



Acceleration of Acid-catalyzed Transesterification Reaction by Minimizing Glycerol to Fatty Acid Methyl Ester Ratio

Watcharin Rattanapong, Kulchanat Prasertsit* and Chakrit Tongurai

Department of Chemical Engineering, Faculty of Engineering, Prince of Songkla University, Songkhla 90110, Thailand

*Author for correspondence; e-mail: kulchanat.k@psu.ac.th

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ABSTRACT

This work aimed to study the acceleration of a slow acid catalyzed transesterification process, retarded by poor blending of two components in a liquid-liquid reaction. Reducing the solution viscosity was achieved by adding fatty acid methyl ester (FAME) into refined palm oil at the beginning of the reaction could improve miscibility and enhance the conversion of triglyceride to FAME. The study also focused on glycerol to FAME ratio on adding FAME. The results show that a lower glycerol to FAME ratio in a conventional reactor increases FAME generation. This can be applied in the two-step transesterification process by maintaining a low glycerol to FAME ratio. To achieve the required ester content of greater than 96.5%, the proposed second step transesterification in a multistage reactor with glycerol removal can reduce the reaction time by up to 91.2% in the second step using heterogeneous acid catalyst, or by 57.5% using acid catalyst in a conventional reactor, respectively.

Keywords: two-phase liquid-liquid reaction, acid-catalyzed transesterification, miscibility, phase separation, glycerol removal

1. INTRODUCTION

On using an acid catalyst for biodiesel conversion, both transesterification and esterification occur simultaneously [1, 2]. There are three second-order consecutive reversible reactions in transesterification. Triglyceride (TG) reacts with alcohol to form diglyceride and ester. Next, diglyceride reacts with alcohol to form monoglyceride and ester; and lastly, monoglyceride reacts with alcohol to form glycerol and ester [3]. Furthermore, some authors have evaluated the same mechanism including fourth- and second-order derivation reactions, and the saponification reaction; whereas others use kinetic models of the first order [4, 5]. In an esterification process, free fatty acids (FFA) in raw oil such as crude

palm oil, waste cooking oil, or waste vegetable oil, react with alcohol to form ester and water [6-8]. Acid catalyzed transesterification of low FFA oil has been studied in the past. Although an advantage of using acid catalyst is that it does not induce soap formation from saponification [9], the reaction is very slow (2 hours) depending on reactants and temperatures [10-12]. Consequently, acid catalyzed transesterification cannot currently be applied in commercial scale.

Moreover, regarding the slow reaction rate on using acid catalyst in transesterification, sulfuric acid in the methanol (MeOH)-rich polar phase cannot blend well with the raw oil non-polar phase because of their different polarities [13-15]. To

accelerate the reaction, mechanical and chemical improvements such as using microwaves, sonication, co-solvent, or supercritical state, are required. In a laboratory scale, acceleration methods using microwaves, sonication, and co-solvent have been studied [16, 17]. These methods can improve the productivity, but microwaves and sonication are not suitable for industrial or commercial scale.

Using co-solvent should be reconsidered. Fatty acid methyl ester (FAME) can be a co-solvent alike Tetrahydrofuran (THF), because the FAME's polarity is between polarities of polar and nonpolar components [18]. FAME co-solvent can assist two-phase miscibility [19] and it is less toxic than THF [20]. Moreover, adding FAME has not induced reversed reaction. Phoopisutthisak et al. showed that transesterification of FAME was not reversible at 60°C. On adding FAME to the reaction, it still moved forward, while adding glycerol caused reversion of reaction direction [21]. Some studies have shown that reaction to produce monoglyceride or triglyceride from

glycerol and FAME occurs at temperatures greater than 150°C [22,23].

The last problem in biodiesel production comes from glycerol. Previous studies have found that glycerol also affects the mixing of the liquid phases. It acts as a barrier preventing catalyst from reaching TG in the MeOH-rich droplets [21, 24]. Therefore, many studies have designed reactors for glycerol removal, such as a diglycerol reactor [25] and reactive distillation [26, 27].

Therefore, the aim of this work was to improve the liquid phase miscibility in acid catalyzed transesterification by blending FAME into low FFA of refined palm oil (RPO). This step focused on the remaining glycerol to FAME ratio. The sulfuric acid distribution to each phase of the reaction was measured. Finally, the study applied a multistage reactor to accelerate acid catalyzed transesterification, comparing it to two-step transesterification in the literature shown in Table 1.

Table 1. Literature data on two-step biodiesel conversion processes.

Raw material oil	Catalyst type Phase/Reaction		Alcohol type	Conditions		Time (h)	Ester content (wt%)	References
	1 st step	2 nd step		1 st step	2 nd step			
Waste vegetable oil	Acid Ho/E	Acid Ho/E	MeOH	10:1 0.41:1 60**	50:1 1.93:1 60**	2	99.50	[1]
Sunflower oil and linseed oil	Alkaline Ho/T	Acid Ho/T	MeOH	10:1 1.15 wt% KOH 60*	15:1 15.9% H ₂ SO ₄ 60*	2	97.00	[25]
RPO	Alkaline Ho/T	Acid He/T	MeOH	5.48:1 0.32%NaOCH ₃ 55*	10:1 12%Amberlyst 15 115*	9.67	98.00	[26]
Waste cooking oil	Alkaline Ho/T	Alkaline Ho/T	MeOH	3:1 0.5%KOH 30*	3:1 0.5%KOH 60*	1	97-98	[27]
Mahua oil	Acid Ho/E	Acid Ho/E	MeOH	14:1 0.3:1 60**	47:1 1.17:1 60**	2	99.20	[28]

*Transesterification conditions: alcohol/oil molar ratio, catalyst (wt%), temperature (°C)

**Esterification conditions: alcohol/FFA, catalyst/FFA ratio, temperature (°C)

Here Ho = Homogeneous phase, He = Heterogeneous phase, E = Esterification reaction, T = Transesterification reaction, EtOH = Ethanol, Time = the overall time required

2. MATERIALS AND METHODS

2.1 Materials

Feed stock RPO (about 0.5 wt% of FFA and 0.2 wt% moisture content) was obtained from Oleen Co., Ltd. (Thailand). A commercial grade FAME (approximately 97.3 wt% purity) was obtained from Specialized R&D Center for Alternative Energy from Palm Oil and Oil Crops, Faculty of Engineering, Prince of Songkla University. Commercial grade methanol (99.8 wt%) was purchased from P-General Co., Ltd. (Thailand). Commercial grade sulfuric acid (98 wt%) was purchased from AGC Chemicals (Thailand) Co., Ltd. Other analytical chemicals and analytical grade ethanediol were obtained from FisherChemical (UK). Analytical grade sodium hydroxide (99.9 wt%), and sodium periodate (99.0 wt%) were ordered from KEMAUS (Australia). All indicators, such as bromothymol blue, methyl orange, and phenolphthalein were ordered from KEMAUS (Australia).

2.2 Methods

2.2.1 Effect of glycerol to FAME ratio in acid catalyzed transesterification

The mixed oil phase with 0, 25, 50, 75, and 95 wt% FAME in RPO and the MeOH-sulfuric acid phase with 1, 5, and 10 wt% sulfuric acid in MeOH were measured for viscosities. The reaction was operated in a 250-mL bottle with the molar ratio of oil to MeOH at 1:10, stirring speed 500 rpm, temperature 60°C, and for 5 minutes reaction time. Then a sample was taken to determine glycerol by titration and TG conversion was estimated for each catalyst concentration.

2.2.2 Phase separation of two-phase liquid-liquid reaction

To ensure that acid catalyzed transesterification was a two-phase liquid-liquid system, and that its solubility was improved, 100 g of mixed oil (mixing FAME in RPO at 0, 25, 50, 75, and 100 wt% FAME in RPO) was blended with MeOH (vary from 38.16, 39.67, and 41.56 g for 1, 5, and 10 wt%

sulfuric acid in MeOH, respectively) in a Duran bottle with magnetic stirring for 5 minutes. After that a sample from each condition was separated into two phases and weight of each phase was measured.

2.2.3 Enhanced rate of acid catalyzed transesterification

A conventional reactor and a multistage reactor with methanol-glycerol removal were compared in terms of glycerol to FAME ratio effects. For the conventional reactor, the initial reactants were started from 50 wt% FAME in RPO and 5 wt% sulfuric acid in MeOH according to the conditions in section 2.3.1. The conventional reactor was run for 30 minutes and a sample was collected every 5 minutes. The products from multistage reactor were sampled every 5 minutes and all polar solution was removed before adding fresh methanol and sulfuric acid to start a new stage until completion in 30 minutes. All samples were phase separated and analyzed for glycerol content and sulfuric acid content by titration methods.

The conditions for the multistage reactor to determine the relation between the initial %FAME in RPO and total FAME content were as follows. The reaction was done in a 1000 mL glass bottle reactor. Glycerol to FAME ratio affected TG conversion. 5 wt% Sulfuric acid in MeOH was added into the mixed oil. The initial mixed oil was at 50 wt% of FAME in RPO, mixed at rotating speed 600 rpm, and reaction temperature was 60°C. After reaction was completed, remaining glycerol was measured by titration. Next the polar phase components were separated and removed in a separation funnel. The amount of FAME was determined. The next stage used the amount of FAME and added MeOH in the same ratio as the previous stage. The reaction was continued in the same pattern until reaching the desired yield. The final product was analyzed by using GC-FID.

The scheme above can be implemented in a two-step transesterification after the reaction reaches some desired point for the first-step

transesterification. Using a model from Thoai et al. shown in Eq. (1) [29] to estimate the reaction time giving ester content of 80% by SOLVER in EXCEL as the starting point and following the steps above until ester content from the reaction reaches 95%.

$$\begin{aligned}
 Y = & -331.56 + 116.51X_1 + 149.21X_2 \\
 & + 0.588X_3 + 1.113X_4 - 10.76X_1^2 - 42.35X_2^2 \\
 & - 0.00969X_3^2 - 0.015964X_4^2 - 7.45X_1X_2 \\
 & + 0.159X_1X_4 - 0.69X_2X_4 + 0.00592X_3X_4
 \end{aligned}
 \quad (1)$$

where x_1 is MeOH/RPO molar ratio, x_2 is CH_3ONa content, x_3 is Reaction time, and x_4 is Temperature.

The proposed experiment was done in a 500 mL three-necked flask with 600 rpm rotating speed. From SOLVER, the required reaction time was estimated as about 21 minutes, with MeOH/RPO molar ratio of 5.24, catalyst content 0.40 wt%, and reaction temperature 60°C.

2.2.4 Analytical methods

Glycerol content was calculated from the total glycerol measured by the titration method (ASTM D7637) [29]. FAME of each condition was determined from the amount of the generated glycerol: one mole of glycerol gives 3 moles of FAME. Only the final FAME product was quantified directly by using Gas Chromatography equipped with flame ionization detector (GC-FID) based on EN 14132 standard [30]. The viscosities of the raw oils were measured by using Ostwald's viscometer based on ASTM D446-12.

3. RESULTS AND DISCUSSION

3.1 Glycerol to FAME Ratio Affected Acid Catalyzed Transesterification

For acid catalyzed transesterification, adding FAME as co-solvent into RPO can decrease viscosity and adding sulfuric acid into MeOH can increase viscosity as shown in Figure 1, because the viscosity of FAME is lower than that of RPO. This clearly boosts the reaction from that without initial FAME added, as shown in Figures 2a and 2b.

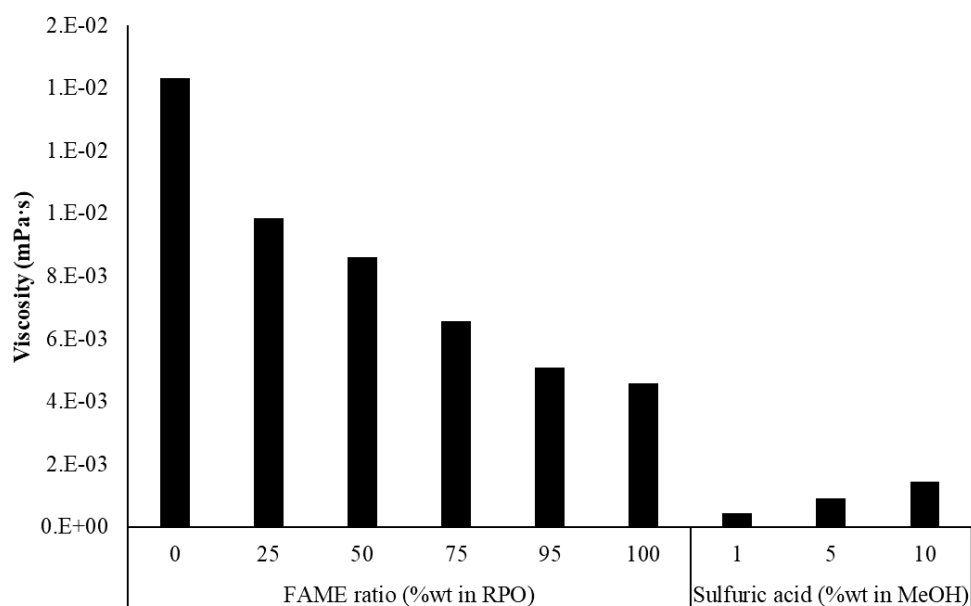


Figure 1. Viscosity of the raw materials; initial FAME ratio and sulfuric acid in MeOH.

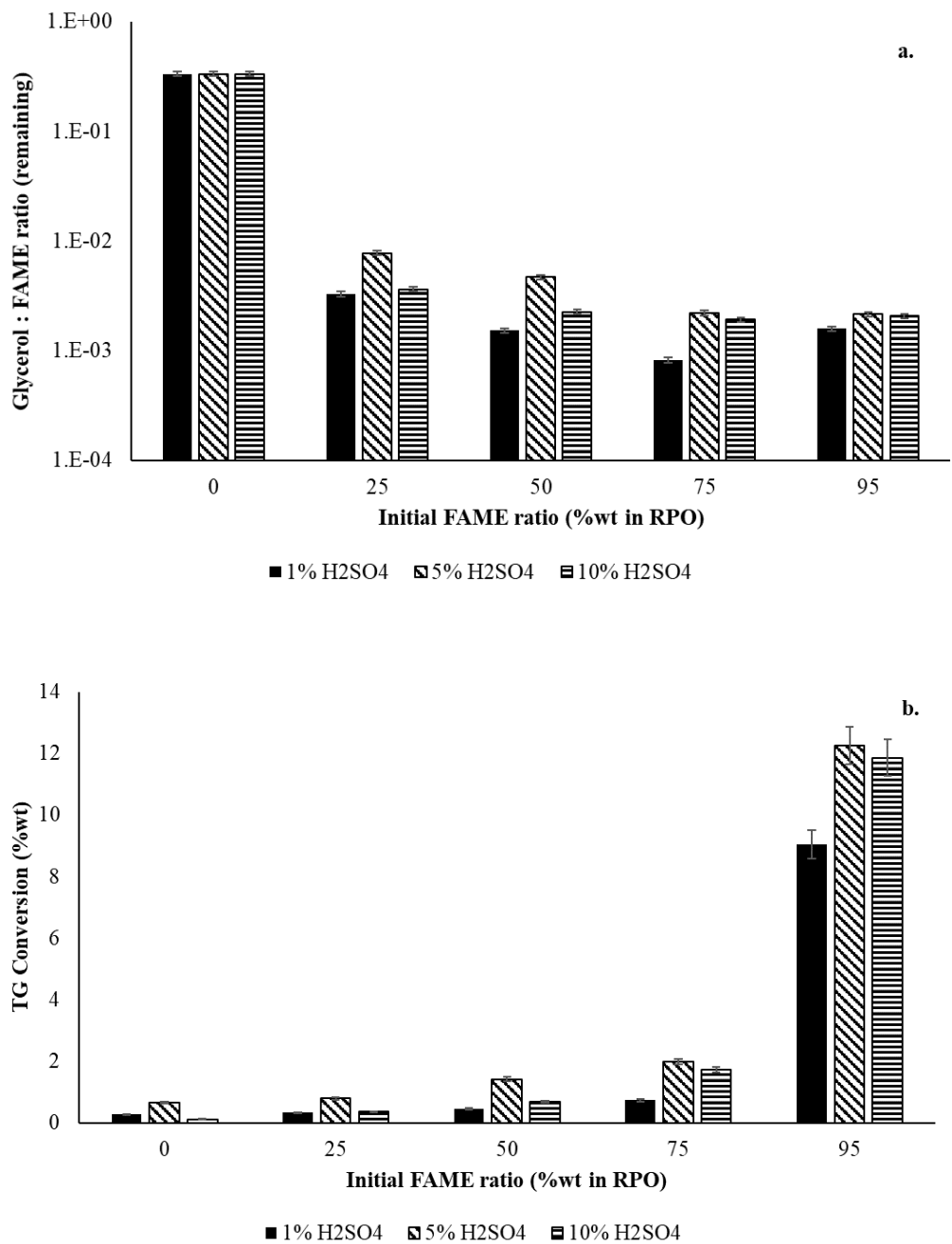


Figure 2. Relation of initial FAME ratio (%wt in RPO) to a) Glycerol : FAME ratio, and b) TG conversion.

Another factor effecting the reaction rate is catalyst concentration. At the ratio of glycerol to FAME greater than 0.5, 1 wt% sulfuric acid gave the lowest conversion as shown in Figure 2a and 2b because of too small amount of hydrogen ions provided for the reaction. Both effects of sulfuric acid concentration and glycerol to FAME ratio can be seen in Figure 2. Using 5 wt% or 10 wt% sulfuric acid gave almost similar conversions. On the other hand, when the glycerol to FAME ratio was lower than 0.01, TG conversion increased dramatically, and 5 wt% sulfuric acid gave its conversion higher than at 10 wt% because the lower polarity of 5wt% gave a better mixing than 10 wt%. Therefore, the condition of the initial FAME to RPO ratio 50 % and 5 wt% sulfuric acid were selected for further study to improve the reaction, as mentioned in section 3.3.

3.2 Solubility Affected to the Two-phase Separation

A contour plot of the 5 minute-reaction in Figure 3 presents a two-liquid liquid-phase reaction. There were two separated phases, polar MeOH phase and non-polar oil phase. A higher

concentration of sulfuric acid, a strong polar chemical in the solution, made polar and nonpolar phases blend with difficulty. This was reflected by the Octanol-water coefficient, $\text{Log } K_{ow}$. Sulfuric acid dispersed into the polar phase more than in the nonpolar phase since $\text{Log } K_{ow}$ of sulfuric acid is near that of MeOH. This means that the acid wholly separated from the mixed oil. It could not actively catalyze the desired reactions.

Since $\text{Log } K_{ow}$ of FAME is in the range of a semi-polar substance, it can serve as a co-solvent for this reaction. Adding FAME in RPO would increase the miscibility of the multi-component mixture. Another point of view is seen using an LCD microscope with an *in vitro* reactor using alkaline catalyst in transesterification. The polar phase (alcohol, catalyst, and glycerol) formed spherical drops in the continuous oil phase. The generated glycerol was a barrier covering the drop. When glycerol content increased, it enlarged drop size and slowed down the reaction rate [21, 24]. Two-step esterification also showed phase separation of polar and nonpolar phases, similar to an alkaline catalyst. Moreover, water also used sulfuric acid in the hydrolysis reaction,

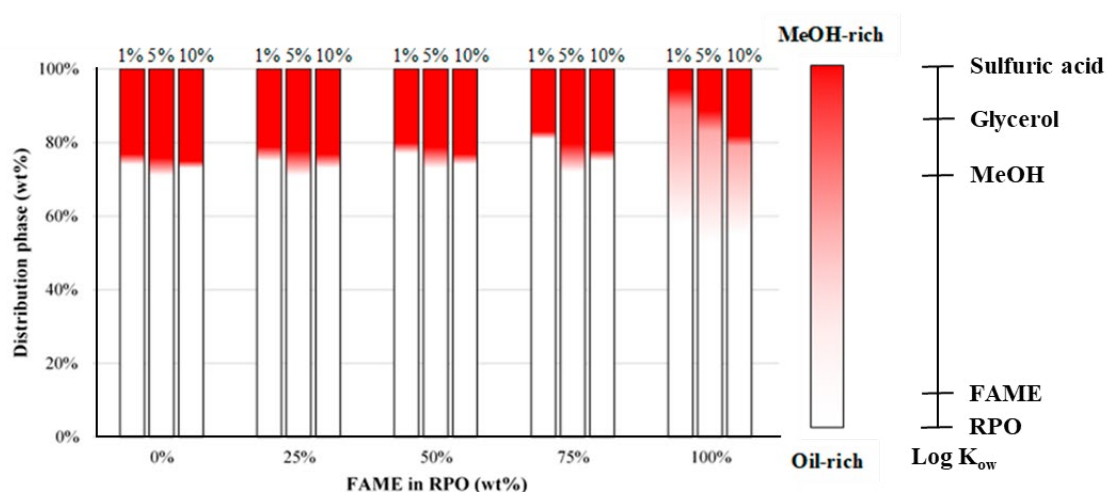


Figure 3. Phase separation in two-phase liquid-liquid reaction, $\text{Log } K_{ow}$, Sulfuric acid [31], Glycerol [32], MeOH [33], FAME [34] and RPO [35].

interrupting the esterification reaction. Hence, water in the system should be separated and removed from the first step before feeding raw oil into the second step [1].

3.3 Enhanced Rate of Acid Catalyzed Transesterification Reaction and Application

3.3.1 A comparison of the mixing methods and applications

Figure 4 shows that the conventional reactor gradually had increased FAME yield from the beginning until 30 minutes, of about 10 wt%, while the multistage reactor gave more than twofold that of the conventional reactor. This relates to solubility and polarity disruptions. In the conventional reactor, all solvent was first blended, and it generated glycerol and FAME. Glycerol can dissolve in the MeOH-sulfuric acid phase, then drove the sulfuric acid out of the oil phase. So, the glycerol generation may disrupt the interaction between raw materials. From

Figure 5 the phase distribution demonstrates that the series of reactions had more oil content than conventional reactor when the reaction reached 30 minutes.

Table 2 shows a comparison of sulfuric acid and glycerol distributions in the two phases. Sulfuric acid preferred to live in the MeOH phase more than in the oil phase. Less acid remaining in the oil phase was not enough to diffuse into oil phase and catalyze the reaction effectively.

Glycerol from the reaction also brought sulfuric acid back to the MeOH solution. After finishing the reaction, the solution was separated into polar phase MeOH and nonpolar oil phase. MeOH-sulfuric acid could dissolve in suspension around the rich oil phase. Therefore, FAME component in oil phase can reduce viscosity, density, and increase polarity. This can make glycerol and other polar components dissolve increasingly in oil phase when adding FAME.

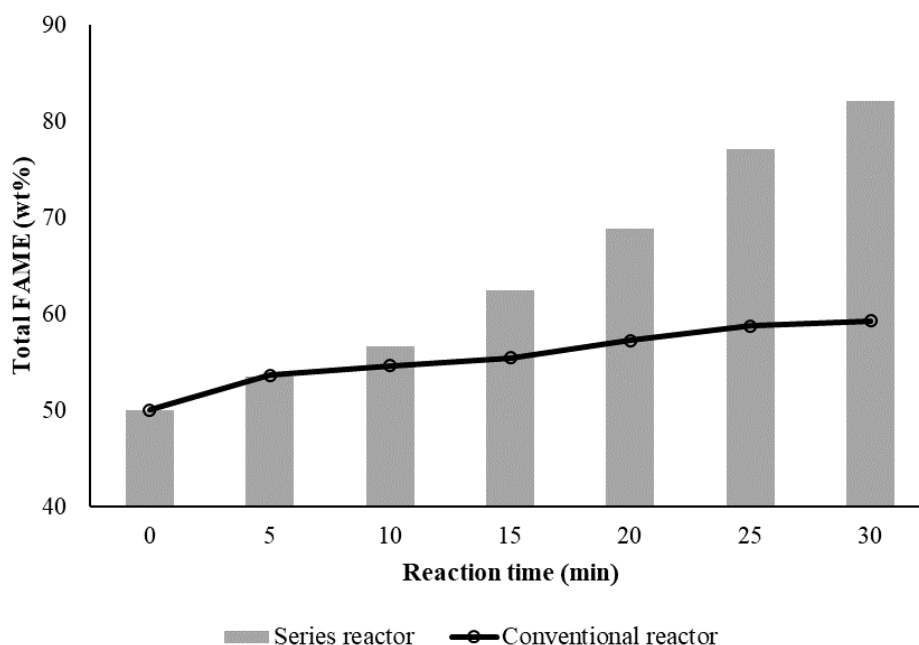


Figure 4. Comparison of two mixing methods: direct reaction and series of stages.

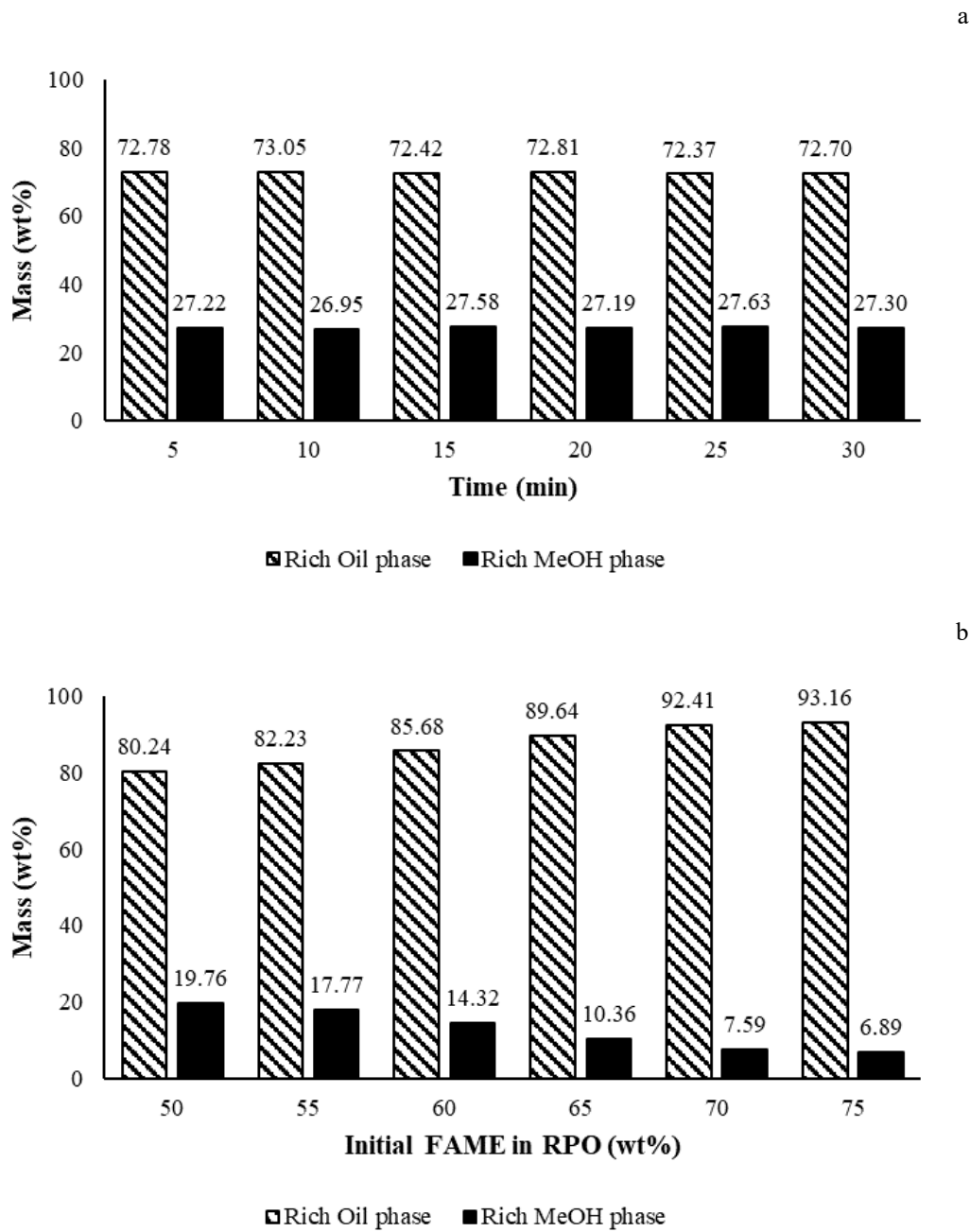


Figure 5. Phase distributions of acid transesterification; a is direct reactor and b is series reactor.

Table 2. Polar component contents in the two-phase system.

Run No.	Conventional reactor				Series reactor			
	Sulfuric acid (wt%)		Glycerol (wt%)		Sulfuric acid (wt%)		Glycerol (wt%)	
	Rich oil	Rich MeOH	Rich oil	Rich MeOH	Rich oil	Rich MeOH	Rich oil	Rich MeOH
1	95.38	4.62	82.29	17.71	67.97	32.03	66.92	33.08
2	96.92	3.08	-	-	67.11	32.89	66.41	33.59
3	95.76	4.24	69.15	30.85	67.97	32.03	66.67	33.33
4	96.56	3.44	-	-	69.85	30.15	66.45	33.55
5	96.78	3.22	-	-	72.48	27.52	66.67	33.33
6	96.13	3.87	77.51	22.49	78.05	21.95	66.32	33.68

Note: Run No. of conventional reactor are included reaction time (min) of about 5, 10, 15, 20, 25, 30, respectively. Then for series reactor are included initial FAME ratio in RPO (wt%) of about 50, 55, 60, 65, 70, respectively.

In a multistage reactor, polar phase including glycerol from the oil phase were removed after 5 minutes of reaction, adding only fresh MeOH-sulfuric acid solution to the reactor to continue the reaction every 5 minutes. This approach improved yield because there was no effect from glycerol barrier. The results corroborate this with decreasing viscosity and density, which can increase the solubility.

The runs of the multistage reactor with the same total reaction time of 30 minutes as the conventional reactor were focused on varied FAME ratios at about 50, 55, 60, 65, 70, and 75 wt%. This experiment shows that one-third mole of generated glycerol was in mixed oil phase and less was in the MeOH rich phase. Figure 6 compares conventional reactor and multistage reactor, and the solvent removal steps in the multistage reactor gave more generated FAME than conventional reactor. In addition, the glycerol to FAME molar ratio of the multistage reactor was higher, parallel with the generated FAME increase, because the conventional reactor did not remove solvent including glycerol. Therefore the glycerol removal step can enhance the reaction rate. Deglycerol reactor should be considered to deliver the reaction

and remove glycerol based on density difference instead of using a continuous stirred tank reactor with hot water to remove it.

3.4 Improving Mixing in the Acid Catalyzed Transesterification Reaction

The relation between initial FAME in RPO and total FAME is shown in Figure 7. FAME in RPO between 50-70 wt%. wt can increase the reaction rate. Ratios greater than 75 wt% slowed down the reaction because of the diminishing precursor content, such as of RPO and methanol, although part of the solubility experiments suggest that adding FAME improved the solubility of substances in the system. From the analytical results of this part, the final product purity was about 98.22 wt% according to titration and 96.17 wt% according to GC-FID analysis, while the prediction model estimated 98.79 wt% [29].

The relation in Figure 3 can be modeled as shown in Eq (2)

$$y = 0.9342x + 0.0955 \quad (R^2=0.9974). \quad (2)$$

where y is % generated FAME, and x is % initial FAME.

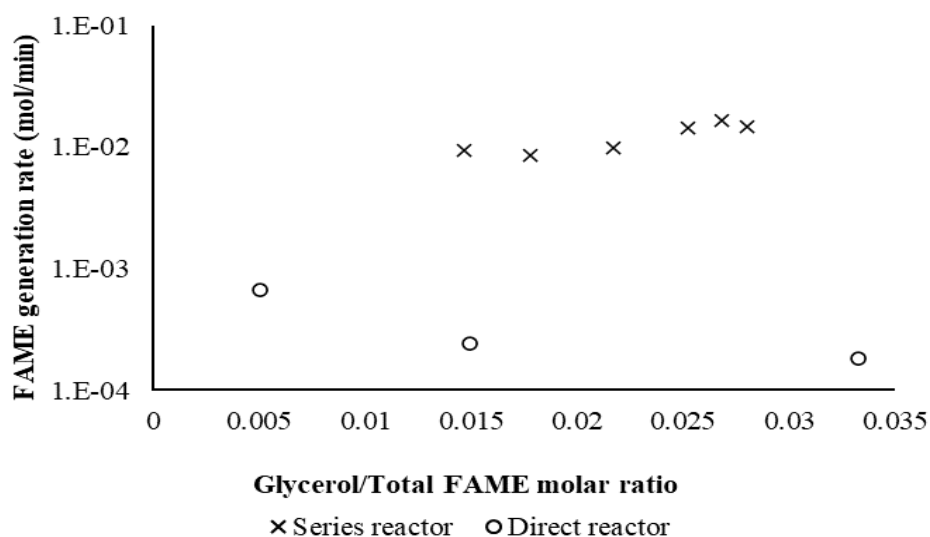


Figure 6. Relationship between FAME generation rate and glycerol to total FAME molar ratio for direct reaction and series reaction.

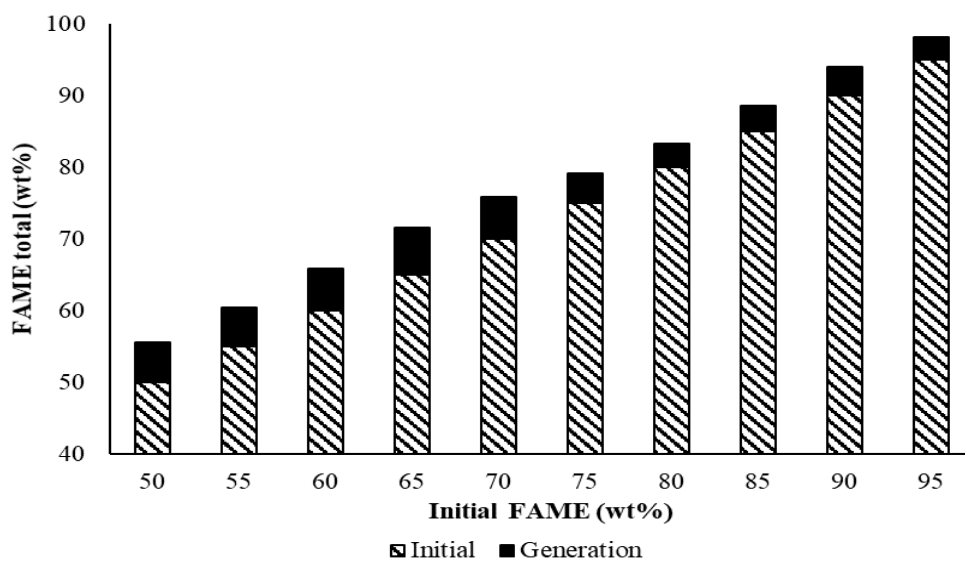


Figure 7. Experimental result for reaction modeling.

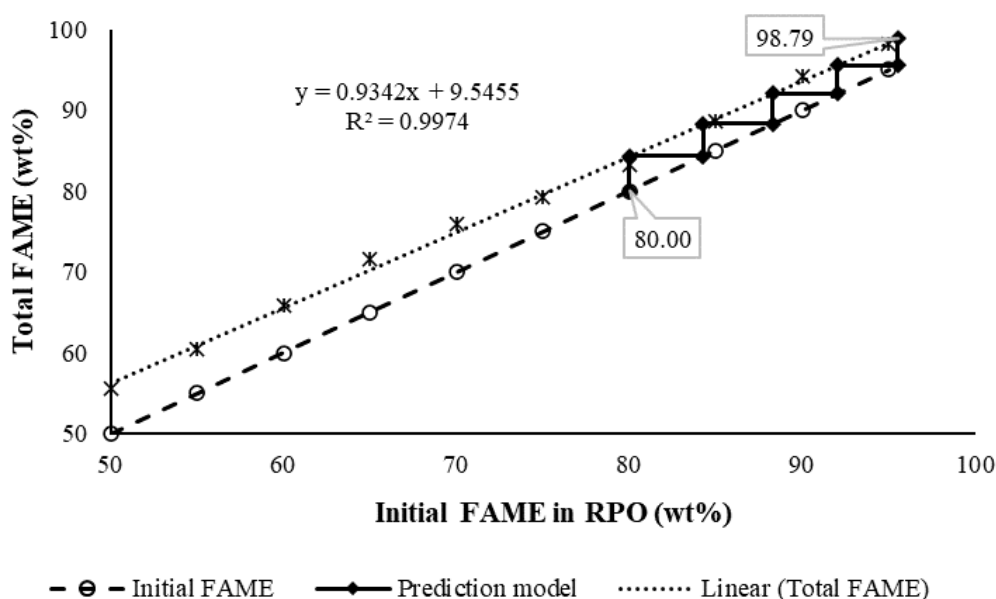


Figure 8. Acid transesterification rate enhancement.

This model of Eq (2) can be applied in the second step transesterification when the first step was alkaline catalyzed. According to FAME prediction model of Thoai et al. [29], it took 21 minutes for the reaction time to get 80% conversion in the first step. This condition occurred at MeOH/ RPO molar ratio of 5.24, 0.40 wt.% catalyst, and reaction temperature of 60°C. This condition was the starting point for the second step transesterification. Initially the stages had no glycerol. From the predicted model (eq (2)), the process should have 5-minutes per stage for 5 stages (or 25 minutes) to 98.75% FAME content from 80% FAME content as shown in Figure 8. But after checking FAME content with GC-FID, the process should have totally 6 stages (total time 30 minutes) to get FAME content pass the standard (96.5%). Therefore, the time required for two step transesterification with glycerol removal in a multistage reactor for the second step was 51 minutes, while a two-step-base-sulfuric acid-transesterification spent

2 hours [28] and a two-step-base-heterogeneous acid catalyzed transesterification required 9 hours and 40 minutes [29]. Our proposed model for the second step indicates shortening the reaction time by about 57.5% from using sulfuric acid catalyst in a conventional reactor, and by 91.2 % from using heterogeneous acid catalyzed transesterification.

4. CONCLUSIONS

Acid catalyzed transesterification reaction is slow because of the poor mutual solubility of the reactant compounds. The two-phase liquid-liquid system is split into polar and non-polar compounds. The slow reaction rate can be improved by adding FAME co-solvent to reduce the system's viscosity and by using a multistage reactor with glycerol removal to reduce the effects of glycerol on esterification rate. In addition, for application of this concept we propose multistage transesterification with glycerol removal in the second step transesterification. Each stage can take about 5 minutes and use the same proportions

of RPO: FAME: methanol: sulfuric acid catalyst. Our proposed method can reduce reaction time by more than 50% from the conventional acid catalyzed transesterification.

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