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FORMULATION OF A CARBON-BASED SOLID ACID CATALYST FROM GROUNDNUT HUSK FOR THE ESTERIFICATION OF OLEIC ACID

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ABSTRACT

In this research, a biochar was prepared from groundnut husk and sulphuric acid. The biochar was sulphonated with chlorosulphonic acid to give a carbon-based sulphonated solid acid catalyst (SAC). The catalyst was characterised by N_2 adsorption and desorption at 77K after degassing overnight under vacuum at 250°C, scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectroscopy, and total acid density measurement. The results of the acid density measurement showed that the sulphonated biochar has a relatively high acid density of 3.2 mmol/g, while that of the non-sulphonated counterpart is 0.56 mmol/g. Comparison of the percentage conversion of oleic acid by esterification with methanol and butanol was carried out under three different conditions, viz: without catalyst, with the non-sulphonated biochar and with the sulphonated biochar, under the same experimental conditions of 5% catalyst weight percent (based on weight of acid), acid-methanol mole ratio of 1:12, reaction temperature of 70 °C, and five hours reaction time. Up to 91.6% percentage conversion of oleic acid to methyl oleate and 86.4% for butyl oleate were achieved, proving the effectiveness of the sulphonated biochar in catalysing the esterification reaction of oleic acid with methanol and butanol. The results of this study are expected to provide insights into the development of sustainable and cost-effective solid acid catalysts for the synthesis of oleate esters and other value-added materials from renewable feedstocks.

Keywords: groundnut husk, sulphonated catalyst, esterification, oleate esters

INTRODUCTION

There is a growing demand for sustainable and eco-friendly catalytic materials (Qian *et. al.*, 2015), and this has driven significant research efforts toward the development of effective solid acid catalysts obtained from renewable resources (Jamil *et. al.*, 2021). Esterification and transesterification reactions, particularly the conversion of long-chain fatty acids like oleic acid from fats and oils into their corresponding esters, are of paramount importance in various industrial processes including the production of biodiesel. The esterification of oleic acid, a long-chain unsaturated fatty acid commonly found in various vegetable oils, presents both technical and environmental challenges due to its high viscosity and susceptibility to oxidation (Zhang *et. al.*, 2020). Traditional homogeneous acid catalysts like sulphuric acid suffer from several disadvantages including corrosion, product contamination, and difficulty in catalyst recovery (Kastner *et. al.*, 2012). Conversely, solid acid catalysts offer distinct advantages such as ease of separation, recyclability, and reduced environmental impact (Jordan *et. al.,* 2016; Rechnia-Gorący*et. al.,* 2020; Sun *et. al.,* 2020).

This article investigates the performance of a carbon-based solid acid catalyst prepared from groundnut husk in the esterification of oleic acid. It presents a simple method for preparing an efficient solid acid catalyst from groundnut husk for the esterification of oleic acid for biodiesel production. Groundnut husk, a lignocellulosic agricultural by-product, rich in cellulose, and hemicellulose, serves as an attractive precursor for the preparation of carbonaceous materials due to its high carbon content (Abdulrazak *et. al.,* 2014; Ajala and Ali, 2020), low ash content, porous structure and low cost (Lewicka, 2017; Madhu and Sharma, 2017). The application of agricultural by-products like groundnut husk, which is an abundant and generally underutilized by-product of groundnut processing in Nigeria, provides a promising avenue for the preparation of value-added carbon-based solid acid catalysts (Deng *et. al.,* 2015; Omogbai*et. al.,* 2019; Geeta *et al*., 2020).

MATERIALS AND METHOD

Materials

Groundnut seeds were purchased from a local market in Port Harcourt, Rivers State, Nigeria. The husks were separated from the kernels and used for the study. All reagents used were of analytical grades except oleic acid which was of industrial grade (76%).

Catalyst Preparation

The solid acid catalyst (SAC) was prepared following the method of Ouyang *et. al.* (2014) with modifications. Groundnut husk (8 g) was soaked in 10% sulphuric acid (16 g) for 24hours. Toluene (10 ml) was added and the mixture was refluxed (5 hours) to give a black carbonaceous solid. The solid was filtered and washed in boiling water to remove residual sulphuric acid and toluene. The char obtained was denoted as carbonaceous groundnut husk (CGH). The CGH (2 g) was refluxed in chlorosulphonic acid (10 ml) for 4 hours. Thereafter, the sulphonated carbonized material (denoted as CGH-Sulph) was filtered and washed with hot distilled water (80 ^oC) until all traces of sulphonate ion was removed, as indicated by $BaCl_2$turbidemetry. The residue was dried overnight in an oven at 105 ^oC, and ground to yield the catalyst.

Catalyst Characterization

The catalyst sample was characterized before and after sulfonation to determine the changes that occurred during the sulfonation process. BET surface area and pore structure were determined by N_2 adsorption and desorption at 77 K (Quarterchrome Instruments) after the samples were degassed under vacuum at 250˚C overnight. The specific surface area (S_{BET}) of the samples was calculated with the Brunauer-Emmett-Teller (BET) equation (Brunauer, Emmett and Teller, 1938) using the N_2 adsorption isotherm data between the relative pressures (P/P0) of 0.05 to 0.25 (Kaneko *et. al.,* 2015). Surface structures were investigated using a scanning electron microscope (SEM) (PRO:X:800-07334, Phenom World). Fourier transform infrared (FT-IR) spectrums of the samples were recorded in the range 400 - 4000 cm^{-1}(FTIR-8400S, Shimadzu), using KBr pellets. The total acid density and sulfonic acid density of CGH-Sulph were obtained by acid-base back titration (Liu *et. al*., 2010). In a typical reaction, the sample (0.1 g) was added to NaOH (50 mL, 0.004 M) with stirring for 1 hour at room temperature. After filtration, excess NaOH was neutralized with HCl (0.02 M).

Preparation of Esters

The esters of oleic acid were prepared according to the method of Orji *et. al.* (2018), with some modifications. In a typical procedure, oleic acid, butanol (mole ratio of 1: 12; acid:alcohol), and benzene (100 ml) were charged into a three-neck round bottom flask equipped with a Dean-Stark water separator, condenser and thermometer. The mixture was heated under reflux on a thermostatted magnetic stirrer until the desired temperature

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(70 ^{o}C) was attained. Thereafter, the catalyst (CGH-Sulph) was added, stirring commenced, and the heating under reflux continued till there was no change in the quantity of water collected in the separator. On completion of the reaction, the mixture was cooled to room temperature and filtered. The filtrate was washed with hot distilled water (60 ^{o}C, 200 ml $\times$ 5) in a separatory funnel and subsequently dried over anhydrous sodium sulphate, and excess butanol was removed by vacuum distillation to afford the ester. In the case of methanol, the reaction was carried out without benzene, and the Dean-Stark apparatus. The progress of the reaction however, was monitored by acid value titration according to AOCS Cd 3d-63 standard, and the percentage conversion of the free fatty acid calculated with Equation 1 (da Luz Corrêa*et. al.*, 2020). The products obtained were designated as MO and BO to represent methyl oleate and butyl oleate respectively.

$$\%\ \text{Conversion} = \frac{A_0 - A_f}{A_0} \times 100\ \% \qquad (1)$$

Where A_0 is the initial acid value and A_f is the final acid value after the esterification reaction, given in mg KOH/g.

These reactions were repeated, first without the catalyst and secondly with the CGH sample that was not sulphonated (CGH), and then with the sulphonated (CGH-Sulph). Finally, the percentage conversion of oleic acid was compared in the three cases.

Esters Characterization

The ester products were analysed by gas chromatography (Agilent GC 7890) and their Fourier transform infrared spectra (FT-IR) recorded in the range 400 - 4000 cm^{-1} (Carg/y 630, Agilent Technology).

RESULTS AND DISCUSSION

Textural Properties of the Catalyst

The result of the pore characteristics presented in Table 1 shows 45% and 4 % reductions in the surface area and pore volume of CGH-Sulph respectively, relative to that of CGH. This could be because the sulphonation process caused the collapse of the pore structure of CGH. Besides, uniform dispersal of H_2SO_4 on the surface of the CGH sample during the sulphonation process, may have introduced sulphonate groups that occupied some of its active sites, bringing about pore plugging of the carbon based support (Cao, et al., 2021).

Table 1: Pore characteristics of the catalyst before and after sulphonation

Samples	BET surface area (m^{2}g^{-1})	Total pore volume (cm^3 g^{-1})	Average pore size (Å)
CGH	103.50	0.13	1.14
CGH-Sulph	56.44	0.09	1.20

However, when compared with the CGH sample, the pore diameter of CGH-Sulph showed a 5% increase from 1.14 to 1.20**Å**, representing a 5% increase in pore diameter. This helps improve the interaction between the active -SO_3H groups of the catalysts and reactants during the esterification reaction, since a large pore volume would easily accommodate a long chain fatty acid like oleic acid (Zhang *et. al.*, 2020).

Total acid density of catalysts

The total acid density of the catalyst samples as calculated from the acid back titration proved that the biochar was sulphonated by the sulphonation process.

The presence of -SO_3H acid sites in the catalysts is likely a result of the sulfonation, as evidenced by the low acid density of the non-sulphonated biochar (0.56 mmol/g) against 3.2 mmol/g recorded for the sulphonated sample.

SEM of the Catalyst

The particles of the CGH-Sulph catalyst have smaller sizes, are uneven and granular in shape, and are without a well-defined surface pore structure (Figure 1B). The micrograph of the non-sulphonated biochar (Figure 1A) shows more pore spaces than the sulphonated sample, though the sulphonated sample has bigger particle sizes as a result of the grafting of the -SO_3H groups on the active sites of the biochar. This is in line with the results obtained from BET analysis.

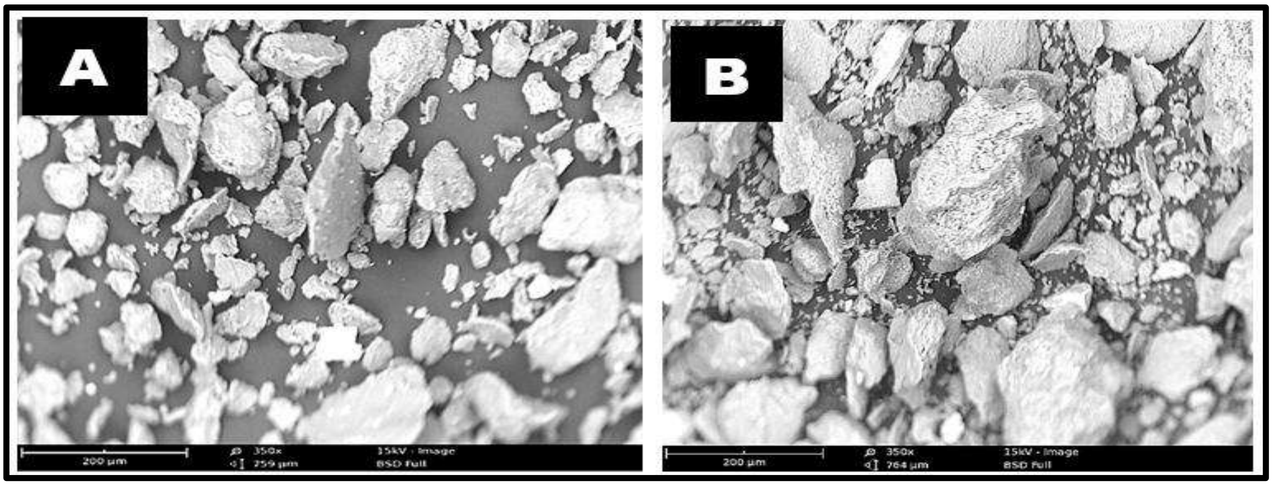

Figure 1: SEM of (A)CGH (B)CGH-Sulph

FTIR of the Catalyst

From Figure 2b, the S=O symmetrical stretching absorption peak at 1335 cm^{-1}, which is completely absent from the IR spectrum of CGH, and the peaks above 3500 cm^{-1}attributed to the absorption peaks of the -OH functional group, are indicative of the presence of -SO_3H groups on CGH-sulph (Chen and Fang, 2011), making it possible for it to act as a Bronsted acid. The absorption peaks in the IR spectrum of CGH-sulph are more prominent than in the sample that was not sulphonated (Figure 2a). The absorption peaks at 1450 and 1519cm^{-1}present in the spectrum of CGH-sulph is, ascribed to the C=C stretching mode of alkenes. There's only one such peak at 1533 cm^{-1}in the IR of the non sulphonated sample. The C=O stretching peak for CGH occurs at 1693 cm^{-1}, this peak was moved to1759 cm^{-1}in CGH-sulph. These peaks prove the existence of unsaturated hydrocarbons and -COOH groups, suggesting that organic materials in the groundnut husk were carbonised to form unsaturated, and possibly aromatic compounds through the treatment with sulphuric acid followed by sulphonation (Phothong *et. al.*, 2021).

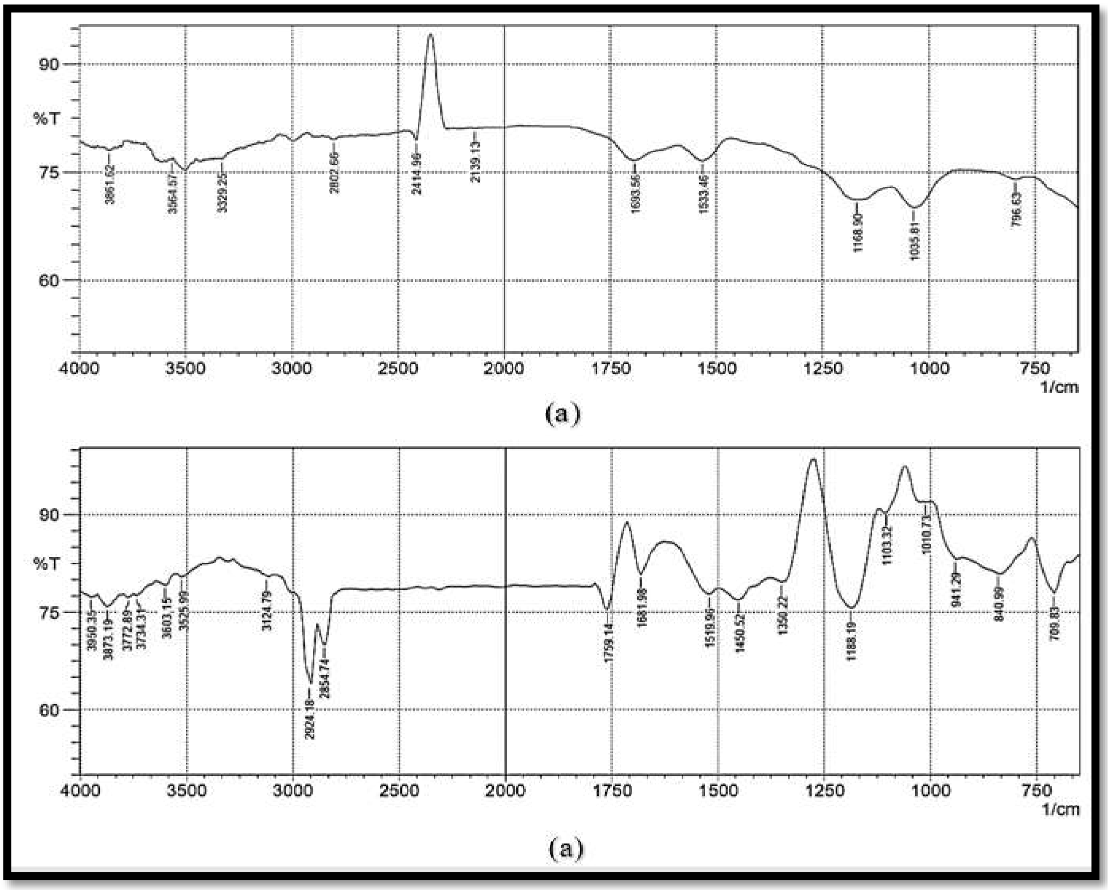

Figure 2: FTIR Spectra of (a)CGH (b)CGH-Sulph

In summary, the physical properties of the groundnut shells were significantly changed by the activation processes to which they were subjected, yielding a sulphonated carbonaceous catalyst with higher acid density, lower surface area and pore volume, bigger particle size, and more active surface functional groups.

Preparation and Characterization of the Esters

The result obtained from calculating the percentage conversion of the acid at the end of the reaction is presented in Figure 3. The esterification of oleic acid with methanol gave a % conversion of 4.5 and 3.3 for the esterification without catalyst and that with CGH respectively. The percentage conversion of the acid rose to 91.6 % and 86.4 % for the methyl and butyl oleates respectively when the sulphonated biochar was employed as catalyst.

Thus, proving that the increase in acid density occasioned by the sulphonation process enhanced the catalytic properties of the sulphonated carbonaceous material (CGH-sulph). The percentage conversion of oleic acid with butanol was lower relative to that obtained with methanol either with or without the two catalysts. This could be explained by the fact that it is relatively easier for the -SO_3H on the surface of the catalyst to sulphonate methanol than butanol owing to the steric effects of the bulkier butanol molecule (Kurczyński*et. al.*, 2022).

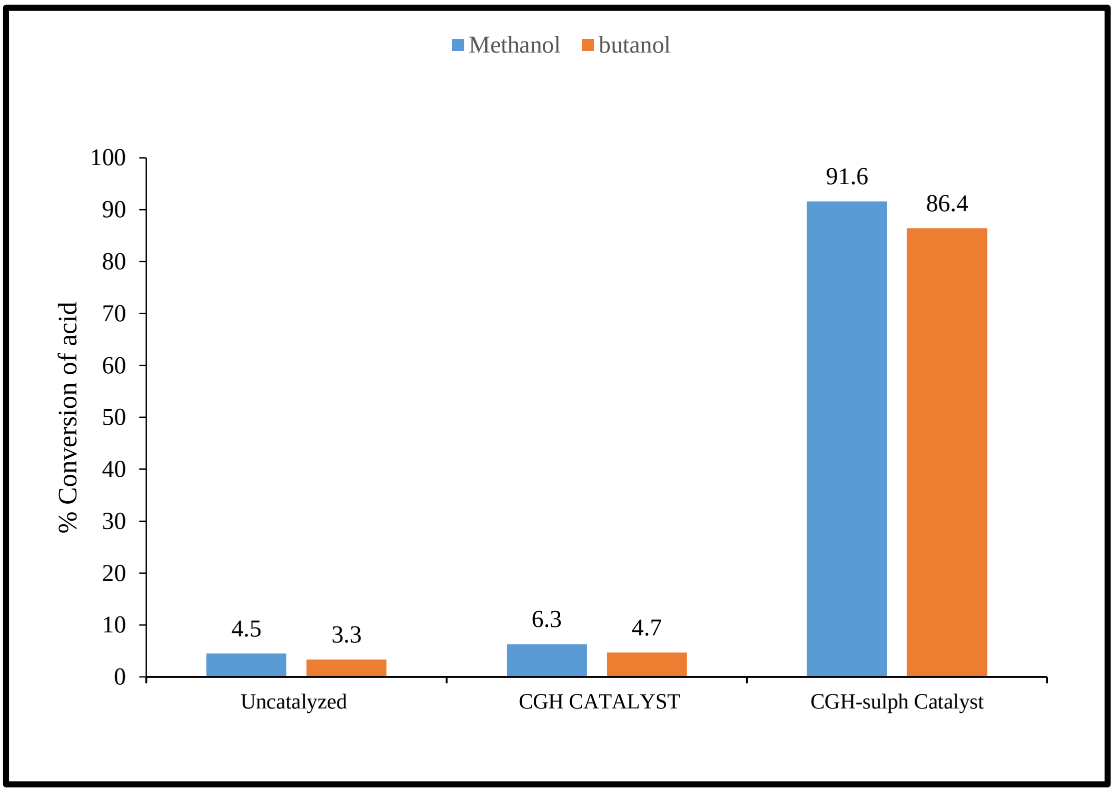

Figure 3: Percentage conversion of the acid

The IR of the esters was obtained and compared with that of oleic acid. The presence of the characteristic ester functional group absorption peaks in the spectra of the compounds synthesized was confirmed by the presence of typical ester absorption peaks observed at 1736cm^{-1}(C=O), 2922cm^{-1}, and 2855cm^{-1}(C-H), and C-O absorption peaks around 1166cm^{-1}and 1114 cm^{-1} for BO (Figure 4B). These absorption peaks in the spectrum of MO occur at 1748 cm^{-1} (C=O), 2922 cm^{-1} and 2855 cm^{-1} for C-H, and C-O absorption peaks around 1162 cm^{-1} and 1095 cm^{-1}(Figure 4C). Comparing these spectra with the standard IR spectrum of oleic acid in Figure 4A demonstrates that the absorption peaks are similar to that of the standard.

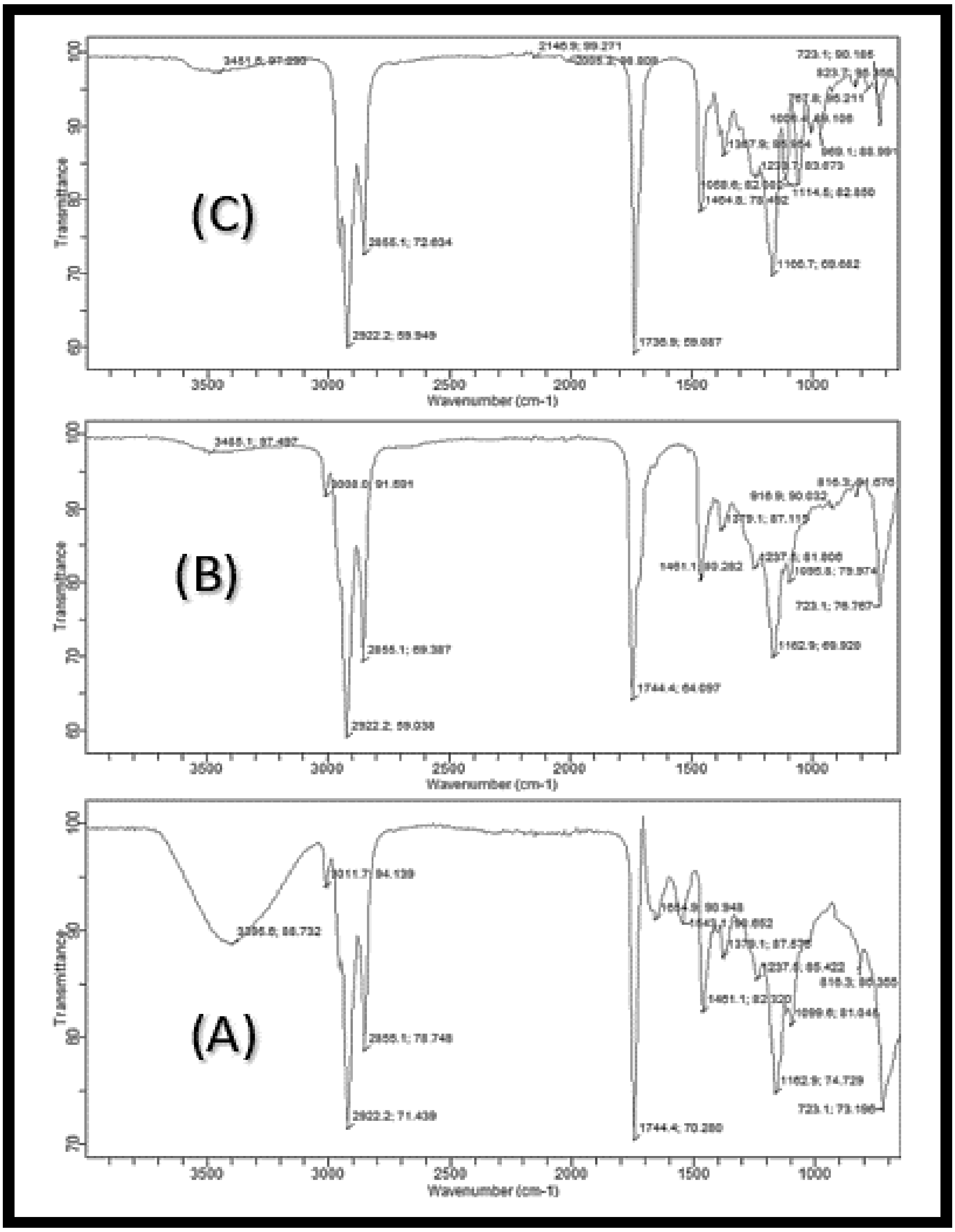

Figure 4: FTIR Spectra of (A)Oleic Acid (B)BO (C)MO

The GC analyses of the synthesised methyl oleate and a standard methyl oleate were compared (Figure 5). The chromatograph shows that both the standard methyl oleate, and the synthesised methyl oleate have the same retention time, further validating the successful synthesis of the ester products.

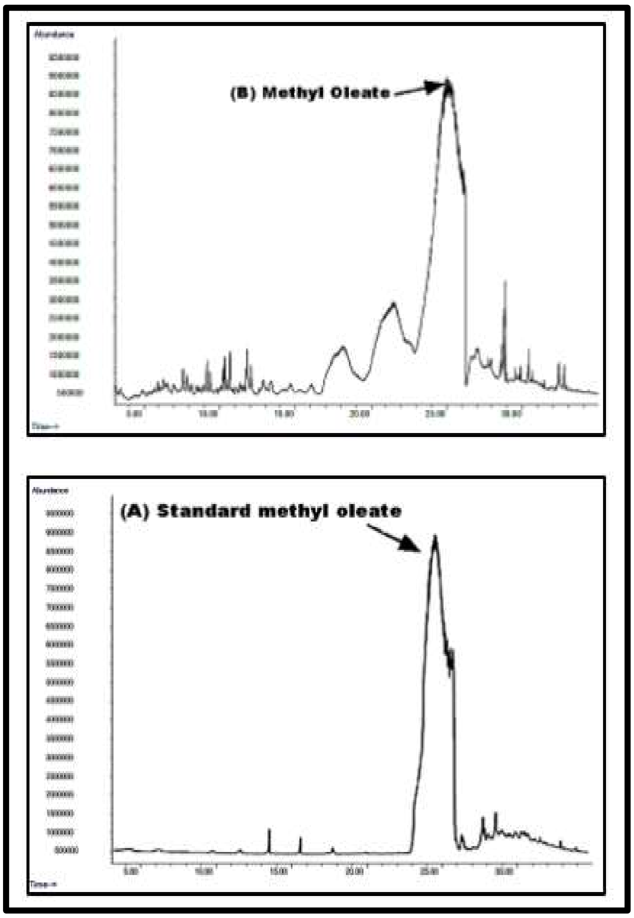

Figure 3: GC of Methyl Oleate

CONCLUSION

A carbon-based solid acid catalyst was prepared from groundnut husk. The catalyst was characterised and used to catalyse the esterification reaction between methanol and butanol with oleic acid. The sulphonated carbonaceous material exhibited better catalytic properties than the non -sulphonated carbonaceous material, leading to 91.6% and 86.4% conversion for methanol and butanol respectively. The findings of this study are expected to provide valuable insights into the development of sustainable and cost-effective solid acid catalysts for the synthesis of biodiesel and other value-added chemicals from renewable feedstocks.

Conflict of Interests

The authors declare that there is no conflict of interest in the course of preparing this article.

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