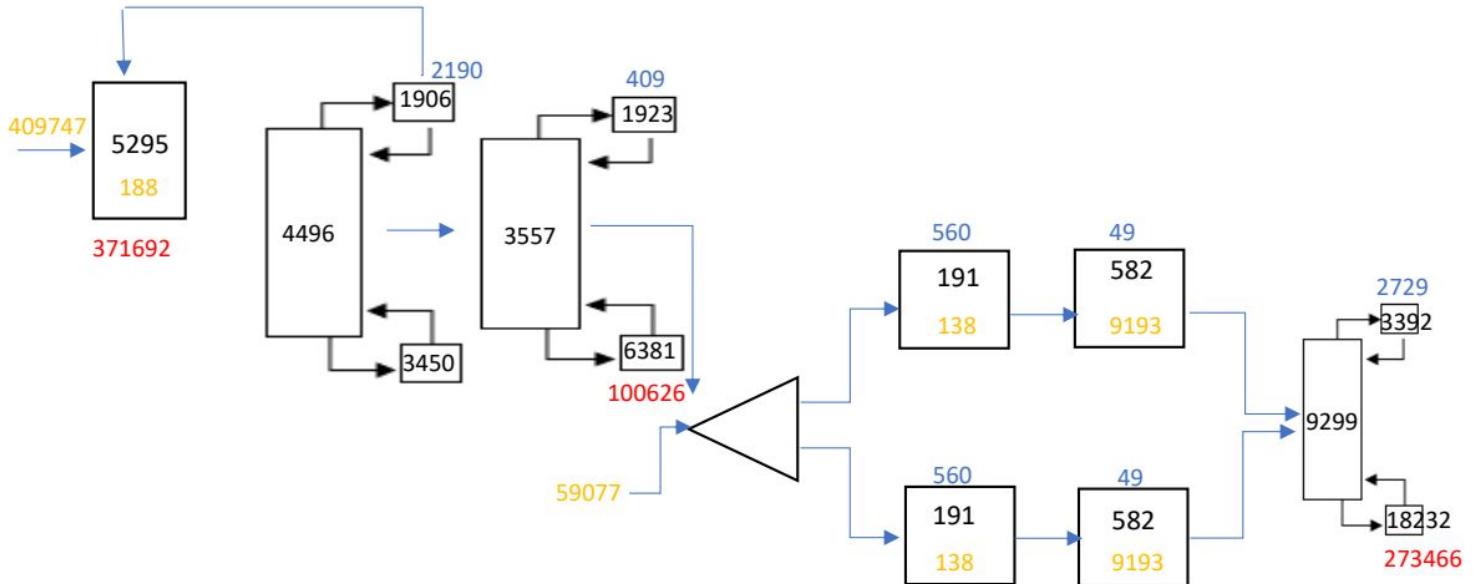


Figure 3.1.1. Flowsheet 1 Cost Estimation Scheme

The summary of the cost estimation can be seen in the figure above. The number represents the estimated cost in 1000 NTD, where the black color shows the equipment cost, the red color represents the steam cost, the blue depicts the coolant cost, and the yellow depict the raw material and catalyst cost.

3.1.1.1. Purchase Cost & Installation Cost

The overall total of the purchase cost and installation cost can be observed in the table below:

Table 3.1.1.1.1. Purchase & installation cost for Flowsheet 1

	Purchase Cost	Installation Cost
Reactor	NTD 2,810,604	NTD 3,976,865
Column	NTD 3,788,873	NTD 11,939,085
Tray	-	NTD 1,669,215
Reboiler	NTD 10,664,340	NTD 206,454,199
Condenser	NTD 2,516,491	NTD 4,731,868
Total	NTD 19,780,308	NTD 228,771,232

3.1.1.1.1. Reactor Cost

The calculation of the reactor cost is as written below. Based on the table, the total purchase cost of the reactors in the first flowsheet is USD 101,336 or around NTD 2,810,604 for each flowsheet. The two in the first flowsheet have an installation cost of USD 143,081 or around NTD 3,976,865. The Marshall & Swift index that we used in all of this economic analysis is the M&S of 2020 which is 2171.6 [45]. Purchase and installation costs were evaluated from the formula in [48]. The shell material chosen is solid stainless steel (hence Fm is 3.67) and the operating pressure is within the range of 1-5 bar (Fp is 1). The detailed calculation for the reactor cost can be seen in the table below:

Table 3.1.1.1.1.1. Purchase Cost of Reactor for Flowsheet 1

Formula	Purchase Cost: $\left(\frac{M\&S}{280}\right) (101.9 \times D^{1.066} \times H^{0.82} \times Fc)$						Purchase Cost	
	Specification							
	No of Tubes	Diameter (ft)	Height (ft)	Fm	Fp	Fc		
CSTR	-	5.25	5.91	3.67	1	3.67	USD 72,921	
PFR (2)	100 / each	0.95	0.95	3.67	1	3.67	USD 5,266	
PFR (2)	500 / each	2.083	2.083	3.67	1	3.67	USD 23,149	
Total Reactor Purchase Cost							USD 101,336	

Table 3.1.1.1.1.2. Installation Cost of Reactor for Flowsheet 1

Formula	Installed Cost: $\left(\frac{M\&S}{280}\right) (101.9 \times D^{1.066} \times H^{0.82} \times (2.18 + Fc))$						Installed Cost	
	Specification							
	No of Tubes	Diameter (ft)	Height (ft)	Fm	Fp	Fc		
CSTR		5.25	5.91	3.67	1	3.67	USD 116,237	
PFR (2)	100/ each	0.95	0.95	3.67	1	3.67	USD 8,394	
PFR (2)	500/each	2.083	2.083	3.67	1	3.67	USD 18,450	
Total Reactor Installation Cost							USD 143,081	

3.1.1.1.2. Distillation Cost

In Flowsheet 1 three distillation columns were used for the process. There are several calculations including the columns, trays, reboilers, and condensers. The material used in the column is carbon steel ($Fm=1$) and the operating pressure is 5 bar in C1, 1 bar in C2-C3 ($Fp=1$). The column tray was designed to be in 24-inch spacing ($Fs=1$), using stainless steel material ($Fm=1.7$), and plate type ($Fs=0$). In the reboiler and condenser, the Fm used is 2.81 (CS/SS), kettle type for the reboiler ($Fd=1.35$) and U-tube type for the condenser ($Fd=0.85$). All of the devices are working under 150 psi hence Fp is 0. The detailed calculation can be seen in the table below. It can be seen that the highest cost in the distillation column is on the third column because the third column did heavier work than the other column.

Table 3.1.1.1.2.1. Distillation Purchase Cost for Flowsheet 1

Formula	Purchase Cost: $\left(\frac{M\&S}{280}\right) (101.9 \times D^{1.066} \times H^{0.82} \times Fc)$						Installed Cost	
	$Fc = FmFp$							
	No of Stages	Diameter (ft)	Height (ft)	Fm	Fp	Fc		
C1	16	2.4	33.07	1	1	1	USD 35,403	
C2	21	1.54	44.88	1	1	1	USD 28,339	
C3	20	3.18	54.33	1	1	1	USD 71,799	
Total Distillation Purchase Cost						USD 135,541		

Table 3.1.1.1.2.2. Installation of Distillation Column for Flowsheet 1

Formula	Installed Cost: $\left(\frac{M\&S}{280}\right) (101.9 \times D^{1.066} \times H^{0.82} \times (2.18 + Fc))$						Installed Cost	
	$Fc = FmFp$							
	No of Stages	Diameter (ft)	Height (ft)	Fm	Fp	Fc		
C1	16	2.4	33.07	1	1	1	USD 112,581	
C2	21	1.54	44.88	1	1	1	USD 90,116	
C3	20	3.18	54.33	1	1	1	USD 228,320	

Total Distillation Installation Cost	USD 431,017
---------------------------------------------	-------------

Table 3.1.1.1.2.3. Installation Tray Installation Cost for Flowsheet 1

Formula	<i>Installed Cost: $\left(\frac{M\&S}{280}\right) (4.7D^{1.55} \times H \times Fc)$</i>						
	Specification						
	No of Stages	Diameter (ft)	Height (ft)	Fm	Fs	Fc	
C1	16	2.4	33.07	1.7	1	2.7	USD 12,642
C2	21	1.54	44.88	1.7	1	2.7	USD 8,626
C3	20	3.18	54.33	1.7	1	2.7	USD 32,128
Total Tray Installation Cost						USD 53,396	

Table 3.1.1.1.2.4. Purchase Cost of Reboiler and Condenser for Flowsheet 1

Formula	<i>Purchase Cost: $\left(\frac{M\&S}{280}\right) (101.3A^{0.65} \times Fc)$</i>						
	Specification						
	Heat Duty (MW)	A (ft ²)	Fp	Fm	Fd	Fc	
C1	6.0315	70.49	0	2.81	1.35	3.79	USD 47,332
C2	2.08	181.56					USD 87,545
C3	-7.4638	912.91					USD 250,120
Total Reboiler Purchase Cost						USD 348,997	
C1	-6.03	47.26	0	2.81	0.85	2.39	USD 23,017
C2	2.08	47.92					USD 23,226
C3	26.48	26.48					USD 40,966
Total Condenser Purchase Cost						USD 87,209	

Table 3.1.1.1.2.5. Installation Cost of Reboiler and Condenser for Flowsheet 1

Formula	Installation Cost: $\left(\frac{M\&S}{280}\right) 101.3 A^{0.65} (2.29 + Fc)$ $Fc = (Fd + Fp)Fm$						
	Specification					Installation Cost	
	Heat Duty (MW)	A (ft ²)	Fp	Fm	Fd		
C1	6.0315	70.49	0	2.81	1.35	3.79	USD 75,931
C2	2.08	181.56					USD 140,442
C3	-7.4638	912.91					USD 401,248
Total Reboiler Installation Cost						USD 617,621	
C1	-6.03	47.26	0	2.81	0.85	2.39	USD 45,071
C2	2.08	47.92					USD 45,479
C3	26.48	26.48					USD 80,217
Total Condenser Installation Cost						USD 170,767	

3.1.1.2. Utility Cost

The utility cost price is based on [40-41]. The detail calculation is described below.

Table 3.1.1.2.1. Utility Cost for Flowsheet 1

Equipment	Utility	Parameter		
		Price	Amount	Cost
C1	Cooling Water	NTD 0.0348/gal	62,946,852	NTD 2,190,551
C2			11,758,291	NTD 409,189
C3			78,431,291	NTD 2,729,423
Reactor 2,4			32,186,236	NTD 1,120,081
Reactor 3,5			2,804,702	NTD 97,603
Total Cost of Cooling Water				NTD 6,546,847
C2	Steam	NTD 0.9/gal	103,738,598	NTD 100,626,440
C3			281,923,742	NTD 273,466,030
Reactor 1			383,187,946	NTD 371,692,308

Total Cost of Steam				NTD 745,784,778
Pump	Electricity	NTD 3.827/kwh	119.46 kwh	NTD 3,785,395

3.1.1.3. Raw Material and Operator Cost

The raw material that used in this experiment is methyl nitrite, nitrite oxide, carbon monoxide, and hydrogen. Total of the raw material cost is USD 16,749,675 or around NTD 464,048,021. The calculation of raw material cost describes in the table below:

Table 3.1.1.3.1. Raw material cost for Flowsheet 1

Raw Material	Unit	Quantity per Year	Unit Price	Cost per Year
Methyl Nitrite	ton	66,240	USD 12	USD 794,880
Nitrite Oxide		8,280	USD 1,630	USD 13,496,400
Carbon Monoxide		49,680	USD 7	USD 347,760
Hydrogen		4,690.3	USD 450	USD 2,110,635
Total Raw Material Cost				USD 16,749,675

Moving on to the operating cost, the wage that is used is NTD 35,000 which equals USD 1,268 per month. The lowest average wage is around NTD 34,600 [49] but to with many considerations we put above the wage to NTD 35,000. The total working hours in the industry is 8280 hours or around 345 days with 3 shifts per day. For the number of particulate handlings in the equation, we used 1 because only the output stream needs to be utilized with the transportation required. For non-particulate handlings in the equation, we put 3 where there are condenser, reboiler, and splitter. The total operator required for this process flowsheet diagram is around 28 people/shift, with 3 shift per day. The total of the operator cost is NTD 33,821,445 per year. Detailed calculation can be seen below:

Table 3.1.1.3.2. Operator Cost Calculation for Flowsheet 1

$N_{OL} = 4.5 \times (6.29 + 31.7P^2 + 0.23N_{np})^{0.5}$	
P	1
N_{np}	3
N_{OL}	28

Wage 1 person per month	NTD 35,000
Total Annual Wage	NTD 33,821,445

3.1.1.4. Catalyst Cost

There are two catalysts that we use in the reactors. For Pd/Al₂O₃ the lifetime is 8000 hours, and the catalyst was used in the CSTR reactor for 0.1036 ton per year with the cost of around NTD 187,168 [46]. For Cu/SiO₂ the lifetime is 3080 hours, and it is used in PFR reactors for 5.051 tons per year with a cost of around NTD 18,531,483 [47]. The total catalyst cost is estimated to be USD 673,466 or around NTD 18,678,916. The detail of the calculation will mention in the table below:

Table 3.1.1.4. Catalyst Cost Calculation for Flowsheet 1

Catalyst	Unit	Quantity per year	Unit Price	Cost per year
Pd/Al ₂ O ₃	ton	0.1036	USD 65,000	USD 6,734
		5.051	USD 132,000	USD 666,732
Total Catalyst Cost				USD 673,466

3.1.2. Flowsheet 2

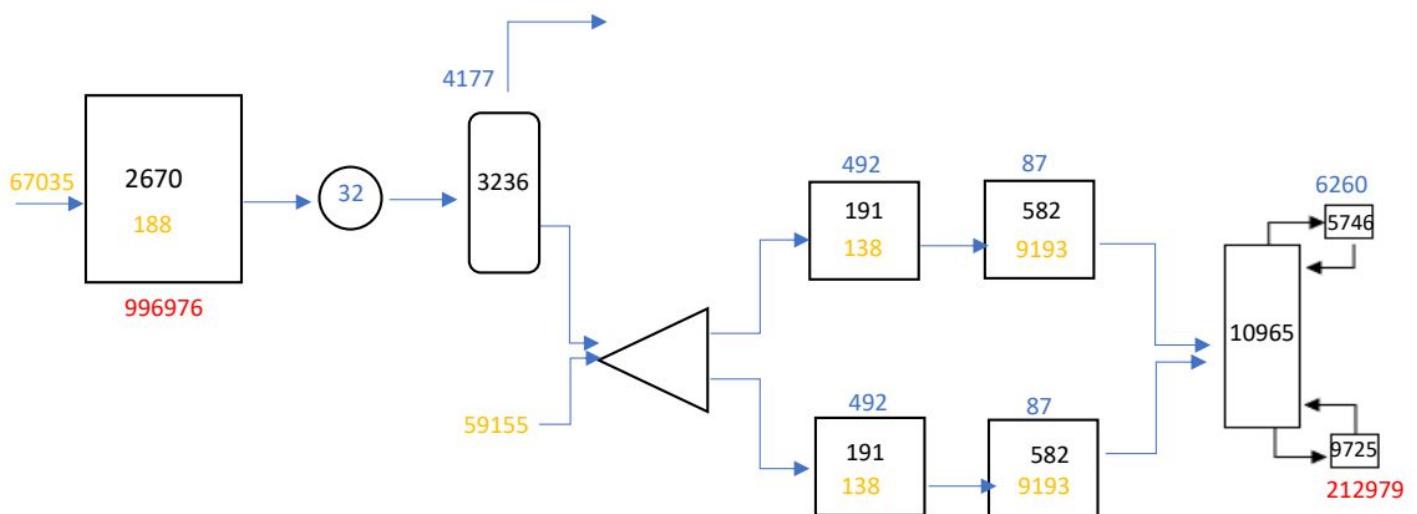


Figure 3.1.2.1. Flowsheet 2 Cost Estimation Scheme

3.1.2.1. Purchase Cost and Installation Cost

Table 3.1.2.1.1 Purchase and Installation Cost for Flowsheet 2

System	Purchase Cost	Installation Cost
Reactor	NTD 1,825,255	NTD 2,393,062
Distillation Column	NTD 2,336,894	NTD 7,431,330
Tray Installation	-	NTD 1,083,395
Reboiler	NTD 3,816,120	NTD 5,909,369
Condenser	NTD 1,746,029	NTD 4,000,532
Flask Tank	NTD 243,194	NTD 2,992,827
Total	NTD 9,967,492	NTD 23,810,515

3.1.2.1.1. Reactor Cost

Similarly, the calculation of the reactor cost is as written below. All of the specifications of the device (F_m , F_p , F_c) are the same as the first flowsheet. The detailed calculation for the reactor cost can be seen in the table below:

Table 3.1.2.1.1.1. Purchase Cost of Reactor for Flowsheet 2

Formula	<i>Purchase Cost: $\left(\frac{M\&S}{280}\right) (101.9 \times D^{1.066} \times H^{0.82} \times F_c)$</i>						Purchase Cost
	Specification						
	No of Tubes	Diameter (ft)	Height (ft)	F_m	F_p	F_c	
CSTR	-	2	3	3.67	1	3.67	USD 36,733
PFR (2)	100 / each	0.95	0.95	3.67	1	3.67	USD 5,266
PFR (2)	500 / each	2.083	2.083	3.67	1	3.67	USD 23,149
Total Purchase Cost of Reactor							USD 65,214

Table 3.1.2.1.1.2. Installation Cost of Reactor for Flowsheet 2

Formula	<i>Installed Cost:</i> $\left(\frac{M\&S}{280}\right) (101.9 \times D^{1.066} \times H^{0.82} \times (2.18 + Fc))$						Installed Cost	
	Specification							
	No of Tubes	Diameter (ft)	Height (ft)	Fm	Fp	Fc		
CSTR	-	2	3	3.67	1	3.67	USD 58,658	
PFR (2)	100/ each	0.95	0.95	3.67	1	3.67	USD 8,394	
PFR (2)	500/each	2.083	2.083	3.67	1	3.67	USD 18,450	
Total Installation Cost of Reactor						USD 85,501		

3.1.1.1.2. Distillation Cost

In Flowsheet 2 there is only one distillation column that was used for the process.

There will be more detailed calculations involving the columns, trays, reboilers, and condensers. The same specification of these devices are used following the first flowsheet. The detailed calculation can be seen below:

Table 3.1.2.1.2.1. Distillation Purchase Cost for Flowsheet 2

Formula	<i>Purchase Cost:</i> $\left(\frac{M\&S}{280}\right) (101.9 \times D^{1.066} \times H^{0.82} \times Fc)$						Installed Cost	
	Specification							
	No of Stages	Diameter (ft)	Height (ft)	Fm	Fp	Fc		
C1	30	3.18	66.14	1	1	1	USD 84,365	
Total Purchase Cost of Distillation Column						USD 84,365		

Table 3.1.2.1.2.1. Installation of Distillation Column for Flowsheet 2

Formula	$\text{Installed Cost: } \left(\frac{M\&S}{280}\right) (101.9 \times D^{1.066} \times H^{0.82} \times (2.18 + Fc))$ $Fc = FmFp$						Installed Cost	
Specification								
No of Stages	Diameter (ft)	Height (ft)	Fm	Fp	Fc			
C1	30	3.18	66.14	1	1	1	USD 268,281	
Total Column Installation Cost						USD 268,281		

Table 3.1.2.1.2.3. Installation Tray Installation Cost for Flowsheet 2

Formula	$\text{Installed Cost: } \left(\frac{M\&S}{280}\right) (4.7D^{1.55} \times H \times Fc)$ $Fc = Fs + Fm + Ft \rightarrow (Ft = 0)$						Installed Cost	
Specification								
No of Stages	Diameter (ft)	Height (ft)	Fm	Fs	Fc			
C1	30	3.18	66.14	1.7	1	2.7	USD 39,112	
Total Tray Installation Cost						USD 39,112		

Table 3.1.2.1.2.4. Purchase Cost of Reboiler and Condenser for Flowsheet 2

Formula	$\text{Purchase Cost: } \left(\frac{M\&S}{280}\right) (101.3A^{0.65} \times Fc)$ $Fc = (Fd + Fp)Fm$						Purchase Cost	
Specification								
Heat Duty (MW)	A (ft ²)	Fp	Fm	Fd	Fc			
C1	11.6235	364.4241	0	2.81	1.35	3.79	USD 137,694	
Total Reboiler Purchase Cost						USD 137,694		
C1	-12.2728	222.6434	0	2.81	0.85	2.39	USD 63,034	
Total Condenser Purchase Cost						USD 63,034		

Table 3.1.2.1.2.5. Installation Cost of Reboiler and Condenser for Flowsheet 2

Formula	Installation Cost: $\left(\frac{M\&S}{280}\right) 101.3A^{0.65}(2.29 + Fc)$						
	$Fc = (Fd + Fp)Fm$						
	Specification					Installation Cost	
	Heat Duty (MW)	A (ft ²)	Fp	Fm	Fd	Fc	
C1	11.6235	345.1436	0	2.81	1.35	3.79	USD 213,223
Total Reboiler Installation Cost						USD 213,223	
C1	-12.2728	222.6434	0	2.81	0.85	2.39	USD 144,348
Total Condenser Installation Cost						USD 144,348	

3.1.2.1.3. Flash Tank Cost

The purpose of the tank has been discussed in the prior section. The total purchase cost of the flash tank is USD 8,775 or around NTD 243,194. The installment cost for the flash tank is USD 107,906 or around NTD 2,992,827. The device is operated at 1.15 bar (Fp=0), using U-tube design type (Fd=0.85), and CS/SS (Fm=2.81). The detailed calculation can be seen in the tables below:

Table 3.1.2.1.3.1. Purchase Cost of Flash Tank for Flowsheet 2

Formula	Purchase Cost: $\left(\frac{M\&S}{280}\right)(101.3A^{0.65} \times Fc)$						
	$Fc = (Fd + Fp)Fm$						
	Specification					Purchase Cost	
	Heat Duty (MW)	A (ft ²)	Fp	Fm	Fd	Fc	
C1	-0.201	10.72	0	2.81	0.85	2.39	USD 8,775
Total Flash Tank Purchase Cost						USD 8,775	

Table 3.1.2.1.3.2. Installation Cost of Flash Tank for Flowsheet 2

Formula	$\text{Installation Cost: } \left(\frac{M\&S}{280}\right) 101.3A^{0.65}(2.29 + Fc)$ $Fc = (Fd + Fp)Fm$						
	Specification						
	Heat Duty (MW)	A (ft ²)	Fp	Fm	Fd	Fc	
C1	-0.201	10.72	0	2.81	0.85	2.39	USD 107,906
Total Flash Tank Installation Cost						USD 107,906	

3.1.2.2. Utility Cost

The utility cost price is based on [40-41]. The detail calculation is described below.

Table 3.1.2.2.1. Utility Cost for Flowsheet 2

Equipment	Utility	Parameter		
		Price	Amount	Cost
Flash 1	Cooling Water	NTD 0.0348/gal	102,022,395	NTD 4,176,779
Cooler			907,883	NTD 31,594
Column			179,887,802	NTD 6,260,096
Reactor 2,4			28,293,924	NTD 984,629
Reactor 3,5			5,004,460	NTD 174,155
Total Cost of Cooling Water				NTD 11,627,235
Column	Steam	NTD 0.9/gal	219,565,902	NTD 212,978,925
Reactor 1			1,027,810,670	NTD 996,976,350
Total Cost of Steam				NTD 1,209,955,275
Pump	Electricity	NTD 3.827/kwh	76.565 kwh	NTD 2,426,158

3.1.2.3. Raw Material and Operator Cost

A lesser amount of materials are used (since it is designed to be in a limited amount). Total of the raw material cost is USD 4,508,443 or around NTD 125,043,921.

The calculation of raw material cost describes in the table below:

Table 3.1.2.3.1. Raw material cost for Flowsheet 2

Raw Material	Unit	Quantity per Year	Unit Price	Cost per Year
Methyl Nitrite	Ton	67,382	USD 12	USD 808,584
Nitrite Oxide		828	USD 1,630	USD 1,349,640
Carbon Monoxide		30,967	USD 7	USD 216,769
Hydrogen		4,741	USD 450	USD 2,133,450
Total				USD 4,508,443

The operator cost, same as the first designed flowsheet, was estimated using NTD 35,000 (USD 1,268) per month, with total working hours of 8280 hours (345 days); 3 shifts/day. For the number of particulate handlings in the equation, we used 1 because only the output stream needs to be utilized with the transportation required. For non-particulate handlings in the equation, we put 3 where those are condenser, reboiler, heat exchanger, and flask tank. The total operator required for this process flowsheet diagram is around 28 people/shift, with 3 shifts per day. The total operator cost is NTD 33,821,445 per year. The detailed calculation will be stated in the table below. (Base salary is from [49]).

Table 3.1.2.3.2. Operator Cost Calculation for Flowsheet 2

$N_{OL} = 4.5 \times (6.29 + 31.7P^2 + 0.23N_{np})^{0.5}$	
P	1
N _{np}	4
N _{OL}	28
Wage 1 person per month	NTD 35,000
Total Annual Wage	NTD 33,821,445

3.1.2.4. Catalyst Cost

The same amount of catalyst is used in the second flowsheet. The total catalyst cost is estimated to be USD 673,466 or around NTD 18,678,916. The detail of the calculation will mention in the table below:

Table 3.1.2.4. Catalyst Cost Calculation for Flowsheet 2 [46-47]

Catalyst	Unit	Quantity per year	Unit Price	Cost per year
Pd/Al ₂ O ₃	ton	0.1036	USD 65,000	USD 6,734
Cu/SiO ₂		5.051	USD 132,000	USD 666,732
Total Catalyst Cost			USD 673,466	

3.2. Comparison and Profitability Analysis

In the profitability analysis, there are many variables that we should calculate. To calculate the total capital investment the variables that we should calculate are onsite cost, offsite cost, start-up cost, working capital, and fixed capital investment. The equation to calculate total capital investment will be described below:

- Offsite Cost = 3 (Onsite Cost)
- Fixed Capital Investment = 1.25 (Onsite Cost + Offsite Cost)
- Start-up Cost = 0.1 (Fixed Capital Investment)
- Total Capital Investment = $\frac{\text{Start-up cost} + \text{Fixed Capital Investment}}{0.85}$
- Working Capital = 0.1 (Total Capital Investment)

Table 3.2.1. Total Capital Investment Calculation

Parameter	Cost per year	
	Flowsheet 1	Flowsheet 2
Purchase Cost	NTD 19,780,308	NTD 9,967,492
Installment Cost	NTD 228,771,232	NTD 23,810,515
Utilities	NTD 756,117,021	NTD 1,224,008,686
Onsite Cost	NTD 1,004,668,561	NTD 1,257,786,693
Offsite Cost	NTD 3,014,005,683	NTD 3,773,360,079
Start-up Cost	NTD 502,334,281	NTD 628,893,347
Working Capital	NTD 975,119,486	NTD 1,220,792,967
Fixed Capital Investment	NTD 5,023,342,805	NTD 6,288,933,465
Total Capital Investment	NTD 6,500,796,571	NTD 8,138,619,778

From **Table 3.2.1.**, we can see that flowsheet 1 is more efficient than flowsheet 2. Even though the purchase and installment cost of the equipment in flowsheet 2 is

cheaper than in flowsheet 1, but we could see the utility cost in flowsheet 2 is much higher due to the hard work that has been done in flowsheet 2. Also, producing the product is more efficient in flowsheet 1 because the quantity of the product is higher in flowsheet 1 due to the revenue. To calculate the profitability analysis many variables should be calculated such as total production cost, profit before tax, depreciation, profit after tax, and cash flow. The equation will be described below:

- Total Production Cost = 1.03(Raw Material + Utility Cost) + 2.13(Operator Cost) + 0.103 (Fixed Capital Cost) + 0.025(Revenue)
- Gross Profit Before Tax = Revenue – Total Production Cost
- Depreciation = 0.181 (Onsite Cost)
- Gross Profit After Tax = (1 – Income Tax) (Gross Profit Before Tax – Depreciation)
- Cash Flow = Gross Profit After Tax + Depreciation

Table 3.2.2. Calculation of profitability analysis

Parameter	Cost per year	
	Flowsheet 1	Flowsheet 2
Revenue	NTD 3,740,409,530	NTD 3,617,263,910
Total Production Cost	NTD 1,939,724,218	NTD 2,199,755,608
Gross Profit Before Tax	NTD 1,800,685,312	NTD 1,417,508,302
Depreciation	NTD 181,845,010	NTD 227,659,391
Gross Profit After Tax	NTD 1,343,637,451	NTD 987,574,596
Cash Flow	NTD 1,525,482,460	NTD 1,215,233,987

From **Table 3.2.2**, cash flow for flowsheet 1 is higher than flowsheet 2. This means that flowsheet 1 is more profitable than flowsheet 2. It will also be proven by profitability analysis comparison.

There are many profitability analyses such as the return of investment, payout time, discounted cash flow rate of return (DCFROR), and Capital Charge Factor (CCF). The return of investment (ROI) and payout time is the simplest calculation to predict the profitability of the process production. But those calculations don't include recent value, so with that disadvantage of ROI and payout time, we should consider DCFROR and CCF because they considered the present value and we can see the value from this

present time until the future. The equation to calculate profitability will be described below:

- Annual Percent Return of Investment Before Tax = $r_b(\%) = \frac{P \times 100}{I}$
- Annual Percent Return of Investment After Tax = $r_a(\%) = \frac{E \times 100}{I}$
- Return of Investment = $ROI(\%) = \frac{\text{Annual Profit} \times 100}{TCI}$
- Payout Time = $\frac{\text{Fixed Capital Investment} + \text{Start-up Cost}}{\text{Cash Flow}}$
- PV Profit = a_j (Gross Profit Before Taxes) $(1 + i)^j$
- PV Investment = $\frac{b_j(\text{Fixed Capital Investment})}{(1+i)^j}$
- $CCF = \frac{\left(\left(\frac{FCI}{4}\right)\left((1+i)^4 - 1\right)\right) + (\text{working capital} + \text{startup cost})i - 0.48(\text{depreciation})}{0.52(TCI)((1+i)^N - 1)(1+i)^{-N}} + \frac{-(\text{Working Capital} + \text{Salvage value})i + 0.48(\text{Depreciation})}{0.52(TCI)((1+i)^N - 1)}$

Table 3.2.3. ROI and Payout Time Calculation

Parameter	Flowsheet 1	Flowsheet 2
Rb (%)	27.7	17.42
Ra (%)	20.67	12.13
ROI (%)	23.47	14.93
Payout Time (Year)	3.6	5.7

From **Table 3.2.3**, we can see that flowsheet 1 is more profitable with a higher ROI value and less payout time value which is only 3.6 years or around 4 years. In the second flowsheet, we can see that the number of ROI is less than the first flowsheet and the payout time is 5.7 years or around 6 years.

Table 3.2.4. DCFROR Calculation

Year	Flowsheet 1		Flowsheet 2	
	i = 0.0894		i = 0.0319	
	Investment	Discount Factor	Investment	Discount Factor
Year 4	NTD 650,079,657	1.4083	NTD 813,861,978	1.1338
Year 3	NTD 2,600,318,628	1.2927	NTD 3,255,447,911	1.0988
Year 2	NTD 2,600,318,628	1.1867	NTD 3,255,447,911	1.0648
Year 1	NTD 650,079,657	1.0894	NTD 813,861,978	1.0319
Working Capital	NTD 975,119,486	1	NTD 1,222,639,971	1
Start-up Cost	NTD 502,334,281	1	NTD 629,844,834	1
PV Investment		NTD 9,548,439,643	PV Investment	NTD 10,655,722,508
Year	Flowsheet 1		Flowsheet 2	
	i = 0.0894		i = 0.0319	
	Cash Flow	Discount Factor	Cash Flow	Discount Factor
Year 1	NTD 915,289,476	0.918	NTD 729,140,392	0.9691
Year 2	NTD 1,372,934,214	0.8427	NTD 1,093,710,588	0.9391
Year 3	NTD 1,449,208,337	0.7736	NTD 1,154,472,288	0.9101
Year 4	NTD 1,525,482,460	0.7101	NTD 1,215,233,987	0.8820
Year 5	NTD 1,525,482,460	0.6518	NTD 1,215,233,987	0.8547
Year 6	NTD 1,525,482,460	0.5984	NTD 1,215,233,987	0.8283
Year 7	NTD 1,525,482,460	0.5493	NTD 1,215,233,987	0.8027
Year 8	NTD 1,525,482,460	0.4629	NTD 1,215,233,987	0.7779
Year 9	NTD 1,525,482,460	0.4249	NTD 1,215,233,987	0.7538
Year 10	NTD 1,525,482,460	0.4249	NTD 1,215,233,987	0.7305
Working Capital	NTD 975,119,486	0.4249	NTD 1,220,792,967	0.7305
Salvage Value	NTD 150,700,284	0.4249	NTD 188,668,004	0.7305
PV Return		NTD 9,548,442,720	PV Return	NTD 10,655,728,326

Table 3.2.5. Table Result of DCFROR and CCF

Parameter	Flowsheet 1	Flowsheet 2
Interest Rate (i)(%)	8.94%	3.19%
CCF	0.542	0.453

From **Table 3.2.5**, we can see that the i value from the first flowsheet is 8.94% while in the second flowsheet i value only 3.19%. From these values, we can conclude that the first flowsheet is more profitable than the second flowsheet with a total PV return of around NTD 9,548,442,720. The CCF also agreed with this results, given the first flowsheet CCF is 0.542, higher than the second flowsheet.

CHAPTER 4

WASTE MANAGEMENT

Every business produces waste, it could be wastepaper or unclean water for some, but it could also be hazardous or toxic waste that requires specific care and disposal for others, just like ours. It is very important to pay attention to the waste that is produced from the plant and to treat it responsibly. Treating waste is not an easy task, it always costs money to treat the waste properly. It cost money to buy the material, and it cost money to treat it or throw it away when it becomes waste. However, waste treatment eliminates pollution that is released, making our community and neighborhood a safer and better place to live. Finally, we benefit, the environment benefits, the community benefits, and our company promotes itself as a decent corporate citizen, yielding tremendous, long-term advantages [50].

4.3. Waste from the production of Ethylene Glycol

Several major pollutants from our production of ethylene glycols are methanol, dimethyl oxalate, nitric oxide, and methyl glycolate. When swallowed or absorbed as fumes, methanol, dimethyl oxalate, and methyl glycolate are extremely harmful to humans. These chemicals should not be consumed in any way, absorbed through the skin, or inhaled directly since they can be dangerous if swallowed, absorbed through the skin, or inhaled [51]. There is no odor of nitric oxide, which is why it is very dangerous when exposed to humans, because the victim may not realize that they have been exposed to nitric oxide. Inhalation is the most common way to be exposed to nitrogen oxides, however, any form of exposure might have systemic consequences. Eyes, skin, mucous membranes, and the respiratory tract can all be irritated by nitrogen oxides [52]. All our pollutants are very dangerous and toxic, which is why we cannot directly release the vapor into the air or dump the liquid waste into the river. Discarding the waste without treating it will be a violation act against the laws and regulations of Taiwan R.O.C. under the Waste Disposal Act article 28 and article 29.

4.4. Method on Vapor Waste Treatment

To treat our vapor waste, there are two possible ways, Absorption and Adsorption method. For absorption, the gas dissolves in the liquid, which is a mass transfer process.

A reaction with one of the liquid's constituents may or may not occur as a result of the dissolution. Three steps in the removal of the pollutant in gas for absorption method are:

1. Diffusion of the pollutant gas to the liquid's surface.
2. Dissolution (transfer across the gas/liquid boundary).
3. Diffusion of the dissolved gas into the liquid away from the interface.

The partial pressure of the pollutant gas can be represented by Henry's law which determines the amount of absorption of a pollutant to a solution [53].

For adsorption, the gas is adsorbed or bonded to a solid (adsorbents), which is also a mass transfer process. Adsorption is a surface phenomenon, which means that the pollutants penetrate and latch themselves into the solid's pores, but not into the lattice of the solid itself. The pollutants bond themselves to the solid in either physical or chemical bonds. The adsorbents are usually held in a fixed bed inside a pressure vessel. Adsorbents that are commonly used such as activated carbon, molecular sieve, silica gel, and activated alumina. The adsorption system uses Langmuir Adsorption Isotherm, it is used to explain the relationship between the amount of pollutant adsorbed and the equilibrium pressure at constant pressure. It is very important to wash the adsorbents in the adsorption system, because the bed will become saturated with pollutant at some point, and the pollutants will begin to flow out of the bed as the saturation point is reached [53].

There are three possible systems that we can use to treat our vapor waste:

1. Absorption tower (Tray column)

In an absorption tower using a tray column, we are able to increase the retention time of the gas pollutant inside the column. There are two types of flow in the column, the more commonly used cross-flow, where the liquid moves in a horizontal direction and the gas moves from bottom to top, and counter flow, where the liquid moves from top to bottom which counters the gas which moves from bottom to top [54].

The gas pollutant travels upward through the trays and makes contact with the down-flowing water stream. This process allows the separation to occur. The exiting gas on top will be clean gas, and the exiting water at the bottom will be wastewater, which will be further treated [55].

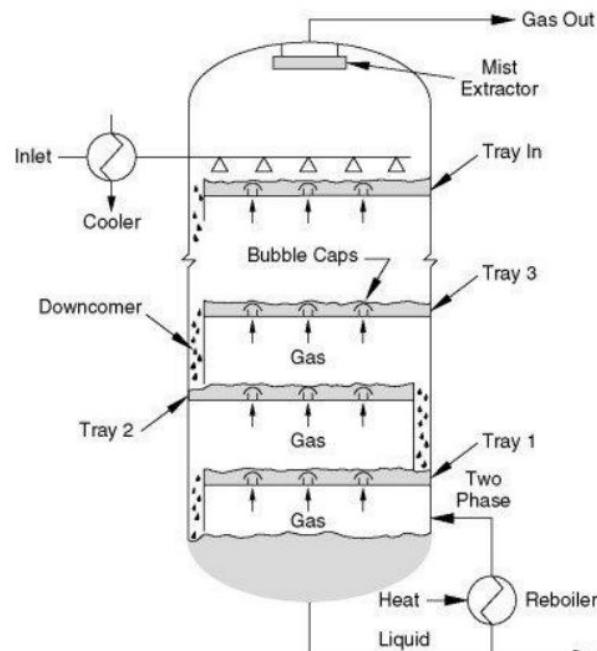


Figure 4.1. Absorption tower (Tray column)

2. Absorption tower (Packed column)

In an absorption tower using a packed column, we are also able to increase the retention time of the gas pollutant inside the column [54]. But the difference with the tray column is that there is more surface contact with the water and gas pollutant with the help of the packings, which means that the mass transfer between gas and liquid will increase. The water flows counter currently from top to bottom against the gas pollutant that flows from bottom to the top.

Same as the tray column, the gas pollutant travels upward through the trays and makes contact with the down-flowing water stream. This process allows the separation

to occur. The exiting gas on top will be clean gas, and the exiting water at the bottom will be wastewater, which will be further treated [55].

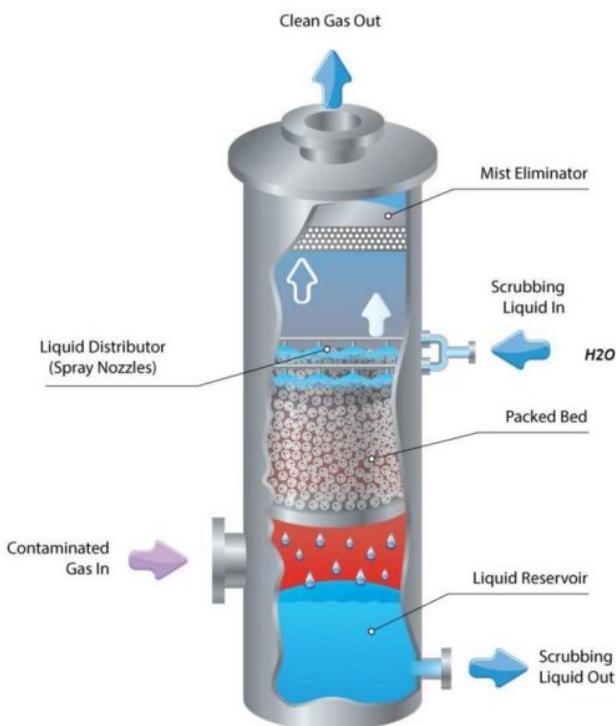


Figure 4.2. Absorption tower (Packed column)

3. Adsorption tower

In an adsorption tower, there will be adsorbents that is packed in the fixed bed inside the column. Adsorbents that are commonly used are activated carbon, molecular sieve, silica gel, and activated alumina.

Pollutant gas will flow into the column with the adsorbent bed, where the reaction will happen. The pollutants will be adsorbed from the gas into the adsorbents, and the exiting gas will be clean gas. This is the adsorption cycle. After some time, steam will be flown into the adsorbent bed, where the desorption cycle happens. The pollutants that are bonded to the adsorbents will be bonded to the steam and carried out by the steam into a condenser. The pollutant-laden steam will then be condensed into a condensed pollutant, which will be treated further. As mentioned above, it is very important to wash the adsorbents in the adsorption system, because the bed will become

saturated with pollutant at some point, and the pollutants will begin to flow out of the bed as the saturation point is reached [53].

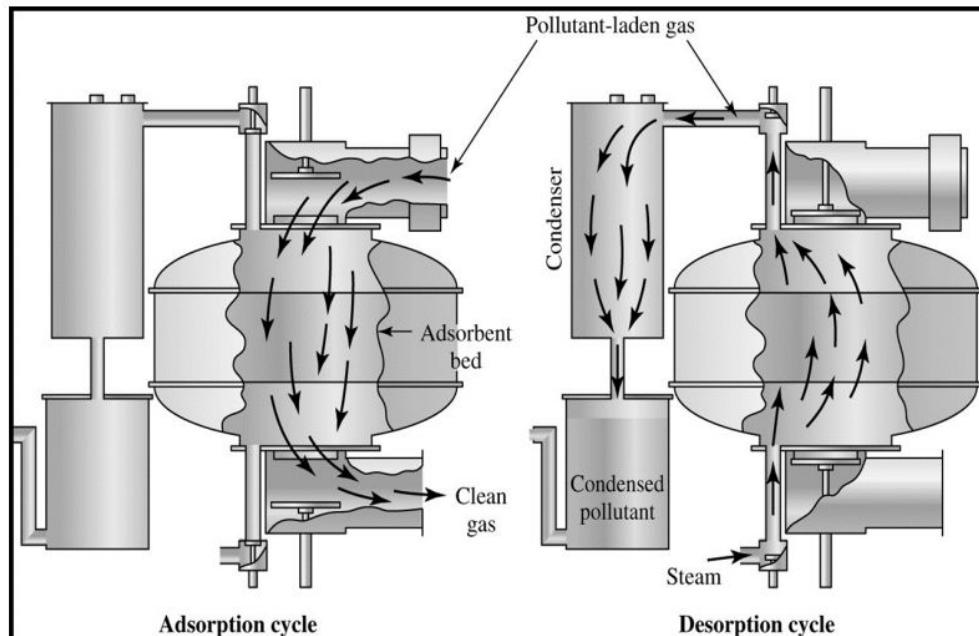


Figure 4.3. Absorption tower system

To treat our gas pollutant before releasing it into the air, we chose Packed Column Absorption tower for our treatment system, since it is the most efficient one. It has the highest surface contact between the gas pollutant and water, making it more efficient in the mass transfer compared to the Tray Column Absorption tower. It is also more cost-efficient than the Adsorption system since we need to change the adsorbent in the fixed bed column after some time since the desorption cycle will not clean the adsorbent perfectly, making it cost-inefficient. However, we do not need to change anything in the Packed Column Absorption system, since there is nothing to change. Though we need to wash the packed column after some time.

CHAPTER 5

PROCESS INTRINSICT AND SAFETY ASSESSMENT

We need to always take into account the safety issues of chemicals, processes, operations, and methods of our plant. Having a plant that takes the safety of the plant seriously will have a huge positive impact on the environment and the employees. Not only will the employee be physically safe, but it takes a positive impact towards their psychology when working in a safe environment. The table below is the MSDS of our chemical components used in the production of ethylene glycol.

Table 5.1. MSDS Table of chemical components for the production of ethylene glycol

Properties	Dimethyl Oxalate	Dimethyl Carbonate	Hydrogen	Oxygen	Methanol	Ethanol
Chemical Formula	(CH ₃) ₂ C ₂ O ₄	(CH ₃ O) ₂ CO	H ₂	O ₂	CH ₃ OH	CH ₃ CH ₂ O H
Chemical Structure			H — H		H ₃ C—OH	
Molecular Weight (g/mol)	118.09	90.08	2.02	31.9999	32.042	46.07
Boiling Point (°C)	163.5	90	-252.879	-183	65	78.37
Melting Point (°C)	50-54	2-4	-259.16	-214.8	-97.6	-114.1
Vapor Pressure at 20°C (bar)	0.003	0.07386	1.01325	-	0.1302	0.0595
Density (g/ml)	1.148	1.069	0.08988	1.429	0.79	0.7893
Safety symbol						
Properties	Nitrogen	Carbon Monoxide	Nitric Oxide	Methyl Nitrite	Methyl Glycolate	Ethylene Glycol
Chemical Formula	N ₂	CO	NO	CH ₃ NO ₂	C ₃ H ₆ O ₃	C ₂ H ₆ O ₂
Chemical Structure						
Molecular Weight (g/mol)	28.014	28.01	30.01	77.04	90.08	62.07
Boiling Point (°C)	-195.8	-191.5	-152	64.6	150-151	197
Melting Point (°C)	-209.86	-205	-164	-82.3	149-151	-12.9

Vapor Pressure at 20°C (bar)	-	-	50.252	-	-	1.0666×10^{-4}
Density (g/ml)	1.1606	0.00114	0.00134	1.2	1.167	1.11
Safety symbol		   	          	   	  	

Dimethyl Oxalate

Dimethyl oxalate is an organic compound with the formula $(CO_2CH_3)_2$. It is a colorless crystalline that is soluble in water, with a low melting point of 54°C. It is made by treating carbon monoxide with methanol and is utilized as a raw material in the production of pharmaceuticals and agrochemicals, as well as etching agents for electronic components.

Even though DMO is not too much of a toxic chemical, but high exposure to it causes severe skin burns and serious eye damage, and it is harmful if swallowed.

Methanol

Methanol (also known as wood alcohol and methyl alcohol) is a non-drinking kind of alcohol that is mostly used to make fuel, solvents, and antifreeze. It is a colorless liquid that is volatile, flammable, and dangerous to humans, unlike ethanol. Methanol is also used to make acetic acid and a range of other compounds. Many living species produce small amounts of methanol as part of their metabolic activities. Methanol, for example, is found in a variety of fruits and vegetables [56].

Methanol is a poisonous chemical and deadly when ingested. It is often used as a method for suicide attempts. All possible symptoms including a reduced level of consciousness, weak or no coordination, vomiting, abdominal pain, and a distinct odor on the breath. As early as twelve hours following exposure, the victim's visual loss might occur. Blindness and renal failure may be long-term consequences. Even a modest amount of methanol can result in toxicity and death.

Carbon Monoxide

Carbon monoxide (CO) is a colorless, odorless, tasteless, flammable gas that is slightly less dense than air. Biologically, carbon monoxide plays a crucial role in all phylogenetic kingdoms.

Carbon monoxide is a famous example of hormesis in mammalian physiology, with low amounts acting as an endogenous neurotransmitter (gasotransmitter) and high quantities acting as a toxin, resulting in carbon monoxide poisoning. Carbon monoxide also plays a part in metal fabrication, used in chemical manufacturing such as acids, esters, and alcohols, used to regenerate catalyst, used as a reduction agent, and even in semiconductor applications.

Carbon monoxide is also a poisonous gas to breathe in, in fact, it's also the most preferred way to commit suicide as well. Headache, dizziness, weakness, upset stomach, vomiting, chest discomfort, and confusion are the most typical symptoms of CO poisoning. The symptoms of CO are frequently described as "flu-like." CO poisoning can cause you to faint out or even kill you if you inhale too much of it. CO poisoning can kill people who are sleeping or inebriated before they show symptoms.

Nitric Oxide

Nitric oxide (NO), also called nitrogen monoxide, colorless toxic gas that is formed by the oxidation of nitrogen. Nitric oxide liquefies at $-151.8\text{ }^{\circ}\text{C}$ ($-241.2\text{ }^{\circ}\text{F}$) and solidifies at $-163.6\text{ }^{\circ}\text{C}$ ($-262.5\text{ }^{\circ}\text{F}$), both the liquid and the solid are blue in color. Nitric oxide is a diatomic molecule with a free radical that is relatively unstable. In humans and other animals, nitric oxide plays a key role in chemical signaling and has a variety of medical applications. It has a limited number of industrial applications. It is a major pollutant released into the atmosphere by automobile engines and thermal power plants [57].

Automobile engines and thermal power plants produce a significant amount of nitric oxide, which contributes to air pollution. Nitric acid is formed when nitric oxide reacts with water vapor in the atmosphere, and it is one of the components of acid rain. The steady loss of the ozone layer in the high atmosphere was also caused by increased amounts of atmospheric nitric oxide as a result of industrial activities. Nitric oxide reacts chemically with ozone in the presence of sunlight, converting ozone to molecular oxygen.

Nitric Oxide is a colorless, non-flammable, toxic, oxidizing gas with an unpleasant odor at room temperature. Nitric oxide is extremely toxic when inhaled, and signs of overexposure might take up to 72 hours to appear. Because the gas is an oxidizer, it will accelerate and increase combustion. Nitric Oxide is a highly reactive oxidizing substance that produces brown nitrogen dioxide fumes when exposed to air. If Nitric Oxide gets into the eyes, it can cause serious injury and swelling of the eye tissue. Low quantities of Nitric Oxide gas cause irritation of the mucous

membranes of the eyes, nose, throat, and lungs, resulting in choking, coughing, headache, nausea, and exhaustion. Methemoglobinemia, cyanosis, delayed pulmonary edema, mental disorientation, coma, and death are all possible side effects of extreme overexposure. High levels of Nitric Oxide gas may result in an oxygen-deficient atmosphere; however, other, more serious health effects will appear before those related to asphyxiation. In the body, nitric oxide can oxidize hemoglobin to methemoglobin in the blood. When methemoglobin levels exceed 70%, coma and death might occur. Methemoglobin's failure to interact with oxygen can cause tissue hypoxia, which can have clinical consequences. Muscle tremors, sleepiness, a brownish-blue hue to the mucous membranes, an elevated heart rate, vertigo, and vomiting are some of the symptoms.

Methyl Nitrite

Methyl nitrite (CH_3ONO) is an organic compound in a gas form and is the simplest alkyl nitrite. The reaction of silver nitrite with iodomethane is used to synthesize methyl nitrite. Methyl nitrite is a heat-sensitive oxidizing agent whose sensitivity increases in the presence of metal oxides. It creates explosive salts with inorganic bases. When combined with air, it creates explosive combinations. It is a monopropellant that's employed as a rocket propellant. It bursts with greater force than ethyl nitrite. Even when kept refrigerated, lower alkyl nitrites might degrade and burst the container. Methyl nitrite is employed as a precursor and intermediate in chemical syntheses, such as in the creation of phenylpropanolamine.

Methyl nitrite is a poisonous asphyxiating gas that can also cause cyanosis. Methemoglobinemia can occur as a result of exposure. Without warning, vapors can cause dizziness or asphyxiation. In short, methyl nitrite is a very dangerous chemical.

CHAPTER 6

CONCLUSION

In conclusion, we achieve the goal of this process design project, which is producing 6,800 ton/year Ethylene Glycol with mass purity of 99 wt%. After comparing both design and economical value, the first flowsheet is more beneficial than the second one. Design wise, the second flowsheet is simpler and using less amount of devices, but the utility cost increased, hence the cost estimation goes higher. The economic conclusion can be seen in the table below.

Parameters	First Flowsheet	Second Flowsheet
ROI (%)	23.47%	14.93%
Payout Time (year)	4 years	6 years
DCFROR	8.94%	3.19%
CCR (year^{-1})	0.542	0.453

The first flowsheet is clearly more profitable and beneficial than the second one. In consideration, the future improvements are going to be implemented in both systems to achieve more benefits of each system.

CHAPTER 7

FUTURE WORK AND SUGGESTION

1. Catalyst Aspect

For the Cu/SiO₂ catalyst, a better method to regenerate Cu/SiO₂ or another type of catalyst can be observed. Regeneration can be more beneficial than just reuse because it can save the catalyst cost.

2. Design Aspect

The EG conversion might be higher if the reactant combination and reactor configuration are correct. In some literature, there is 3-4 recycled product after reaction 2 including MG, DMO, and H₂ into the reactor. This will need a lot of effort, trials, and error, but is not impossible if there is more time. Methanol can also be obtained if more distillation columns are applied in the last separation process.

3. Economic Aspect

In the future, especially if the catalyst regeneration method and cost are available, the economic analysis can be done in a longer period of time, like 5-10 years, to estimate the stability and profitability of our designed process for the long term. In this analysis, the tax, inflation, depreciation, can also be included.

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