Esterification of Non-edible Oil Mixture in Reactive Distillation Column over Solid Acid Catalyst: Experimental and Simulation Study

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ABSTRACT: *Biodiesel is one of the promising energy alternatives to fossil fuel. Among the economical feedstocks of biodiesel is high free fatty acid (FFA) vegetable oil. Production of biodiesel from high FFA oils needs esterification reaction as the pre-treatment step. In this work, esterification reaction of high FFA non-edible oil mixture (used cooking oil, jatropha oil, and nyamplung seed oil) was conducted in reactive distillation (RD) column in the presence of solid acid tin(II) chloride catalyst. RD has potential to be applied at industrial scale. For this purpose, an accurate model is required to scale up the process, predict the RD performance and optimise the process. Experimental work, simulation study and validation were carried out in this work to determine the accurate model and simulation. In experimental work, esterification reaction was conducted by varying the reaction temperature and catalyst concentration. The simulation was performed using ASPEN PLUS V8.8 and validated with the experimental data. Based on the experiment, the optimum FFA conversion was 78.33%, obtained at temperature of 60°C and catalyst concentration of 5% (w/w). The FFA conversion achieved from the simulation was 75.8%. The proximity between the simulation and experimental data demonstrated that this simulation has accurately predicted the conversion of FFA with less than 5% error.*

Keywords: Biodiesel, multiple oil feedstocks, tin(II) chloride, reactive distillation, validation

1.   INTRODUCTION

Nowadays, fuel demand has increased in accordance with the increase of public need for transportation, industries, power plant, household and many other activities. The increasing fuel demand is not in line with the energy sources availability. Based on data, fuel oil consumption in Indonesia has exceeded its domestic production and petroleum resources are expected to be available until the next 10–15 years from now.[1] Due to the depleting fossil fuel reserves, the development of renewable energy resources is important. Renewable energy is generated from renewable resources and can be constantly replenished, such as sunlight, wind, geothermal and various forms of biomass (biofuel), etc. One of the promising biofuels is biodiesel, which can be applied as diesel-engine fuel. Biodiesel exhibits various advantages. For instance, it is clean, environmentally friendly, holds excellent fuel properties, and can be utilised in the diesel engine without any modification of the machine.[2]

Biodiesel is derived from vegetable oils or animal fats through chemical modification. The main compounds of vegetable oils and animal fats are triglycerides and free fatty acids (FFA). Biodiesel is produced through a chemical process by converting vegetable oils/animal fats into fatty acid methyl esters (FAME).[3] In general, FAME (biodiesel) can be synthesised via two distinctive routes, i.e., (1) one-step process of alkaline-catalysed transesterification reaction of low FFA vegetable oils/fats using short-chain alcohols; or (2) two-step process of acid-catalysed esterification of high FFA vegetable oils/fats using short-chain alcohols followed by transesterification of triglycerides of the oils/fats.[4] Esterification reaction is a pre-treatment to reduce the FFA content by converting it into FAME.

High FFA vegetable oils are cheap and non-edible. Hence, they are hardly ever employed for food production. Utilisation of high FFA non-edible oils for biodiesel production is beneficial since it can avoid the crops competition between energy and food needs. There are several studies of biodiesel synthesis using non-edible oils, such as jatropha oils, rubber seed oils, used cooking oils, *nyamplung* (*Calophyllum inophyllum* L.) seed oils, palm fatty acid distillate, etc.[3–8] However, the current studies of biodiesel production are predominated by the application of a single type of oil feed-stocks. For the purpose of feedstock diversification, study on the employment of multiple oil feed-stocks for biodiesel production is essential, thus it should be further investigated.

In this study, a mixture of three different oils were used as a feedstock in biodiesel production. The three oil sources used were cooking oil, jatropha oil and *nyamplung* seed oil, which contain high FFA. Used cooking oil might harm the environment if

it is not properly managed. One of the solutions is by processing it into biodiesel. On the other hand, jatropha and *nyamplung* seed oils are among the high FFA non-edible oils which are potential as biodiesel feedstocks.[3,7]

Biodiesel production is challenging since the process usually involves a reactor followed by a series of separation equipment, which contributes to the complexity and expensive cost of biodiesel production. This challenge can be overcome by the application of multi-functional reactors such as reactive distillation (RD).[4] RD integrates reaction and separation (distillation) in a single column. Thus, it offers many advantages compared with the reactor-separator in terms of the increase in selectivity and conversion, better heat control, reduction of the catalyst consumption, azeotrope avoiding, the effectiveness of heat integration for energy conservation, and lower capital cost due to the reduction of distillation columns as separation unit. Moreover, RD is suitable for reversible reaction such as esterification process since continuous product separation on RD will shift the reaction equilibrium towards product formation.[9]

In this study, RD was used for conducting esterification reaction of high FFA vegetable oil mixture as the pre-treatment step of biodiesel production. Esterification reaction was performed using methanol in the presence of tin(II) chloride solid catalyst. RD is potential for industrial-scale application. However, to scale up the process, predict the RD performance, and optimise the process at large scale operation, an accurate simulation is needed. Hence, this work will focus on the investigation of the accurate simulation of RD process. The investigation involved experimental work, simulation study and validation. In the experimental work, effects of reaction temperature and catalyst concentration were studied on the FFA conversion. Subsequently, a simulation study was carried out based on the equilibrium model (MESH) using ASPEN PLUS V8.8.[4] Several kinetic parameters used in the simulation were obtained from previous study performed by Kusumaningtyas.[10] The process simulation was then validated using the FFA conversion obtained in the experiment. Validation is important since the proximity between the simulation result and the experimental data would indicate that the model and simulation can be applied for the prediction of RD performance at the larger (industrial) scale of process.

2.   EXPERIMENTAL

2.1   Materials

The feedstock used in this study is a mixture of non-edible oil which consists of jatropha oil, *nyamplung* seed oil and used cooking oil. Used cooking oil was collected from home industry Roti Goreng Anggita in Sruweng, Kebumen, Jawa Tengah, Indonesia with FFA content of 15.05%. Crude jatropha oil with FFA content of 30.57% was obtained from PT Jatropha Green Energy, Kudus, Jawa Tengah, Indonesia. *Nyamplung* seed oil with FFA content of 26.37% was obtained from Koperasi Jarak Lestari, Cilacap, Jawa Tengah, Indonesia. Methanol (99 %v/v) and solid acid catalyst tin(II) chloride with purity of 99% were obtained from Merck.

2.2   Esterification Reaction

The apparatus employed for the experiments was composed of the main RD column and the pre-mixer tank combined with pre-heater. The RD column was a Raschig ring packed column equipped with an electrical heating mantle. A condenser and reboiler were placed on the top and bottom of the column, respectively. Esterification reaction of non-edible oil mixture was performed in this RD and the schematic drawing of the equipment is shown in Figure 1.

Non-edible oil mixture which consists of used cooking oil, jatropha oil and *nyamplung* seed oil with a ratio of 1:1:1 (v/v) was reacted with methanol. Oil to methanol molar ratio in this study was 1:60. Previously, tin(II) chloride with certain concentration was diluted in methanol. Oil mixture and catalyst-methanol solution were then preheated and pre-mixed before entering RD column. In this study, esterification reactions were conducted at 40°C, 50°C and 60°C. Tin(II) chloride concentrations were varied at 1%, 3%, 5%, 7% and 9% (w/w) of oil. The product was then collected continuously at the bottom of RD for further analysis.
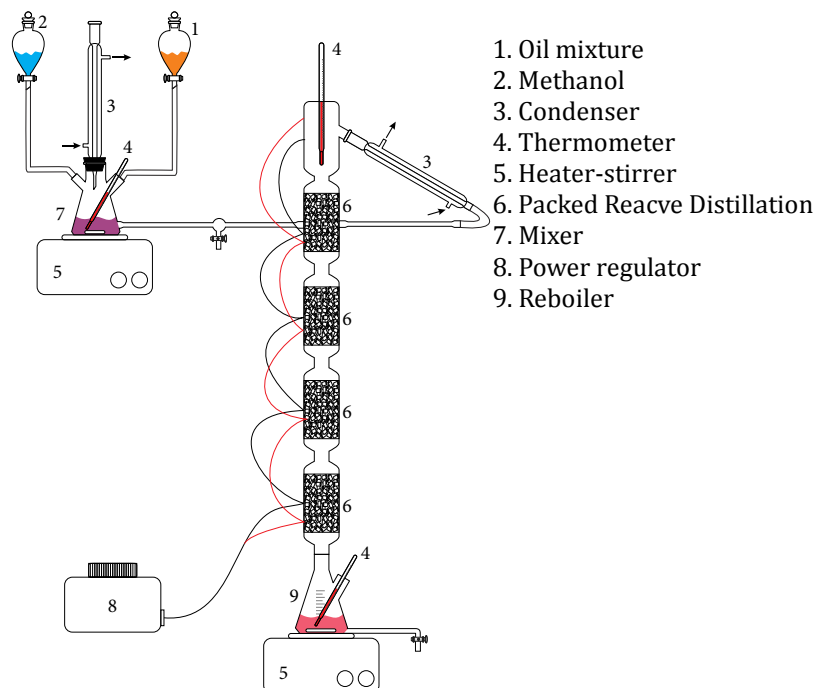
1. Oil mixture
2. Methanol
3. Condenser
4. Thermometer
5. Heater-stirrer
6. Packed Reacve Distillation
7. Mixer
8. Power regulator
9. Reboiler

Figure 1: Reactive distillation apparatus.

2.3   Analytical Procedure

Reaction conversions were estimated from FFA content by KOH titration.[8,9] The sample was first diluted using ethanol 99.9%. Subsequently, it was titrated using KOH 0.1 M. Acidity was calculated by using the following calculation:

$$a = \frac{v_{titration.}Mr\ FFA.\ M\ KOH}{m\ sample.1000} \tag{1}$$

where a = activity index, $v_{titration}$ = titrant volume (ml), $Mr\ FFA$ = molecular weight of free fatty acid, $M\ KOH$ = KOH concentration (ml l^{-1}), and m_{sample} = mass of the sample (g).

The conversion was then calculated using Equation 2:

$$X_A = \frac{a_i - a_t}{a_i} \times 100\% \tag{2}$$

where X_A = FFA conversion, a_i = initial acidity index, and a_t = acidity index at t time.

2.4   Simulation Setup

RD simulation was carried out using a chemical process simulator (ASPEN Plus V 8.8). The RADFRAC steady-state model was used for the RD column. RADFRAC is a rigorous equilibrium stage model which is able to solve the set of equations that describe each equilibrium stage: material balances, phase equilibrium relationship between the vapour and the liquid leaving the stage, summation equation and heat balance. The phase equilibrium was described by assuming the vapour phase as ideal gas and the liquid phase as real solution, on the basis of the UNIQUAC model as it was suggested by Bhatia et al.[11]

Esterification reaction between fatty acid and methanol can be represented as:

$$RCOOH + CH_3OH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} RCOOCH_3 + H_2O \tag{3}$$

The reaction rate can be written as:

$$-\frac{dC_A}{dt} = k_1 C_A C_B - k_2 C_C C_D \tag{4}$$

$$k_i = k_{0i} \exp\left(-E_{ai}/RT\right) \tag{5}$$

where C_A = the concentrations of oleic acid (mole l^{-1}), C_B = the concentrations of methanol (mole l^{-1}), C_C = the concentrations of methyl oleate (mole l^{-1}), C_D = the concentrations of water (mole l^{-1}), k_1 = kinetic rate constants for forward reaction (l mole^{-1} min^{-1}), k_2 = kinetic rate constants for backward reaction (l mole^{-1} min^{-1}), k_{0i} = the pre-exponential factor (min^{-1}), and E_{ai} = activation energy for kinetic reaction (kJ mole^{-1}).

The kinetic rate constants in this work were obtained from the experimental study performed by Kusumaningtyas et al. as presented in Table 1.[9] Whereas, the feed inlet composition and parameters for RD simulation are presented in Table 2 and Table 3, respectively.

Table 1: Kinetic and thermodynamic parameters of the reacting system.

Parameter	Value	
k_1	2.33×10^{10}	$l^{-1} mole^{-1} min^{-1}$
Ea_1	64.5	$kJ mole^{-1}$
k_2	4.29×10^8	$l^{-1} mole^{-1} min^{-1}$
Ea_2	40.7	$kJ mole^{-1}$
T boil methanol	64.7	°C

Kusumaningtyas et al.[9]

Table 2: Feed inlet composition for RD simulation.

Component	Input (kmole h^{-1})
Oleic acid	0.0421
Linoleic acid	0.02
Palmitic acid	0.0291
Stearic acid	0.009
Methanol	6.012
Total	6.1122

Table 3: Parameters for the RD simulation.

Parameter	Value
Number of stage	20
Reaction zone	13
Input feed zone	7
Feed temperature	50°C
Total feed	6.112 kmole h^{-1}
Pressure	Atmospheric
Condenser type	Total
Reboiler type	Kettle

3. RESULTS AND DISCUSSION

The experimental work was conducted to study the effects of reaction temperature and catalyst concentration on the FFA conversion. The simulation was then performed based on the equilibrium model (MESH) using ASPEN PLUS V8.8. Simulation result was compared with the experimental data to examine the proximity of the values and validate the simulation.

3.1   Effect of Temperature on FFA Conversion

Effect of reaction temperature on the reaction conversion was studied at temperatures 40°C, 50°C and 60°C. Table 4 shows the effect of reaction temperature to the FFA conversion at different catalyst concentrations. It can be seen that at catalyst concentration of 1%, 3% and 5%, the increasing temperature also increases the FFA conversion. This phenomenon was in accordance with the research carried out by Supardan and Satriana which found that the optimum reaction temperature for esterification process was at 60°C.[12] It also corresponded with the theory of molecule kinetics stating that a temperature increase will raise the molecule kinetics and the effectiveness of molecule collisions. This phenomenon will lead to a faster reaction and increase the conversion.[13] FFA conversions at different temperatures are presented in Table 4.

Table 4: Effect of reaction temperature at different catalyst concentration.

No	Catalyst (w/w)	Conversion (%)		
		at 40°C	at 50°C	at 60°C
1	1%	66.57	70.17	75.14
2	3%	67.86	72.20	77.95
3	5%	69.15	74.72	78.33
4	7%	74.29	69.15	68.12
5	9%	65.59	65.29	61.76

Different trends were exhibited at the catalyst concentrations of 7% and 9%. As the temperature increased, FFA conversion at certain catalyst concentration was decreasing. This is due to a large amount of catalyst used in the esterification process. With a large amount of catalyst, several parts of the catalyst cannot be completely dissolved in the reactant mixture. The insoluble catalyst will become a phase barrier which will prevent mass transfer process and results in the declining FFA conversion. According to Ferreira et al., the optimum condition for esterification reaction of FFA using tin(II) chloride catalyst will be achieved when the mixture of reactants and catalyst is in homogeneous phase.[14]

3.2   Effect of Catalyst Concentration on the FFA Conversion

A slow and reversible reaction such as esterification process needs a catalyst to increase the reaction rate. The larger the amount of catalyst employed in a process, the more active sites available to accelerate the reaction as reported by Srilatha et al.[15,16] In the esterification of FFA by methanol, a large excess of tin(II) chloride

catalyst will cause side reactions between tin(II) chloride with methanol to form alkyl halide which has blackish colour on the product. This reaction also decreases the amount of methanol and will affect the reactants molar ratio. The decreasing amount of methanol also causes slower reaction rate as stated by Ramadhas et al.[5] Figure 2 demonstrates that the optimum FFA conversion is 78.33%, obtained at the reaction temperature of 60°C with the catalyst concentration of 5%.
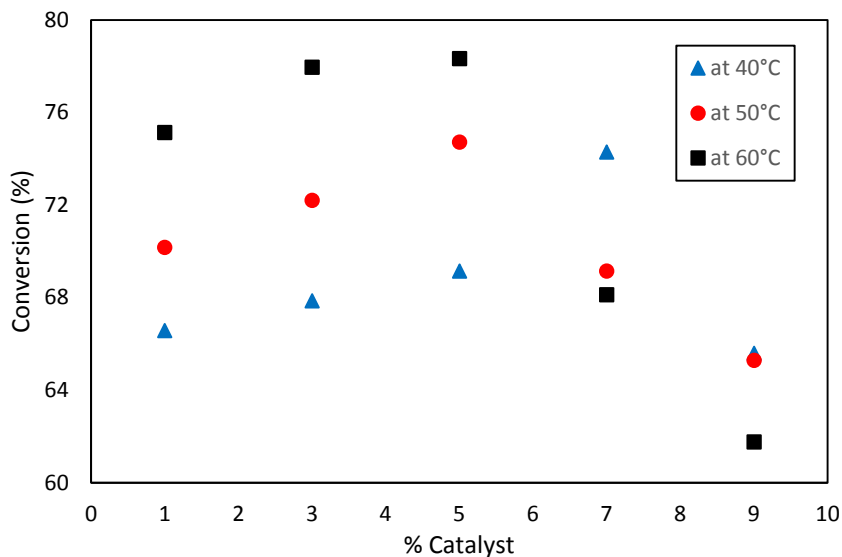

Figure 2: FFA conversion at different catalyst concentrations and reaction temperatures.

3.3   Simulation Results

Simulation of RD for the esterification of mixed non-edible has been conducted in ASPEN PLUS V8.8. Required information to run the simulation is presented in Table 1, 2 and 3. Stream results of the RD simulation are shown in Table 5.

The FFA conversion resulted from the simulation was determined based on the stream data presented in Table 5. It was found that the optimum FFA conversion obtained from the simulation was 75.8%. Compared with the optimum conversion in the experimental study (78.3%), FFA conversion on the simulation has an error of 3.19%. This indicates that result of the simulation was closed to the experimental data, meaning that the model used in this simulation is valid and can accurately predict the conversion of FFA in the esterification of non-edible oil mixture.

Table 5: Feed and product compositions resulted from the RD simulation.

Component	Input (kmole h^{-1})	Output (kmole h^{-1})
Oleic acid	0.0421	0.0101
Linoleic acid	0.02	0.0048
Palmitic acid	0.0291	0.007
Stearic acid	0.009	0.0021
Methanol	6.012	5.9362
Methyl oleate	0	0.0319
Methyl linoleate	0	0.0152
Methyl palmitate	0	0.022
Methyl stearate	0	0.0068

In this study, a sensitivity analysis was also performed to observe the effect of methanol:oil molar ratio to the FFA conversion. Figure 3 shows that the increase of the methanol:oil molar ratio will increase the FFA conversion. This phenomenon was in accordance with the results of research by Gan et al.[13] The research reported that the increase of the mole ratio of methanol to oil would lower the viscosity of the reactants mixture, optimise the process of mixing and mass transfer, so that it will increase the conversion.
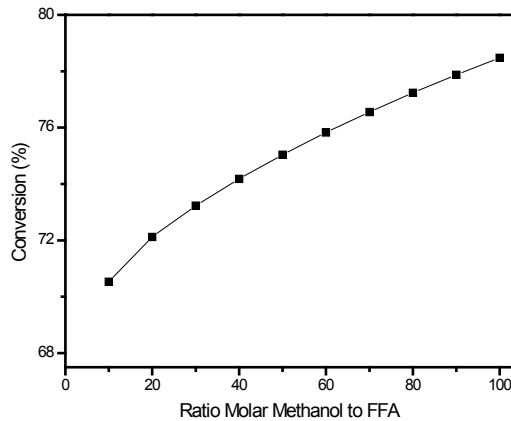

Figure 3: Effect of methanol:oil molar ratio to the FFA conversion.

4.   CONCLUSION

The esterification reaction of FFA by methanol is a slow and reversible reaction. Hence, the addition of catalyst is important to enhance the reaction rate and the application of RD was beneficial to shift the equilibrium to the product formation. To predict the RD performance at large scale operation, an accurate model and simulation is needed. Accurate model and process simulation can be obtained through model validation using experimental data. In this work, the experimental data shows that the optimal FFA conversion of 78.33% was obtained with the addition of catalyst concentration of 5% (w/w) oil and the reaction temperature of 60°C. On the other hand, FFA conversion achieved from simulation study using ASPEN PLUS V8.8 was 75.8%. It can be concluded that the model used in the simulation has accurately predicted the FFA conversion of mixed non-edible oil in reactive distillation. Meanwhile, the results of sensitivity study indicates that the FFA conversion will increase by increasing the methanol:FFA molar ratio.

5.   ACKNOWLEDGEMENTS

6.   REFERENCES

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