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Process Simulation and Design Considerations for Biodiesel Production from Rubber Seed Oil

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Abstract: Indonesia is one of the largest rubber producers worldwide. However, rubber seeds still garner less attention due to their low economic value. In fact, the rubber seeds contain 40–50% (*w/w*) of rubber seed oil (RSO), which is a potential candidate to be used as a feedstock in biodiesel production. In this regard, this study aims to model and simulate the production process of biodiesel from RSO via transesterification reaction, employing methanol and heterogeneous catalyst. The simulation was performed using ASPEN Hysys v11. Acid-based catalyzed esterification was implemented to eliminate soap formation, which may significantly lower biodiesel yield. The results showed that an RSO inlet rate of 1100 L/h with a methanol to oil molar ratio of 1:6 could generate around 1146 L/h biodiesel. Methanol recovery was conducted, an approximately 95% of excess methanol could be regenerated. Simulation results indicated that the properties of the biodiesel produced are compatible with modern diesel engines. Economic analysis also shows that this technology is promising, with excellent investment criteria.

Keywords: biodiesel; rubber seed oil; process simulation; design considerations; ASPEN Hysys

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1. Introduction

Energy and clean air are vital for the survival and prosperity of human beings. A progressive escalation in population, industrialization, and urbanization has been the main cause of an increasing energy demand. Recently, the primary energy source is still supplied by fossil fuels that are limited in resources and full of environmental hazards. The combustion of fossil fuels causes many environmental aftereffects, e.g., global warming, air pollution, acid rain, and ozone layer damage [1]. These aspects render fossil fuels non-renewable and non-sustainable. Abundant research has been conducted in the hope of discovering alternative fuels that have the potential to substitute fossil fuels. These alternative energies can be extracted from solar, wind, hydropower, hydrogen, geothermal, nuclear, and biomass [2]. As a substitute fuel, it is significant for the resources to be technically feasible, economically competitive, environmentally harmless, and available in large quantities at an affordable price. To comply with this perspective, vegetable oils [3], bio-alcohols [4], biogas [5], and biodiesel [6] are deemed to be promising candidates.

Among available fuel resources, biodiesel is considered a complementary fuel to substitute diesel oil and other petroleum-based fuels. Biodiesel has drawn substantial consideration as a remarkable choice because it is safe, renewable, biodegradable, non-toxic, Sulphur-free, and a good lubricant. These advantages of biodiesel over fossil fuels cannot be undervalued. It can be utilized by blending it with diesel oil or as a pure substance. It has notable compatibility with diesel engines without additional modifications and negative impacts on the performance of the engines. In this regard, renewable biological sources, such as biomass, vegetable oils, and fats, can be utilized as biodiesel feedstocks [7].

The types of feedstocks have a significant role in biodiesel characteristics. The raw material spent for producing biodiesel varies across regions depending on their geographical conditions and agricultural systems. Certain physical properties of biodiesel are reliant on the types of feedstocks adopted in the production process. In general, biodiesel is one of the safest fuels since its flash point is considerably higher than fossil fuels. Moreover, the calorific value of biodiesel is ~37.27 MJ/L, or about 9% less than commercial petroleum diesel. The disparity in the energy intensity of biodiesel relies on the compositions of the feedstocks used more than the production methods [8]. Before selecting the raw material for biodiesel production, the selection of certain parameters requires careful consideration, such as the fatty acid profiles and the fat and oil processing techniques.

Increasing the production scale from the laboratory to a larger biodiesel production scale is still a major challenge. Modelling and optimization analysis can predict the scale-up process, which can minimize the scale-up obstacle. Therefore, the process simulation created in this study can be applied as a platform for scale-up design considerations, production approximations and product quality assessments. Process modelling and optimization by simulation for biodiesel production have been conducted for edible oils [9], non-edible oils [7], and waste cooking oils. Our group has carried out various process simulations related to the conversion of vegetable oils into biodiesel or other value-added products [9–12]. We also actively contribute to the waste to energy conversion sector [13,14].

To date, Indonesia is one of the largest rubber producers in the world, supported by a considerable number of rubber plantations in several areas. Rubber seeds have a certain appeal as they are presently unvalued and considered worthless. Rubber seed production is estimated to be in the range of 100–1200 kg/(ha·y). The rubber seeds are composed of a kernel (61% (*w/w*)) enclosed by a hard shell (39% (*w/w*)). The kernel contains 40–50% (*w/w*) oil. By presuming the oil content and the rubber seed production, the annual production of rubber seed oil (RSO) is approximated to be in the range 5–300 kg/(ha·y) [15]. Many laboratory-scale studies have been carried out to convert RSO to biodiesel with promising results [16–22]. In this study, ASPEN Hysys v11 was employed to model and simulate the transesterification process for biodiesel production from RSO by using methanol and a heterogeneous catalyst. A literature review was conducted for design consideration and the characteristics of the biodiesel products obtained were compared. To the best of our knowledge, there are no studies that report process simulation studies and design considerations for biodiesel production from RSO.

2. Design Considerations

Before modeling and simulating the biodiesel production process from RSO, it is necessary to consider various variables that affect the production process and the resulting product. Therefore, an analysis of the following variables is carried out.

2.1. Biodiesel Feedstock

The prohibitive cost of production is the major obstacle to biodiesel expansion into large-scale commercialization and its competition with fossil fuels. The excessive cost is credited to the price of fresh vegetable oil as feedstock. Recent studies focus on decreasing the production cost of biodiesel. One effective method is to replace a fresh edible feedstock with a cooking oil waste due to its more affordable price compared to fresh vegetable oils. Moreover, the utilization of waste cooking oil has environmental benefits since it can reduce a large amount of waste accumulated. Other options are the employment of non-edible oils, which represent an excellent substitute for reducing edible oil reliance. The toxic substances of these oils may create harmful effects on humans if consumed. Thus, it diminishes competition for feed and food use since they are not consumable.

Various raw materials have been studied for biodiesel production, including vegetable oils, animal-fat-based oils, and microbial oils. Vegetable oil can be grouped into edible and non-edible oil. Edible sources that had been studied for biodiesel production include rapeseed [23], peanut [24], coconut [25], palm [26], canola [27], mustard [28], safflower [29], and sunflower [30]. Meanwhile, non-edible sources include polanga (*Calophyllum inophyllum* L.) seed oil [31], pongamia oil [32], castor bean [33], jojoba (*Simmondsia chinensis*) oil [34], rubber seed [16–22], tobacco (*Nicotiana tabacum*) seed oil [35], karanja oil [36], okra (*Hibiscus esculentus*) seed oil [37], and cotton seed oil [38]. The information on various kinds of feedstocks utilized for generating biodiesel and their major fatty acids components are summarized in Table 1.

Table 1. Fatty acids composition in various feedstocks [26,31,36].

Vegetable Oil	Oleic Acid C18:1	Linoleic Acid C18:2	Linolenic Acid C18:3	Palmitic Acid C16:0	Stearic Acid C18:0
Edible Oil					
Rapeseed oil	53–70	15–30	5–13	2.5–6.5	0.8–3.0
Peanut oil	33	13.3	0.2	26.5	2.9
Palm Oil	39	11	-	45	4
Soybean oil	23.4	53.2	7.8	11.0	4.0
Corn Oil	30–50	34–56	0.5–1.5	8–10	1–4
Sunflower Oil	20.6	66.2	0.8	4.8	5.7
Non-edible Oil					
Polanga Oil	34.09	38.26	0.3	12.01	12.95
Castor Bean Oil	36–64	18–45	2.4–3.4	10–17	5–10
Rubber Seed Oil (RSO)	12.8–24.9	18.9–39.6	8–18.2	6.5–10.2	6.6–9.9
Karanja Oil	51.6–72.2	11.8–16.5	0–2.65	9.8–11.65	6.2–7.5
Cotton Seed Oil	13.3–21.7	46.7–58.2	0	11.7–26.4	0.9–5.0
Animal oils and fats					
Chicken fat	34.6	30.9	2.9	19.8	6.1
Lamb meat (oil)	35.0	36.0	-	10.1	6.0
Fish waste (oil)	17.3	1.7	2.9	10.1	6.0
Beef tallow	46.4	2.7	0	24.8	20.6
Microbial lipid					
Fungi	30.1–41.3	8.7–23.3	0.1–0.6	20.1–36.0	10.7–23.6
Algae	13.6–17.2	33.7–40.8	11.3–18.5	24.5–36.4	1.0–2.1
Microalgae	7.8–14.9	6.8–8.3	15.4–25.0	10.8–16.7	2.3–2.6
Yeast	3.5–38.6	2.7–14.6	-	2.8–24.1	4.6–7.7
Waste Cooking Oil	46.0	3.9	0.3	24.6	18.4

The productivity of rubber seeds in Indonesia is approximately about 5 million TPY. Therefore, it is estimated that Indonesia is able to generate RSO with about 2 million TPY. The cost of non-edible oil is much cheaper than edible oil that has continuous growth of demand. Hence, the utilization of RSO as non-edible oil for a feedstock of biodiesel is very assuring [39]. RSO is mainly composed of fatty acids with 18 carbon atoms (Table 1). Meanwhile, hydrocarbons with a carbon chain length of 8 to 10 atoms are the main components of petroleum diesel. The fuel quality for diesel engine is measured by cetane number that will increase linearly with carbon number addition. Branched chains and double bonds existence will also enhance the flow properties. Based on this perspective, the cetane number of biodiesel converted from RSO will likely be high [40].

2.2. Biodiesel Production Technologies

Vegetable oil and animal fat are considered highly viscous to be used directly as biodiesel in diesel engines. The application of highly viscous and dense oils may negatively impact the diesel engine, e.g., the tendency to undergo carbon deposition and engine fouling [16]. Therefore, these feedstocks can be converted to biodiesel through four feasible methods: direct use or blending of oils, micro-emulsion, pyrolysis or thermal cracking, and transesterification process [41]. The advantages and disadvantages of these four production processes are summarized in Table 2.

Table 2. Advantages and disadvantages of main biodiesel production processes [26,41].

Production Process	Advantage	Disadvantage
Direct use and blending	• Does not involve any chemical process (non-polluting) • Technical modifications are not required • Simple production process • Easy to implement • Low investment and production budgets	• Impractical and inapplicable for direct use in diesel engines • Solidification of blend at cold temperatures • Involatile • Highly viscous • Tend to form gum • Prone to lubricating oil thickening • Incomplete combustion • Oil decomposition • High amount of free fatty acid (FFA) • Non-saturated hydrocarbon chains sensitivity • Injector nozzles congestion • Weak atomization • Deterioration of engine durability • Produces more emissions • High cost of maintenance
Microemulsion	• Simple process and produces less pollution • Lower viscosity and higher product liquidity • Lower nitrogen oxide emissions • Free by-product or wasteless • Produces clear, single phase, and thermodynamically stable colloidal equilibrium dispersion of biodiesel fluid	• Insufficient combustion • Lubricating oil thickening • Random injector needle sticking • High viscosity • Low stability • Incomplete combustion, • Carbon residue deposition
Pyrolysis (Thermal Cracking)	• More suitable to be implemented in hydro-processing industry area • Value-added by-products formation like syngas • Produces biofuel with suitable physical and chemical characteristics • Effective, simple, wasteless, and pollution free process	• Excessive production cost • Required complex equipment • No oxygenated value product • Low purity product • The product is more similar to gasoline than diesel fuel
Transesterification	• Is known as the conventional process for production of biodiesel • Recyclable unreacted raw materials • Value-added transformation of by-product (i.e., glycerol) • High conversion with reasonably low expanse • Mild operating parameters • Product characteristics are comparable to the Petro-diesel • Suitable for large-scale production.	• Sensitive to saponification process • Extensive separation and purification process • Complex equipment requirement • Generate large amount of wastewater

In recent years, several production methods have been proposed to reduce the cost of biodiesel. The methods suggest the utilization of supercritical alcohol and eliminate the usage of homogenous catalyst. Furthermore, a short residence time is required in the supercritical process to reach high conversion. Another alternative is to use a heterogeneous/solid catalyst that will shorten the downstream purification stages of the biodiesel. The solid catalyst can be separated easily by physical methods, such as using a hydro cyclone in the situation where a multiphase reactor is operated. On the other hand, a fixed-bed reactor would be able to retain the catalyst phase [42]. A diversity of feedstock (edible, in-edible oil crops and waste oils), varied conversion technologies and products, and potential processing techniques has been widely implemented in biodiesel manufacturing sectors (Figure 1).

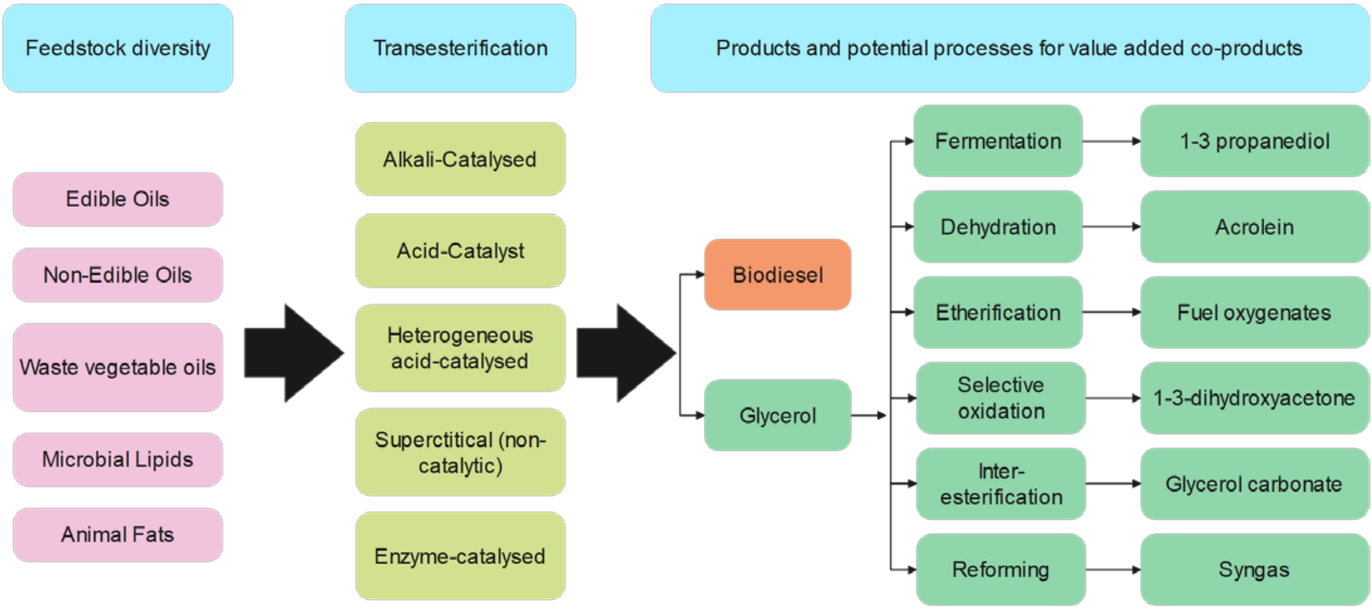

Figure 1. Schematic representation of transesterification process technology and feedstock options for biodiesel production (redrawn and modified from Pasha et al. [43]).

2.3. Transesterification Process

Transesterification is the most preferred among the available methods. Transesterification reactions support the utilization of diverse feedstock categories to produce a fuel with high quality resemblant to conventional diesel. Via this method, oil-bearing crops, animal fats, and algal lipids (triglycerides) can be converted to their alkyl esters with viscosity analogous to commercial diesel fuel. In the transesterification process, the triglycerides in the oil react with alcohols with the help of a catalyst to produce biodiesel in the form of fatty acid alkyl esters and glycerol as the by-product of the reaction. Taking into consideration that methanol is the typical alcohol used in biodiesel production, they are commonly referred as fatty acid methyl esters (FAME) [44]. The process is carried out by using either chemical (acids and bases) or biological catalysts (enzymes), but it is likely that the base catalysts may have better performance. The chemical catalyst involves homogeneous agents (alkali or acid), heterogeneous agents (solid acid or solid alkali), heterogeneous nano catalysts and supercritical fluids (SCFs) [7,44].

Fatty acids in vegetable oils are in the form of triglycerides, diglycerides, monoglycerides and free fatty acids (FFA) [45]. Transesterification reaction catalyzed by base catalyst tends to induce fundamental difficulty for high FFA feedstock. FFA can react with the base catalyst to form soap (saponification) that results in a loss of catalyst, while the soap formed will deactivate the catalyst. To solve this problem, the FFA content must be eliminated or converted to alkyl esters. Two stages are needed to effectively produce biodiesel from raw material with a high amount of FFA. The initial stage is esterification to lower the FFA concentration of the oil. The next stage is transesterification to convert the triglyceride quantity of the oils to mono-alkyl ester and glycerol [39]. Generally, the sulfuric acid catalyst is applied in acid esterification and alkali metal hydroxides and alkoxides are applied as the catalyst for transesterification process [19]. The general biodiesel production process from vegetable oils is depicted in Figure 2.

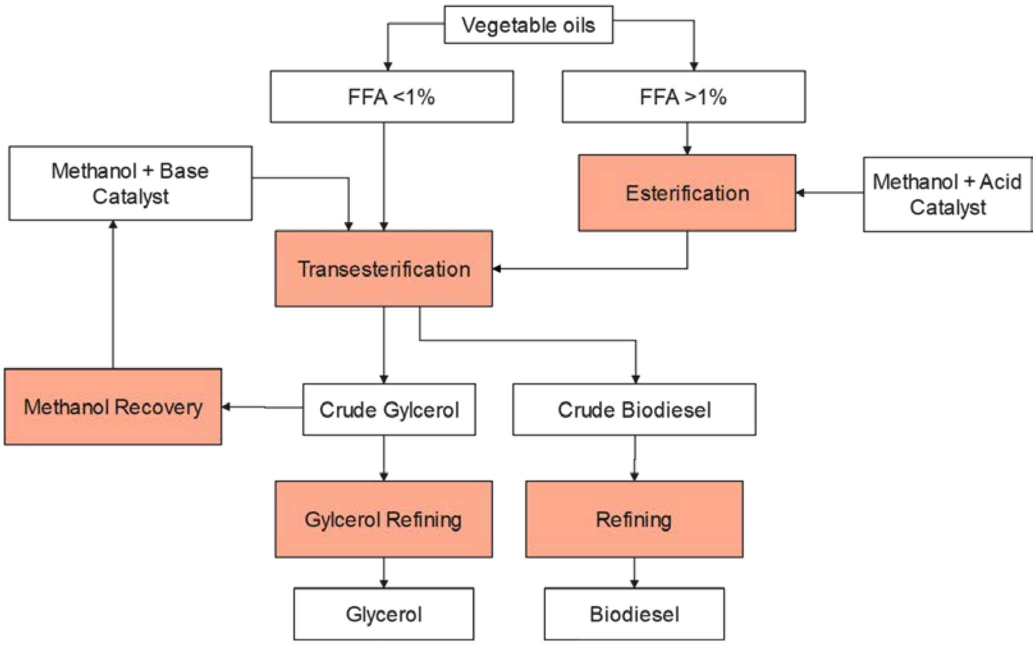

Figure 2. General biodiesel production process.

2.3.1. Esterification Process

Oil feedstocks with more than 1% FFA needs to undergo an acid esterification process to eliminate the negative effect of saponification and reduce the yield of biodiesel. These raw materials are first filtered and pretreated in order to remove water and other contaminants. Afterwards, the mixture flows into the acid esterification reactor. In acid esterification reaction, FFA reacts with alcohol in the presence of catalyst to generate biodiesel (fatty acid alkyl ester) and water. For the esterification process, homogeneous catalyst in the form of acid substance such as sulfuric acid is conventionally used. The acid catalyst is dispersed in methanol and then blended with the pretreated oil. Subsequently, inside the reactor, the mixture is heated and stirred, hence the free fatty acids are converted to biodiesel. After the reaction is accomplished, the water is removed and the reaction proceeds to the transesterification process. The utilization of strong acid as a catalyst has several downsides because of its corrosivity, neutralization issues, and tendency to produce waste. Heterogenous catalysts based on sulfonated carbonaceous material [46] or silica zirconia [47] are some applicable options to substitute the strong acid. The RSO has high amount of FFA concentration that may exceed 40% [22]. The general biodiesel production via esterification reaction with an acidic catalyst is written in Equation (1).

$$\text{FFA} + \text{alcohol} \overset{\text{acid}}{\rightarrow} \text{FAME} + \text{water} \tag{1}$$

2.3.2. Transesterification Process

The transesterification process is the general method of transforming vegetable oils into biodiesel. When triglycerides in vegetable oils react with alcohols in the presence of alkaline/acid catalysts, fatty acid alkyl esters (biodiesel) and glycerol are produced. Oil feedstocks with less than 1% free fatty acids are filtered and pretreated for water and other contaminants removal so they can be directly supplied to the transesterification reactor along with fatty acid alkyl esters from the acid esterification process. Potassium hydroxide, which is commonly used as a catalyst, is dissolved in methanol then blended with the pretreated oil. When an acid esterification process is applied, an additional base catalyst is supplied for acid neutralization. The major co-products (biodiesel and glycerol) are formed two-layer liquid phase that can be separated after the reaction has been accomplished. Commonly, the transesterification reaction has a low reaction temperature (60–70 °C) and pressure (atmospheric). The presence of catalysts in the transesterification process is critical.

Sodium hydroxide is known as a conventional catalyst for this process [48]. Heterogeneous catalysts based on metal oxide is also broadly researched in transesterification reaction for the potential application as catalyst to generate biodiesel [49,50]. Carbon oxides from waste, e.g., eggshell [16,17] and cockle shell [21], have the potential to be utilized as a catalyst in this process. The general biodiesel production via esterification reaction with an alkaline catalyst is written in Equation (2).

$$\text{Trygliceride} + \text{alcohol} \overset{\text{base}}{\rightarrow} \text{FAME} + \text{glycerol} \tag{2}$$

2.3.3. Biodiesel Purification

The transesterification process is conducted in an excess methanol environment. For economic efficiency, the remaining methanol must be removed from the product stream. To fulfill the biodiesel standard, water and glycerol must be removed from the biodiesel product. Several technologies that can be adopted for biodiesel purification include wet washing, dry washing (activated compound, biomass-based adsorbents, silica-based adsorbents), ion exchange, or membrane separation technology [51]. The quality of biodiesel is the controlling factor in determining the most promising technique. Membrane separation can be a potential candidate for glycerol removal from biodiesel [52], but additional works are required to maintain the membrane from fouling and clogging. Other methods such as high voltage electrolysis can also be adopted in the separation of glycerol from biodiesel [53]. Conventionally, distillation can be used as a separation method and recovery of methanol [54]. The adoption of a membrane reactor can also be an option to simplify the purification process [55].

2.4. Effect of Process Parameter

Process parameters, such as the molar ratio of alcohol to oil, reaction temperature, FFA content, catalyst type and concentration, and reaction time, affected the yield of biodiesel. From these parameters, molar ratio, temperature, and catalyst concentration were shown to have a major impact on biodiesel yield [56]. The effect of these process parameters with RSO as feedstock on biodiesel yield is summarized in Table 3.

Table 3. Effect of process parameters on biodiesel yield.

RSO:Methanol	Catalyst	Temperature	Reaction Time	Yield	Ref
1:12	Eggshell-Al_2O_3 3%	65	4 h	98.9	[16]
1:12	Eggsshell 4%	65	3 h	99.7	[17]
1:4	Cement cklinker 5%	65	4 h	96.9	[18]
1:16	SO_3H-MCM-41 14.5%	129.6	48 h	83.10	[19]
1:16	Water cockle shell 9%	60–64	3 h	88.06	[20]
1:6	KOH	55	~1 h	96.8	[57]

2.4.1. Temperature

The reaction temperature greatly influences the yield of biodiesel and reaction kinetics. Generally, by increasing the reaction temperature, the reaction rate will be higher, resulting in a higher yield obtained. The increase in the reaction temperature can be caused by oil thinning due to the reduction of oil viscosity, resulting in a better mixing of oil and alcohol as well as an enhanced separation rate of glycerol from biodiesel. However, a temperature increase beyond the permissible range may cause a considerable reduction in biodiesel yield. These phenomena are expected due to side reactions (e.g., the saponification of triglycerides accelerated by high temperature, hydrolysis of methyl esters of fatty acids to form corresponding acid and alcohol) that occur more rapidly at higher temperatures in comparison to transesterification reactions, resulting in the drop of biodiesel yield [56–58]. Gimbun et al. [18] investigated RSO to biodiesel conversion performed at a temperature in the range of 40–70 °C while keeping other parameters constant. Higher temperature boosts the efficiency of transesterification, which also boosts the RSO conversion. It was also found that a temperature of 65 °C was the optimum temperature for RSO transesterification carried out with limestone-based catalyst. Rising the reaction temperature above 65 °C insignificantly influences the RSO conversion. When the reaction temperature reached 70 °C, the conversion dropped by a small number. This is because the methanol in the mixture evaporates at a temperature beyond the methanol boiling point (64.7 °C), resulting in an undesirable oil to methanol that can inhibit the reaction.

2.4.2. Alcohol to Oil Ratio

The molar ratio is other crucial factors influencing the yield of biodiesel. A small molar ratio of alcohol to oil will impact the conversion rate of triglycerides to FAME negatively. In contrast, a higher molar ratio possibly will reduce the yield and complicate separation process that ultimately impacts production cost and biodiesel yield. The transesterification reaction is reversible, so an excess of alcohol is needed to maintain the reaction towards the product. Methanol has a polar hydroxyl group which can cause the emulsification of glycerol and biodiesel during the process. This facilitates the reverse reaction, i.e., reconnection of glycerol and ester, thereby reducing biodiesel yield [56]. According to the literature, almost all reactions with alkaline catalysts demand approximately a 6:1 M ratio of methanol: oil for biodiesel production (yield of 98% (*w*/*w*)), which is sufficient to enhance fatty acid-glycerol chains. Musa [59] investigated the effects of alcohol to oil molar ratios and the type of alcohol on the transesterification process in biodiesel production and proposed a 6:1 M ratio for methanol and a 9:1 M ratio for ethanol. It has been reported that the biodiesel yield increases linearly with the increase of molar ratio. However, it begins to drop after reaching its peak. Furthermore, the separation process of glycerol and methanol recovery could be complicated in the case of a higher molar ratio.

2.4.3. Catalyst Concentration

Various types of catalysts (alkali, acid, or enzyme) are commonly employed for achieving desirable yields. The disproportionate use of catalysts is reported to create emulsions which can produce a higher viscosity mixture, thus causing the complexity of biodiesel separation and promoting saponification reaction that significantly reduces the final yield of biodiesel [58]. Among the alkali catalysts for biodiesel production, NaOH and KOH are most applied. Recently, the utilization of the heterogeneous catalyst has attracted interests of many researchers. The usage of heterogenous catalysts has greater benefits because of the ability to be recycled and reused [18]. Gimbun et al. studied the performance of CaO catalyst derived from activated cement clinker for biodiesel production from RSO. They found that the highest conversion was 92.3%, with 6% (*w*/*w*) catalyst concentration [18]. Zamberi and Ani investigated the use of CaO catalyst derived from waste cockle shells for RSO to biodiesel conversion. They concluded that the optimum catalyst concentration is 9% (*w*/*w*), which results in the highest yield of 88.06%. The yield starts to drop beyond the optimum concentration [21].

2.5. Simulation Methodology

The biodiesel production process from RSO was simulated using Aspen Hysys v11 with NRTL-ideal as the fluid package. Based on the design considerations in the previous section, we developed the model for the simulation process. The process was constructed referring to the following assumptions. The feedstock used is RSO with FFA > 1%, so before the transesterification process, an esterification process is required to produce biodiesel and glycerol as by-products [39]. The biodiesel purification and excess methanol recovery are handed by distillation [54] and membrane separation [52] methods. The simulation process is simplified by assuming ideal conditions so that the number of heat losses on all process equipment can be ignored. The equipment pressure drop was set at 1.5 psi, and the amount of pressure drop caused by friction inside the pipe was ignored. The RSO triglycerides were represented by the main fatty acids of RSO, triolein and tristearin, and trilinolein and tripalmitin as hypothetical components for better product properties, and FFA was represented by oleic acid. Based on the simulation result, a simple economic analysis was carried out to determine the economic feasibility of the biodiesel production process from RSO. The simulation parameters and composition of RSO are displayed in Table 4. Due to data limitations, both the esterification and transesterification processes were simulated based on reaction conversion (Equation (3)).

$$X_A = \frac{\text{mole of A reacted}}{\text{mole of A fed}} \tag{3}$$

Table 4. RSO to biodiesel simulation parameters.

Parameters	Values
RSO flowrate (L/h)	1100
Methanol to oil ratio	6:1
Reaction temperature (°C)	65
Conversion (%)	10–100
RSO compositions (%-mole)	
• Triolein	24.33
• Trilinolein	32.78
• Tripalmitin	12.37
• Tristearin	3.27
• Oleic Acid (FFA)	27.25

3. Results and Discussion

3.1. Process Simulation

The simulation flowsheet as the model for the biodiesel production process is shown in Figure 3. The process includes esterification, transesterification, excess methanol recovery, and biodiesel purification. The simulation involves different equipment, including reactors, separating units, heat exchangers, and pumps. The code and description of each piece of equipment are summarized in Table 5.

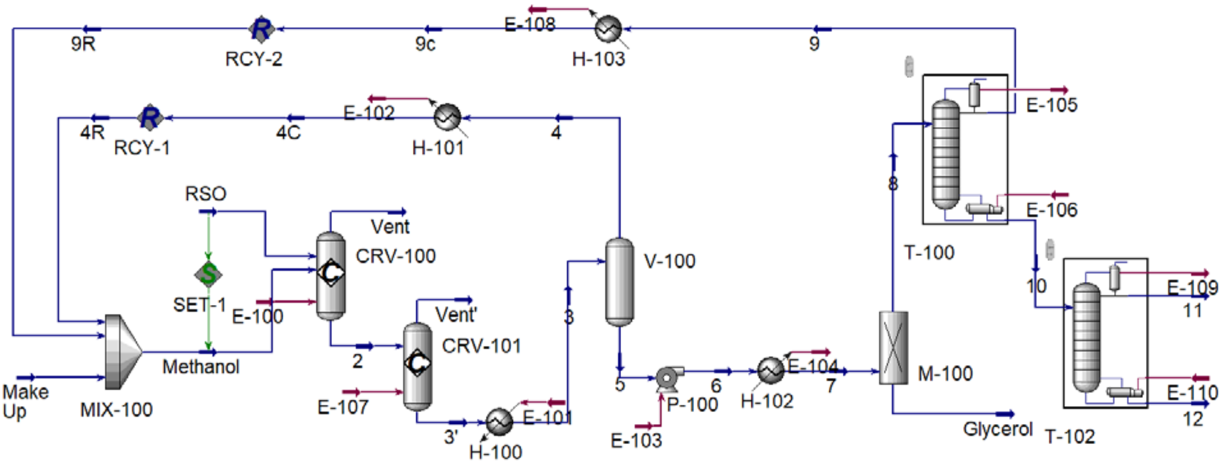

Figure 3. Simulation flowsheet using Aspen Hysys v11.

Table 5. Equipment description of the simulation flowsheet using Aspen Hysys v11.

Code	Description
MIX-100	Mixer
CRV-100	Esterification Reactor
CRV-101	Transesterification Reactor
V-100	Flash drum
M-100	Membrane
T-100 and T-102	Distillation Tower
P-100	Pump
H-100, H-101, H-102, and H-103	Heat Exchanger

3.1.1. Material Balance

The inlets of the system were RSO (1100 L/h) as oil feedstock and methanol as the alcohol source. The RSO stream was simulated using four main fatty acids components: triolein (24.33%), trilinolein (32.78%), tripalmitin (12.37%), tristearin (3.27%), and oleic acid (27.25%) as FFA. Since the RSO has a high FFA content >1%, it needed to undergo the esterification process prior to the transesterification reaction. Based on design consideration, the RSO to methanol molar ratio was set at 1:6. Due to data limitations, both the esterification and transesterification processes were simulated using a conversion reactor. The conversion was set at 100% for the esterification process and varied from 10 to 100% for the transesterification process.

Temperature is another parameter that affects the yield of biodiesel. With regard to the literature study conducted, both reactors were operated at 65 °C and atmospheric pressure [16–18]. The esterification reactor product stream mostly contained the excess methanol, glycerol, and biodiesel. The biodiesel must be separated from the mixture, and for economic efficiency, the excess methanol must be regenerated. For this purpose, the product was then subject to separation phases, methanol recovery, and the glycerol separation process in order to produce high purity biodiesel.

The methanol recovery was carried out in two stages: flash distillation and multi-stage distillation stages. After completing transesterification process, the product stream of the reactor was heated to reach a temperature of 80 °C inside the flash drum, evading the most unused methanol and forming two-phase mixture. The vapor phase that was rich in methanol was then cooled down and employed as feed. This process recovered the majority of excess methanol. In this point, the excess methanol recovery obtained was roughly ~65%.

The liquid phase continued to the next process, which was glycerol separation. Several technologies can be used for this operation as discussed in the previous section: wet washing, dry washing (activated compound, biomass-based adsorbents, silica-based adsorbents), ion exchange and membrane separation technology [51]. Still, membrane separation is one the best candidates because of its high selectivity and rejection rate [52]. Membrane separation was operated at high pressure to fulfil the optimum process conditions. The stream was then pumped and cooled down to 5.5 bar and 25 °C as required for the membrane separation. The retentate was glycerol (74.97 L/h) with high purity of around 99% and other impurities. For biodiesel purification, the permeate streamed to a multi-staged distillation tower (T-100). After a multi-stage distillation, approximately 30% of unreacted methanol could be recovered. The sum of excess methanol that could the be recycled was ~95%. After the purification process, the biodiesel was obtained with an ester content of 99.93% and volumetric flow rate of 1146 L/h for 100% conversion. The assumption in the conversion of RSO into biodiesel greatly affects the yield of biodiesel. As shown in Figure 4, the mass flow rate of biodiesel product increased with increasing conversion. High RSO to biodiesel conversion results in the low number of remaining RSO in the product stream. The effect of RSO to methanol ratio on the flow rate of each reactor product was also investigated (Figure 5). The results indicated that an RSO to methanol molar ratio of 1:3 was sufficient to produce biodiesel with a volumetric flowrate of 1146 L/h. However, this will likely influence the kinetics of the reaction since excess reactants are more desirable in enhancing product conversion in the real application.

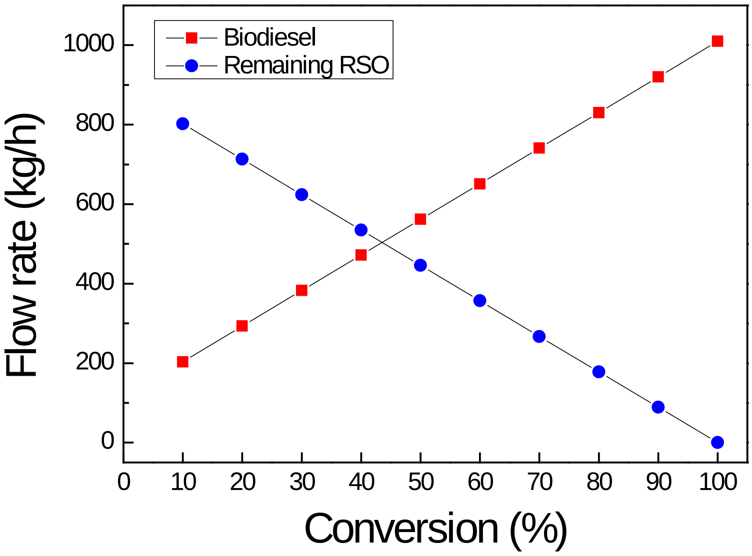

Figure 4. Mass flowrate of biodiesel product and remaining RSO in the product stream with different conversion assumptions.

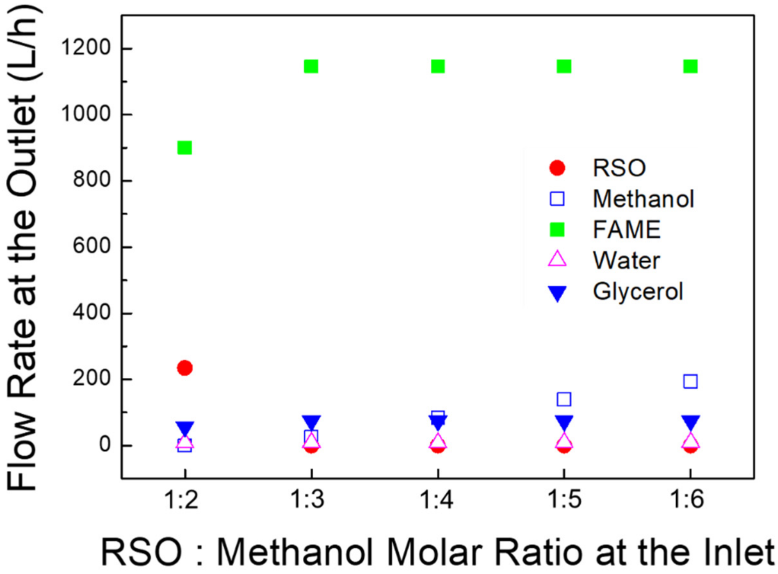

Figure 5. Effect of RSO to methanol ratio on the flow rate of each reactor product.

3.1.2. Energy Balance

The energy balances of the biodiesel production process from RSO are presented in Figure 6. All main equipment requires heating and/or cooling.

Based on the simulated process, the energy consumption for biodiesel production from RSO is summarized in Table 6. The energy is utilized to supply the electricity, heating utility, and cooling utility. Most of the equipment is operated at atmospheric pressure, except the separation membrane which requires a high pressure to operate. In order to achieve the high-pressure condition, the pump P-100 was operated to initiate the membrane separation process. The heating utility (278 W/L biodiesel) is required to operate the flash drum and reboiler that can be supplied with the biodiesel produced and steam. As for the cooling utility (182 W/L biodiesel), water is considered adequate.

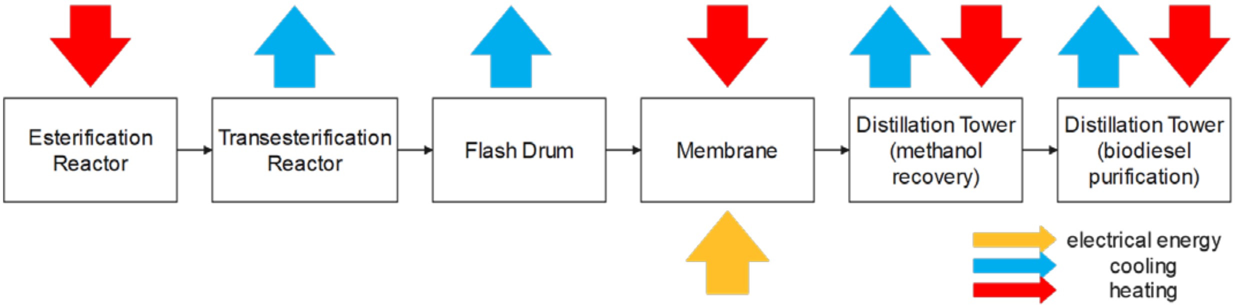

Figure 6. Energy balance concept for the process simulation.

Table 6. Utility requirement in the production of biodiesel from 1100 L/h RSO.

Type	Equipment	Consumption (kW)	Total (kW)
Electricity	E-103	0.23	0.222
Heating stream	E-100	34.42	319.38
	E-101	25.93	
	E-106	172.40	
	E-110	86.63	
Cooling stream	E-102	11.86	208.69
	E-104	44.92	
	E-105	77.31	
	E-107	64.48	
	E-108	5.02	
	E-109	5.10	

The effect of reactor operating temperature on the heating or cooling load of the transesterification reactor and esterification reactor was also observed, as presented in Figure 7. In the graph, the positive value indicates a heating load, while a negative value indicates a cooling load. The results showed that the change in the operating temperature of the transesterification reactor (from 40 to 70 °C) did not significantly affect the cooling load required to cool down the mixture. Meanwhile, increasing the temperature of the esterification reactor from 40 to 70 °C increases the heating load from 13.29 to 55.8 kW.

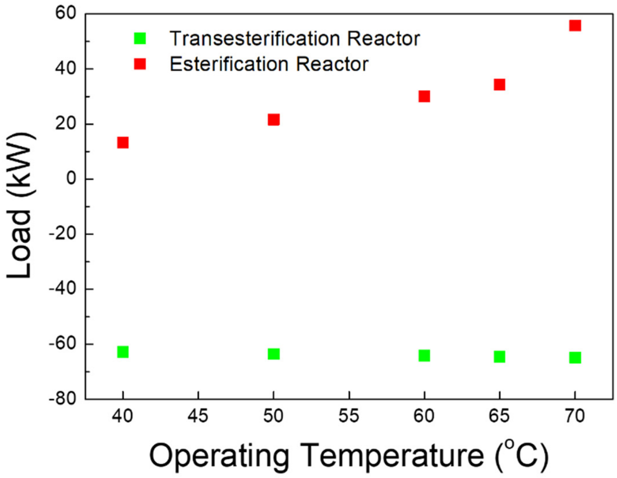

Figure 7. The effect of reactor operating temperature on the heating or cooling load of the transesterification reactor and esterification reactor. The positive value indicates a heating load, while a negative value indicates a cooling load.

3.1.3. Biodiesel Properties

The biodiesel product properties obtained from this study were compared with those from the literature. However, due to data limitations, only a minority of biodiesel properties can be compared (Table 7). The properties of the biodiesel obtained from this study are relatively comparable with other reports on laboratory-scale biodiesel synthesized from RSO. The properties are also in good agreement with ASTM D 6751 standards and EN 14214 standards of biodiesel. It can be observed that the product properties except viscosity fit into the range of biodiesel properties in ASTM D 6751 and EN 14214.

Table 7. Product properties obtained from this study in comparison with other products from the literature.

Properties	ASTM D 6751 Standards	EN 14214 Standards	Onoji et al. [20]	Ahmad et al. [57]	This Study
Water & sediment, max	<0.05	<0.05	0.0062	0.042	0.01
Viscosity (cSt) @ 40 °C	1.9–6.0	3.5–5.0	4.32	3.89	1.811
Density @15 °C (kg/m^3)	870–900	860–900	876	885	880.6
Ester content		>96.5	96.7	96.8	99.93

3.1.4. Economic Analysis

Simple economic analysis for biodiesel production from RSO was performed using the Aspen Process Economic analyzer (APEA). The internal software data (total capital cost and production cost) were used as is, while external data were employed for the rough estimation (RSO, biodiesel, and glycerol price). The estimated yearly expanse and revenue are presented in Table 8.

Table 8. Economic analysis result of biodiesel production from RSO.

Parameter	Value
RSO Price (USD/ton)	550
Biodiesel Price (USD/ton)	2000
Glycerol price (USD/ton)	2100
Biodiesel production capacity (TPY)	8000
Glycerol production (TPY)	750
Total capital cost (million USD)	5.50
Production cost (million USD/year)	1.80
Raw materials cost (million USD/year)	4.24
Biodiesel revenue (million USD/year)	16
Glycerol revenue (million USD/year)	1.6

From the data summarized in Table 8, with additional assumptions of 11% interest rate (i) and eight years project time (t), the payback period (PBP), rate of return on investment (ROROI) and internal rate of return (IRR) can be calculated using Equations (4)–(6), respectively. The projected net present value (NPV) of biodiesel production from RSO is shown in Figure 8. The calculation results show that the biodiesel production from RSO is promising with excellent investment criteria, as summarized in Table 9.

$$\text{PBP} = \frac{\text{Initial Investment} - \text{Opening Cumulative Cash Flow}}{\text{Closing Cumulative Cash Flow} - \text{Opening Cumulative Cash Flow}} \tag{4}$$

$$\text{ROROI} = \frac{\text{Average net annual profit}}{\text{Fixed Capital Investment}} \tag{5}$$

$$\text{IRR} = \text{i}_\text{a} + \frac{\text{NPV}_\text{a}}{\text{NPV}_\text{a} - \text{NPV}_\text{b}}(\text{i}_\text{b} - \text{i}_\text{a}) \tag{6}$$

where:

i_a = lower discount rate chosen

i_b = higher discount rate chosen
NPV_a = Net Present Value at i_a
NPV_b = Net Present Value at i_b

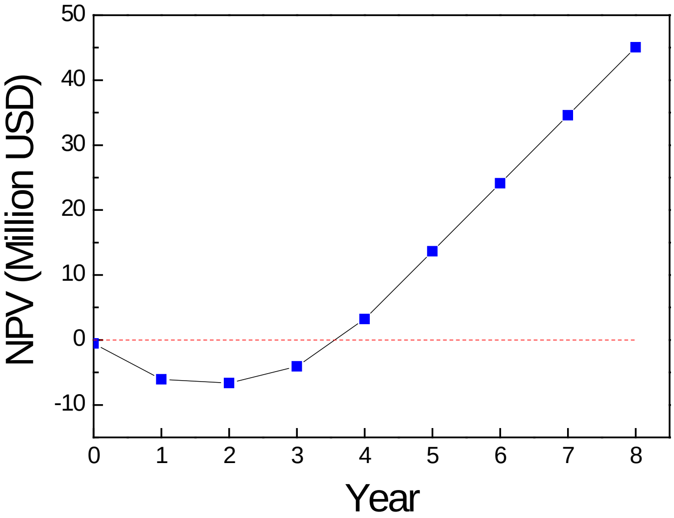

Figure 8. Projected net present value (NPV) of biodiesel production from RSO.

Table 9. Summary of investment criteria of biodiesel production from RSO.

Parameter	Value
PBP	1.60 years
ROROI	144%
IRR	28%

Sensitivity analysis was carried out to determine the influence of production variables on gross profit, including the selling price of biodiesel and production capacity. The sensitivity limits for the input variables are set at −50 and +50% from the base case. The sensitivity analysis results are shown in Figure 9. The production capacity has steep gradient compared to biodiesel production price. It can be concluded that the production capacity has a greater impact on gross profit rather than the biodiesel price.

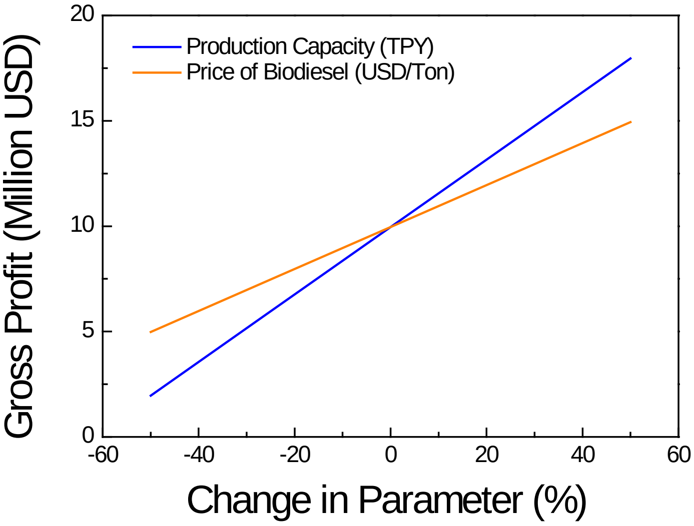

Figure 9. Sensitivity analysis of gross profit for biodiesel production from RSO.

4. Conclusions

Vegetable oil conversion to biodiesel via transesterification is well known and considered a globally acknowledged technology in the biodiesel industry. However, when the utilized feedstocks (oils or fats) have high FFA or water content, the alkali catalyst and FFA are likely to react, resulting in soap formation, which may significantly lower the biodiesel yield. Hence, acid-based catalyzed esterification was implemented in this study to eliminate this drawback. The yield of biodiesel is greatly affected by the alcohol to oil molar ratio, reaction temperature, FFA content, catalyst type, catalyst concentration, and reaction time.

Referring to our simulation results, 1.04 L biodiesel (99.93%) and 680 mL glycerol will be produced per liter of RSO consumed with a methanol to oil molar ratio of 1:6. The excess methanol was recovered using flash and multi-stage distillations. In the methanol recovery process, approximately 95% of excess methanol was regenerated. Simulation results compared with experimental data indicated that biodiesel produced could be used in modern diesel engines. Economic analysis performed in this study also indicated that this technique is promising, with excellent investment criteria.

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