PERINTIS eJournal

PERINTIS eJournal, **2017**, Vol. 7, No. 1, pp. 31-42

PREPARATION AND CHARACTERIZATION OF MICROWAVE-ASSISTED CHLORINATED GLUCOSE USING PALM FATTY ACID DISTILLATE FOR BIODIESEL PRODUCTION

Nur Nazlina Saimon, Muhamad Hariz Adam Hussin Khan, Norzita Ngadi, Mazura Jusoh, Zaki Yamani Zakaria*

Department of Chemical Engineering, Faculty of Chemical & Energy Engineering,
Universiti Teknologi Malaysia, Malaysia

*Corresponding author: zakiyamani@utm.my

ABSTRACT

The development of heterogeneous acid catalyst has gained a broader attention over the last decade. This is due to the incredible solutions to several problems in biodiesel industry including the separation treatment after process, avoid saponification problems and capable to directly esterify low quality feedstock with high content of free fatty acid (FFA). This study was focusing on the development of the chlorinated glucose acid catalyst (CGAC) prepared via microwave assisted method for esterification of palm fatty acid distillate (PFAD) to biodiesel. Preparation of the catalyst was done by varying its power levels (high 800W), medium high 560W, medium low 240W and low 80W). Characterizations of the catalyst were carried out by using Brunauer Emmet and Teller (BET), Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Temperature-Programmed Desorption – Ammonia (TPD-NH_3) and Fourier Transform Infrared (FTIR). For catalytic testing of the catalysts prepared, molar ratio of methanol to PFAD was 10:1, 2.5 wt% of catalysts loading, reaction time at 90 minutes as well as reaction temperature at 70°C were fixed to produce the biodiesel at the same standard. From the Gas Chromatography – Flame Ionization Detector (GC-FID) result, CGAC prepared with medium high power levels showed the highest percentage yield which was up to 90.21%. In addition, the reaction kinetics of biodiesel production for medium high power levels CGAC had been developed. The optimum condition obtained was at 70°C with the rate of reaction of 0.0241 mol dm^{-3} s^{-1} and activation energy of esterification process is 40.471 kJ/mol.K

***Keywords**: Biodiesel, Palm fatty acid distillate, Chlorinated glucose, Microwave-assisted, Esterification, Kinetic.*

ABSTRAK

Pembangunan pemangkin asid heterogen telah mendapat perhatian yang meluas sejak sedekad yang lalu. Ini adalah kerana penyelesaian yang luar biasa untuk beberapa masalah dalam industri biodiesel termasuk rawatan pemisahan selepas proses, mengelakkan masalah saponifikasi dan mampu untuk secara terus mengesterifikasi bahan mentah berkualiti rendah dengan kandungan asid lemak bebas (FFA) yang tinggi. Kajian ini lebih tertumpu kepada pembangunan pemangkin asid glukosa berklorin (CGAC) yang disediakan menggunakan teknologi ketuhar gelombang mikro untuk esterifikasi sulingan asid kelapa sawit kepada biodiesel. Penyediaan pemangkin dilakukan dengan mempelbagaikan tahap kuasanya (tinggi 800W, sederhana tinggi 560W, sederhana rendah 240W dan rendah 80W). Pencirian pemangkin telah dijalankan menggunakan Brunauer Emmet and Teller (BET), Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Temperature-Programmed Desorption – Ammonia (TPD-NH_3) dan Fourier Transform Infrared (FTIR). Untuk ujian pemangkin yang telah disediakan, nisbah molar methanol kepada PFAD adalah 10: 1, 2.5 wt% pemangkin, masa tindakbalas pada 90 minit dan suhu tindak balas pada 70°C adalah ditetapkan untuk menghasilkan biodiesel pada standard yang sama. Dari hasil Gas Chromatography – Flame Ionization Detector (GC-FID), CGAC yang disediakan dengan tahap kuasa pada sederhana tinggi menunjukkan hasil peratusan yang tertinggi iaitu pada 90.21%. Di samping itu, tindak balas kinetik penghasilan biodiesel untuk pemangkin tahap kuasa sederhana tinggi telah dilaksanakan. Keadaan optimum yang diperolehi ialah pada 70°C dengan kadar tindak balas 0.0241 mol/dm^3.s dan pengaktifan tenaga daripada proses pengesteran adalah 40.471 kJ/mol.K.

***Kata kunci**: Biodiesel, Sulingan asid kelapa sawit, Glukosa berklorin, Bantuan ketuhar gelombang mikro, Esterifikasi, Kinetik.*

1. INTRODUCTION

With an increasing awareness of the environment and the depletion of the crude petroleum resources, it has become an imperative issue to look for alternative from renewable or sustainable resources [1]. Biodiesel has been developed since decades and it is continuously improved to produce a high quality of biodiesel with remarkable properties. It is undeniable that the production cost of biodiesel is relatively high [2] and this is essential to formulate a new method to produce a cheaper biodiesel. Most of the biodiesel industries are using palm oil as their feedstock [3-5]. However, the price of palm oil is relatively high and industries cannot bear with the long term expenses. Researchers suggested using a low cost feedstock instead of palm oil. In fact, the low feedstocks are abundantly available and the price is far cheaper compared with palm oil [6].

PFAD is one of the low cost feedstock and abundantly available in every palm oil industry because it is the by-product from refinery stage of palm oil. It has stable properties and cheaper price. PFAD consists of high FFA and cannot be esterified directly with homogeneous acid or base catalyst. Some researchers suggested to use a two steps methods which were esterification and transesterification [6, 7]. However, longer steps will drag a lot more expenses in the production cost. This problem can be solved by using heterogeneous acid catalyst to esterify and transesterify the triglyceride directly [8]. Some researchers already directly esterify their feedstock with high content of FFA level. Their results showed a relatively high yield and conversion. Lokman, Soltani and Konwar had successfully converted 95.4%, 97% and 99% of FFA to fatty acid methyl ester (FAME) respectively using different low cost feedstocks [9-11].

For PFAD cases, high acidity of catalyst will be a core requirement to successfully convert the PFAD to FAME. Recently, heterogeneous acid catalysts have been more widely preferred over homogeneous one since they are easier to be separated and can be recovered. Numerous studies had developed the heterogeneous catalysts for their biodiesel production [5, 12, 13]. High acidity properties and good stability are the main characteristics for ideal heterogeneous acid catalyst [14] and carbohydrate-derived acid catalyst is one of them. As a matter of fact, carbohydrate-derived acid catalyst can be modified from glucose which is cheaper in prices and easier to attain.

Preparation of the heterogeneous acid catalyst is basically involving a series of heating process with higher temperature and time consuming. In order to reduce the time consumption, microwave-assisted technology had been proposed to prepare the heterogeneous catalyst made from D(+)-Glucose. There were various biodiesel productions using microwave however, the preparation of the catalyst was still using the conventional method [15, 16]. Thus, this study was focusing on the preparation method of modified D(+)-Glucose with hydrochloric acid (HCl) to directly esterify and transesterify the triglyceride of PFAD. The main target was to improve and speed up the synthesis duration of the heterogeneous sugar-derived solid acid catalyst in order to produce a high yield and percentage of FAME. The catalysts prepared were then characterized using BET, FTIR, TPD-NH_3, SEM and XRD analysis. The effect of the power levels of the microwave towards the catalytic activity was investigated.

2.0 EXPERIMENTAL

2.1 Chemicals and Materials

PFAD was supplied by Mewaholeo Industries Sdn. Bhd., Pasir Gudang, Malaysia. Commercialized D(+)-Glucose as a source of catalyst was purchased from Qrec (Asia) Sdn. Bhd. Methanol as acyl acceptor was supplied from Merck. Hydrochloric acid (HCl) used in this study was obtained from J.T. Baker, US. 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. No further purification is required for all chemicals used in this study since they were all analytical grade products.

2.2 Catalyst Preparation

Several stages incorporated in this experiment were including heating, milling, and treatment with HCl, dilution, washing, filtering and drying process. 20 g of D(+)-Glucose powder was weighed using a weighing balance. Then the powder was heated in microwave (Brand Sharp R213CST) at medium high power level for about 15 minutes to produce incomplete carbonized glucose (ICG). The ICG was then milled to powder form. 8 g of the ICG was added into 200 mL of concentrated hydrochloric acid and heated inside a microwave for low, medium, medium high and high power levels of the microwave for 7 minutes. The mixture was then filtered and washed using distilled water. The black precipitated was collected and washed again using hot distilled water with temperature of 85°C until the filtrate was clear in colour. This was mainly to remove any impurities from the precipitated. The last step was drying process in a microwave for 15 minutes mainly to remove moisture content in the catalyst.

2.3 Catalyst Characterization

SEM, FTIR, BET and XRD were used for catalyst characterizations. The morphology of the catalyst was studied by using SEM (JEOL – JSM 6390) with 500, 1500, 5000 and 10,000 magnifications. Meanwhile, Shimadzu IRTracer-100 was used for FTIR analysis of the catalysts prepared. The sample was grounded and pelletized by using a hydraulic press to record the infrared spectrum between the ranges of 4000 – 500 cm^{-1}. Micromeritics 3 Flex was used for BET analysis to determine the surface area of the catalysts. The catalyst was degassed at 150°C under vacuum condition for 3 hours. XRD (Bruker, D8 Advance) however was carried out with a scan range of θ from 2° up to 60° at scanning rate of 4° min^{-1} to investigate the crystallinity of the prepared catalysts. For Temperature-Programmed Desorption – Ammonia (TPD-NH_3), Micromeritics AutoChem II was used to determine the density of the acid sites.

2.4 Catalytic Testing

Biodiesel production is involving an esterification process which is mainly to reduce the free fatty acid (FFA) percentage of PFAD. The PFAD and methanol were weighed based on the molar ratio calculation. Then, the PFAD was properly heated at 65°C. Preheated PFAD will be firstly poured into the three necks round bottom flask following by methanol and catalyst. Molar ratio between PFAD and methanol was 10:1. The catalyst used was chlorinated glucose with loading of 2.5 wt%. The solution in the three necks round bottom flask was refluxed to 70°C for about 90 minutes of reaction time. The mixture was poured into a separating funnel and then was allowed to settle for around 3 hours. The biodiesel layer was then separated and purified by water washing process before preparing the sample to be analyzed by using GC-FID.

2.5 Analysis of PFAD Methyl Ester

Standard biodiesel sample was prepared by using ratio of 0.5:40 (biodiesel: methanol). The sample was then sent to analysis laboratory for GC-FID analysis to determine the yield percentage. On the other hand, the conversion of the biodiesel was determined through acid-base titration method. About 1 mL of biodiesel was added into 20 mL of the solvent, methanol. The mixture was then shaken until it dissolved. 2-3 drops of phenolphthalein was added into the flask and titrated with standardized potassium hydroxide (KOH) solution until the first permanent pink colour showed up. The formula to calculate the yield percentage, acid value and percentage of conversion were defined by (Eq) 1, (Eq) 2, and (Eq) 3 respectively.

$$\text{Yield}=\frac{\text{Estercontent} \times \text{weightofproduct(g)} \times 100\%}{\text{massofPFADfeedstock (g)}} \tag{1}$$

$$\text{Acid Value}=\frac{\text{N} \times \text{MW KOH} \times \text{Volume of KOH titrate used (mL)}}{\text{mass of biodiesel (g)}} \tag{2}$$

Where, N is referring to the normality of KOH used and MW indicating the molecular weight of KOH which is 56.11 g/mol.

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

3.0 RESULTS AND DISCUSSION

3.1 Characterization of Catalyst

The catalyst shows the capability to merge with hydrophilic molecules such as –OH as well as -COOH molecules. This type of molecules is easily bonded with –Cl groups in the anchor sites [17]. Figure 1 depicts the IR spectra of the unchlorinated ICG catalyst and the CGAC catalyst. The bands at 3354.27 cm^{-1} and 3325.67 cm^{-1} attributed to the alcohol OH stretch which only present in original and low power levels CGAC [18]. An intensity of peak for all samples at bands 1638.56 cm^{-1}, 1664.60 cm^{-1}, 1619.27 cm^{-1}, 1655.71 cm^{-1} and 1655.92 cm^{-1} represent aromatic ring C-C stretching mode presence in the polyaromatic carbon sketch [19]. There were bands at 664.92, 699.57, 681.06 and 684.80 cm^{-1} for low, medium, medium high and high power levels CGAC indicating the –Cl group bonded to the polyaromatic carbon structure [20].

Figure 2 shows the XRD patterns of ICG after being treated with HCl at low, medium, medium high and high temperature. All samples depicted same trends of one sharp peak at 2θ = 2°-10° and weak peak at 2θ = 10°-25°. Such peaks theoretically were assigned for the amorphous carbon which is composed of the oriented random fashion of aromatic carbon sheets. This indicated that the samples comprised of high content non-graphitic carbon structure. This may be important in the catalyst's activity during the esterification process. The same peaks depicted amorphous carbon comprised of oriented random fashion of aromatic carbon sheets proved by Zong et al [21].

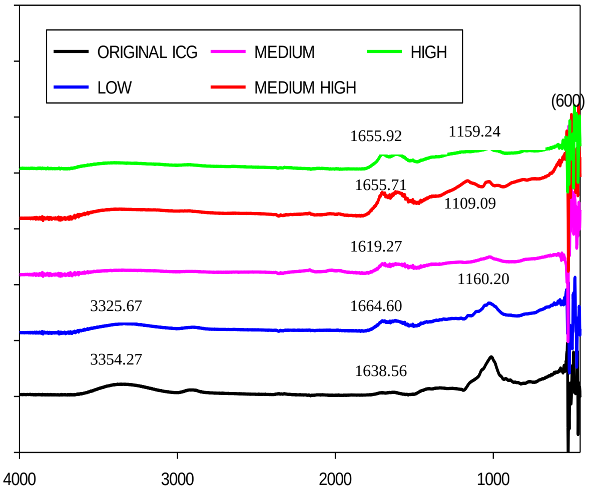

Figure 1. IR spectra of incomplete carbonized glucose (ICG) before and after treated with HCl.

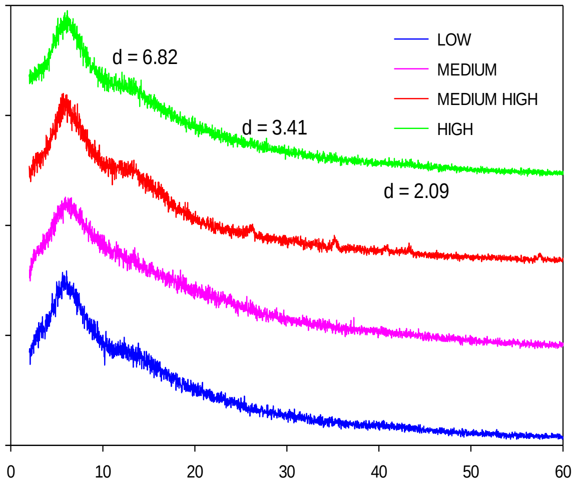

Figure 2. XRD patterns for ICG and after been treated with HCl at various power levels of microwave.

The SEM images for low, medium, medium high and high power levels for CGAC were represented as a), b), c) and d) respectively as well as the unchlorinated ICG as e) in Figure 3. Figure 3b), c) and d) show the irregular and aggregate (amorphous) particles of the chlorinated glucose catalyst. The figure indicates that as the power level of microwave increases, the surface of the catalyst become more aggregate with particle on top of it. For low power level CGAC, showed almost smooth surface with a bit of crack on the top of the ICG. This is almost the same surface with the unchlorinated ICG as shown in 3e).

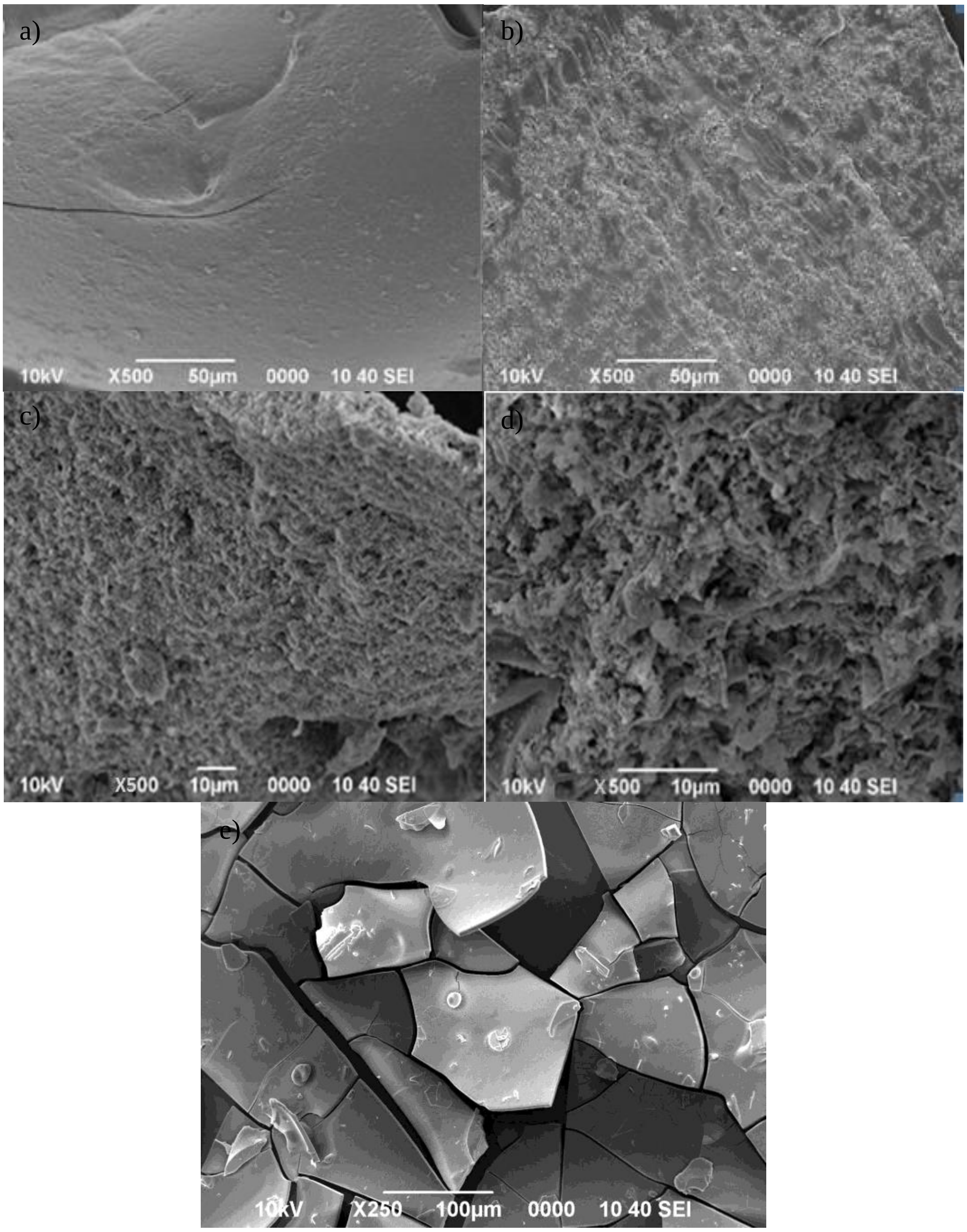

Figure 3. SEM images of incomplete carbonized glucose (ICG) after treated with HCl for low power level, a), medium power level, b), medium high power level, c), high power level, d) and unchlorinated ICG e).

Figure 4 shows the ammonia desorption curves for all CGAC at different power levels of microwave using TPD-NH_3. At low power level of microwave, the CGAC showed lesser ammonia desorption culminating at 337.8 °C compared with the rest of the power level. The figure also indicates the highest ammonia desorption culminating at 343 °C for medium high power level CGAC. Based on Table 1, the acid sites density of the medium high CGAC was 23.301 mmol/g shows the highest number compared to the other power levels CGAC. The highest number of the total acid sites density proves the existence of the strong Brønsted acid sites.

The surface area of the CGAC was determined using BET analysis. Based on Table 1, the biggest surface area was exhibited by the medium high CGAC which was up to 7.39 ± 0.34 m^2/g. It is corresponded linearly with the acid sites density of the CGAC. The low CGAC exhibited smaller surface area due to the smallest power used for low power levels which is around 80W. 80W apparently is not enough to completely form the amorphous surface of the catalyst. Amorphous surface of the catalyst is proven to exhibit higher activity and selectivity compared with crystalline materials [22]. Thus, based on this study, the medium high power level is the optimum power used to prepare CGAC with the best properties.

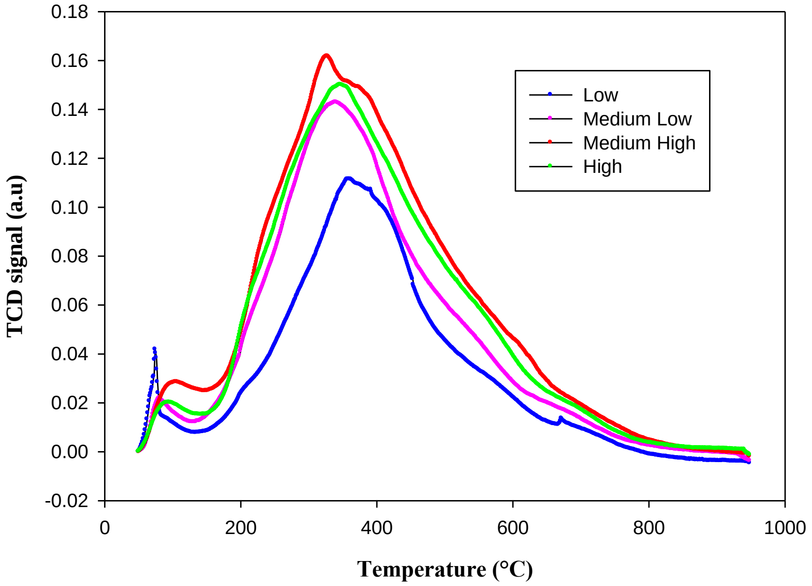

Figure 4. Ammonia desorption curves for low, medium low, medium high and high power levels CGAC.

3.2 Analysis of Biodiesel

Table 1 tabulates the types of catalyst used in this research with their corresponding results for BET analysis, yield and conversion from esterification process. ICG treated with HCl at low power level exhibits the lowest yield and conversion of FFA which were 57.58% and 80.58% respectively. Medium high power level catalyst shows the highest yield and conversion compared to the other catalyst with 90.21% and 93.26% respectively. This shows that the optimum power level for the CGAC for esterification of PFAD was the medium high power level. At a low power level of the microwave, the CGAC could not be able to form completely and exhibit smaller surface area for BET analysis as shown in Table 1.

Table 1. Surface area and total acid site density of each catalysts corresponds to their respective yield and conversion.

Power level for CGAC	BET Surface Area (m^2/g)	Acid Site Density (mmol/g)	Yield (%)	Conversion (%)
Low	0.93 ± 0.10	11.424	57.58	80.58
Medium Low	5.57 ± 0.60	18.813	80.00	87.06
Medium High	7.39 ± 0.34	23.301	90.21	93.26
High	5.76 ± 0.55	21.163	80.43	88.67

BET surface area analysis reflects the experiment results as the larger surface area will increase the yield and conversion of PFAD to biodiesel as shown in table below. The larger surface area provided bigger space for securing the –Cl groups molecules and enhanced the catalytic activity of the catalyst. The esterification of PFAD using the treated ICG for medium high frequency exhibited biggest conversion of FFA which was 93.26 % at 70 °C, 2.5 wt% of the catalyst, 10:1 methanol to PFAD molar ratio, and 90 minutes of reaction time.

Preparation of the glucose catalyst was studied previously by Lokman and colleagues. The paper described a sulfonated glucose acid catalyst prepared via conventional heating method reaches up to 92.3% of yield and 95.4% of conversion. This study proved that the glucose acts as an acid catalyst performs very well for esterification process. However, the preparation of the catalyst required a longer period which consumed about more than 5 days to completely finish the drying process of the catalyst [9]. Instead of wasting time and energy on the preparation of the catalyst, an alternative was taken to shorten the time and energy consumed during the catalyst preparation. Microwave-assisted was proposed because of its capability to delivers the energy directly to the glucose and the heat transfer became more effective compared with conventional heating [23]. In fact, it enhances the speed of reaction and the reaction can be completed in a much shorter time. Table 2 shows the comparison of conventional heating and microwave-assisted heating in preparation of the catalyst which obviously shows the reduction of time taken in microwave-assisted acid catalyst.

Table 2. Comparison of Conventional Heating and Microwave-Assisted Heating in Catalyst Preparation [9].

Preparation Step	Conventional Heating (h)	Microwave-Assisted Heating (min)
D-(+) Glucose heating	12	15
Treatment with acid	5-15	3-9
Drying process	24	15

3.3 Kinetic Study

Kinetic study is the derivation of mathematical models in order to have a better understanding in chemical processes. The procedure of kinetic data was preceded with the determination of rate constant from the graph concentration of ester against time. The slope of the graph represents the initial rates of methyl ester. Then, after the determination of the initial rates of the methyl ester, determination of activation energy was achieved by using Arrhenius plot. Figure 5 shows the conversion of PFAD (X) against time at 50°C, 60°C and 70°C. The conversion of PFAD was obtained using equation 3. Then a graph of ln (1-X) against time was plotted as shown as in Figure 6. By using the equation 4 and 5, graph of natural logarithmic of rates against 1/Temperature will be plotted. The slope of the graph will be represented as the rate constant, k. The activation energy was determined based on the plotting graph of ln k against 1/T as shown as in Figure 7.

$$\ln k = -Ea/RT + C \tag{4}$$

$$\text{Slope} = -Ea/RT \tag{5}$$

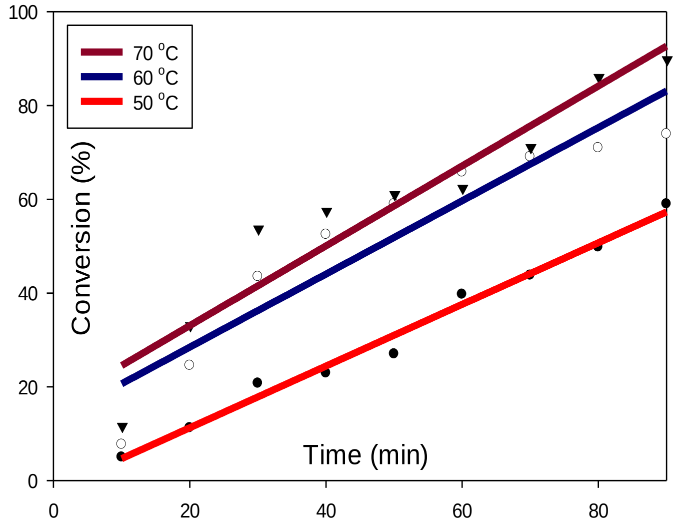

Figure 5. Graph of conversion of PFAD against time at various temperatures.

The rate constant of the reaction can be determined based on the increased amount of the product that occurs in some reaction time interval or alternatively based on the decreased amount of the limiting reactant, i.e. triglycerides. The determination of rate constant also depends on the order of the reaction. Using experimental data, the correct order would be determined by which function of rate equation best fit the linear requirement. Once the order of reaction is established, the rate constants are then estimated from the slope of the linear plot.

$$\text{Rate} = -\frac{d\,[TG]}{dt} \tag{6}$$

$$\ln k = k't \tag{7}$$

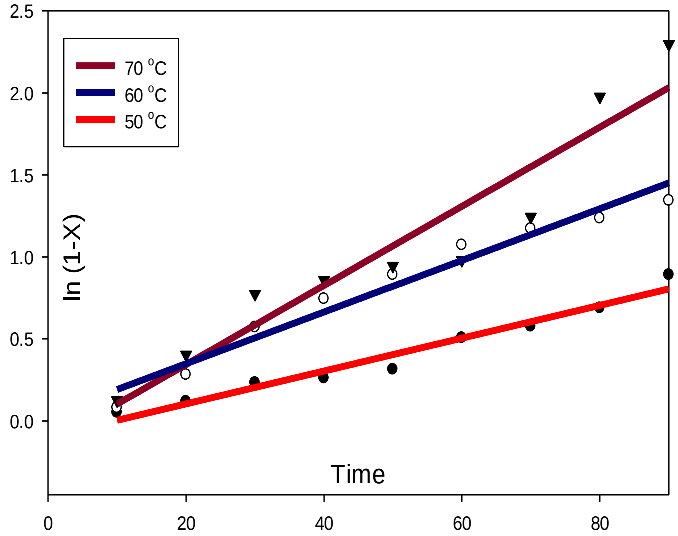

Figure 6. Determination of rate of reaction for each temperature using slope of the graph.

Experiments were carried out at 10:1 molar ratio of methanol to oil and 0.1N of KOH concentration using medium high frequency chlorinated ICG types of catalyst which gave the highest yield 90.21%. 1mL sample from the system was taken out in every 10 minutes. The sample was added with 4 drops of phenolphthalein and then titrated with 0.1N of diluted KOH. The sample of biodiesel was then swirled until the solution turned into pink colour indicates that the neutralization process completed.

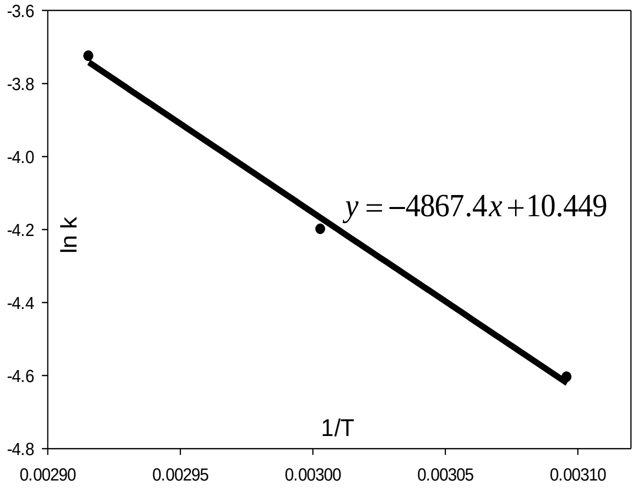

Figure 7. Graph of ln(k) against 1/T.

From Figure 7, slope for the equation is -4867.4, applying equation (5) the activation energy is 40.471 kJ/mol.K. The activation energy was relatively low compared with study from Berrios and Thanh which were 50.745 kJ/mol and 53.717 kJ/mol respectively [24, 25]. Low activation energy is favourable especially in reactor design in any chemical plant. A reaction with high activation energy faces with lots of difficulties in process control due to its rapid changes of its reaction rate as the temperature increases [26].

4.0 CONCLUSION

Transesterification of PFAD using methanol to produce biodiesel was proved to be one of the best alternative due to the low cost of feedstock and also beneficial because PFAD is considered as a waste from the palm oil industry. When using acid-catalyzed glucose, it can help to reduce the cost of preparing the catalyst and ease the separation after the reaction. The use of microwave-assisted reaction towards the introduction of HCl to ICG reduced the catalyst preparation time. From the experiment, the catalyst prepared using medium high frequency gave the highest yield and conversion which are 90.21% and 93.26% respectively. For the kinetic study, the rate constant for the 50°C, 60°C, and 70°C were 0.0100, 0.0158, and 0.0241 respectively while the activation energy calculated for the reaction was 40.471 kJ/mol.

ACKNOWLEDGEMENT

The authors thank the financial support to conduct this study from Ministry of Education and Universiti Teknologi Malaysia under Vote No. 07H81 and 12J43.

REFERENCES

[1] Septevani AA, Evans DAC, Chaleat C, Martin DJ, Annamalai PK. A systematic study substituting polyether polyol with palm kernel oil based polyester polyol in rigid polyurethane foam. Ind Crop Prod. 2015;66:16-26.

[2] El-Galad MI, El-Khatib KM, Zaher FA. Economic feasibility study of biodiesel production by direct esterification of fatty acids from the oil and soap industrial sector. Egyptian Journal of Petroleum. 2015;24:455-60.

[3] Suppalakpanya K, Ratanawilai SB, Tongurai C. Production of ethyl ester from esterified crude palm oil by microwave with dry washing by bleaching earth. Applied Energy. 2010;87:2356-9.

[4] Nongbe MC, Ekou T, Ekou L, Yao KB, Le Grognec E, Felpin F-X. Biodiesel production from palm oil using sulfonated graphene catalyst. Renewable Energy. 2017;106:135-41.

[5] Roschat W, Siritanon T, Yoosuk B, Promarak V. Biodiesel production from palm oil using hydrated lime-derived CaO as a low-cost basic heterogeneous catalyst. Energy Conversion and Management. 2016;108:459-67.

[6] Malvade AV, Satpute ST. Production of Palm Fatty Acid Distillate Biodiesel and Effects of its Blends on Performance of Single Cylinder Diesel Engine. Procedia Engineering. 2013;64:1485-94.

[7] Chongkhong S, Tongurai C, Chetpattananondh P. Continuous esterification for biodiesel production from palm fatty acid distillate using economical process. Renewable Energy. 2009;34:1059-63.

[8] Chabukswar DD, Heer PKKS, Gaikar VG. Esterification of Palm Fatty Acid Distillate Using Heterogeneous Sulfonated Microcrystalline Cellulose Catalyst and Its Comparison with H2SO4 Catalyzed Reaction. Ind Eng Chem Res. 2013;52:7316-26.

[9] Lokman IM, Rashid U, Taufiq-Yap YH, Yunus R. Methyl ester production from palm fatty acid distillate using sulfonated glucose-derived acid catalyst. Renewable Energy. 2015;81:347-54.

[10] Soltani S, Rashid U, Yunus R, Taufiq-Yap YH. Biodiesel production in the presence of

sulfonated mesoporous ZnAl2O4 catalyst via esterification of palm fatty acid distillate (PFAD). Fuel. 2016;178:253-62.

[11] Konwar LJ, Das R, Thakur AJ, Salminen E, Mäki-Arvela P, Kumar N, et al. Biodiesel production from acid oils using sulfonated carbon catalyst derived from oil-cake waste. Journal of Molecular Catalysis A: Chemical. 2014;388–389:167-76.

[12] Al-Sakkari EG, El-Sheltawy ST, Attia NK, Mostafa SR. Kinetic study of soybean oil methanolysis using cement kiln dust as a heterogeneous catalyst for biodiesel production. Applied Catalysis B: Environmental. 2017;206:146-57.

[13] Hidayat A, Rochmadi, Wijaya K, Nurdiawati A, Kurniawan W, Hinode H, et al. Esterification of Palm Fatty Acid Distillate with High Amount of Free Fatty Acids Using Coconut Shell Char Based Catalyst. Energy Procedia. 2015;75:969-74.

[14] Wang J, Chen K, Chen C. Biodiesel Production from Soybean Oil Catalyzed by K2SiO3/C. Chinese Journal of Catalysis. 2011;32:1592-6.

[15] Zhang Y, Xia X, Duan M, Han Y, Liu J, Luo M, et al. Green deep eutectic solvent assisted enzymatic preparation of biodiesel from yellow horn seed oil with microwave irradiation. Journal of Molecular Catalysis B: Enzymatic. 2016;123:35-40.

[16] Wang Y-Y, Chen B-H. High-silica zeolite beta as a heterogeneous catalyst in transesterification of triolein for biodiesel production. Catalysis Today.

[17] Mar WW, Somsook E. Sulfonic-Functionalized Carbon Catalyst for Esterification of High Free Fatty Acid. Procedia Engineering. 2012;32:212-8.

[18] Tan YH, Abdullah MO, Nolasco-Hipolito C, Taufiq-Yap YH. Waste ostrich- and chicken-eggshells as heterogeneous base catalyst for biodiesel production from used cooking oil: Catalyst characterization and biodiesel yield performance. Applied Energy. 2015;160:58-70.

[19] Rosa SML, Rehman N, de Miranda MIG, Nachtigall SMB, Bica CID. Chlorine-free extraction of cellulose from rice husk and whisker isolation. Carbohydrate Polymers. 2012;87:1131-8.

[20] Daeyaert F, Desseyn HO, van der Veken BJ. Vibrational and conformational analysis of chloromethylacetate and some deuterated derivatives. Spectrochimica Acta Part A: Molecular Spectroscopy. 1988;44:1165-84.

[21] Zong M-H, Duan Z-Q, Lou W-Y, Smith TJ, Wu H. Preparation of a sugar catalyst and its use for highly efficient production of biodiesel. Green Chemistry. 2007;9:434-7.

[22] Cocke DL. Heterogeneous Catalysis by Amorphous Materials. JOM. 1986;38:70-5.

[23] Lindstrom P, Tierney J, Wathey B, Westman J. Microwave assisted organic synthesis-a review. Tetrahedron 2001. 2001:9225-83.

[24] Berrios M SJ, Martín MA, Martín A A kinetic study of the esterification of free fatty acids (FFA) in sunflower oil. Fuel, 2007;86(15), 2383-8.

[25] Thanh LT, Okitsu K, Maeda Y, Bandow H. Ultrasound assisted production of fatty acid methyl esters from transesterification of triglycerides with methanol in the presence of KOH catalyst: Optimization, mechanism and kinetics. Ultrasonics Sonochemistry. 2014;21:467-71.

[26] Luyben WL. Impact of Reaction Activation Energy on Plantwide Control Structures in Adiabatic Tubular Reactor Systems. Industrial & Engineering Chemistry Research. 2000;39:2345-54.