



Synthesis of Fatty Acid Methyl Ester (Biodiesel) using Environmentally Benign Catalyst (Yam Peel)

Muhammadu Abdulsalam and *Hamisu Umar Farouk

Department of Pure and Industrial Chemistry, Bayero University, P.M.B. 3011, BUK, Kano, Nigeria

*Correspondence Email: hamiz5@gmail.com

ABSTRACT

Homogeneous alkali-catalyzed transesterification is the typical process used in biodiesel production, complicating the downstream separation processes and causing oversupply of glycerol as by-product. In this work the synthesis of biodiesel by solid heterogeneous acid catalysts using sulphuric and phosphoric acids functionalized yam peel as catalysts and fried oil as the source of glyceride was investigated. The solid acid catalysts were prepared by carbonization followed by direct sulfonation and phosphorylation via reflux. The FTIR Spectra of the catalyst and the XRD confirmed the incorporation of sulphate and phosphate groups on the carbonized yam peels. The amount of catalyst loading was investigated on the biodiesel yield. Sulphuric acid treated catalyst showed highest yield of 62.6 % at 1.0 g catalyst load, with phosphoric acid treated catalyst having slightly lower at 61.2 % and 1.0 g load. The physicochemical analysis of the used oil showed acid value of 27.50 mg KOH/g, free fatty acid (FFA) value of 13.83, density 0.91 g/mL, saponification value 154.28 mgKOH/g. The presence of high free fatty acid in the oil feed indicate that the preferred catalyst to be used is heterogeneous catalyst.

Keywords: Acid-catalyst, Carbonization, Phosphoration, Sulfonation, Transesterification

INTRODUCTION

Energy is the chief mover of economic growth and plays a vital role in sustaining the modern economy and society. The future of economic growth depends on the long-term accessibility to energy from the sources that are easily available, safe and affordable. However, with the increased use and depleting problem of fossil fuels there is a huge demand for an alternative source of energy which can produce sufficient energy of preferred quality in various forms in a sustainable manner and at competitive prices (Ouda *et al.*, 2016).

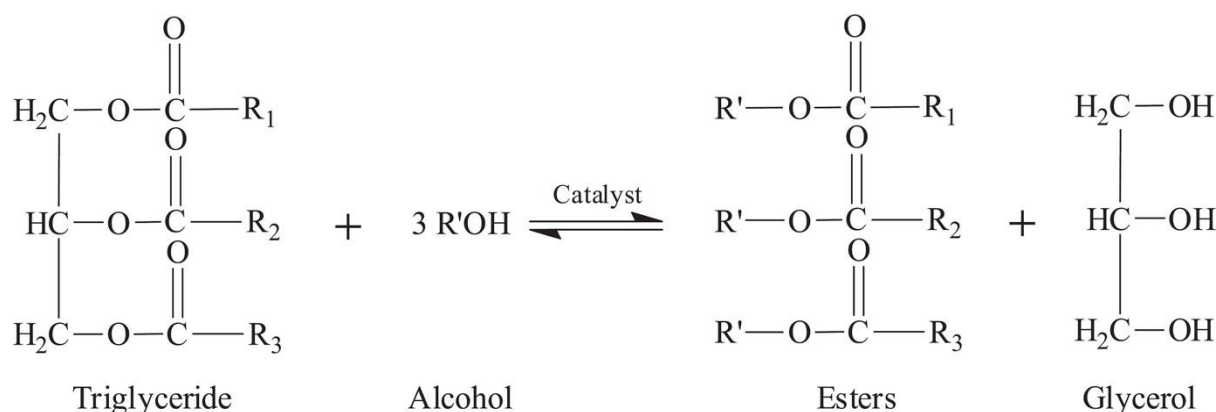
In recent years, there has been increased focus on global warming and the depletion of resources caused by the heavy consumption of finite fossil resources. In order to resolve these problems, biomass is increasingly gaining international attention as a source of renewable energy. Biodiesel fuel produced by the transesterification of vegetable oils and animal fats is expected to be one of the biomass-based alternatives to fossil resources due to its renewability, lack of aromatic compounds, high biodegradability, and low sulphur dioxide (SO₂) and particulate matter content (Kawashima *et al.*, 2007). Apart from the processing methods, biodiesel feedstock also requires some conversions to meet regulatory standards. The application of biodiesel in conventional diesel engines helps to remediate the global warming effect by reducing

significantly the emission of carbon dioxide (CO₂) on a life cycle basis, carbon monoxide (CO), unburned hydrocarbons and particulate matters by 78, 46.7, 45.2 and 66.7 %, respectively (Ezebor *et al.*, 2014). The likelihood of producing biofuels from locally grown sources, as an alternative for various petroleum products is one of the reliable methods of overcoming the energy crisis. Any investments in biofuels will lead to a considerable boost in economic development. It is expected that with suitable production process, biofuels will produce significantly lesser greenhouse gas emissions than fossil fuels (Monisha *et al.*, 2013).

Transesterification is a conventional technique employed for the production of biodiesel. It is a catalyzed reversible reaction which involves a homogeneous or heterogeneous catalyst to produce biodiesel from oleaginous feedstock with the aid of short-chain alcohol. The triglycerides (TG) from the feedstock are converted into fatty acid alkyl esters (FAAEs) referred to as biodiesel and producing glycerol as the by-product which can be separated in a decantation funnel overnight or by centrifugation (Kirubakaran and Selvan, 2018). The overall chemical equation is shown in the reaction process is shown in Scheme 1. Since this process occurs in a liquid-liquid two-phase system, its rate is constrained by the mass transfer contributed by immiscibility of oil and alcohol. Other factors such as high operating cost and

energy requirements further limit its performance

(Tiwari *et al.*, 2018).



Scheme 1: Catalytic Transesterification (Pereira *et al.*, 2014)

Catalytic transesterification using methanol is the typical method employed for the production of biodiesel due to the fact that methanol is relatively cheap and easily accessible. This results in huge production of glycerol as by-product, creating the problem of oversupply and declining their market price (Marx, 2016). Therefore, manufacturing biodiesel via a novel glycerol-free method can be more favorable to improve the processing economics and avoid the by-production of glycerol. For instance, methyl acetate can replace the alcohol reactant in transesterification reaction and form triacetin, a higher added value by-product as compared to glycerol. Catalyst is a crucial element in speeding up the transesterification reaction for biodiesel production. Nowadays, the commercial production of biodiesel makes use of homogeneous catalysts (Domingues *et al.*, 2013). This increases the overall operating cost due to downstream processes to recover the catalysts. Thus, heterogeneous catalyst is preferable. However, although heterogeneous alkaline catalyst offers high catalytic performance, its activity is affected by feedstock with high free fatty acid (FFA) content due to soap formation (Chakraborty *et al.*, 2016). Heterogeneous acidic catalyst is suitable to be used under the conditions of high FFA content and water without soap formation (Ezebor *et al.*, 2014).

Solid acid catalysts are gaining a lot of attention because of their ease in separation of product without the need for high consumption of energy and elimination of the problems associated with corrosion, toxicity and environmental pollution (Dawodu *et al.*, 2014). These kinds of catalysts are capable of catalyzing simultaneous esterification and transesterification of FFAs and triglycerides present in non-edible vegetable oils into biodiesel. Solid acid catalysts such as zeolites, sulphated zirconia, niobic acid, perfluorosulfonated ionomers are currently being used for biodiesel

production (Endalew *et al.*, 2011). Despite their high catalytic activities, they either suffer from low acid densities, deactivation in the presence of water, small pore size or poor stability (Lou *et al.*, 2012). Researchers have reported the synthesis of water-tolerant catalyst from carbon-bearing materials by incomplete carbonization followed by sulfonation with concentrated sulphuric acid (Toda *et al.*, 2005). Various carbon materials such as naphthalene, glucose, starch, cellulose, sucrose, vegetable oil asphalt are presently being used. A prepared carbon-based catalyst from bagasse and its catalytic activity was tested on the esterification of oleic acid with methanol and transesterification of waste cooking oil containing a high amount of FFAs 38.6 wt% (Lou *et al.*, 2012).

In general, the catalysts used for transesterification process can be bases, acids or immobilized enzymes. For the transesterification to give a high yield, the alcohol should be free of moisture and the free fatty acid content must be <0.5 % (Monisha *et al.*, 2013). Transesterification is a reversible reaction but in the production of biodiesel, the backward reaction does not take place or is negligible because the glycerol formed is immiscible with the product leading to a two-phase system.

In this work the synthesis of carbon-based heterogeneous catalyst for both transesterification of triglycerides and esterification of free fatty acids in biodiesel production was carried out. The synthesis of solid acid catalysts was from waste yam peels through two methods; by direct sulfonation (via reflux by sulfuric acid) and phosphorylation (via reflux by phosphoric acid).

The effects of operating parameters such as acid concentration and amount of catalyst loading on the percentage yield of the biodiesel was investigated.

MATERIALS AND METHODS**MATERIALS**

Fresh Yam peels were collected from Kabuga in Gwale Local government, Kano State, Nigeria, the yam peel sample was washed and dried for 48 hours at 60 °C. The sample was crushed into fine powder using mortar and pestle. The fried cooking oil was obtained at Rigiyar Zaki, Ungogo Local Government, Kano State. Phosphoric acid 85 % (H₃PO₄), Sulphuric acid 98 % (H₂SO₄), Methanol (≥99.8 %), 1 M NaOH, distilled water, fried oil (awara), Phenolphthalein indicator 1 g/L, Starch indicator, 0.1 N KOH, 0.5 N alcoholic potassium hydroxide, 0.5 M hydrochloric acid 37 % (HCl), Ethanol (≥99.8 %), Sodium hydroxide pellet (≥85 %), Iodine bromide. All the chemicals and materials were of analytical grade.

METHODS**Physicochemical analysis of oil sample****Acid value determination**

The oil sample (2 g) was weighed and poured into a dried conical flask, 25 mL of absolute ethanol and 2-3 drops of phenolphthalein were both added, the mixture was heated and shaken in water bath for 10 min, after cooling, the solution was titrated against 0.1N KOH until pink color appeared, the titer value recorded. The acid value (AV) and free fatty acids (FFA) were calculated using Equations 1 and 2 respectively (Usman *et al.*, 2013).

$$AV = \frac{\text{mL KOH} \times N \times 56}{\text{weight (g) of sample}} \quad (1)$$

$$FFA = \frac{AV}{2} \times 100\% \quad (2)$$

Where N is the normality of KOH.

Saponification value determination

Approximately 2 g of the oil sample was weighed into 250 mL conical flask, 25 mL of ethanolic KOH was added, a reflux condenser was attached, and the flask content was heated on a boiling water bath for 1 h with occasional shaking. While the solution was still hot, 3 drops of phenolphthalein indicator were added, the mixture was titrated with 0.5M HCl and the titer value recorded, the same procedure without sample was done for the blank (Usman *et al.*, 2013). The saponification value (SV) was calculated from Equation 3.

$$SV = \frac{56.1 (B - S) \times M \text{ of HCl}}{\text{weight (g) of Sample}} \quad (3)$$

Where B is the average titer value for the blank, S is the average titer value for the sample solution and M is the molarity of HCl.

Specific gravity measurement

Density bottle of 50 mL capacity was filled to the mark with distilled water and the

weight taken as W₁ and then filled with oil sample and recorded as W₂ and that of empty bottle was W₃ (Usman *et al.*, 2013). The specific gravity of the oil was calculated using equation 4.

$$\text{Specific gravity} = \frac{W_1 - W_3}{W_2 - W_3} \quad (4)$$

Catalyst preparation

Yam peel powder (10 g) was hydrolyzed using 200 mL of 1 M NaOH followed by refluxing for 2 h, with repeated washings and filtering the glucose content was determined using volumetric method (glucose oxidized method). The residue was dried in an oven for 3 h at 105 °C followed by carbonization for 2 h at 400 °C in a muffle furnace. After carbonization, it was washed with distilled water to remove residual ash and left to dry (Viena *et al.*, 2018), the same steps were repeated 5 times. The carbonized yam peel was divided into two, 1 M sulphuric acid and 1 M phosphoric acid were added differently on the carbonized yam peel and refluxed for 2 h in a ratio of 1:10 for both the two acids concentration (Dawodu *et al.*, 2014; Tamborin, *et al.*, 2015; Endut *et al.*, 2017). It was dried at room temperature after which the catalyst was analyzed using FTIR spectroscopy and XRD analysis.

$$\text{Mass of catalyst} = \frac{\% \text{ of catalyst} \times \text{mass of oil}}{100} \quad (5)$$

At different runs 2 % (0.2 g), 5 % (0.5 g), and 10 % (1.0 g) of the catalyst were used for the production of biodiesel.

Catalyst Characterization and Screening

FTIR and XRD characterization techniques were carried out on all the developed solid acid catalysts before and after incorporation of the acids. Fourier Transform Infrared Spectroscopy (FTIR) was adopted for functional group analysis and possible molecular rearrangement expected for chemical changes by careful inspection of the spectra, X-ray Diffractometer (XRD) was used to study the diffraction patterns of the derived catalysts (Zhang *et al.*, 2014).

Procedure for biodiesel production

The biodiesel production was carried out with a mixture of methanol and oil (1:9) over the yam peel based derived catalysts. The prepared sulfonated catalyst of 0.2 g was placed in a plastic container and 2 mL of methanol was added, the mixture was preheated for few minutes. After preheating the mixture of catalyst and methanol, 18 mL of preheated oil was added, the mixture was put into mechanical shaker for 5 h at 100 revolutions per minute at 60 °C. After 5 h the catalyst was separated, and the filtrate was allowed to settle for 24 h to obtain the glycerol and methyl ester, the methyl ester was washed up with distilled

water and separated with separating funnel to obtain the pure biodiesel. The biodiesel produced was placed in a hot air oven at 105 °C for 30 min to evaporate the remaining water (Dawodu *et al.*, 2014). The same procedure was repeated for 0.5 g and 1 g, as well as for the other catalyst prepared from phosphoration for masses of 0.2 g, 0.5 g and 1 g. After drying, the weight of biodiesel was measured and recorded. Thus, the yield of transesterification process was calculated using the formula as in Equation 6 (Ribeiro *et al.*, 2017).

$$\% \text{ yield} = \frac{\text{weight of biodiesel produced}}{\text{weight of oil used for biodiesel}} \times 100 \quad (6)$$

RESULTS AND DISCUSSION

Physicochemical Analysis of the oil Sample.

Acid value is the measure of mg of KOH required to neutralize FFA in 1 g of the oil. The acid value of the oil feed as shown in Table 1 was 27.50 mg KOH/g hence, this value indicates that there was free fatty acid present in the oil feed that need to be neutralized to obtain good biodiesel quality (Reda, 2014).

Table 1. Physicochemical analytical result of the oil feed

S/N	Parameter	Values
1.	Acid value (mg KOH/g)	27.50
2.	Free fatty acid (mg KOH/g)	13.83
3.	Density (g/mL)	0.91
4.	Saponification value (mg KOH/g)	154.28

The data obtained from acid value allow us to compute the value of free fatty acids present in a given oil, the value of free fatty acids indicate the catalysis method to employ, if the value of FFA is lower than 3 homogeneous catalysis is preferred and if its greater than 3, catalysis use is heterogeneous because at value greater than 3 homogeneous catalysis lead to the formation of soap, which make separation between the biodiesel and the soap to be difficult (Dawudo *et al.*, 2014). The value of FFA gotten from the frayed oil (awara) i.e. 13.83 mg KOH/g allow us to make use of heterogeneous catalysis method. Density has been described as one of the most basic and most important properties of fuel because of its correlation with cetane number, heating values and fuel storage and transportations (Alawu *et al.*, 2007). The density, 0.91 g/mL obtained for the oil feed as shown in Table 1 was close to standard which is within the range of 0.87-0.9 g/mL (Usman *et al.*, 2013). Saponification value was found to be 154.28 mg KOH/g oil which is below the standard range (175 – 205 mg KOH/g) (Usman *et al.*, 2013)

of oil used in the production of soap and shampoo, hence biodiesel production is favored using the catalyst synthesized from yam peel. The glucose content was 99 and is within the standard range of 80-130, it shows that there was adequate glucose content in the yam peel.

Catalysts FTIR spectroscopy and XRD

FTIR Analysis

FTIR analysis was performed within the wave number range of 600 to 4000 cm^{-1} to identify the functional group present on the surface of the catalysts shown in Figure 1. This is a critical analytical test to verify the presence of the acidic group which is the active site in catalyzing the transesterification reaction and leading to biodiesel production. According to Chellappan *et al.* (2018), a solid acid catalyst must possess hydroxyl, -OH, carboxylic acid, -COOH and sulfonic acid, -SO₃H functional groups for it to be efficient. Table 2 lists out the common stretching vibrations in acid catalysts and their corresponding frequencies.

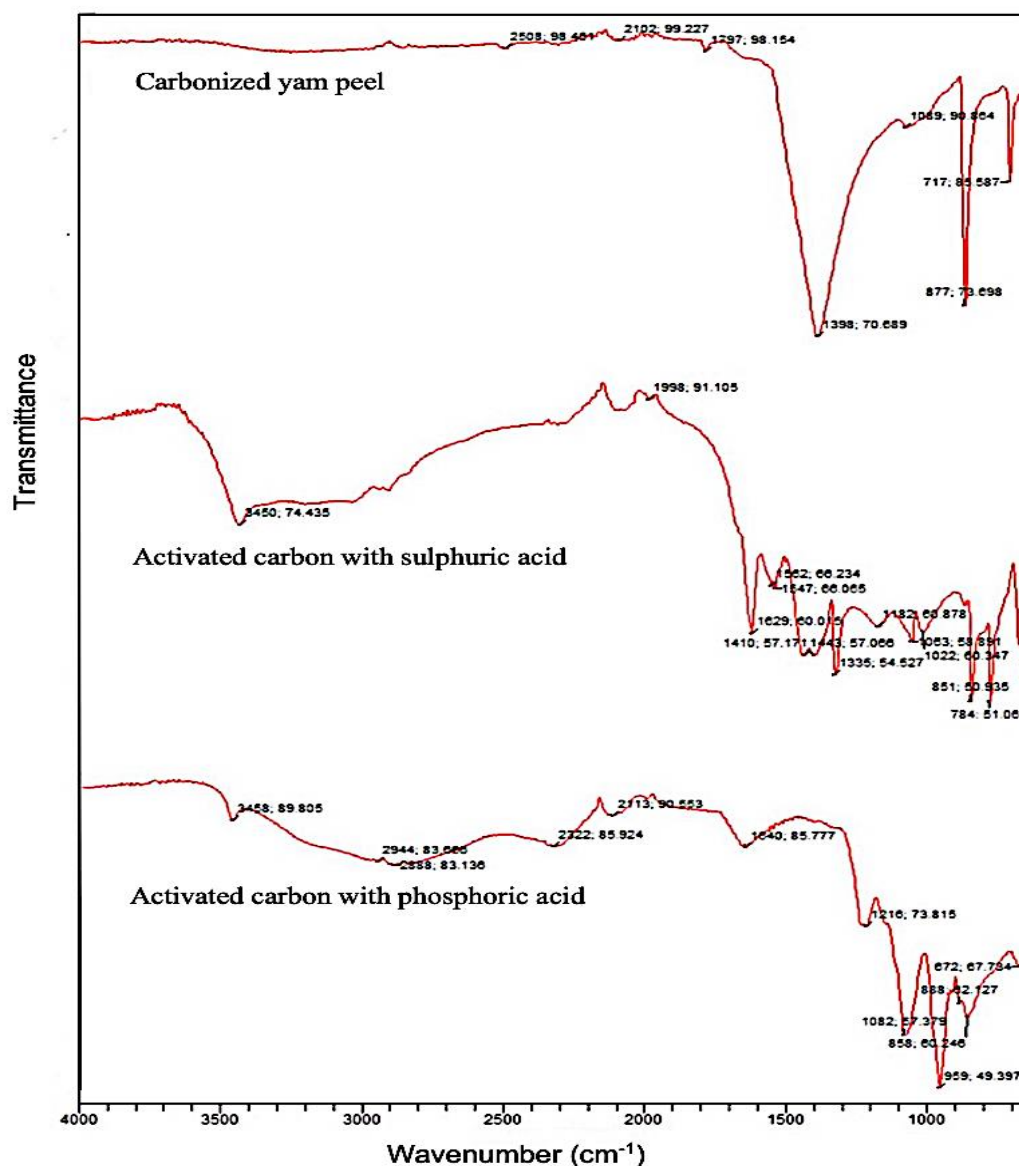


Figure 1. FTIR Spectra of the various produced catalysts

Table 2: FTIR Stretching Frequencies (Thushari and Babel, 2018; Niu *et al.*, 2018).

S/N	Vibrations	Frequency ranges (cm ⁻¹)	Observed frequency ranges (cm ⁻¹)
1.	O-H stretch	3600-2800	3335-2344
2.	C=O stretch	1800-1500	1800-1500
3.	C=C stretch	1600	1600
4.	O=S=O stretch	1200-1100	1629
5.	-SO ₃ H stretch	1296	1153-1053
6.	C-S stretch	715-670	870-672

As shown in Figure 1, three curves representing each sample have revealed well defined differences between carbonized yam peels and the synthesized solid acid catalysts, indicating

the effect of direct sulphonation and phosphorylation method on the catalyst support. For the sulphuric acid support curve, there was observed transmittance peaks at 1629 cm⁻¹, 1153 to 1053cm⁻¹

and 870 to 672 cm^{-1} attributed to O=S=O stretching, $-\text{SO}_3\text{H}$ stretching and C-S stretching respectively. Since concentrated sulfuric acid was used as the sulfonating agent, aliphatic groups of CH_2 or CH_3 could be oxidized to carboxylic acid groups, enhancing the total acid density of the fabricated catalysts (Sandouqa *et al.*, 2018). This was noticed by the presence of vibration bands around 1800 to 1500 cm^{-1} , signifying C=O stretching of the carbonyl or carboxylic acid functional groups at the surface of the solid acid catalyst. Sulfonic acid group was the most prominent functional group since the O=S=O and $-\text{SO}_3\text{H}$ stretching peaks were more significant compared to others. The weak and broad peak at wave number ranging from 3335 to 2344 cm^{-1} was assigned to the stretching mode of O-H in the alcoholic or phenolic group in the samples. The stretching vibration of hydroxyl group was not obvious in both samples, but its presence would enhance the catalytic performance of the synthesized catalysts (Shuit and Tan, 2014). For the phosphoric acid support curve from Figure 1; broad absorption band around 3500 cm^{-1} shows the presence of O-H from HPO_4^{2-} , the peak around 1000 cm^{-1} shows the presence of P=O stretching of HPO_4^{2-} , the intense absorption band at 600 to 560 cm^{-1} indicate P-O stretching of PO_4^{2-} . Comparing the spectra of the carbonized yam peel and catalyst formed, the O-H, P=O and that of P-O confirmed that, phosphate group was successfully incorporated on the carbonized yam peel. Thus, the catalyst synthesized is the expected catalyst. It is worth mentioning that, the catalyst support was expected to have carbonyl or carboxylic region prior to either sulphonation or phosphoration since the relevant peak was also seen in the FTIR spectrum of the carbonized yam peel. This common peak in all the three samples is a stretching mode of conjugated C=C bond at 1600

cm^{-1} , attributable to the aromatic ring formed as a result of incomplete carbonization of carbonaceous materials. Therefore, a more rigid carbon material was formed. This proved that the active sites were well established on the surface of the sulfonated solid acid catalyst.

XRD Analysis

XRD is an analytical technique used to identify the composition, crystalline phase and crystallite size from the constructive interference of monochromatic X-rays and a crystalline sample. Only a solid with crystalline structure can diffract the beams of X-ray. This is due to the fact that unlike amorphous materials, the atoms of crystalline structure are arranged in a periodic array (Chellappan *et al.*, 2018). The XRD patterns of the carbonized yam peels (C-support) compared with the synthesized sulfuric acid catalysts and carbonized yam peels (C-support) compared with phosphoric acid catalysts are shown in Figure 2 and 3 respectively. One noticeable fact is all the samples tested were semi crystalline since only a few crystalline phases were detected. Nonetheless, there was a broad diffraction peak ranging from 20° to 30° in each sample corresponding to aromatic carbon C (Chellappan *et al.*, 2018). This was induced by the presence of amorphous carbon structure which consist of randomly oriented aromatic carbon sheets. Despite all samples having similar curve, patterns of the carbonized yam peels and synthesized catalysts were not the same, indicating that there was a change of crystal structure during thermal treatment. As the broad peak became narrower and more intense trending from carbonized yam peels to synthesized catalysts due to the formation of stable carbonaceous material that is ordered graphitic structure in the fabricated catalysts.

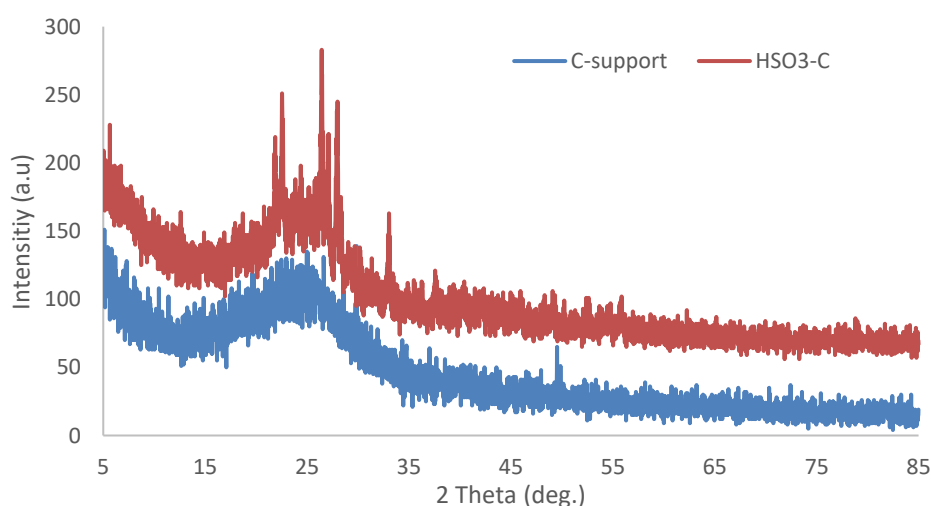


Figure 2: XRD Diffractogram of Sulphuric acid catalyst compared to carbonized yam peel

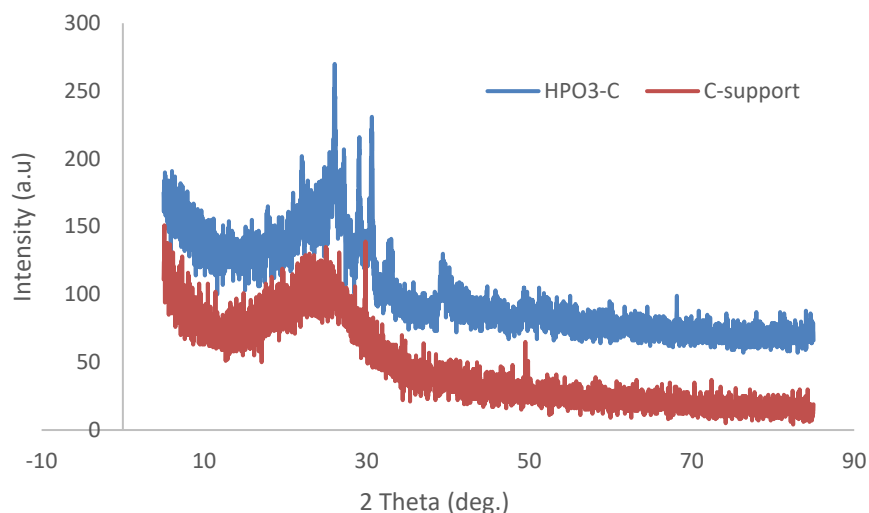


Figure 3: XRD Diffractogram of Phosphoric acid catalyst compared to carbonized yam peel

Biodiesel Yield

From bar chart of Figure 4, the percentage yield obtained, shows that sulphuric acid catalyst has slightly higher yield than Phosphoric acid catalyst. This can be attributed to mutual electron-withdrawal caused by the strong hydrogen bonding to sulfonic groups which subsequently resulted in high acid density, and total acid density of the synthesized catalyst increased with the

concentration of sulfonating agent used (Chellappan *et al.*, 2018). As the concentration of sulfuric acid increased, higher sulfur content will allow more acidic site to anchor on the catalyst support and thus resulting in higher distribution of acidity (Abdullah *et al.*, 2017). It was also observed that, the percent yield of the two biodiesel shows that, the amount of catalyst used in the production slightly affect the yield, as the catalyst amount increases the yield also increases.

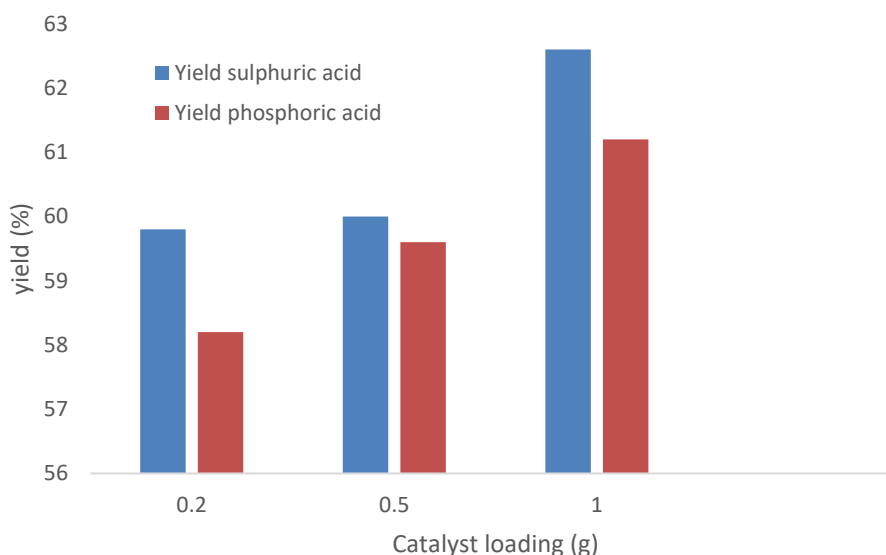


Figure 4: Comparative percentage biodiesel yield in relation to catalyst loading

CONCLUSION

The present work focused on synthesizing solid acid catalyst from biomass waste of yam peels for biodiesel production. From the FTIR analysis, the presence of sulfonic and phosphoric acid groups vibration bands respectively proved its successful attachment on the catalyst support

(carbonized yam peel). Based on the XRD analysis, differences in the XRD patterns of the carbonized yam peels and synthesized catalysts indicates that there is a change of crystal structure during thermal treatment. In the production, the catalyst ratio, type of the acid as well as the concentration of the refluxing acids account on the yield of the biodiesel

produced. It was identified that as the refluxing acid concentration increases the yield also increases, and if the amount in the catalyst loading was increased the biodiesel production also increases in the same proportion. Also, there was improvement in reaction yield using a catalyst synthesized under more concentrated sulfonating agent, indicating the role of sulfonation in surface modification and subsequently the yield.

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