Feasibility Study of Using Waste Cooking Oil and Byproduct from Palm Oil Refinery for Green Diesel Production

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A bio-hydrogenated diesel (BHD) becomes more attractive fuel due to its use without engine modification and high heating value. This work aims to evaluate the possibility of using low-grade, potential resources, i.e., waste cooking oil and palm fatty acid distillate (PFAD), which is a byproduct from palm oil refinery, to produce BHD. A systematic methodology through a thermodynamic insight is applied to designing the BHD production process. Two alternatives in waste cooking oil processing are considered; the first one (A1) involves the esterification process coupled with a hydrotreating process and the second one (A2) concerns about the direct hydrotreating process. The production of BHD from PFAD (B) is based on the hydrotreating process. Modeling of the BHD processes is performed using Aspen Plus simulator. All the proposed processes are designed with the BHD specification of 99.5% purity. Regarding the economic analysis, the use of PFAD for the BHD production offers more benefit than that of waste cooking oil in terms of net present value, return on investment and payback year.

1. Introduction

Global energy demand for household and transportation over the past decades increases the use of conventional fuels such as coal, fossil fuels and natural gas. The use of these petroleum-based fuels leads to the release of gaseous pollutant, such as NO_x, CO_2, and SO_2, from excessive combustion, which affects climate change and global warming. Due to environmental concerns, the development of technologies for producing renewable fuels has played an important role.

Palm oil is considered the alternative renewable feedstock that can be converted into green fuels like biodiesel, which is used as a fuel (i.e., B10 and B100) in diesel engines. Although biodiesel has been widely used as alternative energy, a bio-hydrogenated diesel (BHD) becomes more attractive fuel due to its use without engine modification and high heating value. As a result, many researchers have developed technology and searched for alternative resources for BHD production (Razak et al., 2017). In general, BHD can be produced from all vegetable oils and free fatty acids via catalytic reactions, including hydrodeoxygenation, decarboxylation and decarbonylation. To design a processing system, the effect of process variables and reaction schemes are investigated to achieve a high yield and purity of BHD. However, the current process design needs high energy usage and requires high purity of raw materials. Multiple components in vegetable oils and many reaction pathways in the BHD production lead to undesired products. Although the use of waste vegetable oil for BHD production has been less studied, Glisic et al. (2016) showed that this process could compete with the alkali-catalyzed biodiesel production process in term of economic consideration. To date, a few works concerned about the process development for BHD production using waste cooking oil and palm fatty acid distillate (PFAD), the byproduct from palm oil refineries. As a result, this work focuses on the feasibility study of using low-grade resources for bio-hydrogenated diesel production process. The BHD process is designed using a thermodynamic insight to improve the process efficiency.

2. Methodology

2.1 Design methodology

The design of the BHD process is proposed based on a systematic methodology through a thermodynamic insight. All physical properties, thermodynamic properties, types of catalysts and production yield are considered. Pseudo-components, such as triglycerides, diglycerides, monoglycerides and fatty acids, are generated. The missing properties, i.e., vapor pressure, boiling point and heat of vaporization, are predicted using NRTL as a fluid package. Then, all possible processes are screened through major criterions such as conversion, contamination of feedstocks and stability of catalysts. The sequence of unit operations, such as reactors, flash separators and distillations, is ordered according to key components and their properties. For example, the key component of the distillation is based on the type of fuels (i.e., C13-C15 of jet fuel and C16-C18 of diesel). The number of stages and reflux ratios are determined from driving force of key components (Bek-Pederson and Gani, 2004). Finally, a rigorous simulation is performed using Aspen Plus and the feasible process is determined in term of economic availability.

2.2 Process design of the hydrogenated diesel production process

From the design methodology, the stability of the catalyst needs to be concerned because it reduces the production yield. Thus, the first step is to gather information of operating parameters and reaction time to limit coke formation. The reaction time should be lower than 7 h due to the stability of catalyst (Zhang et al., 2017). CO generation also degrades catalyst via coke formation. The production yield of bio-hydrogenated diesel (BHD) is required because the RSTOIC reactor model in Aspen Plus is used as a hydrotreating reactor. The second step is to propose three possible hydrogenated diesel production processes from waste cooking oil and PFAD. Waste cooking oil contains 84.7% of triglyceride, and 15.2% of free fatty acid. While PFAD contains 87% of free fatty acid, 4.5% of triglyceride, 3.7% of diglyceride, 2.6% of monoglyceride and 1% of water. The process operating conditions are obtained from literature. It is found that the esterification process coupled with hydrotreating process using waste cooking oil (A1) gives the lowest yield of BHD of 44.8 %, whereas the direct hydrotreating process of waste cooking oil (A2) and the hydrogenated diesel process from PFAD (B) give the BHD yield of 75 % and 76.90 %, respectively. For the process A1, the product from the esterification process such as unsaturated fatty acids, unsaturated triglycerides and unsaturated methyl esters have to be converted to saturated fatty acids, saturated triglycerides and saturated methyl esters before they go through the hydrotreating process. These effect causes low yield of BHD. Next, the separation techniques of each task in the designed process is listed, as shown in Table 1.

Table 1: List of the feasible separation techniques

| Tasks	Properties	Separation techniques	Binary ratio
Esterification			
Methanol/water	Vapor pressure	Distillation	5.12
Fatty acid/methyl esters	Vapor pressure	Distillation	10.80
Fatty acid/glycerol	Solubility	LL extraction	1.85
Hydrogenated diesel production			
H_2, CO, CO_2, C_3H_8/water	Vapor pressure	Flash separator	7.72×10^{17}
Water/C13	Vapor pressure	Distillation	376.24
C13/C16	Vapor pressure	Distillation	196.47
C16/fatty acid	Vapor pressure	Distillation	371.80
C16/methyl oleate	Vapor pressure	Distillation	345.00

The properties of the adjacent binary ratio of the components are computed. Table 1 shows the suitable separation techniques relating to the properties giving the highest binary ratio. Figure 1(a) shows the flowsheet of the process A1. Waste cooking oil is reacted with methanol in an esterification reactor using H_2SO_4 as a catalyst. The products are sent to the 5 stages distillation unit for methanol recovery. Then, the decanter is used to separate glycerol. The 5 stages and 20 stages distillation trains are required for the purification of methyl esters (99.65%), which is used as a raw material in the hydrotreating process. Hydrogen is sent to the hydrotreating reactor using NiMo as a catalyst (Yang et al., 2012). The reactor is operated at the H_2/methyl ester flow rate of 300 Nm^3/m^3, temperature of 340 ^oC and pressure of 40 bar. The effluent stream from the reactor is sent to the flash separator to remove excess hydrogen and recycle it back to the reactor. The liquid stream is sent to the distillation with a partial condenser to separate excess gaseous product and water. Then, alkane with a carbon range of C16-C18 is purified (99.5%). Figure 1(b) shows the flowsheet of the direct hydrotreating process of waste cooking oil (process A2). Waste cooking oil and hydrogen are sent to

the two hydrotreating reactors in series with the H_2/oil flow rate of 600 Nm^3/m^3, temperature of 340 ^{o}C and pressure of 40 bar. The liquid stream enters the first distillation column for water removal and then, the second distillation column for the purification of the BHD (99.5%). Figure 1(c) shows the diagram of the direct hydrotreating process of PFAD (process B). The process conditions used is according to the work by Kantama et al. (2015). The PFAD and hydrogen are reacted in the hydrotreating reactor and excess hydrogen is removed using the flash separator. The liquid products are then separated by using the distillations with the partial condenser. The jet fuel (C13-C15) and BHD is separated at the top of the second and third distillation columns, respectively.
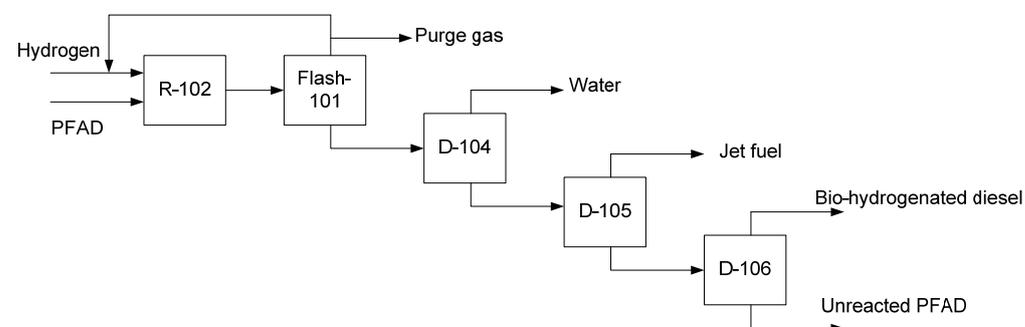
(a)
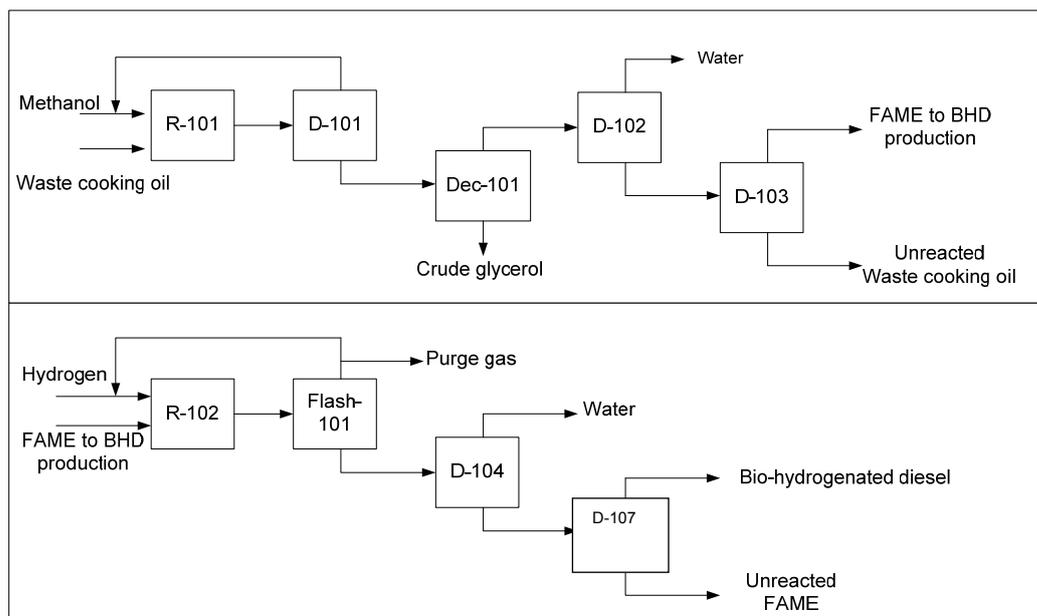
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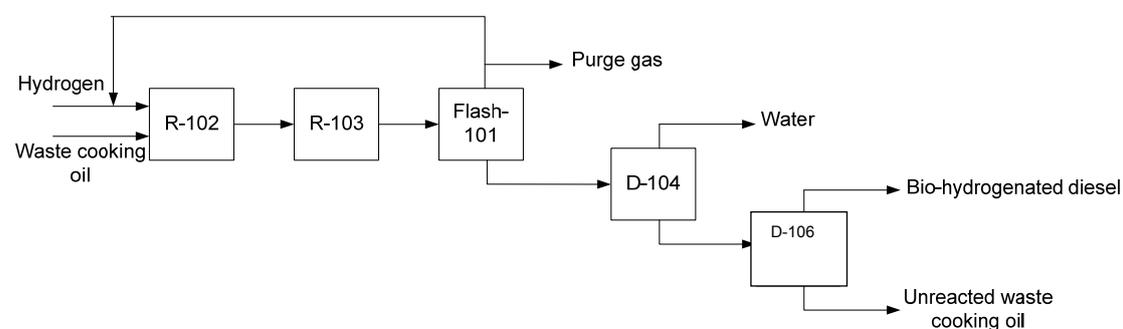
(c)

Figure 1: (a) Esterification and hydrotreating process using waste cooking oil (Process A1), (b) Direct hydrotreating process using waste cooking oil (Process A2) and (c) direct hydrotreating process using PFAD (Process B)

3. Results and discussions

3.1 Distillation design

Design of BHD process mentioned in the previous section includes separation units such as flash separators and distillation columns. Thus, the sequence of these separation units is arranged based on types of the products (i.e., BHD with a carbon range of C16-C18 and jet fuel with a carbon range of C13-C15). The next step of the methodology is to generate the driving force diagram of key components considering a vapor-liquid equilibrium. The minimum reflux ratio and the number of distillation stages are determined from the driving force diagram. The slope of the driving force diagram can be used to predict the minimum reflux ratio. The feed stage is located at the middle of the column. For example, Figure 2(a) shows the driving force diagram of water and C13. Due to the high driving force of 0.97, the number distillation stages of three is required. As a result, the actual reflux ratio is lower than the predicted of 0.4. The simulation shows that the distillation column can separate water from C13. Thus the overhead stream contains water and low gaseous products such as CO_2. This is because the flash separator (Flash-101) does not perform a good separation. Figure 2(b) shows the effect of the number of stages on the driving force of the distillation (D-104). The optimal number of stages is three. Regarding the distillation for separation of jet fuel and BHD in the process B (D-105), C13 and C16 are selected to generate the vapor–liquid equilibrium and driving force diagram, as they represent the main component of jet fuel and BHD, respectively. Figure 3(a) shows the driving force diagram located at 0.358, lower than the binary ratio of water/C13. The minimum reflux ratio is 0.7. Therefore, the number of distillation stages and energy consumption are high to vaporize C13 at the top of the column. The distillation column can provide the jet fuel with 95 wt.% while the remaining hydrocarbon compounds at the bottom of the column is obtained. The optimal number of stages of distillation (D-105) is 24, giving the largest driving force and the lowest energy consumption as shown in Figure 3(b). To obtain the high purity of BHD, the distillation is required to eliminate unreacted raw materials for all the processes. For example, the distillation column (D-107) separates methyl oleate from BHD. Thus, the driving force diagram between C16/methyl oleate is generated as shown in Figure 4(a). There are multi-components in BHD and thus, C16 is used to represent the main component. The binary ratio of C16/methyl oleate vapor pressure is 345 while the binary ratio of boiling point is approximately 1. Hence, the number of distillation stages of 27 can purify the BHD with 99.5% purity. It offers the highest driving as shown in Figure 4(b). The amount of BHD and purity is increased with an increase in reflux ratio. Thus, a reflux ratio of three is an optimal value at the highest driving force. In process B and process A2, the distillation for purification of BHD (D-106) is required. Because the VLE curve of C16/oleic acid is narrow, the largest driving force of C16/oleic acid has low value, compared with other mixtures as shown in Figure 5(a). In addition, the binary ratio of the boiling point of oleic acid/C16 is 1.3. Figure 5(b) presents the optimal distillation stage of 26 for the column D-106 at the highest driving force that offers a high purity of BHD (99.5%).
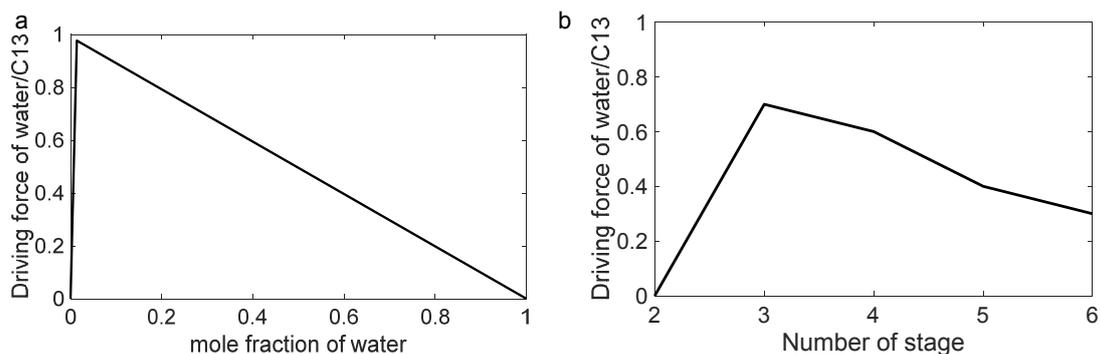

Figure 2: (a) Driving force diagram and (b) Effect of the number of stages on the driving force of water and C13
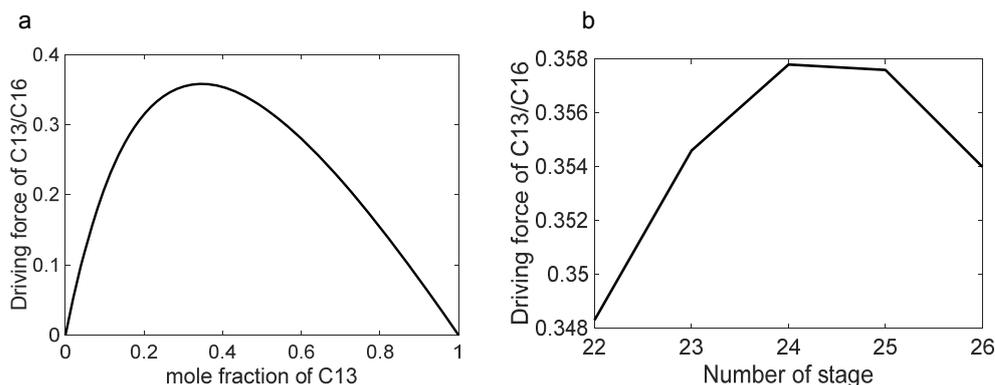
Figure 3: (a) Driving force diagram and (b) Effect of the number of stages on the driving force of C13 and C16
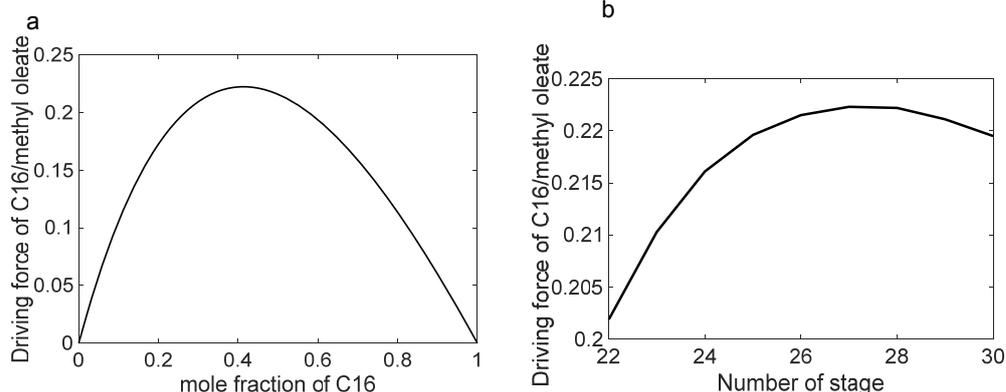

Figure 4: (a) Driving force diagram and (b) Effect of the number of stages on the driving force of C16/methyl oleate
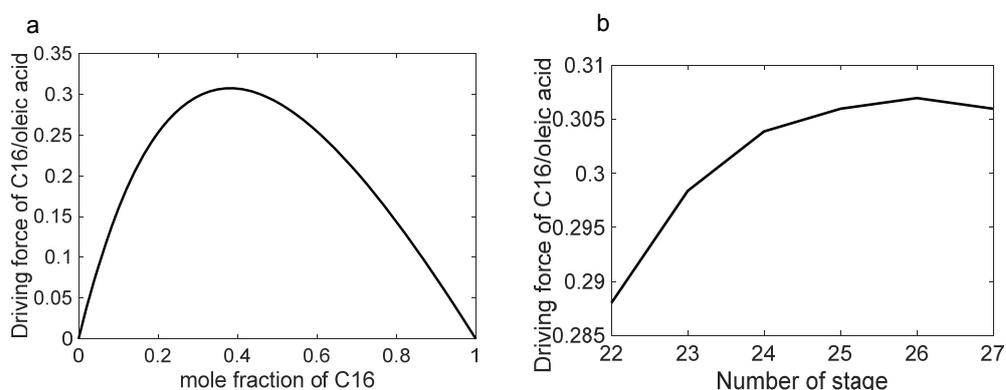

Figure 5: (a) Driving force diagram and (b) Effect of the number of stages on the driving force of C16/oleic acid

3.2 Economic assessment

The economic consideration is a final decision to choose feasible processes. The major investment cost involves equipment costs and installation costs that depend on equipment size. As a result, the process A1 and A2 have high investment cost. In addition, high recirculation stream of H_2 and other gaseous product, such as propane, is required and thus, high energy consumption is needed, causing the large size of the compressor and flash separators. The large distillation columns in process A1 and A2 is determined to remove unreacted feedstock such as free fatty acids and triglycerides. The compressor for pumping H_2 to the hydrotreating section in process A1 and A2 is higher energy consumption than process B. The breakdown of the production cost presents that the raw material costs have played an important role, dominating 80-87% of the production cost, as shown in Figure 6. Raw material costs of process A1 and process A2 is higher than the process B due to H_2 and methanol, respectively. The hot utility cost of the process B is the lowest due to the fact that the energy intensity per kilogram feed of the process A1, A2 and B are 187 Btu/kg, 124 Btu/kg and 443 Btu/kg, respectively. Furthermore, the utility cost of cooling of the process B is lower than other processes. This is because high energy consumes for cooling the product from the hydrotreating reactor and the BHD. Therefore, process B show the lowest production costs. The economic indicators, such as net

present value (NPV), return on investment (ROI) and payback period, are analyzed to show the economic availability under the assumptions: the project year of 10 years and the income cash flow derived from selling BHD of 1.1 $/kg. Table 3 shows the economic indicators of BHD production processes. Because the yield of BHD of the process A1 is lost during the esterification process, the hydrogenation of unsaturated fatty acid and high energy utilization, this process gives the negative ROI and NPV. The investment on process A2 and process B can offer the benefit in term of payback year. Thus, PFAD using as raw material is preferred to the BHD production.
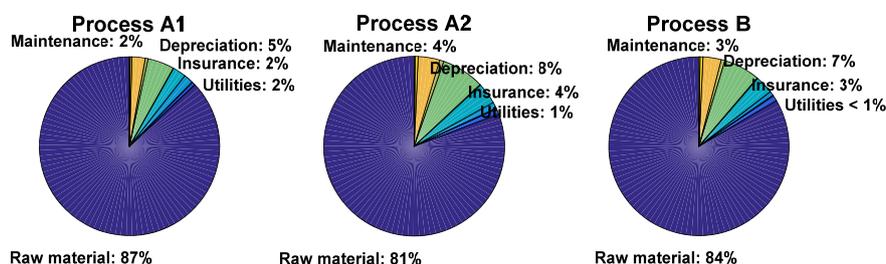

Figure 6: Total production cost of process A1, process A2, process B

Table 3: Economic indicators of BHD processes

Economic indicators	Process A1	Process A2	Process B
Total production cost (x10^7 $/year)	12.3	7.69	7.51
ROI	-1.14	0.18	0.22
NPV (x10^8 $/year)	-8.8	0.635	0.762
Payback year	N.A.	5.47	4.51

4. Conclusions

The feasibility analysis of the bio-hydrogenated diesel (BHD) production from waste cooking oil and palm fatty acid distillate (PFAD), a byproduct from palm oil refinery, was performed. The arrangement of unit operations and the optimal configuration of the distillation columns were determined by considering a thermodynamic insight. The economic indicators of the BHD processes were analyzed based on the net present value, return of investment and payback year. The results showed that a type of raw materials was the important factor. A possibility of using waste cooking oil and PFAD as feedstock for BHD production was done through the direct hydrotreating process. The use of PFAD feedstock is preferred because the process required less unit operations and gave the best payback year.

Acknowledgements

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