

## Preparation of Ti-SO<sub>3</sub>H/ICG Using Microwave-Assisted for Esterification of Palm Fatty Acid Distillate to Methyl Ester

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The utilisation of low-cost yet valuable feedstock such as palm fatty acid distillate (PFAD) in the replacement of edible oils have a great potential in solving high-cost problem in biodiesel industries. Heterogeneous solid acid catalyst is the most proficient to esterify the feedstock containing high free fatty acid (FFA). Most of the prepared catalysts from the previous studies were produced using a conventional heating method which is basically time and energy consuming. The development of heterogeneous solid acid catalyst from sulfonated glucose and impregnation with titanium (Ti-SO<sub>3</sub>H/ICG) was prepared by using a microwave-assisted heating method with various heating time during the sulfonation process. The heating times taken were 3, 5, 7 and 9 min for acid treatment using H<sub>2</sub>SO<sub>4</sub>. The catalysts showed an outstanding result in reducing the catalyst separation problem and efficiently producing high percentage yield of biodiesel. The physical and chemical properties of the modified catalyst were analysed by using Temperature Programmed Desorption-Ammonia (TPD-NH<sub>3</sub>) and Brunauer-Emmett-Teller (BET). 7 min Ti-SO<sub>3</sub>H/ICG showed the best performance catalyst due to its high surface area and acid site density, which were 78.37 m<sup>2</sup>/g and 15.16 mmol/g. The catalyst showed highest percentage yield and conversion of 98.92 % and 80.24 % at 70 °C, with a molar ratio of methanol to PFAD of 10 : 1, 2.5 wt% of catalyst loading and 90 min of reaction time. A kinetic model was studied and the activation energy (E<sub>a</sub>) obtained was 13.43 kJ/mol.K, the lowest value recorded as compared with the activation energy from previous studies in related field.

### 1. Introduction

The study on renewable energy has been widely investigated to fulfil the world's demand for energy. Renewable energy, including solar, wind, hydro and energy from biomass and waste, has been highlighted over the past decade due to its potential to substitute the fossil fuel (Popp et al., 2014). The renewable energy from combustible energies such as biodiesel, should enter the energy market intensively in the near future to diversify the global energy sources.

Palm oil is commonly used as the raw feedstock (Chen et al., 2015) for biodiesel production. However, the increment of the palm oil prices is forcing the researchers to look for another low-cost feedstock. Previous studies revealed the palm fatty acid distillate (PFAD), a by-product from the refinery of crude palm oil, consists more than 85 wt% of free fatty acid (FFA), serving as a promising biodiesel feedstock candidate (Lokman et al., 2016a). Apart of having quite a stable property and abundantly available, PFAD is being proposed to have high potential as a valuable, low-cost raw material for biodiesel production. The conversion of this kind of feedstock into a valuable product requiring a very good acid catalyst because of the high content of FFA (Hidayat et al., 2015). A solid acid (heterogeneous) catalyst is well known to have a unique advantage in esterification and trans-esterification reactions, which enhances the use of high acid value oil as a feedstock for biodiesel synthesis. Previous studies proved the effectiveness of glucose to esterify high FFA feedstock for biodiesel production (Lokman et al., 2016b). A similar study was reported using direct-ultrasonic irradiation to transesterify a high FFA feedstock and successfully reduced the FFA level from 42 % to 0.2 % (Amin et al., 2015). Common preparations of glucose-based acid catalyst involve a series of heating process which consumed lots of time and energy. Instead of preparing the catalyst through traditional methods, a microwave-assisted technology was proposed to replace the heating process of the catalyst. The application of

microwave-assisted process instead of using conventional heating has been fully depicted in the peer-reviewed literature and books. One of the benefits of using microwaves is the reduction in the time scale in conjunction with lower energy consumption (Benavente et al., 2015). Microwave heating is able to reduce the number of steps involved in the global process, eliminating the need for other reagents or devices (Benavente et al., 2015). Microwave heating offers a non-contact heating, rapid heating, quick start-up and stopping, and higher level of safety and automation (Menéndez, 2010).

The efficiency of biodiesel production using microwave-assisted is widely known. The catalyst prepared via microwave-assisted is not being applied in wide range of research. This study showed a novel preparation of sulfonated glucose-based catalyst impregnated with titanium (Ti-SO<sub>3</sub>H/ICG) mainly to esterify the PFAD. This type of heterogeneous acid catalyst is low in cost, easier in preparation process, high effectiveness, greener and suitable for esterification of feedstock containing high FFA (Lokman et al., 2016b). The sugar catalyst are physically robust and there is no leaching of SO<sub>3</sub>H groups during utilisation. This catalysts exhibits a high and stable activity during the esterification reactions (Lou et al., 2008). In this study, the use of microwave irradiation in catalyst preparation for esterification of PFAD was carried out, characterised and analysed to determine its performances. The catalysts were then tested, and the study of the kinetics of the reaction was performed.

## 2. Materials and methods

### 2.1 Chemicals and materials

The main feedstock, PFAD was originally supplied by Mewaholeo Industries Sdn. Bhd., Pasir Gudang, Malaysia. Commercialised D(+)-Glucose was purchased from QReC (Asia) Sdn. Bhd., Selangor, Malaysia. Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), potassium hydroxide (KOH) and Titanium (IV) Isopropoxide were purchased from J.T. Baker. The acyl acceptor used is methanol (95 %), and analytical grade toluene was supplied from Merck. The standard methyl esters for GC analysis such as methyl palmitate, methyl oleate, methyl stearate, methyl linoleate and methyl myristate were purchased from Sigma-Aldrich chemical company.

### 2.2 Preparation of catalyst

The methods were originally from Zong et al. (2007) and Lou et al. (2008) and were modified for the catalyst preparation. Around 20 g of D(+)-Glucose was heated using medium high power level (560W) for 15 min in a microwave model Sharp R213CST. The resultant black carbon, incomplete carbonised glucose (ICG) was then crushed into powder form. Then, 4 g of the ICG was added into 100 mL of concentrated sulfuric acid and heated inside a microwave for 3, 5, 7 and 9 min. The mixture, SO<sub>3</sub>H/ICG was taken out from the microwave and distilled water was used to dilute the catalyst produced. The black precipitate was collected by filtration method and washed again using hot distilled water with temperature of 80 °C until the filtrate became a clear solution. This is mainly to remove any excess sulphate ions and impurities from the precipitate. The SO<sub>3</sub>H/ICG was heated again in a microwave for about 10 min to remove all the moisture. 5 g of dried SO<sub>3</sub>H/ICG was impregnated with 7.5 mL titanium (IV) Isopropoxide by immersed it in 20 mL of toluene. The mixture of titanium and toluene was then stirred until all the toluene was completely evaporated at 100 °C. The solid form inside the beaker was washed with ethanol to remove the residual toluene and subsequently dried at 110 °C in oven for overnight. The last step was calcination of the Ti-SO<sub>3</sub>H/ICG at 500 °C for 2 h in a furnace.

### 2.3 Catalyst Characterisation

The characterisations for the catalyst produced were Temperature Programmed Desorption – Ammonia (TPD-NH<sub>3</sub>) as well as Brunauer-Emmett-Teller (BET). The surface area of the catalyst was measured by using BET (Brunauer-Emmet-Teller). The sample of catalysts were degassed and heated overnight at 150 °C. The TPD-NH<sub>3</sub> (micromeritics AutoChem II) was used to identify the density of the acid sites.

### 2.4 Catalytic activity

The PFAD and methanol were weighed based on the molar ratio of 10 : 1. The PFAD was then liquefied by proper heating at 70 °C. Preheated PFAD will be firstly poured into the three necks round bottom flask following by methanol and 2.5 wt% of catalyst loading. The solution in the three necks round bottom flask was then refluxed to 70 °C for about 90 min of reaction time. The mixture was poured into a separating funnel and was allowed to settle for around 30 min. The biodiesel layer was then separated and purified by the water washing process.

### 2.5 Analysis of PFAD methyl ester

The biodiesel sample for analysis was prepared by using a ratio of 1 : 40 (biodiesel:methanol). The sample was sent to laboratory for GC/FID analysis in order to determine the yield percentage. The conversion of the

PFAD was determined through an acid-base titration method. About 1 mL of biodiesel was added into 20 mL of the solvent, methanol. The mixture was then shaken until completely dissolved. 2 to 3 drops of phenolphthalein was added into the flask and titrated with standardised potassium hydroxide (KOH) solution until the first permanent pink colour showed up. The formulas to calculate the yield percentage, acid value and percentage of conversion were defined by Eq(1), Eq(2) and Eq(3).

$$\text{Yield (\%)} = \frac{\text{Ester content} \times \text{weight of product (g)} \times 100 \%}{\text{Mass of PFAD feedstock (g)}} \quad (1)$$

$$\text{Acid value} = \frac{N \times \text{MW KOH} \times \text{Volume of KOH titrate used (mL)}}{\text{Mass of biodiesel (g)}} \quad (2)$$

Where,

N = Normality of KOH used

MW = Molecular weight of KOH: 56.11 g/mol

$$\text{Percentage conversion (\%)} = \frac{(\text{Acid value of PFAD} - \text{Acid value of sample}) \times 100 \%}{\text{Acid value of PFAD}} \quad (3)$$

### 3. Results and discussions

#### 3.1 Characterisation of catalyst

Table 1 shows the density of the acid sites of the catalyst produced. The acid sites density was determined through TPD-NH<sub>3</sub>. Figure 1 shows all ammonia desorption curves for 3, 5, 7 and 9 min ICG treated with H<sub>2</sub>SO<sub>4</sub> and impregnated with titanium. It was observed that obvious desorption of ammonia occurred at two events, which were around 180 °C - 310 °C and around 450 °C - 700 °C. The broad peak culminated within 450 °C - 700 °C proves the existence of strong acid sites. 7 min Ti-SO<sub>3</sub>H/ICG showed the highest density of the acid site which was up to 15.16 mmol/g. This broad peak at higher temperature proved the presence of strong Brønsted acid sites.

Table 1 reveals that the surface area of the catalyst is significantly reduced after exceeding 7 min of treatment time. 9th min of Ti-SO<sub>3</sub>H/ICG showed the drop of the surface area value. An optimum treatment time can be achieved at 7 min, which is the most favourable for the catalyst to efficiently react in the esterification process of PFAD. The larger surface area provided bigger space for securing the -SO<sub>3</sub>H groups molecules and enhanced the catalytic activity of the catalyst. The esterification of PFAD using the treated ICG for 7 min exhibited highest percentage yield of biodiesel in this study as shown in Figure 2.

The percentage yield of the esterification of PFAD by using catalyst prepared at various heating time were depicted as shown in Figure 2. Based on the results shown, ICG treated with H<sub>2</sub>SO<sub>4</sub> for 7 min exhibits the highest yield and conversion of 98.92 % and 80.24 % as shown in Figure 2 and Table 2. The percentage of conversion was determined through an acid-base titration and it was proven that the highest value obtained was the esterification using treated ICG at 7 min. The lowest yield of Fatty Acid Methyl Ester (FAME) was the esterification using treated ICG at 9 min, which was around 84.79 %. This is due to the open heating system inside the microwave that leads to the vaporisation of the acid, thus reducing the volume of the acid significantly. Less efficiency of the catalyst was observed with longer time of acid treatment. In this case, the ICG could not exhibit a larger surfaces area and acid site density for a longer treatment time due to the vaporised H<sub>2</sub>SO<sub>4</sub>, reducing the chance to be bonded in the anchor sites with the amorphous carbon. This is showed where the ICG treated at 9 min was inefficient to esterify the PFAD because it has exceeded its optimum peak at around 7 min of treatment time.

As shown in Table 1, the lowest BET surface area and pore size of 23.71 m<sup>2</sup>/g and 20.90 Å for ICG treated at 9 min proved the reason of the lowest FAME yield as compared to ICG treated at 3, 5 and 7 min. The low surface area (23.71 m<sup>2</sup>/g) of the 9 min acid treated catalyst indicates that most of the -SO<sub>3</sub>H groups were in the interior of this catalyst. Since it had a small pore size (20.9018 Å), the entry of a bulky of a reactant molecule will be obstructed, causing a reduction in the percentage yield of FAME. It can be summarised that the highest yield and conversion percentage of the PFAD methyl esters was done at ICG optimum treatment time of 7 min, operating parameters of 10 : 1 molar ratio of methanol to PFAD, 2.5 wt% of catalyst loading, 70 °C of reaction temperature and 90 min of reaction time. No significant increment was observed for molar ratio 10 : 1 up to 18 : 1 (Lokman et al., 2015).

Table 1: Properties of treated ICG as catalyst using BET and TPD-NH<sub>3</sub> analysis

Catalyst	Surface area (m <sup>2</sup> /g)	Pore Volume (cm <sup>3</sup> /g)	Pore size diameter (Å)	Acid sites density (mmol/g)	Yield (%)
SO <sub>3</sub> H/ICG 3 min	61.4021	0.127587	83.1156	13.06754	89.76
SO <sub>3</sub> H/ICG 5 min	72.2662	0.120126	66.4910	14.10319	96.37
SO <sub>3</sub> H/ICG 7 min	78.3671	0.160364	81.8527	15.16428	98.92
SO <sub>3</sub> H/ICG 9 min	23.7149	0.012392	20.9018	8.76817	84.79

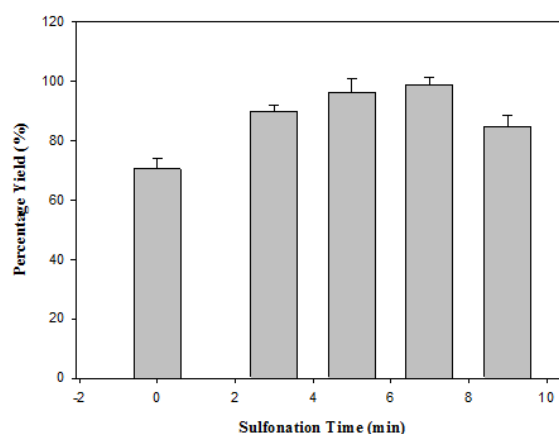
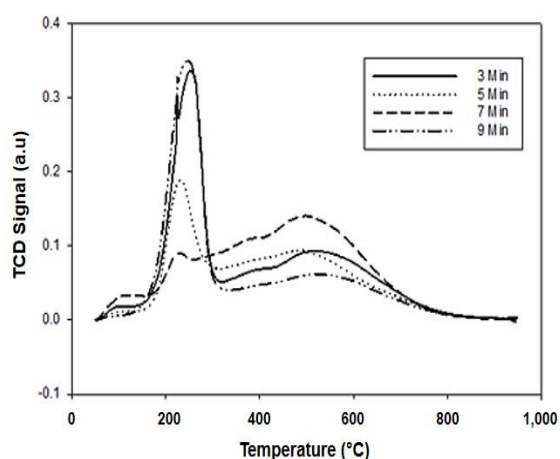
Figure 1: TPD-NH<sub>3</sub> of ICG/SO<sub>3</sub>-Ti at 3, 5, 7 and 9 minutes

Figure 2: Fatty acid methyl ester percent yield at different catalyst acid treated time (minutes)

### 3.2 Reaction Kinetic

Kinetic studies of PFAD esterification have been carried out at the optimum conditions of 10 : 1 molar ratio of methanol to oil, 50 °C, 60 °C and 70 °C reaction temperature, 2.5 wt% catalyst amounts and for a total of 90 minutes reaction. The value of reaction rate constant at different reaction temperature is based on Eq(4).

$$\ln(1 - X) = k't \quad (4)$$

Based on the Arrhenius equation as stated in Eq(5), the reaction rate constant (k) is a function of temperature. Therefore, in this work a reaction conversion at different temperatures 50 °C, 60 °C and 70 °C and time intervals of 10, 20, 30, 40, 60, 70, 80 and 90 min are determined as shown in Table 2. By substituting the conversion into Equation (4), the value of reaction rate constant (k) can be identified from a plotted graph of  $\ln(1 - X)$  versus reaction time as shown in Table 2.

It was observed that there was an increasing trend of reaction rate constants with increasing reaction temperature, with the lowest and highest reaction rate constants observed at 50 °C and 70 °C. In this study, an assumption that the process having a pseudo-first order reaction kinetic has been made. Talebian et al. (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 the same assumption of high methanol concentration employed in the reaction.

$$\ln(k) = Ea/RT + \ln(A) \quad (5)$$

The obtained values of k were then used to find the activation energy (Ea) and the pre-exponential factor for the reaction based on Equation 5. A graph of  $\ln k$  versus  $1/T$  (K) was plotted to determine Ea and A as shown Figure 3.

Table 2: Effect of reaction temperature and time on acid value corresponding % conversion of PFAD after esterification step

Reaction Time (min)	Acid Value			% Conversion		
	50 °C	60 °C	70 °C	50 °C	60 °C	70 °C
10	158.99	135.50	118.45	29.68	40.07	47.61
20	151.75	132.34	115.75	32.89	41.47	48.80
30	151.62	137.60	80.76	32.94	39.14	64.28
40	153.93	133.78	86.14	31.92	40.83	61.90
50	144.62	132.11	69.99	36.04	41.57	69.04
60	156.28	130.15	64.61	30.88	42.44	71.43
70	148.70	128.93	53.84	34.23	42.98	76.19
80	148.39	126.18	51.15	34.37	44.19	77.38
90	144.01	125.60	44.69	36.31	44.45	80.24
Reaction rate constant, $k'$ (1/min)	0.0008	0.001	0.0124	-	-	-
Coefficient of determination ( $R^2$ )	0.4441	0.8007	0.9631	-	-	-

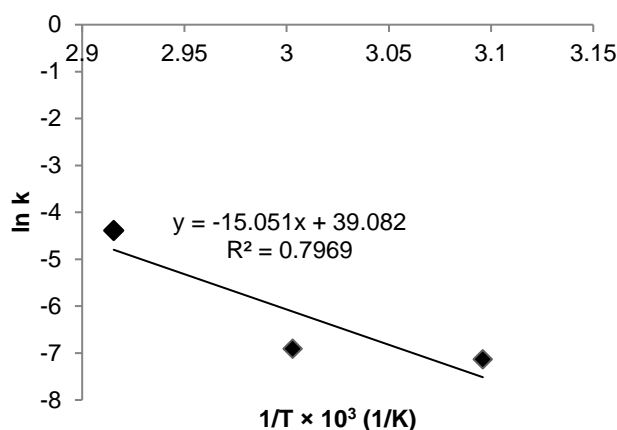


Figure 3: Graph of  $\ln k$  versus  $1/T$  (K) for activation energy,  $E_a$  and Arrhenius factor,  $A$  values

$E_a$  obtained was 13.43 kJ/mol.K is relatively low compared to other previous studies which had shown the highest activation energy of 50.745 kJ/mol.K (Berrios et al., 2007)) and 40 kJ/mol.K (Ang et al., 2015). Smaller value of activation energy will be more favourable in designing a reactor for chemical plant. This is because chemical reactions with higher  $E_a$  exhibit difficulties in control issues due to its rapid increase of the reaction rate as the temperature increases (Luyben, 2000).

#### 4. Conclusions

In this research, a microwave-assisted heating method is introduced to produce a catalyst for the esterification of PFAD instead of using a conventional method, which is time and energy consuming. The results showed that the  $-\text{SO}_3\text{H}$  from sulfuric acid is supporting strongly to the polycyclic aromatic carbon from the glucose. This property enhances the acidity of the catalyst. ICG treated with  $\text{H}_2\text{SO}_4$  for 7 min showed the highest yield and conversion of the biodiesel, which were 98.92 % and 80.24 %. This highest value was obtained from the esterification process at 70 °C of reaction temperature, 10 : 1 molar ratio of methanol to PFAD, 2.5 wt% of the catalyst loading and 90 min of reaction time. It can be concluded that glucose treatment with  $\text{H}_2\text{SO}_4$  and supported to a metal titanium (IV), is a good catalyst to directly esterify a high fatty acid feedstock like PFAD. A high percentage yield of fatty acid methyl ester was produced, and the product obtained in this study is observed to be very stable. No reversible reaction of the product into glycerol was observed as the FAME is stored. The energy and time consumed in the biodiesel production process was significantly reduced through the application of microwave-assisted method in acid treatment of ICG.

### Acknowledgements

The authors would like to express gratitude and many thanks for the financial support to conduct this study from Ministry of Education and Universiti Teknologi Malaysia under vote no. 07H81 and 12J43.

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