

Article

Process Improvement and Economic and Environmental Evaluation of Bio-Hydrogenated Diesel Production from Refined Bleached Deodorized Palm Oil

Amata Anantpinijwatna ¹, Lida Simasatitkul ^{2,*}, Kanokporn Yooyen ², Suksun Amornraksa ³,
Suttichai Assabumrungrat ^{4,5} and Karittha Im-orb ⁶

¹ Department of Chemical Engineering, School of Engineering, King Mongkut's Institute of Technology Ladkrabang, Bangkok 10520, Thailand; amata.an@kmitl.ac.th

² Department of Industrial Chemistry, Faculty of Applied Science, King Mongkut's University of Technology North Bangkok, Bangkok 10800, Thailand

³ Chemical and Process Engineering Program, The Sirindhorn International Thai-German Graduate School of Engineering, King Mongkut's University of Technology North Bangkok, Bangkok 10800, Thailand; suksun.a@tggs.kmutnb.ac.th

⁴ Center of Excellence in Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand; suttichai.a@chula.ac.th

⁵ Bio-Circular-Green-Economy Technology & Engineering Center (BCGeTEC), Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand

⁶ Program in Food Process Engineering, School of Food Industry, King Mongkut's Institute of Technology Ladkrabang, Bangkok 10520, Thailand; karittha.im@kmitl.ac.th

* Correspondence: lida.s@sci.kmutnb.ac.th

Abstract: The co-production of BHD with other renewable fuels (i.e., using a novel process involving carbon dioxide utilization to achieve the global sustainability goal) is presented. The three configurations of BHD production from refined bleached deodorized palm oil (RBDPO), including (1) the conventional BHD process with hydrogen recovery (BHD process), (2) the BHD process coupled with the Fischer–Tropsch process (BHD–FT process), and (3) the BHD process coupled with the bio-jet fuel and methanol processes (BHD–BIOJET–MEOH process) are investigated using the process model developed in Aspen Plus. The effect of the operating parameters is studied, and the condition of each process offering the highest BHD yield is proposed. Then, the pinch analysis and heat exchanger network (HEN) design of each proposed process are performed to find the highest energy-efficient configuration. The economic and environmental analysis is later performed to investigate the sustainability performance of each configuration. The conventional BHD process requires less hydrogen and consumes less energy than the others. The BHD–BIOJET–MEOH process is the most economically feasible, offering the highest net present value (NPV) of USD 7.93 million and the shortest payback period of 3 years and 1 month. However, it offers the highest carbon footprint of 0.820 kgCO₂ eq./kg of BHD, and it presented the highest potential environmental impact (PEI) in all categories.

Keywords: bio-hydrogenated diesel; process improvement; hydrodeoxygenation; economic analysis; carbon footprint



Academic Editor: Javier Martínez-Gómez

Received: 31 October 2024

Revised: 23 December 2024

Accepted: 25 December 2024

Published: 1 January 2025

Citation: Anantpinijwatna, A.; Simasatitkul, L.; Yooyen, K.; Amornraksa, S.; Assabumrungrat, S.; Im-orb, K. Process Improvement and Economic and Environmental Evaluation of Bio-Hydrogenated Diesel Production from Refined Bleached Deodorized Palm Oil. *Processes* **2025**, *13*, 75. <https://doi.org/10.3390/pr13010075>

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1. Introduction

Rising energy demands across the transportation, building, and all industrial sectors lead to a high rate of fossil fuel consumption, which releases large amounts of greenhouse gases during combustion, contributing to air pollution and global warming issues. As a

result, several countries agreed to set a target of net-zero carbon emissions by 2050 [1]. The European Union (EU) has expressed its commitment to reducing greenhouse gas emissions by at least 55% by 2030 [2]. To achieve carbon neutrality, the energy strategy encourages the government to pursue technology for renewable energy production. For example, the Neste company produces renewable diesel and renewable bio-jet fuel to reduce greenhouse gas emissions in accordance with the greenhouse gas protocol by 2035 [3]. Using biomass derived from agricultural crops and residues as an energy source for the production of biofuels and biochemicals is a suitable method for agricultural countries.

For green diesel production, vegetable oils such as canola oil, rapeseed oil, flaxseed oil, soybean oil, and sunflower oil are used as raw materials for hydroprocessing vegetable oils in Canada [4]. In Asia, palm fatty acid distillate, palm oil, and palm kernel oil are more popular due to their large-scale cultivation [5]. Waste cooking oil can also be used in hydroprocessing vegetable oil because the price is less expensive [6,7]. Thailand is an agricultural country with various raw materials that are suitable for the production of bio-hydrogenated diesel (BHD) or green diesel, which mainly contains hexadecane. BHD is a renewable fuel that can be produced from the hydrodeoxygenation of edible and non-edible vegetable oils, animal fats, and used oils. According to the Ministry of Agriculture and Cooperatives [8], animal fats and used oils do not have the potential to be commercially viable for BHD production because the amount that can be collected each year is relatively small. According to business trends and the oil palm industry in 2020–2022, Thailand has approximately 500,000 tons per year of palm oil reserved for consumption and biodiesel production [9]. The oil palm has the highest potential for oil production per area and, thus, the lowest production cost compared with other oil crops [9]. Therefore, it has great potential to be used as a raw material source for BHD production.

In the production of BHD, vegetable oil reacts with hydrogen under certain conditions. The triglycerides (TG) and fatty acids (FA) are transformed into hydrocarbon compounds by the removal of oxygen atoms in the molecules. The main reactions of BHD production include the exothermic cracking of TG, reduction of FA, and hydrogenation reactions for the breaking of a double bond into a single bond. Hydrodeoxygenation (HDO) is the reaction to remove oxygen from the molecule in the form of water in the presence of hydrogen. Decarbonylation (DCO) and decarboxylation (DCO_2) release carbon monoxide and carbon dioxide, respectively. HDO and DCO_2 are exothermic reactions, while DCO is an endothermic reaction [10]. Refined bleached deodorized palm oil (RBDPO) is obtained from refining, bleaching, and deodorizing crude palm oil. It can be used as a raw material for fatty acid methyl ester (FAME) and BHD production. BHD contains hydrocarbon compounds in the same range of FA contents. RBDPO is a commonly used feedstock due to its availability, relatively low cost, and favorable properties for conversion into BHD [10].

A large amount of hydrogen and a high operating pressure are generally required for the reactions to obtain high yield [10–12]. The main products produced are long-chain hydrocarbons (n-alkane), typically in the range of diesel fuel, and thus, they are referred to as BHD. Propane (C_3H_8) and carbon monoxide are also produced as byproducts. The properties of the BHD are similar to petroleum-based diesel, and thus, it can be used in conventional combustion engines without any modifications. In addition, BHD has better properties compared to biodiesel in many aspects [13]. The current technology for BHD production is carried out in a fixed bed reactor with a commercial catalyst (i.e., $\text{NiMo}/\text{Al}_2\text{O}_3$ [14,15]) under high temperature and high pressure. For example, Kaewtrakulchai et al. [16] produced BHD from palm oil under 340–420 °C. They found that a high BHD yield and 100% conversion were achieved [16]. To enhance the hydrogen dispersion in raw material, the solvent, such as dodecane, decane, heptadecane, and mesitylene, was incorporated throughout the reaction to decrease mass transfer resistance [17–19].

The slurry phase reactor was utilized for the hydroprocessing of cottonseed acidic oil and offered a high production rate of BHD [20]. Previously, several studies carried out experiments on BHD production via the hydroprocessing of palm oil and waste cooking oil using a batch continuous fixed-bed reactor [7,21]. Additionally, BHD production was examined using process models developed in commercial software in order to study the effect of operating parameters on process performance [22–24]. As there are some excess hydrogen and gaseous products released from the reactions, conversion of these gases to high-value products not only improves the economic performance but also the environmental one.

The management of byproducts, or wastes, is crucial to the sustainability of any production process. Specifically, it is more preferable if the carbon monoxide byproduct from the BHD production process can be converted into a more valuable product. One possible option is to mix it with hydrogen and utilize it as a syngas feedstock in the Fischer-Tropsch (FT) process to produce synthetic hydrocarbon fuels [25]. The produced fuels are renewable and clean fuels. They can be burnt in existing combustion engines and release less harmful emissions due to their very low sulfur and aromatic contents compared to fossil fuels [26]. Another possible and attractive option to utilize carbon monoxide is to use it as a feedstock to produce a primary chemical such as methanol. Methanol is an important industrial chemical because it is a base substance used to produce many other valuable chemicals, such as formaldehyde, acetic acid, methyl tertiary butyl ether (MTBE), and more [27]. Methanol can be synthesized via the hydrogenation of carbon monoxide. Phichisurathaworn et al. [28] pointed out that the co-production of BHD with methanol could offer more benefits in terms of economics compared with the stand-alone BHD process.

Bio-jet fuel, or sustainable aviation fuel, is another potential product that can be produced from the catalytic cracking of BHD. Bio-jet fuel is a renewable aviation fuel that has been recently developed and used for aircraft. Its use in air transportation has been greatly promoted to mitigate carbon emissions and reach carbon neutrality. It is targeted that, in 2050, 70% of bio-jet fuel will be incorporated into normal aviation fuel consumption [29]. Bio-jet fuel can be produced from renewable feedstocks, such as biomass or vegetable oils, via hydrotreating TG or FA with hydrogen under a high-pressure condition [30]. This hydrodeoxygenation reaction is strongly exothermic and can cause an uncontrollable rise in temperature in the BHD production system [31]. Moreover, the FT reaction to synthesize paraffinic kerosene can also be carried out [32]. Among the studies, in bio-jet fuel production, a hydroprocessing reactor was designed as reactive distillation (RD) to reduce the energy requirement [33,34]. Carrasco-Suárez et al. [35] proposed a bio-jet fuel production process from waste cooking oil, consisting of the esterification process, the transesterification process, and the hydrotreating of biodiesel. Naphtha, BHD, bio-jet fuel, and glycerol were obtained. The co-production of BHD and bio-jet fuel offered an economical process in case of large plant size [36].

To investigate the economic viability of the BHD process, the economic analysis using the payback period, NPV, and return on investment as indicators should be performed. The BHD production from palm fatty acid distillate, a byproduct from palm oil refineries, through the conventional BHD process and the one with heat integration can make a profit and give a payback period of 3 years [37]. However, the stand-alone BHD production was not a feasible process comparable with the conventional biodiesel production process [22]. The processes offering the co-production of BHD with bio-jet fuel and with methanol were more economically feasible than a stand-alone BHD production process [28,36].

For the environmental aspect, a life cycle assessment (LCA) is used to evaluate the environmental impacts under system boundaries such as gate-to-gate, cradle-to-gate, and cradle-to-grave. The inventory data collected from mass balance and energy balance is

used to evaluate the environmental impact. The LCA of BHD production from palm fatty acid distillate and FAME was analyzed in terms of a cradle-to-gate boundary. The result showed that the cultivation and feedstock production stages significantly contributed to environmental impacts in the categories of greenhouse gas emission, human toxicity, freshwater eutrophication, ecotoxicity, natural land transformation for BHD production, and BHD production from the co-products generated during palm oil production [38,39]. Therefore, process improvement based on the bio-circular economy concept is a promising strategy for developing a more sustainable BHD process.

Although BHD production from palm oil has been widely studied, the co-production of BHD with other renewable fuels using a novel process involving carbon dioxide utilization has not been discussed. Therefore, this work aims to enhance the BHD production process in terms of technical, economic, and environmental perspectives. Three different scenarios of the improved process were designed and assessed. The first process is a base case of BHD production, with hydrogen recovery to reduce hydrogen consumption (BHD process). The second process is BHD production coupled with synthesis fuel production via FT synthesis (BHD-FT process). The last process is BHD production coupled with bio-jet fuel and methanol production (BHD-BIOJET-MEOH process). First, the technical performance of the three processes is studied by investigating the effect of the operating conditions. Pinch analysis and heat exchanger network (HEN) design are performed for each configuration that offers the highest BHD yield to minimize energy consumption and improve energy efficiency. The economic analysis is performed using NPV, payback period, and internal rate of return (IRR) as indicators. Then, the LCA is used to evaluate the environmental performance of the three processes. Finally, the process offering the best performance is presented.

2. Methodology

A flow diagram showing the methodology used in this work is illustrated in Figure 1. First, the models of three BHD processes (i.e., the BHD process, BHD-FT process, and BHD-BIOJET-MEOH process) are developed in Aspen Plus V12.1 based on the reaction kinetics of BHD reactions. Then, the effect of the operating parameters is investigated in order to find the suitable condition offering the highest BHD yield. After that, the pinch analysis and heat exchanger network (HEN) design are performed to optimize the use of external utilities and improve the energy efficiency of the process, as well as to maximize the heat recovery of the selected BHD processes. Finally, the selected processes were evaluated by an economic assessment and a life cycle assessment (LCA).

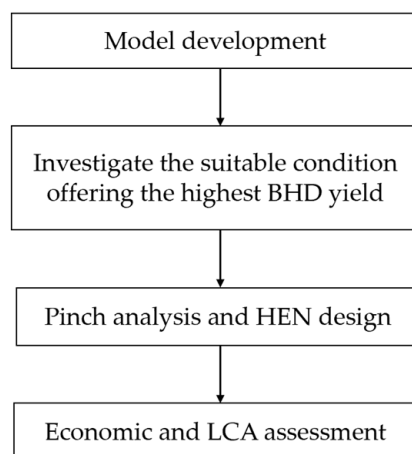


Figure 1. Methodology of the process design.

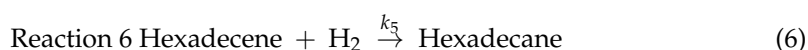
2.1. Process Description

Normally, the raw materials for BHD production are refined bleached deodorized palm oil (RBDPO) and hydrogen. However, since RBDPO contains triglycerides with a wide variety of FA compositions, tripalmitin is used to represent RBDPO in this study in order to simplify the calculation. The reactions involved in BHD production are shown in Equations (1) to (6). There are two reaction pathways involved the BHD production. The first pathway (RP-I) is the decarboxylation of aldehydes, giving pentadecane as the final product. The second pathway (RP-II), the reaction 1 and reaction 2 are similar to the RP-I as shown in Equations (1) and (2). Then other reactions are the reduction of aldehyde and the dehydration of alcohol, giving hexadecane as shown in Equations (4) to (6) as the final product.

RP-I



RP-II



The block flow diagrams of three configurations of BHD production were preliminarily generated prior to the rigorous design. The isothermal and adiabatic conditions of the plug-flow reactor (PFR) were assumed in this study. Three BHD production processes with different downstream managements were created and simulated using Aspen Plus, namely (a) a BHD process, (b) a BHD-FT process, and (c) a BHD-BIOJET-MEOH process, as shown in Figure 2.

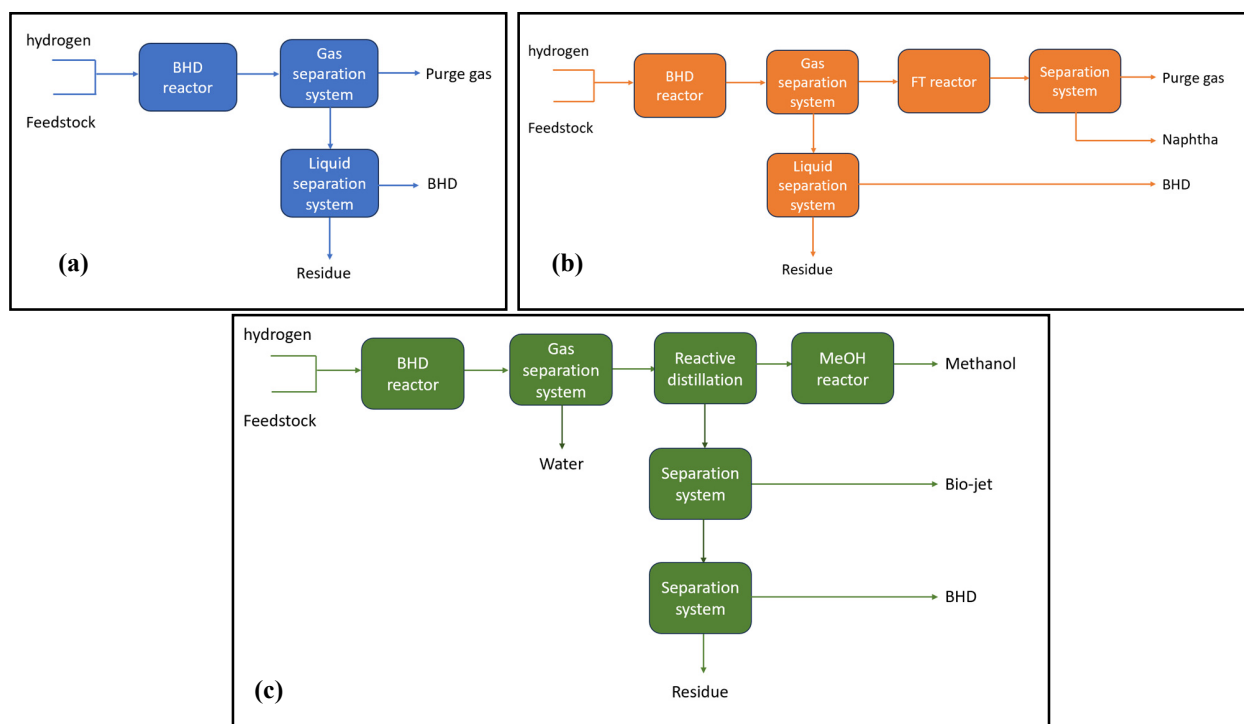


Figure 2. Block flow diagrams of (a) BHD process, (b) BHD-FT process, and (c) BHD-BIOJET-MEOH process.

Mass balances and energy balances for the three processes were performed by Aspen Plus. The tripalmitin is represented by RBDPO. The nonrandom two liquids (NRTL) activity coefficient model was used to calculate the vapor–liquid equilibrium in the BHD reactor, RD, and distillation column because the mixtures consist of ester, alcohol, aldehyde, and water. The Peng–Robinson (PENG-ROB) model, which was a cubic equation of state, was used for nonpolar or mildly polar mixtures, such as hydrocarbon in the FT reactor [40]. The Soave–Redlich–Kwong (SRK) model, which was a cubic equation of state, was applied in the methanol reactor because the mixtures consisted of wet synthesis gas and methanol [28,41,42]. The UNIFAC model was an activity coefficient model, which was used for liquid systems [43]. After all process flowsheets were generated, a pinch analysis and heat integration were applied to the HEN to minimize energy consumption and improve the process’s energy efficiency. High-pressure steam and cooling water were used as hot and cold utilities, respectively. Then, the Aspen Energy Analyzer was used to analyze the energy consumption and design the HEN.

2.2. Economic Evaluation

Economic evaluations of three BHD processes were evaluated and compared. The economic calculation followed the method reported by R. Turton et al. [44]. The assumptions for the economic feasibility assessment of this research are as follows:

- (a) operation of 8 h per day, and 340 working days per year;
- (b) project lifetime is 15 years;
- (c) costs of raw materials and products are based on 2022;
- (d) income and expenses are constant throughout the project’s lifetime;
- (e) the manufacturing cost does not include the waste treatment cost;
- (f) the deactivated catalyst and catalyst regeneration are neglected.

The total investment cost consisted of fixed capital investment cost (FCI) and the working capital cost. The operating cost consisted of the raw materials cost and the utility cost. NPV, payback period, and IRR were used as the economic indicators.

2.3. Environmental Evaluation

For the environmental aspect, the LCA of the BHD processes was analyzed on the basis of cradle-to-gate using LCSOFT software V6.2 from PSE for the SPEED company [45] and normalized by the ILCD 2011 method. The database of RBDPO in LCSOFT included refining, bleaching, and deodorizing. The environmental impacts of cultivation and transportation were constant for all cases. The effects of catalyst regeneration and disposal on the environment were not considered. The carbon footprint was the total amount of GHGs, which were presented as kilograms of CO₂ equivalent and could be calculated from Equation (7).

$$CO_{2,eq} = \frac{(m_{GHG} \times CF_{GHG})}{m_{product}} \quad (7)$$

where m_{GHG} was the mass flow rate of the GHG (kg h^{−1}), and CF_{GHG} was the characterization factor of the GWP.

3. Model Development

After the preliminary flowsheets were generated, the models of three BHD processes were developed in Aspen Plus based on the kinetic data of BHD reactions obtained from Yenumala et al. [11], in which the reactions were the first order of concentration in the liquid phase, and the rate constant (k) of each reaction followed the Arrhenius equation, as shown in Equation (8). To perform the feasibility study of BHD production using various process configurations, an RBDPO of 22,000 kg/day, which was a pilot scale capacity of a refinery

plant, was selected as model input. The model development of three BHD processes was explained in the following sections.

$$k = A \exp(-E_a/RT) \quad (8)$$

3.1. BHD Process

For the BHD process, the NRTL activity coefficient model was used to calculate the vapor–liquid equilibrium in the BHD reactor. And the isothermal and adiabatic conditions of a PFR were maintained. The Aspen Plus model flowsheet of the BHD process is shown in Figure 3. Tripalmitin was fed to a pump (P-01) and a heater (E-03) to increase the pressure to 30 bar with temperatures in the range of 330–460 °C, respectively. The hydrogen gas was fed to multistage compressors (C-01 and C-02) and coolers (E-01 and E-02) until the pressure of 30 bar and a temperature in the range of 330–460 °C were achieved. Hydrogen gas and tripalmitin were mixed at a mixer (M-01) before entering the adiabatic BHD reactor (RE-101) in which Ni/Al₂O₃ was selected as the catalyst. The main products were pentadecane (n-C₁₅) and hexadecane (n-C₁₆), while propane, hexadecanol, water, and carbon monoxide were side products. All products, including hydrogen gas and palmitic acid residue from the reactions, were sent to a chiller (E-04) and a flash tower (F-01) to separate the gaseous products (propane, carbon monoxide, and hydrogen) from the liquid products (pentadecane, hexadecane, hexadecanol, water, and palmitic acid). The gas stream (S12) was sent to pressure swing adsorption (PSA) to adsorb carbon monoxide and propane at the condition reported in previous work [46]. The unadsorbed gas, mainly hydrogen, was then partially purged into the environment. The remaining hydrogen was adjusted to the same pressure and temperature by the compressor (C-03) and heater (E-05) before re-circulation back with the feed stream. The liquid product was sent to a decanter (DE-01) to remove water. A rigorous design of the distillation column by using the RadFrac model, in which the NRTL activity coefficient model was used to calculate the vapor–liquid equilibrium and the UNIFAC model was used for the liquid system [43], was applied for the distillation column. Finally, the propane and BHD were purified to 96.0% and 99.4%, respectively.

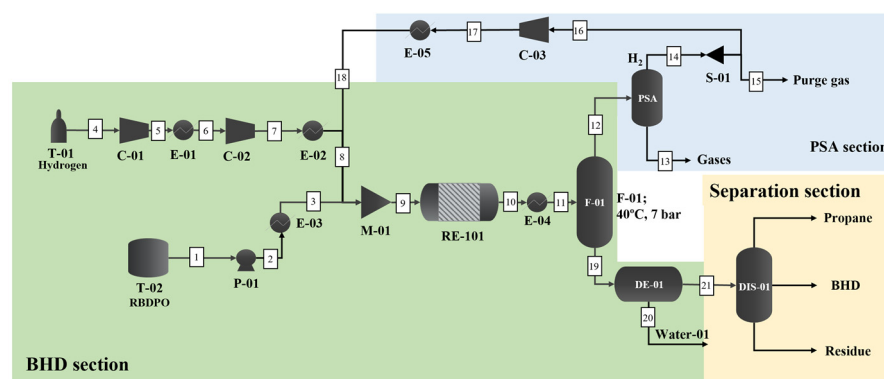


Figure 3. Aspen Plus model flowsheet of BHD process.

3.2. BHD-FT Process

The BHD process in the BHD-FT process was similar to the BHD process explained in Section 3.1, but the FT process was integrated for the production of paraffin from the carbon monoxide and hydrogen gas obtained from the BHD process, as shown in Figure 4. The PENG-ROB model was used to estimate the product composition of the FT reactor [40]. Thus, the product from the BHD reactor (RE-101) was cooled to 100 °C before entering the flash tower (F-01) to separate the gaseous compound from liquids. A gas stream (S12), consisting of hydrogen, carbon monoxide, and propane, was preheated by the heater (E-05)

to increase its temperature in the range of 210–270 °C before entering the FT reactor (RE-201) in which the Co-based catalyst was used. This process could produce naphtha (n-C₅ to n-C₁₀) and a small amount of kerosene (n-C₁₁ to n-C₁₄). The reactor product (S14) was sent to a three-phase flash tower (F-02) to separate the unreacted gases (carbon monoxide and hydrogen) and water from liquid hydrocarbons and propane. The hydrocarbon stream (S16) was then mixed with the treated bottom product (S22) from the first flash tower (F-01) and then sent to the separation section. The gaseous products (carbon monoxide, hydrogen gas, and propane) were separated from naphtha by the first distillation column (D-01). Then, propane and naphtha were purified using the distillation column (D-02). Finally, BHD, consisting of kerosene and diesel, was separated from the palmitic acid and hexadecanol (residue) using the distillation column (D-03).

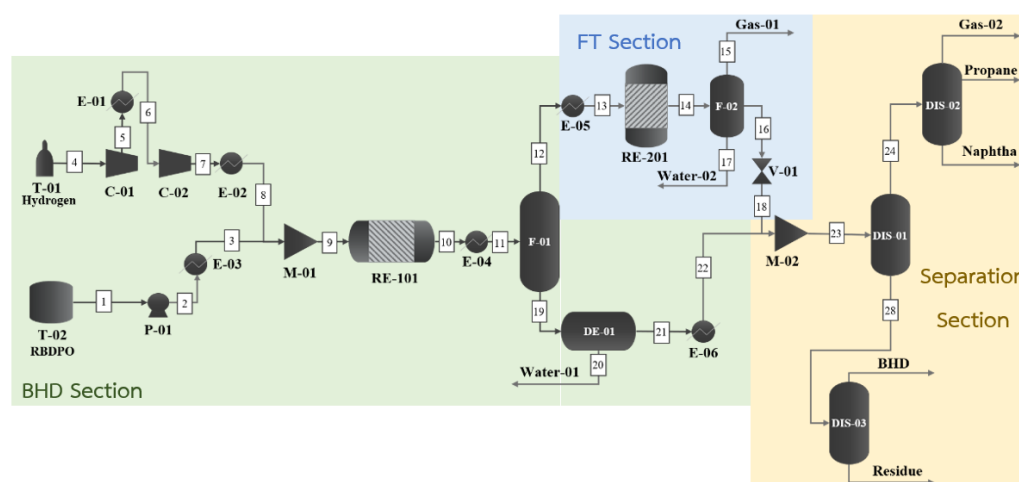


Figure 4. Aspen Plus model flowsheet of BHD-FT process.

3.3. BHD-BIOJET-MEOH Process

The Aspen Plus model flowsheet of the BHD-BIOJET-MEOH process is shown in Figure 5. The BHD process was similar to the BHD process explained in Section 3.1. However, the products from the RE-101 reactor were cooled to 35 °C using a heat exchanger (E-04) and sent to a three-phase flash separation (F-01) to remove water residue. Then, gaseous and liquid products from F-01 were separately heated to 240 °C by using heat exchangers (E-05 and E-06) before feeding to the RD using a Co-Mo/Al₂O₃ catalyst in which the NRTL activity coefficient model was used to calculate the production of jet fuel. This research assumed the cracking of BHD molecules of 10%. A gaseous product from RD (S17), containing synthesis gases (hydrogen gas and carbon monoxide), was heated by the heater (E-07) before entering the MEOH section at which the equilibrium reactor (RE-301) was used to produce methanol from synthesis gas under a Cu/Zn catalyst. As the gaseous product of the RD had low H₂/CO, most of the H₂ was consumed during methanol synthesis. As a result, recirculation of the gas product leaving the methanol reactor to improve methanol yield was not cost-effective to carry out. The SRK model was applied to calculate the product composition of this unit [10,20,21]. The top liquid product from RD (S22), containing jet fuel (n-C₈ to n-C₁₆) and propane, was sent to a valve (V-01) to reduce the pressure to 1 bar. The bottom product from RD (S26), containing BHD, hexadecanol, and palmitic acid residue, was sent to a valve (V-02) and the heat exchanger (E-08) to reduce the pressure and temperature to 1 bar and 340 °C, respectively. In the separation section, methanol was purified using the distillation column (DIS-01) with a partial condenser, resulting in highly purified methanol (99.6% by volume) as the bottom product. Crude propane and crude bio-jet fuel from the V-01 valve were purified by a

flash separation unit (F-02). Highly purified jet fuel (99.9% by volume) was obtained as the bottom product, while propane was derived as the overhead product. BHD in the treated bottom product (S28) was further purified using the distillation column (DIS-02) to obtain the BHD as the overhead product and the other residue at the bottom.

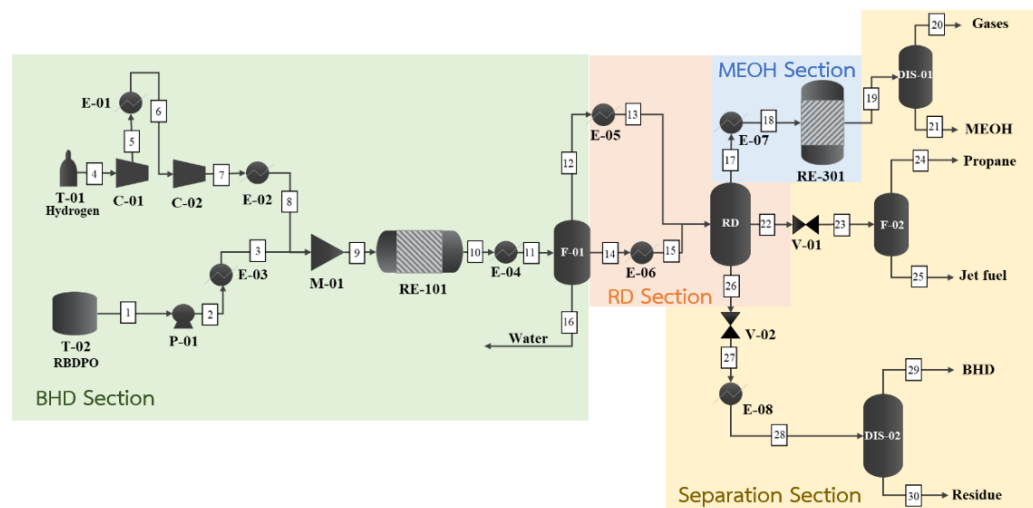


Figure 5. Aspen Plus model flowsheet of BHD-BIOJET-MEOH process.

4. Results and Discussion

The process design and optimization of the three processes were performed. When the optimal operating conditions are found, a HEN was designed to improve energy consumption. Finally, the three configurations of the BHD process were evaluated in terms of economic and environmental aspects.

4.1. Technical Performance

The technical performance of the three BHD processes is performed to investigate the effect of the operating conditions offering the highest BHD yield. The optimal process conditions of BHD, BHD-FT, and BHD-BIOJET-MEOH processes were summarized in Tables 1–3, respectively. And the technical performance of each BHD process is shown in Table 4. It was found that the BHD process offered the highest BHD of 1966.6 kg/h, followed by the BHD-FT process (1961.08 kg/h) and the BHD-BIOJET-MEOH process (1745.96 kg/h), respectively. However, the BHD-FT process offered 60.86 kg/h of naphtha as a co-product. For the BHD-BIOJET-MEOH process, the methanol of 99.08 kg/h and bio-jet of 189.25 kg/h were produced as additional products. Regarding energy consumption, the BHD process released the highest amount of energy, followed by the BHD-FT and BHD-BIOJET-MEOH processes, respectively.

Table 1. Optimal operating conditions of BHD process.

Operating Unit	Parameter	Condition
RE-101	Temperature (°C)	340
	Pressure (bar)	30
	H ₂ /TP ratio	6.4
	L:D reactor	5:1

Table 1. *Cont.*

Operating Unit	Parameter	Condition
RE-102	Temperature (°C)	430
	Pressure (bar)	30
	H ₂ /TP ratio	11.83
	L:D reactor	6:1
F-01	Temperature (°C)	40
	Pressure (bar)	7
DE-01	Temperature (°C)	35
	Pressure (bar)	7
PSA	Pressure (bar)	7
Pressure (bar)	Number of stages	18
	Feed stage	9
	Reflux ratio	0.864
	Distillate-to-feed ratio	0.915
	Distillate vapor fraction	0.1
	Pressure (bar)	7

Table 2. Optimal operating conditions of BHD-FT process.

Operating Unit	Parameter	Condition
RE-201	Temperature (°C)	130
	Pressure (bar)	30
	H ₂ /CO ratio	1.19
	L:D reactor	0.185:0.046
F-01	Temperature (°C)	100
	Pressure (bar)	30
F-02	Temperature (°C)	25
	Pressure (bar)	30
DE-01	Temperature (°C)	100
	Pressure (bar)	12
DIS-01	Number of stages	11
	Feed stage	6
	Reflux ratio	1.045
	Distillate-to-feed ratio	0.2595
	Pressure (bar)	12
DIS-02	Number of stages	7
	Feed stage	4
	Reflux ratio	3
	Distillate-to-feed ratio	0.76
	Distillate vapor fraction	0.7
	Pressure (bar)	12
DIS-03	Number of stages	21
	Feed stage	11
	Reflux ratio	2
	Distillate-to-feed ratio	0.906
	Pressure (bar)	1

Table 3. Optimal operating conditions of BHD-BIOJET-MEOH process.

Operating Unit	Parameter	Condition
RE-301	Temperature (°C)	210
	Pressure (bar)	30
	H ₂ /CO ratio	1.02
	L:D reactor	1.15:0.288
F-01	Temperature (°C)	35
	Pressure (bar)	30
F-02	Temperature (°C)	25
	Pressure (bar)	1
RD	Number of total stages	7
	Feed stage	4
	Reactive stage	4
	Reflux ratio	0.075
	Distillate rate (kmol/h)	22
	Distillate vapor fraction	0.75
	Pressure (bar)	30
DIS-01	Number of stages	5
	Feed stage	3
	Reflux ratio	0.6
	Distillate-to-feed ratio	0.702
	Pressure (bar)	1
DIS-02	Number of stages	9
	Feed stage	5
	Reflux ratio	2
	Distillate-to-feed ratio	0.899
	Pressure (bar)	1

Table 4. Technical performance of the three BHD processes.

Technical Performance	BHD Process	BHD-FT Process	BHD-BIOJET-MEOH Process
BHD (kg/h)	1966.60	1961.08	1745.96
Propane (kg/h)	45.26	35.75	184.17
Naphtha (kg/h)	-	60.86	-
Methanol (kg/h)	-	-	99.08
Bio-jet (kg/h)	-	-	189.25
Overall energy consumption (MW)	−0.52	−0.46	−0.22

4.2. Energy Analysis

An energy analysis was performed using an Aspen Energy Analyzer in Aspen Plus in order to find the energy-efficient conditions of the selected BHD processes. The pinch analysis provided the composite curve with a temperature difference of 10 °C, which is depicted in Figure 6. The high-pressure steam (HP steam) and cooling water were used as hot and cold utilities for all BHD processes. It was found that the BHD process required external hot and cold utilities of 1.85 MW and 2.37 MW, respectively. The BHD-BIOJET-MEOH process showed the same trend, as it required both external hot and cold utilities of 1.35 MW and 1.57 MW, respectively. Specifically, only external hot utilities of 2.30 MW were required for the BHD-FT process.

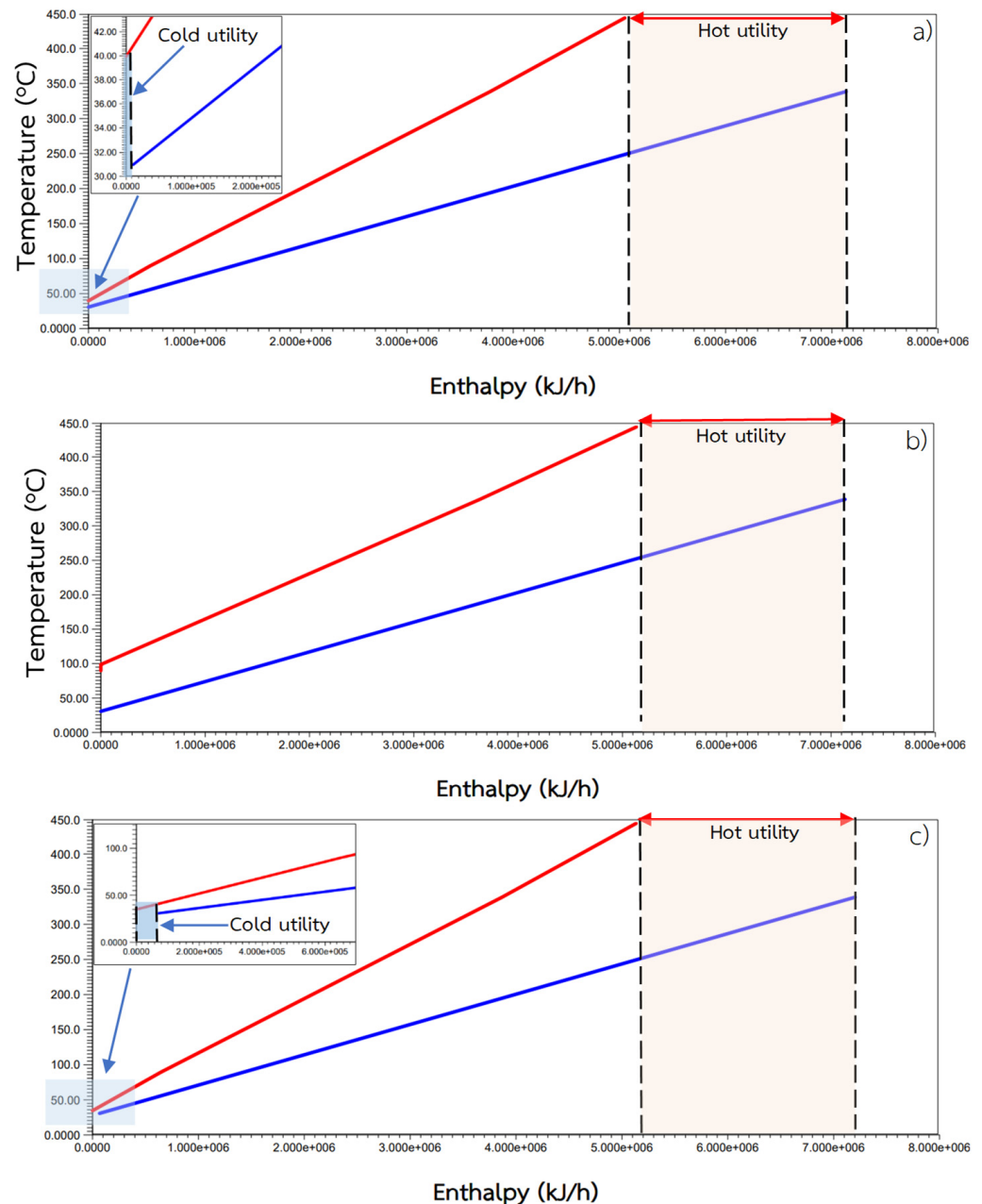


Figure 6. Composite curves of hot and cold utility of (a) BHD process, (b) BHD-FT process, and (c) BHD-BIOJET-MEOH process when red line is hot utility and blue line is cold utility.

The HEN design was later performed to maximize the heat recovery of the selected BHD processes. The HEN design diagram of the BHD process is shown in Figure 7. The red arrows are hot streams, while the blue arrows are cold streams. A HEN analysis indicated that the BHD process required two heaters (i.e., HEAT-01 and HEAT-02), which supply the external heat source, as shown in Figure 8. The HEN design diagram of the BHD-FT process is shown in Figure 9. The newly designed BHD-FT process including HEN required three coolers, namely COOL-01, COOL-02, and COOL-03, as shown in Figure 10. The HEN design diagram of the BHD-BIOJET-MEOH process is shown in Figure 11. After the HEN analysis, one heater and one cooler were required, namely HEAT-01 and COOL-01, as shown in Figure 12.

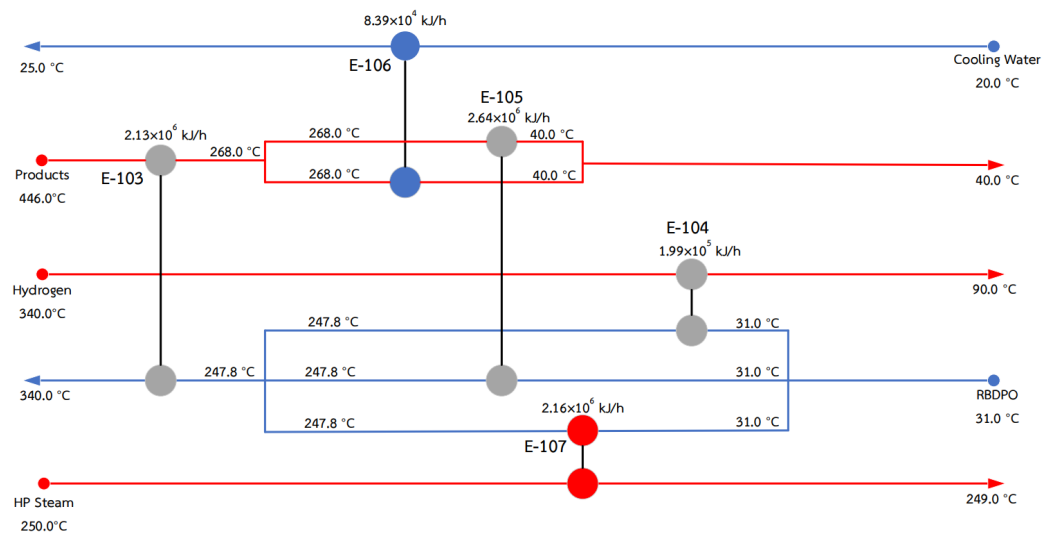


Figure 7. HEN design diagram of BHD process.

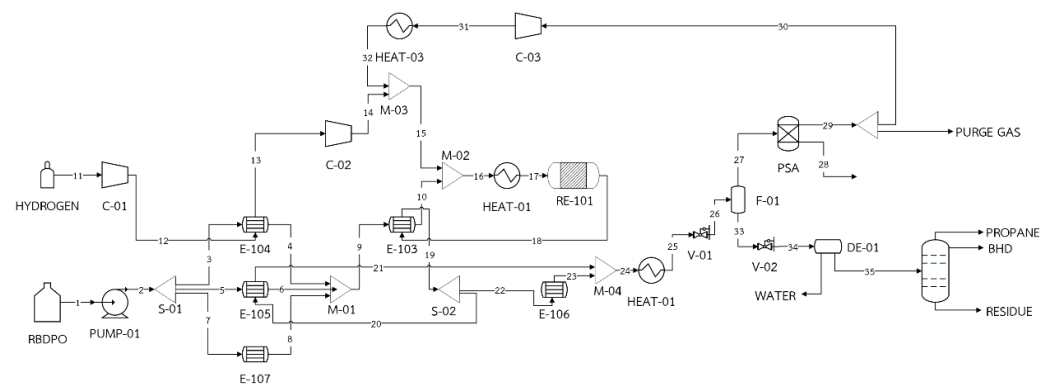


Figure 8. Newly designed BHD process including HEN.

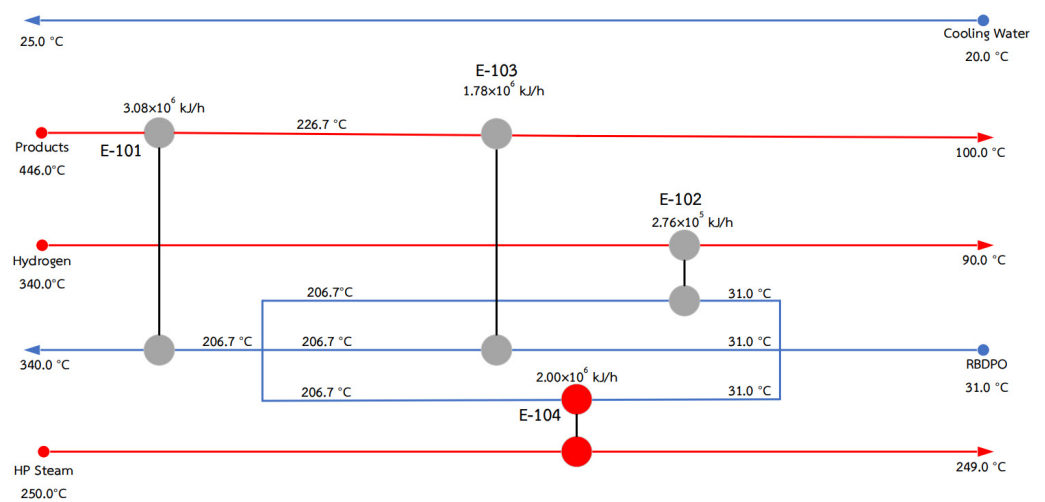


Figure 9. HEN design diagram of BHD-FT process.

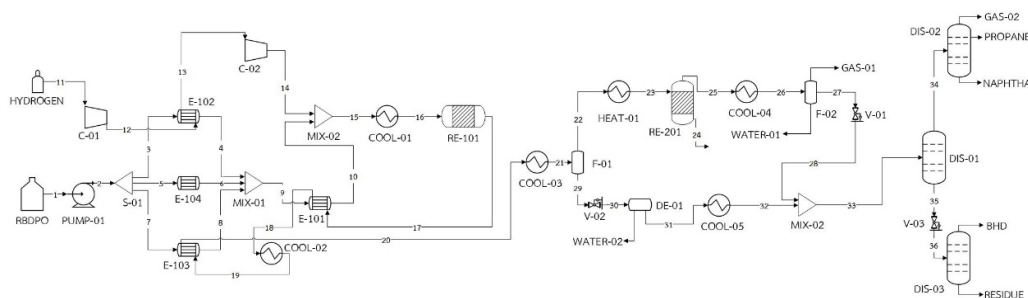


Figure 10. Newly designed BHD-FT process including HEN.

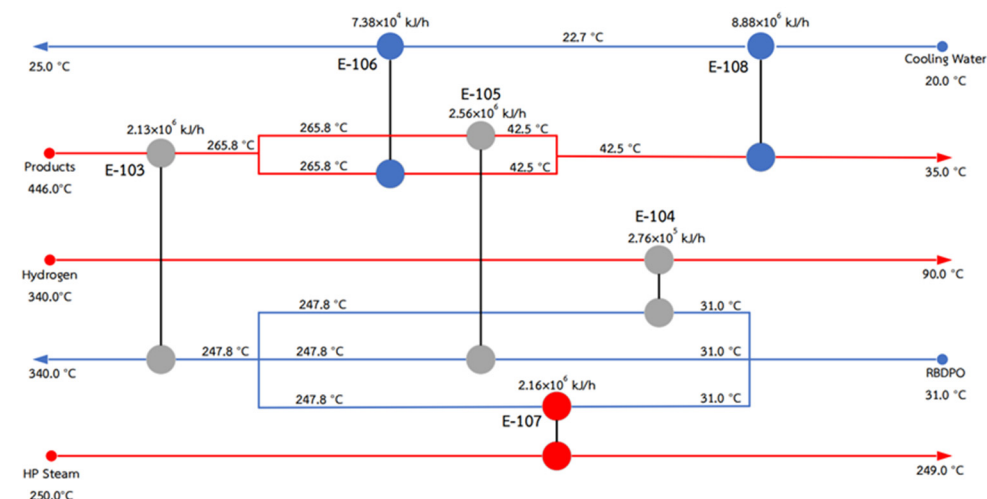


Figure 11. HEN design diagram of BHD-BIOJET-MEOH process.

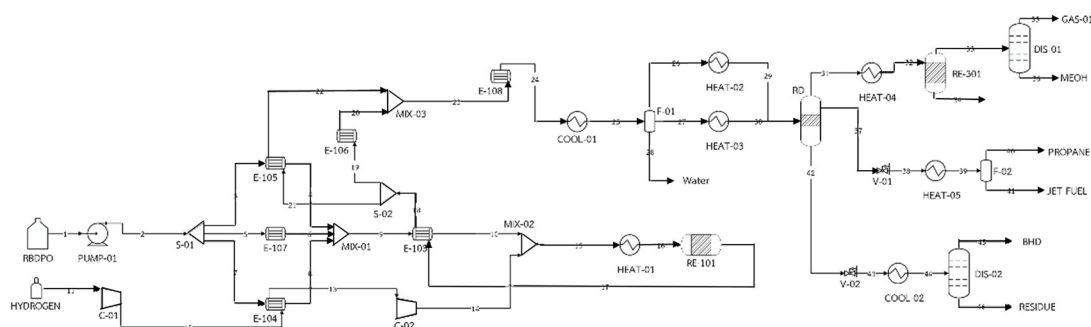


Figure 12. Newly designed BHD-BIOJET-MEOH process including HEN.

After performing the heat integration, the comparison revealed that the energy requirements for heating and cooling in the BHD-FT process were slightly higher than those of the BHD and BHD-BIOJET-MEOH processes due to a specific emphasis on the energy required for the FT reactor and the distillation columns. Notably, the BHD-BIOJET-MEOH process demonstrated the lowest energy demands for heating and cooling due to the simultaneous utilization of energy for reaction and separation in RD. The comparison of energy utilization before and after heat integration for the three BHD processes was illustrated in Figure 13. For the BHD process, the HEN design reduced the hot utility consumption of the process by 31.32% and reduced the cold utility consumption of the process by 26.85%. For the BHD-FT process, the hot and cold utility consumption could be reduced by 34.64% and 29.42%, respectively, after performing the HEN design. While the BHD-BIOJET-MEOH process showed the same trend, the requirement of the hot and cold utilities could be reduced by 29.16% and 26.14%, respectively.

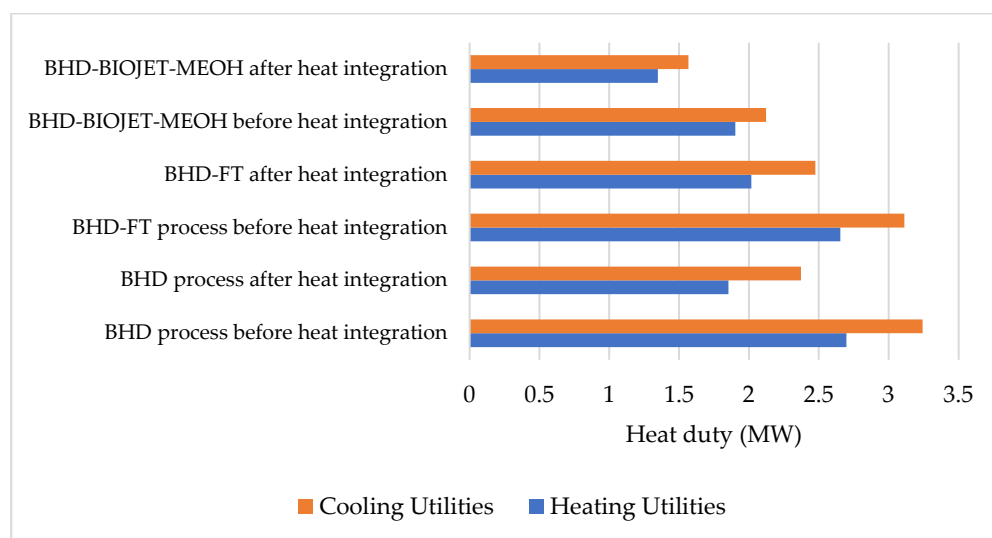


Figure 13. Hot and cold utility requirements before and after heat integration.

4.3. Economic Analysis

The economic analysis was performed for three BHD processes based on the same RBDPO feed rate of 22,000 kg/day. Raw material, product, and catalyst costs are shown in Table 5. The catalyst costs depended on reactor sizing and inlet flow rate. However, these costs were low compared with the cost of raw materials and equipment. Therefore, the catalyst costs had no influence on the total production cost. The economic feasibility assessment indicated that the BHD-FT process offered the highest FCI due to the high costs of the compressor, distillation, and flash separator, as shown in Table 6. The compressor cost and distillation cost accounted for 70% and 30% of the FCI, respectively. The total investment cost of the BHD-FT process was higher than that of the BHD process by approximately 6.93%. Considering the BHD-BIOJET-MEOH process, the additional heaters that provided the external heat source caused a higher cost compared with the BHD process. Thus, the BHD process offered the lowest FCI due to a smaller number of operating units. The total production costs of the three BHD processes are shown in Table 7. The total production costs of the BHD-FT process and the BHD-BIOJET-MEOH process were quite similar and higher than those of the BHD process due to the higher cost of raw materials. It was noted that the BHD process was still preferable in terms of total investment cost and total production cost.

Table 5. Raw material and product price.

Chemicals	Price (USD/kg)	References
Hydrogen	1.15	[47]
RBDPO	0.78	[48]
Ni/ γ -Al ₂ O ₃	10	[49]
Co-Mo/Al ₂ O ₃	7.8	[49]
Cobalt catalyst	751.5	[50]
Cu/ZnO/Al ₂ O ₃	300	[49]
Propane	0.725	[48]
Diesel	1.46	[51]
Naphtha	1.24	[48]
Jet-fuel	1.49	[51]
Methanol	0.48	[48]

Table 6. The summary of total investment cost.

Description	BHD Process (Millions USD)	BHD-FT Process (Millions USD)	BHD-BIOJET-MEOH Process (Millions USD)
Reactor	0.13	0.13	0.13
PSA	0.09	0	0
Flash	0.09	0.19	0.18
Pump	0.04	0.04	0.04
Compressor	1.04	1.11	1.11
Heat exchanger	0.03	0.02	0.03
Heater	0.02	0.01	0.14
Cooler	0.00	0.12	0.10
Decanter	0.08	0.06	0.00
Distillation	0.61	0.59	0.52
Fixed capital investment cost	3.51	3.76	3.74
Working capital cost	0.53	0.56	0.56
Total investment cost	4.04	4.32	4.30

Table 7. The summary of total production cost.

Description	BHD Process (Millions USD)	BHD-FT Process (Millions USD)	BHD-BIOJET-MEOH Process (Millions USD)
Raw material	5.93	5.93	5.98
Utilities	0.05	0.05	0.05
Catalyst	0.002	0.0023	0.03
Labor	0.05	0.05	0.05
Maintenance	0.18	0.19	0.19
Depreciation	0.35	0.38	0.37
Local tax	0.04	0.05	0.04
Insurance	0.18	0.19	0.19
Total production cost	6.72	6.95	7.93

The BHD-BIOJET-MEOH process offered more benefits than the other BHD processes in terms of NPV and IRR. The cumulative cash flow of each process is shown in Figure 14. It was found that the cumulative cash flow continuously increased when the project lifetime increased. And the payback periods of the BHD, BHD-FT, and BHD-BIOJET-MEOH processes were 3 years and 4 months, 3 years and 4 months, and 3 years and 1 month, respectively. Among the three BHD processes, the BHD-BIOJET-MEOH process was the most economically feasible process because it offered the highest NPV and IRR, followed by the BHD-FT and BHD processes, as shown in Table 8.

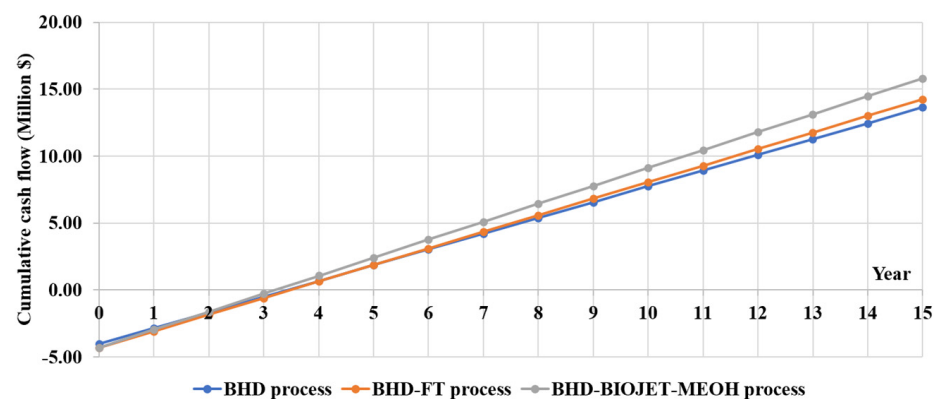
**Figure 14.** Cumulative cash flow of three BHD processes.

Table 8. The NPV and IRR of three BHD processes.

Parameter	BHD Process	BHD-FT Process	BHD-BIOJET-MEOH Process
NPV (Million USD)	6.69	6.95	7.93
Payback period	3 Y 4 M	3 Y 4 M	3 Y 1 M
IRR (%)	28.48	27.92	30.75

Considering the sensitivity analysis of only the BHD-BIOJET-MEOH process, in case the product selling price changes +30% and −30% of the base case, it was found that the NPV was negative when the selling price of the products decreased, as shown in Table 9. According to the literature [52,53], the price of diesel and jet fuel fluctuated according to the market price. Therefore, the BHD-BIOJET-MEOH process was the most attractive process because it could adjust the operating parameters of the RD, such as the distillate-to-feed ratio, the reflux ratio, etc., to maximize the profit.

Table 9. The sensitivity analysis of the BHD-BIOJET-MEOH process in case the product selling price changes.

Sensitivity (%)	Price List (USD/kg)				NPV (Million USD)
	Propane	BHD	Bio-Jet Fuel	MEOH	
−30	0.51	1.02	1.04	0.34	−14.53
−20	0.58	1.17	1.19	0.38	−6.92
−10	0.65	1.31	1.34	0.43	0.28
0	0.73	1.46	1.49	0.48	7.93
10	0.80	1.61	1.64	0.53	15.59
20	0.87	1.75	1.79	0.58	22.79
30	0.94	1.90	1.94	0.62	30.40

4.4. Life Cycle Assessment

In this section, environmental impacts including carbon footprint, human toxicity non-cancer (HTNC), human toxic cancer (HTC), human toxicity by exposure (HTPE), human toxicity by ingestion (HTPI), human toxicity carcinogenics (HTC), photochemical ozone formation (POCP), photochemical oxidation potential (PCOP), ozone depletion potential (ODP), global warming potential (GWP), terrestrial eutrophication, marine eutrophication potential (MEP), acidification potential (AP), terrestrial toxicity potential (TTP), aquatic toxicity (ATP), and freshwater ecotoxicity (ET) are evaluated for all BHD processes. The inputs were raw materials, chemicals, and fuels. The outputs of the process were effluent gas, wastewater, and solid waste.

The carbon footprint of the raw materials (including H₂ and RBDPO) and that of each operating unit of the three BHD processes are shown in Figure 15. Although all processes consumed the same amount of RBDPO, the hydrogen consumption of the BHD process was 28% less than the BHD-FT process and the BHD-BIOJET-MEOH process, resulting in a lower carbon footprint of the raw materials. As the BHD-BIOJET-MEOH process involved a large number of operating units, it offered the highest carbon footprint, followed by the BHD process and the BHD-FT process, respectively. The carbon footprints of each operating unit in the BHD, BHD-FT, and BHD-BIOJET-MEOH processes are shown in Figure 16a–c, respectively. It was found that the distillation columns showed the highest carbon footprint because they consumed a large amount of energy.

The analysis of potential environmental impacts (PEIs) of all BHD processes by normalization was performed using the ILCD 2011 software. The PEIs in the categories of human health and ecosystem are shown in Figure 17a,b, respectively. For the category of human health, the PEI of the BHD-BIOJET-MEOH process was the one that most contributed to

HTNC, while the HTC was comparable among all processes. Regarding the category of the ecosystem, the PEIs in the categories of PCOP and AP were the two biggest impacts for all processes. And the BHD-BIOJET-MEOH process offered the highest effect on the ecosystem.

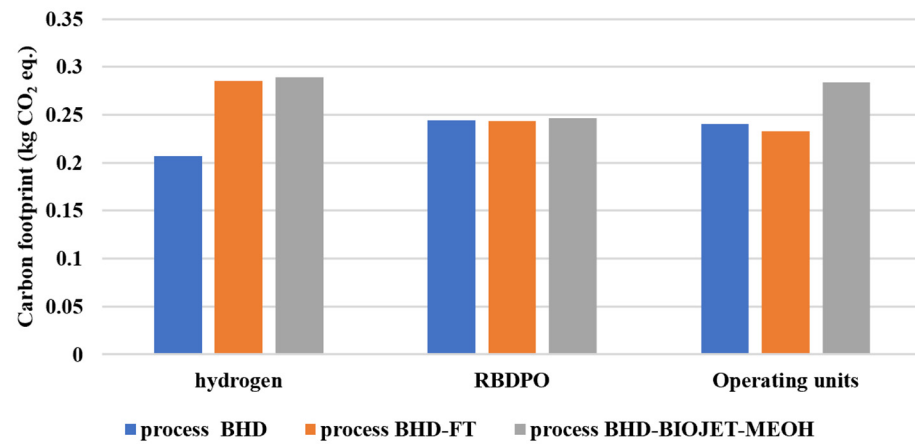


Figure 15. Carbon footprint of operating units and raw materials of three BHD processes.

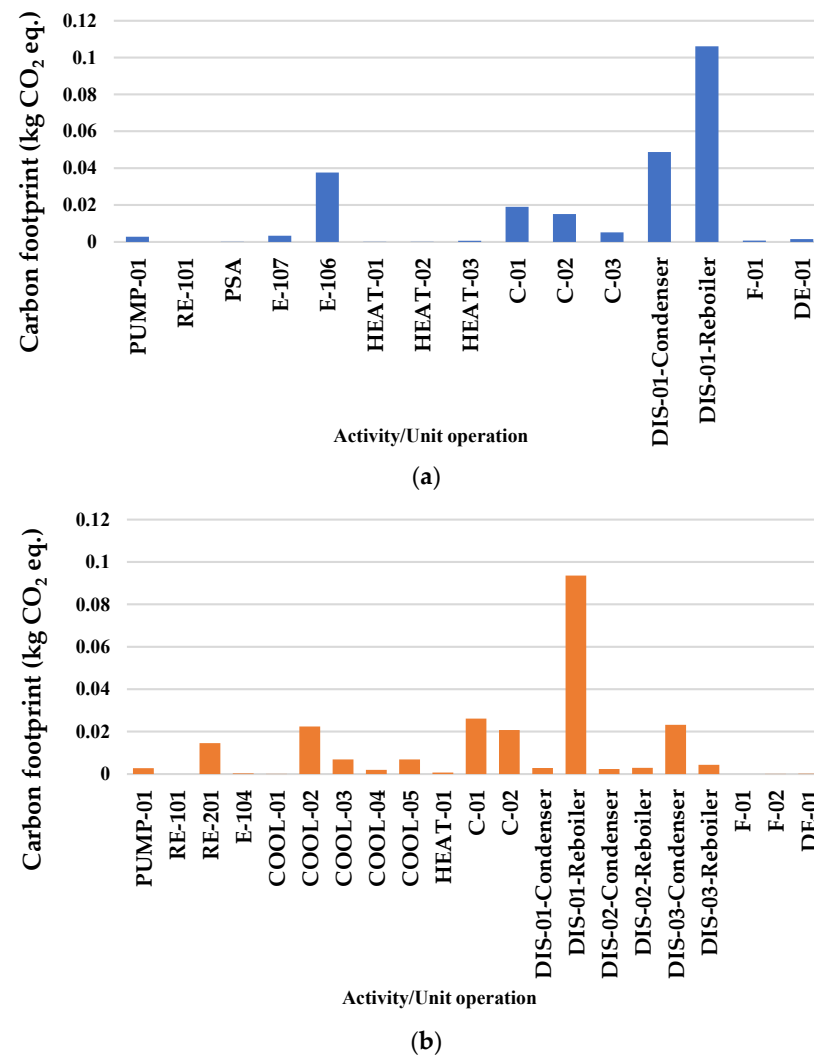


Figure 16. Cont.

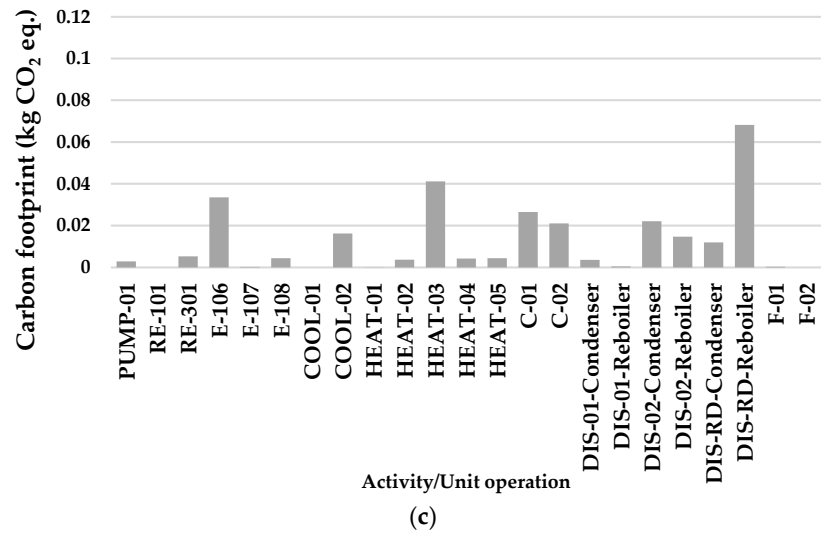


Figure 16. Carbon footprint of each operating unit of (a) BHD process, (b) BHD-FT process, and (c) BHD-BIOJET-MEOH process.

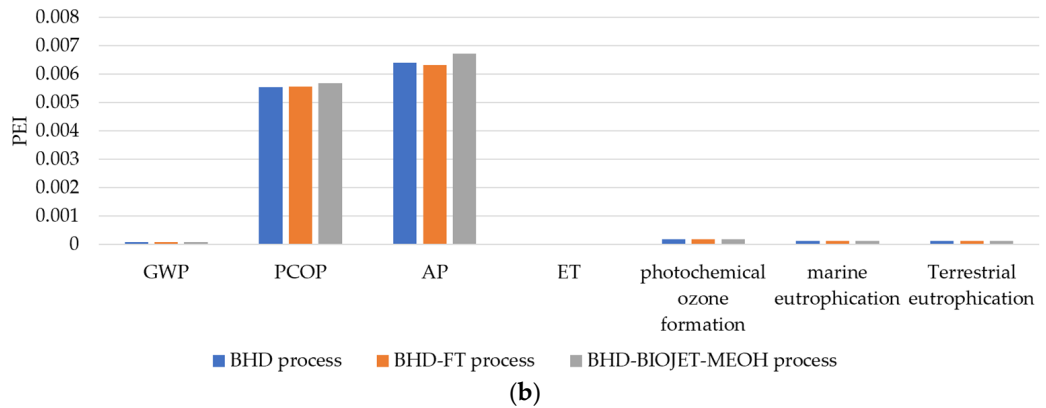
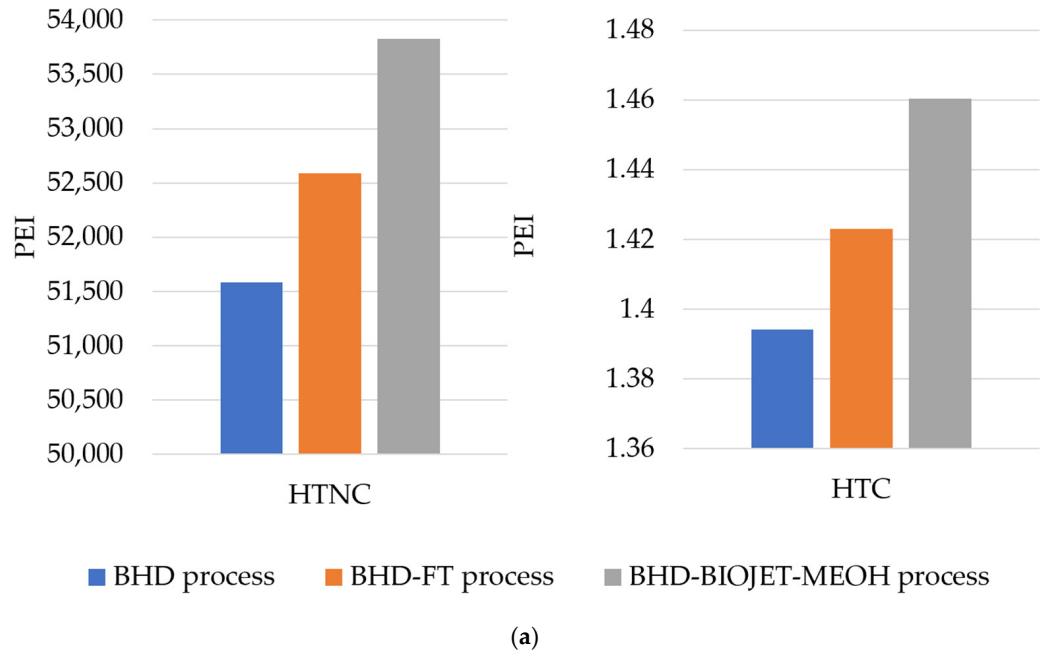


Figure 17. The environmental impact of various BHD processes in categories of (a) human health and (b) ecosystem.

5. Conclusions

In order to enhance process performance and achieve a sustainable objective, the co-production of BHD with other renewable fuels using a unique process including carbon dioxide usage is investigated. Three alternative processes of BHD production from RBDPO, including (1) the conventional BHD process with hydrogen recovery (BHD process), (2) the BHD process coupled with the Fischer–Tropsch process (BHD-FT process), (3) the BHD process coupled with the bio-jet fuel and methanol processes (BHD-BIOJET-MEOH process) are studied and compared with the conventional BHD process, in terms of technical, economic, and environmental aspects. The conventional BHD process requires less hydrogen and consumes less energy than the others. The pinch analysis and HEN design were performed to find the energy-efficient condition of the selected BHD process. The BHD-BIOJET-MEOH process could reduce hot utilities by 50% and cold utilities by 52% compared with the BHD process. The economic analysis indicates that the BHD-BIOJET-MEOH process is the most economically feasible, as it has the shortest payback period of 3 years and 1 month, the highest NPV of USD 7.93 million, and the highest IRR of 30.75%. Regarding environmental performance, the BHD process has the lowest carbon footprint of 0.692 kgCO₂eq./ kg of BHD. The BHD-BIOJET-MEOH process offered the highest PEI in the categories of human health and ecosystem. To exactly justify which process is the most suitable process offering the highest performance regarding the technical, economic, and environmental viewpoints, a multi-objective optimization that combines all criteria should be further performed.

Author Contributions: Conceptualization, L.S., S.A. (Suksun Amornraksa), A.A.; methodology, L.S., S.A. (Suksun Amornraksa), A.A.; software, L.S., S.A. (Suksun Amornraksa); validation, K.Y.; investigation, L.S., S.A. (Suksun Amornraksa), A.A.; resources, K.Y.; writing—original draft preparation, L.S., S.A. (Suksun Amornraksa), K.Y.; writing—review and editing, A.A., S.A. (Suttichai Assabumrungrat); visualization, S.A.; supervision, S.A.; writing—review and editing, K.I.-o. All authors have read and agreed to the published version of the manuscript.

Funding: This work was funded by King Mongkut’s University of Technology North Bangkok, Contract no. KMUTNB-67-BASIC-05.

Data Availability Statement: Data are contained within the article.

Acknowledgments: This work was supported and funded by King Mongkut’s University of Technology North Bangkok, Contract no. KMUTNB-67-BASIC-05. The authors would like to acknowledge the support of Aspen Plus from TGGS- Thai—German Graduate School of Engineering King Mongkut’s University of Technology North Bangkok and the support of LCSOFT from PSE for SPEED Company Limited.

Conflicts of Interest: The authors declare no conflicts of interest.

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