Production of Biodiesel from Oleic Acid Using a Carbon-Based Catalyst

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Abstract— *In this work, the production of biodiesel (FAME) from oleic acid using a sulfonated carbon catalyst derived from glycerol was investigated. The synthesized catalyst was characterized using FTIR, BET, FESEM, XRD and TPD-NH3 to determine its catalytic activity. Simultaneous esterification/ transesterification of oleic acid, was carried out using the synthesized catalyst. The influence of molar ratio of methanol to oleic acid, catalyst loading and reaction time on the conversion and yield of FAME were also studied. For oleic acid conversion, 96% was obtained at optimum conditions of 1:7 methanol/ oleic acid molar ration, 15 wt% catalyst loading and 4h reaction time. The high catalytic ability of the catalyst was associated with the high acid site density formed in the catalyst which was due to high porosity and large pore size of the carbon framework of the catalyst. The catalyst showed good stability when it was recycled. The recyclability of the catalyst and its cheap feedstock makes the overall process much simpler, cost-efficient and environmentally friendly.*

Keywords— *Biodiesel, Carbon- based catalyst Oleic acid, Reusability.*

I. INTRODUCTION

Fuels obtained from fats and oils have become attractive owing to the fact that they are made from renewable sources (Šánek *et al.*, 2016). However, the high cost in its production is still a challenge. Therefore, new and eco-friendly processes needs to be studied to reduce the cost. Some of the processes involved in biodiesel production are the use of homogeneous or heterogeneous catalysts. Studies carried out on biodiesel production using homogeneous alkaline catalysts have shown them to have major setbacks as they produce soap when they come in contact with water and free fatty acids making the separation of biodiesel and glycerol a very difficult task (Keera et al., 2010). Furthermore, they are highly hygroscopic, so they absorb water during storage, thereby, diminishing the catalytic performance. Homogeneous acid catalysts have been found to be very effective. However, it is very corrosive and hard to separate the acid from the final product. On the other and, the application of heterogeneous catalysts in biodiesel production has been found to be of great advantage. They are easily separated from the product by filtration. They are mostly environmentally friendly and also enable the potential of continuous process (Islam *et al.*, 2013).

In this study, a heterogeneous acid (carbon) catalyst was synthesized by sulfonation of glycerol. This catalyst was characterized using FTIR, BET, FESEM, XRD and TPD-NH$_3$ to determine its catalytic activity. Oleic acid was used as the test oil in this work and the effect of different operating parameters such as methanol molar ratio, catalyst amount and reaction time was intensively studied for esterification of the oleic acid. The study on reusability of the catalyst was also appraised

II. EXPERIMENTAL PROCEDURE

2.1 Materials

All chemicals were used without any purification. Oleic acid was obtained from Chempur, Germany. Sulfuric acid (95-97% purity), Ethanol (96% purity), silicon oil, and methanol (> 99.9 % purity) were obtained from Q Rec, New Zealand. Glycerol (>99.5% purity) was purchased from Sigma Aldrich, USA. And other reagents such as methyl oleate standard, methyl palmitate standard with purity of 97%, and phenolphthalein were obtained from Merck, Germany. All of which were of analytical grade. These reagents were used to synthesize a sulfonated carbon catalyst, and carry out the simultaneous esterification/ transesterification of oleic acid.

2.2 Catalyst Preparation

The sulfonated carbon was prepared according to the method proposed by (Devi *et al.*, 2014). 10g glycerol was mixed with 20g concentrated sulfuric acid in a 500ml beaker, and gently heated on a hotplate from 25ºC to 220ºC to ensure incomplete carbonization and sulfonation. The temperature was kept constant for 20 min till it stopped foaming. The product obtained was washed under agitation with hot water until it became neutral to pH. The product (sulfonated carbon) was then filtered and dried at 110ºC for 2hrs in an oven so as ensure it is moisture free.

2.3 Catalyst Characterization

The synthesized sulfonated carbon catalyst was characterized and analyzed in detail. The crystalline structure of the catalyst was determined by X-ray diffraction (Bruker Advanced D8, 40k v, 40mA) with a scanning range of 2-60º at 4º min^{-1}. Its surface area was determined using Braunauer-Emmett- Teller using N$_2$ adsorption isotherm with a BET Surfer Thermoscientific equipment. Prior to the measurement, the samples were degassed at 200ºC for 6h.

The morphology of the synthesized catalyst was investigated using the Field Emission Scanning Electron Microscope (JSM-6700F, JEOL model, Japan) with resolution

(X25,000), 5.0KV with a maximum 2nA probe current. This was fitted with an energy dispersive X-ray spectrometer (EDX) for elemental composition analysis.

To determine the functional groups present on the polycyclic carbon catalyst, infrared spectroscopy (Perkin Elmer Spectrometer, 1725 X) was used. Its acid density was determined using the temperature programmed ammonia desorption (TPD-NH3, micrometrics autochem 112920).

2.4 Reaction Study

The esterification of oleic acid was done using a simple technique. The reaction was carried out in a 100 ml three-necked flask that was connected with a reflux condenser, a thermometer and a stopper. The reaction mixture was stirred vigorously at constant stirring rate for the experiment. Oleic acid: methanol molar ratio (1:3-1:11), catalyst loading (5-30 wt %), reaction temperature ($65^{\circ}C$), and reaction time (1-6h) were varied accordingly. A mixture of oleic acid, methanol, and the sulfonated carbon catalyst was put into the flask, and heated at $65^{\circ}C$ under stirring for 5h. After the reaction reached completion, the catalyst was filtered off, and the product obtained was poured into a separating funnel. The upper layer consists of FAME, which was washed with distilled water and dried in an oven to remove any impurities present. The recovered catalyst was recycled after washing with methanol and drying in an oven at $110^{\circ}C$ for 2h. The catalyst was reused for several times to study its reusability. Lastly, the fatty acid methyl ester (FAME) was collected for further analysis. The conversion rate was calculated using the following formula:

Conversion rate (%) = Initial A.V- Final A.V/ Initial A.V x 100%   (1)

2.5 Recycling of Sulfonated Carbon Catalyst

To investigate the reusability of the catalyst, esterification/transesterification of oleic acid was carried out four times with the same catalyst loading of 15wt%, 1:7 methanol to oil molar ratio, reaction time of 5h and temperature of $65^{\circ}C$. After each reaction, the catalyst was washed with methanol and dried in an oven for 2h at $110^{\circ}C$. The dried catalyst was reused in subsequent reactions for the esterification/transesterification reactions under the sme reaction conditions. For each reaction, new samples of oleic acid at the same concentration as those in the first batch were prepared.

III. RESULTS AND DISCUSSION

3.1 Catalyst characterization

The crystalline structure of the catalyst was determined using X-ray diffraction. Fig 3.1 depicts the pattern obtained by XRD. A broad diffraction peak was observed between $2\Theta=5^{\circ}$-30°. This peak is theoretically attributed to amorphous carbon which is composed of oriented random aromatic carbon (Zong et al., 2007). Ideally, a diffraction is usually seen at 40-50° in X-ray diffractions involving sulfonated carbon. However, this is not the case in this particular catalyst. But then, the results obtained are in agreement with other results obtained from carbon catalysts synthesized by direct carbonization and sulfonation (Ouyang, et al., 2014).

One of the unique properties of amorphous carbon are its ability to be attached with hydrophilic molecules such as the –COOH and –OH. They normally give anchor sites for the bonding of the $-SO_3H$ group. Fig 3.2 shows the IR spectrum of the sulfonated carbon catalyst. The presence of strong absorption bands were observed at $1700cm^{-1}$ and $1595cm^{-1}$ indicating the absorption of the carbonyl, C=O stretching mode of COOH group, and the aromatic C=C carbon structure (Lokman *et al*., 2015). The presence of symmetric and asymmetric C-O-SO_3H functional groups were detected by the bands at 1030 and 1140 stretching vibrations (Guo *et al*., 2012). This confirms the presence of $-SO_3H$ group which are covalently bonded to the polycyclic aromatic carbon structure (Mar and Somsok., 2012). Bands identical to the S=O symmetric and asymmetric were observed at $810cm^{-1}$ and $871cm^{-1}$ which is due to the IR absorption ability of the carbon (C-C) catalyst's framework (Lokman *et al*., 2015). Similar results were also reported by Nakajima and Hara (Nakajima and Hara, 2012). A band was also observed at $2928cm^{-1}$ attributable to the saturated C-H stretching vibration which shows the incomplete carbonization of the catalyst. The results obtained are in accordance with those observed in the X-ray diffraction XRD.
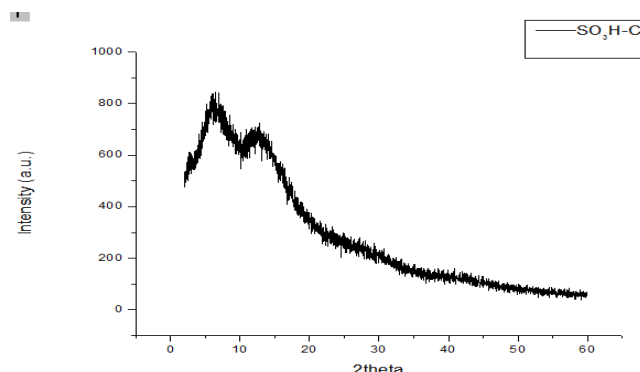

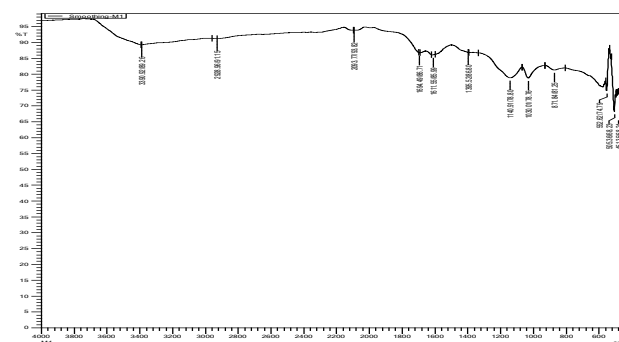Fig. 3.1 X-ray Diffraction image of sulfonated carbon catalyst

Fig. 3.2 FTIR image of sulfonated carbon catalyst.

The FESEM images (Fig 3.3) of the sulfonated carbon catalyst shows that the catalyst contains micropores with irregular shapes and rough edges. The textural properties of the carbon sheets composing mainly of polycyclic aromatic groups are expected to be binded to large amounts of $-SO_3H$ groups. It is capable of providing a successful diffusion of glycerides, FFA and methanol through the catalyst. The binding of S (26.2%) and O (17.1%) was confirmed using Energy Dispersive

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X-ray (EDX) spectroscopy (Figs 3.4). This indicates that the incomplete carbonization and sulfonation resulted in a sulfonated carbon with composition of $CH_{0.26}S_{0.26}O_{0.17}$. This also tallied with the FTIR results which showed the presence of the $-SO_3H$ groups. The result obtained also tallied with that obtained during the BET in which a surface area of $1.806 m^2/g$ and a maximum pore radius of 2.11nm was obtained.

Temperature-Programmed-Desorption (TPD-NH$_3$) was used to determine the density and distribution of acid sites on the sulfonated carbon catalyst. This is shown in fig 3.5. There was one broad desorption peak maximized at 608ºC from 470ºC to 800ºC and another at 907ºC This is attributed to the strong acid sites with the density of the acid site up to 2.63mmol/g, while that of the other peak was 0.01mmol/g indicating the catalyst is chemically and thermally stable.
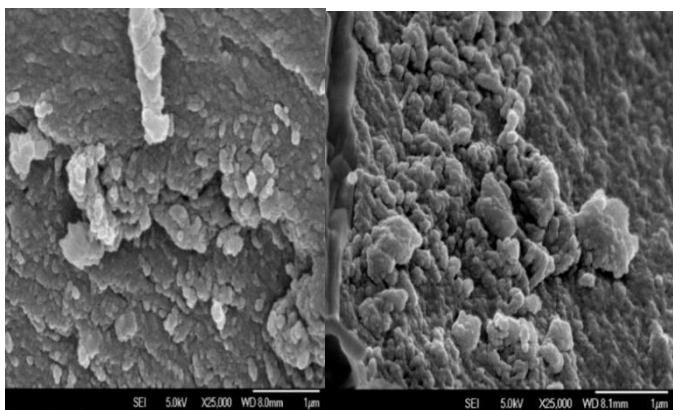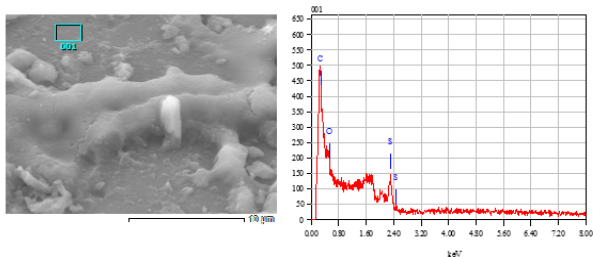

Fig. 3.3 FESEM image of sulfonated carbon catalyst

Fig. 3.4 EDX image showing the binding of S, and O on the sulfonated carbon catalyst.
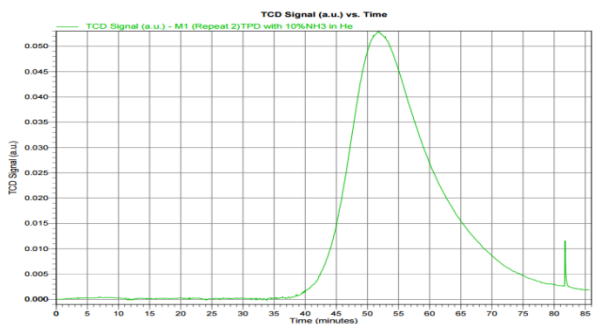

Fig. 3.5 TPD-NH$_3$ image of sulfonated carbon catalyst

3.2 Reaction Studies

3.2.1 Effect of methanol/oil molar ratio

The effect of oleic acid/ methanol molar ratio on the conversion yield of FFA was studied using different molar ratios (1:3, 1:5, 1:7, 1:9, and 1:11). As seen in Fig. 3.6, conversion of FFA in oleic acid increased from 86% with an increases in molar ratio up to 1:7 with a conversion of 96%. This declined when molar ratios greater than 1:7 was applied. This can be explained by the excess methanol content which must have caused over-flooding of the active sites of the catalyst. Thereby, inhibiting effective catalytic activity (Shu *et al.,* 2010). A high molar ratio was required to push the reaction towards the product side, such as those displayed in similar studies relating to carbon catalysts which required higher molar ratios (Dawodu *et. al.*, 2014; Fadhil *et al.*, 2016). This shows the superiority of the synthesized catalyst over similar catalysts that have been studied previously.

3.2.2 Effect of catalyst loading

Since the presence of a catalyst in a reaction quickens the reaction rate by reducing the activation energy for the reaction to progress, an increase in catalyst loading is likely to push the reaction towards the product side at a faster rate (Rao *et al.,* 2011). In this study, catalyst loading had positive influence on the conversion to FAME within the studied range. An increase in conversion was obtained from catalyst loading 5wt%-15wt%. However, a decline was observed after 15 wt% (Fig 3.7). This is in agreement with a study on catalyst loading in literature which was reported as the amount of solid catalyst used in a reaction might lead to a self-agglomeration among particles. And as such, the number of sites in the catalyst will be reduced. Thereby leading to a lower yield in FAME (Chongkhong *et al.*, 2009).
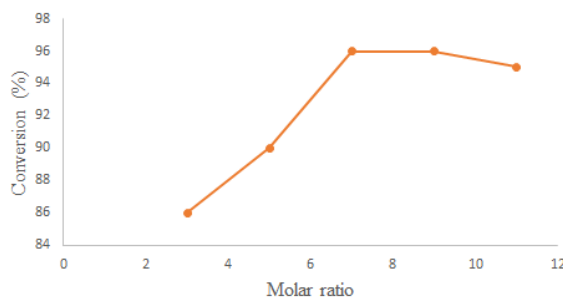

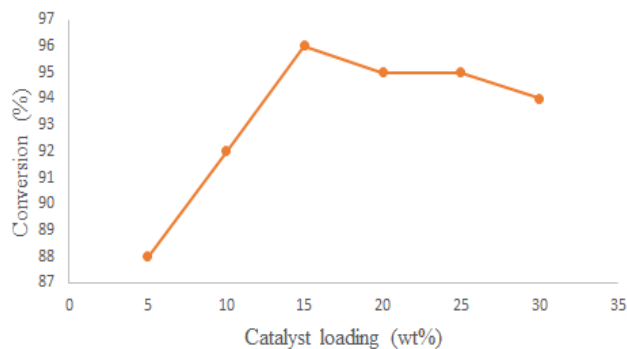Fig. 3.6 The effect of molar ratio on conversion of oleic acid

Fig. 3.7 The effect of catalyst loading on conversion of oleic acid

3.2.3 Effect of reaction time

Reaction time played a very important role in the oleic acid conversion. A range of reaction time 1-6h was studied. As shown in Fig.3.8, the conversion increased from 1- 4h where a

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FA conversion of 96% was achieved. After which there was a decline. This could be attributed to the hydrolysis of the methyl ester with the presence of water as a by-product which deactivates the catalyst (Leong *et al*. 2015).
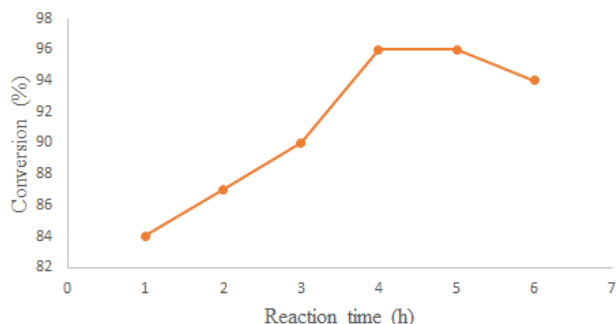

Fig. 3.8 The effect of time on oleic acid conversion

3.3 Recycling of Catalyst

One of the main advantages of heterogenous catalysts over homogeneous catalysts is the ease in which they can be recovered, and reused in subsequent reactions. In order to recycle the catalyst, the reusability of the catalyst was evaluated on completion of the esterification/ transesterification reactions of the oleic acid. The catalyst was seperated from the product by filteration. It was then washed with methanol to remove the residual reactants from the surface of the catalyst. Fianlly, it was dried in an oven at 110ºC for 2h. The catalyst was then used in the subsequent esterification/transesterification reactions of oleic acid. This was done using molar ratio of methanol to oil 1:7, catalyst loading of 15wt%, temperature of 65ºC and 4h reaction time. Fig. 3.9 summarizes the results obtained.
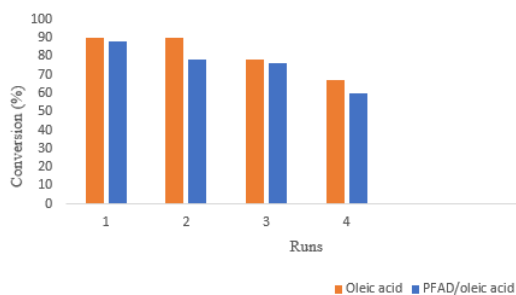

Fig. 3.9 Reusability of Recycled Sulfonated Carbon Catalyst

A marked loss of activity was seen in the reactions after the second recycling of the sulfonated carbon catalyst. There was a decline in conversion after each run. The reasons for the decline in activity can be explained as, first, the presence of a blockage in the pores of the catalyst by large molecules which must have inhibited the diffusion of oleic acid molecules into the pores of the sulfonated carbon. Hara (2010), reported a similar case in which they attributed the loss of activity to the presence of glycerol on the catalyst which cannot be removed by washing with water and forms methyl sulfonate when washed with methanol. Secondly, the loss in activity could have been as a result of leaching of the active components in the washing, and recovery of the catalyst for the recycling process. Dawodu *et al*. (2014) also reported a similar case for one of the catalysts

they synthesized. But then, they attributed the leaching to the presence of smaller carbon sheets which formed a weaker bond with the SO_3H groups. Nevertheless, as can be seen in Fig. 3.9, the sulfonated carbon for this study has a good reusability for the esterification/transesterification of oleic acid, and this can be attributed to its stable C-C framework and the strong attachment of SO_3H groups to the framework.

IV.   CONCLUSION

A sulfonated carbon catalyst for the simultaneous esterification/transesterification of oleic acid, has been synthesized and characterized. The amorphous nature of the catalyst was shown to enhance the surface area and acid strength of the catalyst, which in turn gave a successful simultaneous esterification/transesterification of oleic. A high specific surface area of 7.98 m^2/g was obtained, when compared with those reported in literatures by (Lou *et al*., 2008), (Zong *et al*., 2007), and (Okamura *et al*., 2006), which were less than 5 m^2/g. The acid density at 2.63 mmol/g was also larger than that obtained by (Lokman *et al*., 2015) . The obtained acid density indicated that most of the SO_3H were in the interior part of the catalyst. Thereby, enabling the reactants to have contact with more acid sites, and ensuring a better catalytic activity. Furthurmore, reaction conditions were well studied and optimum conversion of 96% was obtained at metanol:oil molar ratio 1:7, catalyst loading 15wt% and 4h reaction time. Investigations on the recycling of the catalyst showed a good stability after it was recovered successfully from the reaction mixture, and reused for the subsequent esterifications/ transesterifications of oleic acid acid. Conversions of 90% were obtained in the first two runs. However, a decline in conversion was obtained for the subsequent recycling.

From the results obtained in the study, it is proposed that sulfonated carbon is a suitable catalyst for the synthesis of biodiesel from high free fatty acid content feedstocks, owing to its activity. It can be easily recovered and reused after the whole process. The catalytic performance exhibited by this catalyst, has great potential for biodiesel production from feedstocks containing high free fatty acid content, especially when some modifications are done to it.

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