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Esterification pretreatment of free fatty acid in biodiesel production, from laboratory to industry

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ABSTRACT

In the US, biodiesel producers usually follow the 19.8:1 methanol-to-FFA molar ratio for free fatty acid (FFA) esterification, as suggested by the National Renewable Energy Laboratory (NREL) without optimization studies. In this paper, both laboratory studies and industrial practices of the esterification process were compared, and an optimization study of a used vegetable oil with 5% FFA was conducted. The optimal conditions of this oil, i.e., methanol-to-FFA molar ratio of 40:1, and sulfuric acid usage of 10%, fell out of the suggested range of 19.8:1. The activation energy of the esterification reaction is 20.7 kJ/mol at the optimized condition and 45.9 kJ/mol at the 19.8:1 methanol to FFA ratio. It was found that the 19.8:1 methanol-to-FFA molar ratio worked well only within the FFA range of 15–25% while the suggested 5% sulfuric acid worked well only within the FFA range of 15–35%. Outside these ranges, especially at FFA levels less than 15%, optimization study is necessary. Regression models of methanol and acid dosing have been utilized in two industrial scale biodiesel producing facilities and have successfully reduced the FFA level to less than 0.5%.

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1. Introduction

Biodiesel is considered as a “direct-pour” alternative fuel to petroleum diesel, as it requires almost no modification to most modern diesel engines. Biodiesel can be produced locally and therefore reduces foreign oil dependence. It has been reported that biodiesel combustion can result in less air pollutant emissions, such as carbon monoxide, sulfur dioxide, particulate matter, hydrocarbons, but with slightly higher nitrogen oxides [1]. Since the feedstock of biodiesel is mostly renewable, it significantly reduces carbon dioxide emission during its whole life cycle [2]. But the reliance on virgin oil as biodiesel feedstock raised sustainability concerns, such as the “Food vs. Fuel” debate [3], and consumption of resources such as land and water [4]. In addition, it makes biodiesel less competitive in the fuel market due to the high cost of virgin oil. The cost of the feedstock usually accounts for more than 80% of the total cost in biodiesel production [5]. Therefore, the market fraction of biodiesel from virgin oil has decreased in recent years in the U.S. More and more commercial biodiesel producers are capable of

handling multi-feedstocks which include soybean oil, used cooking oil, and animal fats, etc.

Many studies have reported the production of biodiesel from waste oil feedstock with a few cited here to summarize the advantages and challenges of using waste oils [6–9]. The waste feedstock can range from used cooking oil from restaurants to animal fats from rendering companies. The utilization of waste oil reduces the feedstock cost and increases the sustainability of biodiesel production by minimizing resource consumption [9]. Depending on the cooking process and subsequent storage, the used oils may contain impurities such as water, food residues, and a high free fatty acid (FFA) concentration. The major technical challenge of making biodiesel from low-quality used oil is the pretreatment of FFA. FFA is undesirable during the alkali transesterification process due to the formation of soap, yield loss, and increased difficulty in product separation [9,10]. The earlier practice of caustic stripping is to remove the FFA by forming soap with alkali materials. However, this can result in biodiesel yield loss, more alkaline usage and a potentially delayed phase separation by the excess soap formation from neutralization [11]. The acid-catalyzed transesterification can directly convert both FFA and oil into biodiesel. However, it is not much practiced by the biodiesel producers due to the longer reaction time and lower yield [12]. Instead, the two-step conversion process: an acid-catalyzed esterification pretreatment to lower the FFA content followed by the traditional alkali-catalyzed transesterification [7], is widely used in both industry and laboratory. The acid-catalyzed esterification requires additional acid and methanol usage, but the majority of methanol can

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be reclaimed through a methanol recovery system, which is now commonly installed by biodiesel manufacturers. Table 1 compares the chemical costs and yield loss of caustic stripping and acid-catalyzed esterification pretreatment. The esterification process is currently economically favored.

For the dosage of FFA pretreatment, most industrial biodiesel manufacturers adopt the dosing regimen recommended by a National Renewable Energy Laboratory (NREL) report, which is 2.25 g of methanol and 0.05 g of sulfuric acid for every gram of FFA in the oil (equivalent to 19.8:1 of methanol-to-FFA molar ratio and 5% of acid-to-FFA weight percentage) [11]. Dosage optimization is generally not performed by the commercial producers, while optimal operating conditions are usually sought for in laboratory studies and are summarized in Table 2 [13–31]. The industrial and laboratory values of methanol and acid dosages are not in agreement. The discrepancy is especially significant at FFA levels less than 15%. Farage et al. blended a mixture of soybean oil and sunflower oil at 1:1 ratio with oleic acid to create an oil with 8.50% FFA and found that the optimal chemical usage for esterification was 24:1 methanol-to-FFA molar ratio and 29.4% (weight relative to FFA) acid usage [24]. Hayyan et al. found that the optimal dosages for a sludge palm oil (contains 23.2% FFA) were methanol-to-FFA molar ratio of 13:1 and acid amount of 3.23% (weight relative to FFA) [25]. Optimization of chemical usage is necessary for the oils with various FFA contents.

Therefore the goal of this paper is to evaluate the optimal chemical usage differences between industry and laboratory studies. Optimal conditions of used cooking oil with less than 15% FFA were experimentally determined. The results were integrated with existing studies to better evaluate the efficacy of the NREL regimen. Regression analyses were performed to better evaluate the correlation between the initial FFA content and the optimal chemical usage. Kinetic parameters were calculated to better understand the differences of industrial and laboratory studies.

2. Materials and methods

2.1. Materials

The used cooking oil was collected from restaurants inside the Cincinnati Zoo and Botanical Gardens. The esterification reaction used sulfuric acid (HPLC grade, 99.8%, Pharmco-AAPER) as the catalyst and methanol (HPLC grade, 99.9%, Pharmco-AAPER) as the reactant.

2.2. Experimental set-up and procedure

The esterification was performed in a one-liter three-neck round-bottom flask (Ace Glass Inc.). One neck was equipped with a thermometer to measure the temperature. A water cooled condenser was

connected to another neck on top of the reactor to reduce evaporative loss of methanol. The third neck is used for chemical addition and taking samples. The reactor was placed in a water bath and heated on a hotplate (Fisher Scientific, 11-100-100SH). Methanol and H₂SO₄ were mixed before the reaction and oil were heated to the desired temperature before the addition of methanol and H₂SO₄ mixture. The methanol and oil are immiscible so the agitating speed was kept at 600 revolutions per minute (rpm) to ensure efficient mixing, as suggested by a previous study [13]. For each run, 400 ml of used cooking oil was added into the flask and heated to the desired temperature. 5-ml aliquot of samples was withdrawn from the flask for titration at 5, 10, 20, 30, 60, 90, and 120 minute intervals after the onset of the reaction. The titration of FFA followed AOCS Cd 3d-63, which is a standard method for FFA titration in oil [32].

The effects of three essential operating parameters i.e., reaction temperature, methanol dose and acid catalyst dose on the FFA conversion rates were investigated. The studied temperatures were 35, 45, 55 and 65 °C (approximately the boiling point of methanol) at atmospheric pressure. The quantities of methanol were expressed as methanol-to-FFA molar ratio that varied from 20:1 to 60:1 with 10:1 interval (equal to 3.1, 4.7, 6.3, 7.8, and 9.4 vol.% to oil). Although the esterification reaction requires one mole of methanol for one mole of FFA, in practice excessive methanol is often added since this reaction is reversible [13]. The quantity of sulfuric acid was expressed as weight percentage to FFA and ranged from 5% to 15% with 2.5% increment.

Both the acid value (the absolute value) and the FFA conversion rate (a relative scale) can be used to indicate the completion of acid esterification reaction. The target acid value suggested is less than 2 mg KOH/g (roughly 1% FFA) in order to proceed to the alkali-catalyzed transesterification. In this study, the initial acid value of the used cooking oil was 10 ± 1 mg KOH/g. Hence the FFA conversion rate of 80% was set as a cutoff point to evaluate the effectiveness of the esterification reaction, i.e. whether the end product had reached less than 1% FFA and was suitable for the subsequent alkali-catalyzed transesterification. The FFA conversion rate was calculated by Eq. (1).

$$\text{FFA Conversion} = \frac{(\text{Initial FFA} - \text{Final FFA})}{\text{Initial FFA}} \times 100\% \quad (1)$$

Where:

Initial FFA initial acid value (mg KOH/g)

Final FFA final acid value (mg KOH/g)

2.3. Analytical methods

The properties of the used cooking oil were analyzed by the ASTM and AOCS standard testing procedures as listed in Tables 3.1 and 3.2. The glycerides were analyzed by a Hewlett-Packard gas chromatograph (model 5890) with a flame ionization detector and an auto sampler (model 7673). A Restek Rx-Biodiesel TG column (10 m * 0.32 mm * 0.1 μm) with a 2 m * 0.53 mm guard column was used. The operating conditions followed the ASTM D6584. A small amount of the oil was converted into biodiesel via acid-catalyzed esterification and alkali-catalyzed transesterification for fatty acid compositional analysis (Table 3.1). The chemical composition of methyl esters was analyzed by a Hewlett-Packard gas chromatography (model 5890) and mass spectrometry (model 5970) (GC-MS) system with an auto sampler (model 7673). The operating conditions were: Restek Rxi-5 ms column (30 m * 0.25 mm * 0.25 μm), injector temperature at 250 °C and detector temperature at 250 °C, flow rate of helium 1 ml/min, split ratio of 5:1, oven temperature starting at 40 °C with holding time of 2 min, increasing to 180 °C at 10 °C/min, then to 230 °C at 5 °C/min, and finally to 300 °C at 15 °C/min with holding time of 4 min.

Table 1
Cost comparison FFA pretreatment methods.

FFA% in oil		2.5%	5%	10%	15%
Caustic stripping	Yield loss	2.5%	5%	10%	15%
	Cost (\$/gal)	0.119	0.238	0.476	0.715
	Cost (\$/L)	0.031	0.063	0.126	0.189
Acid esterification	Yield loss	1%	1%	1%	1%
	Cost (\$/gal)	0.040	0.080	0.160	0.240
	Cost (\$/L)	0.011	0.021	0.042	0.063

Notes: The costs of chemicals and sale price of biodiesel are all based on current industrial scale values: prices of sulfuric acid, sodium methylate and methanol are \$5/gal, \$4/gal, and \$1.6/gal respectively, and \$4/gal of sale price for biodiesel is used (due to various federal and local tax credit and incentives program, the sale price of biodiesel could change dramatically). The methanol recovery efficiency is assumed at 80%.

Table 2
Summary of published results on FFA pretreatment.

References	Oil type	FFA (% weight of oil)	Methanol ^a (to FFA molar ratio)	Acid ^b (% weight of FFA)	Temperature (°C)
13	Sunflower	2.99	60:1	5	60
14	Rubber seed	16.88	13:1	6	45 ± 5
15	Pongamia pinnata oil	8.13	37:1	12.3	60
16 First step ^c	<i>Mahua</i> oil (crude extracted oil)	19	16:1	10.76 ^c	60
16 Second step ^c		2.27	103:1	90.06 ^c	
17	Jatropha (crude seed oil)	14.9	36:1	6.7	50
18	Jatropha	14	24:1	20.88	60
19	Palm fatty acid distillate	93.0	8:1	1.83	70
20 First step ^c	Rice bran oil	20	11:1	5 ^e	60
20 second step ^c		2.4	95:1	42 ^e	
21	Crude palm oil	7.5	24:1 (ethanol)	4 ^f	Microwave
22	Tobacco oil	35	18:1	5.71	60
23	Crude palm and rubber seed oil (1:1)	11.90	44:1	4.20	65
24	Sunflower and soybean oil (1:1)	8.50	24:1	29.41	60
25	Sludge palm oil	23.20	13:1	3.23	60
26	Mixed crude palm oil	10	10:1	10	60
27	Waste frying oil	1.01	201:1 ^d	67.3	51
28	Karanja oil	8.80	34:1	0.42 ^f	Microwave
29	Sludge palm oil	22.33	17:1	3.36	60
30	Waste cooking oil	37.96	18:1	10.54	95
31	Waste cooking oil	8.71	23.4:1	5.74 ^f	Microwave

In this study, methanol-to-FFA molar ratio and acid to FFA weight percentage are used instead of reactant to oil ratio or reactant to FFA ratio for easy comparison purposes. The conversion equations are as follows:

$$\text{Methanol} \rightarrow \text{FFA}_{\text{molar\_ratio}} = \left(\frac{\text{methanol}_{\text{to\_oil}}}{\text{MW}_{\text{oil}}} \right) / \left(\frac{\text{FFA}_{\%}}{\text{MW}_{\text{FFA}}} \right)$$

$$\text{Acid} \rightarrow \text{FFA}_{\% \text{weight}} = \frac{\text{acid}_{\text{to\_oil}}}{\text{FFA}_{\%}}$$

The average molecular weights of FFA and oil are calculated by the acid profiles reported in the literatures. Otherwise, 885.46 g/mol, molecular weight of triolein is used as the average molecular weight of oil; and 282.46 g/mol, molecular weight of oleic acid is used as the average molecular weight of FFA [11].

^a The ratio from the original publication has been converted into methanol-to-FFA molar ratio.

^b The acid usage from the original publication has been converted into sulfur acid to FFA wt%.

^c The literature used 2-step acid-catalyzed esterification to lower the FFA level, the optimal conditions of the first and second esterifications were listed separately.

^d The optimal methanol usage was determined in another study by the same authors, we don't have the access to the original thesis.

^e The acid usage was fixed, so the results were not included in the acid usage comparison.

^f The heating resource was different from all other studies, the results were not included in the acid usage comparison due to the lack of temperature control.

3. Results and discussion

The chemical composition of the used cooking oil is listed in Tables 3.1 and 3.2. The fatty acid profile resembled canola oil. The 5% FFA content was higher than the allowable level for direct alkali-catalyzed transesterification. As used cooking oil, the triglycerides level is lower than that of the virgin oil. The FFA is hydrolysis/oxidation by-products of oil due to cooking and storage, and monoglyceride and diglycerides are degrade products of oil. The water, MIU (moisture, insoluble, and unsaponifiables), phosphorous and sulfur levels of the used cooking oil were all in reasonable ranges for making biodiesel. For a biodiesel producer, this used oil is of reasonably good quality.

3.1. Optimization of the esterification process

Fig. 1 shows the effect of reaction temperature on FFA conversion under different methanol usage. The reaction time of 2 h was used based on industrial practices of the pretreatment time. In industrial practice, prolonging reaction time can be used to fix a batch but usually not favored due to resultant cost increase. All of the four figures suggested that the higher the reaction temperature, the more complete the FFA conversion would be. The optimal reaction temperature range was 55–65 °C, which is consistent with most studies listed in Table 2, and also consistent with the industrial practice. In practice, biodiesel manufacturers need to balance the reaction time (2 h) and temperature (~60 °C) to obtain both high yield and low energy consumption.

Table 3.1
Profile of the fatty acid methyl ester from used cooking oil.

Fatty acid profile	Relative wt.%
Lauric acid methyl ester C12:0	0.02%
Myristic acid methyl ester C14:0	0.03%
Palmitic acid methyl ester C16:0	3.34%
Palmitoleic acid methyl ester C16:1	0.13%
Stearic acid methyl ester C18:0	2.09%
Oleic acid methyl ester C18:1	79.75%
Linoleic acid methyl ester C18:2	12.39%
Linolenic acid methyl ester C18:3	2.04%
Arachidic acid methyl ester C20:0	0.22%
Unsaturated methyl esters	94.31%

Table 3.2
Chemical analysis of the used cooking oil used in this study.

Test	Result	Method
Free fatty acid	5.0 wt.%	AOCS Cd 3d-63
Triglycerides	89.6 ± 1.0 wt.%	ASTM D6584
Diglycerides	5.2 ± 0.2 wt.%	
Monoglycerides	1.4 ± 0.2 wt.%	
Density	0.920 g/ml	ASTM D 1298
Water	0.23 v/v%	AOCS Ca 2e-84
Sediment	~0.5 v/v%	AOCS Ca 3d-02
MIU	<1 wt.%	AOCS Ca 3a-46 and AOCS Ca 6b-53
Phosphorous	9.0 ppm	AOCS Ca 20-99
Sulfur	5.6 ppm	AOCS Ca 17-01

Fig. 1. Effect of reaction temperature on acid value.

Meanwhile, Fig. 1 also suggested that FFA reduction is also affected by the methanol-to-FFA molar ratio. When using 50:1 methanol-to-FFA molar ratio and 10% acid, the 2-hour acid values decreased to less than 2 mg KOH/g for all test temperatures. At 40:1 methanol-to-FFA molar ratio, FFA conversions at 45, 55, and 65 °C met the 2 mg KOH/g target, but not at 35 °C (2.2 mg KOH/g). At methanol-to-FFA molar ratio of 30:1, the target FFA value under was only met at 55 and 65 °C. Further reducing methanol-to-FFA molar ratio to 20:1, which is the NREL suggested value, the target acid value could not be met at any temperature.

The impacts of methanol-to-FFA molar ratio on the 2-hour FFA conversion rates are further explained in Fig. 2. The target FFA concentration of 1% is represented by the 80% FFA conversion rate, and all results shown in this figure were with 10% sulfuric acid concentration. The FFA conversion rate increased with methanol-to-FFA molar ratio increasing from 20:1 to 40:1, regardless of reaction temperature. Increasing the methanol-to-FFA molar ratio to 50:1 or 60:1, the 2-hour FFA conversion rates slightly changed. An ANOVA (analysis of variance) single factor test was performed to evaluate if there were statistically significant differences between FFA conversion rates and methanol-to-FFA molar ratios from 40:1 to 60:1. The *p*-values at 45 °C, 55 °C, and 65 °C were 0.35, 0.40, and 0.08 respectively, all larger than the significance level at 0.05, which indicated that changes of conversion rates were not statistically significant when the methanol-to-FFA increased beyond 40:1. Therefore, the optimal methanol-to-FFA molar ratio was determined as 40:1. This result is qualitatively in agreement with some studies,

which reported that the additional methanol did not improve the conversion beyond a certain ratio [13,14].

Fig. 3 shows the effect of catalyst quantity on FFA conversion rate. The methanol-to-FFA molar ratio was fixed at 40:1 for this plot. The range of catalyst quantity, 5–15% (weight, relative to FFA), fitted in the

Fig. 2. Effect of methanol molar ratio to FFA ratio on the 2-hour FFA conversion rate.

Fig. 3. Effect of acid catalyst amount on the 2-hour FFA conversion rate.

ranges reported in Table 2. The conversion rate increased with the catalyst usage from 5 to 10%, and then decreased with further increase of the acid catalyst to 15%. The optimal acid amount was 10% (weight, relative to FFA). Similar result has also been observed by another study, where the conversion rate was reduced with further addition of sulfuric acid after the maximum conversion rate was achieved at a certain sulfuric acid amount [14,27]. This may be due to the excess quantity of sulfuric acid consumes more KOH during neutralization, but is accounted as FFA.

3.2. Comparison of chemical usage

Fig. 4(a and b) summarizes the optimal chemical usages and initial FFA levels from a combination of literature [14–31], the NREL suggested value used by biodiesel producers, and data from this study. Fig. 4a indicates that the methanol dosage is reasonably correlated to the FFA level, with an R^2 of 0.77. It is also suggested that the NREL suggested dose is suitable for the oil with 15 to 25% FFA. For the oil with FFA higher

than 25%, the 20:1 methanol ratio is overdosed, which results in unnecessary methanol input and more energy input for methanol recovery. For FFA less than 15%, the methanol ratio is underdosed and the esterification reaction may not be complete in the desired time period. As shown in this study, when using 20:1 methanol-to-FFA ratio (Fig. 1), none of the experiments could reach the target yield in the reaction time window. The longer reaction time was necessary to complete the reaction, which required extra energy input and slowed down the production. Unfortunately, the major underdosed range lies in the yellow grease range, which is defined as the oil with FFA less than 15% by biodiesel industry. Generally, the acid esterification could pretreat the oil with FFA up to 20%, so the biodiesel industry strongly prefers yellow grease to brown grease. For oils with less than 15% FFA, an optimization study is necessary to not only maintain high reaction yield and good final product quality, but also lower the chemical cost and energy consumption. Fig. 4b shows the optimal acid usages and initial FFA levels from various studies [13,14,18–20,22–27,29–31]. Similar to the methanol usage, the relationship between optimal acid amount and the initial FFA percentage is not linear. The lower R^2 for the regression suggests that the FFA to acid correlation is not as strong as that of FFA to methanol. In the middle FFA level, roughly between 15 and 35%, the NREL suggested dose is close to the regression curve, while in the low FFA range (<15%), NREL dose is underdosed and in the high FFA range (>35%), NREL dose is overdosed. Again, this suggests the necessity of optimization tests for yellow grease.

Two biodiesel producers, Bluegrass Biodiesel (10 million gallons per year production capacity) and Greenleaf Biofuels (20 gpm feedstock flow rate), have used both the NREL dosing suggestion, and the optimized dosage based on the regression model (Fig. 4a and b) with their feedstock. Results shown in Table 4 indicated that using optimized dosage improved product yield as compared to the NREL suggested value when FFA ranges were outside of the effective NREL range of 15–35%.

3.3. Parametric analysis

The experimental results indicated that the 2-hour FFA conversion rate could be affected by the reaction temperature, methanol and sulfuric acid quantities. To evaluate the relative contribution of each factor, a multivariable linear model and a multivariate quadratic model were

Fig. 4. a. Comparison of methanol usage between laboratory and industrial practices. b. Comparison of H_2SO_4 usage between laboratory and industrial practices.

Table 4

Yield of esterification comparison between the suggested and optimized dosages by two biodiesel producers.

Initial FFA content	NREL dose			Optimized dosage from Fig. 4 (tested in two biodiesel plants)		
	Methanol-to-FFA molar ratio	Catalyst-to-FFA wt%	Yield %	Methanol-to-FFA molar ratio	Catalyst-to-FFA wt%	Yield %
2.5%	19.8:1	5%	80.0	89.3	19.8	92.0
6%			86.7	48.9	12.4	95.8
10%			90.0	34.3	9.4	96.6

employed. Similar approach was applied in other environmental data analysis [13,14]. The parametric analysis results could be used as a guide for industrial production to predict the reaction yields.

The linear model is expressed as the following Eq. (2).

$$y = \beta_0 + \beta_1 T + \beta_2 A + \beta_3 M \quad (2)$$

Where:

y the FFA conversion rate after two hours;
 β_i ($i = 0 \sim 3$) coefficient for each variable
 T temperature ($^{\circ}\text{C}$)
 A catalyst amount weight percentage to FFA
 M methanol-to-FFA molar ratio

The non-linear model is expressed as the following second-order polynomial Eq. (3).

$$y = \beta_0 + \beta_1 T + \beta_2 A + \beta_3 M + \beta_{11} T^2 + \beta_{22} A^2 + \beta_{33} M^2 + \beta_{12} T \times A + \beta_{13} T \times M + \beta_{23} A \times M \quad (3)$$

β_{jk} ($j = 1 \sim 3, k = 1 \sim 3$) correlation coefficients for each variable to be determined.

Other denotations are the same as in Eq. (2).

The results of analysis of variance (ANOVA) are listed in Table 5. Both linear and non-linear models have high F -values, at 35.41 and 32.21 respectively. The R^2 of the linear model is 0.57, and the non-linear model has an R^2 of 0.77, which indicates that the non-linear model fits the experimental data better. The correlation coefficients between the 2-hour FFA conversion rate and each contributing parameter in the non-linear model are listed in Table 6. The four highest correlation coefficients are $T \times M$ (Temperature * Methanol-to-FFA molar ratio), T (Temperature), Methanol, and T^2 (Temperature²) at 0.70, 0.57, 0.55, and 0.54 respectively. This indicates that reaction temperature has the highest

impact on FFA conversion rate, followed by methanol-to-FFA molar ratio. These results are consistent with experimental observations, as well as other studies in Fig. 4a and b. The comparison of experimental and predicted two hour conversion rates is shown in Fig. 5. Almost 90% of the experimental conversion rates (76 out of 85) are within $\pm 15\%$ of the predicted range.

3.4. Reaction kinetics

The acid-catalyzed esterification is a reversible reaction. However, given the significantly excessive methanol use as compared with FFA, the reverse reaction could be neglected [13]. Some studies have suggested that the experimental data could fit into a first-order reaction [13]. Hence, the activation energy can be determined by Arrhenius equation, shown below:

$$k = Ae^{-\frac{E_a}{RT}} \quad (4)$$

where: k is the reaction rate constant (min^{-1}) derived from pseudo-first order reaction. A is the pre-exponential factor (min^{-1}) and E_a denotes the activation energy ($\text{J} \cdot \text{mol}^{-1}$). R and T stand for ideal gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) and temperature (K), respectively.

E_a and A can be determined by plotting the “ $\ln(k)$ vs T^{-1} ” graph, and the results are listed in Table 7. The R^2 for all calculations are between 0.95 and 0.99, which indicate a good fit of experimental data with the equation. With H_2SO_4 as the catalyst, the activation energy ranged from 20.7 to 45.9 kJ/mol, which is within the range of the existing results [13,15,33,34]. Using methanol-to-FFA molar ratio of 40:1, the activation energies decreased from 5 to 12.5% acid usage and then greatly increased at 15% acid usage. With the fixed acid usage of 10%, the activation energy decreased with the increasing methanol-to-FFA molar ratio from 60:1 to 50:1 and then sharply increased. The low activation energies at methanol-to-FFA molar ratio of 40:1 to 50:1 and 10–12.5% (weight relative to FFA) acid quantity were consistent with higher FFA conversion rate observed at these reaction conditions. Furthermore, if we were to use the NREL suggested methanol-to-FFA molar ratio of 20:1 or 5% acid, the resultant E_a would be the largest, which would affect the effectiveness of the pretreatment.

4. Conclusions

In this study, the differences of laboratory and industrial practices on the FFA pretreatment reaction were evaluated, and the used vegetable oil with $5 \pm 0.5\%$ FFA was pretreated via an acid-catalyzed esterification to better understand the difference. The optimal condition of this used cooking oil: 55–65 $^{\circ}\text{C}$, the methanol-to-FFA molar ratio of 40:1, and sulfuric acid (catalyst) usage of 10% (weight relative to FFA), fell out of the suggested values used by the biodiesel industry. It is found that the suggested 20:1 methanol-to-FFA molar ratio worked well within FFA range of 15–25% and the suggested 5% acid amount worked well within the FFA range of 15–35%. Outside these ranges, an optimization study is necessary since the esterification reaction might not proceed with these conditions. For yellow grease (FFA less than 15%), the suggested 20:1 methanol-to-FFA molar ratio and 5% acid use may result in underdose. The correlation between the initial FFA level and the methanol-to-FFA ratio was found stronger than that between the initial

Table 5

Statistical analyses of linear and non-linear regression models.

	Linear model		Non-linear model	
	Coefficient	p -Value	Coefficient	p -Value
β_0	0.105	0.214	−1.25	1.36E−5
β_1	0.0083	4.76E−10	0.058	7.5E−8
β_2	−0.9E−3	0.827	−	−
β_3	0.0073	1.76E−9	0.016	0.03
β_{11}			−0.4E−3	0.16E−3
β_{22}			−0.004	5.64E−5
β_{33}			−0.3E−3	5.97E−7
β_{12}			−0.5E−3	0.198
β_{13}			−0.2E−3	0.029
β_{23}			0.0027	0.1E−3
R^2	0.567		0.77	
Standard error	0.106		0.080	
F -value	35.41		32.21	
Significance F	<0.001		<0.001	

Table 6

Correlation coefficients between 2-hour FFA conversion rate and factors.

	T	A	M	T ²	A ²	M ²	T × A	T × M	A × M
2-hour FFA conversion rate	0.57	0.0073	0.55	0.54	−0.011	0.49	0.31	0.70	0.40

FFA and sulfuric acid dosages, indicating quantity of methanol is more crucial to the esterification reaction. The activation energies of the esterification reaction for the test oil ranged from 20.7 to 45.9 kJ/mol. The lowest activation energy was obtained with the optimized chemical dosage, while the highest activation energy was obtained under the operation conditions used by the industry (NREL recommended dosages).

Disclaimer

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Fig. 5. Comparison of predicted and experimental the 2-hour FFA conversion rate.**Table 7**

Energies of activation and frequency factors of acid-catalyzed esterification of FFA.

Methanol-to-FFA molar ratio	Sulfuric acid % wt to FFA	Ea (J/mol)	A	R ²
40	15%	38798.94	19747.85	0.99
40	12.5%	20746.76	43.25	0.99
40	10%	24440.67	207.41	0.96
40	7.5%	34370.91	6666.83	0.96
40	5%	42007.32	97831.32	0.95
60	10%	29235.35	1241.90	0.96
50	10%	23132.04	128.32	0.97
40	10%	24440.67	207.41	0.96
30	10%	43106.43	150843.8	0.95
20	10%	45936.51	179512.5	0.96

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