A Catalyst Reusability Study in Palm Fatty Acid Distillate and Glycerol Esterification using Multi-Criteria Decision Analysis and Reaction Kinetics Approach

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ABSTRACT As a byproduct of the physical refinement of crude palm oil, palm fatty acid distillate or PFAD has a potential to be transformed into monoglycerides by means of irreversible esterification with glycerol over a cation exchange resin catalyst. Irreversibility of the esterification can be assured by continuous azeotropic removal of water by adding xylene as an entrainer. Because PFAD-glycerol esterification demands high temperatures for fast conversion and high selectivity of monoglycerides, it is necessary to test catalyst reusability performance. In this research, evaluation of catalyst reusability performance was based on five parameters: free fatty acid conversion, the rate of free fatty acid decomposition, the selectivity of monoglycerides, monoglyceride concentration, and the cation exchange capacity of the catalyst. The cation exchange resin used was Tulsion T-42 SM. The evaluation was conducted using the simple multi-attribute rating technique extended to ranking (SMARTER) method. The results showed that the optimum reaction temperature was 180°C. Ultimately, a kinetic study at 180°C was also performed to model the reaction after using similar catalysts for certain times. This kinetic study revealed that the reaction mechanism changed from Langmuir-Hinshelwood to Eley-Rideal after several cycles of catalyst reuse.

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1. INTRODUCTION

Palm fatty acid distillate (PFAD) is a side product of crude palm oil production, which is majorly comprised of free fatty acids (>80%), or FFA (Abdul Kapor et al. 2017). With this composition, PFAD has an economic potential to be transformed into more valuable products such as monoglycerides. The high value of monoglycerides is generated by interesting properties of their chemical structure that consists of an aliphatic lipophilic chain and two replaceable hydroxyl groups in the hydrophilic sides (Wang and Marangoni 2016; Yusoff and Abdullah 2016). The chemical structure of monoglycerides allows the emulsion to be stabilized when monoglyceride is added as a surfactant in a mixture. Furthermore, monoglycerides can also be used as food additives in prepared foods (O'Brien 2009; Lee et al. 2014), and in any other drug products (Rouxhet et al. 2009). For instance, monoglycerides can function as a homogenizing agent to maintain the consistency of processed peanut butter, or function as a thickener in baking.

Monoglycerides can be produced from PFAD through esterification with glycerol, a byproduct of biodiesel production (Chetpattananondh and Tongurai 2008; Chung and Park 2009; Hermida et al. 2011). In this study, the reaction between PFAD and glycerol was catalyzed by the cation exchange resin Tulsion T-42 SM. This is a cation exchange resin of Na⁺ form mainly used in the water treatment process. Although the cation resin is in Na⁺ form, the sodium ion can be exchanged by H⁺ by conditioning with an acid solution to turn the cation resin to be acidic. Given the

insolubility of cation resin, it can be used as a heterogeneous acid catalyst in esterification. This heterogeneous reaction has received attention as it allows catalyst separation in simpler processes (Pouilloux et al. 1999; Özbay et al. 2008). Having said that, one challenge present in the esterification process is catalyst separation that can feasibly be done by filtration (Gee and Fisher 2015).

A cation exchange resin is usually used in water treatment that employs a much milder condition than the one used in this study. As a consequence, the reusability of the catalyst might be an issue that limits its application. Therefore, this study investigated the catalytic performance of the cation exchange resin for successive esterification.

This investigation was conducted through a lab experiment and mathematical modeling. The mathematical model was built based on the suitable reaction mechanism that theoretically depends on the polarity of the reactants in this case. Although PFAD is classified as non-polar, its carboxylic group still provides partial polarity so that PFAD may still attach on the surface of the solid acidic catalyst (Pedneault et al. 2007; Mitran et al. 2013). As a chemical species of alcohol group, glycerol is absolutely polar and can be adsorbed by the acid catalyst (Liu et al. 2012).

Because both reactants could attach to the catalyst surface, the Langmuir-Hinshelwood (LH) model was used to describe the esterification reaction (Kumar et al. 2008; Miao and Shanks 2011; Abidin et al. 2016; Olutoye and Hameed 2016). The rate equations of the glyceride formation, according to the LH model are shown in Equations 1, 2, and 3 (Sudibyo et al. 2017). The meanings of

the corresponding symbols and subscripts in the following equations are explained in Appendix A.

a. Monoglycerides:

$$r_M = k_{r1} \cdot C_P \cdot C_G \cdot \left(\frac{1}{(1 + K_P \cdot C_P + K_G \cdot C_G + K_M \cdot C_M + K_D \cdot C_D + K_T \cdot C_T + K_W \cdot C_W)} \right)^2 \quad (1)$$

b. Diglycerides:

$$r_D = k_{r2} \cdot C_P \cdot C_G \cdot \left(\frac{1}{(1 + K_P \cdot C_P + K_G \cdot C_G + K_M \cdot C_M + K_D \cdot C_D + K_T \cdot C_T + K_W \cdot C_W)} \right)^2 \quad (2)$$

c. Triglycerides:

$$r_T = k_{r3} \cdot C_P \cdot C_G \cdot \left(\frac{1}{(1 + K_P \cdot C_P + K_G \cdot C_G + K_M \cdot C_M + K_D \cdot C_D + K_T \cdot C_T + K_W \cdot C_W)} \right)^2 \quad (3)$$

These equations were subsequently used in the mass balance of the batch experiment. The resulting simultaneous ordinary differential equations (ODEs) of each component in the reaction mixture are shown in Equations 4–9. The ODEs were numerically solved using the *ode15s* solver accompanied by a determination of rate constants by using an optimization solver, namely *fmincon* (interior-point algorithm) in MATLAB 2016b (Sudibyo et al. 2017).

$$\frac{dC_P}{dt} = r_3 + r_5 + r_7 \quad (4)$$

$$\frac{dC_G}{dt} = r_3 \quad (5)$$

$$\frac{dC_M}{dt} = -r_3 + r_5 \quad (6)$$

$$\frac{dC_D}{dt} = r_5 + r_7 \quad (7)$$

$$\frac{dC_T}{dt} = -r_7 \quad (8)$$

$$\frac{dC_A}{dt} = -(r_3 + r_5 + r_7) \quad (9)$$

2. MATERIALS AND METHODS

2.1 Materials

PFAD was obtained from PT. Alkindo Mitrajaya (Indonesia). Glycerol 79 wt.% was obtained from Bratachem (Indonesia), and other chemicals were obtained from Merck (United States): ethanol 96%, xylene, NaOH, H₅IO₆, H₂SO₄ 98%, Na₂SO₄, ethyl ether, n-hexane, chloroform, and methanol. The cation exchange resin Tulsion T-42 SM was supplied by PT. Pupuk Sriwijaya (Indonesia). Chemical standards for analytical routine consisting of monoglycerides, diglycerides, triglycerides, and fatty acids were supplied by Fluka. Quantification of reaction products were by means of thin-layer chromatography (TLC) conducted on an alumina plate (10 cm × 20 cm) using a mobile phase made by mixing ethyl ether, n-hexane, chloroform, and methanol at a volume ratio of 80:2:2, respectively.

2.2 Cation resin preparation

Prior to every use, cation resin was pretreated with acid regeneration using HCl 7% solution for 60 min, followed by air drying to remove the moisture. The cation exchange capacity (CEC) was then measured by submerging in 1N Na₂SO₄ for 2 h, following which the cation resin was separated. The CEC was then measured based on the difference of the 0.1N HCl volume needed to titrate the fresh 1N Na₂SO₄ and to titrate the used 1N Na₂SO₄ solution. The aforementioned procedures (from HCl 7% regeneration) were repeated after 360 min reactions to check the activity of the catalyst.

2.3 Esterification experiment

The esterification was conducted in a 0.5-L round-bottom flask with three necks connected to the refluxing line, a thermometer, and a regulable stirrer (Figure 1). The mass ratio of PFAD and technical grade glycerol was 1.5:1 (by approaching PFAD as linoleic acid) to achieve a molar ratio of 3:1 (Sudibyo et al. 2017). The catalyst amount was 3 wt.% of the reaction mixture. PFAD, xylene, and cation resin were mixed (PFAD mixture) and were heated until the desired temperature. Meanwhile, glycerol was heated until the reacting temperature. Afterward, both the PFAD mixture and glycerol were fed into the reactor, with the timer set for 360 min. Four different reaction temperatures (180°C, 190°C, 200°C, and 210°C) were applied in the experiment. The lowest temperature of 180°C was to support azeotropic water removal from the reaction mixture so that the reaction ran irreversibly (Sudibyo et al. 2017). A sample was taken every 30 min for the first 4 h and every 60 min for the remaining 2 h.

The reusability test of the catalyst was conducted by completing four cycles of the esterification experiment (1 cycle = 6 h of reaction). In every cycle, the analytical routines were performed to the samples taken by following similar sampling times. A certain amount of cation resin was separated to have its cation exchange capacity (CEC) measured.

2.4 Thin-layer chromatography (TLC) analysis

The concentration of the glycerides in the products was quantified using TLC analysis. Samples (0.1 g) were diluted in 10 mL chloroform. The diluted samples were dropped on the determined spot of the activated TLC plate. The TLC plate was developed in a vertical position in the TLC chamber containing a mobile phase solution for 60 min. The developed TLC plate was then scanned using a CA-MAG TLC Scanner 3 to quantify the product composition

FIGURE 1. Apparatus set-up for the esterification experiment.

based on the photo-densitometry. This quantification was performed by previously analyzing (with TLC) the chemical standards with a known concentration (Sudewi et al. 2014).

2.5 Determination of optimum reaction temperature

The reusability test was performed at the optimum reaction temperature. Because there were four criteria to decide the optimum temperature in this study, a multi-criteria decision analysis (MCDA) method was used. The MCDA is the most well-known branch of decision-making, and recently there have been four techniques used most frequently (Kigozi et al. 2014):

- The analytic hierarchy process (AHP).
- Analytic network process (ANP).
- Simple multi-attribute rating technique extended to ranking (SMARTER).
- Case-based reasoning (CBR).

According to Stillwell et al. (1981) and Barfod and Leleur (2014), the simple multi-attribute rating technique

extended to ranking (SMARTER) method has many advantages over the other methods. In the case of this study, AHP and ANP were eliminated due to the need for experts to make the decision. In CBR, problem-solving is conducted according to the judgment of similar past problems and experiences. Therefore, SMARTER was used in this study. In the SMARTER method, the decision is made independently of the options, and the determination of the ratings of each option is based on natural scales (Barron and Barrett 1996). To maintain accuracy of decision-making, the weighting of each criterion, along with the ratings of available options, were conducted with the help of a linear scale value function (Barfod and Leleur 2014).

Criteria weighting can be vague for decision-makers. In SMARTER, expert opinions are often needed for traditional weighting. Fortunately, several methods of numerical weighting have been developed, and this is what makes SMARTER more advantageous. The weighting of criteria can be done by establishing a rank order on the attribute in terms of importance (from worst to best rank). Several surrogate weighting factor formulae based on the ranking have been proposed, namely rank sum, rank reciprocal, and rank order centroid (ROC) (Stillwell et al. 1981). ROC has been proven to be better at weighting based on rank than rank sum and rank reciprocal. The formula of ROC is shown in Equation 10.

$$W_i^{ROC} = \frac{1}{n} \sum_{k=i}^n \frac{1}{k} \quad (10)$$

where i is the i^{th} rank and n is the number of attributes. Afterward, the correlation of the obtained kinetics constants with the cycle of catalyst reuse was verified using Pearson's correlation coefficient (Puth et al. 2014).

FIGURE 2. Free fatty acid conversion profile at the end of four cycles of reactions at the temperatures of 180°C, 190°C, 200°C, and 210°C.

FIGURE 3. Free fatty acid concentration profiles for (a) 180°C and (b) 190°C for each cycle.

FIGURE 4. Free fatty acid concentration profiles for (a) 200°C and (b) 210°C for each cycle.

FIGURE 5. Monoglycerides concentration profile at the end of esterification reaction.

3. RESULTS AND DISCUSSION

The final FFA conversion of all temperatures showed a decreasing trend after four successive esterifications, as shown in Figure 2. The most significant decrease (indicated by the highest slope) was demonstrated by 210°C. Although the 180°C and 190°C reaction temperatures initially showed a lower FFA conversion, successive esterification under these conditions showed a relatively smaller reduction in FFA conversion. In addition to FFA conversion, it was also necessary to assess the rate of FFA conversion, so as to determine the optimum esterification temperature.

Figures 3 and 4 show the rate of FFA conversion of every cycle of four temperatures. At 180°C and 190°C, the slope was relatively the same after being used for four cycles as the curve of each cycle was adjacent. However, a significant reduction of conversion rate started to be seen at 200°C, as reflected in the increasing distance between curves, especially until the 180 minute mark before it reached a plateau afterward. The rate decrease was much worse at 210°C after four cycles of esterification.

Reusing the catalyst also affects the product composition. Figure 5 shows that the concentration of monoglycerides consistently decreased after being used for four cycles. The highest concentration of monoglycerides was achieved by a 200°C reaction between 0.42 and 0.47 mol/L. Based on the ratio of monoglycerides concentration over the sum of diglycerides and triglycerides, the esterification at 190°C resulted in the highest ratio (Figure 6). Although the ratio showed stable values for all reactions according to Figure 6, it seems that 190°C was the optimum reaction temperature due to the highest ratio of monoglycerides over di- and tri-glycerides, the second-highest monoglycerides concentration, and a relatively stable rate of FFA conversion. To statistically verify the conclusion of optimum

TABLE 1. The rate of decrease of parameters related to the reusability performance of the catalyst.

Criteria	Rate of decrease ($\times 10^5$)			
	180°C	190°C	200°C	210°C
Cation exchange capacity (eq/(L.min))	10.74	15.56	30.28	37.04
FFA conversion (%/min)	4.63	2.91	3.82	8.92
Selectivity of monoglycerides production	95.62	1923.22	2140.36	353.15
Highest concentration of monoglycerides achieved (mol/(L.min))	1.05	1.00	2.52	3.79

FIGURE 6. The selectivity of monoglycerides production over the sum of diglycerides and triglycerides production.

reaction temperature, multi-criteria decision analysis was subsequently used.

To explain why a higher reaction temperature could lead to degradation in the performance of the catalyst after reuse for several cycles, the cation exchange capacity was measured after each cycle, and the reaction kinetics was studied. The cation resin experienced the most significant decrease in cation exchange capacity (CEC) after being exposed to 210°C (Figure 7). Tolerable performance degradation was found at 180°C and 190°C reactions, whose exchange capacity showed a declivous negative trend. According to the manufacturer's specifications of Tulsion T-42 SM, it has a tolerable operating temperature of 120–140°C, and therefore higher temperature causes the active sites of the cation resin to decay and retards the reaction.

This study determined the optimum reaction temperature using the SMARTER method. The first step was calculating the average rate of decrease of each criterion in the given time period (Table 1), followed by the weighting factor of each criterion using Equation 10 (Table 2). In this case, the cation exchange capacity was the top priority followed by the FFA conversion, the monoglycerides selectivity, and

TABLE 2. Weighting factor determination of each parameter using ROC.

Rank	Criteria	Weighting factor
1	Cation exchange capacity	0.5208
2	FFA conversion	0.2708
3	Selectivity of monoglycerides production	0.1458
4	Highest concentration of monoglycerides achieved	0.0625
Total		1

TABLE 3. The overall score for each reaction temperature based on the weighted score of each criterion.

No.	Criteria	Weighted score			
		180°C	190°C	200°C	210°C
1	Cation exchange capacity	52.08	42.55	13.39	0.00
2	FFA conversion	19.32	27.08	22.99	0.00
3	Yield of monoglycerides production	14.58	1.55	0.00	12.75
4	Highest concentration of monoglycerides achieved	6.13	6.25	2.83	0.00
Overall score		92.13	77.43	39.20	12.75

FIGURE 7. Profile of the change of cation exchange capacity of the cation resin.

the monoglycerides concentration, since the focus was on the reusability of the catalyst. These values would be the basis in calculating the score and the weighted score of each criterion for each reaction temperature.

The calculation of the weighted score focused on the highest and the lowest value (shown in Table 1) for each criterion (Barron and Barrett 1996). On the linearization, the preference value was selected to be as low as possible, since it was related to the rate of the catalyst's performance degradation so that the gradient and the constant of the linear equation would follow. According to Table 3, the optimum reaction temperature was 180°C, with the highest overall score.

The degradation of the active site in the cation resin significantly influenced the reaction kinetics of PFAD-glycerol esterification. Taking 180°C as the optimum reaction temperature to study the reaction kinetics, the value changes experienced by each reaction rate constant can be interpreted (Table 4). The value of kr_1 decreased, while kr_2 and kr_3 both increased with the increasing cycle of catalyst uses. This indicated that after several cycles, monoglyceride produced by the reaction between glycerol and the fatty acid of PFAD would esterify further to form diglycerides and triglycerides. In other words, the preference of esterification after several cycles tended to produce more diglycerides and triglycerides than monoglycerides.

From the kinetics study, another important interpretation was also derived, related to the reaction mechanism. As the value of K_G increased, this indicated that the catalyst decay causing the affinity of the cation resin to adsorb fatty acid molecules decreased, so that the active site could only adsorb glycerol molecules. The increases of K_M , K_D , and K_T after four cycles also affirmed that the cation resin could no longer adsorb fatty acid molecules that are considered to be partially polar. This result also indicates that

FIGURE 8. Transformation of reaction mechanism from Langmuir-Hinshelwood to Eley-Rideal after several cycles of catalyst reuse in PFAD-glycerol esterification.

the reaction products (the glycerides), which were less polar than glycerol, can be easily desorbed. Additionally, the increase of the K_W value as the catalyst used for a longer period also indicates that after the reaction, the desorption of water as the byproduct of the esterification reaction might be spontaneous. From these changes in the values of K_G and K_W , there was an indication that the reaction mechanism changes from Langmuir-Hinshelwood to Eley-Rideal after prolonged esterification. This possible reaction mechanism change is illustrated in Figure 8.

4. CONCLUSIONS

This study showed that higher reaction temperatures led to a degradation in the performance of the catalyst after several cycles of reuse. The optimum reaction temperature was 180°C, which allowed for complete azeotropic H_2O removal from the reaction mixture as well as maintaining the catalyst activity for a long-time reaction. An inevitable phenomenon for reusing the catalyst for several cycles is the change of the reaction mechanism from Langmuir-Hinshelwood into Eley-Rideal. This change in reaction mechanism is important to note, particularly where equipment design is concerned. Potential equipment designs are suggested to follow the Eley-Rideal mechanism for continuous long-term operation because the Langmuir-Hinshelwood mechanism can only be applied when the catalyst is still fresh. Further investigation is necessary to confirm the technical feasibility of using a cation exchange resin in high-temperature continuous esterification.

TABLE 4. Reaction kinetics constants to determine the possible physical phenomenon existed in the reaction mixture at 180°C.

Constants	First 360'	Second 360'	Third 360'	Fourth 360'	Pearson's correlation coefficient	Correlation
kr_1	6.89	5.24	4.76	4.04	-0.96	Strong
kr_2	0.44	0.66	0.68	0.84	0.96	Strong
kr_3	0.20	0.22	0.26	0.31	0.99	Strong
K_P	2.48	1.37	1.47	1.16	-0.85	Moderate
K_G	23.77	24.55	24.38	24.51	0.73	Moderate
K_W	10.33	10.25	10.23	10.19	-0.96	Strong
K_M	10.32	10.25	10.23	10.19	-0.96	Strong
K_D	5.64	5.50	5.46	5.39	-0.96	Strong
K_T	5.64	5.50	5.46	5.39	-0.96	Strong

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AUTHORS' CONTRIBUTIONS

Conceptualization: R, MF; analysis and investigation: HS, R; data analysis: HS, FS; writing and preparation of the manuscript: HS; funding acquisition: R, MF. All authors have read and agreed to the published version of the manuscript.

COMPETING INTERESTS

The authors have no conflicts of interest to declare.

APPENDIX A

Appendix A. Nomenclature.

Symbols		
kr_1	L/(mol.min)	Rate constant of monoglycerides formation
kr_2	L/(mol.min)	Rate constant of diglycerides formation
kr_3	L/(mol.min)	Rate constant of triglycerides formation
K_i	L/mol	Equilibrium constant for adsorption or desorption of component i
C_i	mol/L ⁻¹	Concentration of species i
Subscripts		
P		Palm fatty acid distillate
G		Glycerol
M		Monoglyceride
W		Water
D		Diglyceride
T		Triglyceride
Abbreviations		
PFAD		Palm fatty acid distillate
FFA		Free fatty acid
CEC		Cation exchange capacity
TLC		Thin-layer chromatography
ROC		Rank order centroid
SMARTER		Simple multi-attribute rating technique extended to ranking
MCDA		Multi-criteria decision analysis

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