Catalyst Activity of Solid Acid Catalyst Derived From Agricultural Biomass for Biodiesel Production From Waste Cooking Oil

S.H.Y.S. Abdullah, F. Lananan, A. Endut

Abstract: *Homogeneous alkali catalyst produces soap as a by-product and generates a large amount of wastewater. This study investigates the potential of three types of biomass namely oil palm frond, coconut shell and groundnut shell to be developed as a solid acid catalyst for transesterification of waste cooking oil into biodiesel. The synthesis of solid acid catalyst is conducted by incomplete carbonization of biomass followed by sulfonation using concentrated sulfuric acid to incorporate the sulfonic group in the carbon body. The porosity of prepared catalyst was characterized by adsorption/desorption technique and surface acidity was evaluated by means of back titration method. Coconut shell showed the highest acid density of 0.51 mmol/g followed by groundnut shell and oil palm frond with 0.16 mmol/g and 0.12 mmol/g respectively. The biodiesel production was carried out at reaction conditions of methanol-to-oil ratio 20:1, reaction temperature 60 ºC, reaction time 6 h and catalyst loading 6 wt%. The highest biodiesel conversion was achieved using a coconut shell as a catalyst with 86.5%, followed by groundnut shell and oil palm frond. The use of solid acid catalyst derived from biomass could explores new market value for waste material while minimizing the solid waste production and further reduces cost and energy consumption in biodiesel production.*

Index Terms: *Biodiesel, Biomass, Energy production, Solid acid catalyst, Waste cooking oil.*

I. INTRODUCTION

The term biodiesel refers to a long chain fatty acid monoalkyl ester (FAME) that is derived from biological sources including plant oils and animal fats [1]. Attributable to the rising of environmental awareness among the public, biodiesel has become a preference by the individual and large industrial player as their source of energy. The use of biodiesel as an alternative energy source is considered to be highly advantageous as it has proven to be environmental-friendly, non-toxic and renewable [2]. Often, transesterification reaction was used for biodiesel production due to its simplicity in reaction, mild reaction conditions and financially viable options [3]. In addition, the characteristic of biodiesel produced using this method is similar to that of petroleum-based diesel surpass with lower viscosity and valuable by-product.

Transesterification involves a chemical reaction of fats or oils and alcohol i.e. mostly methanol, in the presence of a catalyst i.e. acid, base or enzymatic to produce FAME and glycerol. According to the stoichiometric equation, three moles of methanol is required to react with triglyceride and produced three moles of FAME and glycerol as the by-product [4]. Transesterification has been widely used to convert numerous oils into biodiesel including soybean oil [5], palm oil [6], sunflower oil [7], jatropha oil [8], and waste cooking oil (WCO) [9]. However, high cost of vegetable oil feedstock is the main concern for biodiesel production. The cost of vegetable oils is approximately contributed to 75% of the total manufacturing cost in biodiesel production. When the production cost is included, it was found that the total cost for biodiesel production is much more higher compared to petroleum diesel production [10]. In addition, the growing population of developing countries like Malaysia has resulted in the increment in the food consumption as well as WCO production. Hence, the conversion WCO into biodiesel is an alternative to eliminate the easy and inevitable disposal of the waste oil by the user. On top of that, the manufacturing cost can be reduced since the price of WCO is much more cheaper compared to virgin plant oils [11].

The application of heterogeneous catalyst in transesterification reaction is advantageous since it is easier for product separation and has a high potential for catalyst reusability. Hence, it contributes to cost and energy saving associated with purification and separation process as well as a reduction in wastewater generation. Further research and studies have led to the development of a green catalyst for biodiesel production. Green catalyst can be defined as solid catalyst derived from biological sources or biomass. Biodiesel has been successfully produced by using various biomass-derived catalyst including waste shell [12], animal bones biochars [13] and activated carbon [14]. The application of biomass-derived solid acid catalyst (SAC) is advantageous as it exhibits high catalytic activity due to their porous nature [15]. Moreover, it comes from cheap and renewable resources, non-toxic and environmental friendly [16]. In this study, three types of indigenous biomass were selected to be the precursor carbon for SAC. Oil palm frond, coconut shell and groundnut shell are the major agricultural waste that can be found in Malaysia.

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These biomasses are abundantly available and have low market value. Since biodiesel production required dealing with high FFA feedstock, the utilization of biomass-derived SAC may provide a green and sustainable biodiesel production [17]. On top of that, utilization of biomass-derived SAC may add some commercial value to the waste material as well as up-cycling the waste into a more useful end product.

The main objective for this study was to compare three different types of biomass namely oil palm frond, coconut shell and groundnut shell as the potential SAC for biodiesel production. Surface morphology and chemical composition of each type of biomass were carefully assessed. The performance of the produced biomass-derived SAC was investigated by the conversion of WCO into biodiesel in transesterification reaction.

II. MATERIALS AND METHODS

A. Raw Materials

Three types of biomass were used in this study including oil palm frond (OPF), coconut shell (CS) and groundnut shell (GS). The biomass was locally obtained from local plantation area and market. The initial characteristic of these biomass including the moisture content, volatile matter content, ash content and fixed carbon content were determined according to the ASTM standard. WCO was obtained from a food stall. All the chemicals used are reagent-grade including methanol, concentrated sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), hydrochloric acid (HCl), potassium hydroxide (KOH) and sodium chloride (NaCl). The chemicals were obtained from Merck and Sigma-Aldrich.

B. Preparation of Catalyst

20 g of the biomass sampled (oven-dried) was carbonized in a muffle furnace for 8 h at a specific temperature. The carbonized product was cooled down prior to being grounded into powder form. The activated carbon (AC) powder was sulfonated using concentrated H_2SO_4 for approximately 15-20 min and residual acid was removed from the mixture. The remaining wet solid mixture was heated in the muffle furnace at 150 °C for 15 h. The sulfonated carbon product was cool down to ambient temperature and rinsed with excessive distilled water until the wash water became neutral (pH 7). The solid acid catalyst was dried at 105 °C then sealed and kept for experimental use.

C. Characterization of Catalyst

The characterization of catalyst was performed using Scanning Electron Microscopy (SEM) using SEM-JEOL to determine the catalyst surface morphology. Further evaluation on the surface porosity was conducted by means of nitrogen adsorption/desorption technique using Micromeritics V4.02. Thermogravimetric analysis (TGA) was used to evaluate the thermal stability of the prepared SAC at specific temperature range. Acid base titration method described by Thushari et al. [18] was conducted to determine the surface acidity of the SAC samples.

D. Catalyst Activity

The catalyst activity was carried out following the method depicted in Velasquez-Orta et al. [19]. 1 g of WCO is filled into a 50 mL centrifuge tube. The process conditions were as follows; methanol to oil ratio of 20:1 and catalyst dosage of 6 wt%, the reaction was conducted at a temperature of 60 °C for 6 h. The centrifuge tubes that contained reaction mixture were kept at 200 rpm stirring rate throughout the reaction. When the reaction time completed, the centrifuge tubes were cooled to ambient temperature. Following that, remaining solid phase (biomass and solid catalyst) were removed through filtration. The liquid product (mixture of excess methanol, biodiesel and by-product) were stored in a pre-weighed tubes. Final weight of each tube were documented. Acid value of biodiesel end product was determined using potentiometric titration method [20]. The acid value can be determined using the following equation:

$$AV = (A - B) \times C \times M/W \qquad (1)$$

where AV is the the acid value of biodiesel sample in mg KOH/g, A is the volume of KOH standard solution consumed in the biodiesel sample in mL; B is the volume of KOH standard solution consumed in the blank titration in mL, C is the concentration of the standard KOH solution in mol/L, M is the molecular weight of KOH (g/mol) and W represents the weight of biodiesel sample (g). The FFA conversion was calculated as follows:

$$FFA\ conversion\ (\%) = (AV_0 - AV_1)/AV_0 \times 100 \qquad (2)$$

where AV_0 and AV_1 are the acid value of WCO and biodiesel respectively.

E. Statistical Analysis

Statistical analysis was performed using Minitab 17 (Minitab Inc., Pennsylvania, USA) with an alpha set at 0.05 (significance at $P < 0.05$). The reported mean values of total acid density, sulfonic density, and percentage conversion were compared by using one-way ANOVA. Tukey-HSU pairwise comparison was used if there were significant differences at a significant level 0.05 in order to identify the significant difference between the catalytic ability of different SAC samples.

III. RESULTS AND DISCUSSION

A. Proximate Analysis

The chemical compositions of each biomass were determined using proximate analysis and the results are tabulated in Table 1.

Table 1. Proximate analysis of three types of biomass

Parameter	Precursor Carbon		
	OPF	CS	GS
Moisture content (%)	5.17[b] ± 0.17	6.72[a] ± 0.18	5.17[b] ± 0.09
Volatile matter (%)	72.67[a] ± 0.72	64.24[b] ± 1.44	78.43[a] ±1.04
Ash content (%)	4.16[a] ± 0.18	1.03[c] ± 0.09	3.21[b] ± 0.04
Fixed carbon (%)	18.00[a] ± 1.49	28.01[a] ± 1.64	13.19[b] ± 1.00

OPF: Oil palm frond, CS: Coconut shell, GS: Groundnut shell
Values are expressed as mean ± standard error (n=3). The different superscript alphabet indicates that the values are significantly different at p < 0.05.

The difference in the biomass composition might affect the structural and textural properties of the developed SAC. All of the biomass selected comprised mainly of volatile matter with highest found in GS (78%), OPF (73%) and CS (64%). Volatile matter content in OPF and GS show no significant difference from one another with higher ash content than CS. The high ash content in both biomasses is an indicator that the formed activated carbon will contain a high amount of calcium and potassium. Previous study by Mahamad et al. [20] mentioned that low ash content is one of the characteristic for an effective carbon catalyst. Low ash content will reduce the potential competition for carbon adsorption and prevent side-reaction with other compound to occur. Apart from that, CS showed high moisture content compared to both OPF and GS. However, no significant difference was found in moisture content for both OPF and GS. On the other hand, CS showed highest carbon content compared to OPF (18%) and GS (13%).

B. Surface Morphology

The morphology of AC and SAC were investigated through SEM analysis and presented in Fig. 1.
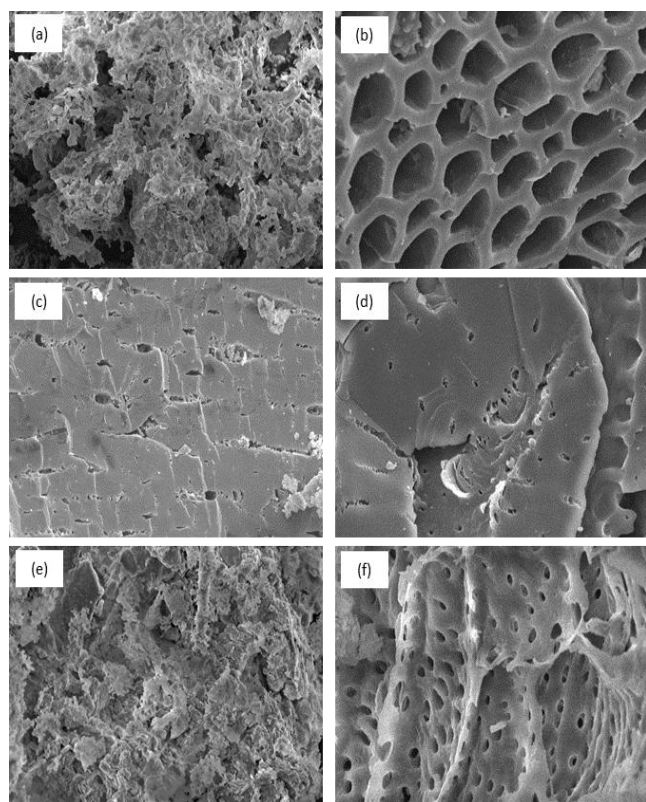

Fig. 1. SEM images of AC and SAC samples at 500 °C carbonization temperature. (a) AC oil palm frond (b) SAC oil palm frond (c) AC coconut shell (d) SAC coconut shell (e) AC groundnut shell (f) SAC groundnut shell

From observation, AC derived from OPF presented a rather loose irregular structure with no obvious pores as shown in Fig. 1(a). However, upon the introduction of the sulfonic group ($-SO_3H$) into the carbon skeleton, a network of pores is started to develop as illustrated in Fig. 1(b). A similar observation was found when GS was used as the starting material as shown in Fig. 1(e) and Fig. 1(f). This might due to the similar nature of the carbon material by both OPF and GS as presented in the proximate analysis. On the contrary, the surface morphology of CS sample shows no difference between AC and SAC samples. Nevertheless, both samples presented a porous catalyst structure as evident in Fig. 1(c) and Fig 1(d).

C. Surface Porosity

The porosity characterization of AC and SAC samples of the biomass was carried out using the nitrogen-adsorption method and the results are tabulated in Table 2.

Table 2. Textural properties of biomass-derived activated carbon and solid acid catalyst

Parameter		Activated Carbon	Solid Acid Catalyst
BET Surface area (m^2/g)	OPF	28.32	33.85
	CS	144.62	24.17
	GS	64.58	228.95
Average pore volume (cm^3/g)	OPF	0.0065	0.0261
	CS	0.0609	0.0115
	GS	0.0555	0.1065
Pore size (Å)	OPF	91.81	30.85
	CS	16.84	19.02
	GS	34.35	18.60

OPF: Oil palm frond, CS: Coconut shell, GS: Groundnut shell

The results indicated that the porosity of AC samples for OPF and GS are improved with further sulfonation with concentrated H_2SO_4. Accordingly, BET surface area and pore volume of SAC derived from OPF was increased to 33.8563 m^2/g and 0.0261 cm^3/g. On the other hand, an increment of BET surface area and pore volume to 228.9573 m^2/g and 0.1065 cm^3/g were found in GS. Evaluation on the surface morphology using SEM analysis confirmed the occurrence of pores on the catalyst surface of OPF and GS as shown in Fig. 1(b) and Fig. 1(f), respectively.

On the contrary, this effect was not observed in the CS sample. Sulfonation process of AC derived from CS has caused the reduction in BET surface area from 144.6253 m^2g^{-1} to 24.1703 m^2/gas observed in the SAC samples. The average pore volume was also reduced from 0.0609 cm^3/g to 0.0115 cm^3/g. AC derived from CS showed high porosity nature as evident by the BET surface area value and surface morphology evaluation using SEM. Nevertheless, the pore distribution reduces upon sulfonation process. This might be explained by the fact that $-SO_3H$ group has incorporated in the catalyst surface hence reduces the surface area. This can be confirmed by the high value of sulfonic acid density in CS derived SAC compared to the other biomass derived catalyst. Previously, Sandouqa et al. [21] stated that the accumulation of $-SO_3H$ group in the pores may be the main reason why lower surface area and pore volume were obtained in sulfonated catalyst despite having a high acid density value. A similar outcome was also reported by Zuo et al. [22] in a study of solid acid catalyst using functionalized SBA-15 materials. The sulfonation process has resulted in the production of solid acid catalyst with a low surface area as a result of $-SO_3H$ intercalation. Regardless of that, the catalyst activity remains the highest.

D. Thermal Stability

Fig. 2 shows the TGA and DSC curvatures of SAC samples derived from OPF, CS and GS over a temperature range of 30 to 800 °C.
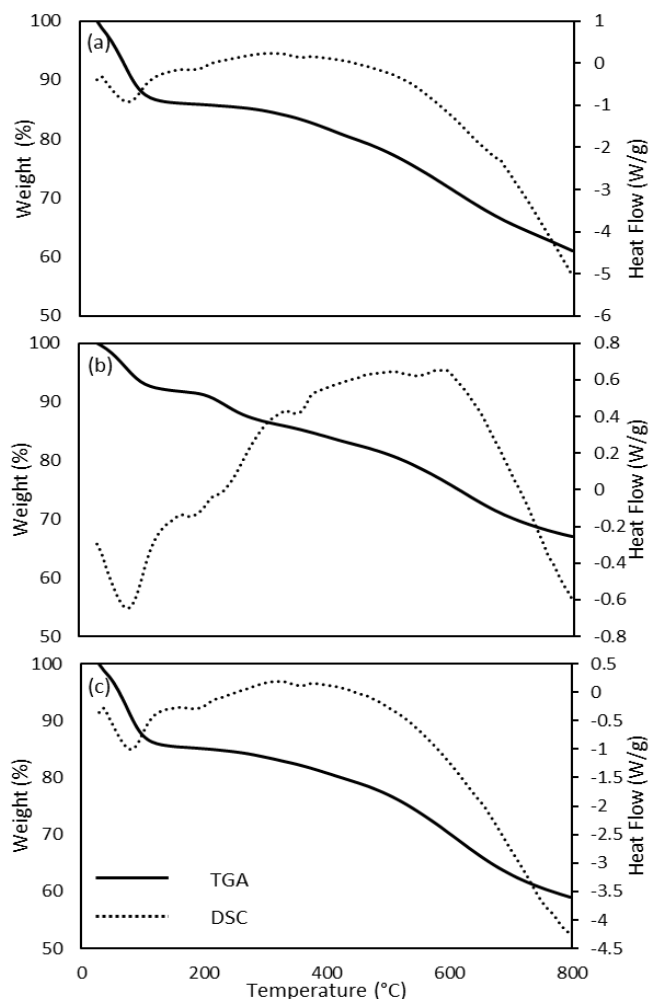

Fig. 2. TGA and DSC analysis of solid acid catalyst derived from (a) OPF (b) CS and (c) GS

A two-step weight reduction trend was observed in the TGA analysis of all the prepared sample. The first reduction step occurred in the temperature region below 200 °C. A slight reduction was observed in the TGA curve which is due to the weight loss from evaporation of adsorbed water in the sample body. Evaluation using DSC analysis showed a noticeable peak at this region reflects the evaporation of water within the compound [23]. The second step of weight loss in TGA analysis was confirmed by the continuous and steep weight reduction from the temperature of 350 °C up to 800 °C which accounted for a greater weight loss in all three samples. This situation can be explained by the fact that during this temperature range, the disintegration of macromolecules and other organic substance occur due to combustion process [24]. In addition to that, the decomposition of -SO$_3$H in the catalyst also occur in this region. Similar findings were reported on significant weight loss in the region 150-400 °C due to thermal decomposition and desorption of –SO$_3$H group [25].

E. Surface Acid Density

The value of surface acidity for the prepared SAC was evaluated at different carbonization temperature. The results are tabulated in Table 3. From the result, it was found that different carbonization temperature gives a significant effect to the formation of total acid sites and sulfonic acid sites in the developed solid acid catalyst. Increase in the carbonization temperature produced SAC with higher acid densities. From post-hoc Tukey-HSU analysis, SAC derived from OPF showed a significant difference compared to CS and GS.

Table 3. Total acid density and sulfonic acid density of solid acid catalyst prepared at different carbonization temperature

Sample	Carbonization Temperature (°C)	Total acid density (mmol/g)	Sulfonic acid density (mmol/g)
OPF	400	2.200[e] ± 0.100	0.307[bc] ± 0.000
	500	3.300[b] ± 0.040	0.113[cd] ± 0.031
	600	3.767[a] ± 0.253	0.053[d] ± 0.031
CS	400	2.807[d] ± 0.064	0.620[a] ± 0.064
	500	3.213[bc] ± 0.103	0.507[ab] ± 0.144
	600	3.500[ab] ± 0.174	0. 627[a] ± 0.164
GS	400	3.143[bcd] ± 0.180	0.253[cd] ± 0.031
	500	3.417[ab] ± 0.091	0.127[cd] ± 0.000
	600	2.853[cd] ± 0.110	0.154[cd] ± 0.012

OPF: Oil palm frond, CS: Coconut shell, GS: Groundnut shell
Values are expressed as mean ± SEM (n=3). Means with the different superscripts within column are significantly different at p < 0.05.

The highest total acid density was recorded at 600 °C with 3.767 mmolg^{-1} in SAC derived from OPF. The value of total acid density increased as carbonization temperature was raised from 400 to 600 °C. A similar observation was found in SAC CS that showed improvement in total acid density from 2.807 to 3.5 mmol/g at carbonization temperature of 400 and 600 °C respectively. On the other hand, the total acid density in SAC GS dropped to a value of 2.87 mmol/g at 600 °C. Wang et al. [26] reported that at 400 °C the formed carbon network is unstable and may collapse during sulfonation. At higher carbonization temperature (500-600 °C), hydrogen and oxygen were removed from carbonaceous material resulting in the formation of pores and increase in the surface area thus improved the total acid density of SAC. However, further increment in the carbonization temperature might cause the formation of an ordered pattern to the carbon sheet that is unfavorable for the catalytic reaction [23].

Nevertheless, the results indicated that large fractions of acidity in the prepared catalyst were comprised of weak acid groups including phenolic (-OH) and carboxylic (-COOH). These groups existed as a result of oxidation of aliphatic group due to strong sulfonation and incomplete carbonization of the precursor [27]. However, these weak acidic groups did not contain the ability to catalyze the transesterification reaction and producing FAME [28]. It should be noted that only -SO$_3$H (strong acid) are active as catalytic sites for transesterification and esterification reaction [29]. Thus a simple back titration of the SAC suspended in aqueous sodium chloride was conducted to confirm the presence of strong acid functionality in the carbon sheet.

The results are tabulated in Table 3 indicated that SAC derived from CS presented the highest content of -SO₃H with sulfonic acid density value ranging from 0.507-0.620 mmol/g. The increase in carbonization temperature improved the functionalization of -SO₃H group onto catalyst surface as observed in coconut shell as precursor carbon.

On the contrary, the increase in carbonization temperature gave an adverse effect to SAC derived from OPF and GS. The sulfonic acid density values for both catalysts significantly reduced as higher carbonization temperature was utilized. This is mainly due to the formation of soft aggregate carbon structure observed in both oil palm frond and groundnut shell after incomplete carbonization process. Even though high surface area was observed in both activated carbon products of OPF and GS, the soft carbon structure considerably dissolved into liquid upon the addition of concentrated sulfuric acid into the carbonized product. This reflects low stability of both oil palm frond and groundnut shell in an acidic environment. Nevertheless, the values of sulfonic acid density and total acid density of the prepared catalysts in this study are comparable to the acid density values reported in previous literatures [30,31].

F. Catalyst Activity

The SAC was further subjected to transesterification reaction with methanol and WCO to investigate the catalyst activity. Fig. 3 shows the results of the transesterification activity of the SAC at different carbonization temperature. The transesterification reaction was carried out at a reaction temperature of 60 °C for 6 h with methanol-to-oil ratio of 20:1 and 6 wt% catalyst loading. All biomass-derived SAC were demonstrated to be catalytically active for the transesterification of WCO. The highest conversion was obtained using SAC derived from CS with > 80% conversion. On the other hand, mild catalytic activity was shown by SAC derived from OPF and GS.
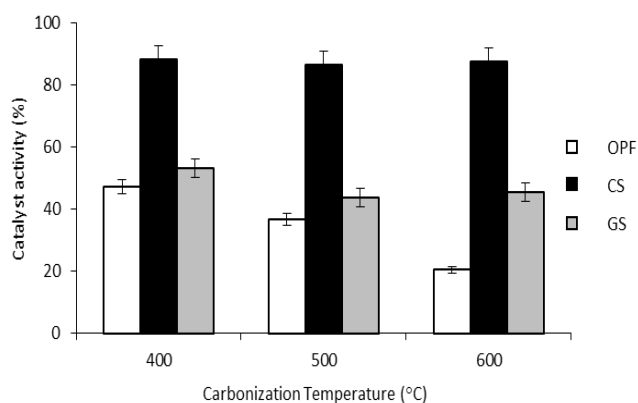

Fig. 3. Catalyst activity of solid acid catalyst derived from biomass for transesterification of waste cooking oil into biodiesel

The superior catalytic activity of SAC derived from CS over the other catalysts can be related to its high sulfonic acid density that leads to the increase in the active sites available for the reaction. There was no significant difference ($p < 0.05$) on the biodiesel conversion when different carbonization time was employed in SAC derived from CS. This confirmed that the porosity nature of coconut shell is not greatly affected by the difference in carbonization temperature. Thus, by employing a low carbonization temperature is sufficient to produce high activity SAC whilst reducing the energy required for this process.

In contrast, a significant reduction in the biodiesel conversion was observed when higher carbonization temperature was utilized in SAC derived from OPF and GS. The biodiesel conversion using SAC derived from OPF showed significantly higher mean value at carbonization temperature of 400 °C with 47.33% compared to 20.46% at carbonization temperature of 600 °C. In the presence of SAC derived from GS, the biodiesel conversion also shows a reduction from 53.67% to 45.50% with the increase in carbonization temperature from 400 to 600 °C. The main reason for low transesterification activity is might be due to the low sulfonic acid density of the prepared catalyst. This result is consistent with the previously mentioned low sulfonic acid density presented in both SAC derived from OPF and GS. According to Zhang et al. [32] acid density especially sulfonic acid density plays a major role in determining the catalytic activity of a SAC. Fewer numbers of active sites hindered the reaction to take place hence reducing the capacity for efficient biodiesel conversion [33].

IV. CONCLUSION

SAC was successfully generated in this study via incomplete carbonization of biomass followed by sulfonation using concentrated sulfuric acid. Several types of biomass were selected to be the precursor carbon for SAC including oil palm frond, coconut shell and groundnut shell. The selection criteria are based on its availability, low cost, high carbon content and agricultural waste biomass. The resultant SAC consists of aromatic carbon framework with a sulfonic acid functional group attached to it. All the studied biomass or waste materials are reported to be catalytically active, however, the findings from this study showed that coconut shell-derived SAC has the highest potential for biodiesel production. The SAC derived from CS presented superior performance than SAC derived from OPF and GS. The use of CS as the precursor carbon for solid acid catalyst synthesis provides advantages in the reduction and recycling of waste biomass as well as an environmental-friendly solution in biodiesel practice as opposed to homogeneous acid catalyst.

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