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Characterisation of Microwave-Assisted Sulfonated Glucose Catalyst for Esterification of Palm Fatty Acid Distillate to Biodiesel

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This study was carried out to solve the problem involving catalyst usage by practicing a heterogeneous solid acid catalyst, which require a low-cost production, easy preparation process, high effectiveness, environmental friendly and suitable to be used in the esterification process involving waste oil containing high level of free fatty acids. This paper investigated the sulfonated incomplete carbonised glucose (SO_3H/ICG) catalysts prepared via microwave-assisted which involve carbonisation and sulfonation processes. Thorough screening covering the power level of microwave (W), heating time (min) as well as weight of D(+)-glucose (g) were studied to generate the optimum condition for carbonisation process. Sulfonation of the catalyst were prepared at 7 min using 4 g of ICG; 100 ml H_2SO_4 and medium high power level (560 W).The physical and chemical properties of the sulfonated catalyst were analyzed by X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Brunauer-Emmett-Teller (BET) and Ammonia Temperature Programmed Desorption (TPD-NH_3). For the esterification of palm fatty acid distillate (PFAD), a classic conventional reflux system was used. It is found that 20 g of D(+)-glucose heated at 20 min in medium power level (400 W) provides the optimum carbonisation parameters due to its highest yield of fatty acid methyl ester (FAME) produced, 91.41 %.

1. Introduction

Alternative energy, especially renewable energy, is the main key in solving problem involving the depletion of energy sources as it has significant potential to meet the demand of the world's energy usage. Fatty acid methyl ester (FAME) or known as biodiesel had been widely chosen as an alternative source to replace the readily fuel. Aside from its non-toxicity property, its biodegradability characteristic and the low emission profiles by which it can reduce the emissions of carbon dioxide up to 78.5 % with comparison to petroleum fuel (Manzetti and Andersen, 2015).

Not only that, the usage of conventional refined vegetables oil; assist by alkali-catalyst, had been proven as non-economical since the production cost consume about 75 % of the manufacturing cost which causes the production cost to incline 1.5 times greater than the conventional diesel (Samuel et al., 2013). Conventional heating method is the most adopted technique due to the smooth heating process as the heat accumulated on the object surface is gradually transferred to the object interior, in which a slow process is restricted to the highest temperature and inevitable deviations of temperatures (Cheng et al., 2013).

Hence, researchers had been trying to formulate new methods for low cost biodiesel production. The usage of used oils and the refined oil's by product, palm fatty acid distillate (PFAD) for production of biodiesel apparently capable to solve the problems.

To cope with low quality feedstock; which is unrefined and much cheaper than the refined oil, researcher had preferred to use heterogeneous catalyst as it is suitable to be used with low quality feedstock include animal fats(5-10 %), palm fatty acid distillate (PFAD, 80-95 %), trap grease(100 %), and cooking oils (2-7 % free fatty acid (FFA)) (Yahya et al., 2017). The carbon solid acid catalyst derived from the incomplete carbonised carbohydrate had gained much attention form the researchers for its low-cost of production, easy process of

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catalyst preparation, high effectiveness, friendlier environmental as well as suitable for the esterification of waste oil involving high FFA content (Saimon et al., 2017).

Therefore, the objectives of this research is to produce a solid acid catalyst of sulfonated-incomplete carbonised glucose (SO_3H/ICG) at optimum condition and study the characterization of the catalyst produced as well as the yield and conversion of the FFA into biodiesel by using the acid-catalyst. With the presence of this carbon-based catalyst, FFA will undergo the process of esterification to produce FAME in a reflux system. The usage of SO_3H/ICG catalyst as compared to the commonly used homogenous catalyst showed lots of improvement in term of its corrosiveness and reusability of the catalyst.

The preparation of this carbon-based catalyst is carried out using One Factor at A Time (OFAT) method at various operating condition which is weight of D(+)-glucose (g), time for heating (min) and power level (W). This is crucial to determine the best condition to be used to provide with the optimum yield and conversion.

2. Methodology

20 g of D(+)-glucose powder was first heated in microwave to produce 4 g of ICG which was then being sulfonated with concentrated H_2SO_4. The preparation of this carbon-based catalyst is carried out using One Factor at A Time (OFAT) method at various operating condition which is weight of D(+)-glucose used, time for heating and power level. The weights of the D(+)-glucose ranged between 10 g to 30 g, meanwhile the heating time for carbonisation ranged between 5 min to 25 min. Power level of the microwave ranged between 80 W to 720 W.

2.1 Catalyst characterizations

Characterization methods for the catalyst include BET, XRD, FESEM and TPD-NH_3. XRD method was used to study the crystallinity structure of the SO_3H/ICG catalyst while BET was applied to analyze the surface area, pore are and pore volume of the solid catalyst and FESEM was used to observed the morphology of the catalyst. TPD-NH_3 was performed to observe acid strength of the SO_3H/ICG catalyst prepared.

3. Results and discussion

3.1 Characterizations of catalyst

Figure 1a, Figure 1b and Figure 1c show the effects of the heating time (min), weight of D(+)-glucose (g) and microwave power level (W) used for carbonisation screening process. The catalyst was then sulfonated with H_2SO_4 at fixed conditions before being used to esterify the PFAD.

Figure 1a depicted the biodiesel yield percentage increases when D(+)-glucose was carbonised from 15 up to 20 min but decreases slightly when the time further increases to 25 min. ICG were not completely produced at 5 and 10 min since the color and structure of the glucose remain the same. Thus, esterification using incompletely formed ICG was quite impossible.

Figure 1b on the other hand indicates the effect of D(+)-glucose's weight on biodiesel yield percentage. The trend shows an increment towards the biodiesel yield as the weight of D(+)-glucose increase from 10 g to 20 g but reduces slightly as the weight escalates gradually to 30 g. 20 g of D(+)-glucose was the optimum weight for carbonisation. An increment in weight of D(+)-glucose results a surge in the drying coefficient, k due to sudden and volumetric heating thus, generating high pressure inside the glucose samples and resulting a faster drying (Haghi and Amanifard, 2008). Drying coefficient, k is a parameter which indicates the drying capability of an object. Figure 1c shows the effect on the MW power level towards the biodiesel yield. The power level provided with certain ranges of Watt. The trend was quite similar to Figure 1b since further increment of power level resulting a rise of the biodiesel yield from 59.22 % to 91.41 % at medium power level. However, after a surge to the power level, a decrease of biodiesel yield occurs. From the carbonisation screening, 20 min of heating time, 20 g of D(+)-glucose and medium power level of microwave were found to be the optimum parameters to produce the effective ICG for sulfonation.

5 of the samples from the screening were selected to be characterized by using XRD, FESEM, BET and TPD-NH_3. The XRD pattern of the sulfonated glucose acid catalyst is shown in Figure 2. The pattern with two broad and weak diffraction peaks at 2θ of 5° – 15° and 20°–30°, which are assigned for the graphitic C(002) and C(101) planes. Typically, the first peak of the C (002) plane was assigned for the amorphous carbon that consists of disordered polycyclic aromatic carbon sheets. The weak peak of the C (101) plane was normally assigned for the graphitic structure of the carbon (Dehkhoda et al., 2010). Both structure are crystalline which indicates the glassy structure of the catalyst. The XRD pattern of catalyst A, B and E show the increment of intensity substantially between 2° to 10° compared to the sample C. This change explains the growing crystallinity of the catalyst is attributed to carbonisation factor using different power level of the microwave. C sample was carbonised by using low power level which is about 80 W of power. 80 W is basically used for

gentle defrosting because of the irradiation produced through low power level is relatively small and previous study showed that low power level only indicates low temperature which basically not exceeding the melting point of the D(+)-glucose (Li et al., 2010). Klinbun and Rattanadecho (2012) proved that high power level is able to penetrate through the surface far over than low power level that lead to higher amplitude of transmitted wave within water layer.

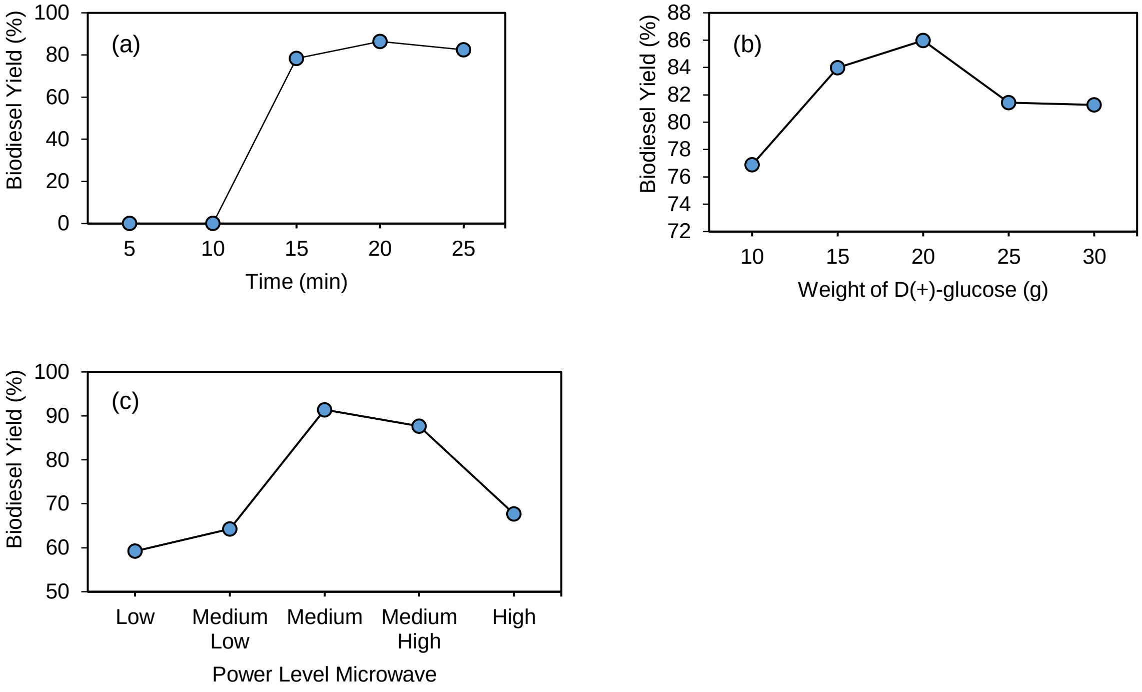

Figure 1: Effect of (a) time, (b) weight of D(+)-glucose and (c) power level microwave on biodiesel yield during esterification of PFAD. Sulfonated glucose produced at 7 min using 4g ICG; 100 ml H_2SO_4; medium high power level. Reaction conditions: 2.5 wt% catalyst loading; 75 °C reaction temperature; 10:1 molar ratio of methanol to PFAD; 2 h of reaction time.

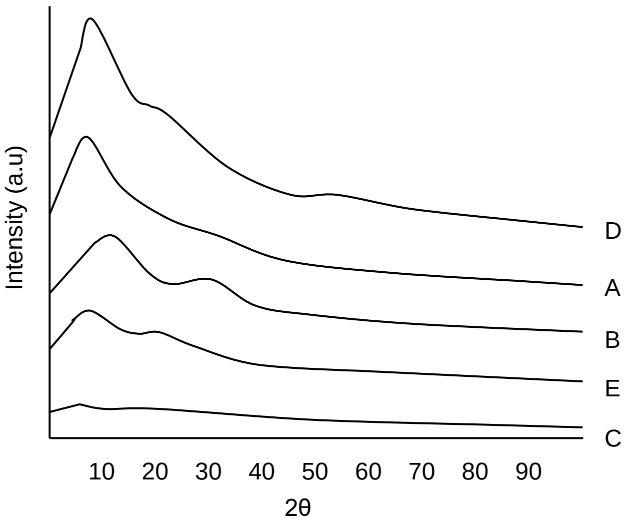

Figure 2: XRD Diffractogram of sulfonated glucose; A (20g D(+)-glucose; 15 min; Medium), B (30g D(+)-glucose; 20 min; Medium), C (20g D(+)-glucose; 20 min; Low), D (20g D(+)-glucose; 20 min; Medium) and E (20g D(+)-glucose; 20 min; Medium Low).

The morphology and microstructure of the catalyst prepared at different time of acid treatment were examined by FESEM. Figure 3 represents the FESEM micrographs of the sulfonated glucose prepared with different parameters. A, B, C, D and E are catalyst sample from different range of parameters. The image represents the range of the diameter particles of the sulfonated glucose ranging from 10 to 200 μm sizes. The images of A, B and D were homogenously decorated with well dispersed particles.

Lokman and colleagues proved that the raw glucose exhibits a microstructure of mesoporous feature, an irregular as well as aggregation shape of the sample in micrometer dimension (Lokman et al., 2015). The structure was quite similar to the sample A, B and D. Sample C and E on the other hand exhibited quite bulky, mossy type of the surface. This is due to the different power level used during the carbonisation process. Low power level indicates lower intensity of the radiation towards the surface of the catalyst. Thus, bulky and mossy surface was established for low power level. Under lower carbonisation power level, polycyclic carbon sheets are formed through dehydration condensation and massive of oxygen-containing functional groups subsequently abscise to be favorable for the sulfonic acid group introduction. Nevertheless, excess high power level aggravates stack of the polycyclic aromatic carbon frames and leads to a rigid structure, which is not favor for the active sites introduction. Hence, the optimal carbonisation power level is supposed to be medium in this study.

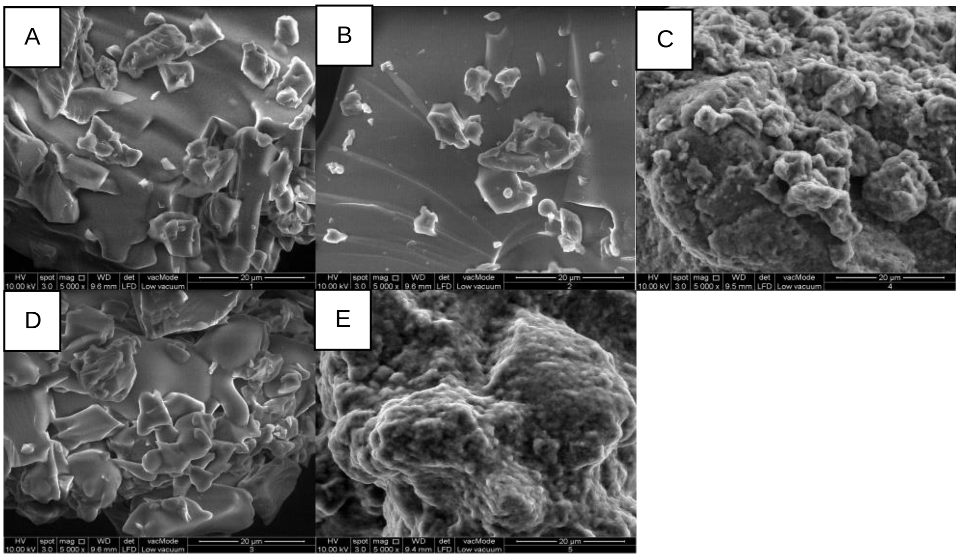

Figure 3: FESEM image of sample of A (20g D(+)-glucose; 15 min; Medium), B (30g D(+)-glucose; 20 min; Medium), C (20g D(+)-glucose; 20 min; Low), D (20g D(+)-glucose; 20 min; Medium) and E (20g D(+)-glucose; 20 min; Medium Low).

Through carbonisation process, surface area of the catalyst will basically decompose thus reducing the particles size. High surface area defines the formation of pores on the carbon surface. Using low power level of microwave exhibited small surface area (2.03 m^2/g) due to relatively low heating supplied to the incomplete carbonised glucose for decomposition and restructuring the carbon bonding to shrink the particle size and enlarge the formation of pores. For C and E sample catalyst, the small difference in surface area is due to low decomposition of organic compound and slow increment of pore formation. Large surface area is required for sulfonated glucose to act as catalyst for reaction to occur. High total acidity is obtained at different carbonisation microwave power level although the strength of the acidity somewhat reduces with increasing power level. The carbonisation power level is selected at medium as the ICG corresponds to both large surface area (16.94 m^2/g) and acidity (25.45 mmol/g). The effect of carbonisation time prevails as the surface areas increases with increasing heating time as tabulated in Table 1. The surface area increases with carbonisation time from 9.32 $m^2/$ g to 16.94 m^2/g for 15 min and 20 min. The carbonisation time selected at 20 min corroborate with large surface area of 16.94 m^2/g and high acidity of 25.65 mmol/g. area. Heating time plays an important role for carbonisation due to the formation of polycyclic aromatic carbon sheets which basically occurs for certain duration (Ning and Niu, 2017). Further increment of the heating time is insignificant once the polycyclic aromatic carbon sheets formed. As proven from this study, the optimum carbonisation duration able to reach was 20 min with 86.72 % of biodiesel yield produced. After a prolonged duration, the biodiesel yield seems to be reduced to 82.41 % at 25 min. Hence, the optimal carbonisation duration ought to be at 20 min. To date, many acid catalyst from various carbon based have been used. Corn straw was used by Liu et al and he found the optimal carbonisation duration was 1 h via conventional method (Liu et al., 2009). Touhami et al however used rice husk as a heterogeneous acid catalyst and established 30 min for the optimal carbonisation duration using MW heating method (Touhami et al., 2017). This study is comparable to previous research done by Touhami et al and provides an alternative for carbonisation process in shorter time yet capable to produce high yield of biodiesel. Figure 4 shows the distribution of the catalyst's acid site density based on TPD-NH_3 analysis. Catalyst D exhibits the sharp peak at 330 °C from 250 °C to 400°C and a weak desorption peak can be seen at 250 °C within 230 °C – 270 °C. The strong peak is appointed as strong acid sites with 25.65 mmol/g density as tabulated in Table 1. The weak desorption peak is occurred due to the contact of $–NH_3$ with incomplete carbon sheets as well as the interaction with the $–SO_3H$ (Kastner et al., 2012). Broad peak depicted at 350 °C and 500 °C is the catalyst C with lowest desorption of ammonia of 12.93 mmol/g acid site density. The preparation of the catalyst involved different power level indicating different temperatures. The rise of temperature during carbonisation will initiate the growth of the carbon sheet (Shu, 2010). Nevertheless, too high power level or temperature of the microwave is not preferable due to accumulation of the discontinuities to shorten the molecular orientation and vibration (Chen and Cui, 2016).

Table 1: BET surface area and acid site density for selected parameter for sulfonated glucose

Catalyst	ICG Preparations	Surface area[a] (m^2/g)	Acid sites density[b] (mmol/g)	Yield (%)
A	20g D(+)-glucose; 15 min; Medium	9.32 ± 0.30	25.31	86.72
B	30g D(+)-glucose; 20 min; Medium	4.78 ± 0.40	23.85	79.27
C	20g D(+)-glucose; 20 min; Low	2.03 ± 0.30	12.93	59.22
D	20g D(+)-glucose; 20 min; Medium	16.94 ± 0.30	25.65	91.41
E	20g D(+)-glucose; 20 min; Medium Low	2.39 ± 0.20	17.52	69.68

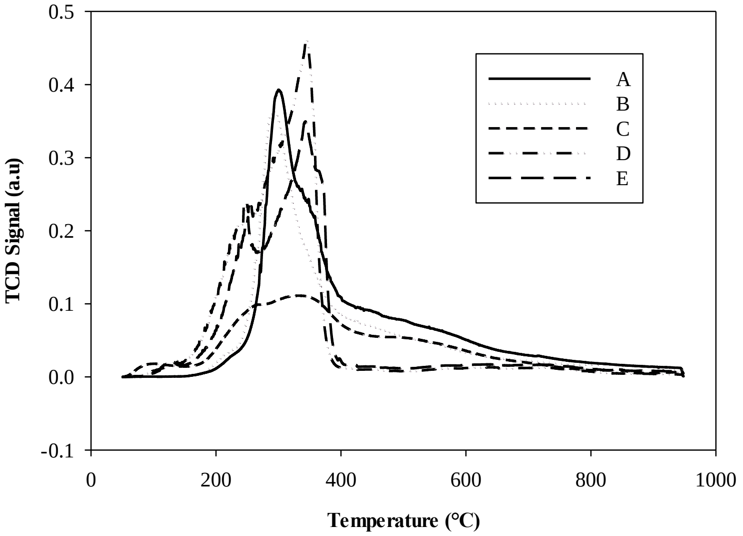

Figure 4: TPD-NH3 for sulfonated glucose at selected parameters of ICG preparation

4. Conclusions

From the preparation of ICG-SO_3H catalyst through microwave heating-assisted done by using One Factor At a Time (OFAT) method, the best condition to prepare this heterogeneous solid acid catalyst were 20 min heating time, 20g of D(+)-Glucose and medium power level of the microwave. The optimum parameters for carbonisation successfully generates a heterogeneous acid catalyst that delivered 91.42 % FAME yield with high surface area and acid site density of 16.94 m^2/g and 25.65 mmol/g.

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