

Kinetic Study of Esterification of Palm Fatty Acid Distillate Using Sulfonated Glucose Prepared via Microwave-Assisted Heating Method

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Kinetic models play an important role especially in designing reactor, simulation and optimization of a particular chemical reaction. In this study, kinetic model of the esterification of palm fatty acid distillate (PFAD) using sulfonated incomplete carbonized glucose (SO₃H/ICG) prepared via microwave-assisted heating method was developed. D(+)-Glucose was carbonized in a microwave to produce incomplete carbonized glucose (ICG). Then the ICG was sulfonated with H₂SO₄, heated in a microwave and stirred. The catalyst prepared was then used for esterification of PFAD at reaction temperatures of 65 °C, 75 °C and 85 °C. The highest conversion exhibited was 95.76 % performed at 85 °C, 2.5 wt% catalyst, 10:1 molar ratio of methanol to PFAD, 120 min reaction time. A kinetic model of PFAD's esterification was developed and the model was described as a pseudo first-order reaction rate law. The value of the activation energy was 28.8 kJ/mol with R² of 0.985.

1. Introduction

Biodiesel, scientifically identified as fatty acid methyl esters (FAME) is getting acknowledged due to its properties which effectively reduce the emission of greenhouse gases (GHG) to atmosphere. The usage of biodiesel especially in transportation provides the environment a possible solution to the alarming air pollution problems. However, synthesis of biodiesel consumes high cost and energy (Mohammadshirazi et al., 2014). Part of it was due to that fact that vegetable oil which was used as biodiesel feedstock competes with the food industry. Hence, second and third generation biodiesel that employs inedible sources emerged in the form of biomass and engineered crops. Palm fatty acid distillate (PFAD) (Saimon et al., 2018) and algae (Peralta-Ruiz et al., 2018) had been used as biodiesel feedstock which possess substantial potential in cost reduction.

Esterification of the feedstock with high free fatty acid (FFA) requires the existence of heterogeneous acid catalyst to avoid saponification and separation problem (Gaurav et al., 2019). The biodiesel production is started with a lab-scale to a pilot-scale and demonstration scale and finally develops into an industrial-scale production. In order to operate an industrial-scale biodiesel production efficiently, kinetic study is the most important aspect to be comprehended. It is a powerful tool in designing reactor for synthesis of higher added-value products of chemical processes. The development of kinetic model will be a great help for the process simulation (Harsha Hebbar et al., 2018). In order to scale up a process, the concentration of reactants, temperature of the reaction as well as the pressure profile should be determined through reactor modeling (Chai et al., 2014).

Through a kinetic study on the esterification reaction, the parameters to predict the extent of reaction under particular reaction conditions will be provided. Basically a kinetic study will be covering the determination of reaction rate equation, rate constant as well as activation energy (Marchetti et al., 2011). Years of study shown that description of the kinetics of esterification for biodiesel remains controversial. There are conflicting findings on the reaction order and the estimation of reaction rate constants (Turner, 2005). Various researchers are more focused on determining the best fit of empirical data to simple models of reaction order (Silva et al., 2009). Common acid or base catalyst esterification adopt kinetic model developed by (Bernard Freedman et al., 1986). This study promotes the development of acid heterogeneous catalyst prepared via

microwave-assisted heating technique to esterify the PFAD with methanol. The main objective of this study is to develop a kinetic model from esterification of PFAD with methanol using the prepared catalyst. It is imperative to investigate the performance of reaction kinetic resulted from the catalyst that is prepared from a non-conventional approach. Most of the previous study is mainly developed a kinetic model from transesterification. This kinetic model is also applicable to esterification of high free fatty acid using sulfonated glucose via microwave-heating method.

2. Methodology

2.1 Materials

PFAD was supplied by Mewaholeo Industries Sdn. Bhd., Pasir Gudang, Johor and and methanol (95 %) was supplied by Merck chemical company. Materials to synthesis catalyst include D(+)-Glucose, potassium hydroxide (KOH) as well as sulphuric acid (H_2SO_4), which were bought from J.T. Baker. All chemicals were all analytical grade products, thus no further purification is required.

2.2 Catalyst preparation

ICG was produced from heating 20 g of D(+)-glucose powder in microwave. The ICG produced was crushed into powder form. Sulfonated glucose is prepared by heating 4g of ICG with 158.11 mL concentrated H_2SO_4 at 7.5 min, using 400 W of microwave's power level and stirred at 700 rpm. All parameters were obtained from the result of optimization of the sulfonation process. The mixture was then washed with hot distilled water and filtered until the filtrate turn to a clear solution. The purpose of the washing is to remove the excess sulphate ions and impurities from the precipitate. The moisture of the sulfonated glucose produced was removed by heating inside a microwave for 10 min. Characterizations of the sulfonated glucose catalyst have been described in our previous work (Saimon et al., 2019).

2.3 Esterification of PFAD

PFAD was liquefied at 70 °C. The amount of the feedstock was prepared based on the 10:1 molar ratio of methanol and PFAD. The preheated PFAD was poured into a 100 mL three-necks-round-bottom-flask. The reflux condenser was installed onto the neck of the flask mainly to re-condense the evaporated methanol. As shown in Figure 1. The methanol and 2.5 wt% sulfonated glucose catalyst were added into the flask and heated at 65 °C, 75 °C and 85 °C for 2 h. 2.5 wt% of the prepared catalyst is selected based on the previous literature review (Lokman et al., 2015). Then the liquid was poured into a separating funnel and was allowed to settle for around 60 min. The bottom layer containing FAME was collected and the conversion of the PFAD to methyl ester was calculated using Eq(1) and (2):

$$\text{Acid value} = N \times M_w \text{ KOH} \times \text{Volume of KOH titrate used (mL)} / \text{mass of biodiesel} \quad (1)$$

where N is normality of KOH and M_w is molecular weight of KOH (56.11 g/mol).

$$\text{FFA conversion (\%)} = (\text{Acid value of PFAD} - \text{Acid value of sample}) \times 100 / (\text{Acid value of PFAD}) \quad (2)$$

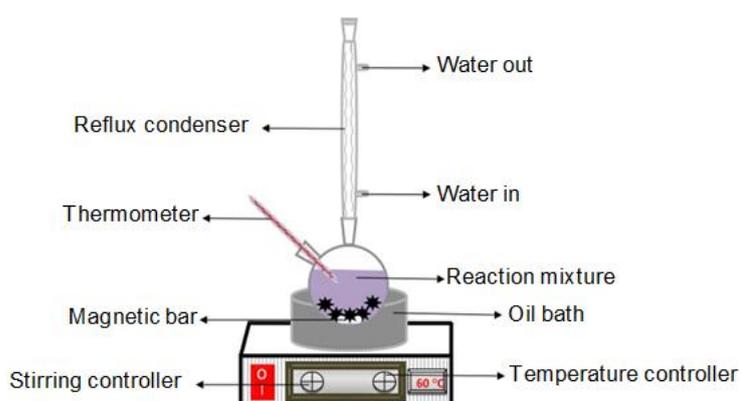


Figure 1: Experimental set-up for the esterification reaction.

2.4 Kinetic Modelling

The activation energy (E_a) can be determined by using Arrhenius Eq(3) as shown below:

$$k = Ae^{-E_a/RT} \quad (3)$$

where A is the frequency factor, R is $8.31 \text{ Jmol}^{-1}\text{K}^{-1}$ and T is temperature in K.

The E_a can be calculated via integration of the Eq(3) and expressed as Eq(4) and Eq(5) as follow:

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

$$\ln k = -E_a/R (1/T) + \ln A \quad (5)$$

Generally, Eq(5) can be defined as $y=mx+c$ thus, E_a can be determined by the slope of the $\ln k$ against $1/T$ graph as shown in Eq(6) below:

$$\text{Slope} = E_a/RT \quad (6)$$

Thus, the activation energy can be calculated by Eq(7):

$$E_a = \text{slope} \times RT \quad (7)$$

Esterification of PFAD with methanol catalyzed by $\text{SO}_3\text{H/ICG}$ to produce FAME and water can be described by the reaction in Eq(8):



Eq(8) can be simplified as Eq(9) as follows:



The rate of reaction for Eq(9) can be described mathematically as Eq(10):

$$-r_A = -d[A]/dt = k_1 [A]^a [B]^b - k_2 [C]^c [D]^d \quad (10)$$

which $-r_A$ is the reaction rate of the PFAD; k_1 and k_2 are reaction rate constant and equilibrium constant; [A] is the concentration of PFAD; [B] is the concentration of methanol; [C] is concentration of FAME while [D] is concentration of water.

The kinetic model is based on several assumptions: (i) concentration of methanol is constant due to the excess of methanol used (ii) the reverse reaction can be neglected due to the excessive methanol (Berrios M, 2007). Thus, $[B]^b$ is assumed fixed and $k_1[B]^b$ can be symbolized as k . The reversible reaction from Eq(9) can be ignored. The rate of reaction after following the assumptions can be written as in Eq(11) and Eq(12) as follow:

$$-r_A = -d[A]/dt = k[A] \quad (11)$$

$$d[A]/[A] = -kdt \quad (12)$$

the integration of Eq(12) will obtain following Eq(13):

$$\ln [A_0] / [A] = -kt \quad (13)$$

which $[A_0]$ is the initial concentration of the PFAD and [A] is the concentration of the PFAD at time t. k value is obtained using non-linear regression which basically provides the Sum of Square Quake Error (SSE) between the experimental data and the calculated data as shown in Eq(14) below.

$$\text{SSE} (k) = \sum (X_{\text{exp}} - X_{\text{calc}})^2 \quad (14)$$

3. Results and discussion

Table 1 tabulates the conversion of PFAD to biodiesel for both experimental and calculated esterification reaction taking place at 10:1 molar ratio of methanol to PFAD; 2.5 wt% catalyst; for 120 min of reaction time. Based on Table 1, highest conversion obtained from the esterification process of PFAD and methanol using the prepared sulfonated incomplete glucose acid catalyst was 95.76 % at 85 °C of reaction temperature. Figure 2 illustrates the experimental and calculated PFAD conversion (%) at 65 °C, 75 °C and 85 °C. Via best fit curve, it can be observed that the percentage FFA conversion increased from between 31-36 % to between 80-100% at the end of the experiment. Extending experiment time would result in 100 % FFA conversion but may not be economically viable due to various cost factor such as power consumption management and

others. Hence, it is best to optimize the reaction synergistically through the operating temperature, catalyst mass, catalyst acid strength and other factors.

Table 1: Conversion of PFAD (X), experimental and calculated in esterification of PFAD at 10:1 molar ratio of Methanol to PFAD; 2.5 wt% catalyst; for 120 min of reaction time

Temp °C	65			75			85		
time, min	$X_{A_{exp}}$	$X_{A_{calc}}$	Error ²	$X_{A_{exp}}$	$X_{A_{calc}}$	Error ²	$X_{A_{exp}}$	$X_{A_{calc}}$	Error ²
0	33.67	49.0742	0.2093	35.63	52.9575	0.2365	32.33	54.2949	0.4616
12	38.97	51.2552	0.0994	39.55	54.9018	0.1507	41.02	58.9414	0.1909
24	43.75	53.2221	0.0469	43.19	56.7072	0.0980	48.19	62.7752	0.0916
36	49.33	55.5183	0.0157	50.93	60.5463	0.0357	59.61	68.8815	0.0242
48	55.04	57.8680	0.0026	59.31	64.7028	0.0083	66.34	72.4800	0.0086
60	64.66	61.8266	0.0019	69.21	69.6132	0.0000	72.44	75.7417	0.0021
72	68.22	63.2915	0.0052	75.73	72.8471	0.0014	79.52	79.5273	0.0000
84	71.09	64.4725	0.0087	81.66	75.7884	0.0052	83.31	81.5539	0.0004
96	75.49	66.2831	0.0149	85.83	77.8567	0.0086	89.16	84.6819	0.0025
108	78.31	67.4436	0.0193	87.04	78.4568	0.0097	92.31	86.3662	0.0041
120	80.44	68.3201	0.0227	87.43	78.6503	0.0101	95.76	88.2109	0.0062
		k=	0.4466		k=	0.5641		k=	0.7922

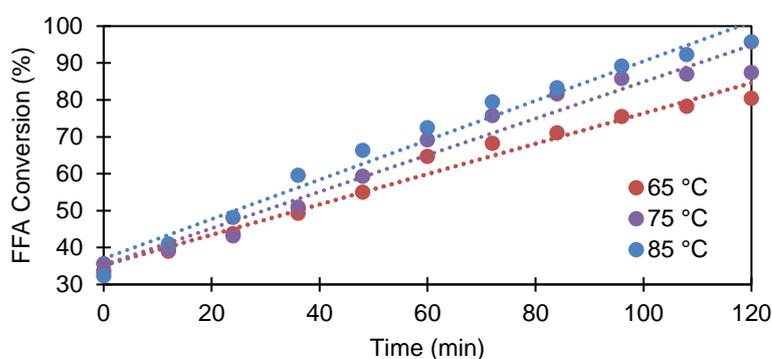


Figure 2: Experimental and calculated PFAD conversion (%) at 65 °C, 75 °C and 85 °C.

Based on Figure 3, the slope obtained is 3,464, thus the activation energy calculated is 28.8 kJ/mol and the collision frequency factor, A is equivalent to $8.124 \times 10^{-5} \text{ min}^{-1}$. The data shows that the increment of temperature will increase the k value as well. Reaction occur when particles collide with each other. If temperature is increased, the particles are frequently move and collide thus speeding up the rate of reaction (Gaurav et al., 2019). This study fits to first order reaction. Talebian-Kiakalaieh (2013) also found the same order of reaction for the forward reaction in trans-esterification of free waste cooking oil (WCO) by heteropoly acid (HPA) catalyst by making similar assumption of high methanol concentration employed in the reaction (Talebian-Kiakalaieh et al., 2013).

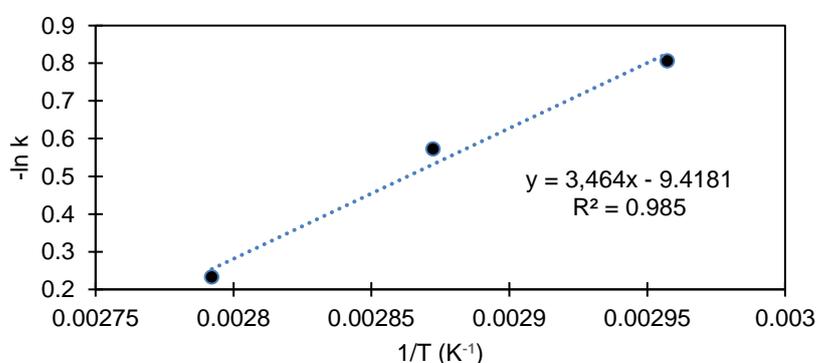


Figure 3: Graph of $-\ln k$ versus $1/T$ (K^{-1}) for Arrhenius equation of the esterification reaction

Table 2 shows the comparison of the kinetic study of esterification from various feedstocks using acid heterogeneous catalyst. Based on the Table 2 below, it can be seen that activation energy of this study is comparable and the lowest among the activation energy from other study. Wang et al. (2019) obtained the lowest activation energy which is 24.7 kJ/mol, however the catalyst prepared took quite a long time since the catalyst is conventionally prepared by sulfonation for 16 h. Shu et al. (2019) manages to obtain E_a value of 32.7 kJ/mol from esterification of oleic acid and F-SO₂⁻⁴/MWCNTs catalyst. The catalyst was also prepared in 30 to 60 min at higher temperature which was between 500 to 700 °C. Li et al. (2018) managed to obtain 47.9 kJ/mol of the activation energy, a little bit higher than the rest by using rubber seed oil as the feedstock and SO₄²⁻/ZrO₂ as the catalyst which was prepared at 550 °C for 4 h. Lieu et al. (2016) however obtained the highest activation energy of 53.7 kJ/mol using Ceiba pentandra seed oil and H₂SO₄ as a catalyst. The esterification of the seed oil was done in a microwave and obtained 94.43 % of FFA conversion. Mazubert et al. (2014) also study the esterification of waste cooking oil in a microwave using H₂SO₄ as a catalyst and obtained 37.1 kJ/mol of activation energy. These two studies were proofs that the microwave irradiation is an effective tool for biodiesel pretreatment. However, most of kinetic study using microwave heating method offered within the range of esterification process and not covering the preparation of catalyst using microwave-irradiation thoroughly. Most of the activation energy values in Table 2 are almost analogous with this study, however, the preparation of the catalyst offers significant differences in term of the energy utilization and time consumption.

Table 2: Comparison of kinetic study using acid heterogeneous esterification reaction

Feedstock	Catalyst	Reaction order	Activation Energy, E_a (kJ/mol)	Pre-Exponential factor, A	References
Oleic Acid	Zr-SO ₃ H	1 st	24.7	134.4 min ⁻¹	(Wang et al., 2019)
Oleic Acid	F-SO ₂ ⁻⁴ /MWCNTs	2 nd	32.7	1.88 L/mol.h	(Shu et al., 2019)
Canola + 10 % Palmitic Acid	HSiW/Al ₂ O ₃	2 nd	32.9	7.9 x 10 ⁻² mol/g.min	(Gaurav et al., 2019)
Rubber Seed Oil	SO ₄ ²⁻ /ZrO ₂	1 st	47.9	7.71 x 10 ⁶ mol/L.min	(Li et al., 2018)
PFAD	Tulsion 42SM	1 st	34.0	n/a	(Augustia et al., 2018)
Ceiba Pentandra Seed Oil	H ₂ SO ₄	2 nd	53.7	3.98 x 10 ⁹ min ⁻¹	(Lieu et al., 2016)
Waste Cooking Oil	H ₂ SO ₄	-	37.1	1.3 x 10 ⁶ L/mol/min	(Mazubert et al., 2014)
PFAD	ICG/SO ₃ H	1 st	28.8	8.124 x 10 ⁻⁵ min ⁻¹	This study

4. Conclusions

This study revealed that the sulfonated glucose catalyst prepared via microwave-assisted heating method produced better PFAD conversion to methyl ester as reaction temperature increase. The PFAD conversion obtained was 95.76 % using 2.5 wt% sulfonated glucose catalyst. The esterification of PFAD followed pseudo first-order reaction with R² value 0.985 and 28.8 kJ/mol of activation energy. The study attained in this work is comparable with others recent investigations.

For future work, it is highly recommended to use the pre-exponential factor (A) and activation energy (E_a) obtained from this study to expand the reaction to pilot and commercial scale. This is imperative to evaluate the viability of the reaction on a higher scale and to enable adjustment to be made if necessary.

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