

Preparation and Characterisation of Microwave Assisted Chlorinated Glucose for Biodiesel Production from Palm Fatty Acid Distillate

Nur Nazlina Saimon, Mazura Jusoh, Norzita Ngadi, Zaki Yamani Zakaria*

Chemical Engineering Department, Faculty of Chemical and Energy Engineering Universiti Teknologi Malaysia, 81310, Skudai, Johor
zakiyamani@utm.my

Biodiesel has a remarkable potential in substituting petroleum based fuel because it is non-toxic, biodegradable, renewable and sulphur free. In this work, the esterification of palm fatty acid distillate (PFAD) over microwave assisted chlorinated glucose catalysts was investigated. PFAD is being chosen due to its lower cost compared to palm oil and stable its properties. Incomplete carbonised glucose (ICG) was prepared by heating the D-(+)-Glucose in microwave and crushed into powder form. The ICG powder was mixed with concentrated HCl acid and heated for 5, 7 and 9 min in microwave. The catalyst was then diluted with distilled water and washed using hot distilled water. The catalyst was then dried prior to the catalytic activity. Esterification conditions were molar ratio methanol: oil of 10 : 1, temperature at 70 °C, 2.5 wt% of catalyst loading and 90 min reaction time. Characterisation of catalyst was carried out by using Brunauer-Emmett-Teller (BET), Scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier transform-infrared (FTIR). The maximum biodiesel yield obtained was 91.78 % using the optimal chlorinated glucose catalyst which was heated for 5 min in the microwave. It can be deduced that microwave assisted chlorinated glucose acid catalyst could potentially reduce substantial amount of time, energy and cost to produce low cost feedstock biodiesel.

1. Introduction

Petroleum demand increased each year with the rise of human population and rapidly growing industries. It became significantly imperative in the transportation sector and world economy (Li et al., 2013). High consumption of petroleum result to the fast depletion of petroleum resources recently. The automobile and energy-based industry will have to deal with the consequences or in worst case scenario they might have to be closed (Bharathiraja et al., 2014). Fatty acid methyl ester (FAME) or known as well as biodiesel is one of the alternatives in solving the depletion of the petroleum sources. It can be derived from transesterification of triglycerides which is basically fine grade edible oil. Besides palm oil, potential feedstocks for the production of biodiesel include jatropha oil, cotton seed oil, soybean oil as well as corn oil. Despite of various feedstocks available, the transesterification process is still expensive, partly contributed by the cost of feedstocks. Hence, a cheaper low cost feedstock is favourably crucial to be used to improve the economic viability of biodiesel industry.

Recent study involving palm fatty acid distillate (PFAD) has gained attention due to its stable properties and cheaper price. PFAD is a by-product from crude palm oil refinery consisting more than 85 wt% of free fatty acid (FFA) (Cho et al., 2012). High level of FFA percentage in the feedstock will trigger problem in biodiesel production especially with the utilisation of common catalyst such as H₂SO₄ and NaOH. Utilisation of NaOH will generate saponification and deactivate the catalyst, thus an acid catalyst, for instance H₂SO₄ is proposed to overcome the issue (Chongkhong et al., 2007). The final product of biodiesel uses H₂SO₄ as catalyst which subsequently creates additional further treatment to recover the methyl ester from the acid. Due to this dilemma, a heterogeneous acid catalyst was suggested to eliminate the problems that occurs from using NaOH and H₂SO₄ (Nakpong and Wootthikanokkhan, 2010).

Various heterogeneous acid catalysts were proposed such as sulphated zirconia (Shi et al., 2016), aluminium alginate (Cheryl-Low et al., 2015), sugar-derived (Lokman et al., 2015a), HZSM-5zeolites (Vieira et al., 2015), and heteropolyacid (Alcañiz-Monge et al., 2013). High acidity properties and good stability are the main characteristics for ideal heterogeneous acid catalyst (Chen et al., 2011) 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.

In line with that, research on sugar-derived acid catalyst was conducted by (Lokman et al., 2015a) and showed promising biodiesel percentage yield from PFAD. The process in the catalyst preparation seems tedious, time and energy consuming. In this study, microwave-assisted sugar-derived acid catalyst was synthesised in quest to simplify, reduce time and energy of the catalysts preparation. The main target for this study is to improve and enhance the heterogeneous sugar-derived solid acid catalyst in order to produce a high yield and percentage of FAME. The catalyst was then characterised by using BET, FTIR, SEM and XRD analysis. The effect of the chlorination time towards the catalytic activity was investigated.

2. Experimental

2.1 Chemicals and materials

The PFAD was freshly obtained from Mewaholeo Industries Sdn. Bhd., Pasir Gudang, Malaysia. Commercialised D-(+)-Glucose as a source of catalyst was purchased from Qrec (Asia) Sdn. Bhd. Methanol as acyl acceptor was supplied from Merck. 37 % of 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

The catalyst preparation involved several stages which were heating, milling, treatment with HCl, dilution, washing, and drying process. Twenty grams of D-(+)-Glucose powder was weighed and then heated in a microwave for about 10 min to produce incomplete carbonised 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 5, 7 and 9 min. The mixture was then filtered and washed using distilled water. The black precipitated was collected and washed again using hot distilled water with temperature higher than 80 °C. This was mainly to remove any impurities from the precipitated. The last step was drying process in an oven at 80 °C for around 5 h to remove moisture content in the catalyst.

2.3 Catalyst characterisations

Several characterisations were selected including SEM, FTIR, BET and XRD. FTIR (Shimadzu IRTracer-100) was used to determine the functional group of the sample of catalyst. The analysis was performed at Analytical Laboratory, Faculty of Chemical and Energy Engineering, UTM. SEM and XRD were conducted in Ibnu Sina, Universiti Teknologi Malaysia. JEOL, JSM-6390LV was used to perform SEM in order to study the morphology of the catalyst. Meanwhile the XRD which is mainly to study the crystallinity of the catalyst was determined by Bruker D8 Advance diffractometer with the scan range of θ from 2° up to 60° at 4° min⁻¹ scanning rate. The surface area of the catalyst was measured by using BET instrument located in C19, Faculty of Science, UTM. The sample of catalysts were degassed and heated overnight at 150 °C.

2.4 Esterification of PFAD

Biodiesel production involved 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 between 35 °C to 45 °C regarding to PFAD's melting point which is around 38 °C to 41.5 °C (IBM Malaysia, 2005). Preheated PFAD will be firstly poured into the three-neck round-bottom flask following by methanol and catalyst. Molar ratio between PFAD and methanol was 10 : 1. The catalyst used is 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 min of reaction time. Since the catalyst is heterogeneous, the solution was separated from the catalyst by centrifugation. Then the solution was poured into a separating funnel and allowed to settle for around 30 min to separate the glycerol and methyl ester. The biodiesel layer was then separated and purified by water washing process before preparing for the standard sample to be analysed using GCFID.

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 Analytical Laboratory for GCFID 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 dissolved. About 2 to 3 drops of phenolphthalein was added into the flask and titrated with standard potassium hydroxide (KOH) solution until a faint pink colour persist for about 5 s. The formula 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 is referring to the normality of KOH used and MW indicating the molecular weight of KOH which is 56.11 g/mol.

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

3. Results and discussion

3.1 Characterisation of catalyst

Figure 1 depicts the IR spectra of the original ICG catalyst and chlorinated ICG for 5, 7 and 9 min heating time. The bands at $3,388.02 \text{ cm}^{-1}$, $3,348.48 \text{ cm}^{-1}$, $3,302.19 \text{ cm}^{-1}$, and $3,362.95 \text{ cm}^{-1}$ for all samples were assigned to the O-H stretching mode of the alcohol group. The bands at $1,619.27 \text{ cm}^{-1}$, $1,636.63 \text{ cm}^{-1}$, and $1,637.59 \text{ cm}^{-1}$ from ICG 5, 7, and 9 min were attributed to the straight chain C=C stretching mode presence. This is unlike the original ICG which detected no bands within this range. The presence of chlorine groups was confirmed by strong vibration bands at 667.38 cm^{-1} , 636.52 cm^{-1} , 624.95 cm^{-1} for symmetric stretching ICG 5, 7 and 9 min as shown in Figure 1 proving the presence of the C-Cl functional group. There were bands at $1,160.20 \text{ cm}^{-1}$, $1,109.09 \text{ cm}^{-1}$, and $1,159.24 \text{ cm}^{-1}$ from ICG 5, 7, and 9 min indicating the -Cl group covalently bonded to the polyaromatic carbon structure.

Irregular and aggregate particles with lots of crevices and cracks were shown through the SEM images as illustrated in Figure 2(a) at $100 \mu\text{m}$ scale. After the catalyst was treated with HCl, the surface of the catalyst exhibited heterogeneous surface morphology with various porous structures. As the heating time of the treated glucose increased, the structures became smaller in size which requires a higher magnification to observe the particles.

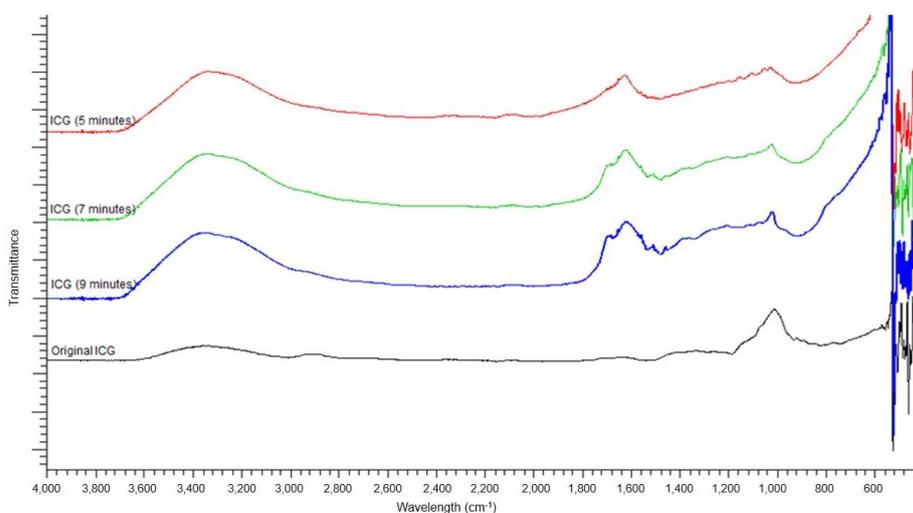


Figure 1: IR spectra of incomplete carbonised glucose (ICG) before and after treated with HCl

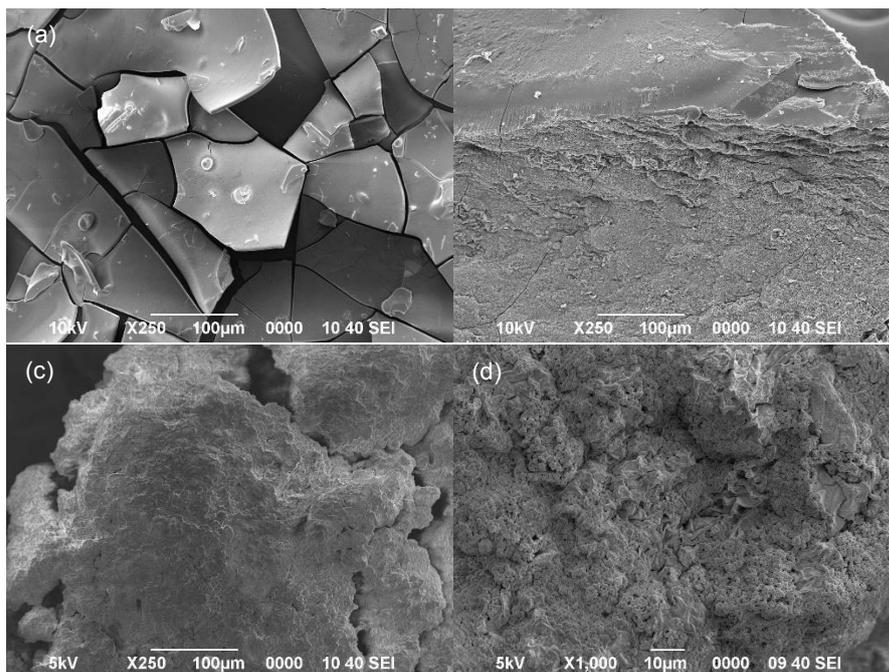


Figure 2: SEM images of incomplete carbonised glucose (ICG) (a) before and (b) after treated with HCl for 5 min, (c) 7 min and (d) 9 min

Figure 3 shows the XRD patterns of original ICG, and ICG after being treated with HCl for 5, 7 and 9 min. All samples depicted same trends of one sharp peak at $2\theta = 2^\circ - 10^\circ$ and weak peak at $2\theta = 10^\circ - 25^\circ$. As heating time increased, the sharp peak exhibited broader peak as shown in ICG-HCl for 7 and 9 min. The peaks depicted amorphous carbon comprised of oriented random fashion of aromatic carbon sheets (Zong et al., 2007). Since the glucose was heated in microwave system, the C-O-C bonding is breaking the cleavage thus forming a clearer polycyclic carbon sheets.

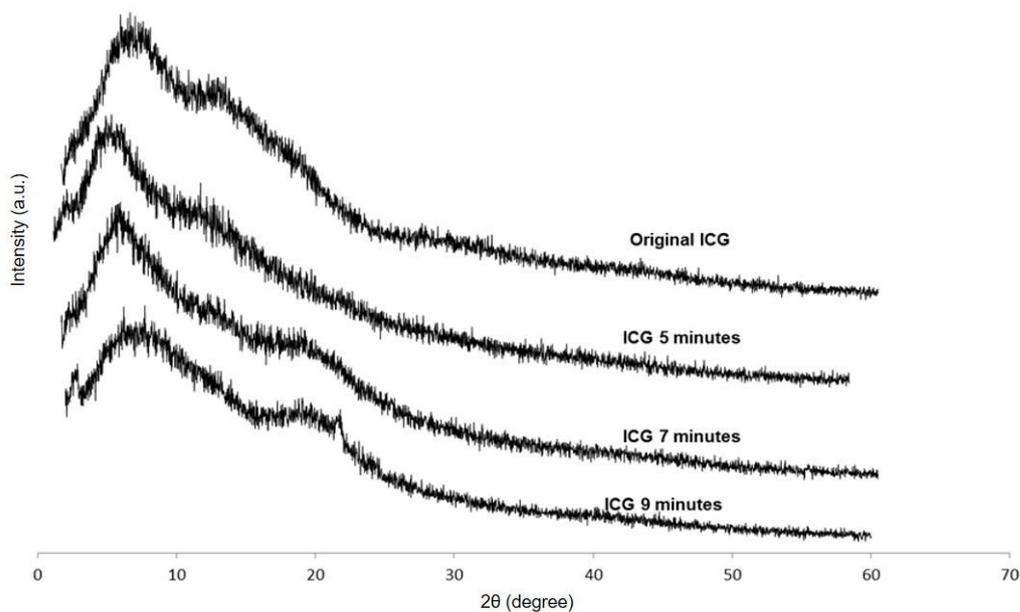


Figure 3: XRD patterns for original ICG and after been treated with HCl for 5 min, 7 min and 9 min

Table 1 showed the physicochemical properties of the original ICG and treated ICG for different treatment times (5, 7 and 9 min). Original ICG and ICG treated with HCl for 9 min exhibited lower conversion of FFA which was 70.43 % and 67.14 %. This was proven by looking at the lower BET surface area as compared to ICG treated at 5 min and 7 min. The treated ICG with HCl for 5 min exhibited a larger surface area as high as $7.57 \pm 0.60 \text{ m}^2/\text{g}$. It was larger than previous study reported by Lou et al. (2008). The study showed that optimum treatment time for ICG treated with HCl was achieved at 5 min. The results revealed that a longer treatment time of the ICG reduced the BET surface area. The larger surface area provided bigger space for securing the $-\text{Cl}$ groups molecules and enhanced the catalytic activity of the catalyst. The esterification of PFAD using the treated ICG for 5 min exhibited biggest conversion of FFA which was 95.51 % at 70°C , 2.5 wt% of the catalyst, 10 : 1 methanol to PFAD molar ratio, and 90 min of reaction time.

Table 1: Physicochemical properties of original ICG and treated ICG as catalyst in biodiesel production

Catalyst	Thermal treatment in microwave (min)	Treatment with HCl (min)	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size diameter (A°)	Conversion (%)
Original ICG	15	-	3.03 ± 0.10	3.10×10^{-1}	3.5	70.43
ICG 5 min	15	5	7.57 ± 0.60	8.40×10^{-1}	8.1	95.51
ICG 7 min	15	7	5.39 ± 0.34	5.32×10^{-1}	5.7	86.08
ICG 9 min	15	9	0.76 ± 0.55	8.41×10^{-2}	2.2	67.14

3.2 Effect of different chlorination time on catalytic activity

The percentage yield and conversion for the esterification of PFAD using different types of catalyst prepared at various heating time are presented in Figure 4. Based on the results shown, ICG treated with HCl for 5 min exhibits the highest yield and conversion of the biodiesel which were 91.78 % and 95.51 %. This is due to the heating system inside the microwave is open, thus most of the acid will be vaporised and could not be recovered back to the system. Since the vaporised acid was reduced as heating time increased, the ICG could not be exhibiting a larger surface area and acid site density. This might lead to the inefficiency of the ICG to esterify the PFAD directly. The highest yield and conversion percentage of the PFAD methyl esters was done at 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 observed for molar ratio 10 : 1 up to 18 : 1 (Lokman et al., 2015b).

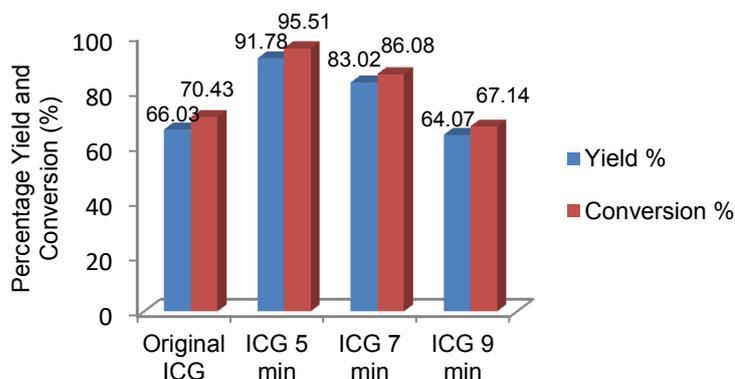


Figure 4: The yield and conversion percentage of the PFAD methyl esters from esterification process of PFAD at 70°C , 10 : 1 molar ratio, 2.5 wt% of catalyst loading and 90 min of reaction time.

4. Conclusions

Biodiesel from PFAD has been successfully produced using chlorinated glucose catalyst via esterification process. Instead using a conventional method for heating which is of high temperature and time consuming, a microwave assisted method is applied in the preparation of the catalyst, and offers lower temperature and less time. Incomplete carbonised glucose (ICG) was prepared by heating the D-(+) Glucose in microwave then the ICG powder was mixed with concentrated HCl acid and heated for various heating time in microwave. The results showed that the $-\text{Cl}$ from hydrochloric acid is supporting strongly to the polycyclic aromatic carbon from the glucose. This property directly enhances the acidity of the catalyst. ICG treated with HCl for 5 min

showed the highest yield and conversion of the process which were 91.78 % and 95.51 %. These parameters for the esterification process were reaction temperature = 70 °C, 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 the glucose treated with HCl catalyst using microwave assisted method has tremendous potential as a good candidate to directly esterify high free fatty acid feedstock to produce high yield of biodiesel at relatively low temperature, low energy and less time.

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