

## Original Article

Post-treatment for high content of ethyl ester  
from esterification of palm fatty acid distillate\*

Waritorn Kanjaikaew, Chakrit Tongurai, and Sininart Chongkhong\*

*Department of Chemical Engineering, Faculty of Engineering,  
Prince of Songkla University, Hat Yai, Songkhla, 90112 Thailand*

Received: 7 December 2020; Revised: 5 June 2021; Accepted: 4 August 2021

**Abstract**

Ethyl ester from palm fatty acid distillate is of interest as biodiesel. However, the standard biodiesel quality free fatty acid (FFA) content is hard to achieve due to reversible reactions at low FFA content. The post-treatment of ethyl ester (1.5 wt% FFA) by esterification was investigated using homogeneous catalysts or heterogeneous catalysts, and comparing the short-chain alcohols ethanol and methanol. An approximate equilibrium was attained more easily when using methanol or the heterogeneous catalysts, and the goal of 0.25 wt% FFA content was achieved. First-order reaction kinetics were postulated, and three alternative kinetic models were formulated for cases with large excess in some reactants. The simplest such model gave the forward rate constant as 13.32 which was higher than that of the reverse reaction. The water generated during esterification contributed with total initial water, which also was a key factor affecting the water balance.

**Keywords:** post-treatment, palm fatty acid distillate, esterification, ethyl ester, kinetics**1. Introduction**

Alternative low-quality feedstocks with a high FFA content, such as non-edible oil, used cooking oils, or palm fatty acid distillate (PFAD), can reduce biodiesel production costs by 60-90% (Bonet-Ragel, Canet, Benaiges, & Valero, 2015; Eze, Phan, & Harvey, 2018; Kadapure *et al.*, 2017; Li, Wang, Faiza, Yang, & Wang, 2017; Talebian-Kiakalaieh, Amin, & Mazaheri, 2013). Palm fatty acid ethyl ester (FAEE) is another interesting liquid biofuel for Thailand, because nowadays there is a very large surplus of ethanol production capacity, exceeding the regular consumption, and PFAD is about 5 wt% of crude palm oil from the refined palm oil plants (Gapor Md Top, 2010; Zero and Rainforest Foundation Norway, 2015). The integrated biodiesel plants in Thailand, with feedstock from palm oil mills, apply glycerolysis for converting PFAD to glycerides, the common reactant of transesterification. However, the direct conversion of PFAD

to ester via esterification has some advantages over the previous glycerolysis process.

The esterification reaction is usually acid-catalyzed, normally with sulfuric acid ( $H_2SO_4$ ). The esterification of FFA to ester is a reversible reaction, as shown in Equation (1). To avoid the undesirable reverse reaction, multistep esterification is used in ester production from high free fatty acid content reactants. The alcohol-water phase is separated from the hydrocarbon phase of fatty acid and ester, before going to the next esterification step with a fresh acid-alcohol stream. When the system has a high concentration of ester and a very low concentration of FFA, the reverse esterification reaction is difficult to avoid. Kanjaikaew, Tongurai, and Chongkhong (2018) studied two-step esterification from PFAD, which was carried out using ethanol and  $H_2SO_4$ . The results showed that the conversion effectiveness was comparable to that of using methanol. However, at the end of the reaction, the residual FFA content remained above 0.25 wt%. This high FFA content is unacceptable by standard specifications of biodiesel fuel. The high-water content of the system was presumed to be a key compound affecting reversible esterification reaction.

An investigation of the post-treatment of the off-spec ethyl ester (OEE) affected by reversible esterification of

\*Peer-reviewed paper selected from The 9<sup>th</sup> International Conference on Engineering and Technology (ICET-2021)

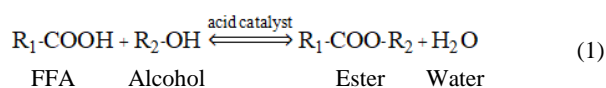
\*Corresponding author

Email address: csininart@yahoo.com

water and ester was the focus of our study. The simple aim was to attain the standard fatty acid content in biodiesel specification, 0.25 wt%, or an acid value of 0.5 mg KOH/g. Due to the OEE having a very low 1.5 wt% of FFA, competition between forward esterification of FFA with ethanol and reverse reaction of ester and water was expected. Farag, El-Maghraby, & Taha (2011) confirmed this when studying the esterification of various types of oil with varying amounts of FFA.

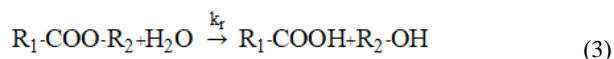
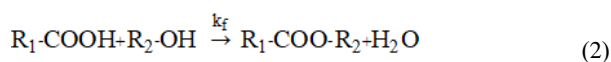
A low-priced commercial  $H_2SO_4$  contains approximately 2.0 wt% water and the commercial ethanol contained 0.5 wt% water, which is more than that in methanol at 0.2 wt%. The high molar ratio of ethanol to free fatty acid as a drawback contributed to the water, which caused the undesirable reverse esterification at a high concentration of ester. A high amount of  $H_2SO_4$  should also give a large amount of water, but testing should be done to verify this expectation.

The minimization of water content from homogeneous acid-catalyzed reaction via  $H_2SO_4$  was studied by using low water content methanesulfonic acid (MsOH). The MsOH is a strong Brønsted acid catalyst and has a purity of 99.5 wt% (Gernon, Wu, Buszta, & Janney, 1999; Palden, Onghena, Regadio, & Binnemans, 2019). The homogeneous and heterogeneous acid catalysts have advantages and disadvantages: an advantage of heterogeneous acid catalysts is the absence of water, and a disadvantage is the high operating costs. The heterogeneous acid catalysts Amberlyst 15 and Amberlyst BD20 were also of interest. The usability of solid catalysts was also studied in a few trials. Finally, the lower water content in methanol (0.2 wt%) was used for enlightening our understanding about the water effects.



In this study, OEE with a low 1.5 wt% FFA content, was introduced into post-treatment by esterification using two types of acid catalysts, namely homogeneous acid catalysts MsOH and  $H_2SO_4$ , as well as heterogeneous catalysts Amberlyst 15 and Amberlyst BD20. The commercial short chain alcohols ethanol and methanol (having different water contents) were also used in the study.

The reaction rate constant at equilibrium, which was the barrier hindering low FFA content in the final product, was another focal point of our studies. The postulated simple first-order reaction was used to explain our results as shown in Equation (2) for the forward reaction and in (3) for the reverse reaction



where  $k_f$  and  $k_r$  are reaction rate constants of the forward and reverse reaction, respectively.

## 2. Materials and Methods

### 2.1 Materials

Synthesized ethyl ester mixed with 1.5 wt% PFAD was used as the initial reactant in this post-treatment study. This mixture called OEE could be normally obtained from a two-step esterification (Kanjaikaew *et al.*, 2018). Sulfuric acid ( $H_2SO_4$ , 98.0 wt% purity) was obtained from Merck Ltd., Thailand, while methanesulfonic acid (MsOH, 99.5 wt% purity) was acquired from Sigma-Aldrich, Thailand. Amberlyst 15 and Amberlyst BD20 were purchased from Rohm & Haas, France. Properties of heterogeneous catalysts are shown in Table 1. Commercial grade methanol (MeOH) and ethanol (EtOH) were bought from P-General Ltd. and Union Intraco PCL., respectively. The water contents determined by Karl Fischer titration were 0.1 wt% for methanol, 0.33 wt% for ethanol and 0.05 wt% for OEE. Sodium hydroxide and isopropanol were used in the analysis of the FFA content.

### 2.2 Experimental

Based on prior investigations (Kaddour, 2017; Mansir *et al.*, 2018; Pan *et al.*, 2016; Saejio & Prasertsit, 2018), our experiments were conducted under a 90:1 molar ratio of alcohol to FFA (alcohol:OEE of 1.47:1) and at reaction temperature of 70 °C for a reaction time of 5 h, which was long enough for the heterogeneous catalysts. One hundred grams of OEE was heated to and maintained at the desired temperature. The desired amount of a mixture of alcohol and catalyst was added to the heated OEE and stirred continuously in a 250 mL three-necked round bottom flask, which was immersed in an oil bath equipped with a reflux condenser to maintain the temperature and minimize the loss of alcohol. The apparatus of the experimental set-up can be seen in Figure 1. After the desired reaction time, the reaction mixture was allowed to settle in a separating funnel for 1 h. The ester phase was purified by water washing and dried at 105 °C for 0.5 h.

On using heterogeneous catalysts, the procedure was similar to that with a homogeneous catalyst. After the reaction, the solid catalyst was separated by filtration before the reaction mixture was settled in a separating funnel.

#### 2.2.1 Homogeneous catalyst

The  $H_2SO_4$  and MsOH were used in these experiments. The amount of catalyst was 1, 3, 5, or 7 wt% of

Table 1. Properties of heterogeneous catalysts

Catalyst	Type and Ionic form	Surface area	Concentration of acid sites*	Limit of temperature	moisture content
Amberlyst 15	Strong acid, Hydrogen	53 m <sup>2</sup> /g	4.74 eq/kg	120°C	≤1.6 wt.%
Amberlyst BD20	Strong acid, Hydrogen	0.11 m <sup>2</sup> /g	5.10 eq/kg	500°C	75-80 wt.%

\*(Park *et al.*, 2010)

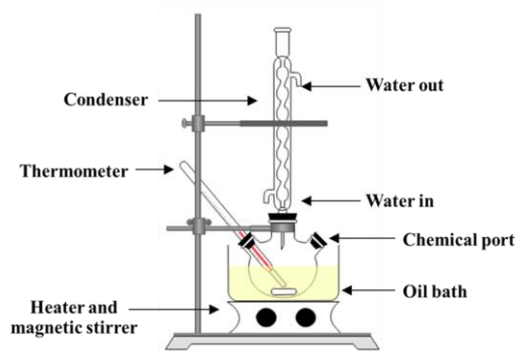


Figure 1. The apparatus set-up for post-treatment

OEE. With each catalyst amount, methanol and ethanol were also employed to assess effects from water contents in these alcohols.

### 2.2.2 Heterogeneous catalyst

The amounts of both Amberlyst 15 and Amberlyst BD20 used in our trials were 5, 10, 20, or 30 wt% of OEE. The as-received Amberlyst BD20 was fully saturated with water and required drying for activation. This resin (50 g) was mixed with 300 ml of methanol for 10 min, and then filtered to remove the methanol. After filtration, the wet catalyst was dried in an oven at 105 °C for 24 h. To dry Amberlyst 15, it was simply put in an oven at 105 °C for 24 h. Then, both catalysts were cooled to room temperature in a desiccator (Kaddour, 2017).

### 2.2.3 Regeneration of heterogeneous catalysts

The filtered heterogeneous catalyst was rinsed three times with methanol. The amount of methanol used in each washing was 5 times the catalyst weight. Then, the catalyst was dried in an oven at 105 °C for 24 h.

### 2.3 Analysis

FFA contents were determined by titration according to AOCS Ca 5a-40. The water contents of raw materials were analyzed by the Karl Fischer method (ISO 12937). The conversion of FFA was determined using Equation (4).

$$\text{FFA conversion (\%)} = \frac{\text{FFA}_0 - \text{FFA}}{\text{FFA}_0} \times 100 \quad (4)$$

where  $\text{FFA}_0$  is the initial FFA content, and FFA is the residual FFA in the product.

## 3. Results and Discussion

### 3.1 Effect of catalyst amount

#### 3.1.1 Homogeneous catalyst

Sulfuric acid and MsOH were chosen as the homogeneous acid catalysts in our trials. It was known that the acid strength of  $\text{H}_2\text{SO}_4$  was slightly higher than that of MsOH. However, the purity of  $\text{H}_2\text{SO}_4$  was 98% and that of MsOH was 99.5%. It was therefore assumed that the water contents in the catalysts were 2% and 0.5%, respectively. Therefore, the water in our system came from initial ester, ethanol, catalyst, and the water produced by esterification reaction. Figure 2 shows the effects of the amounts of each catalyst on the residual FFA content. As can be seen in this figure, increasing the amount of catalyst had a positive effect on FFA reduction by accelerating the rate limiting reaction between the catalyst and the hydrocarbon reactants (both for forward esterification and the reverse reaction). On allowing the same 5 hours reaction time, the system with the highest 7 wt% catalyst amount got closest to the equilibrium state. The effect of water in the system was presumed to dominate over the acid strength, and was detailed in the 7 wt% trials in Table 2. The initial concentrations of water in the reactor from

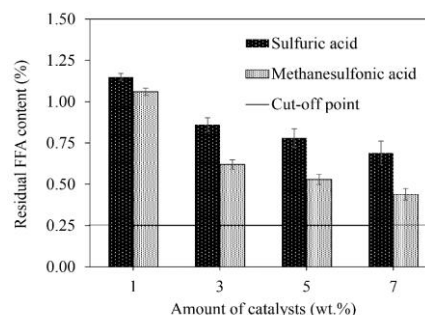


Figure 2. The effect of homogeneous catalyst amount on residual FFA content (90:1 molar ratio of ethanol to FFA and 70 °C reaction temperature for 5 h)

Table 2. Material Balances of the selected trials using 7 wt% of  $\text{H}_2\text{SO}_4$  or MsOH

Component	$\text{H}_2\text{SO}_4$			MsOH		
	Initial		Final	Initial		Final
	wt. (g)	Conc. (mol/L)	Conc. (mol/L)	wt. (g)	Conc. (mol/L)	Conc. (mol/L)
FFA	1.500	0.036	0.016	1.500	0.036	0.010
FAEE	98.450	2.121	2.141	98.450	2.112	2.137
EtOH	23.000	3.211	3.191	23.000	3.196	3.170
Catalyst	7.000	0.459	0.459	7.000	0.465	0.465
Water						
(Total)	0.266	0.096	0.116	0.161	0.057	0.082
(FAEE)	0.050			0.050		
(EtOH)	0.076			0.076		
(Cat.)	0.140			0.035		
(Generated)	0.050			0.070		

H<sub>2</sub>SO<sub>4</sub> and MsOH catalysts were 0.096 and 0.057 mol/L, yielding the respective final concentrations of 0.116 and 0.082 mol/L. The generated amount of water from MsOH catalyst was higher than from H<sub>2</sub>SO<sub>4</sub> (0.07 to 0.05 g) due to better FFA conversion (71 and 54% conversions), and the final concentrations of FFA were 0.016 and 0.010 mol/L, respectively. The initial water content in the H<sub>2</sub>SO<sub>4</sub> system was higher than with MsOH by 0.105 g of the overall 0.266 g water (based on H<sub>2</sub>SO<sub>4</sub>). This large water content significantly contributed to reverse esterification (hydrolysis) that limited the FFA conversion. Unfortunately, our experimental conditions were not good enough to meet the 0.25 wt% FFA limit in biodiesel standard specification, even on using the high 90:1 molar ratio of ethanol to FFA. A discussion of esterification and hydrolysis reaction kinetics is provided in section 3.2 on “Equilibrium of the reverse esterification reaction”.

### 3.1.2 Heterogeneous catalyst

Amberlyst 15 and Amberlyst BD20 are known as heterogeneous catalysts with good esterification efficiency (Pan *et al.*, 2016). In this case, the catalytic reactions happened on the surfaces of the catalyst particles. Therefore, larger amounts of these heterogeneous catalysts were needed than of the homogeneous catalysts, to have enough active catalyst sites that enhanced the reaction rate and lessened the reaction time. To study the effects of heterogeneous catalyst amount, the amounts were varied between 5wt% and 30 wt% (Kaddour, 2017). Other parameters were kept constant at the same values as for the reactions with homogeneous catalysts.

Figure 3 presents the residual FFA content achieved with various amounts of the heterogeneous catalysts. As expected, the residual FFA content of OEE decreased with the amount of catalyst, due to an increase in acid sites. The FFA conversion using Amberlyst BD20 was slightly better than with Amberlyst 15, due to the higher concentration of acid sites (Table 1). The results conformed to the studies of Pan *et al.* (2016) and Park, Kim, & Lee (2010) who reported that Amberlyst BD20 showed better performance than Amberlyst 15. Our objective of reducing the residual FFA content to 0.25 wt% was attained by using Amberlyst BD20 at 20 wt%. Also on using Amberlyst 15 at 30 wt% the residual FFA content reached the 0.25 wt% threshold, but there was no noticeable change between using Amberlyst BD20 at 20 wt% or 30 wt%. Possibly the equilibrium state of esterification and hydrolysis (reverse esterification) reactions was nearly attained.

From Tables 2 and 3, the initial water concentrations in the system on using acid-catalysis with H<sub>2</sub>SO<sub>4</sub>, MsOH, Amberlyst BD20, and Amberlyst 15 at the best conditions were 0.096, 0.057, 0.048, and 0.048 mol/L, respectively. The final water concentration was increased by the water from esterification, and this varied with the FFA conversion. The final water concentrations were certainly the lowest at 0.079 and 0.078 mol/L on using Amberlyst 15 and Amberlyst BD20, respectively, and the targeted final residual FFA content of 0.25 wt% was achieved. The effect of water concentration in the system was further assessed by using methanol instead of ethanol: that lessened the amount of water entering with the alcohol reactant.

In addition, According to Park *et al.* (2010), the SEM images of Amberlyst 15 and Amberlyst BD20 showed

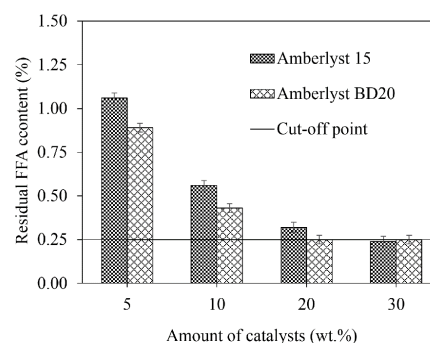


Figure 3. The effect of heterogeneous catalyst amount on residual FFA content (90:1 molar ratio of ethanol to FFA and 70 °C reaction temperature for 5 h)

similar outer surfaces, and the BET surface area of Amberlyst BD20 was <0.1 m<sup>2</sup>/g. With such low specific surface area, the catalysts might be completely deactivated by the water adsorbing on the active sites. This led to decreased catalytic activity. Thus, the post-treatment using lower amounts of the catalysts (<30 wt%) provided ester with FFA content more than 0.25 wt%.

### 3.2 Equilibrium of the reverse esterification reaction

Certainly, the acid-catalyzed methanolysis allowed better results than ethanolysis, due to high reactivity. Farag *et al.* (2011) reported that the esterification rate decreased markedly when the molecular weight of alcohol increased. Furthermore, not only did methanolysis give a higher reaction rate, methanolysis also caused fast and complete phase separation after the reaction (Nikhom & Tongurai, 2014). However, our focus was on the effects of water content in the post-treatment system, on equilibrium state in relation to the final biodiesel specifications.

The selected optimal conditions of the post-treatment of OEE using the four acid catalyzed runs (5 or 7 wt% homogeneous catalyst, and 20 or 30 wt% heterogeneous catalyst) with ethanol were considered for replacement of ethanol with methanol. Figure 4 shows the residual FFA content for each catalyst with both alcohols.

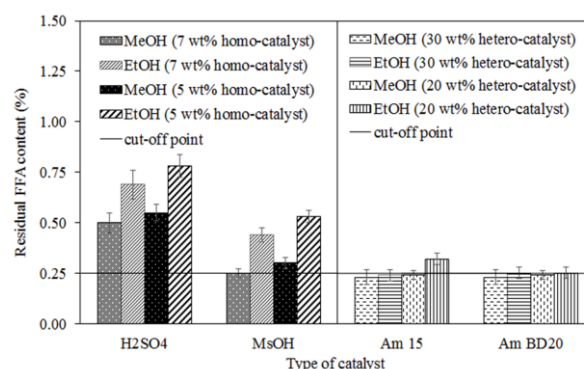


Figure 4. The effect of alcohol type on residual FFA content in the post-treatment, using homogeneous and heterogeneous acid-catalyzed esterification (90:1 molar ratio of alcohol to FFA and 70 °C reaction temperature for 5 h)

Table 3. Material Balances of selected trials with 30 wt% Amberlyst 15 or Amberlyst BD20

Component	Amberlyst 15			Amberlyst BD20		
	Initial		Final	Initial		Final
	wt. (g)	Conc. ol/L	Conc. ol/L	wt. (g)	Conc. mol/L	Conc. mol/L
FFA	1.500	0.037	0.006	1.500	0.037	0.006
FAEE	98.450	2.178	2.209	98.450	2.178	2.208
EtOH	23.000	3.296	3.265	23.000	3.296	3.265
Catalyst	30.000			30.000		
Water	(Total)	0.126	0.079	0.126	0.048	0.078
	(FAEE)	0.050		0.050		
	(EtOH)	0.076		0.076		
	(Generated)	(0.080)		(0.080)		

The different water contents in methanol and ethanol had almost no effect on the overall rate of esterification reaction, but should be seriously considered in relation to the final state, especially for the post-treatment of OEE. Moreover, in this study the moisture content of methanol (0.1 wt%) was lower than that of ethanol (0.33 wt%). The results in term of residual FFA contents obtained from the use of methanol and ethanol at the highest amounts of homogeneous catalysts ( $H_2SO_4$  and  $MsOH$  at 7 wt%) and heterogeneous catalysts (Amberlyst 15 and Amberlyst BD20 at 30 wt.%) in the post-treatment are shown in Figure 4. The second-best conditions using 5 wt% of homogeneous catalyst and 20 wt% of heterogeneous catalyst are also presented in Figure 4. On using heterogeneous catalysts at 20 wt% or 30 wt% with methanol, the conversions of FFA were equal with Amberlyst 15 and Amberlyst BD20. These steady values of the lowest residual FFA content indicate that the reaction reached an equilibrium state. The final and initial concentrations of all the reactants and products in the four tests with methanol are summarized in Table 4. Also, the same details with ethanol are shown in Table 5. The final concentrations were the main results of interest.

We assumed that the final state of esterification was at an equilibrium of first-order reactions. The forward rate of reaction depended on the reaction rate constant ( $k_f$ ) and the product of both reactant concentrations of FFA and alcohol  $[(C_{FFA})(C_{alc})]$ . However, when one of the reactants was present in a large excess, the reaction rate should strongly depend on the limiting reactant. The concentration ratio of alcohol to FFA in our trials indicated that alcohol excess increased towards the final concentration. The reverse rate of reaction was  $k_r(C_{ester})(C_{water})$ , and the concentration ratio of ester to water turned from a large excess to a moderate excess by end of a run.

We postulated that the slight changes of all the component concentrations in progress to the final concentrations had resulted from the approach to the equilibrium state. The ratio of the forward reaction rate constant to reverse constant was  $(C_{ester})(C_{water})/(C_{FFA})(C_{alc})$ . We proposed 3 models to determine the  $k_f/k_r$  ratio: the first model was the standard  $(C_{ester})(C_{water})/(C_{FFA})(C_{alc})$ ; the second had excess alcohol so that  $k_f/k_r$  ratio was  $(C_{ester})(C_{water})/(C_{FFA})$ ; and the third had both alcohol and ester in excess, giving  $(C_{water})/(C_{FFA})$ . These 3 models are shown in Table 6.

The final concentrations of water in the methanol treatments were lower than in the ethanol trials. But, if we

focused on the trials that had final FFA contents less than 0.25 wt% (B, C, D, G, and H), these approximated the equilibrium state. The reaction rate constant ratio was of the same magnitude in all 3 models. The higher reaction rate constant of the forward reaction was due to the slightly exothermic esterification reaction (Hinde & Hall, 1998; Liu, Liu, Yan, Zhou, & Zhou, 2019; Sert & Atalay, 2011; Snee, Barcons, Hernandez, & Zaldivar, 1992). The 3<sup>rd</sup> model gave a limiting molar concentration ratio of water to FFA at a maximum of 13.32.

Actually, when we used methanol for the post-treatment of OEE, the ester content was not 100% of ethyl ester. But, based on the US specifications, ASTM D6751 defined biodiesel as mono-alkyl esters of long-chain fatty acids derived from vegetable oils and animal fats. The type of alcohol used was not specified. Thus, mono-alkyl esters could be produced with any alcohol (methanol, ethanol, etc.) as appropriate to the economy and resources of each country.

#### 4. Conclusions

For the reversible esterification reaction, the equilibrium conditions should be critically considered for high purity of the ester. The post-treatment by esterification is reasonable in this case. The concentration of water obviously plays a significant role in the reverse (hydrolysis) reaction. The equilibrium state is attained when the forward and reverse reaction rates are equal. Then the final concentration of water should be low enough according to the very low required final FFA content. The water content in the esterification of biodiesel comes from both hydrocarbon and alcohol reactants. Moreover, water was added as an impurity in the acid catalyst. The water from esterification reaction is also a contribution that should be considered. The water content in the off-spec fatty acid ester has to be kept as low as possible. The commercial methanol or ethanol have typically different water contents and the choice should be done wisely.

Our study showed final residual FFA contents generated from use of 2 homogeneous ( $H_2SO_4$  and  $MsOH$ ) and 2 heterogeneous (Amberlyst 15 and Amberlyst BD20) acid catalysts. Both the commercial short-chain alcohols, methanol and ethanol, were tested. Simple first-order reaction kinetics were used to explain the equilibrium of the forward and reverse reactions. Three alternative models of concentration effects on equilibrium were employed, by eliminating the concentrations of substances in excess from

Table 4. Final and initial concentrations of reactants and products of the methanol post-treatment

Reactant or product	H <sub>2</sub> SO <sub>4</sub>		MsOH		Amberlyst 15		Amberlyst BD20	
	initial	Final	initial	Final	initial	Final	initial	Final
Conc. FFA (mol/L)	0.0383	0.0128	0.0382	0.0064	0.0394	0.0060	0.0394	0.0060
Conc. MeOH (mol/L)	3.423	3.397	3.407	3.374	3.521	3.486	3.521	3.486
Conc. ratio of MeOH/FFA	89.38	265.41	89.18	527.21	89.36	581.06	89.36	581.06
Conc. ester (mol/L)	2.262	2.287	2.251	2.282	2.326	2.359	2.326	2.359
Conc. water (mol/L)	0.0799	0.1054	0.0379	0.0696	0.0274	0.0608	0.0274	0.0608
Conc. ratio of ester/water	28.31	21.70	59.39	32.79	84.90	38.80	84.90	38.80

Table 5. Final and initial concentrations of reactants and products of the ethanol post-treatment

Reactant or product	H <sub>2</sub> SO <sub>4</sub>		MsOH		Amberlyst 15		Amberlyst BD 20	
	initial	Final	initial	Final	initial	Final	initial	Final
Conc. FFA (mol/L)	0.0360	0.0165	0.0358	0.0105	0.0369	0.0059	0.0369	0.0062
Conc. EtOH (mol/L)	3.211	3.191	3.196	3.170	3.296	3.265	3.296	3.265
Conc. ratio of EtOH/FFA	89.18	193.40	89.27	301.90	89.33	553.40	89.33	526.60
Conc. ester (mol/L)	2.121	2.141	2.112	2.137	2.178	2.209	2.178	2.208
Conc. water (mol/L)	0.0963	0.1157	0.0568	0.0821	0.0476	0.0786	0.0476	0.0784
Conc. ratio of ester/water	22.03	18.50	37.18	26.03	45.75	28.10	45.75	28.17

Table 6. Three models of the forward to reverse reaction rate proportions at equilibrium

Final state	MeOH				EtOH			
	A	B	C	D	E	F	G	H
	H <sub>2</sub> SO <sub>4</sub>	MsOH	Am 15	Am BD	H <sub>2</sub> SO <sub>4</sub>	MsOH	Am 15*	Am BD**
Conc. FFA (mol/L)	0.0128	0.0064	0.0060	0.0060	0.0165	0.0105	0.0059	0.0062
Conc. Alc. (mol/L)	3.397	3.374	3.486	3.486	3.191	3.170	3.265	3.265
Conc. ester (mol/L)	2.287	2.282	2.359	2.359	2.141	2.136	2.209	2.208
Conc. water (mol/L)	0.1054	0.0696	0.0608	0.0608	0.1157	0.0821	0.0786	0.0784
1 <sup>st</sup> Model	5.54	7.35	6.85	6.85	4.70	5.27	9.01	8.55
2 <sup>nd</sup> Model	18.83	24.82	23.91	23.91	15.01	16.71	29.43	27.93
3 <sup>rd</sup> Model	8.23	10.88	10.13	10.13	7.01	7.82	13.32	12.65

\* Am 15 = Amberlyst 15

\*\* Am BD20 = Amberlyst BD20

the second and the third model. In the simplest model only the final concentrations of water and FFA affected the equilibrium.

The reversible esterification is slightly exothermic, so that the forward reaction rate constant ( $k_f$ ) should be larger than the reverse rate ( $k_r$ ). Our results showed the ratio 13.32 of molar concentrations of water to FFA at the approximate equilibrium reached experimentally. This number could guide considerations of post-treatment of off-spec fatty acid ester.

The post-treatment of the off-spec fatty acid ester should be evaluated from the initial and the final FFA contents. For example, if the initial concentration of FFA is less than 1.5 wt%, the specification FFA content at 0.25 wt% can be achieved easily because only a small amount of water is produced from conversion of the FFA, adding to the initial water content. The end state will be quite distant from equilibrium. The choice of catalysts remains an open question, but if the US specification, ASTM D6751, were implemented, methanol should be applied in the post-treatment process.

## Acknowledgements

The authors would like to gratefully thank Mr. Seppo Karrila and the Research and Development Office, Prince of Songkla University, for assistance with proofreading the English. Technical equipment and many other supporting facilities were generously provided by the Specialized R&D Center for Alternative Energy from Palm Oil and Oil Crops, as well as by the Department of Chemical Engineering, which are deeply appreciated.

## References

- Bonet-Ragel, K., Canet, A., Benaiges, M. D., & Valero, F. (2015). Synthesis of biodiesel from high FFA *alperujo* oil catalysed by immobilised lipase. *Fuel*, 161, 12–17.
- Eze, V. C., Phan, A. N., & Harvey, A. P. (2018). Intensified one-step biodiesel production from high water and free fatty acid waste cooking oils. *Fuel*, 220, 567–574.



- Farag, H. A., El-Maghraby, A., & Taha, N. A. (2011). Optimization of factors affecting esterification of mixed oil with high percentage of free fatty acid. *Fuel Processing Technology*, 92(3), 507–510.
- Gapor Md Top, A. (2010). Production and utilization of palm fatty acid distillate (PFAD). *Lipid Technology*, 22(1), 11–13.
- Gernon, M. D., Wu, M., Buszta, T., & Janney, P. (1999). Environmental benefits of methanesulfonic acid: Comparative properties and advantages. *Green Chemistry*, 1(3), 127–140.
- Hinde, N. J., & Hall, C. D. (1998). Kinetics and mechanism of the formation of mono- and di-phthalate esters catalysed by titanium and tin alkoxides. *Journal of the Chemical Society, Perkin Transactions*, 2(5), 1249–1256.
- Kadapure, S. A., Kiran, A., Anant, J., Dayanand, N., Rahul, P., & Poonam, K. (2017). Optimization of conversion of *Pongamia pinnata* oil with high FFA to biodiesel using novel deep eutectic solvent. *Journal of Environmental Chemical Engineering*, 5(6), 5331–5336.
- Kaddour, M. (2017). *Esterification of free fatty acid by selected homogeneous and solid acid catalysts for biodiesel production* (Master's thesis, The University of Western Ontario, Canada). Retrieved from <https://ir.lib.uwo.ca/etd/4345/>
- Kanjaikaew, U., Tongurai, C., Chongkhong, S., & Prasertsit, K. (2018). Two-step esterification of palm fatty acid distillate in ethyl ester production: Optimization and sensitivity analysis. *Renewable Energy*, 119, 336–344.
- Li, D., Wang, W., Faiza, M., Yang, B., & Wang, Y. (2017). A novel and highly efficient approach for the production of biodiesel from high-acid content waste cooking oil. *Catalysis Communications*, 102, 76–80.
- Liu, Y., Liu, J., Yan, H., Zhou, Z., & Zhou, A. (2019). Kinetic study on esterification of acetic acid with isopropyl alcohol catalyzed by ion exchange resin. *ACS Omega*, 4(21), 19462–19468.
- Mansir, N., Teo, S. H., Rashid, U., Saiman, M. I., Tan, Y. P., Alsultan, G. A., & Taufiq-Yap, Y. H. (2018). Modified waste egg shell derived bifunctional catalyst for biodiesel production from high FFA waste cooking oil. A review. *Renewable and Sustainable Energy Reviews*, 82, 3645–3655.
- Nikhom, R., & Tongurai, C. (2014). Production development of ethyl ester biodiesel from palm oil using a continuous deglycerolisation process. *Fuel*, 117, 926–931.
- Palden, T., Onghena, B., Regadó, M., & Binnemans, K. (2019). Methanesulfonic acid: A sustainable acidic solvent for recovering metals from the jarosite residue of the zinc industry. *Green Chemistry*, 21(19), 5394–5404.
- Pan, Y., Alam, A., Wang, Z., Wu, J., Zhang, Y., & Yuan, Z. (2016). Enhanced esterification of oleic acid and methanol by deep eutectic solvent assisted Amberlyst heterogeneous catalyst. *Bioresource Technology*, 220, 543–548.
- Park, J. Y., Kim, D. K., & Lee, J. S. (2010). Esterification of free fatty acids using water-tolerable Amberlyst as a heterogeneous catalyst. *Bioresource Technology*, 101, S62–S65.
- Saejio, A., & Prasertsit, K. (2018). Kinetics and control of palm fatty acid distillate esterification for a feasible biodiesel production. *Songklanakarin Journal of Science and Technology*, 40(1), 79–86.
- Sert, E., & Atalay, F. S. (2011). Esterification of acetic acid with butanol: Operation in a packed bed reactive distillation column. *Chemical and Biochemical Engineering Quarterly*, 25(2), 221–227.
- Snee, T. J., Barcons, C., Hernández, H., & Zaldívar, J. M. (1992). Characterisation of an exothermic reaction using adiabatic and isothermal calorimetry. *Journal of Thermal Analysis*, 38(12), 2729–2747.
- Talebian-Kiakalaieh, A., Amin, N. A. S., & Mazaheri, H. (2013). A review on novel processes of biodiesel production from waste cooking oil. *Applied Energy*, 104, 683–710.
- Zero and Rainforest Foundation Norway. (2015). *Palm Fatty Acid Distillate (PFAD) in biofuels*. Retrieved from <https://d5i6is0eze552.cloudfront.net/documents/Annex/Palm-Fatty-Acid-Distillate-in-biofuels.-ZERO-and-Rainforest-Foundation-N.pdf?mtime=20160302113207>