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# Preparation and characterization of solid acid catalysts derived from coffee husks

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**Abstract**
Carbonization of coffee husks (CHs) at different temperature, 350°C, 400°C, 450°C and 500°C followed by sulfonation with sulfuric acid gave solid carbon acid catalysts: CHs-350-$SO_3H$, CHs-400-$SO_3H$, CHs-450-$SO_3H$ and CHs-500-$SO_3H$. The results of total acid density of the catalysts determined by titrimetry method range from 2.88 to 3.88 mmol/g and the –$SO_3H$ density from 0.64 to 1.24 mmol/g. The catalysts were found by XRD to have a unique amorphous structure. FT-IR results show that the catalysts contain three functional Brönsted acid sites: weak acidic OH and COOH groups and strong acidic $SO_3H$ groups. The solid acid catalyst prepared at 400°C (CHs-400-$SO_3H$) have exhibited the highest catalytic activity and good stability for the esterification of free fatty acids (FFA) in palm kernel oil with ethanol. This study provides an insightful knowledge on the resourceful transformation of a non-edible lignocellulosic solid waste precursor to a highly efficient, benign, and recyclable solid acid catalysts.

**Keywords:** carbon-based solid acid catalyst, coffee husks, characterization, sulfonation, esterification

## 1. Introduction
The acid catalyzed reactions are very important in chemical industry. Sulfuric acid is frequently used as catalyst in various acid catalyzed reactions, such as alkylation, esterification, isomerization, hydration and etherification [1]. However the use of homogeneous acid pose a lots of serious problems such as difficulties of separation and recovery, environmental pollution by the waste, sensitivity to water and equipment corrosion [2, 4]. To date, enormous efforts have been made to replace homogeneous acid with solid acid catalysts.
Various solid acids have been prepared and studied, including zeolites acid, meso structured silica functionalized with sulfonic groups, tungsten oxide zirconia, sulfonated polymers (Amberlyst-15), Nafion-based composites [5], solid superacids (e.g., $SO_4^{2-}/ZrO_2$) and sulfonated carbon materials [1]. However, a metal oxide or a zeolite catalyst has low acidic site density and hydrophilic surface. Nafion contain abundant sulfonic acid groups (-$SO_3H$) that can function as strong acid sites but their catalytic activities are generally lower due to their low surface area [3]. Nafion and Amberlyst with their large pore, are more expensive than mineral acid catalysts which restrict their practical use in acidic cation-exchangeable reactions.
Recently, considerable efforts have been focused on the synthesis and applications of carbon materials containing -$SO_3H$ groups catalysts, due to their low cost, excellent catalytic property, high recycling capacity and strong mechanical stability. The sulfonated carbon solid acid catalysts derived from incomplete carbonization of natural organic material and biomass resources have shown better catalytic performance with high stability for esterification of fatty acids than sulfonated meso-porous silica [6]. Carbon derived materials from palm empty fruit bunch [7], Irul wood sawdust [8], Orange peel [9], coconut shell [10], Yulin coal [11], rice husk [3], camphor tree branches [12], oil palm trunk and sugarcane bagasse [13], cassava stillage residue [14], corn straw [15], seed shells of karanja [16] have been used as carbon precursors for solid acid catalyst synthesis. In general, carbon catalysts containing -$SO_3H$ groups are synthesized via sulfonation of an incompletely carbonized organic compound, which possesses polycyclic aromatic carbon sheets consisting of amorphous carbon structure [11], The carbon rich material is generally obtained by slow pyrolysis that generate a highly cross-linked, multi ringed aromatic structure anchored to lignin [17] that further can be functionalized to make it as strong solid acid catalysts.
Coffee is among the largest export agriculture products of the Democratic Republic of Congo. Treatment of coffee beans yield a large amount of waste (about 80.000 tons per year) which is discarded [18]. Coffee husks (CHs), obtained after de-hulling of coffee cherries during dry processing are probably the major residues from the processing of coffee, for which there are no profitable uses, and their adequate disposal constitutes a major environmental problem. The generated coffee husks (CHs) are rich in organic matter and nutrients and contain compounds such as caffeine, tannins, and polyphenols. Due to the presence of these secondary metabolites, these organic solid residues are toxic and constitute not only a problem of environmental pollution but also restricts its use as animal feed [19] and making it completely inedible with little or no economic value. These solid wastes have been used in the present study for preparation of solid acid catalysts. It is worth mentioning that activated carbon from coffee husks has used as potential bio sorbents for the treatment of contaminated waters with phenol, methylene blue and Cr (VI) ions [20, 21].
The main objective of the present work is to prepare sulfonated carbon-based solid acid from the lignocellulosic waste, coffee husks (CHs) by incomplete carbonization followed by sulfonation with sulfuric acid. The catalytic activity of the synthesized catalysts was investigated in the esterification of free fatty acid in palm kernel oil with ethanol.

## 2. Materials and methods

### 2.1 Materials

Coffee husks (CHs) was collected from the African Coffee Company in Kinshasa Kingabwa. Proximate analysis was performed in accordance to the ASTM standard (D1762-84 method) and the results are presented in Table 1.

### 2.2 Catalyst synthesis

Coffee husks (CHs) was primarily washed with distilled water and sun dried for 5 days before grinding into powder (<1 mm). The powder was dried in an oven at 80 °C for 24 h and stored in a desiccator.

The CHs-derived carbon-based solid acid catalysts were prepared according to a slightly modified procedure reported by Toda *et al*.; [22] Chellappan *et al*., [8] and Mardhiah *et al*. [23] In a typical run, 15 g of coffee husks powder (CHs) in a lid-closed porcelain crucible was heated in a muffle furnace for 4 hours, under nitrogen ($N_2$) flow at different temperature: 350, 400, 450 and 500°C to produce incompletely carbonized materials. Upon cooling the obtained carbon material was manually grinded and labeled as CHs-Tc, in which Tc denote carbonization temperature.

The carbon precursors (CHs-Tc) powder were then heated in a concentrated $H_2SO_4$ solution (98 wt %) at 90 °C for 5 hours in a 250 ml conical flask (the ratio of carbon material mass to sulfuric acid was 1 g to 10 ml). After sulfonation, the resulting mixture was cooled to room temperature and precipitated by addition of distilled water. The sulfonated carbon (CHs-Tc) black solid residue was separated by vacuum filtration and washed several times with warm distilled water (> 80 °C) until the filtrate reach neutral pH. Finally, the resulting solid acid catalyst was dried in oven at 105°C for 3h.

The synthesized catalysts were denoted as CHs-350-$SO_3H$, CHs-400-$SO_3H$, CHs-450-$SO_3H$ and CHs-500-$SO_3H$, according to their carbonization temperature.

### 2.3 catalyst characterizations

The elemental analysis was done on Vario-Elementar Microcube® ELIII. Functional groups in the catalysts were characterized by Fourier transform infrared (FT-IR) spectroscopy (Perkin Elmer Spectrum 100 FT-IR). Each sample was subjected to 8 scans in the frequency range from 650 to 4000 $cm^{-1}$ and data were processed using the software FT-IR Spectrum and plotted with OriginPro 8. SEM experiments were carried out on a TESCAN VEGA® Scanning Electron Microscope for analysis of surface morphology and topology of the catalysts. An energy dispersive X-ray spectrometer (EDX) (using an INCA PENTA FET connected to the VAGA TESCAM operating at 20 kV accelerating voltage) was used for assessment of elemental surface composition of the catalysts. Crystallinity state of sulfonated catalysts was evaluated with X-ray diffraction (XRD). The experiments were conducted using Cu-Kα radiation set at 1.5404 angstrom (Å) with a nickel filter, on Bruker D8 Discover instrument equipped with a Lynx Eye detector. Data were plotted using OriginPro 8 software.

The density of surface acid sites was measured by neutralization using titration method. In short, the strong acid group density (–$SO_3H$) of the sulfonated catalysts was determined as follow: 0.05 g of sulfonated samples and 30 mL aqueous solution of NaCl (2 mol/L) were placed in a flask and subjected to ultrasonic oscillation for 30 min. Then, the mixture was filtered, and the filtrate was titrated with aqueous NaOH (0.02 mol/L) solution using phenolphthalein as an indicator. The –$SO_3H$ acid group density was calculated as follows:

$$D\text{–}SO_3H\ (mmol/g) = \frac{C(OH-)\times \Delta V}{m} \quad (1)$$

Where *D*–$SO_3H$ represents the strong acid (–$SO_3H$) density of the sulfonated samples (mmol/g); *C*($OH^-$) represents the concentration of the NaOH solution; $\Delta V$ represents the volume of the NaOH solution used; and *m* the mass of the solid catalyst used. Meanwhile, the total acid density, was also estimated by back titration using standard solutions of NaOH (0.01 mol/L), and HCl (0.01 mol/L) as reported in literatures [24].

### 2.4 Evaluation of catalytic activity

The catalytic activity of sulfonated solid acid catalyst (CHs-Tc-$SO_3H$) was investigated for the esterification of free fatty acid (FFA) in palm kernel oil (PKO) which has the following characteristic: acid value 10.6 mg KOH/g and saponification value 246.2 mg KOH/g. The experiments were carried out in a three-neck round bottom flask equipped with a reflux condenser and a thermometer. In a typical run, to a mixture of ethanol and palm kernel oil in a weight ratio of 20 to 1, was added 2.5 wt % of catalyst. The mixture was heated at 80° C for 4 hrs. Upon cooling the catalyst was removed by filtration and ethanol in vacuo. The FFA in the remaining oil was determined as previously and the conversion rate calculated according to the following relation (2).

$$\text{FFA conversion (\%)} = \left(1 - \frac{AVf}{AVi}\right) \times 100 \quad (2)$$

where $AV_i$ is the initial acid value of the oil, and $AV_f$ is the final acid value after the esterification reaction.

## 3. Results and discussion

### 3.1 Catalyst characterization

The chemical composition of coffee husks (CHs) is shown in Table 1. Determination of biomass composition is essential because it might affect the structure and textural properties of a solid acid catalyst [10]. The proximate analysis of coffee husks (CHs) was done, before carbonized in order to know the moisture content, volatile matter, ash content and the fixed carbon content of the raw materials (CHs).

Table 1 shows that coffee husks comprises of mainly volatile matter 67.12 wt % and fixed carbon 18.24 wt %. The content of ash in coffee husks was up to 4.51 wt %. Ash content measures the amount mineral elements mostly calcium and potassium.[25] On the other hand, coffee husks also contain 10.21 wt % of moisture. The results obtained for coffee husks proximate analysis are closed to those reported elsewhere [20, 26]. Among the proximate analysis parameters, special interest is given to the fixed carbon content, as it allows an estimation of the minimum amount of catalyst that could be obtained after synthesis.

**Table 1:** Proximate analysis of coffee husks as precursor carbon for solid acid catalyst.

| Biomass | Proximate composition (wt %) | | | |
|---|---|---|---|---|
| | Moisture | Volatile matter | Ash content | Fixed carbon |

| | | | | |
|---|---|---|---|---|
| Coffee husks | 10.21 | 67.12 | 4.51 | 18.24 |

### 3.1.1 Elemental analysis

The elemental composition of the raw biomass and prepared catalysts reported in Table 2, reveals the presence of carbon, hydrogen, nitrogen, oxygen, and sulfur in the raw biomass (CHs) and in carbonized biomass (CHs-Tc) as well in prepared catalysts (CHs-Tc-S0$_3$H). The composition of the different elements is clearly different before and after sulfonation. The percentage of sulfur in the prepared catalysts decrease in the following order CHs-400-$SO_3H$ (3.54 wt. %) > CHs-450-$SO_3H$ (2.76 wt. %) > CHs-300-$SO_3H$ (2.69 wt. %) > CHs-500-$SO_3H$ (1.94 wt. %).The sulfur content were about 7 time higher in the prepared catalysts than in the coffee husk raw materials, indicating successful introduction of –$SO_3H$ into the aromatic carbon rings via sufonation. This observation is further confirmed by FT-IR spectra that shows the presence of –$SO_3H$ group on the surface of the carbon catalysts.

**Table 2:** Elemental analysis of CHs (wt %), carbonized CHs and CHs-Tc-S0$_3$H catalysts.

| Samples | C | H | O | N | S | 0/C |
|---|---|---|---|---|---|---|
| Coffee Husks (CHs) | 43.38 | 5.89 | 48.84 | 1.40 | 0.49 | 1.12 |
| CHs-400 | 63.48 | 3.73 | 30.09 | 2.19 | 0.51 | 0.47 |
| CHs-350-$SO_3H$ | 54.33 | 2.27 | 38.87 | 1.84 | 2.69 | 0.72 |
| CHs-400-$SO_3H$ | 56.68 | 2.97 | 34.91 | 1.90 | 3.54 | 0.62 |
| CHs-450-$SO_3H$ | 58.62 | 2.99 | 33.76 | 1.87 | 2.76 | 0.58 |
| CHs-500-$SO_3H$ | 59.54 | 2.16 | 34.44 | 1.92 | 1.94 | 0.58 |

In addition, it is found from the elemental analysis that the carbon and sulfur content of the catalysts increases while hydrogen and oxygen content decreases compared to the raw biomass (CHs). These changes in elemental composition are due to various phenomena, such as carbonization, sulfonation, de-hydration and de-oxygenation of the biomass during incomplete carbonization and activation with $H_2SO_4$ during catalysts preparation. Similar observations were reported by Malins *et al.*, [27] Zhou *et al.* [28] and Thushari and Babel [7] during the preparation of a carbon-based solid acid catalyst using cellulose, bamboo and palm empty fruit bunch (PEFB) respectively. It has been also stated that the increase of the ration of oxygen to carbon indicates an increase of weak acid groups in the carbon-based solid acid catalysts [29, 30]. From the results in Table 2, the ration of oxygen to carbon ranges from 0.58-0.72 and seems to depend on the carbonization temperature. Therefore, it can be concluded that the CHs-Tc-$SO_3H$ catalysts could have incorporated high density of both strong ($SO_3H$) and weak (COOH, OH) acid sites.

### 3.1.2 Acid density analysis

The surface acid densities of the samples determined by the titration method are presented in Table 3. Total acid density of the catalysts ranges from 2.88 to 3.88 mmol/g. As stated by Su and Guo [31], total acid density of biomass derived solid acid catalysts is associated with sulfonic, carboxyl, and phenolic OH groups. Among them, sulfonic acid groups (pka=-7) are the major contributor for catalyzing esterification and transesterification reactions [32]. The sulfur content is a proper parameter to understand the sulfonic acid density of the catalysts. In table 3, The sulfur content of the catalysts ranged from 1.94 to 3.54 wt.% and correlate well with the – $SO_3H$ acid density.

**Table 3:** The $SO_3H$ density and total acid site density of the coffee husks-derived catalysts

| Catalysts | S[a] w t.% | Acid density (mmol/g) | |
|---|---|---|---|
| | | –$SO_3H$[b] | Total [c] |
| CHs-350-$SO_3H$ | 2.69 | 0.84 | 3.88 |
| CHs-400-$SO_3H$ | 3.54 | 1.24 | 3.54 |
| CHs-450-$SO_3H$ | 2.76 | 0.88 | 2.88 |
| CHs-500-$SO_3H$ | 1.94 | 0.64 | 3.22 |

[a] Estimated by elemental analysis.
[b] Based on acid-base titration.
[c] Based on acid-base back titration

The sulfonic acid density in the catalyst seems to depend on the carbonization temperature (see Table 3). The higher content of sulfonic acid groups (1.24 mmol/g) was obtained for the CHs-400-$SO_3H$ that were generated from carbonized at 400 °C. Similar observation is mentioned in the literature, which states that, at low carbonization temperature, many degradation products remain in the carbonaceous structure, thereby not allowing complete sulfonation of the material. At elevated temperatures, the increase in size and organization of the aromatic sheets brings about fewer sites accessible for the anchoring of sulfonic acid groups. A higher carbonization temperature also makes the carbonaceous structure more rigid and the entry of reagents more difficult [33, 35]. Hence, there is a point of maximum efficiency for the sulfonation of coffee husks carbon, and this value seems to be 400°C. It is worth mentioning that this optimal value is close to the 375°C found for carbonization of sugarcane bagasse [34]. From our results and those reported in the literature it could be inferred that the optimum carbonization temperature depends on the type of raw material used; for lignocelulosic material it is between 300 to 400 °C. The densities of sulfonic acid groups found (0.64-1.24 mmol/g) are in agreement with data reported in the literature for similar materials [25, 34, 36, 37].

### 3.1.3 Scanning Electron Microscopy (SEM) and energy dispersive X-ray (EDX) analysis

Scanning electron microscopy (SEM) images of coffee husk, carbonized coffee husk and the derived acid are shown in Fig. 1. Rough and highly folded surface was observed for coffee husks (Fig. 1a). Similar morphological features were observed by Oliveira *et al.* [20] in their study of activated carbons from coffee husks using $FeCl_3$ and $ZnCl_2$ as activating agents. Fig. 1b and 2c exhibits the SEM images of carbonized coffee husks and coffee husks-based solid acid catalyst. In comparison to the raw material (Fig. 1a), a remarkable morphological transformation of coffee husks is observed in panels (Fig. 1b).

When thermally treated at 400°C, the fibrous coffee husks network was disrupted and carbon network with small regular particles started forming, indicating carbonization of coffee husks occurring in the thermal process.

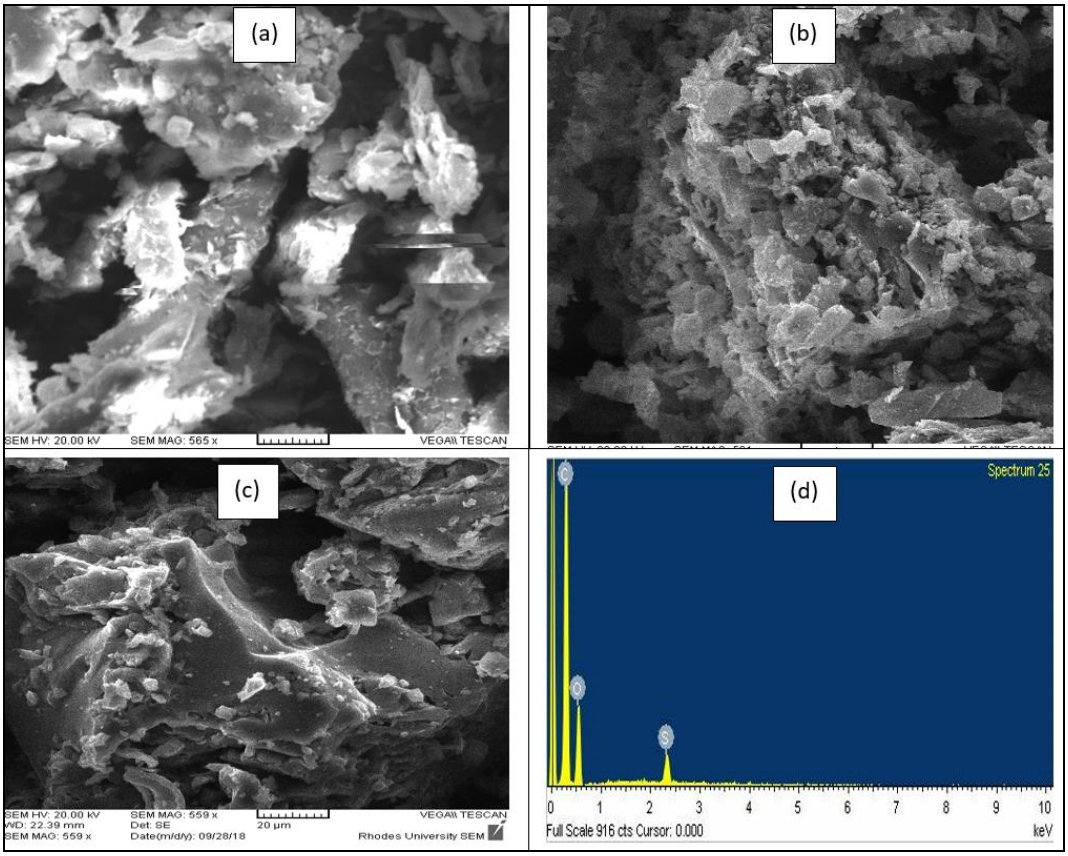


**Fig 1:** SEM images and energy dispersive X-ray (EDX) analysis of carbon materials: (a) coffee husks, (b) Carbonized coffee husks (CHs-400), (c) SEM image of CHs-400-$SO_3H$, and (d) EDX spectra of CHs-400-$SO_3H$

After sulfonation, the solid acid derived from coffee husks showed a completely different morphology (Fig 1c). The morphology of the carbon materials revealed by SEM gives information on the surface area and porosity of the prepared materials. Further oxidation with of $H_2SO_4$ and the intercalation of $SO_3H$ groups make small particles to disappear and aggregate to form large particle with irregular shapes and rough edges. Similar morphological features were observed in a carbon-based catalyst prepared from corncob [37]. It is expected that the carbon sheets composed mainly of polycyclic aromatic groups bind large amounts of $SO_3H$ group. The binding of S and O was investigated with Energy Dispersive X-ray Spectroscopy (EDX) connected to SEM (Fig. 1d). The EDX analysis results of the surface elemental composition of the CHs-400-$SO_3H$ catalyst revealed the presence of carbon, oxygen, and sulfur element characteristics peaks at 0.27, 0.51 and 2.31 keV, respectively, suggesting the attachment of the sulfonic acid group on the surface of the CHs-400. The same characteristic peak of S elements was also observed in the EDX spectra of CHs-350-$SO_3H$, CHs-450-$SO_3H$ and CHs-500-$SO_3H$ sulfonated catalysts. Nakajima *et al* [36]. mentioned that, the Sulphur component detected are basically originated from the -$SO_3H$ functional groups that have been generated and covalently bonded by $sp^2$ hybridized on the polycyclic carbon network of the catalyst.

### 3.1.4 Fourier transform infrared (FT-IR) spectroscopy

The presence of acidic functional groups in the catalyst is confirmed by FT-IR spectra (Fig.2) of the partial carbonized coffee husks at different temperatures. According to Sasmal *et al*., [38] the main characteristics in the FT-IR spectra in biomass are attributed to the presence of different functional groups in hemicellulose, cellulose and lignin in the fibers. FT-IR spectrum of coffee husks (CHs) show an intense absorption band at 3336 $cm^{-1}$ which could be attributed to the O–H stretching [39, 40], probably due to the OH functional groups present in cellulose, hemicellulose and lignin in the original coffee husks. The bands at 2921 $cm^{-1}$ and 2885 $cm^{-1}$ are assigned to symmetric and asymmetric stretching of C–H bonds in $CH_3$, respectively, and bands at 873–750 $cm^{-1}$ are identified as isolated aromatic C–H out-of-plane bending vibrations [41].

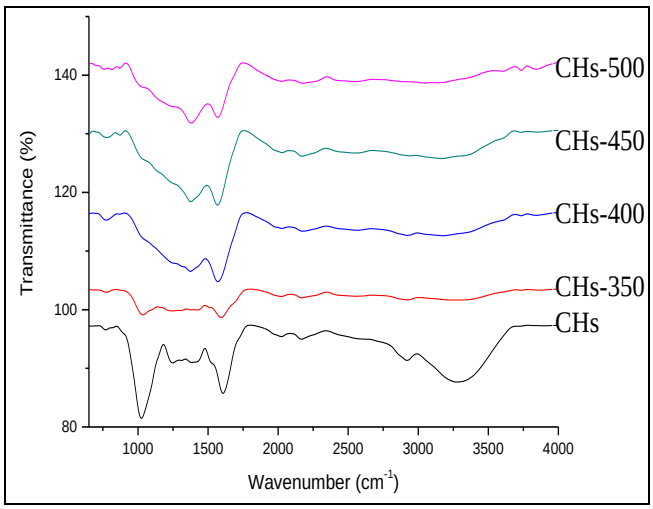


**Fig 2:** FT-IR spectra for coffee husks before and after carbonization at different temperatures

The spectrum of coffee husks showed higher values wavenumber between 1700 and 1500 $cm^{-1}$. In this region,

the bands at 1608 $cm^{-1}$ and 1576 $cm^{-1}$ could be associated to the C=O stretching vibration of carbonyl group and the C=C aromatic stretching vibration [11, 39]. The appearance of bands at 1232 $cm^{-1}$ and 1025 $cm^{-1}$ is attributed to C–O–C and C–OH bending vibration respectively, reflecting the cellulose, hemicellulose and lignin structures in the original coffee husks [13, 28].

After carbonization at different temperatures respectively 350, 400, 450 and 500°C, significant structure changes are observed in the FT-IR spectra, where all the stretching vibration functional groups, like O–H (3336 $cm^{-1}$), C–H (2921-2885 $cm^{-1}$), C=O (1608 $cm^{-1}$), C–O–C (1232 $cm^{-1}$) and C–OH (1029 $cm^{-1}$), gradually disappear with increasing carbonization temperature, supporting the oxygen-containing compounds release during carbonization. It is indicated that the molecular structures of cellulose, hemicellulose and lignin in the original coffee husks are suffering from dehydration for the crack of the ether, hydroxyl and carboxyl bonds. Moreover, the C=C stretching vibration band in the aromatic ring mode (1576 $cm^{-1}$) is enhanced obviously at 400 °C, which labels the significant partial carbonization of coffee husks and favors sulfonation [28].

Sulfonation of lignocellulosic materials resulted in production of stable solids with strong acid density and many active sites. Such an approach can simplify the synthesis of highly active catalysts from inexpensive, naturally occurring materials. Figure 3 presents the FT-IR spectra of unsulfonated partial carbonized materials from coffee husks and sulfonated catalysts. The FTIR spectra of CHs-350-$SO_3H$, CHs-400-$SO_3H$, CHs-450-$SO_3H$ and CHs-500-$SO_3H$ exhibited new characteristic absorption peaks at 1029, 1171 $cm^{-1}$, which are attributed to the S=O symmetric stretching vibration, S=O asymmetric stretching vibration, respectively [42, 43]. This finding proved that the –$SO_3H$ functional group anchored on the surface of the coffee husks carbon. The stretching at 3440 cm-1 is assigned to the O-H stretching mode of phenolic -OH and -COOH groups. Similarly, node stretching at 1710 $cm^{-1}$ is representative of C=O bonds due to -COO- and -COOH group stretching vibrations. The aromatic C=C stretching mode, similar to graphite-like, polyaromatic materials, was ascribed to the broad, intense bands centered at 1587 cm-1. These results are similar to the findings of Zhang *et al*. [44]. The analysis of FT-IR spectra confirmed that the CHs based catalysts consist of acidic group such as sulfonate, phenolic, and carboxyl functional groups.

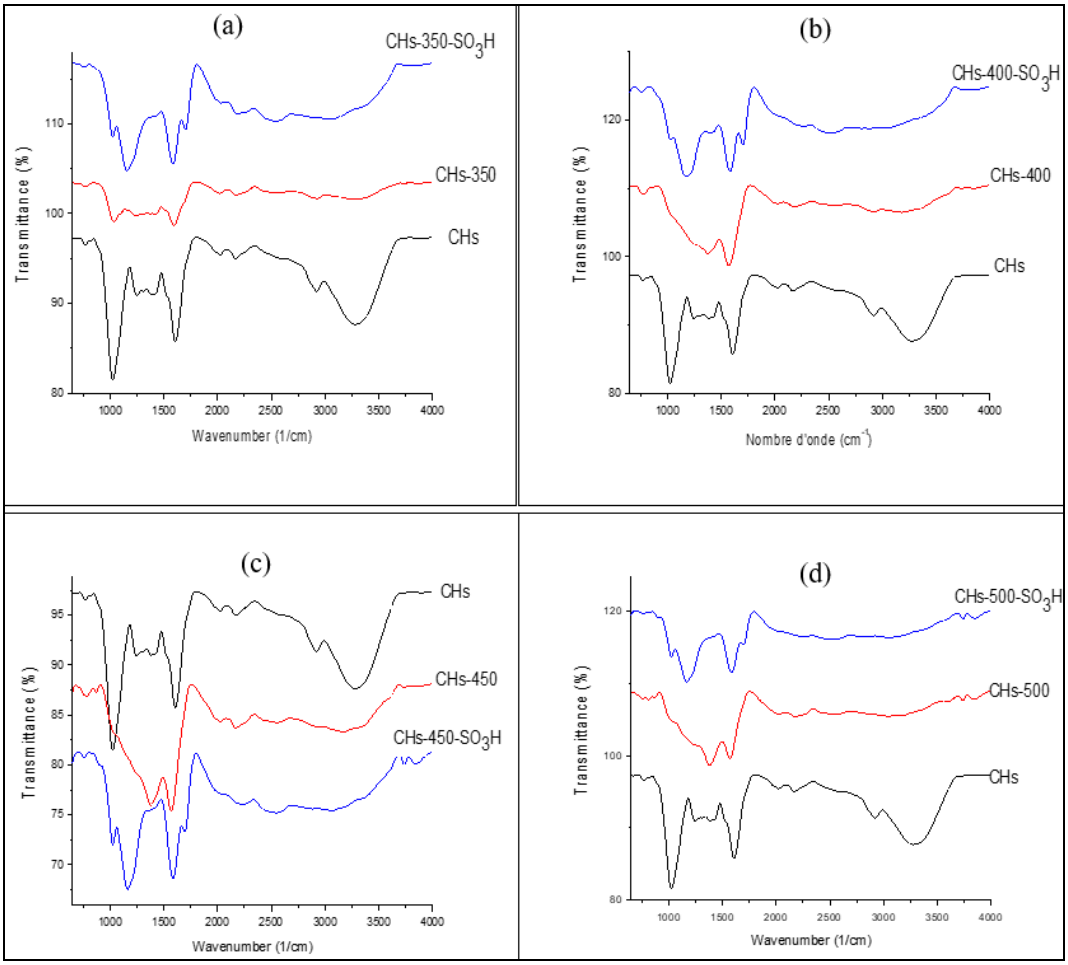


**Fig 3:** FT-IR spectra of the sulfonated carbon-based catalysts: (a) CHs-350-$SO_3H$; (b) CHs-400-$SO_3H$; c) CHs-450-$SO_3H$; and (d) CHs-500-$SO_3H$

### 3.1.5 X-ray diffraction (XRD) spectroscopy

Fig. 4 shows the XRD patterns of coffee husk based solid acid catalyst synthesized under different conditions. All of the XRD patterns of coffee husks-derived catalysts exhibited a broad diffraction peak (2θ =15−30°) attributable to amorphous carbon composed of polycyclic aromatic carbon sheets oriented in a considerably random fashion.[45-46] This structure is far from crystal and favorable for anchoring

the-$SO_3H$ groups. And the weak diffraction peak at 2θ = 40–50° is ascribed to graphite-like structure. These findings are similar to those of the cellulose based carbon catalysts reported by Fukuhara *et al.* [47]. Consequently, we can infer that the solid acid is an amorphous carbon catalyst with relatively high BET surface area. Moreover, the diffraction peak gets sharp when carbonization temperature reaches 500 °C, demonstrating further degree of carbonation, which may be responsible for the low –$SO_3H$ groups attached to carbon structure. However, there is no significant difference in XRD patterns with different carbonization conditions, indicting weak effect on the structure of catalyst. Yu *et al.* [11] reported the same behavior in the XRD structure of sulfonated carbon-based catalysts prepared using Yulin coal (YLC).

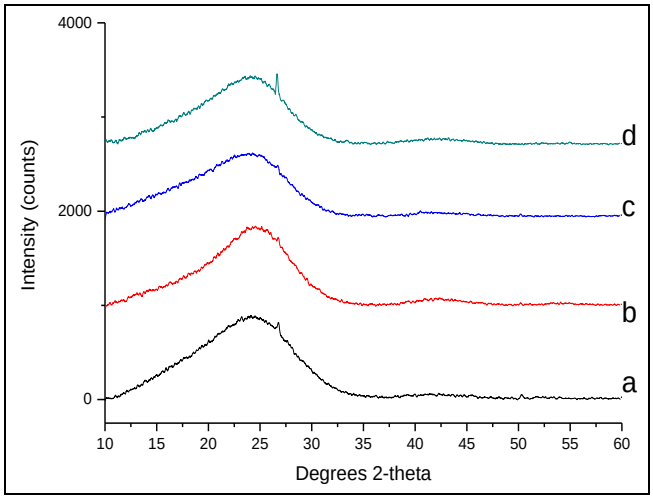


**Fig 4:** XRD Patterns of Sulfonated Carbon-based Catalyst (a) CHs-350-$SO_3H$, (b) CHs-400-$SO_3H$, (c) CHs-450-$SO_3H$, and (d) CHs-500-$SO_3H$

Fig. 5 shows XRD patterns of the original coffee husks and its derived catalyst. Peaks at 2θ = 15.8° and 22.5° in the original coffee husks for the crystalline structure of cellulose disappear in the carbonised and sulfonated coffee husks carbon implying the destructive effect of carbonization and sulfonation on the physical and chemical structures of the raw biomass. The broad diffraction peak at 2θ = 15–30° and weak diffraction peak from 2θ = 35–50° of the carbonized coffee husks are assigned to the randomly arranged amorphous carbon structures containing low content of crystalline graphite [27, 28]. With an increasing carbonization temperature, time, and sulfonation temperature, the amorphous carbon diffraction peak became more obvious and shifted to higher angles (Fig. 5), indicating the production of more carbonized structure and rigid structure, composed of large carbon sheets. Simultaneously, the weak diffraction peak (2θ =40−45°) became more visible as well. This suggests that further carbonization during sulfonation yields a graphite-like carbon structure in the catalysts. This also contributed to a lower $SO_3H$ content in the catalyst, which is consistent with the result of elemental analysis. General analysis of the X-ray diffraction patterns results indicate that both Coffee husks carbon CHs-400 and sulfonated coffee husk solid acid CHs-400-$SO_3H$ consist of disordered polycyclic aromatic carbon sheets. The existence of aromatic compound in prepared carbon materials was confirm by FT-IR spectra, and supported by the XRD patterns.

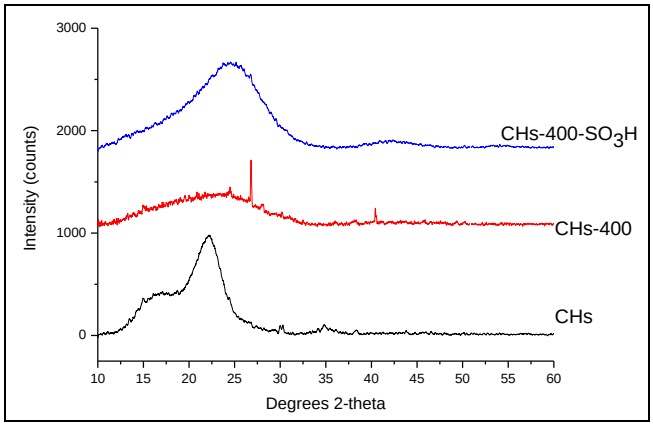


**Fig 5:** XRD patterns of raw coffee husks (CHs), carbonized coffee husks at 400°C (CHs-400) and sulfonated carbon-based solid acid catalyst (CHs-400-$SO_3H$).

### 3.2 Catalytic activity

Fig. 6 shows that catalytic activities of the catalysts mostly depend on their acid density, especially of sulfonic acid group density (-$SO_3H$ groups). With an increase in the -$SO_3H$ groups density, the catalytic activity of the catalyst increased. At 400°C carbonization temperature, the catalyst exhibits a high catalytic activity with the highest % FFA conversion of 90.28 % for CHs-400-$SO_3H$ catalyst (1.24 mmol/g –$SO_3H$ density). The acid value of PKO reduces below 2 mg KOH/g, which is a requirement for transesterification reaction with alkali catalyst. Although CHs-350-$SO_3H$ has a higher –$SO_3H$ acid density than CHs-500-$SO_3H$, the latter exhibits a higher catalytic activity, which could be attributed probably to a relatively high specific surface area and pore volume.

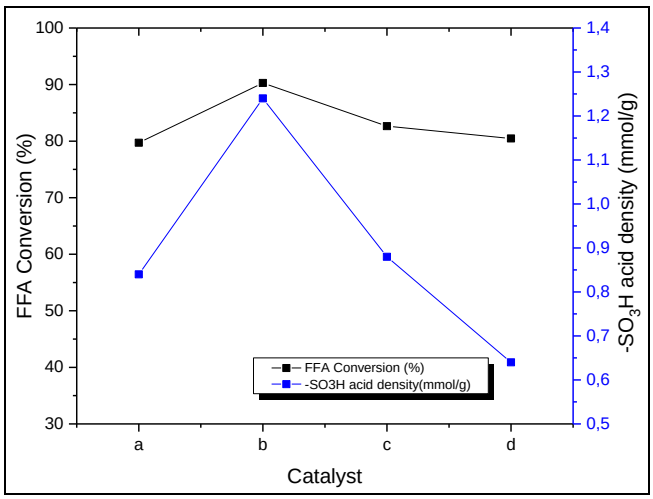


**Fig 6:** Catalytic activity of the coffee husks-derived catalysts: a. CHs-350-$SO_3H$; b. CHs-400-$SO_3H$; c. CHs-450-$SO_3H$; d. CHs-500-$SO_3H$.

### 3.3. Reusability of catalyst

The reusability of CHs-derived carbon-based solid acid catalyst was investigated by performing the esterification reaction under the same conditions through five successive cycles. After each cycle, the CHs-400-$SO_3H$ catalyst was removed from the reaction mixture by vacuum filtration, washed with ethanol, dried at 105 °C for 4 h and then reused in the next cycle. As shown in Fig.7, esterification efficiency gradually decreases slightly with successive run.

The conversion value of FFA decreased from 90.28 % (the

first cycle) to 85.86 % (the fourth cycle) and remained above 82% after the fifth run, confirming the reusability of sulfonated carbon catalyst. Even though some loss of activity is noticeable the catalyst possesses satisfactory operational stability. It is probably that $–SO_3H$ leaching (percent leached 20.42%) takes place during the first cycle run and become less in subsequent cycles. Similar observations were reported in literature [48]. Deactivation, a common problem for the sulfonated carbon-based catalysts is probably due to the leaching of sulfonate groups in the solvent.[49]

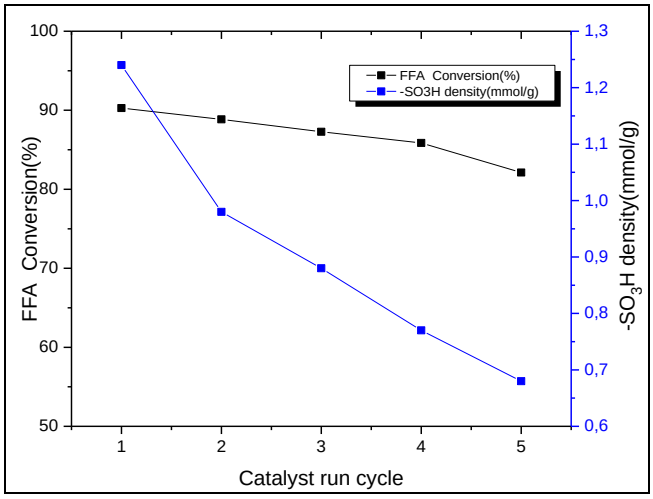


**Fig 7:** Effect of the recycling of catalyst (CHs-400-$SO_3H$) on esterification efficiency and $–SO_3H$

## 4. Conclusion

We prepared sulfonated carbon-based solid acid catalysts from coffee husks as carbon precursor and concentrated $H_2SO_4$ (98%) as sulfonation reagent. The influence of carbonization temperature on surface acid density and catalytic activity were systematically investigated. The characterization results show that the prepared solid acid catalysts have a unique amorphous structure with total acid density of 2.88, 3.22, 3.54 and 3.88 mmol/g for CHs-450-$SO_3H$, CHs-500-$SO_3H$, CHs-400-$SO_3H$ and CHs-350-$SO_3H$ respectively and $–SO_3H$ acid density of 0.64, 0.84, 0.88 and 1.24 mmol/g respectively for CHs-500-$SO_3H$,CHs-350-$SO_3H$, CHs-450-$SO_3H$ and CHs-400-$SO_3H$. In addition, the FT-IR characterization results show that sulfonation of the coffee husks carbon containing three functional Brønsted acid sites: weak acidic OH and COOH groups, strong acidic $SO_3H$ groups. The carbon-based solid acid catalyst CHs-400-$SO_3H$, exhibits the highest catalytic activity and good stability during the catalytic esterification reaction tests, the free fatty acid (FFA) conversion reaches 90.28% after 4 h reaction and it can be reused for 5 cycles with FFA conversion >82%. This good catalytic performance could be attributed to the, high -$SO_3H$ density and hydrophobic surface of CHs-400-$SO_3H$, which can effectively accommodate the long chain FFAs and reject formed water, making the active sites easily accessible. Applications of the prepared carbon-based solid acid catalysts are being extended to other acid-catalyzed reactions.

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## 6. Conflicts of Interest

The authors declare no conflict of interest.

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