PALM FROND AND SPIKELET AS ENVIRONMENTALLY BENIGN ALTERNATIVE SOLID ACID CATALYSTS FOR BIODIESEL PRODUCTION

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Abstract- Carbonization–sulfonation method was used in synthesizing sulfonated mesoporous catalysts from palm tree biomass. BET, XRD, EDX and FE-SEM analyses elucidated the structural and textural properties of the catalysts. Further, FT-IR and titrimetric analyses measured the strong acid value and acidity distribution of the materials. Results obtained from these analyses indicated large mesopore volume, surface area, uniform pore size and high acid density on the catalysts. The catalytic activity exhibited by esterifying used frying oil containing high (48%) free fatty acids (FFAs) corroborated these properties. All catalysts exhibited high activity with sPTS/400 converting more than 98.15% FFA into FAMEs. The catalyst exhibited the highest acid density of 1.2974 mmol/g from NaOH titration. This is outstanding considering the lower reaction parameter of 5 h, 5:1 methanol-to-oil ratio and moderate temperature range between 100 and 200 °C. The study further illustrates prospects of converting wastes into highly efficient, benign and recyclable solid acid catalysts.

Keywords- Biomass, Esterification, High Free Fatty Acid, Mesoporous Carbon Sulfonation, Solid Acid Catalyst.

I. INTRODUCTION

Despite the recent fall in the price of Brent crude oil, the search for sustainable and ecologically benign alternative persists. This is due to environmental pollution caused by its exploration and combustion [1,2] coupled with weaker demand for petroleum fuels. The renewable alternative gaining great research is transesterification of triglycerides, TG with methanol into biodiesel or fatty acids methyl esters, FAME [3]. However, feedstocks containing high free fatty acids (FFAs) for this process such as used frying oil (UFO), animal fats and vegetable oils usually incur postproduction costs in separating soap from alkali-catalyzed transesterification. This further decreases the biodiesel yield produced substantially [4]. Therefore, reducing the FFA content from these feedstocks to ca. 1% (acid value of less than 2 mg KOH/g) is thus necessary before transesterification [5,6]. Similarly, several drawbacks hinder the two-step process via H_2SO_4 pre-esterification of FFA into esters by acid-catalyzed followed byalkali-catalyzed transesterification [3,6-10]. These include equipment corrosion, difficulty in product separation from homogeneous mixtures, non-recyclability of catalyst and high-energy consumption during purification [11]. These highlight the increasingly urgent need for affordable acid catalysts with good catalytic performance that could ameliorate the above mentioned hitches.

The discovery of sugar catalyst proved carbon-based solid acids as promising alternatives for homogeneous alkaline and liquid acid catalysts [12]. Recently, incorporating $-SO_3H$ via carbonization-sulfonation method into carbon biomass such as cellulose, corn straw, starch, glucose, sucrose as carbon precursor [13] displayed good catalytic performance in esterification [12,14-19]. This is despite low surface area and low porosity which have the tendency of limiting diffusing reactant to active sites [13]. However, [20,21-26] and [27] recently synthesized sulfonated ordered mesoporous carbons via nanocasting with SBA-15 as template and phenolic resol and F127 self-assembly under acidic condition respectively. Similarly, [28,29] reported how to prepare catalyst for esterification by high temperature sulfonation of carbon nanotubes. The acidity, large pore size and high BET area exhibited by these materials ensured accessibility of long-chain FFA molecules and high catalytic activity. However, a literature survey shows that no reports are available on acid catalyzed reactions using biomass from palm tree. Developing efficient solid catalysts from low-value biomass is essential in making the process fully ecologically friendly and economical. Malaysia being the world second largest producer and exporter of palm oil generates deluge (85.5%) of biomass with little or no economic value [30]. These include palm trunks, mesocarp fibre (PMF), empty fruit bunches (EFB), palm fronds, spikelets and kernel shells (PKS) [31]. Incidentally, agricultural residues from renewable sources which are both abundant and inexpensive will come-in handy as remarkable feedstock for fuel production and catalyst development [32]. Consequently, this paper demonstrate the synthesis of sulfonated mesoporous carbon catalysts with concentrated H_2SO_4 (98%) as sulfonating reagent and palm tree frond and spikelet as carbon precursors. The study investigated the effect of

the resultant catalysts in simultaneously esterifying FFA into FAME.

II. EXPERIMENTAL

A. Materials and methods

Room temperature drying ensured steady moisture loss from the oil palm residues (fronds and spikelets) before oven drying at 120 °C for 24 h followed by milling and sieving (mesh size: 05 mm). The catalysts preparation followed a modified procedure [12,33]. Low temperature incomplete carbonization induces polycyclic aromatic carbon rings formation from the cellulosic palm residues. Heating the dried powder in tubular furnace at 400 °C; 2°C/min for 24 h under N_2 produced incomplete carbonized materials. Treatment with concentrated sulfuric acid introduces sulphonite groups (-SO_3H) into the materials. This is by heating the brown-black solids (20 g) in 200 cm^3 conc. H_2SO_4 (98%) at 150 °C. Adding distilled water (1000 cm^3) after heating for 10 h and then cooling to room temperature formed a black precipitate. Washing the precipitate with hot distilled water (>80 °C) ensures the absence of impurities such as sulfate ions from the wash water. The material was then oven dried at 70 °C before homogenized with succinic acid. Mixing the carbon material (10 g) with 5 g succinic acid and 40 cm^3 de-ionized water and then heating at 150 °C for 5 h warrants proper sulfonation. After filtering and washing with distilled water followed by methanol, oven-drying the resulting product at 100 °C for 5 h produced rigid carbon materials. The sulfonated palm fronds were designated sPTF/SA/T where T stands for carbonization temperature (300 or 400 °C). A reference material not homogenized with succinic acid, SA designated sPTF/400 was synthesized to decipher the effect of SA addition. Catalyst prepared from palm tree spikelet were designated sPTS/T without adding SA. These differences in reacting conditions helped in determining the optimum sulfonated catalyst synthesized from oil palm residues for esterification.

B. Catalyst characterization

FEI QUANTA™ 450 FEG type 2033/14 with S/N: 9924341 (Czech Republic) unit with 30 kV accelerating voltage performed the field emission scanning electron microscopy (FE-SEM) in analyzing the surface morphology and topology. Energy dispersive X-ray spectrometer (EDX) from the same unit revealed the surficial elemental composition of the catalysts. Further, XRD and BET analyses elucidated the structural and textural properties of the catalysts. XRD patterns were analyzed by Phillips xpert diffractometer with CuKα radiation (λ= 1.54056 Å) at a scanning speed of 0.05° s^{-1} within 2θ range of 5 to 70° at 40 mA and 40 kV. Micromeritics equipment with accelerated surface area porosity (ASAP)-2000 at -196 °C determined the specific surface area of the catalytic materials using liquid nitrogen. Degassing the catalysts at 120 °C for 3 h under vacuum eliminates any physisorbed volatiles and impurities. Rapid (scan speed 3 velocities, 2.2 - 20 kHz) identification and quantification of the catalysts was performed with Bruker FT-IR Tensor 27 IR. The equipment has spectral range of 7,500 to 370 cm^{-1} with more than 1 cm^{-1} apodized resolution and standard KBr beam splitter.

C. Production of fatty acid methyl esters

Heating the catalysts at 150 °C for 1 h before the reaction evacuated adsorbed water and other volatiles. Methanol with aid of the catalyst transesterified used frying oil, UFO at 100 to 200 °C in 100 ml autoclave (250 °C, 100 bar) reactor supplied by AmAr Equipment Pvt Ltd Mumbai. Constant stirring ensured contact between the catalyst and reacting mixture. A reflux condenser attached to the autoclave maintained the set temperature during the reaction. A preliminary optimization showed that 5:1 methanol-oil molar ratio and 1 wt% catalyst loading are optimal reaction conditions. Simple decantation recovers the FAME at the end of 3 to 15 h reaction. Drying, methanol washing and heating at 120 °C for 1 h regenerate the catalyst. The catalyst retained its activity after regeneration for up to 8 recycles.

D. Acid density analysis

Exchanging Na^+ with H^+ in the form of -SO_3H by stirring 0.1 g sulfonated material with 30 mL 0.6 M NaCl solution for 2 h facilitates acid strength determination of the catalysts. Titrating the filtrate from this mixture with 0.1001 mol/L NaOH standard solution and methyl orange as indicator indicates NaOH consumed. A change from slightly red to bright yellow maintained for 30 s highlights the end point. To ascertain the initial unconsumed volume of the NaOH standard solution, it is instructive to perform a blank titration. Employing equation 1 enables accurate calculation of the strong acid (-SO_3H) density.

$$D_{-SO_3H} = \frac{C_{OH^-} \times [V_1 - V_0]}{m_{cat.}} \qquad (1)$$

Where strong acid (-SO_3H) density of the catalyst (in mmol/g) concentration of standard NaOH solution are represented by D_{-SO_3H} and C_{OH^-} respectively. Volume of NaOH standard solution consumed in the blank test and catalyst titration are represented by V_0 and V_1respectively. While $m_{cat.}$ represents the mass of catalyst employed for the acid density analysis.

E. Determination of acid value

Determining oil acid value was by titration analysis according to DIN EN ISO 660 (Application Bulletin 141/4e, available from: http://www.metrohmsiam.com/foodlab/FL_22/FL22_1443613_AB-141_4_EN.pdf). Expected acid value of used frying oil, UFO is between 15 to 75 mg KOH/g. The (0.1 mol/L KOH) titrant neutralizes the solvent mixture comprising of 50 mL ethanol-diethyl ether

(1:1; v/v) mixed with 0.5 g catalyst sample. Thereafter, employing equations 2 to 4 simplifies accurate calculation of the titre and acid values, and FFA conversion respectively.

$$\text{Titre value} = \frac{m_S}{V_{EP_1} \times c(KOH) \times M_A} \quad (2)$$

$$\text{Acid value} = \frac{V_{EP_1} \times f \times c(KOH) \times M_A}{m_S} \quad (3)$$

$$\text{FFA conversion, \%} = \frac{V_{EP_1} \times f \times c(KOH) \times M_A}{10 \times m_S} \quad (4)$$

Where V_{EP_1} represents titrant consumed at end of the first equivalent point in mL. The term $c(KOH)$ represents concentration of KOH titrant (0.1 mol/L in this study). The term M_A represents molecular weight of the analyte (112.12 g/mol in this case). The term f represents correction factor ≪ titre ≫ without unit while M_A represents molecular weight of palmitic acid (256 g/mol) and m_s in Eq. 4 represents sample size in g.

III. RESULTS AND DISCUSSION

A. Characterization of biomass

Previous study [34] showed the approximate oil palm biomass composition as: carbon (45-50%), oxygen (43-48%), nitrogen (0.5%), hydrogen (5%) and sulfur (0.4%). Similarly, proximate analysis revealed that oil palm biomass consisted of volatile matter (72-75%), fixed carbon (14-16%), moisture (6-8%) and ash (2-5%). Further, FE-SEM analysis revealed large pores, sharp edges and agglomeration on surface of the catalysts.Fig. 1 shows the small angle XRD pattern for sPTF/SA-300 and sPTF/SA-400. The Figure displays one broad XRD peak at 2θ value of 24° with d value calculated from Bragg equations as 3.86 nm. The N_2 adsorption results presented in Table 1 confirmed the presence of mesopores on the prepared catalytic materials which are consistent with aromatic sheets of amorphous carbon orientation. The absence of crystallinity also indicate the affinity for anchoring -SO3H groups.

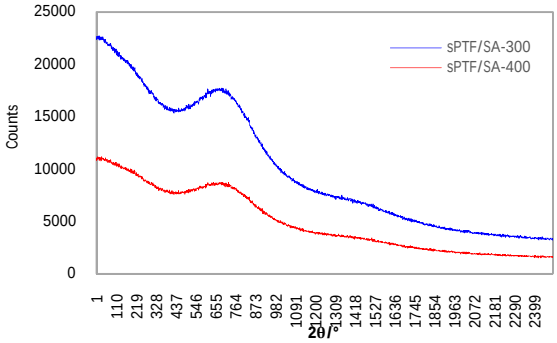


Fig. 1. Small angle XRD pattern of sPTF/SA-300 andsPTF/SA-400

Titrimetric, structural and surficial analysis reveal high strong acid (-SO_3H) densities (Table 1) and amorphous carbon sheets bearing hydroxyl (-OH) and carboxyl (-COOH) groups. Interestingly, the carbon catalysts remained insoluble over boiling temperatures of water, methanol, oleic acid, benzene and hexane [12].Fig. 2a presents the surface microstructure of sulfonated sPTF/SA-400 carbon catalyst studied using FESEM. The different constituents appeared to have beenhomogeneously processed into solid particles of varying dimensions. The surficial elemental composition by EDX analysis revealed the presence of carbon, oxygen, nitrogen and sulfur (Fig. 2b).Similarly, Fig. 3(a) presents the surface microstructure (size and shape of topographic features) of sulfonated sPTF/SA-300 carbon catalyst studied using FE-SEM. The surface morphology appeared to have been heterogeneously processed into solid particles with the succinic acid not fully incorporated. The surficial elemental composition by EDX analysis (Fig. 3b) also revealed the presence of carbon, oxygen, nitrogen and sulfur. Further, FE-SEM analysis revealed large pores on the agglomerated catalyst surface with sharp edges.

Table 1. Surface properties and total acid density (-SO_3H) of the tested catalysts

Catalyst	Surface area (m^2/g)	Pore size (nm)	Pore volume (cm^2/g)	Total acid (-SO_3H) density (mmol/g)
sPTF/SA/400	28.1057	10.1712	0.033078	0.7851
sPTF/SA/300	27.7805	10.0154	0.030178	1.1283
sPTF/400	17.8048	9.1975	0.028308	1.0873
sPTS/400	12.7037	5.1565	0.019907	1.2974

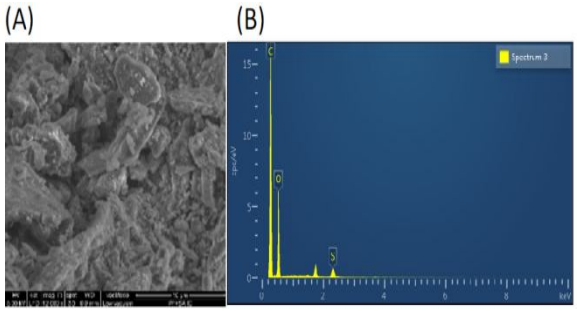


Fig. 2. (a) Results of the surface microstructural analysis of the sPTF/SA-400 via FE-SEM and (b) surficial elemental composition of the sPTF/SA-400 via EDX analysis

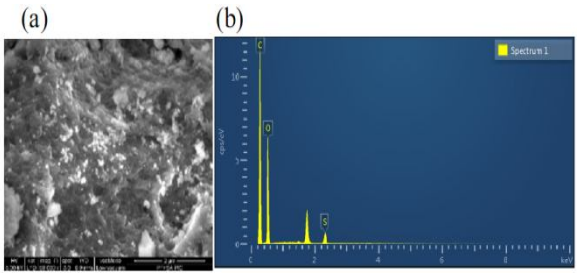


Fig. 3. (a) Results of the surface microstructural analysis of the sPTF/SA-300 via SEM and (b) surficial elemental composition of the sPTF/SA-300 via EDX analysis

Fig. 4(a) presents the surface microstructure (size and shape of topographic features) of sulfonated sPTS-400 carbon catalyst studied using FE-SEM. High carbonization temperature made the carbon structure have fully incorporated the succinic acid into homogeneously processed amorphous solid. Fig. 4(b) presents a cross-sectional surficial composition and distribution of elements on sPTS-400 by EDX analysis. The result also revealed the presence of carbon, oxygen, nitrogen and sulfur. However, the presence of large pores and sharp edges were not evident from the FE-SEM analysis. The analysis only revealed agglomerated amorphous solid with almost uniform protrusions on the catalyst surface.

Sulphonating cellulosic materials produces stable solids with strong acid density constituting high active sites. These facilitates synthesis of highly active catalysts from inexpensive naturally occurring (green) molecules. The FT-IR spectra of unsulfonated mesoporous carbon from palm tree spikelet and sulfonated catalysts are shown in Fig. 5. These results confirmed the findings of [13,23]. Successful incorporation of -SO_3H groups on the sulfonated catalysts is evidently observed from the FT-IR spectrum bands stretching mode at 1040 cm^{-1}. This vibration attributed to symmetric S=O is absent from the unsulfonated material. It is however observed that S=O bond represented by the 1080 cm^{-1} spectra is asymmetric. The FT-IR spectra also revealed O=S=O symmetric bonds from vibration band at 1027 and 1167 cm^{-1} and those for -OH bond at 3424 and 3429 cm^{-1} stretch. The node stretching at 3440 cm^{-1} is assigned to O-H stretching mode of phenolic OH and -COOH groups. Similarly, nodestretching at 1719 cm^{-1} is representative of C=O bonds due to -COO- and -COOH groups stretching vibrations.

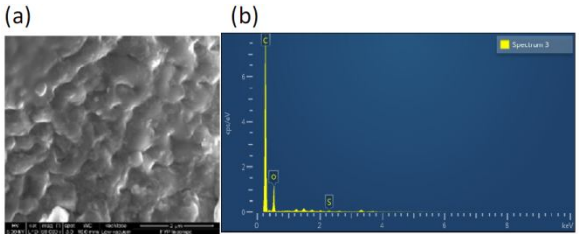


Fig. 4. (a) Results of the surface microstructural analysis of the sPTS-400 via SEM and (b) surficial elemental composition of the sPTS-400 via EDX analysis

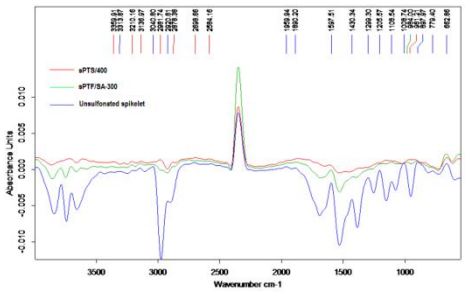


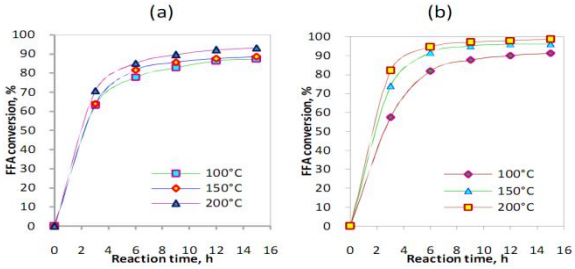
Fig. 5.FTIR spectra of sPTF-300, sPTS-400 catalysts and unsulfonated-PTS-400 mesoporous carbon at different conditions.

The aromatic C=C stretching mode similar to graphite-like polyaromatic materials is ascribed to the broad and intense bands centered at 1610 cm^{-1}. The effect ofcarbonization is observed from the disappearance of C-H peaks stretching at 675 cm^{-1} and 700 to 900 and 3046 cm^{-1} ascribed to polycyclic aromatic and aromatic hydrocarbons respectively. This is because mesoporous carbon skeleton gets dehydrogenated and graphitized at relatively high carbonization temperature. Consequently, it could be deduced that low carbonization temperature is favorable in synthesizing sulfonated carbon catalysts rich in C-H. This is evident from the gradual disappearance of C-H stretching and the difference in -SO_3H incorporated on sPTF/SA/400 (0.7851 mmol/g) and sPTF/SA/300 (1.1283 mmol/g). This corroborates the report by [13].

B. Catalytic performance of the solid acid catalysts in biodiesel production

The catalytic activity of the catalysts synthesized from palm frond and spikelet in producing biodiesel from UFO with methanol was evaluated. The study employed the following conditions: catalyst loading of 1 wt%, methanol-to-oil molar ratio of 5:1 within a temperature range of 100 to 200 °C. The mesoporous sulphonated solid acid catalysts exhibited high activity comparable to conventional solid acid catalysts. They were able to convert high FFA (48%) UFO feedstock obtained from household in Malaysia to more than 98.51% FAMEs. Figs. 6 (a) to (d) show the catalytic activity of the sulfonated solid acid catalysts prepared at different conditions. It is instructive to note that despite low alcohol molar ratio, more than 80% conversion was achieved by all the catalysts after 5 h reaction time. This is encouraging considering 18:1 molar ratio employed by [13], though at lower temperature.

A similar trend is observed for all the reactions with equilibrium setting in after 5 h reaction time. The highest catalytic activity (98.51% FAME) was obtained from reaction with sPTS/400 with 1.2974 mmol/g total -SO3H acid density. This was closely followed by sPTF/SA/300 with 1.1283 mmol/g total -SO3H acid density. Interestingly, the surface area and pore size of sPTF/SA/300 (27.78 m2/g and 10.02 nm) are twice that of sPTS/400. Again, this highlights that successful incorporation of surface strong acid density combined with well-ordered mesoporosity are essential for FFA conversion.



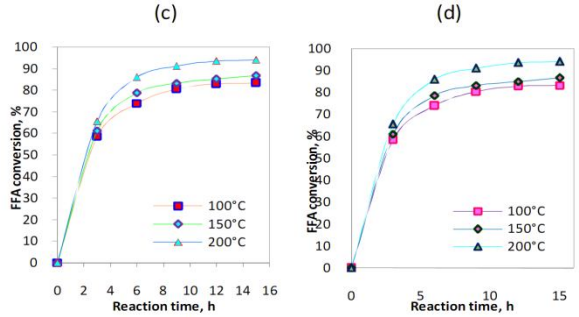


Fig. 6. Comparative catalytic activity of mesoporous (a) sPTF/SA-400, (b) sPTS/400,(c) sPTF/400and (d)sPTF/SA-300 catalysts prepared at different conditions.

Further, the catalyst retained most of its activity after 8 recycles without leaching of its strong (-SO_3H) groups. The catalyst is regenerated by simple decantation, washing and drying. Consequently, this highlights the prospects of producing environmentally benign alternative catalysts from waste palm biomass.

This process is also economical as it employs moderate reaction conditions such as lower catalyst-loading, low temperature (100 °C) and 5:1 alcohol-to-oil ratio. Furthermore, deluge of waste generated from cultivating palm trees and subsequent palm oil production could be easily converted into alternative catalysts with the possibility of wider application in other acid-catalyzed reactions.

CONCLUSIONS

1. Sulfonated mesoporous carbon catalysts prepared from waste palm tree biomass with concentrated H2SO4 (98%) as sulfonating reagent converted more than 98.51% FFA into biodiesel.
2. The study employed 400 °C and 150 °C carbonization and sulfonation temperature to avoid destroying the well-ordered mesostructure of the carbon materials. This ensured good catalytic activity by retaining high acid density on the catalysts.
3. It is instructive to highlight the low process parameters employed in this study; 100 °C, 5 h reaction time, 5:1 methanol-oil ratio with 1 wt% catalyst loading.
4. The catalyst sPTS/400 with specific surface area of 12.7037 m2/g, average pore size of 10.02 nm, mesopore volume of 0.02 cm3/g and 1.2974 mmol/g total -SO3H acid density exhibited the highest activity of 98.51 % after reaction for 5 h. Further, it converted more than 90% FFA after regenerating for 8 consecutive cycles.
5. The observed high catalytic performance is attributed to the large and uniform pore size, good surface area, large mesopore volume, high -SO3H density and hydrophobic surface of sulfonated catalyst. The mesostructure is large enough to effectively accommodate the long FFA chains.
6. Further, the catalysts mesostructure makes accessing the active sites by any water molecules from the UFO feedstock or formed in the course of reaction difficult.
7. This catalyst from waste biomass is promising in the application of solid acid catalysis with good prospects in other acid-catalyzed reactions.

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