TECHNO-ECONOMIC FEASIBILITY ANALYSIS OF HYDROGEN RECOVERY IN BIO-HYDROGENATED DIESEL FROM PALM OIL FOR METHANOL SYNTHESIS VIA ASPEN PLUS

Mr. Nitipat Phichitsurathaworn

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การวิเคราะห์ความเป็นไปได้ในทางด้านเทคนิคและทางด้านเศรษฐศาสตร์ในการนำกลับของไฮโดรเจนในกระบวนการผลิตน้ำมันดีเซลชีวภาพจากน้ำมันปาล์มเพื่อการสังเคราะห์เมทานอลผ่านโปรแกรมแอสเพน พลัส

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By	Mr. Nitipat Phichitsurathaworn
Field of Study	Chemical Engineering
Thesis Advisor	Professor Dr. SUTTICHAI ASSABUMRUNGRAT
Thesis Co Advisor	Assistant Professor Dr. Lida Simasatitkul

Accepted by the FACULTY OF ENGINEERING, Chulalongkorn University in Partial Fulfillment of the Requirement for the Master of Engineering

.... Dean of the FACULTY OF ENGINEERING
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THESIS COMMITTEE

.... Chairman
(Assistant Professor Dr. PALANG BUMROONGSAKULSAWAT)
.... Thesis Advisor
(Professor Dr. SUTTICHAI ASSABUMRUNGRAT)
.... Thesis Co-Advisor
(Assistant Professor Dr. Lida Simasatitkul)
.... Examiner
(Dr. Akawat Sirisuk)
.... External Examiner
(Assistant Professor Dr. Suksun Amornraksa)

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น้ำมันดีเซลชีวภาพหรือกรีนดีเซลสามารถผลิตได้จากน้ำมันปาล์มที่ผ่านกระบวนผลิตโดยใช้ปฏิกิริยาเคมี การจำลองกระบวนการผลิตน้ำมันดีเซลชีวภาพสามารถทำได้ผ่านโปรแกรม Aspen Plus โดยในปัจจุบันมีการผลิตผ่านปฏิกิริยาไฮโดรดีออกซีจิเนชัน โดยใช้ตัวเร่งปฏิกิริยาวิวิธพันธุ์ และจำเป็นต้องใช้อัตราส่วนโดยปริมาตรระหว่างแก๊สไฮโดรเจนต่อน้ำมันปาล์มที่สูง จึงทำให้ต้องปล่อยแก๊สไฮโดรเจนทิ้งในปริมาณที่มากก่อนที่จะนำกลับมาทำปฏิกิริยาใหม่ กระบวนการผลิตน้ำมันดีเซลชีวภาพควบคู่กับการผลิตเมทานอลถูกออกแบบเพื่อที่จะลดปริมาณการปลดปล่อยแก๊สไฮโดรเจน โดยนำแก๊สไฮโดรเจนที่หลงเหลืออยู่ทำปฏิกิริยากับแก๊สคาร์บอนไดออกไซด์ที่เป็นสารตั้งต้นหลัก ความเป็นไปได้ในทางเทคนิคและเศรฐศาสตร์จะใช้เป็นตัวชี้วัดในการพิจารณา พบว่า ในด้านเทคนิค กระบวนการผลิตน้ำมันดีเซลชีวภาพควบคู่กับการผลิตเมทานอลสามารถลดการปลดปล่อยแก๊สไฮโดรเจนได้ถึง 46.3 เปอร์เซ็นต์ และลดการปลดปล่อยแก๊สคาร์บอนไดออกไซด์ และแก๊สคาร์บอนมอนอกไซด์ 14 เปอร์เซ็นต์ ส่วนด้านเศรษฐศาสตร์ กระบวนการผลิตน้ำมันดีเซลชีวภาพควบคู่กับการผลิตเมทานอลมีอัตราผลตอบแทนได้ถึง 39.65 เปอร์เซ็นต์ รวมถึงใช้เวลาในการคืนทุนเพียง 1.68 ปี และมีมูลค่าหลังดำเนินการถึง 65.57 ล้านดอลลาร์สหรัฐ

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Nitipat Phichitsurathaworn : TECHNO-ECONOMIC FEASIBILITY ANALYSIS OF HYDROGEN RECOVERY IN BIO-HYDROGENATED DIESEL FROM PALM OIL FOR METHANOL SYNTHESIS VIA ASPEN PLUS. Advisor: Prof. Dr. SUTTICHAI ASSABUMRUNGRAT Co-advisor: Asst. Prof. Dr. Lida Simasatitkul

A bio-hydrogenated diesel (BHD) or green diesel can be produced from refined palm oil obtained from palm oil refinery. A simulation model of BHD production process from palm oil is developed by Aspen Plus. The conventional process which is the heterogeneous catalytic hydro-deoxygenation reaction of triglycerides required high H_2/oil volumetric ratio. To reduce high hydrogen loss in gaseous by-product, the design of hydrogen gas recovery process of the BHD process by coupling with methanol synthesis is proposed. The two processes (i.e., conventional BHD process and BHD process coupled with methanol synthesis) are compared in terms of hydrogen recovery and economic indicators. The second process can recover 46.3 percent of discharged hydrogen and reduces 14 percent of carbon dioxide and carbon monoxide emission. Furthermore, it provides high rate of return of 39.65 percent, payback period of 1.68 years, and net present value of 65.57 million US dollars.

Field of Study:	Chemical Engineering	Student's Signature ....
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Nitipat Phichitsurathaworn

TABLE OF CONTENTS

Page

CHAPTER 1 Introduction

1.1 Motivation of Research

The depletion of fossil fuel results in high energy consumption in the world continuously over the past decades [1]. Diesel is one of the most utilized fuel in vehicles and diesel engine [2-5]. Thus, demand growth of petroleum diesel from the crude oil fractionation distillation is increasing significantly which leads to import the fuel [6, 7]. To reduce either the lack of energy or high crude oil price, searching the renewable energy for replacing petroleum diesel is an interesting option [8]. Biomass which is the organic matter is used as raw material for biofuel production [9]. Biodiesel is the first-generation type of renewable diesel which is produced from the transesterification reaction of animal fats and plant oil with methanol. The properties of biodiesel are similar to diesel, thus it can be used to replace petroleum diesel directly or blended in the petroleum diesel [10]. The differences of the petroleum diesel and biodiesel are the composition in the molecules and the physical properties. The petroleum diesel contains long chain hydrocarbons (mainly $C_{16}H_{34}$ and $C_{18}H_{38}$) with single bond. However, the biodiesel contains ester bonding components which have 2 atoms of oxygen inside the molecule. The disadvantages of biodiesel are the high viscosity, high cloud point, chemical stability, incompatibility for diesel engine and poor cold flow [11-13]. To improve the biofuel properties, the second generation type of renewable diesel which is called “Bio-hydrogenated diesel (BHD)” or “Green diesel” is recovered[13]. The chemical formula of BHD is similar to petroleum diesel. It is produced from heterogeneous catalytic reactions such as deoxygenation of plant oil and animal fats with or without using hydrogen gas [14].

The parameters (i.e., catalyst, temperature, feed flow rate, type of feedstock, volumetric ratio of H_2/oil ratio) have played an important role for production yield [15]. Generally, the reactions are operated under high pressure, high temperature, and high H_2/oil ratio in the presence of heterogeneous catalyst. Due to high H_2/oil ratio, gaseous by-product consists of excess hydrogen, carbon monoxide, carbon dioxide, some of light hydrocarbons. Furthermore, this stream is recirculated back to the process. As a result, the by-product is continuously accumulated in the system. Thus, the purification process is an important issue for separation of the by-product from the hydrogen gas. Not only it reduces the accumulation of by-product, but it also decreases the discharging of carbon dioxide to the atmosphere which causes the global warming crisis.

From the literature studies, there are several ways for gas separation (i.e., amine absorption and chemical reaction of by-product) which depends on thermos-properties and physical properties. The most common method is amine absorption because it is able to remove acid gas (CO_2 and CO) and produce high purity of hydrogen [16]. However, the utilization of carbon monoxide and carbon dioxide conversion from the BHD process is not mentioned in the literatures. Alternatively, chemical reaction of by-product which is known as waste is an interesting option to produce high value-added product. Methanol is one of valuable chemical which is used as main feedstock in many of chemicals industries such as formaldehyde production and acetic acid production which are used in manufacture of car, building material, perfume or medical treatment [17]. Methanol is a colorless, volatile and flammable chemical which can be used as the fuel. It can be produced by waste gas from this process. Carbon dioxide, carbon monoxide and hydrogen are main raw materials for methanol synthesis. Generally, methanol synthesis is obtained from synthesis gas through a petroleum-based pathway. Methanol is usually produced by steam reforming of natural gas or gasification of coal [18]. At present, the gasification of biomass is converted to synthesis gas before the methanol production [18].

Therefore, this research focused on the design of BHD process coupled with the hydrogen recovery from by-product through the methanol synthesis reaction. Refined bleached deodorized palm oil (RBDPO) was considered as raw material for the BHD process. The optimal process flowsheet was carried out by optimizing operating condition, equipment design, utility design and heat integration. Finally, the techno-economic analysis of proposed process was performed comparing with the conventional BHD process in term of economic point of view.

1.2 Objective of Research

1 To evaluate the techno-economic feasibility of the BHD process coupled with methanol synthesis process.

2 To optimize the operating condition and sizing the equipment in BHD process with and without methanol synthesis process.

1.3 Scope of Research

1 This research was conducted by using the simulation software "Aspen Plus ver.9.0" and studied by using the commercial process of the BHD production in the simulation.

2 RBDPO was a representative of the renewable source.

3 Operating condition of the reaction was referred to that reported in the literature in lab-scale experiments.

4 This research evaluated the optimized condition, equipment type selection and equipment size approximation.

5 This research studied the feasibility of techno-economic assessment and showed the differences between the BHD process with and without methanol synthesis.

1.4 Expected Benefits of Research

The new BHD process can provide for green energy in the future. So it is important to study the optimization of the process and the analysis of techno-economic feasibility. Therefore, the existing BHD process will be improved and will be able to interpret in the commercial scale feasibility.

CHAPTER 2 Fundamentals and Literature Reviews

This chapter describes literature reviews including the BHD synthesis, methanol synthesis, and BHD production process.

2.1 BHD synthesis

The BHD is long chain hydrocarbon which mainly composes of hexadecane and octadecane and used as the bio-fuel. It is different from biodiesel because it requires the catalyst and hydrogen gas to eliminate the oxygen atom of the triglyceride. Then the linear long chain hydrocarbon is obtained [19]. The plant oil and animal fats are deoxygenated over heterogeneous catalyst. In this research, RBDPO [20] was used as reactant which composed of the fatty acid as Table 1.

Table 1 Composition of fatty acid in RBDPO [20]

Fatty acid	**Concentration [%wt.]**
Lauric acid (C12:0)	0.4
Myristic acid (C14:0)	0.8
Palmitic acid (C16:0)	37.4
Palmitoleic acid (C16:1)	0.2
Stearic acid (C18:0)	3.6
Oleic acid (C18:1)	45.8
Linoleic acid (C18:2)	11.1
Linolenic acid (C18:3)	0.3
Arachidic acid (C20:0)	0.3
Eicosenoic acid (C20:1)	0.1

To compare BHD and biodiesel with petroleum diesel [21], the UOP Honeywell studied and found that the chemical structure of BHD was similar to petroleum diesel due to no oxygen content and high energy density. Moreover, BHD also has more advantages than the petroleum diesel because it has higher cetane number, low sulfur content, and good cold flow and oxidative stability as shown in the Table 2. The Eni Company performed the comparison of the physical properties in the Table 3. It found that the properties are similar to the UOP Honeywell.

Table 2 Comparison of Petroleum diesel, Biodiesel, and BHD [21]

Comparison	**Petroleum Diesel**	**Biodiesel**	**BHD**
Percent of oxygen [%]	0	11	0
Cetane number	40-55	50-65	75-90
Energy density [MJ/kg]	43	38	44
Sulfur content [ppm]	<5	<10	<2
Cold flow	Base	Poor	Excellent
Oxidative Stability	Base	Poor	Excellent

Table 3 Comparison of Physical Properties each diesel [16]

Comparison	**Petroleum Diesel**	**Biodiesel**	**BHD**
Bio content	0	100	100
Specific gravity [g/cm^3]	0.840	0.880	0.780
Cloud point [ºC]	-5	-5 to +15	Up to -20
CFPP additive sense.	Base	Base	Excellent
Distillation [ºC]	200 to 350	340 to 355	200 to 320
Polyaromatics [%wt.]	11	0	<2
NO_x Emission	Base	+10 %	-10 %

The BHD is synthesized of triglycerides with the hydrogen gas over catalyst. The liquid reactant consisting of fatty acids, fatty acid esters, and triglycerides can be converted to alkane by releasing the carbon monoxide and carbon dioxide and light hydrocarbon [22] as shown in Figure 1**.**

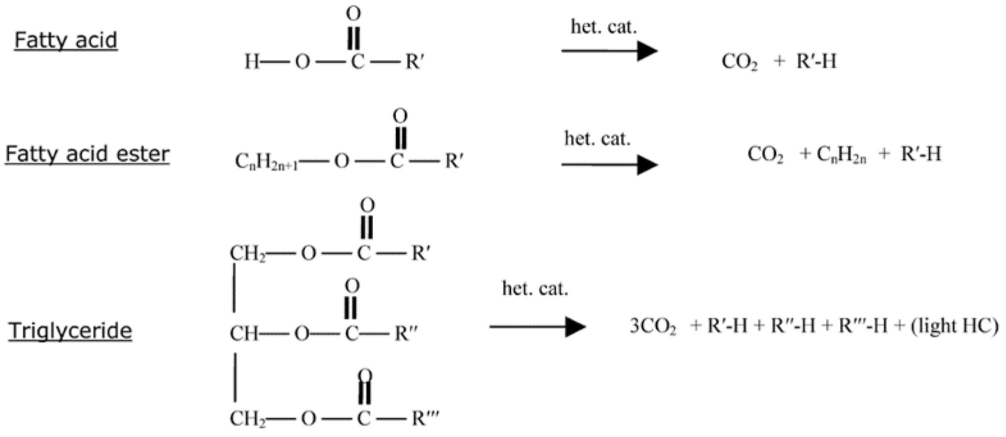

Figure 1 Catalytic carboxylation [22]

The catalysts for the BHD synthesis are the significant parameter. A. Srifa and colleagues in 2014 [23] claimed that the catalyst was active after pre-reduction by hydrogen gas. The catalytic activity is in the order of Co > Pd > Pt > Ni. Normally, the 3 main reactions such as hydro-deoxygenation (HDO), decarboxylation (DCO2) and decarbonylation (DCO) are performed simultaneously as in the Figure 2**.** The reactions can also continue through isomerization and cracking as shown in the Figure 3**.** The results of their experiment showed that RBDPO was converted almost completely and the liquid products were the normal alkane as shown in Table 4. The contribution of each reaction are shown as Table 5**.**

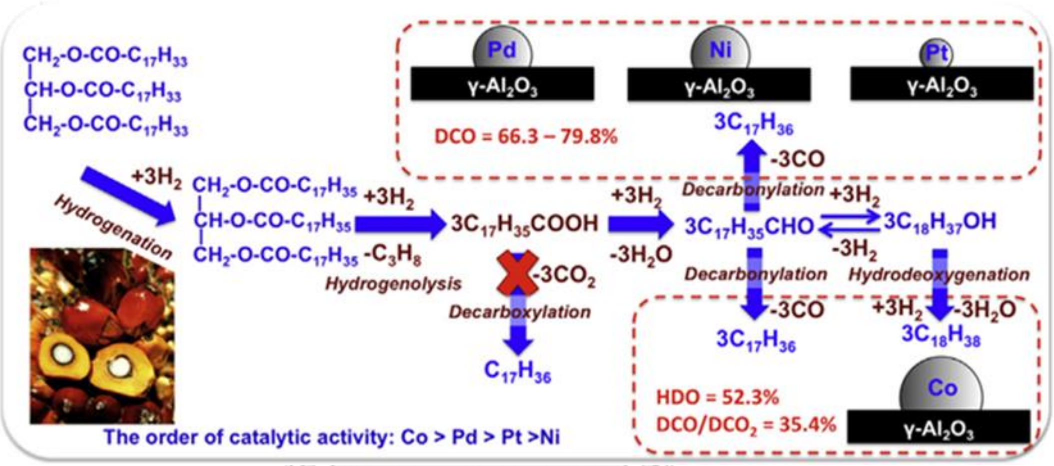

Figure 2 Heterogeneous catalytic reaction for BHD [23]

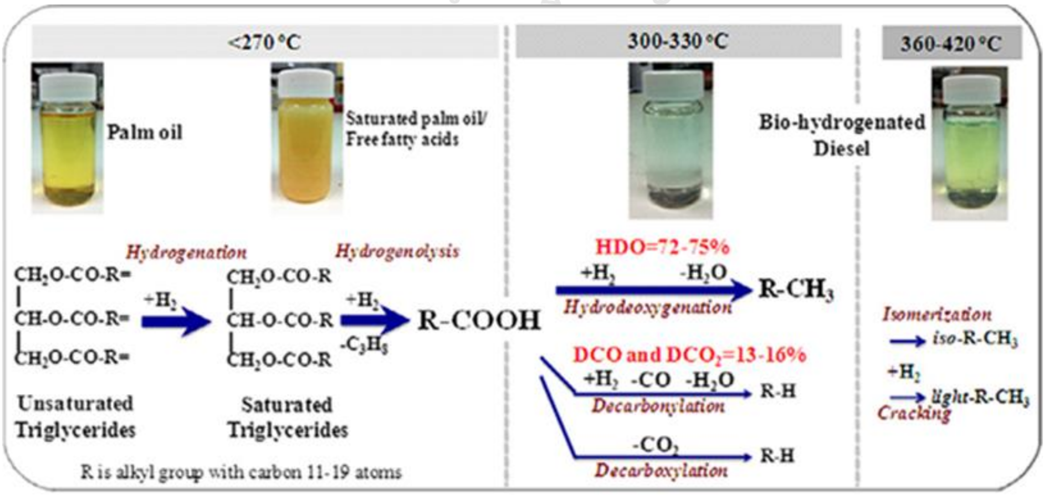

Figure 3 Heterogeneous catalytic reaction for BHD continuously [23]

Table 4 Compositions of the liquid product from palm oil deoxygenation over catalyst [23]

Catalysts Types	**Conversion [%]**	**Liquid product [% wt.]**					**Liquid phase**
		n-C_8H_{18}-n-$C_{14}H_{30}$	**n-$C_{15}H_{32}$**	**n-$C_{16}H_{34}$**	**n-$C_{17}H_{36}$**	**n-$C_{18}H_{38}$**	
5CoAl	100	3.5	14.8	23.2	21.9	34.4	Liquid
10CoAl	100	5.1	16.7	21.7	23.5	29.7	Liquid
5NiAl	100	0.8	25.3	1.3	40.4	1.6	Solid
10NiAl	100	1.6	33.8	1.8	54.6	1.3	Liquid
2PdAl	99	0.3	14.9	1.2	22.8	1.8	Solid
5PdAl	100	0.6	31.4	2.1	51.5	3.2	Liquid
2PtAl	95	0.2	10.4	1.3	16.3	2.3	Solid
5PtAl	100	0.7	28	3.1	46.2	5.2	Liquid

Table 5 Percent of contribution of HDO and DCO/DCO2 from palm oil deoxygenation over catalyst [23]

Catalyst Types	**DCO/DCO2 [%]**	**DCO/DCO2 [%]**	**HDO [%]**	**HDO [%]**
	n-$C_{15}H_{32}$	**n-$C_{17}H_{36}$**	**n-$C_{16}H_{34}$**	**n-$C_{18}H_{38}$**
5CoAl	37.7	33.8	55.6	50.1
10CoAl	42.3	35.9	51.4	42.9
5NiAl	67.7	65.3	3.3	2.5
10NiAl	82.1	80.1	4.0	1.8
2PdAl	39.5	36.6	3.1	2.7
5PdAl	80.9	79.5	4.9	4.7
2PtAl	29.1	27.5	3.5	3.7
5PtAl	71.6	71.9	7.3	7.6

A. Srifa and colleagues [20] studied the effect operating condition on the conversion, liquid product composition, and percent contribution of each reaction by using the γ-Al_2O_3 supported $NiMoS_2$ as a catalyst. The results were shown in the Table 6 and Table 7 and Figure 4 to Figure 7. The summary of operating parameters as below;

1. Temperature: The increasing temperature promotes the rate of the reaction until temperature of 330 ^oC is reached. Then, it leads to cracking, isomerization, and cyclization due to the fact that light hydrocarbon is observed. However, the temperature is lower than 270 ^oC, the liquid will be solidified.

2. Hydrogen pressure: It does not effect on the conversion significantly. The conversion slightly increases to 95.2 percent with an increase in hydrogen pressure to 80 bar from 15 bar. Because the rate of HDO is improved but the rate of DCO and DCO2 are declined.

3. Liquid hourly space velocity: This parameter affects the contact time between feed and catalyst. The effect of LHSV on conversion is not significantly because the conversion reaches 100 percent at 0.25 - 5 h^{-1}.

4. Hydrogen gas to oil ratio (H_2/oil): This parameter effects on the hydro-deoxygenation significantly. The conversion increases from 45.2 percent to 93.3 percent with an increase in hydrogen gas to oil ratio from 250 to 1500 cm^3/cm^3

Table 6 Effect of operating parameters on liquid product composition [20]

Parameters	T [°C]	P [Bar]	LHSV [h^{-1}]	H_2/oil Ratio [Ncm^3/cm^3]	Liquid Product Composition [% wt.]					Product Phase	
					C_8H_{18}-$C_{14}H_{30}$	$C_{15}H_{32}$	$C_{17}H_{36}$	$C_{16}H_{34}$	$C_{18}H_{38}$	**Phase**	**Color**
Temperature	270	50	1	1000	0.2	1.7	9.1	2.9	14.1	Solid	Yellow
	300	50	1	1000	0.8	6.3	30.3	10.7	47.7	Liquid	Clear
	330	50	1	1000	1	4.9	32.1	8	48.7	Liquid	Clear
	360	50	1	1000	2.5	3.2	33.5	4.6	44.6	Liquid	Light Green
	390	50	1	1000	5.7	3.1	31.8	3.5	33	Liquid	Light Green
	420	50	1	1000	12.8	3.8	22.3	2.8	12.7	Liquid	Green
Pressure	300	15	1	1000	0.9	6	29.3	10.3	43.9	Liquid	Green
	300	30	1	1000	0.9	7.6	29.3	12.8	45.5	Liquid	Clear
	300	50	1	1000	0.8	6.3	30.3	10.7	47.7	Liquid	Clear
	300	80	1	1000	0.8	5.9	31.7	10.3	50.4	Liquid	Clear
LHSV	300	50	0.25	1000	0.6	3.4	34.3	6.1	54.7	Liquid	Clear
	300	50	0.5	1000	0.6	5.6	31.9	10	49.4	Liquid	Clear
	300	50	1	1000	0.6	6.3	30.7	10.9	47.4	Liquid	Clear
	300	50	1.5	1000	0.6	5.8	30.7	9.7	46	Liquid	Clear
	300	50	2	1000	0.6	5.6	31.2	9.2	46.1	Liquid	Clear
	300	50	3	1000	0.6	5.3	30.6	8.8	45.3	Liquid	Clear
	300	50	5	1000	0.6	5.3	29.9	8.8	44.5	Liquid	Clear
H_2/oil Ratio	300	50	1	250	0.3	4.3	12.9	7.3	20.1	Solid	Yellow
	300	50	1	500	1	7.2	29	12.2	46.3	Liquid	Clear
	300	50	1	750	0.8	6.6	30.2	11.3	47.9	Liquid	Clear
	300	50	1	1000	0.6	6.6	30.9	11.1	48.2	Liquid	Clear
	300	50	1	1500	0.8	7.1	31.1	12.1	48.3	Liquid	Clear
	300	50	1	2000	0.8	6	31.9	10.1	49.4	Liquid	Clear

Table 7 Effect of temperature and hydrogen pressure on percent of contribution of each n-alkane [20]

Parameters	**T [ºC]**	**P [Bar]**	**$C_{16}H_{34}$ HDO [%]**	**$C_{18}H_{38}$ HDO [%]**	**$C_{15}H_{32}$ DCO/DCO2 [%]**	**$C_{17}H_{36}$ DCO/DCO2 [%]**
Temperature	270	50	22.7	21.4	4.4	4.7
	300	50	74.1	71	16.4	17.1
	330	50	78.5	72.4	12.9	12.8
	360	50	83.3	66.4	8.1	6.9
	390	50	78.4	49.6	8.1	5.6
	240	50	51.9	17	9.5	4.2
Pressure	300	15	72.6	66.4	15.8	16.5
	300	30	72.6	68.7	19.8	20.3
	300	50	74.1	71	16.4	17.1
	300	80	79.1	76.4	15.6	16.5

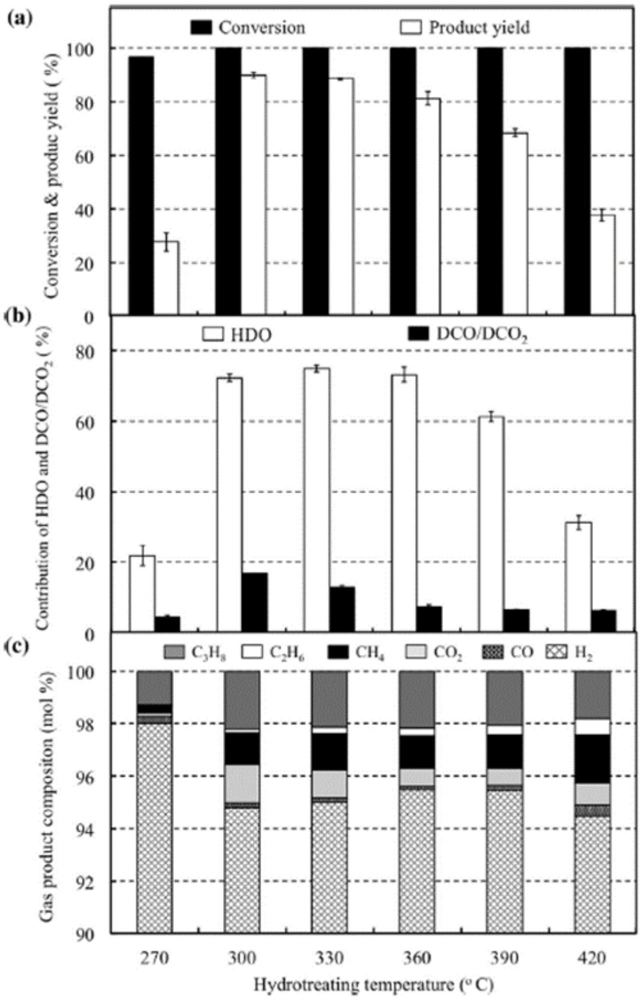

Figure 4 The effect of temperature on the conversion and contribution of deoxygenation reaction and gaseous product composition [20]

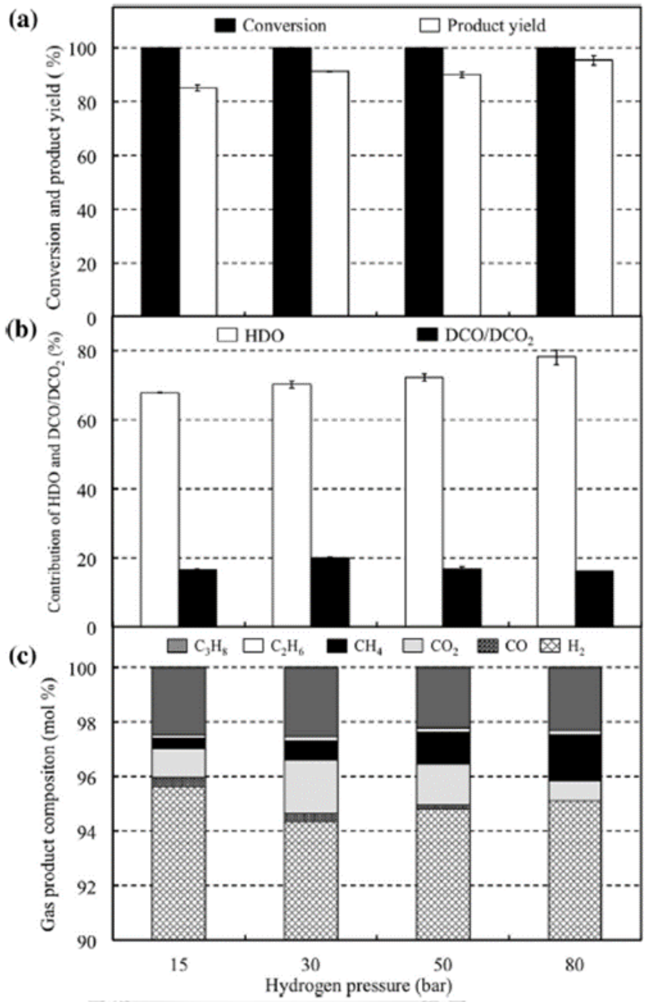

Figure 5 The effect of hydrogen pressure on the conversion and contribution of deoxygenation reaction and gaseous product composition [20]

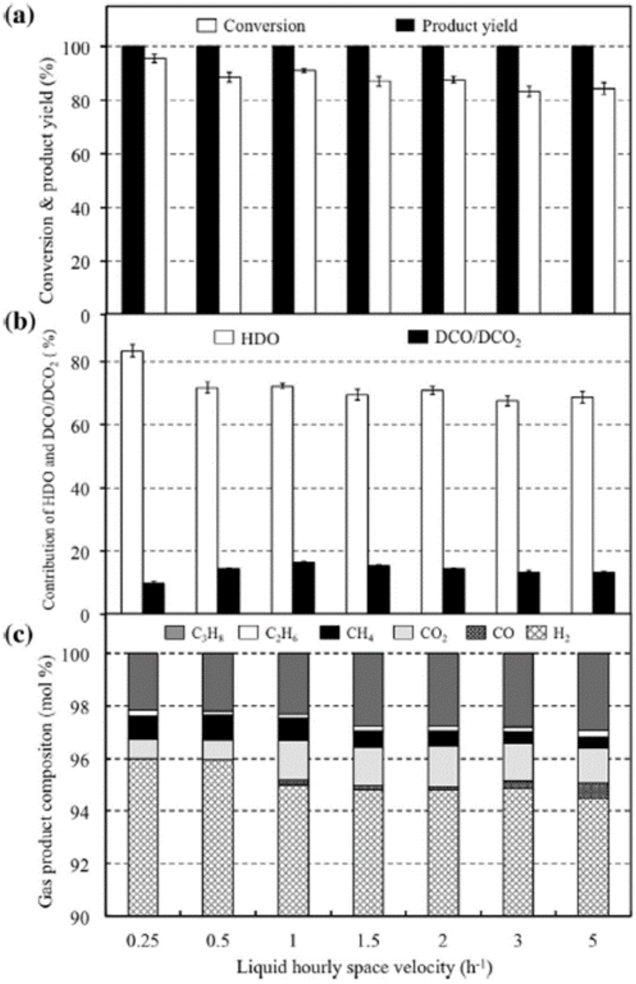

Figure 6 The effect of liquid hourly space velocity on the conversion and contribution of deoxygenation reaction and gaseous product composition [20]

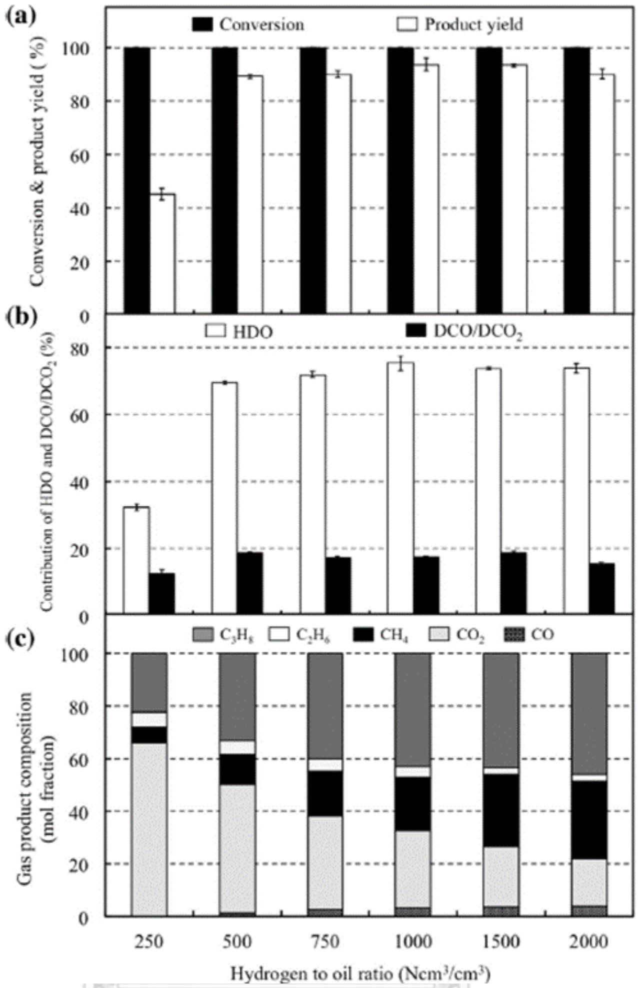

Figure 7 The effect of hydrogen gas per oil ratio on the conversion and contribution of deoxygenation reaction and gaseous product composition [20]

2.2 BHD Process

There are 2 bio-based diesels (i.e., biodiesel and BHD). Bio-diesel is produced by transesterification reaction of the triglyceride and methanol in the continuous flow stirred tank reactor over the catalyst as shown in the Figure 8. But BHD is produced by the heterogeneous catalytic reactions in the 3-phases reactor as the process in the Figure 9 [24].

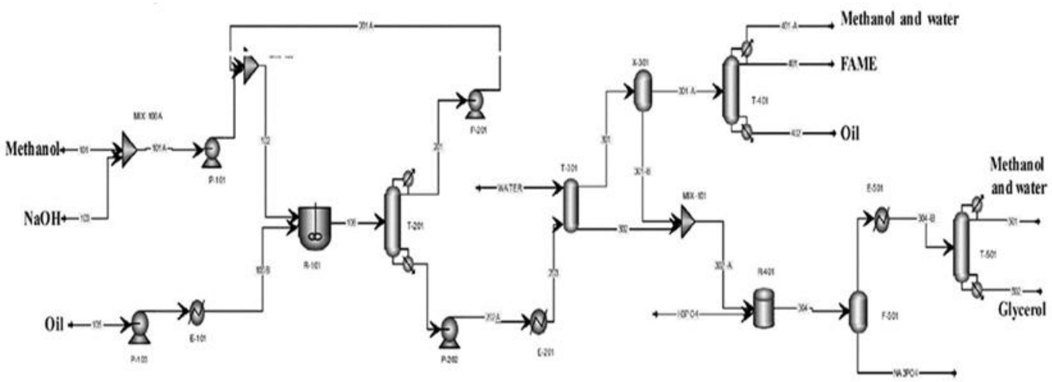

Figure 8 Biodiesel process [24]

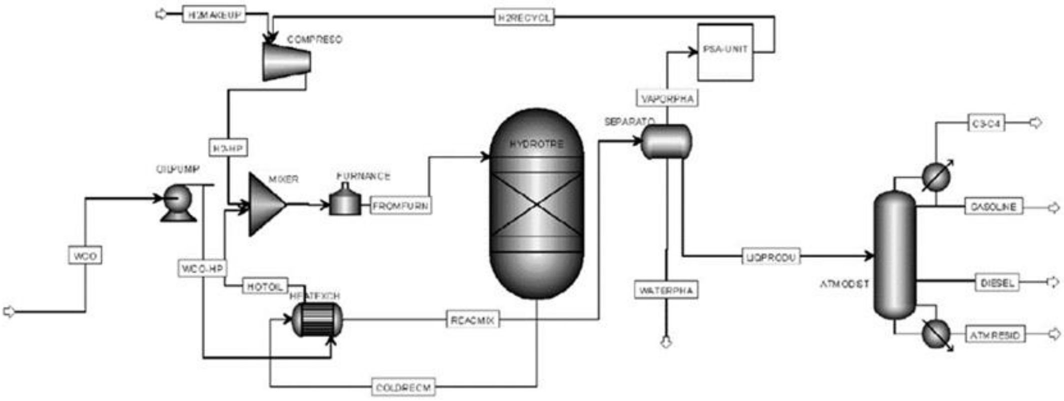

Figure 9 Waste Vegetable Oil for BHD process [24]

The techno-economic showed that the capacity of unit and feedstock cost are the major factors of the production. The co-process of BHD and petroleum plant was preferable to stand-alone BHD plant because of low investment cost compared with stand-alone BHD plant [24].

For the energy recovery, P. Kittisupakorn studied the process for 25000 kg per hour of BHD as shown in Figure 10 [25]. Three strategies to minimize the energy consumption was proposed. It was found that the best process in term of energy recovery could reduce 89.36 percent of energy, approximately 111,195 kW. For heat recovery, the hot product streams were divided into two streams. One hot stream was used to preheat the reactant before outsource utility was required to heat up or cool down each stream to its set point.

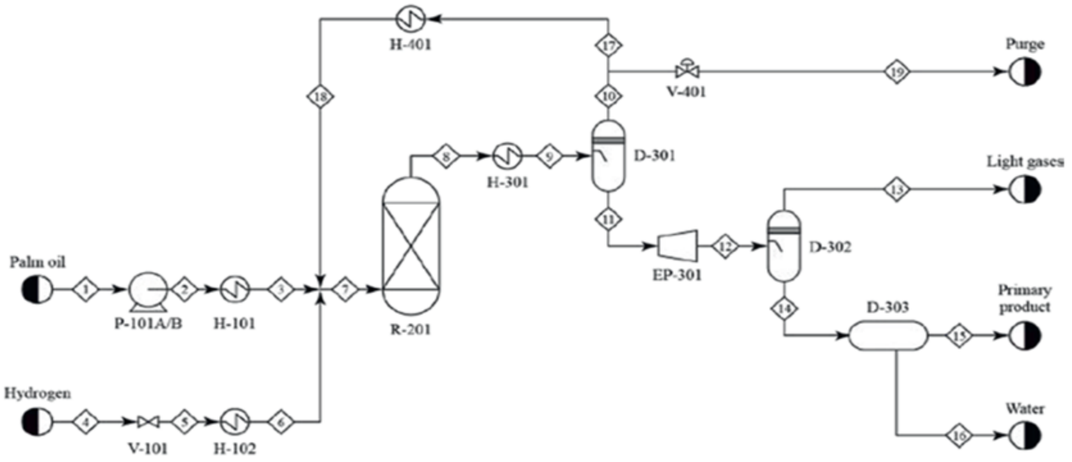

Figure 10 Palm oil for BHD process [25]

2.3 Methanol Synthesis

For the methanol synthesis, this reaction is occurred over commercial catalyst such as $Cu/ZnO/Al_2O_3$ catalyst, at 210-270 ^oC and 50-100 bar. There were a lot of catalyst which were studied for methanol synthesis by carbon dioxide or carbon monoxide conversion. Shanshan Danga and team collected the information about methanol synthesis catalyst in “A review of research progress on heterogeneous catalysts for methanol synthesis from carbon dioxide hydrogenation” as shown in Table 8 [26]. The research claimed that copper alone catalyst is not efficient for methanol synthesis. The catalyst’s support could improve the stabilization of active site and interaction between component and promoter. For Cu/ZnO catalyst, ZnO was used for improvement of copper dispersion and stabilization [26]. The synthesis of methanol from carbon monoxide, carbon dioxide, and hydrogen gas consists of 2 routes [27];

1 Direct hydrogenation to methanol of carbon dioxide

Equation 1 $CO_2\,(g) + 3H_2\,(g) \leftrightarrow CH_3OH\,(l) + H_2O\,(g)$

$\Delta H = -87\ kJ/mole$

2 Reverse water gas shifts followed by hydrogenation to methanol

Equation 2 $CO_2\,(g) + H_2\,(g) \leftrightarrow CO\,(g) + H_2O\,(g)$

$\Delta H = +40\ kJ/mole$

Equation 3 $CO\,(g) + 2H_2\,(g) \leftrightarrow CH_3OH\,(l)$

$\Delta H = -128\ kJ/mole$

Table 8 Effect of reaction conditions and catalyst types on CO_2 conversion and methanol selectivity [26]

Catalyst Type	**T [ºC]**	**P [MPa]**	**H_2/CO_2**	**WHSV [mL/gh]**	**CO_2 conversion [%]**	**CH_3OH Selectivity [%]**
Cu/ZnO	250	3	3:01	18000	~11.0	–
Cu@ZnO	250	3	3:01	18000	–	–
Cu/ZrO_2	260	8	3:01	3600	15	86
CuO/ZnO	250	2	3:01	3750	8.6	45
$Cu/ZnO/Al_2O_3$	270	5	3:01	4000	23.7	43.7
$Cu/ZnO/Al2O_3/ZrO_2$	190	5	3:01	4000	10.7	81.8
$Cu/ZnO/Al2O_3/Y_2O_3$	230	9	3:01	10000	29.9	89.7
$Cu/ZnO/ZrO_2/Al_2O_3/SiO_2$	250	5	2.8:1	10000	–	99.72
$Cu/ZnO/Ga_2O_3$	240	4.5	2.8:1	18000	27	50
Cu/TiO_2	260	3	3:01	3600	–	64.7
$Cu/ZrO_2/CNTs$	260	3	–	3600	16.3	43.5
CnZnO@UiO-bpy	250	4	3:01	18000	3.3	100
CuZnO/rGOae	250	1.5	3:01	16,000	–	–

In this study [27], one step reaction was required as shown in the Equation 1 to Equation 3. The kinetics and rate of each reaction are as Equation 4 to Equation 6, also the kinetic parameters were shown as the Table 9**.** 33 percent of carbon oxide was converted to product. The catalyst characteristic and feed stream information are shown in Table 10 and Table 11. The chemical composition along the reactor length was shown as the Figure 11.

Equation 4 $$r_{CH_3OH} = \frac{k_1 P_{CO_2} P_{H_2} - k_6 P_{H_2O} P_{CH_3OH} P_{H_2}^{-2}}{(1 + k_2 P_{H_2O} P_{H_2}^{-1} + k_3 P_{H_2}^{0.5} + k_4 P_{H_2O})^3} \quad [\frac{kmol}{kg_{cat} s}]$$

Equation 5 $$r_{RWGS} = \frac{k_5 P_{CO_2} - k_7 P_{H_2O} P_{CO} P_{H_2}^{-1}}{1 + k_2 P_{H_2O} P_{H_2}^{-1} + k_3 P_{H_2}^{0.5} + k_4 P_{H_2O}} \quad [\frac{kmol}{kg_{cat} s}]$$

Equation 6 $$ln\, k_i = A_i + \frac{B_i}{T}$$

Table 9 Kinetics parameter [27]

Kinetic parameter	**Constant**	**Value**
k_1 [kmol/kg_{cat}sbar^2]	A_1	-29.87
	B_1	4811.2
k_2 [-]	A_2	8.147
	B_2	0
k_3 [1/bar$^{0.5}$]	A_3	-6.452
	B_3	2068.4
k_4 [1/bar^1]	A_4	-34.95
	B_4	14,928.90
k_5 [kmol/kg_{cat}sbar]	A_5	4.804
	B_5	-11,797.50
k_6 [kmol/kg_{cat}s]	A_6	17.55
	B_6	-2249.8
k_7 [kmol/kg_{cat}sbar]	A_7	0.131
	B_7	-7023.5

Table 10 Catalyst Characteristic [27]

Density [kg_{cat}/m^3_{cat}]	1775
Fixed bed porosity [-]	0.5
Mass [g]	34.8
Pellet diameter [m]	0.0005

Table 11 Feed Stream Information [27]

Feed condition	
Mass Flow [kg/s]	$2.8x10^{-5}$
Pressure [bar]	50
Temperature [°C]	220
Feed composition [%mole]	
CO	4
H_2O	0
Methanol	0
H_2	82
CO_2	3
Inert (Ar)	11

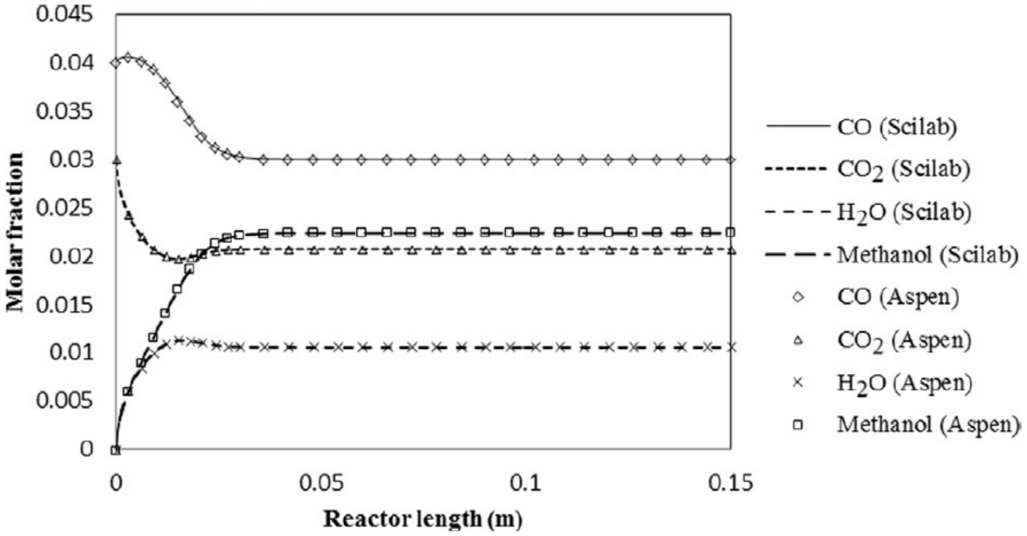

Figure 11 Chemical composition along the methanol synthesis reactor length [27]

2.4 Methanol Synthesis Process

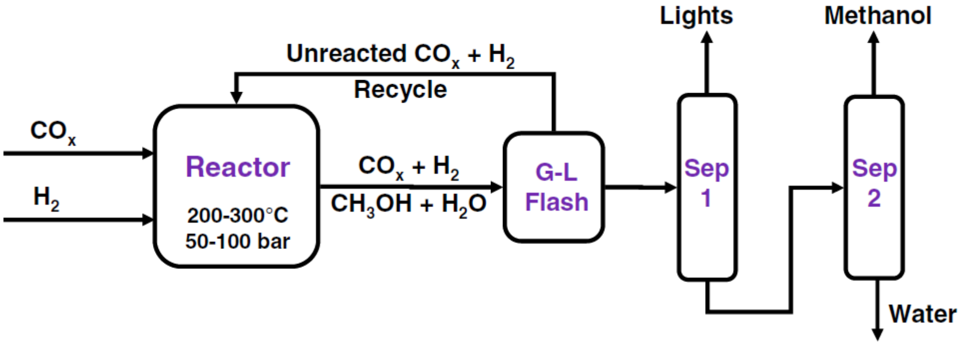

Figure 12 Generic processing scheme for methanol synthesis from syngas or by CO_2 *hydrogenation [28]*

Anton A. Kiss and team showed the typical process for methanol synthesis unit, recycle unit, separation unit and purification unit as Figure 12. Reactor was operated at 200-300 °C and 50-100 bar. Flash drum removed the vapor phase which were unreacted reactant and recycled back to reactor. The liquid phase were sent to separate light gas in separation unit1 (Sep1) and methanol was purified in separation unit2 (Sep2) [28].

The 10 kiloton per year of methanol production process was designed by Anton A. Kiss and team and shown in Figure 13 [28]. The key of their designed process was that there was stripping unit where the hydrogen gas stream which was saturated in water contacted with the product stream. This resulted in carbon dioxide in the product stream could be recycled back to reactor completely and the moisture in hydrogen gas was removed before feeding to the reactor. Then, the raw material was ready for reaction and sent to reactor. After that, the effluent stream from reactor was sent to high-pressure separation unit for removing light gas and low-pressure separation unit for methanol purification.

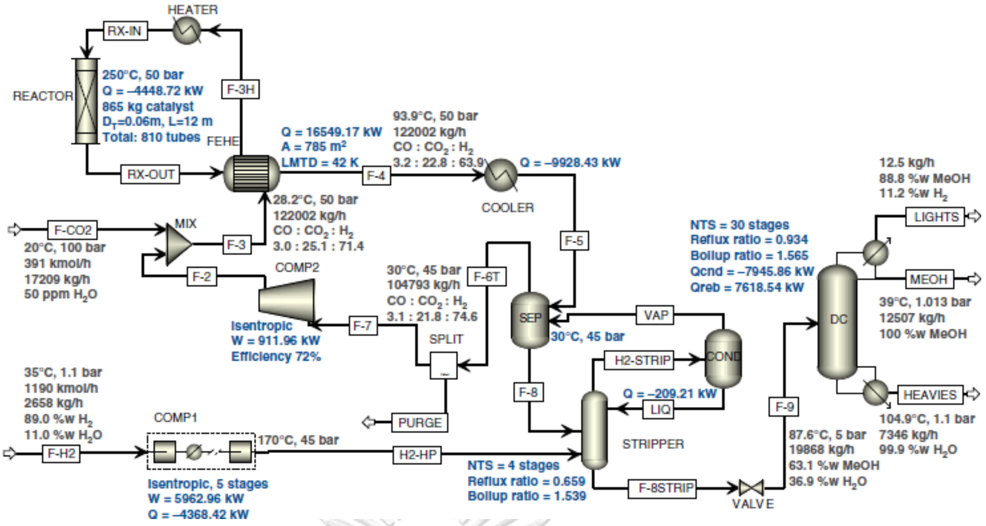

Figure 13 Efficient process for methanol synthesis by CO_2 hydrogenation [28]

Éverton Simões Van-Dal and Chakib Bouallou showed the design and simulation of a methanol in fuel grade production plant from carbon dioxide hydrogenation for methanol production [27]. The process consists of coal plant unit, carbon dioxide capture, methanol synthesis, and water electrolysis unit as shown in Figure 14.

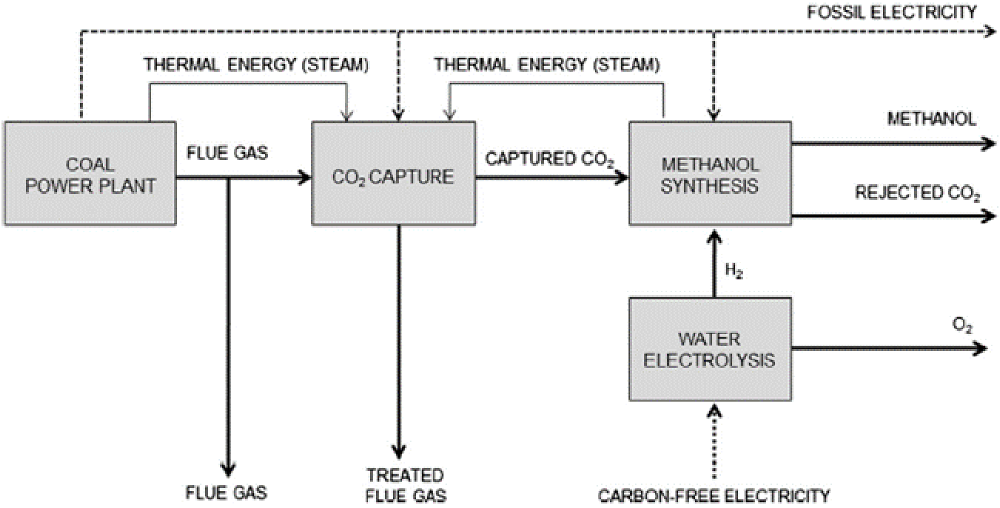

Figure 14 Block diagram of methanol production plant process [27]

Material balance and heat balance were performed by Aspen Plus version 7.3. Modified Hurone-Vidal mixing rules Soave Redlich Kwong (SRK-MHV2), equation of state, was used as the thermodynamics model. The methanol synthesis and purification unit were designed as shown in Figure 15. The number of compressors to pressurize the hydrogen gas was optimized until the desired operating condition was met. The Cu/ZnO/Al_2O_3 catalyst in a catalytic fixed bed reactor was required for the adiabatic operation. The result showed that the reaction yield was 0.67 ton of methanol per ton of carbon dioxide and Table 12 showed the inlet and outlet mass flow of the block diagram.

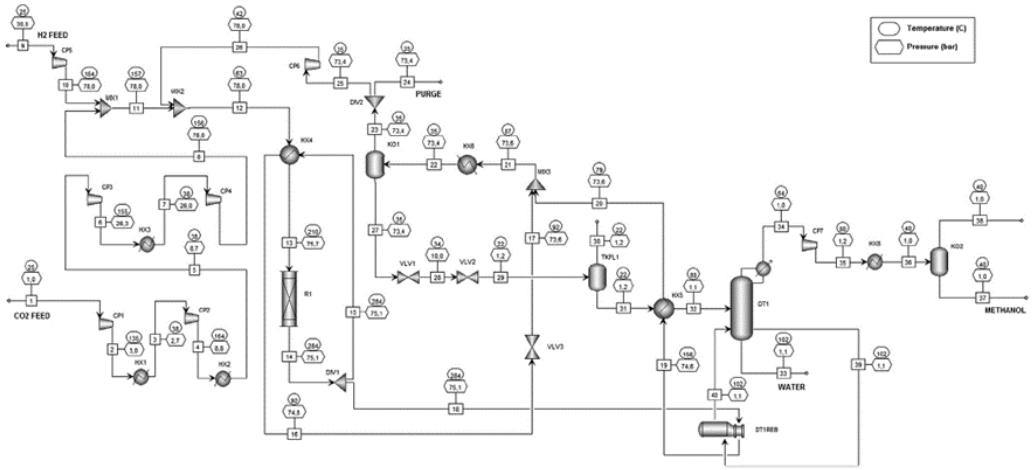

Figure 15 The process design for methanol synthesis and purification unit [27]

Table 12 The mass balance of block flow diagram [27]

Compound	**Inlet [ton/h]**	**Outlet [ton/h]**
CO_2	88	5.82
CO	0	0.51
H_2	0	0.87
H_2O	108.1	33.7
Methanol	0	59.3
O_2	0	96
Monoethanolamine	0.09	0.09

CHAPTER 3 Methodology

This research applied the Aspen Plus version 9 to design and optimize the BHD process and evaluate the feasibility. This methodology in this research was divided to 6 sections, there were

3.1 Verification and Validation

First of all, the important parameters such as operating condition, kinetics of reaction, conversion, selectivity, and yield were required for verification. The conversion of carbon monoxide and carbon dioxide, and yield of BHD were verified with the experimental data which Srifa claimed in Production of BHD by catalytic hydrotreating of palm oil over $NiMoS_2$ -Al_2O_3 catalyst.

For the BHD process, this research applied the process of P. Kittisuppakorn as shown in Figure 10 [25]. Refined palm olein was used as a feedstock consisting of simple triglycerides. The feed composition of refined palm oil was shown as Table 1 [20]. The heterogeneous reaction with the γ-Al_2O_3 supported $NiMoS_2$ catalyst were operated at high temperature, high pressure, and high H_2/oil ratio. This research required data of yield and composition of hydrocarbons. So, the contribution of HDO and DCO/DCO2 reactions were shown as Table 5 and the composition of the BHD product was shown as Table 4 [20].

For the methanol synthesis, the kinetics of the reaction of methanol synthesis and reverse water gas shift were studied and validated to the experiment of E.S. Van-Dal [27] in a fixed bed reactor. The reaction of methanol synthesis was operated adiabatically and the fed gas was at 50 bar and 220 ^{o}C. The reaction condition and kinetics of methanol synthesis unit were implemented in this research.

3.2 Process Design

After both models of the reaction part were verified and validated with the experimental data, the BHD process was designed precisely. In this research, the basis for design was around 25,000 kg/hour of BHD as the commercial process [25] and integrated with the 400 kg/hour of methanol synthesis unit. After combining methanol synthesis to BHD production process, the BHD production process coupled with methanol synthesis could be provided high performance which are reactor unit, vapor-liquid separations process, liquid-liquid separation process, and purification process. Equipment type selection and sizing are selected. Also, the heat integration was performed by pinch analysis. The suitable process consisted of liquid product composition (alkane) as shown in Table 4. Then, the methanol production was designed to reach methanol laboratory grade that was the purity of 99.6 percent by volume [29].

3.3 Utility Design

To minimize the energy consumption, the integration of energy would be analyzed by pinch analysis of the process streams. After that the remaining energy was supplied by utilities such as hot oil, chilling water or cooling water. Selection of utility was analysis in this section.

3.4 Optimization

The optimization was the very important section to find the optimum condition for the operation in units. This work concerned the minimization of methanol synthesis reactor and methanol purification unit. For the methanol synthesis reactor, amount of catalyst was calculated for the 33 percent of conversion as the Éverton Simões Van-Dal claimed [27] by using the design specification tool in Aspen Plus. The inlet temperature was determined after studying effect of inlet temperature on the methanol yield by sensitivity tool. Also, the methanol purification unit was studied for the high purity methanol product. Total stage and reflux ratio of distillation column were studied and the suitable design would be selected.

3.5 Design of Equipment

After the operating conditions of each equipment were optimized, the size of the equipment would be designed accurately. All equipment were sized by Aspen Plus except the reactor design for BHD reactor and methanol synthesis reactor. Both reactors were designed by using information from the literature reviews (i.e., liquid hourly space velocity and conversion of reaction).

3.6 Evaluation of Feasibility

The last section was the feasibility evaluation. This section was to evaluate the designed process for scaling-up to commercial plant. Techno-economic feasibility was concerned with the BHD process and BHD process coupled with methanol synthesis in term of hydrogen and carbon dioxide emission, net present value, internal rate of return and payback period based on the R. Turton and team's method [30]. The optimal process should be worthwhile for investment.

CHAPTER 4 Results and Discussion

In this research, the technical and economic feasibility for BHD production process coupled with the methanol synthesis were studied by using the Aspen Plus version 9.

4.1 Verification and Validation Results

The results are divided to 3 parts

4.1.1 Validation of thermodynamic model

A number of unit operations operated at high pressure, so the equation of state approach was more appropriate than activity model or split approach. The behavior of hydrogen gas and hexadecane ($C_{16}H_{34}$) mixture was selected for thermodynamic validation because these are 2 main components in the process and there is the data in National Institute of Standards and Technology database (NIST) in Aspen Plus. Figure 16 shows the behavior of hydrogen gas and hexadecane ($C_{16}H_{34}$) at 269 ^{o}C compared with NIST. According to the operating condition at 50 bar of pressure and 220-300 ^{o}C of temperature in BHD production process, the Predictive Soave-Redlich-Kwong (PSRK) was used as the thermodynamics model to explain the behavior of gas-liquid equilibrium because it was in good agreement with the data [31].

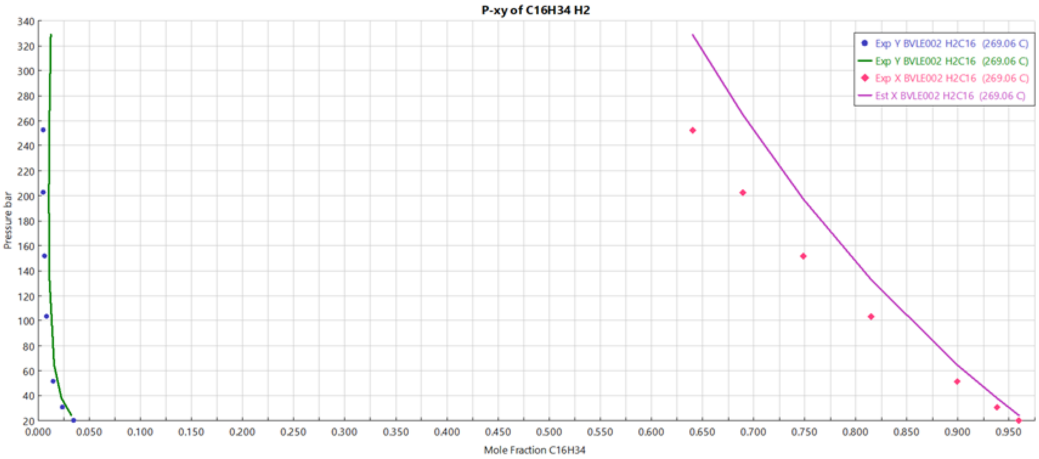

Figure 16 The behavior of hydrogen gas and hexadecane ($C_{16}H_{34}$) at 269 ^{o}C

4.1.2 Verification of BHD production process

The BHD production was the 25,000 kg/hr as P. Kittisupakorn claimed. In Appendix A, the preliminary design for input-output structure was shown in Figure 34 and the BHD production process without heat exchanger network was shown in Figure 36. The rigorous process with heat exchanger network for BHD production was designed and shown as Figure 17. The RBDPO was passed through the pump (P-101) to increase the pressure to 50 bar then heated to 300 ^oC by using 2 heat exchangers (E-101 and E-102). The make-up hydrogen gas reduced the pressure to 50 bar by a pressure reducing valve (V-101). It was preheated (E-103) by the product stream from a reactor (R-101) and then heated up by heat exchanger (E-104) to 300 ^oC by using hot oil as heat resource. After that, the recycle gas stream, make-up hydrogen gas and RBDPO were mixed prior to sending to hydro-deoxygenation reactor (R-101). The complete reactions were taken place in the reactor under 50 bar of pressure and 300 ^oC of temperature. The product stream from the reactor was passed through heat exchangers (E-101, E-103, E-105, and E-107) to transfer heat between product stream and reactants and cooling water, respectively until the temperature of stream was reached to 45 ^oC. Then the effluent stream from heat exchanger (E-107) was sent to a flash separator (F-101) to remove gaseous products from liquid products at 45 ^oC which was limited by cooling water. The 95 % of gaseous products were heated to 300 ^oC by using heat exchangers (E-105 and E-106) and recycled back to the process. However, the remaining gas was purged to the environment. For the liquid product, the pressure was decreased to ambient pressure (1 bar) and flashed by a pressure reducing valve (V-102) and a flash drum (F-102), respectively. The remaining gas was vent out. The liquid product was sent to a decanter (D-101) to separate the BHD from water. Stream compositions and conditions were shown in Table 30 in Appendix A.

The final composition of product (Stream 24) and vent gas (Stream 30) from simulation result were compared with the experimental result of A. Srifa [20] which performed production of BHD by catalytic hydrotreating of palm oil over $NiMoS_2$ -Al_2O_3 catalyst. As shown in Figure 18 and Figure 19, only 5.6 and 8.1 percent error of product and vent gas composition were found. In addition, only 2.8 percent of yield from simulation result was higher than this literature’s result.

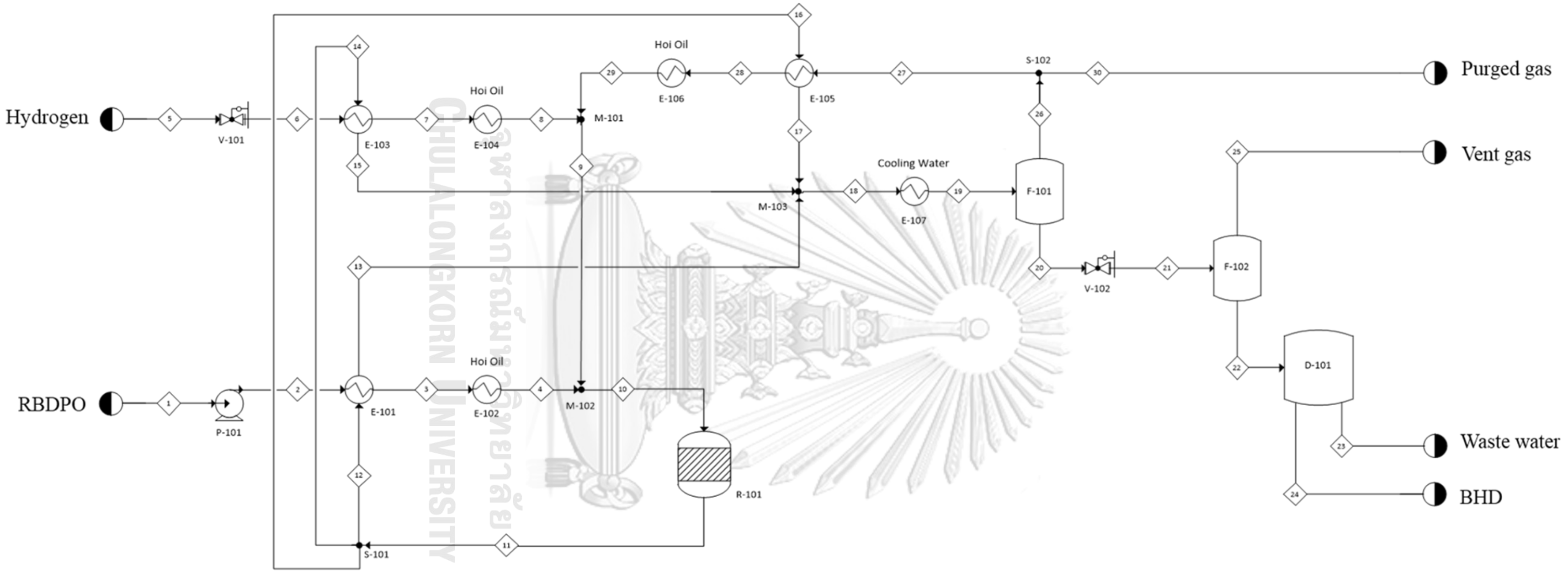

Figure 17 The BHD production process (based case)

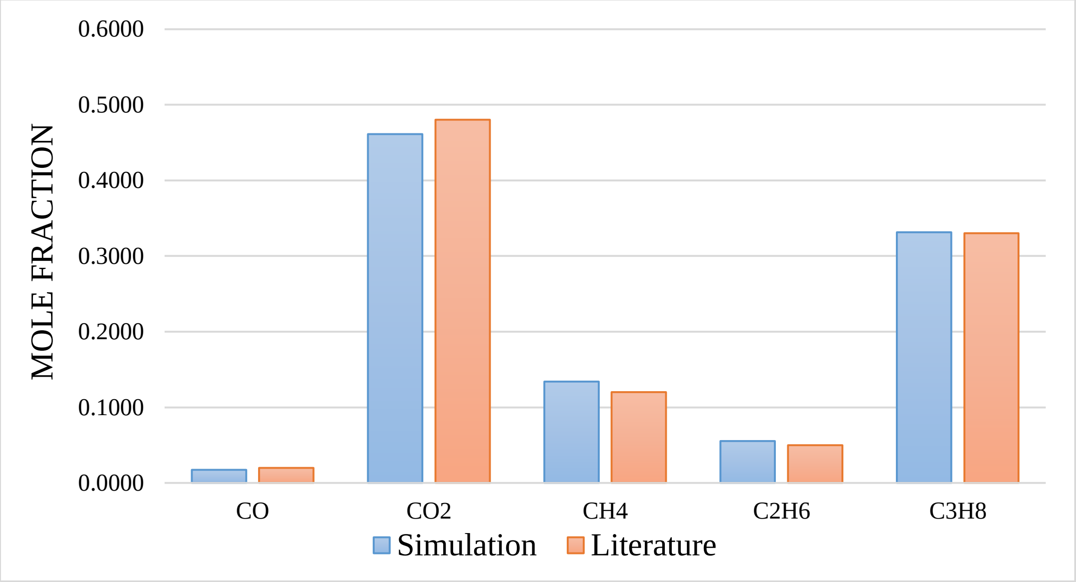

Figure 18 The comparison of composition of by-product gas between simulation results and literature results

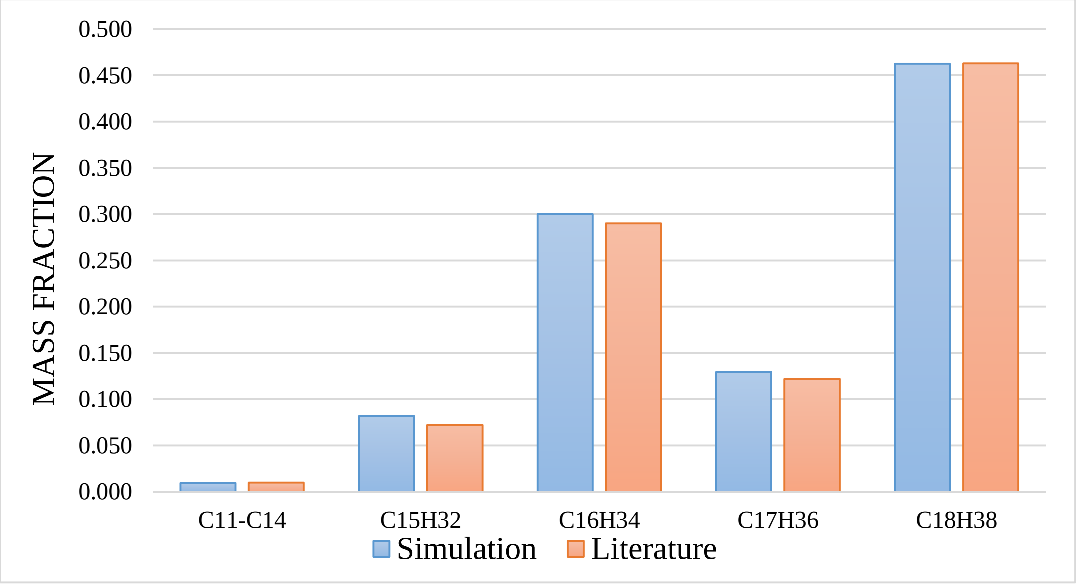

Figure 19 The comparison of composition of BHD composition between simulation results and literature result

4.1.3 Validation of kinetic parameters for methanol synthesis

The kinetic parameters for methanol synthesis provided by Éverton Simões Van-Dal in “Design and simulation of a methanol production plant from CO_2 hydrogenation” [27] shown in Table 9 were applied in this study. Also, the thermodynamic models applied for reactor was modified Hurone-Vidal mixing rules Soave-Redlich-Kwong (SRK-MHV2).

The reaction conditions and feed compositions were shown in Table 11. The simulation used the Langmuir-Hinshelwood-Hougen-Watson model (LHHW) as the reaction rate model [27]. Figure 20 showed the composition along the reactor length from simulation results and they were in good agreement with experimental data. Table 31 in Appendix B showed the raw data of chemical composition along the reactor length for model calculation and experimental data from Éverton Simões Van-Dal [27].

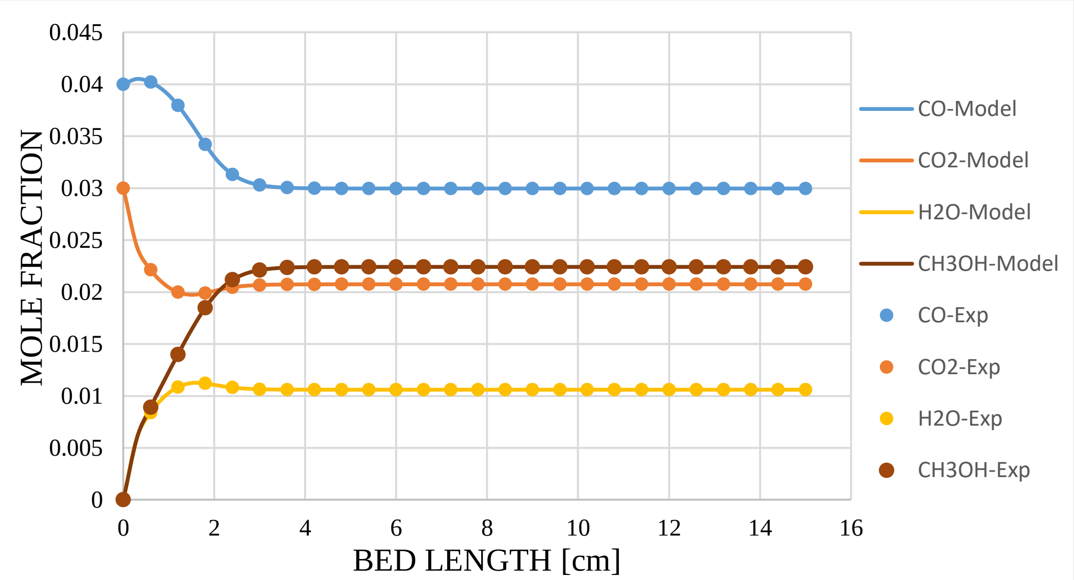

Figure 20 The composition along the reactor length from simulation

4.2 Process Design

The process design for the based case of BHD production process had been designed and shown in the verification section. In this section, the alternative process was developed from the BHD process (based case). So the BHD production process coupled with methanol synthesis was proposed as shown in Figure 21. Figure 35 and Figure 37 in Appendix E show input-output structure and process flow diagram before heat integration for the BHD production process coupled with methanol synthesis, respectively.

The BHD production was the 25,000 kg/hr. It began with pumping the RBDPO to 50 bar by a pump (P-201) and then heating to 300 ^{o}C by using 2 heat exchangers (E-201 and E-202). The make-up hydrogen gas reduced the pressure to 50 bar by a pressure reducing valve (V-201) and it was heated to 300 ^{o}C by the product stream from reactor and hot oil by (E-203 and E-204), respectively. After that, the recycle gas stream, make-up hydrogen gas and RBDPO were mixed prior to sending to hydro-deoxygenation reactor (R-201). The complete conversion was assumed. Thus, all reactants were converted to BHD and by products under pressure of 50 bar and temperature of 300 ^{o}C of temperature. Next, the product stream was cooled down to 45 ^{o}C by heat transfer with the reactants and cooling water (E-201, E-203, E-205, E-207, E-208 and E-209). Then the effluent stream from heat exchanger (E-207) was sent to a flash separator (F-201) to remove gaseous products from liquid products. The 95 % of gas were heated to 300 ^{o}C by using heat exchangers (E-205 and E-206) and recycled back to the process; however, the remaining gas was sent to the methanol synthesis unit. For the liquid phase, the pressure was decreased to ambient and flashed by a pressure reducing valve (V-202) and a flash drum (F-202), respectively. The remaining gas was vent out. The liquid product was sent to a decanter (D-201) to separate the BHD and water.

For the methanol synthesis, the purged gas (Stream 33) from hydro-deoxygenation reaction consisting of excess hydrogen, carbon dioxide, carbon monoxide, water, and some light hydrocarbons were mixed with the additional pure carbon dioxide. Then it was heated to 220 ^{o}C by a heat exchanger (E-208) and mixed with another recycle gas (Stream 65) at the same condition. Then this stream was sent to a fixed bed reactor for methanol production (R-202). The methanol synthesis reaction and reverse water gas shift reaction took place in the reactor. The product from the reactor was sent to heat exchangers (E-210, E-211, and E-212) and a flash drum (F-203) for heat removal to 60 ^{o}C and vapor-liquid separation, respectively. 5 % of gas from vapor stream of flash drum was purged while the other was heated to 220 ^{o}C by E-209 and E-210 before recirculation to R-202. The liquid from F-203 was sent to a pressure reducing valve (V-203) to release the pressure to 3 bar. Then the other flash drum (F-204) was used for gas ventilation. While all liquid product from F – 204 was released the pressure by V-204 to 2.7 bar. Then it passed through the heat exchanger (E-211) to heat to bubble point temperature (101.6 ^{o}C) before entering to the distillation column (T-201) with mixed condenser for methanol purification. Thus, remaining light gas could be removed at the overhead stream. Water was separated from methanol at the bottom stream and it passed through V-206 and E-216 before sending to the waste treatment process. Finally, high purity methanol was obtained at the overhead of column. At the end, it was sent to a valve (V-204) and a heat exchanger (E-214) for the operation at product condition as shown in Table 32 in Appendix C.

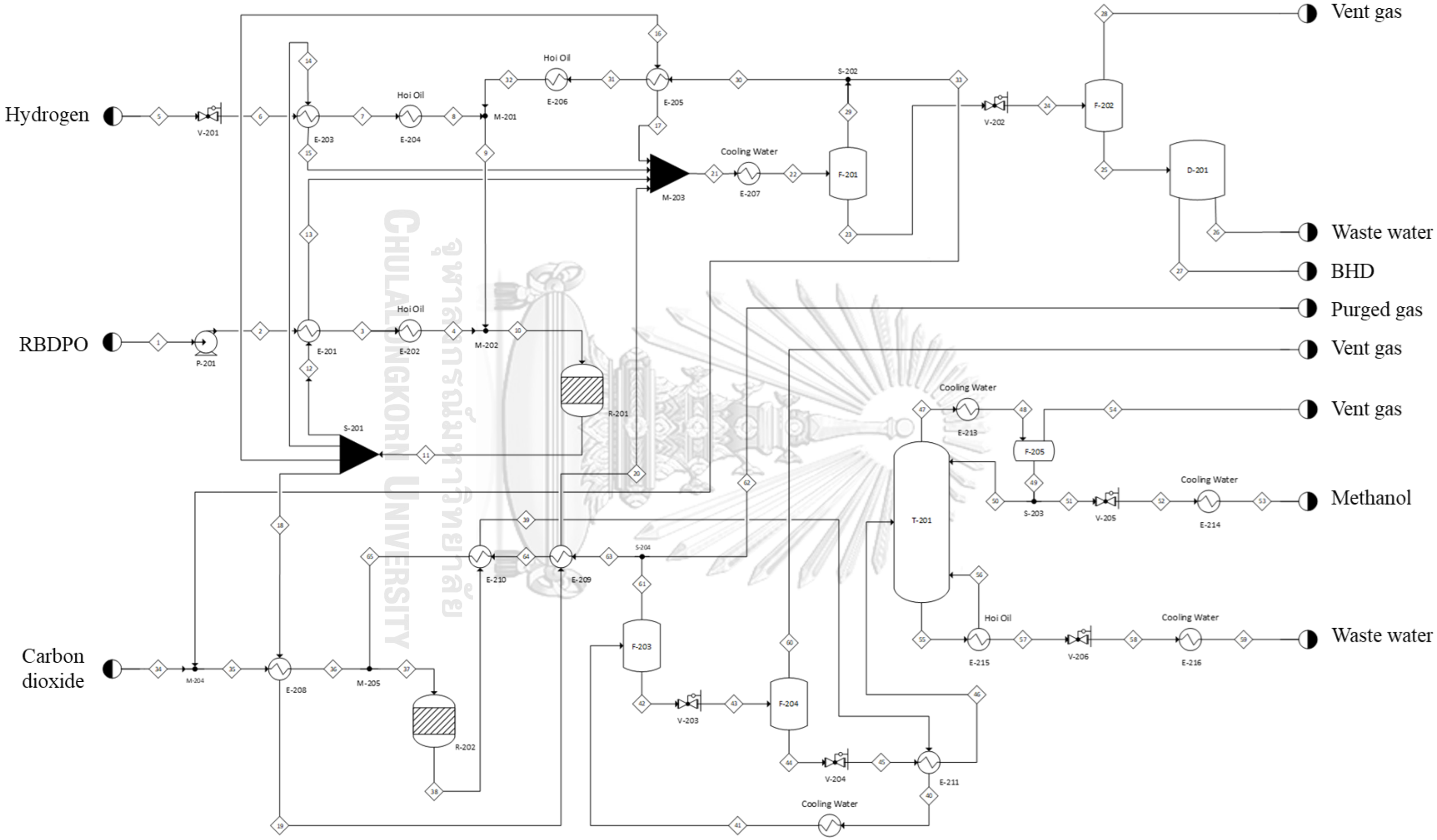

Figure 21 The BHD production process coupled with methanol synthesis

4.3 Utility Design

In this section, heat integration was focused on reducing hot utilities and cold utilities. This study showed how to minimize the utility sources for BHD production and BHD production coupled with methanol synthesis. Figure 37 in Appendix E showed process before heat integration. Table 43 and Table 44 in Appendix E showed the temperature-enthalpy of the stream for each heat exchanger after heat integration in both processes.

For the BHD production, there were 3 cold streams (i.e., make-up hydrogen stream (Stream 5), RBDPO stream (Stream 1) and recycled gas stream (Stream 27)) and 1 hot stream (Stream 11). The hot stream could supply heat for feed preparation before the reaction. Thus, minimum number of heat exchanger was 4 units. In this process, it required 14763 kilowatt for cold utility and 11851 kilowatt for hot utility. After heat integration, the cold streams received the energy from hot stream and this process required 3 more heat exchangers. The outsource utility was required in case energy management through heat integration was not sufficient. Figure 22 showed the utility requirement for BHD production before and after heat integration. The heat exchanger network could reduce the 77 percent of cold utility and 96 percent of hot utility of this process or 11384 kilowatt.

For the BHD production coupled with methanol synthesis, there were 7 cold streams (i.e., make-up hydrogen stream (Stream 5), RBDPO stream (Stream 1), recycled gas stream for BHD synthesis (Stream 30), feed stream of methanol synthesis (Stream 37), recycled gas stream for methanol synthesis (Stream 63), feed stream for methanol purification (Stream 46), bottom stream of distillation column (Stream 55)) and 5 hot streams (BHD product stream from BHD synthesis reactor (Stream 11), methanol product stream from methanol synthesis reactor (Stream 38), overhead product stream of distillation column (Stream 47), methanol product stream (Stream 52), and waste water stream (Stream 58)). The minimum number of heat exchanger was 12 units. Figure 23 showed the utility requirement for BHD production coupled with methanol synthesis before and after heat integration. Without the heat exchanger network, this process required 18177 kilowatt for cold utility and 14985 kilowatt for hot utility. After heat integration, outsource utility was required only 4202 kilowatt for cold utility and 1010 kilowatt for hot utility. The heat exchanger network could reduce the 77 percent of cold utility and 93 percent of hot utility of this process or 13975 kilowatt. But this process required 4 more heat exchangers.

For both processes, the cooling water was used as the cold utility because its temperature was able to remove heat from the overall process. Also, the hot oil was required for using as the hot utility instead of the furnace due to very high temperature range (280-320 ^{o}C) [32] and easy for operation.

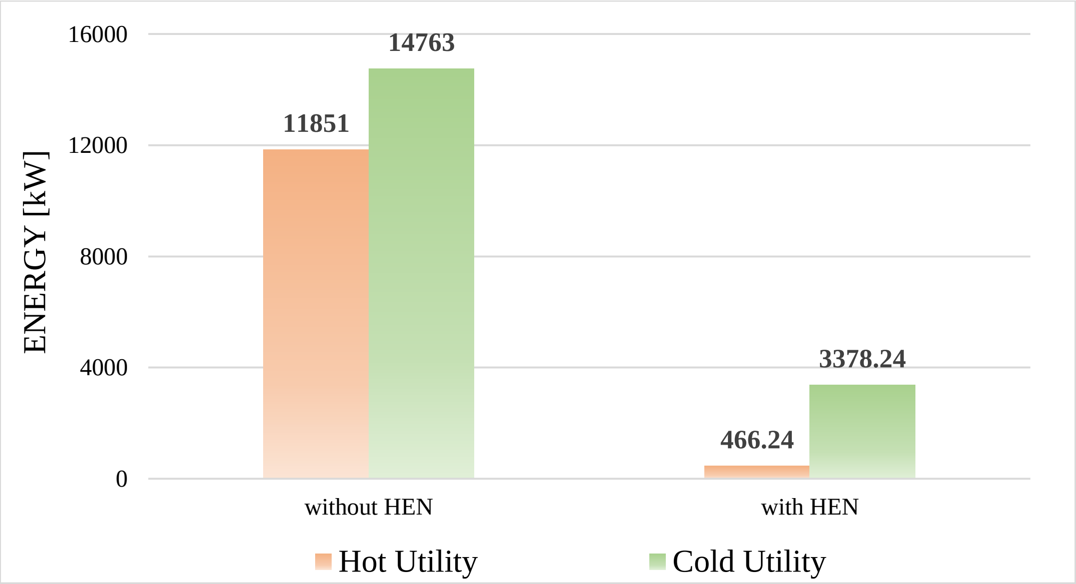

Figure 22 Hot and cold utilities for BHD production process

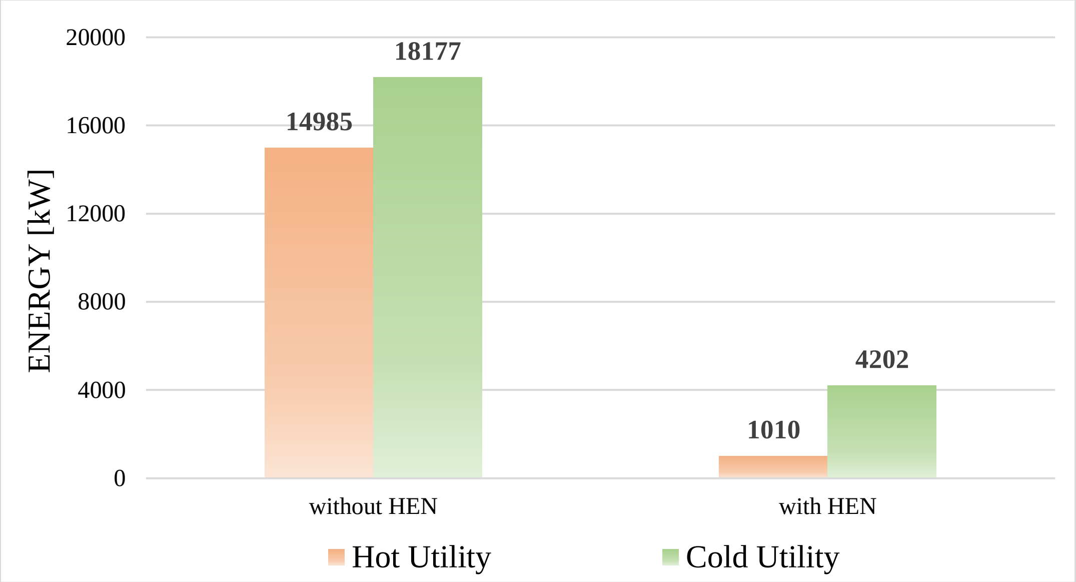

Figure 23 Hot and cold utilities for BHD production process coupled with methanol synthesis

4.4 Optimization

This study showed the optimization of the methanol synthesis unit in BHD coupled production process with the methanol synthesis. The operation of condition of methanol synthesis reactor and purification unit were discussed in this section.

4.4.1 Methanol synthesis reactor

From the literature review, the operating condition studied in Design and simulation of a methanol production plant from CO_2 hydrogenation was at 50 bar and 220 ^{o}C [27]. It provided the kinetic model parameters as LHHW model. This study showed the optimization of operating condition such as inlet temperature and catalyst weight which resulted in high yield of methanol. Figure 24 and Figure 25 showed the effects of inlet temperature and catalyst weight on amount of methanol in effluent stream from the reactor.

The inlet temperature could improve the methanol yield as shown in Figure 24. The maximum yield of methanol of 28.9 kilomole per hour was performed in 220 °C of inlet temperature. Figure 24 also performed that the outlet temperature was increasing with an increase in an inlet temperature due to the exothermic reaction of methanol synthesis reaction [27]. The temperature difference between inlet stream and outlet stream was less than 10 percent of inlet temperature, so it could be operated adiabatically.

Methanol yield was improved with an increase in inlet temperature. However, the opposite trend was performed when temperature is higher than 220 °C. The higher temperature increased reverse water-gas shift reaction equilibrium constant due to the endothermic reaction and decreased the methanol synthesis reaction equilibrium constant which is the exothermic reaction [27].So the carbon dioxide was likely to convert to carbon monoxide more than methanol.

Amount of packing catalyst in the reactor could also improve the methanol yield because it related to the reaction rate. But increasing catalyst weight was not worth for increasing yield as shown in Figure 25. In this study, the optimal amount of catalyst weight for 33 percent of conversion as claimed in literature review [27] was 1041 kilogram which was the result from design specification tool in Aspen plus.

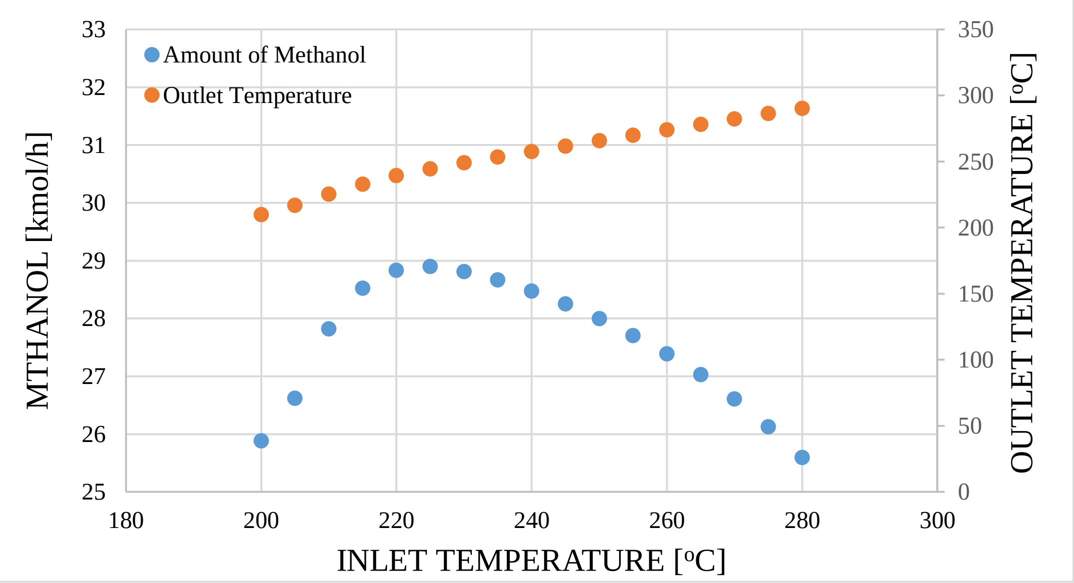

Figure 24 Effect of inlet temperature on amount of methanol and outlet temperature

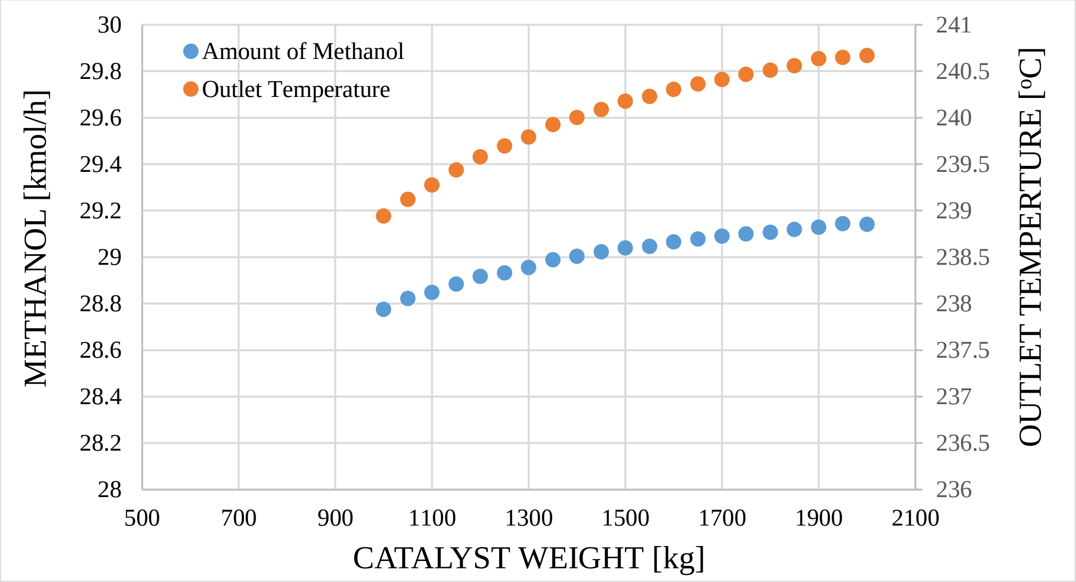

Figure 25 Effect of catalyst weight on amount of methanol and outlet temperature

4.4.2 Methanol purification unit

Methanol product required 96.5% by volume of purity [29]. So, the product from methanol synthesis reactor was sent to separate the unreacted reactant and by-product from the methanol by flash drums and distillation column with partial condenser. The flash drum removed vapor of unreacted reactant from the reactor (R-202) at 60 °C under high pressure and low pressure, respectively. Then, the methanol was sent to purify by distillation column. The methanol product was obtained at the overhead product and water was obtained at the bottom product. The distillation column was preliminary designed by DSTWU model before rigorous designed by Radfrac model. The preliminary design by DSTWU model from Aspen plus shows that distillation column required 18 stages, feed stage was above the 12th stage and the reflux ratio was at 3 for 93% of high purity methanol yield. The condenser was operated at 2 atm and 78.9 °C and reboiler was operated at 2.7 atm and 123.8 °C. After studying rigorous design by RadFrac model, the number of stages vs reflux ratio was shown in Figure 26. To select the suitable condition, it should be considered between construction cost and utility cost which depends on number of stages and reflux ratio, respectively. The 18 stages distillation column and operated the reflux ratio at 3 was selected for this study.

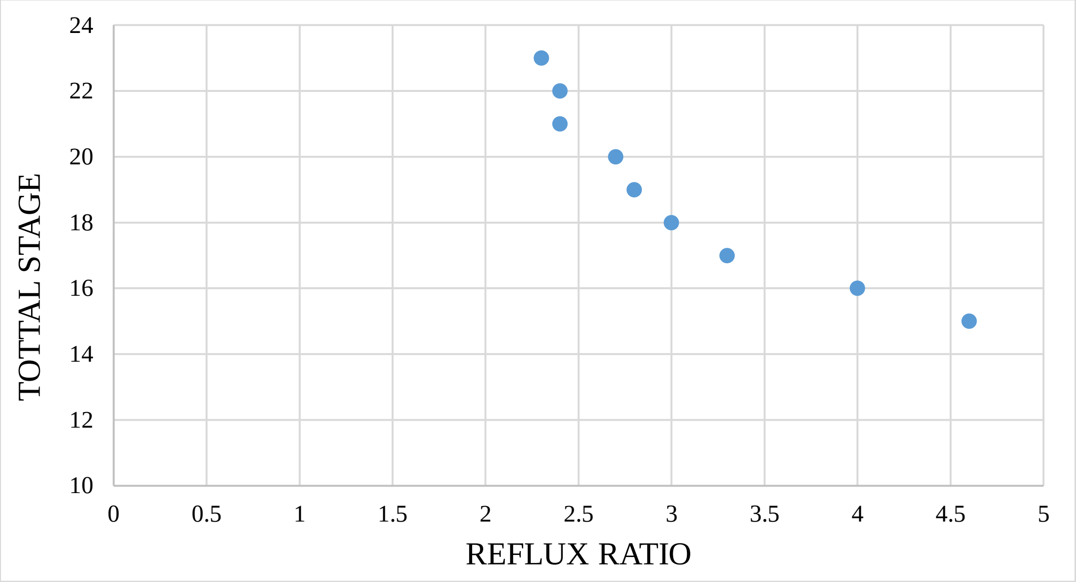

Figure 26 The number of stages vs reflux ratio for methanol distillation column

4.5 Design of the Equipment

There were a lot of equipment in the BHD production process and the BHD production process coupled with methanol synthesis. Table 13 shows the number of each equipment in both processes. Most of equipment in BHD production process were similar to the second process except the numbers of heat exchangers. So they were the same size in both processes except heat exchangers.

Table 13 Number of equipment in each process

Equipment	BHD Production Process	BHD Production Process with Methanol Synthesis
Reactor	1	2
Pump	1	1
Valve	2	6
Heat Exchanger	7	16
Flash Drum	2	5
Decanter	1	1
Distillation Column	0	1

For material of construction, stainless steel was be selected for all equipment in both process. Because it can be used at high temperature and high pressure [33]. And it was compatible with hydrogen, RBDPO, BHD, methanol, and waste water which was main chemicals in process [34].

4.5.1 BHD production process

1 Design of reactor

In this process, there was only 1 reactor for the BHD production. This reactor was designed as the trickle-bed reactor due to the heterogeneous catalytic reaction and operated under isothermal condition as shown in the Table 14. Therefore, this reactor sizing was determined based on heat exchanger. The influent stream was divided to 10 streams for 10 parallel trickled-bed reactors because it required very low flowrate for reaction (LHSV = 1 h^{-1}). Then, all 10 streams were combined after reactor. Table 15 shows the reactor type and size. Calculation of equipment design was shown in Appendix E.

Table 14 BHD reaction condition

Parameters	**Value**
Pressure [bar]	50
Temperature [ºC]	300
H_2/Oil ratio [Ncm^3/cm^3]	500
Liquid hourly space velocity [h^{-1}]	1
Catalyst weight [ton]	76.4

Table 15 BHD reactor type and size for BHD production process

Reactor	**Heat transfer area [m^2]**	**Front end TEMA**	**Shell TEMA**	**Rear end TEMA**
R-101	1742.5	B	E	M

2 Design of pump

There was a pump in this process for feed preparation. The RBDPO was pressurized to reaction condition at 50 bar. This design was calculated from Aspen plus, the result was shown in Table 16.

Table 16 Pump information (BHD production process)

Pump	**Type**	**Liquid flow rate [l/min]**	**Fluid head [m]**	**Design pressure [barg]**	**Efficiency [fraction]**
P-101	Centrifugal	1878	1678.62	52.43	0.70

3 Design of decanter and flash drum

In this process, flash drums were used for vapor-liquid separation under high and low pressure. Decanter separated two liquid phases which were BHD and water. Table 17 showed the design of decanter and flash drum at the optimal condition from Aspen plus. Thickness of vessel can be determined by Equation 12 as shown in Appendix F.

Table 17 Decanter and flash drum information (BHD production process)

Drum	**Vessel thickness [m]**	**Vessel diameter [m]**	**Vessel height [m]**	**Design pressure [barg]**
D-101	0.0063	1.524	4.72	1.03
F-101	0.0870	1.68	4.88	52.43
F-102	0.0063	1.52	4.88	1.03

4 Design of heat exchanger

There were 7 heat exchangers in this process after heat integration. All heat exchangers were shell and tube heat exchanger which were BEM of TEMA symbol. Table 18 showed the heat transfer area for heat exchanger from Aspen plus estimation.

Table 18 Heat exchanger information (BHD production process)

Heat Exchanger	**Heat transfer area [m^2]**	**Front end TEMA**	**Shell TEMA**	**Rear end TEMA**
E-101	203	B	E	M
E-102	17	B	E	M
E-103	63	B	E	M
E-104	3.62	B	E	M
E-105	292	B	E	M
E-106	20	B	E	M
E-107	229	B	E	M

4.5.2 BHD production process coupled with methanol synthesis

1 Design of reactor

In this process, there were 2 reactors which are BHD reactor and methanol synthesis reactor. The reactor sizing of BHD reactor was similar to the first process. For methanol synthesis reactor, it was adiabatically operated under the high pressure and high temperature condition as shown in Table 19. It was designed as packed bed reactor. The design was shown in Table 20.

Table 19 Methanol synthesis reaction condition

Parameters	Value
Pressure [bar]	50
Temperature [°C]	220
Catalyst weight [kg]	1041

Table 20 BHD reactor and methanol synthesis reactor type and size

Reactor	**Heat transfer area [m^2]**	**Front end TEMA**	**Shell TEMA**	**Rear end TEMA**
R-201	1742.5	B	E	M
Reactor	**Vessel thickness [m]**	**Vessel diameter [m]**	**Vessel height [m]**	**Design pressure [barg]**
R-202	0.027	0.48	9.4	52.43

2 Design of pump

In this process, only 1 pump was required in the BHD production unit. The equipment sizing from Aspen plus result was similar to the first process as shown in Table 21. However, there was no pump installation in the methanol synthesis production unit.

Table 21 Pump information (BHD production process coupled with methanol synthesis)

Pump	**Type**	**Liquid flow rate [l/min]**	**Fluid head [m]**	**Design pressure [barg]**	**Efficiency [fraction]**
P-201	Centrifugal	1878	1678.62	52.43	0.70

3 Design of decanter and flash drum

There were 1 decanter and 5 flash drums in BHD production process coupled with methanol synthesis. Table 22 showed the design of each vessel from Aspen plus. There were only F-203, F-204, and F-205 which were added from the bio-hydrogenated production process for vapor-liquid separation in methanol synthesis part. Equation 12 in Appendix F showed the calculation method for vessel thickness.

Table 22 Decanter and flash drum information (BHD production process coupled with methanol synthesis)

Drum	**Vessel thickness [m]**	**Vessel diameter [m]**	**Vessel height [m]**	**Design pressure [barg]**
D-201	0.0063	1.524	4.72	1.03
F-201	0.0870	1.68	4.88	52.43
F-202	0.0063	1.52	4.88	1.03
F-203	0.0489	0.91	3.66	52.43
F-204	0.0063	0.91	3.66	2.43
F-205	0.0063	0.91	2.74	2.43

4 Design of heat exchanger

There were 16 heat exchangers for BHD production process coupled with methanol synthesis. Most of these were BEM type of TEMA symbol except the reboiler of distillation column which was BKU or reboiler type. Table 23 showed the results of heat transfer area for each unit from Aspen plus.

Table 23 Heat exchanger information (BHD production process coupled with methanol synthesis)

Heat Exchanger	Heat transfer area [m^2]	Front end TEMA	Shell TEMA	Rear end TEMA
E-201	1461	B	E	M
E-202	101	B	E	M
E-203	310	B	E	M
E-204	15	B	E	M
E-205	1659	B	E	M
E-206	86	B	E	M
E-207	1092	B	E	M
E-208	11	B	E	M
E-209	68	B	E	M
E-210	455	B	E	M
E-211	6	B	E	M
E-212	180	B	E	M
E-213	17	B	E	M
E-214	6	B	E	M
E-215	10	B	K	U
E-216	7	B	E	M

5 Design of distillation column

The distillation column was required for methanol purification. The design of distillation column was obtained from Aspen plus was shown as Table 24. It required 18 stages including reboiler and condenser to purify the methanol.

Table 24 Distillation Column information (BHD production process coupled with methanol synthesis)

Tower (T-201)	Tower thickness [m]	Tower diameter [m]	Tower height [m]	Design pressure [bar]
Vessel	0.0063	0.6096	17.68	3.43
Tower (T-201)	**Tray type**		**Tray spacing [m]**	
Tray	Sieve		0.6096	

4.6 Evaluation of Feasibility

This section revealed the technical feasibility and economic feasibility for the BHD production process coupled with methanol synthesis compared with the BHD production process. Hydrogen recovery and carbon dioxide and carbon monoxide emission were considered for technical feasibility comparison. For the economic feasibility, this study compared payback period, internal rate of return, and net present value as the main parameters.

4.6.1 Technical feasibility

Hydrogen was one of main raw materials for producing the BHD. According to high H_2/oil volume ratio for reaction, excess hydrogen remained in the effluent stream of the BHD reactor. Thus, the excess hydrogen was returned to the process. However, the purged hydrogen before recirculation was required to attain the convergent material balance. This purged hydrogen stream could be converted to high-value added product such as methanol and it reacted with make-up carbon dioxide. The benefits of this process were hydrogen recovery and the reduction of carbon dioxide emission. Appendix D showed the calculation of technical feasibility for both processes.

Figure 27 showed the discharged hydrogen from the BHD production process compared with the BHD production process coupled with methanol synthesis. It implied that the BHD production process coupled with methanol synthesis could reduce the purged hydrogen 46.26 percent or 87.82 kilogram per hour. Moreover, it could deduct the carbon dioxide and carbon monoxide emission from the process and utility 9.51 percent or 350 kilogram per hour. In addition, make-up the carbon dioxide from the other process was saved 4.5 percent of process or 164.5 kilogram per hour.

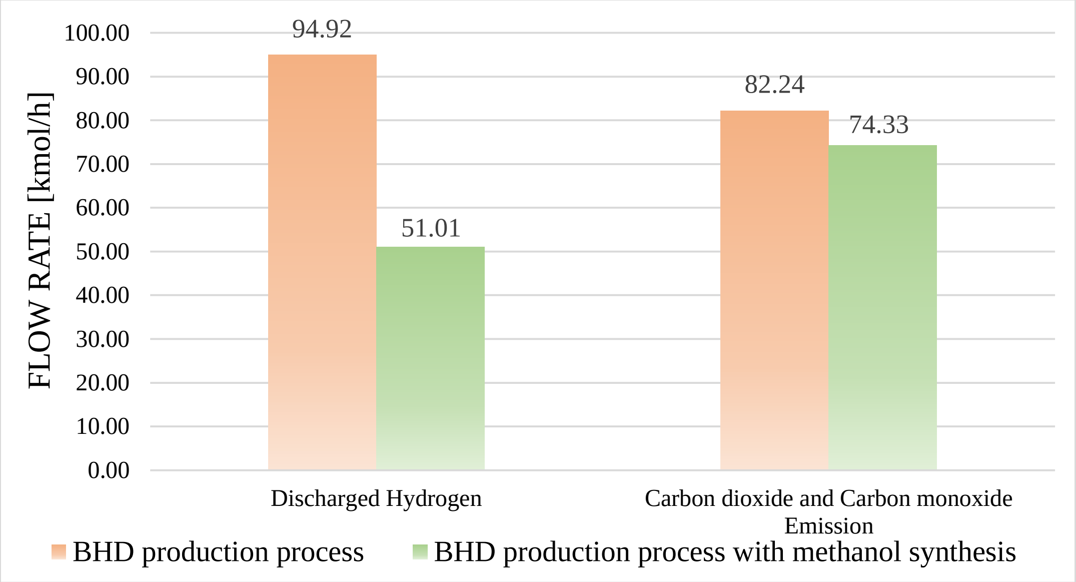

Figure 27 Comparison of discharged hydrogen and carbon dioxide emission

4.6.2 Economic feasibility

Economic analysis was an indicator that could perform the suitable process in terms of economic criteria such as fixed capital investment, net present value, rate of return and payback period. All calculation method of each parameter by using R. Turton and team method [30] was shown in Appendix F.

The capital cost or fixed capital investment (FCI_L) was shown in Figure 28. According to a lot of equipment in methanol synthesis unit, the FCI_L of the BHD process coupled with methanol synthesis was higher than the first process around 34.0 percent or 5.54 million US dollars. Most of fixed capital investment of both processes was spent for BHD reactor around 12.46 million US dollars because of the large size and the number of BHD synthesis reactor.

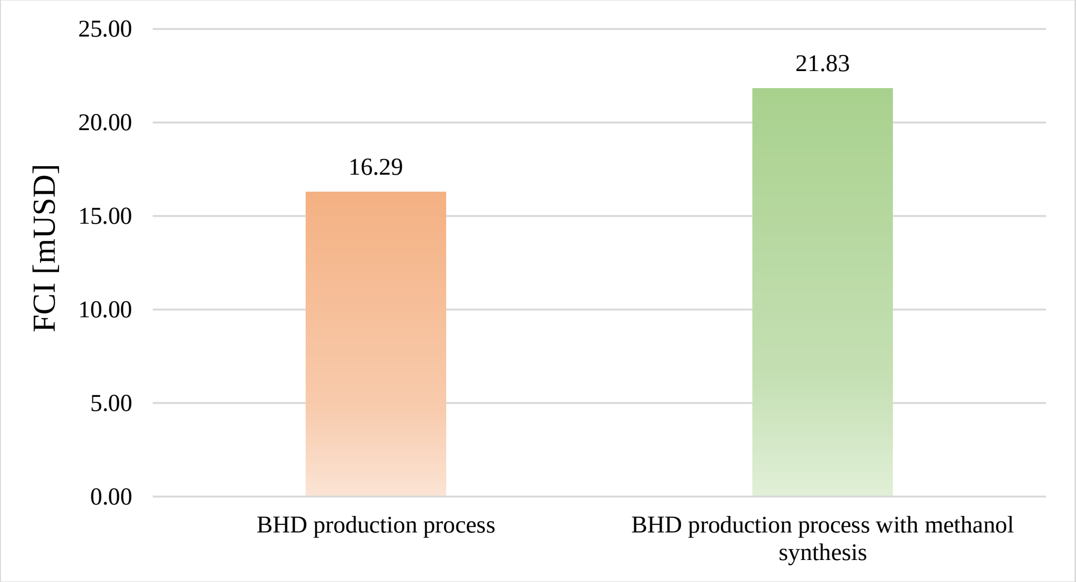

Figure 28 Comparison of fixed capital investment of both processes

Also, Table 25 showed the comparison of cost of raw materials, cost of utilities, cost of waste treatment, and cost of operation labor. These costs were the main parameter of the manufacturing cost. Appendix F showed the cost of each raw materials and utilities in Table 55 and Table 56, respectively. For the operating labor cost and waste treatment cost estimation were shown in Appendix F. Table 26 showed the manufacturing cost which consisted of direct manufacturing cost, fixed manufacturing cost, and general manufacturing expense of both processes. It seemed that there was no significant difference in manufacturing cost for both processes. Because cost of raw materials and other costs of both processes were similar.

Table 25 Comparison of cost of utilities, cost of raw material, cost of waste treatment, and cost of operation labor

Cost [mUSD/year]	**BHD production process**	**BHD production process coupled with methanol synthesis**
Raw material	152.1	152.1
Utility	0.58	0.91
Waste treatment	0.0013	0.0015
Operating labor	0.85	0.98

Table 26 Cost of manufacturing for both process

Cost of Manufacturing without depreciation		**BHD Process [mUSD]**	**BHD Process with Methanol Synthesis [mUSD]**
1. Direct Manufacturing Cost			
	a. Raw material	152.09	152.11
	b. Waste treatment	0.0013	0.0015
	c. Utilities	0.58	0.91
	d. Operating Labor	0.85	0.98
	e. Direct supervisory & clerical labor	0.15	0.18
	f. Maintenance & repairs	0.98	1.31
	g. Operating supplies	0.15	0.20
	h. Laboratory Charges	0.13	0.15
	i. Patents and royalties	5.79	5.85
2. Fixed Manufacturing Cost			
	a. Depreciation	1.63	2.18
	b. Local taxes & insurance	0.52	0.70
	c. Plant overhead cost	1.19	1.48
3. General Manufacturing Expenses			
	a. Administration costs	0.30	0.37
	b. Distribution & selling costs	21.23	21.44
	c. Research & development	9.65	9.74
Total Cost of Manufacturing without depreciation		193.04	194.88

For the engineering economic analysis in this study, the economic parameters were payback period, internal rate of return, and net present which were considered under assumptions as shown below;

1. 8000 hr of production per year and 10 years operation
2. Working Capital = 15 percent of FCI_L [30]
3. Tax rate = 35 percent [30]
4. Salvage = 5 percent of FCI_L [30]
5. Land = 2 percent of FCI_L [35]
6. Discount rate = 10 percent per annual [30]
7. Depreciation was calculated by Modified Accelerated Cost Recovery System (MACRS).
8. Product price = $0.78 USD per L of BHD [36] and 6 USD per kg of methanol [37]
9. Each costs were calculated to the cost based on 2018.
10. Plant was constructed in 2 years which was divided into 2 phases. 50 percent was built in the first year. And another was done in the second year.

The cumulative cash flow for each process was shown as the Figure 29. It implied that although BHD production process coupled with methanol synthesis had to be spent more in fixed capital investment, the internal rate of return of this process was also more than BHD production process. Moreover, this process spent shorter time to payback and had more net present value due to higher price of high purity methanol.

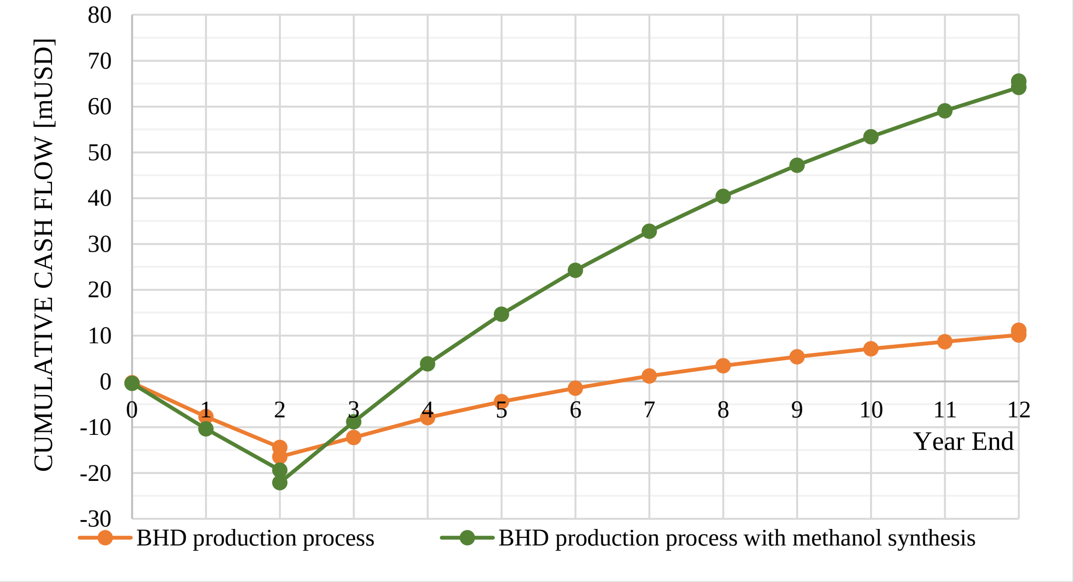

Figure 29 Cumulative cash flow for both process

The additional product which was high purity methanol could improve the existing process economy as shown in Figure 30. In spite of higher investment cost, it increased the internal rate of return from 16.47 percent to 39.65 percent. Additional construction cost of methanol synthesis unit did not effect on economic indicators such as NPV and IRR. Furthermore, the price of high purity methanol was very high. The second process was able to shorten the payback period from 4.49 years to 1.68 years or 62.58 percent. Also, the net present value after 10 years-operation was increased from 11.16 million US dollars to 65.57 million US dollars which was around 487 percent.

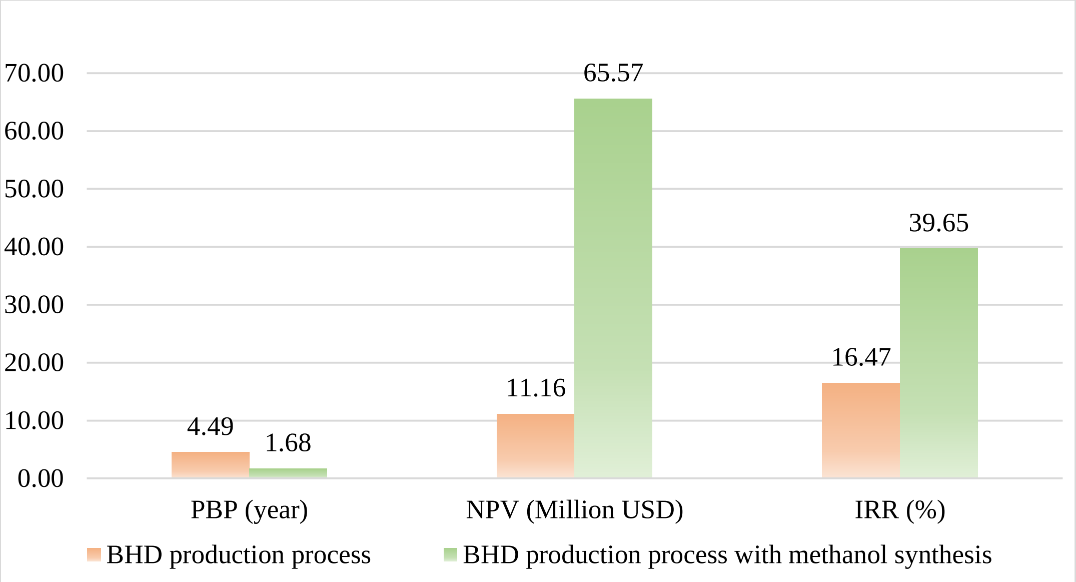

Figure 30 Comparison of economic engineering parameters

It was an interesting issue to investigate the fluctuation of RBDPO cost [38] and diesel price [36] because the raw material cost and product price were used to estimate the revenue and it effected on decision for investment in each process. Figure 31 showed the RBDPO cost and diesel price since 2000 until 2018. Figure 32 and Figure 33 showed the internal rate of return and net present value which are determined from the RBDPO cost and diesel price in each year, respectively. For the methanol price, it is around 4 to 8 US dollars per kilogram [37]. It is higher than BHD's price around 5 to 10 times. The values of payback period, net present value and internal rate of return for the lowest price of methanol, 4 US dollars per kilogram, are around 2.2 years, 44 million US dollars, and 29.79 percent, respectively. So, BHD production process coupled with methanol synthesis was still better than the BHD production process in terms of economic feasibility. Therefore, the fluctuation of methanol price did not effect on the economic feasibility significantly.

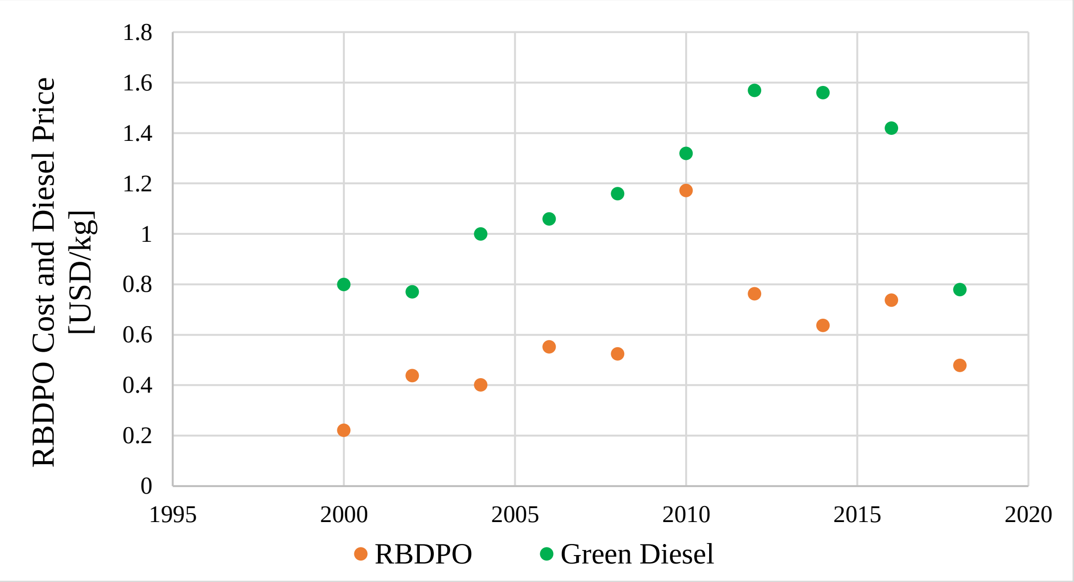

Figure 31 The RBDPO cost [38] and diesel price [36] since 2000

In 2010, the results were shown in negative internal rate of return and net present value for both processes because gap between diesel price and RBDPO cost was less than 0.521 USD per kilogram which was acceptable difference for profit. Although there is an additional methanol production, it cannot improve these economic parameters. In 2002 and 2018, the gap was between 0.521-0.80 USD per kilogram. The more gap difference led to an increase in internal rate of return and net present value of the combination process than the BHD production process. Because profit from methanol increased the total revenue, so it could improve all economic parameters.

Unless the gap was less than 0.80 US dollars per kilogram the BHD production process could enhance high internal rate of return because the stand-alone BHD production resulted in higher revenue than methanol production. So, profit obtained from methanol was not worth for additional methanol synthesis. But the methanol synthesis still made higher net present value.

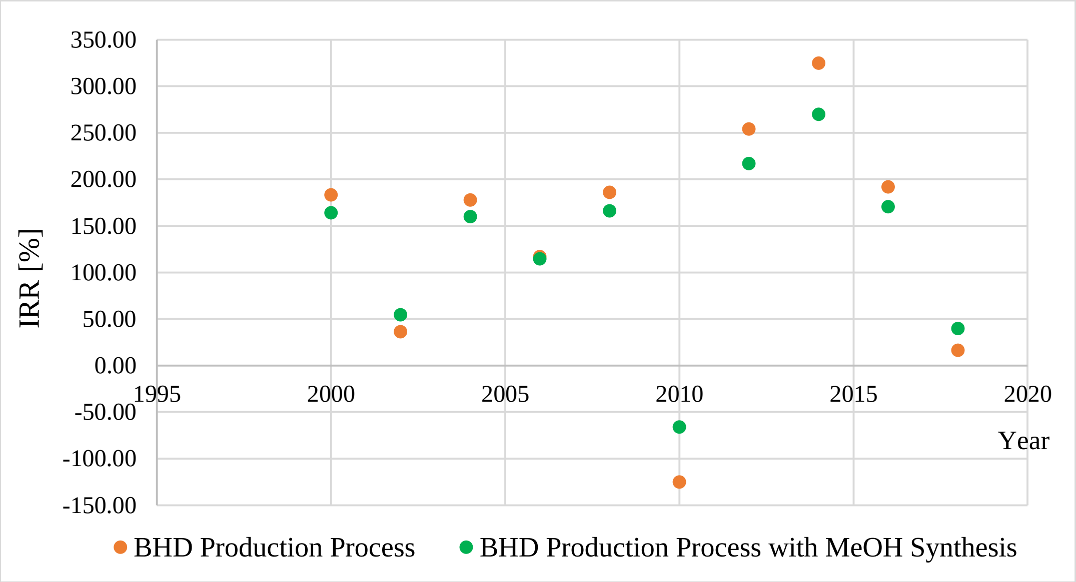

Figure 32 The internal rate of return for RBDPO cost and diesel price in each year since 2000 until 2018

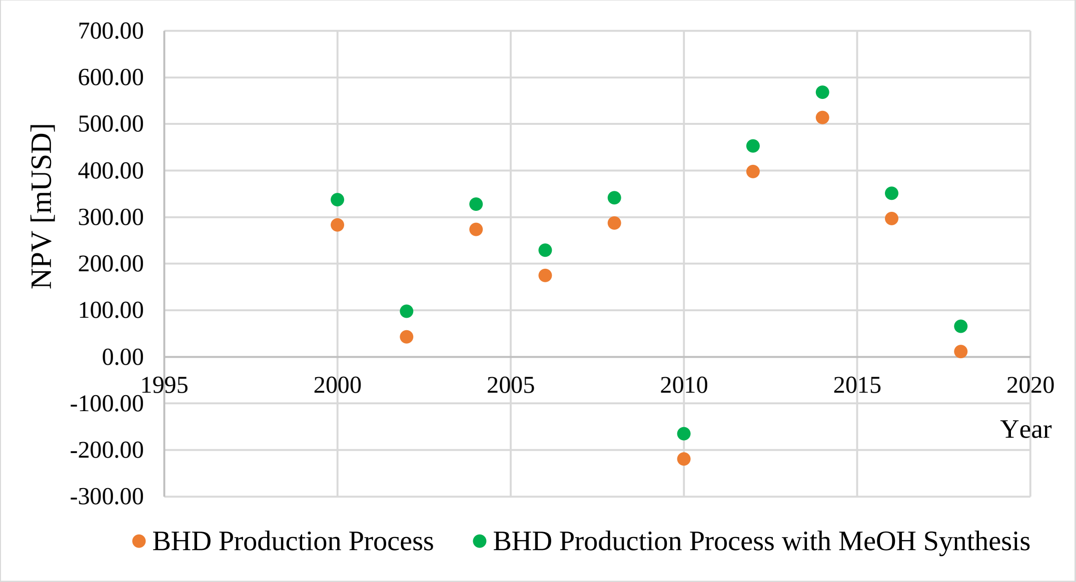

Figure 33 The net present value for RBDPO cost and diesel price in each year since 2000 until 2018

CHAPTER 5 Conclusion

The bio-hydrogenated diesel or green diesel is an alternative fuel which can be used instead of the petroleum diesel and biodiesel in the future. Because BHD structure is more similar and the properties are also closer to the petroleum diesel than the biodiesel. The BHD production requires high temperature, high pressure, low liquid hourly space velocity, and high H_2/oil ratio to convert the RBDPO which contains triglyceride to straight chain hydrocarbons. According to a large amount of hydrogen gas for reaction, it remains in the gaseous by-product which are carbon dioxide and carbon monoxide. This study proposed the method to improve the hydrogen recovery process by converting the gaseous by-product to another product which was methanol that could be produced under high temperature and high pressure. In this study, the BHD production process and BHD production process coupled with methanol synthesis were determined the technical and economic feasibility in terms of payback period, internal rate of return, and net present value. As the result, the BHD production process coupled with methanol synthesis was more interesting than the BHD production process because it recovered the hydrogen gas up to 46.3 percent and also reduced carbon dioxide and carbon monoxide emission 14.0 percent. For the economic feasibility, including methanol synthesis could improve BHD production process by increasing the internal rate of return 23.18 percent, shortening payback period 2.81 years, and also increasing net present value 54.41 million US dollars based on 2018. But this value should be seriously considered because economic feasibility mainly depended on product prices and raw material costs.

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VITA

NAME	Nitipat Phichitsurathaworn
DATE OF BIRTH	01 November 1994
PLACE OF BIRTH	Bangkok
INSTITUTIONS ATTENDED	School: Assumption College Samutprakarn Bachelor degree: Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University
HOME ADDRESS	525/185 Moo 7 Sukhumvit Rd. Samrong Nuea, Mueang, Samut Prakan 10270

APPENDIX A
Design of Bio-Hydrogenated Diesel Production Process

This design was for 25,000 kilograms per hour of BHD which was produced by heterogeneous catalytic reaction of RBDPO with hydrogen. Figure 34 showed the input-output structure of this process including the mass balance of process.

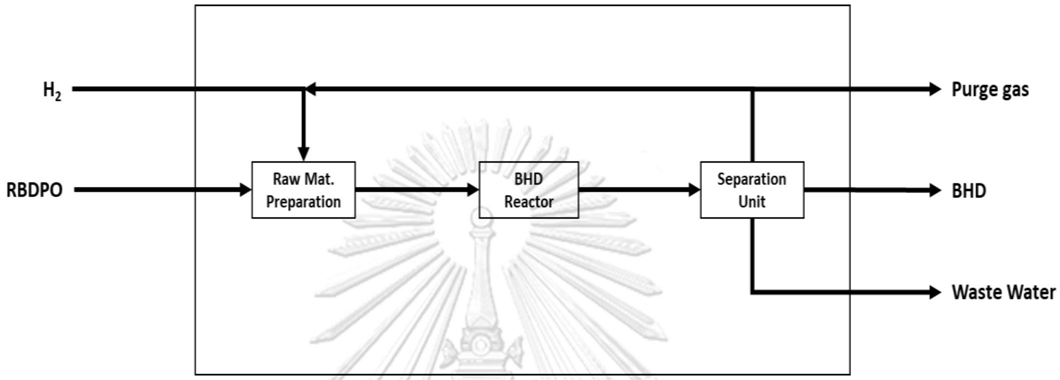

Figure 34 Input-output structure BHD production process

From the result of Aspen plus, it showed the input structure as below;

1.) RBDPO = 30535 kilogram per hour
2.) Hydrogen gas = 1095 kilogram per hour
Input structure = 30535+1095
= 31630 kilogram per hour

Also, the output structure was

1.) Purge gas which composes of H_2, CO_2, CO, CH_4, C_2H_6 and C_3H_8
= 3988 kilogram per hour
2.) BHD
= 25000 kilogram per hour
3.) Waste water = 2642 kilogram per hour
Output structure = 3988+25000+2642
= 31630 kilogram per hour

This process was divided to 4 sections as shown as the block flow diagram in Figure 34. First section was reactor feed preparation or raw material preparation which prepared the condition of raw materials to reactor condition. Second section, it was reactor where the reaction occurs. Third section, the phase separation was used the unreacted gaseous separation and the liquid product separation. Last section was used for recycle stream preparation.

The feed preparation was used to prepare the RBDPO and hydrogen gas to reactor condition. The refined palm oil which was at ambient condition, 1 bar and 35 ^oC was pumped by P-101 to 50 bar and then pass through the heat exchanger, E-101 and E-102, to be heated to 300 ^oC. The hydrogen gas which was available at 400 bar and 35 ^oC was released by V-101 to 50 bar after that it goes to E-103 and E-104 for increasing temperature 300 ^oC. Flow rate of the RBDPO was fixed due to the production rate. The hydrogen gas was from the recycle stream and make-up hydrogen which was also fixed by the reactor condition, H_2/oil ratio = 500 cm^3/cm^3 at standard temperature pressure condition. According to recycle stream, there was 3368 kilograms of hydrogen. So, it requires additional hydrogen 1095 kilogram. The calculation of hydrogen gas flow rate for reaction was shown below;

RBDPO flow rate
= 30535 kilogram per hour (or 35.78463 kmol/hr)
= 35.78463 kmol/hr x (1 mL/0.00035056 mol) x (1000 mol/1 kmol)
= 99246502.7 mL RBDPO/hr

Hydrogen flow rate
= 99246502.7 mL RBDPO/hr x (500 mL H_2/ mL RBDPO)
= 4.96×10^{10} mL H_2/hr x (1 atm) / (273 K) / (0.0821 atmL/molK) x (1 L/1000mL)
= 2214009 mol H_2/hr x (1 kmol/1000mol)
= 2214 kmol H_2/hr

Next section, the reactor was operated at 50 bar and 300 ^oC. There were many reactions which occur in the reactor and convert the RBDPO to product in 100 percent of conversion. The main reactions were hydrogenation, hydrogenolysis, hydro-deoxygenation, decarboxylation and decabonylation. But it might be cracked or isomerized to the smaller molecule or its isomer. All reactions were shown in Table 27. Reaction 1-3 were the hydrogenation reaction which convert the unsaturated triglycerides to saturated triglycerides. Reaction 4-7 were cracking reaction or hydrogenolysis. The saturated triglycerides were cracked to fatty acid and propane. After that the fatty acids were converted to straight chain hydrocarbon by hydrodeoxygenation (Reaction 8-11), decarboxylation (Reaction 12-15) and decabonylation (Reaction 16-19).

Table 27 The reaction in bio-hydrogenation reactor

Reaction	**Stoichiometry**
1	3 H_2 + C18:1TG --> C18:0TG
2	6 H_2 + C18:2TG --> C18:0TG
3	9 H_2 + C18:3TG --> C18:0TG
4	3 H_2 + C12:0TG --> C_3H_8 + 3 C12:0FA
5	3 H_2 + C14:0TG --> C_3H_8 + 3 C14:0FA
6	3 H_2 + C16:0TG --> C_3H_8 + 3 C16:0FA
7	3 H_2 + C18:0TG --> C_3H_8 + 3 C18:0FA
8	3 H_2 + C12:0FA --> $C_{12}H_{26}$ + 2 H_2O
9	3 H_2 + C14:0FA --> $C_{14}H_{30}$ + 2 H_2O
10	3 H_2 + C16:0FA --> $C_{16}H_{34}$ + 2 H_2O
11	3 H_2 + C18:0FA --> $C_{18}H_{38}$ + 2 H_2O
12	C12:0FA --> $C_{11}H_{24}$ + CO_2
13	C14:0FA --> $C_{13}H_{28}$ + CO_2
14	C16:0FA --> $C_{15}H_{32}$ + C_{O2}
15	C18:0FA --> $C_{17}H_{36}$ + CO_2
16	H_2 + C12:0FA --> $C_{11}H_{24}$ + CO + H_2O
17	H_2 + C14:0FA --> $C_{13}H_{2}8$ + CO + H_2O
18	H_2 + C16:0FA --> $C_{15}H_{32}$ + CO + H_2O
19	H_2 + C18:0FA --> $C_{17}H_{36}$ + CO + H_2O
20	H_2 + $C_{18}H_{38}$ --> C_2H_6 + $C_{16}H_{34}$
21	16 H_2 + $C_{17}H_{36}$ --> 17 CH_4
22	15 H_2 + 2 $C_{17}H_{36}$ --> 17 C_2H_6
23	14 H_2 + 3 $C_{17}H_{36}$ --> 17 C_3H_8
24	4 H_2 + $C_{15}H_{32}$ --> 5 C_3H_8

After the product was produced from reactor. The separation unit was needed for purify product and remove the by-product liquid and gas. The effluent stream was cooled to 45 ^{o}C by E-107 and sent to flash drum, F-101, to remove the gaseous by-product. Gaseous by-product was divided into 2 streams, 95 percent was sent to recycle section. The other was purge stream. Liquid phase was released to ambient pressure by V-102 and separated by F-102, respectively. Gas was vented but liquid was sent to decanter, D-101, to separate the waste water from BHD.

The recycle stream was the 95 percent of gaseous stream. It was heated to 300 ^{o}C by 2 heat exchangers, E-106 and E-107. After that it was sent back to reactor for reaction. Then, the required make-up hydrogen gas can be determined as below;

Make-up hydrogen flow rate
= Hydrogen for reaction – Hydrogen in recycle stream
= 2214 kmol H_2/hr – 1671 kmol H_2/hr
= 543 kmol H_2/hr

For the validation this process, this study was validated the purge gas composition and BHD product composition with the result of A. Srifa claimed in Production of BHD by catalytic hydrotreating of palm oil over $NiMoS_2$ -Al_2O_3 catalyst [20]. Table 28 shows the comparison result of by-product gas composition between this literature and simulation. Table 29 shows the comparison result of BHD product composition. Figure 17 shows the BHD production process and Table 30 shows the composition, flow rate, and condition of each stream.

Table 28 The comparison result of by-product gas composition between this literature and simulation

Gas composition [%mole]	Simulation	Literature
CO	0.0174	0.02
CO_2	0.4613	0.48
CH_4	0.1342	0.12
C_2H_6	0.0555	0.05
C_3H_8	0.3316	0.33

Table 29 The comparison result of BHD product composition.

Product composition [%wt.]	Simulation	Literature
$C_{11}H_{24}$-$C_{14}H_{30}$	0.010	0.010
$C_{15}H_{32}$	0.082	0.072
$C_{16}H_{34}$	0.300	0.290
$C_{17}H_{36}$	0.130	0.122
$C_{18}H_{38}$	0.463	0.463

Table 30 The composition, flow rate, and condition of each stream in BHD production process.

List	Unit	Streams				
		1	2	3	4	5
H_2	KMOL/HR	0.0	0.0	0.0	0.0	543.4
H_2O	KMOL/HR	0.0	0.0	0.0	0.0	0.0
CO	KMOL/HR	0.0	0.0	0.0	0.0	0.0
CO_2	KMOL/HR	0.0	0.0	0.0	0.0	0.0
CH_4	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C_2H_6	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C_3H_8	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{11}H_{24}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{12}H_{26}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{13}H_{28}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{14}H_{30}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{15}H_{32}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{16}H_{34}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{17}H_{36}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{18}H_{38}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C12:0TG	KMOL/HR	0.1	0.1	0.1	0.1	0.0
C14:0TG	KMOL/HR	0.3	0.3	0.3	0.3	0.0
C16:0TG	KMOL/HR	13.5	13.5	13.1	13.1	0.0
C18:0TG	KMOL/HR	1.3	1.3	1.3	1.3	0.0
C18:1TG	KMOL/HR	16.4	16.4	16.0	16.0	0.0
C18:2TG	KMOL/HR	4.0	4.0	3.9	3.9	0.0
C18:3TG	KMOL/HR	0.1	0.1	0.1	0.1	0.0
CH_3OH	KMOL/HR	0.0	0.0	0.0	0.0	0.0
Mole Flow	KMOL/HR	35.8	35.8	34.8	34.8	543.4
Mass Flow	KG/HR	30534.8	30534.8	29713.0	29713.0	1095.5
Pressure	BAR	1.0	50.0	50.0	50.0	400.0
Temperature	^oC	35.0	39.6	290.0	300.0	35.0
Vapor Fraction		0.0	0.0	0.0	1.0	1.0

Table 30 The composition, flow rate, and condition of each stream in BHD production process.

List	Unit	Streams				
		6	7	8	9	10
H_2	KMOL/HR	543.4	543.4	543.4	2214.0	2214.0
H_2O	KMOL/HR	0.0	0.0	0.0	18.4	18.4
CO	KMOL/HR	0.0	0.0	0.0	9.0	9.0
CO_2	KMOL/HR	0.0	0.0	0.0	240.1	240.1
CH_4	KMOL/HR	0.0	0.0	0.0	69.9	69.9
C_2H_6	KMOL/HR	0.0	0.0	0.0	28.9	28.9
C_3H_8	KMOL/HR	0.0	0.0	0.0	172.6	172.6
$C_{11}H_{24}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{12}H_{26}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{13}H_{28}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{14}H_{30}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{15}H_{32}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{16}H_{34}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{17}H_{36}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{18}H_{38}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C12:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.1
C14:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.3
C16:0TG	KMOL/HR	0.0	0.0	0.0	0.0	13.5
C18:0TG	KMOL/HR	0.0	0.0	0.0	0.0	1.3
C18:1TG	KMOL/HR	0.0	0.0	0.0	0.0	16.4
C18:2TG	KMOL/HR	0.0	0.0	0.0	0.0	4.0
C18:3TG	KMOL/HR	0.0	0.0	0.0	0.0	0.1
CH_3OH	KMOL/HR	0.0	0.0	0.0	0.0	0.0
Mole Flow	KMOL/HR	543.4	543.4	543.4	2753.0	2788.8
Mass Flow	KG/HR	1095.5	1095.5	1095.5	25219.6	55754.3
Pressure	BAR	50.0	50.0	50.0	50.0	50.0
Temperature	^{o}C	50.1	290.0	300.0	299.9	299.5
Vapor Fraction		1.0	1.0	1.0	1.0	1.0

Table 30 The composition, flow rate, and condition of each stream in BHD production process.

List	Unit	Streams				
		11	12	13	14	15
H_2	KMOL/HR	1765.5	720.9	720.9	164.3	164.3
H_2O	KMOL/HR	178.0	72.6	72.6	16.6	16.6
CO	KMOL/HR	9.6	3.9	3.9	0.9	0.9
CO_2	KMOL/HR	267.4	108.7	108.7	24.8	24.8
CH_4	KMOL/HR	75.8	31.0	31.0	7.1	7.1
C_2H_6	KMOL/HR	33.2	13.6	13.6	3.1	3.1
C_3H_8	KMOL/HR	230.0	93.9	93.9	21.4	21.4
$C_{11}H_{24}$	KMOL/HR	0.1	0.0	0.0	0.0	0.0
$C_{12}H_{26}$	KMOL/HR	0.3	0.1	0.1	0.0	0.0
$C_{13}H_{28}$	KMOL/HR	0.2	0.1	0.1	0.0	0.0
$C_{14}H_{30}$	KMOL/HR	0.6	0.3	0.3	0.1	0.1
$C_{15}H_{32}$	KMOL/HR	9.6	3.9	3.9	0.9	0.9
$C_{16}H_{34}$	KMOL/HR	33.1	13.5	13.5	3.1	3.1
$C_{17}H_{36}$	KMOL/HR	13.5	5.5	5.5	1.3	1.3
$C_{18}H_{38}$	KMOL/HR	45.4	18.6	18.6	4.2	4.2
C12:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C14:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C16:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:1TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:2TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:3TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
CH_3OH	KMOL/HR	0.0	0.0	0.0	0.0	0.0
Mole Flow	KMOL/HR	2662.5	1086.8	1086.8	247.7	247.7
Mass Flow	KG/HR	55754.3	22747.8	22747.8	5185.2	5185.2
Pressure	BAR	50.0	50.0	50.0	50.0	50.0
Temperature	^{o}C	300.0	300.0	93.6	300.0	84.6
Vapor Fraction		1.0	1.0	1.0	1.0	0.9

Table 30 The composition, flow rate, and condition of each stream in BHD production process.

List	Unit	Streams				
		16	17	18	19	20
H_2	KMOL/HR	881.7	881.7	1767.0	1767.0	7.0
H_2O	KMOL/HR	88.8	88.8	178.0	178.0	158.7
CO	KMOL/HR	4.8	4.8	9.6	9.6	0.1
CO_2	KMOL/HR	133.0	133.0	266.5	266.5	14.6
CH_4	KMOL/HR	37.9	37.9	76.0	76.0	2.2
C_2H_6	KMOL/HR	16.6	16.6	33.3	33.3	2.8
C_3H_8	KMOL/HR	114.9	114.9	230.3	230.3	48.3
$C_{11}H_{24}$	KMOL/HR	0.1	0.1	0.1	0.1	0.1
$C_{12}H_{26}$	KMOL/HR	0.2	0.2	0.3	0.3	0.3
$C_{13}H_{28}$	KMOL/HR	0.1	0.1	0.2	0.2	0.2
$C_{14}H_{30}$	KMOL/HR	0.3	0.3	0.6	0.6	0.6
$C_{15}H_{32}$	KMOL/HR	4.8	4.8	9.6	9.6	9.6
$C_{16}H_{34}$	KMOL/HR	16.5	16.5	33.0	33.0	33.1
$C_{17}H_{36}$	KMOL/HR	6.7	6.7	13.5	13.5	13.5
$C_{18}H_{38}$	KMOL/HR	22.7	22.7	45.6	45.6	45.4
C12:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C14:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C16:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:1TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:2TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:3TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
CH_3OH	KMOL/HR	0.0	0.0	0.0	0.0	0.0
Mole Flow	KMOL/HR	1329.2	1329.2	2663.7	2663.7	336.7
Mass Flow	KG/HR	27821.4	27821.4	55754.3	55754.3	30360.6
Pressure	BAR	50.0	50.0	50.0	50.0	50.0
Temperature	^oC	300.0	86.4	89.2	45.0	45.0
Vapor Fraction		1.0	0.9	0.9	0.9	0.0

Table 30 The composition, flow rate, and condition of each stream in BHD production process.

List	Unit	Streams				
		21	22	23	24	25
H_2	KMOL/HR	7.0	0.0	0.0	0.0	7.0
H_2O	KMOL/HR	158.7	146.8	146.5	0.2	11.9
CO	KMOL/HR	0.1	0.0	0.0	0.0	0.1
CO_2	KMOL/HR	14.6	0.5	0.0	0.5	14.1
CH_4	KMOL/HR	2.2	0.0	0.0	0.0	2.2
C_2H_6	KMOL/HR	2.8	0.2	0.0	0.2	2.7
C_3H_8	KMOL/HR	48.3	8.6	0.0	8.5	39.7
$C_{11}H_{24}$	KMOL/HR	0.1	0.1	0.0	0.1	0.0
$C_{12}H_{26}$	KMOL/HR	0.3	0.3	0.0	0.3	0.0
$C_{13}H_{28}$	KMOL/HR	0.2	0.2	0.0	0.2	0.0
$C_{14}H_{30}$	KMOL/HR	0.6	0.6	0.0	0.6	0.0
$C_{15}H_{32}$	KMOL/HR	9.6	9.6	0.0	9.6	0.0
$C_{16}H_{34}$	KMOL/HR	33.1	33.1	0.0	33.1	0.0
$C_{17}H_{36}$	KMOL/HR	13.5	13.5	0.0	13.5	0.0
$C_{18}H_{38}$	KMOL/HR	45.4	45.4	0.0	45.4	0.0
C12:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C14:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C16:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:1TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:2TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:3TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
CH_3OH	KMOL/HR	0.0	0.0	0.0	0.0	0.0
Mole Flow	KMOL/HR	336.7	259.0	146.6	112.4	77.6
Mass Flow	KG/HR	30360.6	27641.6	2642.4	24999.3	2718.9
Pressure	BAR	1.0	1.0	1.0	1.0	1.0
Temperature	^oC	31.7	31.7	40.4	40.4	31.7
Vapor Fraction		0.2	0.0	0.0	0.0	1.0

Table 30 The composition, flow rate, and condition of each stream in BHD production process.

List	Unit	Streams				
		26	27	28	29	30
H_2	KMOL/HR	1758.5	1670.6	1670.6	1670.6	87.9
H_2O	KMOL/HR	19.3	18.4	18.4	18.4	1.0
CO	KMOL/HR	9.5	9.0	9.0	9.0	0.5
CO_2	KMOL/HR	252.8	240.1	240.1	240.1	12.6
CH_4	KMOL/HR	73.6	69.9	69.9	69.9	3.7
C_2H_6	KMOL/HR	30.4	28.9	28.9	28.9	1.5
C_3H_8	KMOL/HR	181.7	172.6	172.6	172.6	9.1
$C_{11}H_{24}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{12}H_{26}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{13}H_{28}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{14}H_{30}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{15}H_{32}$	KMOL/HR	0.001	0.001	0.001	0.001	0.0
$C_{16}H_{34}$	KMOL/HR	0.001	0.001	0.001	0.001	0.0
$C_{17}H_{36}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{18}H_{38}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C12:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C14:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C16:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:1TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:2TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:3TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
CH_3OH	KMOL/HR	0.0	0.0	0.0	0.0	0.0
Mole Flow	KMOL/HR	2325.9	2209.6	2209.6	2209.6	116.3
Mass Flow	KG/HR	25393.7	24124.0	24124.0	24124.0	1269.7
Pressure	BAR	50.0	50.0	50.0	50.0	50.0
Temperature	^{o}C	45.0	50.2	290.0	300.0	50.2
Vapor Fraction		1.0	1.0	1.0	1.0	1.0

APPENDIX B

Validation of Kinetics Parameter for Methanol Synthesis

In this study, there were 2 reactions in the reactor for methanol production as shown below. The reactions occur by heterogeneous catalytic reaction by $Cu/ZnO/Al_2O_3$ catalyst which was the commercial catalyst. The kinetic parameters [27], catalyst characteristic, and feed stream were shown as Table 9, Table 10, and Table 11, respectively.

$$r_{CH_3OH} = \frac{k_1 P_{CO_2} P_{H_2} - k_6 P_{H_2O} P_{CH_3OH} P_{H_2}^{-2}}{(1 + k_2 P_{H_2O} P_{H_2}^{-1} + k_3 P_{H_2}^{0.5} + k_4 P_{H_2O})^3} \qquad [\frac{kmol}{kg_{cat} s}]$$

$$r_{RWGS} = \frac{k_5 P_{CO_2} - k_7 P_{H_2O} P_{CO} P_{H_2}^{-1}}{1 + k_2 P_{H_2O} P_{H_2}^{-1} + k_3 P_{H_2}^{0.5} + k_4 P_{H_2O}} \qquad [\frac{kmol}{kg_{cat} s}]$$

$$\ln k_i = A_i + \frac{B_i}{T}$$

Aspen plus was used for analysis the composition along the reactor length by using the RPLUG reactor. The simulation result shows the same trend as the literature result as shown in Table 31.

Table 31 The composition along the reactor length from simulation

Length [cm]	**Mole percentage**					
	CO	**CO_2**	**H_2**	**H_2O**	**CH_3OH**	**Ar**
0	0.0400	0.0300	0.8200	0.0000	0.0000	0.1100
0.3	0.0405	0.0243	0.8118	0.0060	0.0060	0.1113
0.6	0.0402	0.0221	0.8084	0.0084	0.0089	0.1120
0.9	0.0394	0.0208	0.8059	0.0099	0.0115	0.1125
1.2	0.0380	0.0200	0.8041	0.0109	0.0140	0.1131
1.5	0.0362	0.0197	0.8029	0.0112	0.0164	0.1136
1.8	0.0342	0.0199	0.8021	0.0112	0.0185	0.1141
2.1	0.0325	0.0202	0.8018	0.0110	0.0201	0.1144
2.4	0.0313	0.0205	0.8016	0.0108	0.0212	0.1147
2.7	0.0307	0.0206	0.8015	0.0107	0.0218	0.1148
3	0.0303	0.0207	0.8014	0.0106	0.0221	0.1149
3.3	0.0301	0.0207	0.8014	0.0106	0.0223	0.1149
3.6	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
3.9	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
4.2	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
4.5	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149

Table 31 The composition along the reactor length from simulation

Length [cm]	**Mole percentage**					
	CO	**CO_2**	**H_2**	**H_2O**	**CH_3OH**	**Ar**
4.8	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
5.1	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
5.4	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
5.7	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
6	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
6.3	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
6.6	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
6.9	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
7.2	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
7.5	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
7.8	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
8.1	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
8.4	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
8.7	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
9	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
9.3	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
9.6	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
9.9	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
10.2	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
10.5	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
10.8	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
11.1	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
11.4	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
11.7	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
12	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
12.3	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
12.6	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
12.9	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
13.2	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
13.5	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
13.8	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
14.1	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
14.4	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
14.7	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149
15	0.0300	0.0207	0.8013	0.0106	0.0224	0.1149

APPENDIX C

Design of Bio-Hydrogenated Diesel Production Process Coupled with Methanol Synthesis

This production process was designed for improving the conventional process which purge a lot of hydrogen out of the process due to the high H_2/oil ratio for reaction. The purged gas was designed to convert the carbon dioxide to valuable product such as methanol. Figure 35 showed the input-output structure of this process.

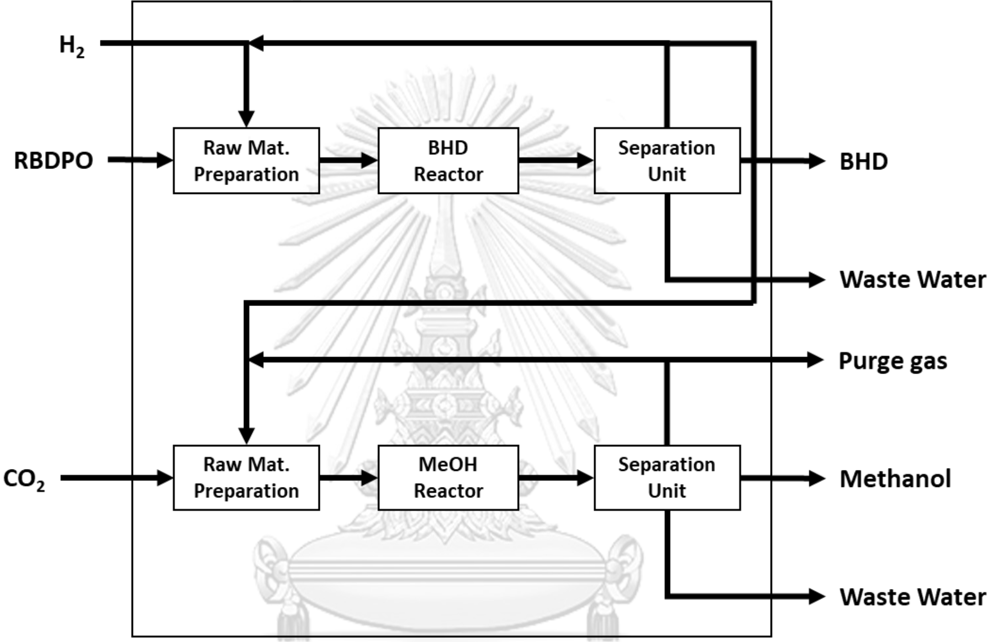

Figure 35 Input-output structure BHD production process coupled with methanol synthesis

From the result of Aspen plus, it shows the input structure as below;

1.) RBDPO = 30535 kilogram per hour
2.) Hydrogen gas = 1095 kilogram per hour
3.) Carbon dioxide = 165 kilogram per hour
Input structure = 30535+1095+165
= 31795 kilogram per hour

Also, the output structure was

1.) Purge gas which composes of H_2, CO_2, CO, CH_4, C_2H_6, C_3H_8 and CH_3OH
= 3452 kilogram per hour
2.) BHD = 25000 kilogram per hour
3.) Waste water = 2936 kilogram per hour
4.) Methanol = 407 kilogram per hour
Output structure = 3452+25000+2936+407
= 31795 kilogram per hour

For the BHD production process, it was quite similar to the first process. But the methanol synthesis needed to be designed. The reactor feed preparation was only heating the raw material which was the mixed gas between purged gas from the first process and additional carbon dioxide to 220 °C by E-208. After that it was mixed with the recycle stream. Then, it was sent to reactor, R-201.

The amount of additional carbon dioxide was also fixed by the reactor condition, CO_2/H_2 ratio was approximately 0.04 mole/mole. According to recycle stream, there were 1680 kilogram of hydrogen (833 kilomoles) and 1257 kilogram of carbon dioxide (28.55 kilomoles). But there were 177 kilogram of hydrogen (88 kilomoles) and 556 kilogram of carbon dioxide (12.6 kilomoles) from the first process. So, it requires additional carbon dioxide 165 kilogram (3.74 kiomoles)

Additional carbon dioxide flow rate
= CO_2/H_2 [mole/mole] x H_2 from first process [mole] – CO_2 remaining in recycle [mole] - CO_2 from first process [mole]
= 0.0487 kmol CO_2/kmol H_2 x (833+88 kmol H_2/hr) – 28.55 kmol CO_2/hr – 12.6 kmol CO_2/hr
= 3.74 kmol CO_2/hr

Next, the separation section was used for methanol purification. The reactor effluent stream was cooled by E-210, E-211, and E-212. The gaseous phase was separated by flash drum, F-203. Then, 95 percent of gas was sent to recycle section which heats to 220 ^{o}C and sent back to reactor. The rest was purged out from process. After that the liquid phase was released by V-203 to separate vapor at low pressure by F-204. The liquid phase was prepared for high purity methanol distillation by releasing pressure to 2.7 bar and heating to 101 ^{o}C. The reboiler operates at 2.7 bar and 123.8 ^{o}C. Condenser operates as partial condenser at 2 bar 79 ^{o}C. The overhead stream was prepared for methanol product by reducing valve, V-205. And it was cooled to ambient temperature. Figure 21 shows the overall process of this design. Also, Table 32 shows the composition and condition of each stream.

Table 32 The composition, flow rate, and condition of each stream in BHD production process coupled with methanol synthesis.

List	Unit	Streams				
		1	2	3	4	5
H_2	KMOL/HR	0.0	0.0	0.0	0.0	543.5
H_2O	KMOL/HR	0.0	0.0	0.0	0.0	0.0
CO	KMOL/HR	0.0	0.0	0.0	0.0	0.0
CO_2	KMOL/HR	0.0	0.0	0.0	0.0	0.0
CH_4	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C_2H_6	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C_3H_8	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{11}H_{24}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{12}H_{26}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{13}H_{28}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{14}H_{30}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{15}H_{32}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{16}H_{34}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{17}H_{36}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{18}H_{38}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C12:0TG	KMOL/HR	0.1	0.1	0.1	0.1	0.0
C14:0TG	KMOL/HR	0.3	0.3	0.3	0.3	0.0
C16:0TG	KMOL/HR	13.5	13.5	13.5	13.5	0.0
C18:0TG	KMOL/HR	1.3	1.3	1.3	1.3	0.0
C18:1TG	KMOL/HR	16.4	16.4	16.4	16.4	0.0
C18:2TG	KMOL/HR	4.0	4.0	4.0	4.0	0.0
C18:3TG	KMOL/HR	0.1	0.1	0.1	0.1	0.0
CH_3OH	KMOL/HR	0.0	0.0	0.0	0.0	0.0
Mole Flow	KMOL/HR	35.8	35.8	35.8	35.8	543.5
Mass Flow	KG/HR	30535.7	30535.7	30535.7	30535.7	1095.7
Pressure	BAR	1.0	50.0	50.0	50.0	400.0
Temperature	^oC	35.0	39.6	290.0	300.0	35.0
Vapor Fraction		0.0	0.0	0.0	0.0	1.0

Table 32 The composition, flow rate, and condition of each stream in BHD production process coupled with methanol synthesis.

List	Unit	Streams				
		6	7	8	9	10
H_2	KMOL/HR	543.5	543.5	543.5	2214.0	2214.0
H_2O	KMOL/HR	0.0	0.0	0.0	18.4	18.4
CO	KMOL/HR	0.0	0.0	0.0	9.0	9.0
CO_2	KMOL/HR	0.0	0.0	0.0	240.1	240.1
CH_4	KMOL/HR	0.0	0.0	0.0	69.9	69.9
C_2H_6	KMOL/HR	0.0	0.0	0.0	28.9	28.9
C_3H_8	KMOL/HR	0.0	0.0	0.0	172.6	172.6
$C_{11}H_{24}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{12}H_{26}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{13}H_{28}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{14}H_{30}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{15}H_{32}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{16}H_{34}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{17}H_{36}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{18}H_{38}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C12:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.1
C14:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.3
C16:0TG	KMOL/HR	0.0	0.0	0.0	0.0	13.5
C18:0TG	KMOL/HR	0.0	0.0	0.0	0.0	1.3
C18:1TG	KMOL/HR	0.0	0.0	0.0	0.0	16.4
C18:2TG	KMOL/HR	0.0	0.0	0.0	0.0	4.0
C18:3TG	KMOL/HR	0.0	0.0	0.0	0.0	0.1
CH_3OH	KMOL/HR	0.0	0.0	0.0	0.0	0.0
Mole Flow	KMOL/HR	543.5	543.5	543.5	2753.0	2788.8
Mass Flow	KG/HR	1095.7	1095.7	1095.7	25219.5	55755.2
Pressure	BAR	50.0	50.0	50.0	50.0	50.0
Temperature	^oC	50.1	290.0	300.0	299.9	299.5
Vapor Fraction		1.0	1.0	1.0	1.0	1.0

Table 32 The composition, flow rate, and condition of each stream in BHD production process coupled with methanol synthesis.

List	Unit	Streams				
		11	12	13	14	15
H_2	KMOL/HR	1765.4	663.8	663.8	158.9	158.9
H_2O	KMOL/HR	178.0	66.9	66.9	16.0	16.0
CO	KMOL/HR	9.6	3.6	3.6	0.9	0.9
CO_2	KMOL/HR	267.4	100.5	100.5	24.1	24.1
CH_4	KMOL/HR	75.8	28.5	28.5	6.8	6.8
C_2H_6	KMOL/HR	33.2	12.5	12.5	3.0	3.0
C_3H_8	KMOL/HR	230.1	86.5	86.5	20.7	20.7
$C_{11}H_{24}$	KMOL/HR	0.1	0.0	0.0	0.0	0.0
$C_{12}H_{26}$	KMOL/HR	0.3	0.1	0.1	0.0	0.0
$C_{13}H_{28}$	KMOL/HR	0.2	0.1	0.1	0.0	0.0
$C_{14}H_{30}$	KMOL/HR	0.6	0.2	0.2	0.1	0.1
$C_{15}H_{32}$	KMOL/HR	9.6	3.6	3.6	0.9	0.9
$C_{16}H_{34}$	KMOL/HR	33.1	12.5	12.5	3.0	3.0
$C_{17}H_{36}$	KMOL/HR	13.5	5.1	5.1	1.2	1.2
$C_{18}H_{38}$	KMOL/HR	45.4	17.1	17.1	4.1	4.1
C12:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C14:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C16:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:1TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:2TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:3TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
CH_3OH	KMOL/HR	0.0	0.0	0.0	0.0	0.0
Mole Flow	KMOL/HR	2662.4	1001.1	1001.1	239.6	239.6
Mass Flow	KG/HR	55755.2	20964.0	20964.0	5018.0	5018.0
Pressure	BAR	50.0	50.0	50.0	50.0	50.0
Temperature	^oC	300.0	300.0	77.9	300.0	77.1
Vapor Fraction		1.0	1.0	0.9	1.0	0.9

Table 32 The composition, flow rate, and condition of each stream in BHD production process coupled with methanol synthesis.

List	Unit	Streams				
		16	17	18	19	20
H_2	KMOL/HR	845.6	845.6	97.1	97.1	97.1
H_2O	KMOL/HR	85.3	85.3	9.8	9.8	9.8
CO	KMOL/HR	4.6	4.6	0.5	0.5	0.5
CO_2	KMOL/HR	128.1	128.1	14.7	14.7	14.7
CH_4	KMOL/HR	36.3	36.3	4.2	4.2	4.2
C_2H_6	KMOL/HR	15.9	15.9	1.8	1.8	1.8
C_3H_8	KMOL/HR	110.2	110.2	12.7	12.7	12.7
$C_{11}H_{24}$	KMOL/HR	0.1	0.1	0.0	0.0	0.0
$C_{12}H_{26}$	KMOL/HR	0.2	0.2	0.0	0.0	0.0
$C_{13}H_{28}$	KMOL/HR	0.1	0.1	0.0	0.0	0.0
$C_{14}H_{30}$	KMOL/HR	0.3	0.3	0.0	0.0	0.0
$C_{15}H_{32}$	KMOL/HR	4.6	4.6	0.5	0.5	0.5
$C_{16}H_{34}$	KMOL/HR	15.9	15.9	1.8	1.8	1.8
$C_{17}H_{36}$	KMOL/HR	6.5	6.5	0.7	0.7	0.7
$C_{18}H_{38}$	KMOL/HR	21.8	21.8	2.5	2.5	2.5
C12:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C14:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C16:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:1TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:2TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:3TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
CH_3OH	KMOL/HR	0.0	0.0	0.0	0.0	0.0
Mole Flow	KMOL/HR	1275.3	1275.3	146.4	146.4	146.4
Mass Flow	KG/HR	26706.7	26706.7	3066.5	3066.5	3066.5
Pressure	BAR	50.0	50.0	50.0	50.0	50.0
Temperature	^{o}C	300.0	76.9	300.0	238.6	70.0
Vapor Fraction		1.0	0.9	1.0	1.0	0.9

Table 32 The composition, flow rate, and condition of each stream in BHD production process coupled with methanol synthesis.

List	Unit	Streams				
		21	22	23	24	25
H_2	KMOL/HR	1765.4	1765.4	7.0	7.0	0.0
H_2O	KMOL/HR	178.0	178.0	158.7	158.7	146.8
CO	KMOL/HR	9.6	9.6	0.1	0.1	0.0
CO_2	KMOL/HR	267.4	267.4	14.6	14.6	0.5
CH_4	KMOL/HR	75.8	75.8	2.2	2.2	0.0
C_2H_6	KMOL/HR	33.2	33.2	2.8	2.8	0.2
C_3H_8	KMOL/HR	230.1	230.1	48.3	48.3	8.6
$C_{11}H_{24}$	KMOL/HR	0.1	0.1	0.1	0.1	0.1
$C_{12}H_{26}$	KMOL/HR	0.3	0.3	0.3	0.3	0.3
$C_{13}H_{28}$	KMOL/HR	0.2	0.2	0.2	0.2	0.2
$C_{14}H_{30}$	KMOL/HR	0.6	0.6	0.6	0.6	0.6
$C_{15}H_{32}$	KMOL/HR	9.6	9.6	9.6	9.6	9.6
$C_{16}H_{34}$	KMOL/HR	33.1	33.1	33.1	33.1	33.1
$C_{17}H_{36}$	KMOL/HR	13.5	13.5	13.5	13.5	13.5
$C_{18}H_{38}$	KMOL/HR	45.4	45.4	45.4	45.4	45.4
C12:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C14:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C16:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:1TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:2TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:3TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
CH_3OH	KMOL/HR	0.0	0.0	0.0	0.0	0.0
Mole Flow	KMOL/HR	2662.4	2662.4	336.7	336.7	259.0
Mass Flow	KG/HR	55755.2	55755.2	30361.6	30361.6	27642.5
Pressure	BAR	50.0	50.0	50.0	1.0	1.0
Temperature	^oC	78.2	50.0	45.0	31.7	31.7
Vapor Fraction		0.9	0.9	0.0	0.2	0.0

Table 32 The composition, flow rate, and condition of each stream in BHD production process coupled with methanol synthesis.

List	Unit	Streams				
		26	27	28	29	30
H_2	KMOL/HR	0.0	0.0	7.0	1758.4	1670.5
H_2O	KMOL/HR	146.5	0.2	11.9	19.3	18.4
CO	KMOL/HR	0.0	0.0	0.1	9.5	9.0
CO_2	KMOL/HR	0.0	0.5	14.1	252.8	240.1
CH_4	KMOL/HR	0.0	0.0	2.2	73.6	69.9
C_2H_6	KMOL/HR	0.0	0.2	2.7	30.4	28.9
C_3H_8	KMOL/HR	0.0	8.5	39.8	181.7	172.6
$C_{11}H_{24}$	KMOL/HR	0.0	0.1	0.0	0.0	0.0
$C_{12}H_{26}$	KMOL/HR	0.0	0.3	0.0	0.0	0.0
$C_{13}H_{28}$	KMOL/HR	0.0	0.2	0.0	0.0	0.0
$C_{14}H_{30}$	KMOL/HR	0.0	0.6	0.0	0.0	0.0
$C_{15}H_{32}$	KMOL/HR	0.0	9.6	0.0	0.0	0.0
$C_{16}H_{34}$	KMOL/HR	0.0	33.1	0.0	0.0	0.0
$C_{17}H_{36}$	KMOL/HR	0.0	13.5	0.0	0.0	0.0
$C_{18}H_{38}$	KMOL/HR	0.0	45.4	0.0	0.0	0.0
C12:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C14:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C16:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:1TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:2TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:3TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
CH_3OH	KMOL/HR	0.0	0.0	0.0	0.0	0.0
Mole Flow	KMOL/HR	146.6	112.4	77.6	2325.7	2209.4
Mass Flow	KG/HR	2642.5	25000.0	2719.1	25393.5	24123.8
Pressure	BAR	1.0	1.0	1.0	50.0	50.0
Temperature	^oC	40.4	40.4	31.7	45.0	50.2
Vapor Fraction		0.0	0.0	1.0	1.0	1.0

Table 32 The composition, flow rate, and condition of each stream in BHD production process coupled with methanol synthesis.

List	Unit	Streams				
		31	32	33	34	35
H_2	KMOL/HR	1670.5	1670.5	87.9	0.0	87.9
H_2O	KMOL/HR	18.4	18.4	1.0	0.0	1.0
CO	KMOL/HR	9.0	9.0	0.5	0.0	0.5
CO_2	KMOL/HR	240.1	240.1	12.6	3.7	16.4
CH_4	KMOL/HR	69.9	69.9	3.7	0.0	3.7
C_2H_6	KMOL/HR	28.9	28.9	1.5	0.0	1.5
C_3H_8	KMOL/HR	172.6	172.6	9.1	0.0	9.1
$C_{11}H_{24}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{12}H_{26}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{13}H_{28}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{14}H_{30}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{15}H_{32}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{16}H_{34}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{17}H_{36}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{18}H_{38}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C12:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C14:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C16:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:1TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:2TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:3TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
CH_3OH	KMOL/HR	0.0	0.0	0.0	0.0	0.0
Mole Flow	KMOL/HR	2209.4	2209.4	116.3	3.7	120.0
Mass Flow	KG/HR	24123.8	24123.8	1269.7	164.5	1434.2
Pressure	BAR	50.0	50.0	50.0	50.0	50.0
Temperature	^oC	290.0	300.0	50.2	50.0	48.6
Vapor Fraction		1.0	1.0	1.0	1.0	1.0

Table 32 The composition, flow rate, and condition of each stream in BHD production process coupled with methanol synthesis.

List	Unit	Streams				
		36	37	38	39	40
H_2	KMOL/HR	87.9	921.1	877.2	877.2	877.2
H_2O	KMOL/HR	1.0	5.3	20.1	20.1	20.1
CO	KMOL/HR	0.5	14.7	15.0	15.0	15.0
CO_2	KMOL/HR	16.4	44.9	30.1	30.1	30.1
CH_4	KMOL/HR	3.7	73.1	73.1	73.1	73.1
C_2H_6	KMOL/HR	1.5	29.7	29.7	29.7	29.7
C_3H_8	KMOL/HR	9.1	174.3	174.3	174.3	174.3
$C_{11}H_{24}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{12}H_{26}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{13}H_{28}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{14}H_{30}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{15}H_{32}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{16}H_{34}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{17}H_{36}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{18}H_{38}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C12:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C14:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C16:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:1TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:2TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:3TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
CH_3OH	KMOL/HR	0.0	14.3	28.8	28.8	28.8
Mole Flow	KMOL/HR	120.0	1277.4	1248.3	1248.3	1248.3
Mass Flow	KG/HR	1434.2	14549.7	14549.7	14549.7	14549.7
Pressure	BAR	50.0	50.0	50.0	50.0	50.0
Temperature	^{o}C	220.0	220.0	239.1	129.4	125.8
Vapor Fraction		1.0	1.0	1.0	1.0	1.0

Table 32 The composition, flow rate, and condition of each stream in BHD production process coupled with methanol synthesis.

List	Unit	Streams				
		41	42	43	44	45
H_2	KMOL/HR	877.2	0.2	0.2	0.0	0.0
H_2O	KMOL/HR	20.1	15.6	15.6	15.5	15.5
CO	KMOL/HR	15.0	0.0	0.0	0.0	0.0
CO_2	KMOL/HR	30.1	0.0	0.0	0.0	0.0
CH_4	KMOL/HR	73.1	0.0	0.0	0.0	0.0
C_2H_6	KMOL/HR	29.7	0.0	0.0	0.0	0.0
C_3H_8	KMOL/HR	174.3	0.4	0.4	0.1	0.1
$C_{11}H_{24}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{12}H_{26}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{13}H_{28}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{14}H_{30}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{15}H_{32}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{16}H_{34}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{17}H_{36}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{18}H_{38}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C12:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C14:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C16:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:1TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:2TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:3TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
CH_3OH	KMOL/HR	28.8	13.8	13.8	13.7	13.7
Mole Flow	KMOL/HR	1248.3	30.0	30.0	29.3	29.3
Mass Flow	KG/HR	14549.7	744.0	744.0	723.2	723.2
Pressure	BAR	50.0	50.0	3.0	3.0	2.7
Temperature	^{o}C	60.0	60.0	58.2	58.2	58.2
Vapor Fraction		1.0	0.0	0.0	0.0	0.0

Table 32 The composition, flow rate, and condition of each stream in BHD production process coupled with methanol synthesis.

List	Unit	Streams				
		46	47	48	49	50
H_2	KMOL/HR	0.0	0.0	0.0	0.0	0.0
H_2O	KMOL/HR	15.5	0.1	0.1	0.1	0.1
CO	KMOL/HR	0.0	0.0	0.0	0.0	0.0
CO_2	KMOL/HR	0.0	0.0	0.0	0.0	0.0
CH_4	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C_2H_6	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C_3H_8	KMOL/HR	0.1	0.1	0.1	0.1	0.0
$C_{11}H_{24}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{12}H_{26}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{13}H_{28}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{14}H_{30}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{15}H_{32}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{16}H_{34}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{17}H_{36}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{18}H_{38}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C12:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C14:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C16:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:1TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:2TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:3TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
CH_3OH	KMOL/HR	13.7	51.3	51.3	50.7	38.0
Mole Flow	KMOL/HR	29.3	51.6	51.6	50.9	38.2
Mass Flow	KG/HR	723.2	1652.7	1652.7	1630.4	1222.8
Pressure	BAR	2.7	2.0	2.0	2.0	2.0
Temperature	^{o}C	101.6	83.5	83.5	78.9	78.9
Vapor Fraction		0.1	0.1	0.1	0.0	0.0

Table 32 The composition, flow rate, and condition of each stream in BHD production process coupled with methanol synthesis.

List	Unit	Streams				
		51	52	53	54	55
H_2	KMOL/HR	0.0	0.0	0.0	0.0	0.0
H_2O	KMOL/HR	0.0	0.0	0.0	0.0	52.8
CO	KMOL/HR	0.0	0.0	0.0	0.0	0.0
CO_2	KMOL/HR	0.0	0.0	0.0	0.0	0.0
CH_4	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C_2H_6	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C_3H_8	KMOL/HR	0.0	0.0	0.0	0.1	0.0
$C_{11}H_{24}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{12}H_{26}$	KMOL/HR	0.0	0.0	0.0	0.0	0.1
$C_{13}H_{28}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{14}H_{30}$	KMOL/HR	0.0	0.0	0.0	0.0	0.1
$C_{15}H_{32}$	KMOL/HR	0.0	0.0	0.0	0.0	0.4
$C_{16}H_{34}$	KMOL/HR	0.0	0.0	0.0	0.0	0.8
$C_{17}H_{36}$	KMOL/HR	0.0	0.0	0.0	0.0	0.3
$C_{18}H_{38}$	KMOL/HR	0.0	0.0	0.0	0.0	0.2
C12:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C14:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C16:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:1TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:2TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:3TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
CH_3OH	KMOL/HR	12.7	12.7	12.7	0.6	7.0
Mole Flow	KMOL/HR	12.7	12.7	12.7	0.7	61.7
Mass Flow	KG/HR	407.6	407.6	407.6	22.3	1617.9
Pressure	BAR	2.0	1.0	1.0	2.0	2.6
Temperature	^oC	78.9	63.5	45.0	78.9	112.8
Vapor Fraction		0.0	0.0	0.0	1.0	1.0

Table 32 The composition, flow rate, and condition of each stream in BHD production process coupled with methanol synthesis.

List	Unit	Streams				
		56	57	58	59	60
H_2	KMOL/HR	0.0	0.0	0.0	0.0	0.2
H_2O	KMOL/HR	37.3	15.5	15.5	15.5	0.0
CO	KMOL/HR	0.0	0.0	0.0	0.0	0.0
CO_2	KMOL/HR	0.0	0.0	0.0	0.0	0.0
CH_4	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C_2H_6	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C_3H_8	KMOL/HR	0.0	0.0	0.0	0.0	0.3
$C_{11}H_{24}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{12}H_{26}$	KMOL/HR	0.1	0.0	0.0	0.0	0.0
$C_{13}H_{28}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{14}H_{30}$	KMOL/HR	0.1	0.0	0.0	0.0	0.0
$C_{15}H_{32}$	KMOL/HR	0.4	0.0	0.0	0.0	0.0
$C_{16}H_{34}$	KMOL/HR	0.8	0.0	0.0	0.0	0.0
$C_{17}H_{36}$	KMOL/HR	0.3	0.0	0.0	0.0	0.0
$C_{18}H_{38}$	KMOL/HR	0.2	0.0	0.0	0.0	0.0
C12:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C14:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C16:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:1TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:2TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:3TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
CH_3OH	KMOL/HR	6.5	0.4	0.4	0.4	0.1
Mole Flow	KMOL/HR	45.8	15.9	15.9	15.9	0.7
Mass Flow	KG/HR	1324.6	293.3	293.3	293.3	20.7
Pressure	BAR	2.7	2.7	1.0	1.0	3.0
Temperature	^{o}C	123.8	123.8	96.0	45.0	58.2
Vapor Fraction		1.0	0.0	0.1	0.0	1.0

Table 32 The composition, flow rate, and condition of each stream in BHD production process coupled with methanol synthesis.

List	Unit	Streams				
		61	62	63	64	65
H_2	KMOL/HR	877.0	43.9	833.2	833.2	833.2
H_2O	KMOL/HR	4.5	0.2	4.3	4.3	4.3
CO	KMOL/HR	15.0	0.7	14.2	14.2	14.2
CO_2	KMOL/HR	30.1	1.5	28.6	28.6	28.6
CH_4	KMOL/HR	73.0	3.7	69.4	69.4	69.4
C_2H_6	KMOL/HR	29.7	1.5	28.2	28.2	28.2
C_3H_8	KMOL/HR	173.9	8.7	165.2	165.2	165.2
$C_{11}H_{24}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{12}H_{26}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{13}H_{28}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{14}H_{30}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{15}H_{32}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{16}H_{34}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{17}H_{36}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
$C_{18}H_{38}$	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C12:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C14:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C16:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:0TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:1TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:2TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
C18:3TG	KMOL/HR	0.0	0.0	0.0	0.0	0.0
CH_3OH	KMOL/HR	15.0	0.8	14.3	14.3	14.3
Mole Flow	KMOL/HR	1218.2	60.9	1157.3	1157.3	1157.3
Mass Flow	KG/HR	13805.7	690.3	13115.4	13115.4	13115.4
Pressure	BAR	50.0	50.0	50.0	50.0	50.0
Temperature	^{o}C	60.0	60.0	60.0	98.8	220.0
Vapor Fraction		1.0	1.0	1.0	1.0	1.0

APPENDIX D
Technical Feasibility Analysis

This technical analysis showed the comparison of discharged hydrogen from each process and carbon dioxide emission. BHD production process coupled with methanol synthesis can improve the conventional process since additional carbon dioxide converts the discharged hydrogen to methanol.

There were 2 streams which releases the hydrogen in conventional process. They were stream25 and stream30. Table 33 shows the amount and composition of vent gas stream. Stream30 has more hydrogen, so this stream will be the main raw material for new process. Also, Table 34 showed the released carbon dioxide released from the required utility which was calculated by CO_2 emission data source: US EPA Rule E9-5711 from Aspen Plus software.

Table 33 The amount and composition of vent stream in BHD production process

List	Unit	Streams	
		25	30
H_2	KMOL/HR	7.0	87.9
H_2O	KMOL/HR	11.9	1.0
CO	KMOL/HR	0.1	0.5
CO_2	KMOL/HR	14.1	12.6
CH_4	KMOL/HR	2.2	3.7
C_2H_6	KMOL/HR	2.7	1.5
C_3H_8	KMOL/HR	39.7	9.1
Mole Flow	KMOL/HR	77.6	116.3
Mass Flow	KG/HR	2718.9	1269.7
Pressure	BAR	1.0	50.0
Temperature	^{o}C	31.7	50.2
Vapor Fraction		1.0	1.0

Table 34 The amount of carbon dioxide from utility in BHD production process

List	Unit	Utility
CO_2	KMOL/HR	54.94
Mole Flow	KMOL/HR	54.94
Mass Flow	KG/HR	2417.9
Pressure	BAR	N/A
Temperature	°C	N/A
Vapor Fraction		1.0

For the new process, there were 4 streams which were the outlet gas streams as shown in Table 35. One stream was the same stream as conventional process. The others were from the methanol synthesis process. Also, Table 36 shows the released carbon dioxide released from the required utility.

Table 35 The amount and composition of vent stream in BHD production process coupled with methanol synthesis

List	Unit	Streams			
		28	54	60	62
H_2	KMOL/HR	7.0	0.0	0.2	43.9
H_2O	KMOL/HR	11.9	0.0	0.0	0.2
CO	KMOL/HR	0.1	0.0	0.0	0.7
CO_2	KMOL/HR	14.1	0.0	0.0	1.5
CH_4	KMOL/HR	2.2	0.0	0.0	3.7
C_2H_6	KMOL/HR	2.7	0.0	0.0	1.5
C_3H_8	KMOL/HR	39.8	0.1	0.3	8.7
CH_3OH	KMOL/HR	0.0	0.6	0.1	0.8
Mole Flow	KMOL/HR	77.6	0.7	0.7	60.9
Mass Flow	KG/HR	2719.1	22.3	20.7	690.3
Pressure	BAR	1.0	2.0	3.0	50.0
Temperature	°C	31.7	78.9	58.2	60.0
Vapor Fraction		1.0	1.0	1.0	1.0

Table 36 The amount of carbon dioxide from utility in BHD production process coupled with methanol synthesis

List	Unit	Utility
CO_2	KMOL/HR	57.84
Mole Flow	KMOL/HR	57.84
Mass Flow	KG/HR	2545.5
Pressure	BAR	N/A
Temperature	^oC	N/A
Vapor Fraction		1.0

The comparison of effluent hydrogen, carbon dioxide, and carbon monoxide gas from each production process were shown in Table 37. It implies that the new process can reduce the purged hydrogen 46.2 percent. Moreover, it can deduct the carbon dioxide and carbon monoxide emission from the process and utility 9.5 percent. In addition, it safe the carbon dioxide from the other process 4.5 percent of process. The calculation was shown below;

Hydrogen recovery
= (Released H_2 from conventional process – Released H_2 from new process) / (Released H_2 from conventional process) x 100
= (94.9-51.1) / 94.9 x 100
= 46.2 %

Carbon dioxide and carbon monoxide emission reduction
= (Released CO_2 and CO from conventional process – Released CO_2 and CO from new process) / (Released CO_2 and CO from conventional process) x 100
= (82.24-74.24) / 82.24 x 100
= 9.7 %

Carbon dioxide and carbon monoxide emission reduction from the other process
= (Released CO_2 and CO from other process) / (Released CO_2 and CO from conventional process) x 100
= 3.7 / 82.24 x 100
= 4.5 %

Table 37 Comparison amount of released hydrogen, carbon dioxide, and carbon monoxide from process and utility

List	Unit	BHD production process	BHD production process coupled with methanol synthesis
H_2	KMOL/HR	94.9	51.1
CO	KMOL/HR	0.6	0.8
CO_2	KMOL/HR	81.64	73.44

APPENDIX E
Design of Equipment

This section showed the equipment designs which were equipment type selection and equipment sizing for both production process. Table 38 shows the number of each equipment of both processes.

Table 38 Number of equipment in each process

Equipment	BHD Production Process	BHD Production Process with Methanol Synthesis
Reactor	1	2
Pump	1	1
Valve	2	6
Heat Exchanger	7	16
Flash Drum	2	5
Decanter	1	1
Distillation Column	0	1

For the BHD reactor (R-101 and R-201), it needs very low liquid hourly space velocity. So, very low flow rate was required. This design was based on the reactor condition from literature “production of BHD by catalytic hydrotreating of palm oil over $NiMoS_2$ -Al_2O_3 catalyst” which A. Srifa [20] claimed. The reactor condition was shown as Table 39.

Table 39 BHD reactor condition from literature

Parameter	Literature Lab. Scale Reactor
Volume [L]	0.012 L
LHSV [h^{-1}]	1 h^{-1}
Flow Rate [L/min]	$Q/V = 1\ h^{-1}$ $Q = V \times 1\ h^{-1} = 12\ mL/h$
Catalyst wt. [g]	8.5 g
Cross Sectional Area [m^2]	Tube reactor $A = Pi / 4 \times (0.007m)^2$ $= 0.0000385\ m^2$

According the very high flow rate from the process design, the influent stream of reactor should be separated to 10 reactors for low LHSV. Each reactor was designed as similar as the shell and tube heat exchanger. All of these reactors were operated under isothermal condition because the result of simulation shows that if the operation was adiabatic system, the outlet temperature was 461 °C which was more than 10 percent of inlet temperature. Table 40 showed the calculation of BHD reactor design.

Table 40 BHD reactor design

Parameter	**BHD Reactor Design (R-101, R-201)**
LHSV [h^{-1}]	1 h^{-1}, Fixing parameter
Flow Rate [l/min]	Q = 1797 L/min x 60 min/h = 107820 L/h So, Total Volume = 107820 L
Catalyst wt. [g]	Catalyst wt. = 107820 L x (8.5 g/0.012 L) = 76372.5 kg
Cross Sectional Area [m^2]	$Re_{lab} = Re_{design}$ $(\rho du/\mu)_{lab} = (\rho du/\mu)_{design}$; ρd/μ were equal and u = Q/A $(Q/A)_{lab} = (Q/A)_{design}$; 0.012/0.0000385 = 107820/A; $A_{design} = 346\ m^2$ <u>Assume</u> tube diameter = 1 inch = 2.54 cm (A = 0.0005 m^2) So, there were 346/0.0005 = 682405 tubes. And flow per tube is 107820/682405 = 0.158 L/h V = Q / (1 h^{-1}) = 0.158 L; Length = V/A = 0.158 L/0.0005 = 0.32 m
Heat Transfer Area [m^2]	Required heat transfer area = 340.5 m^2 ; from Aspen But total heat transfer area = 682405 x (Pi x 0.0254 x 0.32) = 17425 m^2
Volume per Reactor [l]	Separate reactor to 10 reactors (shell and tube); Total area per reactor = 17425/10 = 1742.5 m^2

For methanol synthesis reactor design (R-202), this reactor was designed as similar as the reactor from literature “Design and simulation of a methanol production plant from CO_2 hydrogenation” which Éverton Simões Van-Dal [27] claimed. The assumption for this reactor was that 33 percent of carbon dioxide was converted to methanol. This reactor was also designed as the shell and tube heat exchanger. The 1041 kg of catalyst was required which calculated from the design specification result in Aspen plus. So, the number of tubes was calculated as below. Table 41 shows the methanol synthesis reactor design.

Number of tubes
= Required catalyst weight / Catalyst weight per tube
= 1041 kilogram / (0.04 kilogram per tube)
≈ 26000 tubes

Total volume of reactor
= 26000 tubes x (π x 0.016^2 / 4 x 0.15 m^3/tube)
= 0.78 m^3

L/D parameter was fixed at 9.375 (0.15/0.016 = 9.375) as literature [27], so diameter and length of packed bed could be determined from total volume as below;

$V = \pi \times D^2 / 4 \times L_{bed}$
$0.78\ m^3 = \pi \times D^2 / 4 \times (D \times 9.375)$
$D = 0.47\ m$
$L_{bed} = 4.43\ m$

Glass beads for packing the bed was assumed around 0.2 m at the beginning and the end of bed. So, reactor length was around 4.83 m.

Table 41 Methanol synthesis reactor design

Parameter	Literature	Methanol Synthesis Reactor Design (R-202)
Flow rate [kg/s]	2.8×10^{-5}	4.04
Catalyst weight [kg]	0.04	1041
Reactor diameter [m]	0.016	0.47
Reactor length [m]	0.15	4.83

The designs of pump (P-101 and P-201) which were needed for pressurize the liquid for these two processes were the same design. Also, a decanter and 3 flash drums volume were the same designed for liquid-liquid separation and vapor-liquid separation. But there were 3 additional flash drums for methanol synthesis unit which were F-203, F-204, and F-205. The result was from the Aspen plus calculation. These designs were shown in Table 16 and Table 17, respectively.

Heat exchangers were the major equipment for heating and cooling the process streams to the set temperature. There were 3 cold streams and 1 hot stream in BHD production process as shown in Figure 36. But there were 7 cold streams and 5 hot streams in BHD production process coupled with methanol synthesis as shown in Figure 37. Figure 17 and Figure 21 show both of these process after heat integration. Table 42 shows the comparison of energy from utility which were served for each process before and after doing the heat exchanger network. Total area for heat transfer was determined by Aspen plus and the design uses the tubular exchanger manufacturers association system (TEMA) as shown in Table 18 and Table 23. The composite temperature-enthalpy information of each heat exchanger in each process were shown in Table 43 and Table 44.

Table 42 Comparison of energy from utility which were required for each process before and after heat integration

Process	**BHD production process**		**BHD production process with methanol synthesis**	
	Hot Utility	**Cold Utility**	**Hot Utility**	**Cold Utility**
without HEN	11851	14763	14985	18177
with HEN	466.24	3378.24	1010	4202

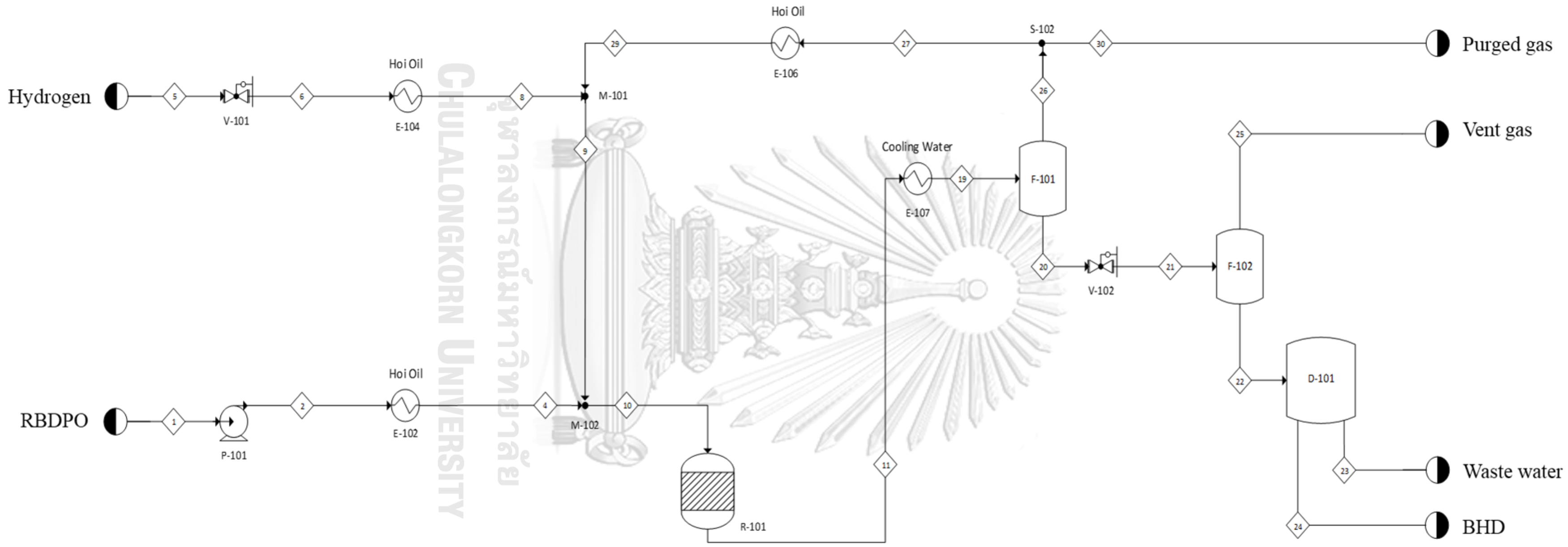

Figure 36 BHD production process before heat integration

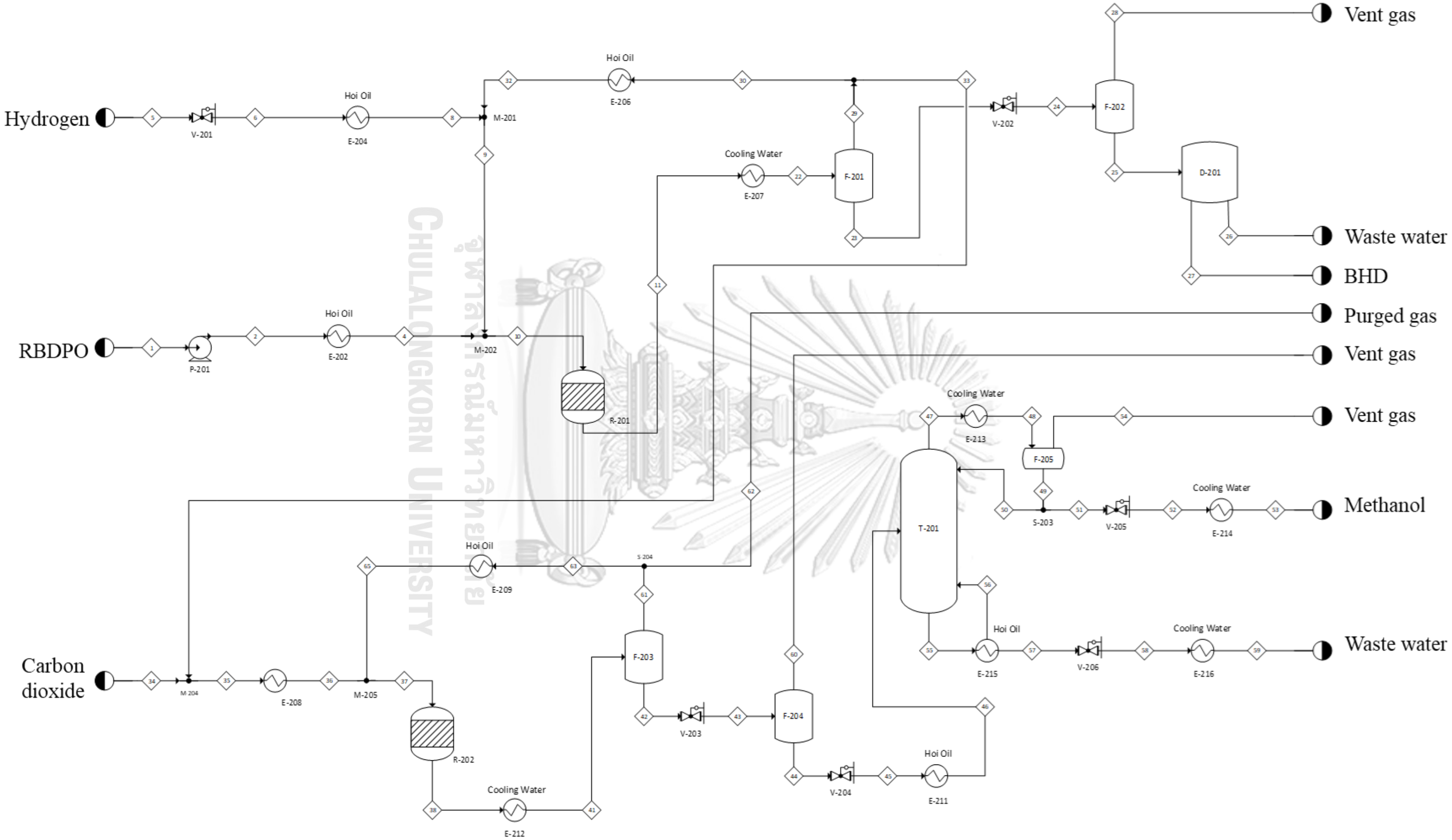

Figure 37 BHD production process coupled with methanol synthesis before heat integration

Table 43 Temperature-enthalpy of the stream for each heat exchanger (BHD production process)

E-101			**E-102**			**E-103**		
Heat duty	**Cold stream temperature**	**Hot stream temperature**	**Heat duty**	**Cold stream temperature**	**Hot stream temperature**	**Heat duty**	**Cold stream temperature**	**Hot stream temperature**
cal/sec	**ºC**	**ºC**	**cal/sec**	**ºC**	**ºC**	**cal/sec**	**ºC**	**ºC**
0.00	290.00	300.00	0.00	300.00	320.00	0.00	290.00	300.00
51093.68	279.83	292.65	2418.65	299.53	319.05	12089.67	278.58	292.37
102187.36	269.56	285.06	4837.29	299.05	318.10	24179.33	267.17	284.47
153281.03	259.16	277.21	7255.94	298.58	317.15	36269.00	255.76	276.30
204374.71	248.64	269.10	9674.59	298.10	316.20	48358.66	244.34	267.85
255468.39	237.98	260.73	12093.24	297.63	315.25	60448.33	232.93	259.11
306562.07	227.18	252.10	14511.88	297.15	314.30	72537.99	221.52	250.09
357655.75	216.24	243.19	16930.53	296.68	313.34	84627.66	210.11	240.78
408749.43	205.14	234.03	19349.18	296.20	312.39	96717.32	198.71	231.19
459843.10	193.86	224.60	21767.83	295.73	311.44	108806.99	187.30	221.32
510936.78	182.41	214.93	24186.47	295.25	310.49	120896.65	175.89	211.18
562030.46	170.76	205.01	26605.12	294.77	309.54	132986.32	164.48	200.79
613124.14	158.91	194.86	29023.77	294.30	308.58	145075.98	153.07	190.15
664217.82	146.83	184.49	31442.42	293.82	307.63	157165.65	141.65	179.29
715311.49	134.51	173.93	33861.06	293.34	306.68	169255.31	130.23	168.22
766405.17	121.93	163.18	36279.71	292.87	305.72	181344.98	118.81	156.97
817498.85	109.07	152.27	38698.36	292.39	304.77	193434.64	107.38	143.53
868592.53	95.91	139.15	41117.01	291.91	303.82	205524.31	95.94	131.86
919686.21	82.41	127.86	43535.65	291.43	302.86	217613.97	84.49	120.07
970779.88	68.54	116.47	45954.30	290.96	301.91	229703.64	73.04	108.20
1021873.56	54.28	105.03	48372.95	290.48	300.95	241793.30	61.56	96.31
1072967.24	39.59	93.59	50791.59	290.00	300.00	253882.97	50.08	84.59

Table 43 Temperature-enthalpy of the stream for each heat exchanger (BHD production process)

E-104			**E-105**			**E-106**		
Heat duty	**Cold stream temperature**	**Hot stream temperature**	**Heat duty**	**Cold stream temperature**	**Hot stream temperature**	**Heat duty**	**Cold stream temperature**	**Hot stream temperature**
cal/sec	**ºC**	**ºC**	**cal/sec**	**ºC**	**ºC**	**cal/sec**	**ºC**	**ºC**
0.00	300.00	320.00	0.00	290.00	300.00	0.00	300.00	320.00
504.25	299.52	319.05	64377.86	279.14	292.43	2835.02	299.52	319.05
1008.50	299.05	318.10	128755.72	268.23	284.59	5670.04	299.05	318.10
1512.75	298.57	317.15	193133.59	257.28	276.49	8505.06	298.57	317.15
2017.00	298.10	316.20	257511.45	246.27	268.11	11340.08	298.10	316.20
2521.25	297.62	315.25	321889.31	235.21	259.44	14175.10	297.62	315.25
3025.50	297.14	314.30	386267.17	224.10	250.50	17010.12	297.15	314.30
3529.75	296.67	313.34	450645.03	212.93	241.28	19845.14	296.67	313.34
4033.99	296.19	312.39	515022.89	201.71	231.77	22680.16	296.20	312.39
4538.24	295.71	311.44	579400.75	190.43	222.00	25515.18	295.72	311.44
5042.49	295.24	310.49	643778.62	179.09	211.96	28350.20	295.24	310.49
5546.74	294.76	309.54	708156.48	167.69	201.66	31185.22	294.77	309.54
6050.99	294.29	308.58	772534.34	156.22	191.13	34020.24	294.29	308.58
6555.24	293.81	307.63	836912.20	141.05	180.37	36855.26	293.81	307.63
7059.49	293.33	306.68	901290.06	129.26	169.40	39690.27	293.34	306.68
7563.74	292.86	305.72	965667.92	117.39	158.26	42525.29	292.86	305.72
8067.99	292.38	304.77	1030045.78	105.45	144.93	45360.31	292.38	304.77
8572.24	291.90	303.82	1094423.65	93.44	133.37	48195.33	291.91	303.82
9076.49	291.43	302.86	1158801.51	81.38	121.68	51030.35	291.43	302.86
9580.74	290.95	301.91	1221218.56	69.63	110.27	53865.37	290.95	301.91
10084.99	290.48	300.95	1223179.37	69.37	109.91	56700.39	290.48	300.95
10589.24	290.00	300.00	1287557.23	60.15	98.11	59535.41	290.00	300.00
			1351935.09	50.23	86.42			

Table 43 Temperature-enthalpy of the stream for each heat exchanger (BHD production process)

E-107		
Heat duty	**Cold stream temperature**	**Hot stream temperature**
cal/sec	**°C**	**°C**
0.00	50.00	89.15
40431.23	49.29	85.54
80862.46	48.57	82.01
121293.69	47.86	78.70
202156.15	46.43	78.15
242587.38	45.72	78.10
283018.61	45.00	77.16
323449.84	44.29	75.79
363881.07	43.57	74.15
404312.30	42.86	72.32
444743.53	42.14	70.33
485174.76	41.43	68.20
525605.99	40.72	65.96
566037.22	40.00	63.62
606468.45	39.29	61.19
646899.68	38.57	58.67
687330.91	37.86	56.07
727762.14	37.14	53.39
768193.37	36.43	50.65
808624.60	35.71	47.85
849055.83	35.00	45.00

Table 44 *Temperature-enthalpy of the stream for each heat exchanger (BHD production process coupled with methanol synthesis)*

E-201			**E-202**			**E-203**		
Heat duty	**Cold stream temperature**	**Hot stream temperature**	**Heat duty**	**Cold stream temperature**	**Hot stream temperature**	**Heat duty**	**Cold stream temperature**	**Hot stream temperature**
cal/sec	**°C**	**°C**	**cal/sec**	**°C**	**°C**	**cal/sec**	**°C**	**°C**
0.00	290.00	300.00	0.00	300.00	320.00	0.00	290.00	300.00
52508.96	279.83	291.79	2485.61	299.53	319.05	12095.47	278.58	292.10
105017.93	269.55	283.27	4971.23	299.05	318.10	24190.94	267.16	283.92
157526.89	259.16	274.43	7456.84	298.58	317.15	36286.40	255.74	275.44
210035.86	248.63	265.26	9942.46	298.10	316.20	48381.87	244.33	266.67
262544.82	237.98	255.77	12428.07	297.63	315.25	60477.34	232.91	257.58
315053.79	227.18	245.95	14913.69	297.15	314.30	72572.80	221.50	248.20
367562.75	216.24	235.80	17399.30	296.68	313.34	84668.27	210.09	238.50
420071.72	205.14	225.32	19884.92	296.20	312.39	96763.74	198.68	228.51
472580.68	193.86	214.53	22370.53	295.73	311.44	108859.21	187.26	218.22
525089.65	182.41	203.44	24856.15	295.25	310.49	120954.68	175.85	207.65
577598.61	170.76	192.06	27341.76	294.77	309.54	133050.14	164.44	196.80
630107.58	158.91	180.42	29827.38	294.30	308.58	145145.61	153.02	185.71
682616.54	146.83	168.54	32312.99	293.82	307.63	157241.08	141.60	174.38
735125.50	134.51	156.44	34798.61	293.34	306.68	169336.55	130.18	162.84
787634.47	121.93	142.11	37284.22	292.87	305.72	181432.01	118.75	151.12
840143.43	109.07	129.54	39769.84	292.39	304.77	193527.48	107.32	137.13
892652.40	95.90	116.85	42255.45	291.91	303.82	205622.95	95.88	124.98
945161.36	82.40	104.07	44741.06	291.43	302.86	217718.42	84.43	112.73
997670.33	68.54	91.32	47226.68	290.96	301.91	229813.88	72.96	100.43
1050179.29	54.28	79.13	49712.29	290.48	300.95	241909.35	61.49	88.21
1102688.26	39.59	77.87	52197.91	290.00	300.00	254004.82	50.00	77.07

Table 44 Temperature-enthalpy of the stream for each heat exchanger (BHD production process coupled with methanol synthesis)

E-204			**E-205**			**E-206**		
Heat duty	**Cold stream temperature**	**Hot stream temperature**	**Heat duty**	**Cold stream temperature**	**Hot stream temperature**	**Heat duty**	**Cold stream temperature**	**Hot stream temperature**
cal/sec	**ºC**	**ºC**	**cal/sec**	**ºC**	**ºC**	**cal/sec**	**ºC**	**ºC**
0.00	300.00	320.00	0.00	290.00	300.00	0.00	300.00	320.00
504.32	299.52	319.05	64440.47	279.13	292.10	2834.86	299.52	319.05
1008.65	299.05	318.10	128880.95	268.21	283.90	5669.73	299.05	318.10
1512.97	298.57	317.15	193321.42	257.24	275.42	8504.59	298.57	317.15
2017.30	298.10	316.20	257761.90	246.23	266.63	11339.46	298.10	316.20
2521.62	297.62	315.25	322202.37	235.16	257.54	14174.32	297.62	315.25
3025.95	297.14	314.30	386642.84	224.03	248.14	17009.19	297.15	314.30
3530.27	296.67	313.34	451083.32	212.85	238.43	19844.05	296.67	313.34
4034.59	296.19	312.39	515523.79	201.62	228.43	22678.92	296.20	312.39
4538.92	295.71	311.44	579964.26	190.33	218.12	25513.78	295.72	311.44
5043.24	295.24	310.49	644404.74	178.97	207.54	28348.64	295.24	310.49
5547.57	294.76	309.54	708845.21	167.56	196.68	31183.51	294.77	309.54
6051.89	294.29	308.58	773285.69	156.08	185.57	34018.37	294.29	308.58
6556.22	293.81	307.63	837726.16	140.90	174.23	36853.24	293.81	307.63
7060.54	293.33	306.68	902166.63	129.09	162.68	39688.10	293.34	306.68
7564.87	292.86	305.72	966607.11	117.20	150.94	42522.97	292.86	305.72
8069.19	292.38	304.77	1031047.58	105.25	136.93	45357.83	292.38	304.77
8573.51	291.90	303.82	1095488.05	93.23	124.77	48192.70	291.91	303.82
9077.84	291.43	302.86	1159928.53	81.15	112.51	51027.56	291.43	302.86
9582.16	290.95	301.91	1221191.38	69.62	100.80	53862.42	290.95	301.91
10086.49	290.48	300.95	1224369.00	69.19	100.19	56697.29	290.48	300.95
10590.81	290.00	300.00	1288809.48	59.95	87.96	59532.15	290.00	300.00
			1353249.95	50.00	76.90			

Table 44 Temperature-enthalpy of the stream for each heat exchanger (BHD production process coupled with methanol synthesis)

E-207			**E-208**			**E-209**		
Heat duty	**Cold stream temperature**	**Hot stream temperature**	**Heat duty**	**Cold stream temperature**	**Hot stream temperature**	**Heat duty**	**Cold stream temperature**	**Hot stream temperature**
cal/sec	**°C**	**°C**	**cal/sec**	**°C**	**°C**	**cal/sec**	**°C**	**°C**
0.00	50.00	78.21	0.00	220.00	300.00	0.00	98.80	238.61
27275.51	48.57	77.79	2460.23	212.19	297.40	5732.82	96.98	230.88
54551.02	47.86	77.06	4920.45	204.35	294.78	11465.64	95.15	222.98
81826.53	47.14	76.15	7380.68	196.48	292.12	17198.45	93.32	214.91
109102.04	46.43	75.11	9840.91	188.59	289.42	22931.27	91.48	206.66
136377.55	45.72	73.96	12301.13	180.66	286.70	28664.09	89.65	198.26
163653.06	45.00	72.73	14761.36	172.71	283.95	34396.91	87.81	189.70
190928.57	44.29	71.42	17221.58	164.73	281.16	40129.73	85.97	180.99
218204.08	43.57	70.05	19681.81	156.72	278.34	45862.55	84.13	172.16
245479.59	42.86	68.61	22142.04	144.17	275.48	51595.36	82.29	163.19
272755.10	42.14	67.13	24602.26	135.92	272.59	57328.18	80.44	154.12
300030.61	41.43	65.59	27062.49	127.64	269.67	63061.00	78.59	142.90
327306.12	40.72	64.01	29522.72	119.32	266.72	68793.82	76.74	133.54
354581.63	40.00	62.39	31982.94	110.97	263.73	74526.64	74.89	124.10
381857.14	39.29	60.72	34443.17	102.59	260.71	80259.45	73.03	114.60
409132.65	38.57	59.02	36903.40	94.18	257.65	85992.27	71.18	105.07
436408.15	37.86	57.28	39363.62	85.75	254.56	91725.09	69.32	95.53
463683.66	37.14	55.51	41823.85	77.29	251.44	97457.91	67.46	86.11
490959.17	36.43	53.70	44284.07	68.83	248.28	103190.73	65.60	77.48
518234.68	35.71	51.87	44329.71	68.67	248.22	108923.54	63.73	78.11
545510.19	35.00	50.00	46744.30	62.40	245.09	114656.36	61.87	74.88
572785.70			49204.53	55.66	241.87	120389.18	60.00	70.01
			51664.75	48.60	238.61			

Table 44 Temperature-enthalpy of the stream for each heat exchanger (BHD production process coupled with methanol synthesis)

E-210			**E-211**			**E-212**		
Heat duty	**Cold stream temperature**	**Hot stream temperature**	**Heat duty**	**Cold stream temperature**	**Hot stream temperature**	**Heat duty**	**Cold stream temperature**	**Hot stream temperature**
cal/sec	**^{o}C**	**^{o}C**	**cal/sec**	**^{o}C**	**^{o}C**	**cal/sec**	**^{o}C**	**^{o}C**
0.00	220.00	239.00	0.00	101.00	129.38	0.00	50.00	125.80
18909.95	214.51	234.00	596.22	100.77	129.21	14065.83	49.29	121.76
37819.89	208.99	228.98	1192.45	100.50	129.04	28131.66	48.57	117.71
56729.84	203.46	223.94	1788.67	100.17	128.87	42197.49	47.86	113.66
75639.79	197.90	218.89	2384.90	99.77	128.70	56263.32	47.14	109.59
94549.74	192.32	213.82	2981.12	99.25	128.53	70329.15	46.43	105.51
113459.69	186.72	208.74	3577.35	98.56	128.36	84394.97	45.72	101.42
132369.63	181.10	203.63	4173.57	97.64	128.18	98460.80	45.00	97.31
151279.58	175.45	198.51	4769.80	96.40	128.01	112526.63	44.29	93.20
170189.53	169.78	193.37	5366.02	94.76	127.84	120089.56	43.90	90.98
189099.47	164.08	188.22	5962.25	92.71	127.67	126592.46	43.57	89.93
208009.42	158.36	183.04	6558.47	90.28	127.50	140658.29	42.86	87.62
226919.37	152.62	177.84	7154.69	87.56	127.33	154724.12	42.14	85.28
245829.32	146.06	172.63	7750.92	84.63	127.16	168789.95	41.43	82.91
264739.26	140.24	167.40	8347.14	81.55	126.99	182855.78	40.72	80.52
283649.21	134.40	162.15	8943.37	78.36	126.82	196921.61	40.00	78.09
302559.16	128.54	156.87	9539.59	75.09	126.65	210987.44	39.29	75.63
321469.11	122.64	151.58	10135.82	71.75	126.48	225053.27	38.57	73.14
340379.05	116.72	145.49	10732.04	68.37	126.31	239119.09	37.86	70.61
359289.00	110.77	140.14	11328.27	64.94	126.14	253184.92	37.14	68.03
378198.95	104.80	134.77	11924.49	61.49	125.97	267250.75	36.43	65.41
397108.90	98.80	129.38	12520.72	58.00	125.80	281316.58	35.71	62.73
						295382.41	35.00	60.00

Table 44 Temperature-enthalpy of the stream for each heat exchanger (BHD production process coupled with methanol synthesis)

E-214			**E-216**		
Heat duty	**Cold stream temperature**	**Hot stream temperature**	**Heat duty**	**Cold stream temperature**	**Hot stream temperature**
cal/sec	**°C**	**°C**	**cal/sec**	**°C**	**°C**
0.00	50.00	63.50	0.00	50.00	96.00
127.48	49.29	63.43	298.52	49.29	95.90
254.95	48.57	63.34	597.05	48.57	95.80
382.43	47.86	63.24	895.57	47.86	95.69
509.91	47.14	63.11	1194.10	47.14	95.57
637.38	46.43	62.94	1492.62	46.43	95.45
764.86	45.72	62.74	1791.15	45.72	95.32
892.34	45.00	62.47	2089.67	45.00	95.13
1019.81	44.29	62.11	2352.42	44.37	93.40
1147.29	43.57	61.63	2388.20	44.29	92.96
1274.77	42.86	61.01	2686.72	43.57	89.27
1402.24	42.14	60.20	2985.25	42.86	85.58
1529.72	41.43	59.20	3283.77	42.14	81.89
1607.89	40.99	58.45	3582.30	41.43	78.19
1657.20	40.72	57.84	3880.82	40.72	74.50
1784.67	40.00	56.26	4179.34	40.00	70.81
1912.15	39.29	54.66	4477.87	39.29	67.11
2039.63	38.57	53.07	4776.39	38.57	63.42
2167.11	37.86	51.46	5074.92	37.86	59.73
2294.58	37.14	49.86	5373.44	37.14	56.04
2422.06	36.43	48.24	5671.97	36.43	52.36
2549.54	35.71	46.62	5970.49	35.71	48.68
2677.01	35.00	45.00	6269.02	35.00	45.00

Distillation Column (T-201) was required for the methanol synthesis part which was designed for methanol purification. This column was designed to be the sieve-tray column which has 18 trays. The condenser operates as partial condenser to separate the light gas which were hydrogen, methane, ethane, and propane at 2 bar and 79 ^{o}C. The high purity methanol was obtained as the overhead product. The reboiler was operated at 2.7 bar and 123.8 ^{o}C and the water was obtained. Table 24 showed the dimension of distillation column, and tray space from Aspen plus results.

APPENDIX F
Economic Feasibility Analysis

This section showed the calculation of capital cost investment and economic feasibility of both process based on R. Turton and team method [30]. The economic engineering analysis were considered in term of internal rate of return, payback period, and net present value. This study assumed to analyze base on in 2018 cost. So, the chemical engineering plant cost index (CEPCI) would be applied for changing cost from calculation to the cost in 2018 which could be calculated by using Equation 7. The CEPCI of each year were shown in Table 45.

Equation 7

$$C_{2018} = \frac{I_{2018}}{I_i} x\ C_i$$

Where C_{2018} = Purchased cost in 2018
C_i = Purchased cost in year i
I_{2018} = CEPCI in 2018
I_i = CEPCI in year i

Table 45 The CEPCI of each year

Year	CEPCI
2001	394
2010	550.8
2018	603

The fixed capital investment was determined by calculating for equipment purchased cost. Bare module cost of each equipment can be calculated by product of bare module factor and purchase cost as Equation 8. Purchased cost was calculated by using the Equation 9 by using the constant K_i as shown in Table 46 for calculation. F_{BM} was calculated by Equation 10 by using constant as shown in Table 47. F_P could be determined by Equation 11 and constants were shown in Table 48.

Equation 8

$$C_{BM}^0 = F_{BM} C_p^0$$

Equation 9

$$log_{10} C_p^0 = K_1 + K_2 log_{10} A + K_3 (log_{10} A)^2$$

Where C_P^0 = Purchased cost
K_i = Constant
A = Capacity or size parameter for each equipment

Table 46 Constant Ki for purchased cost calculation

Equipment	**A**	**K_1**	**K_2**	**K_3**
Pump	Power [kW]	3.8696	0.3161	0.122
Shell and tube heat exchanger	Area [m^2]	4.3247	-0.303	0.1634
Tubular reactor	Area [m^2]	4.3247	-0.303	0.1634
Vessel	Volume [m^3]	3.4974	0.4485	0.1074
Tower Vessel	Volume [m^3]	3.4974	0.4485	0.1074
Tray	Area [m^2]	2.9949	0.4465	0.3961

Equation 10

$$F_{BM} = B_1 + B_2 F_M F_p$$

Table 47 Constant Bi and material factor for bare module factor calculation

Equipment	**B_1**	**B_2**	**F_M**
Pump	1.89	1.35	2.5
Shell and tube heat exchanger	1.63	1.66	2.7
Tubular reactor	1.63	1.66	2.7
Vessel	3.1	2.25	1.82
Tower Vessel	3.1	2.25	1.82
Tray	F_{BM} = 1.8		

Equation 11

$$log_{10}F_P = C_1 + C_2 log_{10}P + C_3(log_{10}P)^2$$

Where F_P = Pressure factor
C_i = Constant
P = Operating pressure [bar]

Table 48 Constant Ci for pressure factor calculation

Equipment	**C_1**	**C_2**	**C_3**
Pump	-0.245382	0.259016	-0.01363
Shell and tube heat exchanger	0.038810	-0.112720	0.08183
Tubular reactor	0.038810	-0.112720	0.08183

Pressure factor for vessel could be calculated by using the correlation of thickness as shown in Equation 12. Table 49, Table 50, and Table 51 show the thickness of each vessel and pressure factor of each equipment in both process.

Equation 12

$$t = \frac{PD}{2SE-1.2P} + CA$$

$F_P = 1$ If $t < t_{min}$ and $P > -0.5$ bar
$F_P = t/t_{min}$ If $t > t_{min}$ and $P > -0.5$ bar
$F_P = 1.25$ If $P < -0.5$ bar

Where t = Thickness [m]
P = Operating pressure [bar]
D = Diameter [m]
S = Maximum allowable pressure (944 bar)
E = Weld efficiency (0.6)
CA = Corrosion allowance (0.00315 m)
t_{min} = Minimum allowable thickness (0.0063 m)

Table 49 The thickness of each vessel and pressure factor for vessel in both process

Equipment	**Thickness [m]**	**F_P**
D-101, D-201	0.0063	1.00
F-101, F-201	0.0870	13.80
F-102, F-202	0.0063	1.00
F-203	0.0489	7.76
F-204	0.0063	1.00
F-205	0.0063	1.00
R-202	0.027	4.23
T-201 (Vessel)	0.0063	1.00

Table 50 The pressure factor for each equipment in BHD production process

Equipment	F_P
P-101	1.44
E-101	1.22
E-102	1.22
E-103	1.22
E-104	1.22
E-105	1.22
E-106	1.22
E-107	1.22
R-101	1.22

Table 51 The pressure factor for each equipment in BHD production process coupled with methanol synthesis

Equipment	F_P	Equipment	F_P
P-201	1.44	**E-210**	1.22
E-201	1.22	**E-211**	1.15
E-202	1.22	**E-212**	1.22
E-203	1.22	**E-213**	1.02
E-204	1.22	**E-214**	2.87
E-205	1.22	**E-215**	1.00
E-206	1.22	**E-216**	2.87
E-207	1.22	**R-201**	1.22
E-208	1.22	**R-202**	4.23
E-209	1.22	**T-201 (Tray)**	1.00

The bare module factor, purchased cost, and bare module cost of each equipment for both production process as shown in Table 52 and Table 53.

Table 52 The bare module factor, purchased cost, and bare module cost of each equipment for BHD production process

Equipment	**F_{BM}**	**C_P^0 [USD]**	**C_{BM} [USD]**
P-101	6.77	25865.36	174984.96
D-101	7.89	10254.27	80926.70
F-101	80.14	11874.73	951603.51
F-102	7.89	10468.38	82616.49
R-101	7.11	114597.99	8142768.16
E-101	7.11	31271.89	222202.62
E-102	7.11	15853.74	112648.82
E-103	7.11	20366.36	144713.30
E-104	7.11	16087.27	114308.24
E-105	7.11	37233.23	264560.96
E-106	7.11	16141.40	114692.81
E-107	7.11	33111.56	235274.43

Table 53 The bare module factor, purchased cost, and bare module cost of each equipment for BHD production process coupled with methanol synthesis

Equipment	**F_{BM}**	**C_P^0 [USD]**	**C_{BM} [USD]**
P-201	6.77	25865.36	174984.96
D-201	7.89	10254.27	80926.70
F-201	80.14	11874.73	951603.51
F-202	7.89	10468.38	82616.49
F-203	46.01	4826.54	222082.17
F-204	7.89	4826.54	38091.06
F-205	6.20	4559.70	28279.27
R-201	7.11	114597.99	8142768.16
R-202	26.12	2908.26	75948.72
E-201	7.11	100519.32	714240.72
E-202	7.11	23648.60	168035.31
E-203	7.11	38388.25	272767.94
E-204	7.11	15675.90	111385.22
E-205	7.11	110420.20	784591.46
E-206	7.11	22422.17	159320.90
E-207	7.11	81742.04	580818.61
E-208	7.11	15377.55	109265.30
E-209	7.11	20829.14	148001.60
E-210	7.11	47211.84	335464.07
E-211	6.77	15440.09	104474.86
E-212	7.11	29681.43	210901.63
E-213	6.19	15817.23	97905.60
E-214	14.51	15367.61	223051.06
E-215	6.11	21545.78	131689.51
E-216	14.51	15302.50	222105.96
T-201 (Vessel)	7.89	7439.65	58713.70
T-201 (Tray)	1.80	826.47	34215.66

So, the total bare module cost or fixed capital investment cost (FCI_L) in 2001 and 2018 of these processes were calculated by Equation 13 and shown in Table 54.

Equation 13
$$FCI_L = \sum_i C^0_{BM,i}$$

Table 54 Fixed capital investment in 2001 and 2018 for each process

Equipment	BHD production process	BHD production process coupled with methanol synthesis
FCI in 2001 [USD]	10641301.00	14264250.15
FCI in 2018 [USD]	16286052.03	21830819.4

Manufacturing cost consisted of raw material cost, utility cost, waste treatment cost, and operating labor cost. All of these costs have to invest as annual cost due to 8000 hours operation. The calculations were shown as below.

Raw materials for producing the BHD in both processes were hydrogen gas, RBDPO, $NiMoS_2/Al_2O_3$ catalyst. Also, feed rates of both raw materials for each process were similar. But there was some additional carbon dioxide and $Cu/ZnO/Al_2O_3$ catalyst which was used for methanol production. Table 55 showed the raw material cost of each process in 2018.

Table 55 Raw material cost of each process in 2018 [36, 39-41]

Raw Material	Cost [USD/kg]	Flow Rate [kg/hr]	BHD production process [USD/y]	BHD production process coupled with methanol synthesis [USD/y]
H_2	4	1095.512	1095.512	1095.512
RBDPO	0.479	30534.75	30534.75	30534.75
CO_2	0	164.5	0	0
$NiMoS_2/Al_2O_3$	0.375	76500	28687.5	28687.5
$Cu/ZnO/Al_2O_3$	15	1041	0	15615
Total cost			152094233.5	152109800.7

Utility for the process was used for heating and cooling the process stream after heat integration. Amount of utility was minimized. Hot oil was selected for hot utility and cooling water was cold utility. Because Maximum temperature in this process was 300 ^{o}C which was the influent and effluent of BHD reactor. Hot oil was the suitable utility for this process because its range was between 300-320 ^{o}C. Also, cooling water which was able to cool down the process stream to ambient temperature due to low temperature range (35-45 ^{o}C). Another major utility required for production process was electricity. Table 56 showed the amount of energy required for both processes.

Table 56 Utility for each process

Utility	**BHD production process**	**BHD production process coupled with methanol synthesis**
Hot oil [kJ/hr]	1822507.64	46367384.8
Cooling water [kJ/hr]	44038606.87	3662740.26
Electricity [kW]	15.15	15.15

Cost of utility calculation, this study also used the cost from “Analysis, Synthesis, and Design of Chemical Processes” book. Hot oil cost was assumed to be 13.88 USD per Gigajoule and cost of electricity was assumed to be 0.06 USD per kilowatt hour [30]. For the cooling water, the calculation was shown as below;

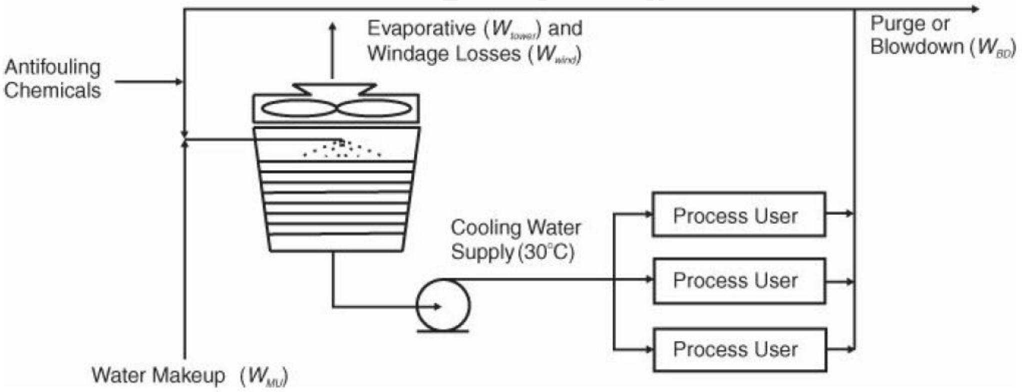

Figure 38 Cooling water system [30]

Figure 38 shows the cooling water system that there was some cooling water loss such as evaporative water, windage water, and blowdown water. Also, there was some inorganic chemical which was added into the cooling water to reduce the fouling in heat exchanger. So, amount of make-up water and amount of chemicals was the main cost for this utility.

Make-up water balance calculation

Equation 14 $$W_{Make-up} = W_{Evap} + W_{Wind} + W_{BD}$$

Inorganic chemical balance calculation

Equation 15 $$S_{in} W_{Make-up} = S_{loop}(W_{Wind} + W_{BD})$$

Where $W_{Make\text{-}up}$ = Mass flow rate of make-up water [kg/h]
W_{Evap} = Mass flow rate of evaporative water [kg/h]
W_{Wind} = Mass flow rate of windage water [kg/h]
W_{BD} = Mass flow rate of blow down water [kg/h]
S_{in} = Concentration of chemical in make-up water [-]
S_{loop} = Concentration of chemical in cooling water loop [-]

Normally, W_{Evap} can be calculated by total heat removal divided by latent heat of water. W_{Wind} was approximately 3 percent of cooling water. S_{loop}/S_{in} was assumed to be 5. So, W_{BD} and $W_{Make\text{-}up}$ can be calculated as below;

Equation 16 $$W_{BD} = \frac{S_{in}}{S_{loop}-S_{in}} W_{Evap} - W_{Wind}$$

Equation 17 $$W_{Make-up} = W_{Evap} + W_{Wind} + W_{BD}$$

In addition, there were pump and fan which was used in the cooling water loop. This equipment utilized electricity, so there was some additional cost in cooling water cost. Electricity for pump was calculated by the total pressure drop as Equation 18. This study assumed as Turton assumption that pump efficiency (**ϵ**) was around 75 percent and total pressure drop (ΔP) was 38.7 psi or 266.7 kPa because of 15 psi of pipe losses, 5 psi of exchanger losses, 10 psi of control valve loss, and 8.7 psi of static head.

Equation 18

$$Pump\ power = \frac{1}{\varepsilon} V\Delta P$$

Fan power calculation in kilowatt was assumed that the total surface area in the tower was 0.5 ft^2/gpm and the fan horsepower per square foot of tower area was 0.041 hp/ft^2. It can be determined be Equation 19.

Equation 19

$$Fan\ power = CW\ mass\ flow\ rate\ x\ Surface\ area\ in\ tower\ x\ Fan\ power\ per\ tower\ area$$

The required amount of make-up water, amount of inorganic chemical, power for pump and power for fan were shown in the Table 57. Cost of make-up water was around 0.156 USD per 1000 kilograms, chemicals cost was approximately 0.067 USD per 1000 kilogram of make-up water. Electricity cost was also 0.06 USD per kWh. So, total cost of cooling water was shown in Table 58. Total cost of utility of both processes were compared in the Table 59.

Table 57 Cooling tower information

Cooling Water Requirement	BHD production process	BHD production process coupled with methanol synthesis
Total cooling water [kg/h]	703570.29	740775.3431
Evaporative water [kg/h]	18220.36	19183.86
Windage water [kg/h]	21107.11	22223.26
Blowdown water [kg/h]	25662.20	27019.22
Make-up water [kg/h]	64989.67	68426.34
Pump power [kW]	69.50	73.17
Fan power [kW]	47.49	50.01

Table 58 Cooling water cost of each process in 2018

Cooling Water Requirement	BHD production process [USD/y]	BHD production process coupled with methanol synthesis [USD/y]
Make-up water cost	81107.10	85396.08
Inorganic chemical cost	34834.46	36676.52
Pump power cost	33358.61	35122.63
Fan power cost	22797.09	24002.61

Table 59 Utility cost of each process in 2018

Utility	Cost [USD/unit]	BHD production process [USD/y]	BHD production process coupled with methanol synthesis [USD/y]
Hot oil	13.88 /GJ	202371.25	406710.68
Cooling water	-	172097.27	181197.83
Electricity	0.06 /kWh	7271.96	7271.96
Total cost in 2001		381740.47	595189.13
Total cost in 2018		584237.32	910911.29

Waste treatment was the major section of these both process due to the large amount of water by-product. Cost for waste water removal was around 41 USD per 1000 m^3 [30]. Waste treatment cost of both processes were shown in Table 60.

Table 60 Waste treatment cost

Cooling Water Requirement	**BHD production process**	**BHD production process coupled with methanol synthesis**
Waste water [kg/h]	2642.38	2935.71
Total cost in 2001 [USD/y]	866.70	962.91
Total cost in 2008 [USD/y]	1326.45	1473.70

Cost of operating labor was determined based on the information in "Analysis, Synthesis, and Design of Chemical Processes" book. Number of operations per shift can be approximated by Equation 20.

Equation 20

$$N_{OL} = \left(6.29 + 31.8P^2 + 0.23N_{np}\right)^{0.5}$$

Where N_{OL} = Number of operations per shift
P = Number of equipment involving the solid

N_{np} = Number of equipment which were heat exchanger, tower, reactor, compressor

Actually, 1 operator can work approximately 49 weeks per year and operate 5 8-hour shifts per week. So, he can operate 245 shifts per year. In 1 year, there were 365 days and 3 shifts per day. Thus, the chemical plant requires 1095 shifts per year. Therefore, the chemical plant needs 4.5 operators per operation. Labor cost in 2010 was around 59,580 USD per year. So, Table 62 summarizes the raw material cost, utility cost, waste treatment cost, and operating labor cost for both production process.

Table 61 Operating labor cost

Operating labor	**BHD production process**	**BHD production process coupled with methanol synthesis**
Number of equipment involving the solid [P]	0	0
Number of equipment which were heat exchanger, tower, reactor, compressor [N_{np}]	8	19
Number of operations per shift [N_{OL}]	2.85	3.26
Total operating labor	13	15
Total cost in 2010 [USD/y]	774540.00	893700.00
Total cost in 2008 [USD/y]	847944.12	978397.06

Table 62 Summary of raw material cost, utility cost, waste treatment cost, and operating labor cost for both production process

Cost [USD/y]	**BHD production process**	**BHD production process coupled with methanol synthesis**
Raw material cost	152094234	152109801
Utility cost	584237	910911
Waste treatment cost	1326	1474
Operating labor cost	847944	978397

Cost of manufacturing were divided into 3 groups which were direct manufacturing cost, fixed manufacturing cost, and general expense. Direct manufacturing cost was the cost that depends on the production rate. But fixed manufacturing cost was the cost that does not depend on the production rate. General expense was the cost that was needed to carry out business functions including sales, management, research, and financing functions. This cost can be estimated by Equation 21. Factor of each parameter was approximate as shown in Table 63.

Equation 21 $$COM_d = 0.180FCI + 2.73C_{OL} + 1.23(C_{UT} + C_{WT} + C_{RM})$$

Where COM_d = Cost of manufacturing without depreciation
FCI = Fixed capital investment [USD]
C_{OL} = Cost of operating labor [USD/year]
C_{UT} = Cost of utility [USD/year]
C_{WT} = Cost of waste treatment [USD/year]
C_{RM} = Cost of raw material [USD/year]

Table 63 Cost of Manufacturing Calculation

Cost of Manufacturing without depreciation		**Factor**	**Variable**
1. Direct Manufacturing Cost			
	a. Raw material	1	C_{RM}
	b. Waste treatment	1	C_{WT}
	c. Utilities	1	C_{UT}
	d. Operating Labor	1	C_{OL}
	e. Direct supervisory & clerical labor	0.18	C_{OL}
	f. Maintenance & repairs	0.06	FCI_L
	g. Operating supplies	0.009	FCI_L
	h. Laboratory Charges	0.15	C_{OL}
	i. Patents and royalties	0.03	COM
2. Fixed Manufacturing Cost			
	a. Depreciation	0.1	FCI_L
	b. Local taxes & insurance	0.032	FCI_L
	c. Plant overhead cost	0.708	C_{OL}
		0.036	FCI_L
3. General Manufacturing Expenses			
	a. Administration costs	0.177	C_{OL}
		0.009	FCI_L
	b. Distribution & selling costs	0.11	COM
	c. Research & development	0.05	COM

APPENDIX G
Engineering Economic Analysis

This section showed the calculation for economic feasibility in term of payback period, internal rate of return, and net present value for each process and also compares benefit of each process. Assumption for this section were

1. 8000 hr. of production per year and 10 years operation
2. Working Capital = 15 percent of FCI_L [30]
3. Tax rate = 35 percent [30]
4. Salvage = 5 percent of FCI_L [30]
5. Land = 2 percent of FCI_L [35]
6. Discount rate = 10 percent per annual [30]
7. Depreciation was calculated by Modified Accelerated Cost Recovery System (MACRS).
8. Product price = $0.78 USD per L of BHD [36] and 6 USD per kg of methanol [37]
9. Each cost was calculated to the cost based on 2018.
10. Plant was constructed in 2 years which was divided into 2 phases. 50 percent was built in the first year. And another was done in the second year.

According to equipment lifetime, the value of equipment decreases with time call "depreciation". In this study, modified accelerated cost recovery system was applied. Table 64 shows depreciation allowance of capital investment in each year.

Table 64 Depreciation allowance of capital investment

Year	**Depreciation allowance (% of FCI_L)**
1	20.00
2	32.00
3	19.20
4	11.52
5	11.52
6	5.76

Most of corporations, 35 percent was the basic federal taxation rate for tax calculation. The annual revenue, expenses, income tax, after-tax profit, and after-tax cash flow were determined by the equations below;

Equation 22
$$E = COM_d + d$$

Equation 23
$$T = (R - E)xt$$

Equation 24
$$R = \sum(P_i C_i)$$

Equation 25
$$P = R - E - T$$

Equation 26
$$C = P + d$$

Where E = Annual expenses
COM_d = Cost of manufacturing without depreciation
d = Depreciation
T = Income tax
t = Tax rate (35%)
R = Revenue
P_i = Price of product i
C_i = Production rate of product i
P = After tax net profit
C = After tax cash flow

For this study, it was assumed that construction period spends 2 years before starting up the plant. Revenue from BHD was around 199.99 million USD per year and revenue from methanol was 19.56 million USD per year due to each production rate. Table 65 and Table 66 show the cumulative cash flow calculation of each production.

Table 65 The cumulative cash flow calculation of BHD production process [USD]

End of year	Investment	Depreciation	Revenue	COM_d	Revenue-Expense	After tax net profit
0	325721.04 (Land)					
1	8143026.02 (1st FCI)					
2	8143026.02 (2nd FCI)					
2	2442907.80 (Working Capital)					
3		3257210.41	199994000.00	193042527.45	3694262.14	5658480.80
4		5211536.65	199994000.00	193042527.45	1739935.90	6342494.98
5		3126921.99	199994000.00	193042527.45	3824550.56	5612879.85
6		1876153.19	199994000.00	193042527.45	5075319.36	5175110.78
7		1876153.19	199994000.00	193042527.45	5075319.36	5175110.78
8		938076.60	199994000.00	193042527.45	6013395.95	4846783.97
9			199994000.00	193042527.45	6951472.55	4518457.16
10			199994000.00	193042527.45	6951472.55	4518457.16
11			199994000.00	193042527.45	6951472.55	4518457.16
12			199994000.00	193042527.45	6951472.55	4518457.16
12	-325721.04 (Land)					
12	-2442907.80 (Working Capital)					
12			814302.60 (Salvage)		814302.60	529296.69

Table 65 The cumulative cash flow calculation of BHD production process [USD]

End of year	Cash flow	Discount cash flow	Discount. cumulative cash flow
0	-325721.04	-325721.04	-325721.04
1	-8143026.02	-7402750.92	-7728471.96
2	-8143026.02	-6729773.57	-14458245.53
2	-2442907.80	-2018932.07	-16477177.60
3	5658480.80	4251300.38	-12225877.22
4	6342494.98	4332009.42	-7893867.81
5	5612879.85	3485156.79	-4408711.02
6	5175110.78	2921215.12	-1487495.91
7	5175110.78	2655650.11	1168154.20
8	4846783.97	2261060.49	3429214.69
9	4518457.16	1916266.92	5345481.61
10	4518457.16	1742060.84	7087542.45
11	4518457.16	1583691.67	8671234.11
12	4518457.16	1439719.70	10110953.81
12	325721.04	103784.76	10214738.58
12	2442907.80	778385.71	10993124.29
12	529296.69	168650.24	11161774.52

Table 66 The cumulative cash flow calculation of BHD production process coupled with methanol synthesis [USD]

End of year	**Investment**	**Depreciation**	**Revenue**	**COM_d**	**Revenue-Expense**	**After tax net profit**
0	436616.39 (Land)					
1	10915409.70 (1st FCI)					
2	10915409.70 (2nd FCI)					
2	3274622.91 (Working Capital)					
3		4366163.88	219558665.60	194817859.80	20374641.88	17609681.10
4		6985862.21	219558665.60	194817859.80	17754943.55	18526575.51
5		4191517.32	219558665.60	194817859.80	20549288.43	17548554.8
6		2514910.39	219558665.60	194817859.80	22225895.36	16961742.38
7		1508946.24	219558665.60	194817859.80	23231859.52	16609654.92
8		502982.08	219558665.60	194817859.80	24237823.68	16257567.47
9			219558665.60	194817859.80	24740805.76	16081523.74
10			219558665.60	194817859.80	24740805.76	16081523.74
11			219558665.60	194817859.80	24740805.76	16081523.74
12			219558665.60	194817859.80	24740805.76	16081523.74
12	-436616.39 (Land)					
12	-3274622.91 (Working Capital)					
12			1091540.97 (Salvage)		1091540.97	709501.6304

Table 66 The cumulative cash flow calculation of BHD production process coupled with methanol synthesis [USD]

End of year	Cash flow	Discount. cash flow	Discount cumulative cash flow
0	-436616.39	-436616.39	-436616.3879
1	-10915409.70	-9923099.73	-10359716.11
2	-10915409.70	-9020999.75	-19380715.87
2	-3274622.910	-2706299.93	-22087015.79
3	17609681.10	13230414.05	-8856601.741
4	18526575.51	12653900.36	3797298.616
5	17548554.80	10896271.87	14693570.48
6	16961742.38	9574461.38	24268031.87
7	16609654.92	8523379.27	32791411.13
8	16257567.47	7584275.21	40375686.34
9	16081523.74	6820135.92	47195822.26
10	16081523.74	6200123.56	53395945.82
11	16081523.74	5636475.97	59032421.79
12	16081523.74	5124069.06	64156490.85
12	436616.38	139119.44	64295610.28
12	3274622.91	1043395.78	65339006.06
12	709501.63	226069.08	65565075.14

According to cumulative cash flow of each production process, the economic feasibility was considered. The first parameter was internal rate of return (IRR) which was the average annual net profit after operation per fixed capital investment. It can be estimated by Equation 27 [30]. Next parameter, payback period (PBP) was the minimum time period of operation which was able to recover the fixed capital investment. The last was net present value (NPV). It was the overall value of production plant including the product price after 10 years operation. Table 67 shows the comparison of economic feasibility parameter of each process.

Equation 27

$$IRR = \frac{Total\ profit\ during\ operation\ period}{Operation\ period\ x\ FCI} x100$$

Table 67 The comparison of economic feasibility parameter of both process

Parameter	**BHD production process**	**BHD production process coupled with methanol synthesis**
IRR [%]	16.47	39.65
PBP [Years]	4.49	1.68
NPV [USD]	11161774.52	65565075.14

According to fluctuation of raw material cost and product price, it was the interesting thing for consideration. Table 68 shows the raw material cost and product price since 2000 until 2018. This fluctuation makes high risk for investment because raw material cost and product price can be increased and decreased. So, this fluctuation would be studied.

Table 68 RBDPO cost and BHD price since 2000 until 2018 [36, 38]

Year	RBDPO Cost [USD/kg]	BHD Price [USD/L]
2018	0.479	0.78
2016	0.737	1.42
2014	0.638	1.56
2012	0.763	1.57
2010	1.172	1.32
2008	0.525	1.16
2006	0.553	1.06
2004	0.402	1.00
2002	0.438	0.77
2000	0.222	0.8

Table 69 shows the net present value and internal rate of return of each process when the raw material cost and product prices were varied. It shows that worthiness of each process depends of this fluctuation. The year which have a large difference, higher than 0.80 USD per kilogram of BHD, the methanol synthesis unit might not need to improve these parameters. But if difference was less than 0.521 USD per kilogram of BHD, both processes have possibility to loss. If the difference was between 0.521 to 0.80 USD per kilogram of BHD, the methanol synthesis was the potential process that was able to increase the internal rate of return. For the methanol price, it varied between 4 to 8 USD per kilogram [37]. So, the fluctuation of methanol price did not effect on the economic feasibility because it was significantly higher than the BHD price. For example, the values of payback period, net present value and internal rate of return for the lowest price of methanol, 4 USD per kilogram, were around 2.2 years, 44 million USD, and 29.79 percent, respectively. Therefore, BHD production process coupled with methanol synthesis was still better than the BHD production process.

Table 69 Net present value and internal rate of return in each year for both process

Year	**Gap [USD/kg of BHD]**	**BHD production process**		**BHD production process coupled with methanol synthesis**	
		NPV [mUSD]	**IRR [%]**	**NPV [mUSD]**	**IRR [%]**
2018	0.521	11.16	16.47	65.57	39.65
2016	1.084	296.94	191.94	351.34	170.56
2014	1.362	513.61	324.97	568.01	269.81
2012	1.250	398.10	254.06	452.51	216.90
2010	0.520	-219.11	-124.92	-164.71	-65.83
2008	0.962	287.15	185.93	341.55	166.07
2006	0.806	174.74	116.91	229.15	114.58
2004	0.880	273.72	177.69	328.12	159.92
2002	0.549	43.36	36.24	97.76	54.40
2000	0.804	282.97	183.37	337.38	164.16