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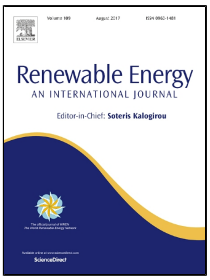

Synthesis of biodiesel from palm fatty acid distillate using sulfonated palm seed cake catalyst

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Graphical Abstract

Research Highlights

- Palm seed-based acidic catalyst was synthesized.
- Synthesized catalyst showed high acid density (12.08 mmol/g).
- 97.8% biodiesel yield was achieved at 60 ^{o}C for 2 hr reaction.
- Catalyst was successfully reused for esterification cycles (8 times) without treatment.

Synthesis of biodiesel from palm fatty acid distillate using sulfonated palm seed cake catalyst

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ABSTRACT

The use of a sulfonated soaked palm seed cake (SPSC-SO_3H) derived catalyst for the production of biodiesel from palm fatty acid distillate (PFAD) (the byproduct obtained during palm oil production) has been demonstrated. The activated carbon material from the soaked palm seed cake (SPSC) was sulfonated and then used for esterification of PFAD (containing 85% of free fatty acid (FFA), 10% of triglycerides, 3% of diglycerides, 0.3% of monoglycerides and some traces of impurities). The synthesized SPSC-SO_3H catalyst was characterized using powder X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), fourier transform infrared (FTIR) spectroscopy, field emission scanning electron microscope (FESEM), NH_3-temperature programmed desorption (NH_3-TPD), N_2 physisorption and thermogravimetric analysis (TGA). The SPSC-SO_3H catalyst showed higher acid density (12.08 mmol g^{-1}) and surface area (483.07 m^2 g^{-1}). The optimized reaction conditions, *i.e.* 9:1 methanol/PFAD molar ratio; 60 °C reaction temperature; 2.5 wt.% of the SPSC-SO_3H catalyst and 2 h of reaction time was employed to achieve FFA conversion (98.2%) and FAME yield (97.8%). The SPSC-SO_3H catalyst underwent eight reaction cycles and catalytic activity was dropped by 24% during recyclability study. The SPSC-SO_3H catalyst demonstrates a promising and effective application for biodiesel synthesis especially for feedstocks containing high free fatty acid content.

Keywords: Palm seed cake; Palm fatty acid distillate; Heterogeneous catalyst; Sulfonation; Reusability, Biodiesel

1. Introduction

In recent years, biodiesel production as an alternative fuel source, has received more attention due to the increased carbon emissions, dwindling traditional fossil resources, unstable cost, and the non-renewability of petroleum fuel. Biodiesel is derived from various animal and vegetable oils and it is basically comprised of a mixture of alkyl esters of fatty acids, and other glycerides compounds [1]. The transesterification of vegetable oils and fats have been employed to lower the viscosity levels of these fats and oils so as to meet the permissibility limit of petroleum fuel [2]. Moreover, biodiesel is a clean-burning fuel because of its environmentally benign, easily degradable and bio-renewable nature, good transport and storage properties, and it can be directly used in modern day compression-ignition engines with no modification step needed [3].

Currently, different sources of vegetable oil have been used as an attractive feedstock for the production of biodiesel, *i.e.* canola [4], palm [5], Jatropha [6], sunflower [7] and rapeseed [8] oils. However, food grade vegetable oils have not been exploited for the production of biodiesel because they will inadvertently lead to an increase in the prices of edible vegetable oils and an unhealthy competition between food and fuel. Hence, there is a necessary need to explore new suitable feedstock for biodiesel production. As a result, palm fatty acid distillate (PFAD), a by-product from the palm oil industry has emerged as the prime candidate for biodiesel production. Of the total 59 million tons of palm oil produced globally in 2014, Malaysia, being the second largest global producer and exporter of palm oil, produced 19.4 million tons of palm oil which is approximately 33% of the global production [9]. PFAD primarily consists of high free fatty acid (FFA, 85 wt. %), triglycerides (10 wt.%) and other small contents of sterols, vitamin E and squalene.

In industry, a base catalyst is used to convert PFAD to methyl esters, saponification usually occurs, due to the high free fatty acid contents of the feedstock. In conventional esterification process, homogeneous acid catalysts (H_2SO_4) are used with high quantities of alcohol, which is the main factor affecting economics of biodiesel production from PFAD [10]. This also creates many drawbacks *i.e.* corrosion to reactor, multiple purification steps which generates wastewater and unreacted H_2SO_4 catalyst [11].

In other to avert this shortcoming, different types of heterogeneous solid acids such as ferric hydrogen sulfate [11], ferric alginate [12], carbohydrate-derived solid acid [13], sulfonated-carbon nanotubes [14], niobium-MCM-41 [15] catalysts have been investigated as viable catalysts for esterification reaction. Moreover, carban based catalysts i.e. sugars [13], starch [16], fiber [17], resin [18], polymer [19] and glycerol [20] have also been reported. However, the expensive materials, synthesis routes, low activity and reusability, reduced their industrial applicability. Therefore, the development of sulfonated carbon catalysts derived from low cost biomass wastes to produce biodiesel from acidic oil could be a potential and considerable interest. Palm biomass accounts for about 85.5% of the total biomass generated from agricultural activities, and only about 10% of oil is produced, thus Malaysia has a rich source of palm biomass suitable as feedstock for catalyst synthesis [9].

In previous study, Guldhe et al. [21] synthesized chromium-aluminum mixed oxide (CRAL) heterogeneous catalyst and utilized for esterifying the PFAD. They had achieved FAME conversion (98.28%) at optimum reaction conditions; reaction temperature of 80 °C, catalyst concentration of 15 wt. % and 15:1 methanol-to-oil molar ratio. In another related study, rice husk-derived sodium silicate was utilized for transesterification of oils at the optimal reaction conditions; catalyst loading of 2.5 wt. %, methanol-to-oil molar ratio of 12:1, at 65 °C for 30 min

and FAME yield was 97% [22]. Similarly, the methanolysis of RBD palm oil was demonstrated using calcium oxide synthesized catalyst at the following optimal conditions; 9 wt. % catalyst loading, 12:1 methanol-to-oil ratio, 2 h reaction time and 60 °C and observed the conversion of 90.11% [23].

To our best knowledge, no study on the catalytic performance of sulfonated soaked palm seed cake (SPSC-SO_3H) catalyst has been reported yet, for biodiesel production from PFAD. In this work, the main aim was to synthesize the highly acidic palm seed cake-based catalyst and its utility to generate biodiesel from PFAD. A thorough physicochemical characterization *i.e.* X-ray diffraction (XRD), thermogravimetric analysis (TGA), Fourier Transform infrared (FTIR), Brunauer–Emmett–Teller (BET), NH_3-temperature programmed desorption (NH_3-TPD), field emission scanning electron microscope (FESEM) and carbon hydrogen nitrogen sulfur (CHNS) analyses were carried out for the SPSC-SO_3H catalyst. Important reaction variables (methanol to PFAD molar ratio, catalyst loading, time and temperature) were also optimized for a higher PFAD conversion yield. Furthermore, the reusability study of SPSC-SO_3H catalyst was further appraised to test its usability for eseterification reaction without further treatment.

2. Experimental

2.1. Reagents and materials

The palm seed cake and PFAD were obtained from Jomalina R&D and Sime Darby Group Sdn. Bhd., Malaysia, respectively. The PFAD consists of 85 wt.% of FFA (43.2% palmitic, 30.1% oleic, 7.1% linoleic, 3.6% stearic and 1.0% myristic). It also contains 10% triglycerides (TG), 3% diglycerides (DG), 1% monoglycerides (MG) and some traces of impurities. Ethyl alcohol (96%), methanol (99.8%), propanol (99.97%) and *n*-hexane (85%) were purchased from Merck & Co, pharmaceutical company, USA. Concentrated H_2SO_4 (98%) and KOH (86%) were bought from J.

T. Baker. Phenolphthalein and H_3PO_4 (50%) were purchased from Sigma-Aldrich. Methyl palmitate, methyl linoleate, methyl oleate, methyl heptadecanoate, methyl myristate and methyl steatrate were ≥99.0% analytical grade standards purchased from Fisher Scientific and used for the FAME yield determination using gas chromatography (GC). The saponification value of the crude PFAD was measured using AOCS method Cd 3-25.

2.2. Chemical activation process

Two samples were prepared in order to check the progression in surface area and pore volume. The first sample was measured and pyrolized without H_3PO_4, whereas the other powdered palm seed cake was chemically activated by soaking (20 g) with orthophosphoric acid (H_3PO_4; 50%) in the impregnation ratio of 2:1 (w/w) for 24 h at self a generated temperature to facilitate high porous and specific surface area development [14]. After the soaking the PSC, the resultant material was kept for calcination.

2.3. Catalyst preparation

Briefly, the palm seed cake-based acidic catalyst was synthesized using sulfonation process after the pyrolysis of soaked palm seed cake. The preparation of the sulfonated solid acid catalyst from the SPSC was adopted and slightly modified from the previous procedure [24]. The soaked/unsoaked PSC was then transferred and calcined with tube furnace in N_2 atmosphere at 400 °C for 2 h until black material was produced. The black solid materials produced were extensively washed with hot distilled/de-ionized water (> 80 °C) until reaching pH~7, followed by drying in an oven at 80 °C for 24 h to obtained the palm seed cake based activated carbon. After drying, a mortar pestle was used to powder the PSC-AC and SPSC-AC materials. The attachment of a sulfonic group ($-SO_3H$) was performed by sulfonating on the SPSC-AC (4 g) with 100 mL of

concentrated H_2SO_4 at 150 ˚C under a nitrogen flow in a reflux system for 12 h. At the end of the heating, the sample was allowed to cool down to room temperature and then slowly diluted with distilled water and the black precipitate was afterwards collected. The sulfonated soaked palm seed cake (SPSC-SO_3H) catalyst was then washed with hot (> 80 ˚C) distilled water in order to remove the possible remnants of the sulfate ions and unwanted impurities. The excess moisture was gotten rid of by drying the SPSC-SO_3H catalyst in an oven for 24 h at 80 °C.

2.4. Catalyst characterization

The catalyst's structural and crystallinity were checked by X-ray diffraction (XRD). The machine used for the analysis was the XRD (Shimadzu, XRD 6000) which has a scanning rate of 4 degrees min^{-1} and a scanning range of theta (θ) from 2˚ to 60˚. The average crystallite size of the PSCW-SO_3H samples was estimated by Scherrer's formula ($D = 0.89\ \lambda / \beta\ Cos\ \theta_\beta$), where D is the average crystallite size, λ is the wavelength of the X-ray beam, β is the full width half maximum (FWHM) values of the peaks, and θ_β is the Bragg angle. To investigate for the thermal stability, the thermogravimetric analysis (TGA) was performed with differential thermogravimetry (DTG), using the Mettler Toledo 990. In order to ascertain the presence of the functional group attached on the catalyst, the Fourier Transform Infrared (FTIR) from Perkin Elmer (1725 X) was deployed. Prior to the surface area analysis (BET), the sample was degassed at 150 ˚C and heated overnight. The Sorptomatic 1990 series (Thermo Finnigan) instrument was used for the surface area measurement. The acid density and active acid sites were determined by using the ammonia-temperature programmed desorption (NH_3-TPD) (Thermo Finnigan, TPDRO 1100 series) and helium was used as a carrier gas. A morphological study of the samples was carried out using a high magnifying field emission scanning electron microscope (FESEM) (JEOL, JSM-6400).

2.5. Catalytic activity of the SPSC-SO_3H catalyst

In the present study, experiments were planned to appraise the effect of different reaction parameters such as methanol/PFAD molar ratio (3:1-13:1); SPSC-SO_3H catalyst loading (0.5-3.5 wt.%), reaction temperature (55-75 °C) and reaction time (1-6 h). The esterification reaction involving the PFAD and SPSC-SO_3H catalyst in the presence of a calculated amount of alcohol, a conventional reflux system was used. The 250 mL of a 2-necked flat bottom flask, containing the mixture of reactants, was coupled to the condenser to re-condense the evaporated methanol back into the reaction. The flask was immersed in a semi-filled silicon oil bath for the esterification reaction as per scheme 1. The esterification reactions were performed by varying the amount of catalyst, methanol to PFAD molar ratio, time and temperature of the reaction. Typically, 0.1g of catalyst, 4 g of PFAD and 4.27 g of methanol were mixed together in the reaction system, a stirrer was placed along in the flask, with a stirring speed set at 600 rpm. At the end of the reaction, the reaction mixture (depending on the volume) was poured into a 50 mL centrifuge tube for centrifugation at 5000 rpm for 15 min in order to ease the separation. The catalyst was further washed with ethanol (30 mL at room temperature) after separation and dried at 80 °C for 4 h and tested in the reuse experiments. As for the FAME, it was heated at 65 °C for 1 h to remove the excess remaining methanol.

2.6. PFAD methyl ester analysis

According to the AOCS 5a-40 standard, the fatty acid (FA) conversions were calculated, according to the differences of the free fatty acid (FFA) of the feedstock and the product [9], as the following equation (Eq. 1), where; FFA_f and FFA_p represents the acid value of the feedstock and the free fatty acid value of the FAME phase, respectively.

$$\text{FFA conversion (\%)} = \frac{\text{FFA}_f - \text{FFA}_p}{\text{FFA}_f} \times 100 \quad (1)$$

Gas chromatography equipped with a flame ionization detector (FID) was used to analyze the FAME yield using EN 14103 method. A highly polar capillary column BPX 70, from the SGE Company (length: 60 m, ID: 0.25 mm and capillary: 0.25 mm) was used for separating the various compound compositions of the FAME. The n-hexane was used to dilute the samples. All reference standards *i.e.* methyl oleate, methyl palmitate, methyl linoleate, methyl myristate and methyl stearate were diluted to become 1000 ppm, respectively and methyl heptadecanoate was prepared as the internal standard. For a typical GC analysis injection, 1 mL of the prepared sample solution was injected into the GC injector pot. The temperature for the inlet was set at 250^0C whilst the FID temperature was set at 270 ˚C. The GC oven's starting temperature was programmed to start at 100 ˚C and increase to 250 ˚C with the temperature rate set at 10 ˚C min^{-1}. Eq. (2) showed the formula to calculate the FAME yield:

$$\text{FAME yield (\%)} = \frac{\text{weight of FAME produced}}{\text{weight of theoritical FAME}} \times 100 \quad (2)$$

2.7. Catalyst reusability analysis

The reusability was carried out for the spent SPSC-SO_3H catalyst. After each esterification cycle, separation of the FAME, SPSC-SO_3H catalyst and water residue were performed. The spent catalysts were recovered from the reaction mixture and washed with ethanol to remove all possible oil residues and afterwards with hexane to remove polar and non-polar compounds from the catalyst. The SPSC-SO_3H catalyst was dried for 12 h at 80 °C and then reused for the next reaction cycle. The reusability study of SPSC-SO_3H catalyst was performed at optimized reaction parameters (*i.e.* 2.5 wt. % of the SPSC-SO_3H catalyst, reaction temperature of 60 °C, reaction time

of 2 h and methanol to PFAD molar ratio of 9:1) and FAME yield and FFA conversion were calculated using Eq. (1) and (2). The same procedure was repeated for all the cycles.

2.8. CHNS analysis

The CHNS analysis was used to measure the amount of sulfur leached during the esterification reaction. Typically, the 0.05 g of SPSC-SO_3H catalyst was collected after each run and analyzed using CHNS instrument (LECO CHNS-932 spectrometer) to determine the amount of leached active site (-SO_3H) from SPSC-SO_3H catalyst.

2.9. Statistical analysis

In order to analyze the data for the catalytic activities, samples were individually studied in set of three as the mean ± SD.

3. Results and discussion

3.1. Effect of chemical activation on surface area

The Brunauer–Emmett–Teller (BET) surface area analysis was carried out to investigate the effect of H_3PO_4 treatment on the PSC. Two samples; the palm seed cake-activated carbon (PSC-AC) and soaked palm seed cake activated carbon (SPSC-AC) were analyzed for nitrogen adsorption/desorption measurements and results are summarized in Table 1. The SPSC-AC showed a type 4 mesoporous structure with H4 hysteresis loop which is a typical feature of a slip-shaped pore which clearly defines a mesoporous material. On the other hand the PSC showed a type 1 structure which is a main feature of a microporous material [19]. Based on the nitrogen quantity adsorbed at different relative pressures, the specific surface area of the PSC-AC (107 m^2 g^{-1}) and the SPSC-AC (658 m^2 g^{-1}) was calculated by the Brunauer–Emmett–Teller (BET) method. The recorded pore diameter for the SPSC-AC was 5.09 nm and pore volume of 1.18 cm^3 g^{-1},

whereas the PSC-AC pore diameter and pore volume was 0.95 nm and 0.15 cm^3 g^{-1}, respectively. Therefore, there was an apparent increment in the specific surface area, pore volume and pore diameter of the SPSC-AC as depicted in Table 1. These results indicate that H_3PO_4 is an effective activating agent that promotes the development of porosity and can help to increase the surface area to a reasonable margin [25-26].

3.2. Characterization of the SPSC-SO_3H catalyst

3.2.1. XRD analysis

The x-ray diffraction patterns (Fig 1), confirms the amorphous nature of PSC, SPSC-AC and SPSC-SO_3H catalyst. They all revealed weak but broad diffraction peaks of (002) and (101) at 2θ values ranged from 10-30° and 38-45°, respectively, which is attributed to the amorphous carbon natures composed of aromatic carbon sheets oriented in a relatively random manner in the carbonaceous materials [16, 27]. The bio-based material becomes completely black which might be indication of dehydration process to form polyaromatic/carbon on the surface [27], whereas, the sharp peaks may indicate the presence of inorganic substances [28].

3.2.2. FT-IR analysis

The FTIR spectra of typical absorption signals observed from Fig 2 shows band recorded at 1118 cm^{-1} which confirms the presence of the sulfonic group (-SO_3H), covalently bonded to polyaromatic carbon structure on the SPSC-SO_3H catalyst. The stretching bands at range of 1500-1700 cm^{-1} for both the SPSC-AC (Fig. 2b) and SPSC-SO_3H catalyst (Fig. 2c) was indication for typical carbonyl functional groups (C=O); which is characteristic peaks of incompletely carbonized carbons [29]. Other stretching band that appeared at 1180 (P=O stretching), indicated the incorporation of H_3PO_4 as an acid activation agent on the non-sulfonated carbon surfaces of the PSC-AC (Fig. 2b) [29].

3.2.3. FESEM and EDX analysis

Fig. 3 shows the FESEM images of the PSC, SPSC-AC and SPSC-SO_3H catalyst. All the materials exhibited aggregate and irregular particles. The surface texture of the PSC changed significantly after soaking with H_3PO_4 and sulfonation with H_2SO_4. Upon the H_3PO_4 acid treatment of PSC (Fig. 3b) and sulfonation of SPSC-AC (Fig. 3c), the porosity of the carbon materials, increased in arrangement of PSC < SPSC-AC < SPSC-SO_3H catalyst, respectively, as clearly seen in the FESEM images (Fig. 3). The EDX and CHNS analysis (Table 2) data clearly depicts that the predominantly the carbon, hydrogen and sulfur in all the materials. The existing of sulfur in SPSC-SO_3H catalyst was proved to confirm the sulfonation of the -SO_3H functional group on the surface of the catalyst.

3.2.4. NH_3-TPD analysis

The total amount of acidity and active acid site distributions were determined by the NH_3-TPD analysis. The NH_3 desorption profiles of PSC, SPSC-AC, and SPSC-SO_3H catalyst are depicted in Fig 4 and the amount of acidity of the SPSC-SO_3H catalyst is summarized in Table 2. For PSC (Fig. 4a), the appearance of two broader desorption peaks were observed as weakly and moderately of acid sites which may be due to the interaction between -NH_3 and residue of the unreacted carbon sheets [30]. The NH_3-TPD profile of the SPSC-AC (Fig. 4b) exhibited the NH_3 desorption peaks in ranges of 100-300 °C and 400-700 °C after the chemical activation process with H_3PO_4 acid. This indicated that a Lewis acid site and a Brønsted acid site were found at the desorption peak with T_{max} of 180 ˚C and 630 ˚C [31], respectively. The SPSC-SO_3H catalyst (Fig. 4c) showed strong acid sites desorption peak at the T_{max} of 780 ˚C after sulfonation, but it also showed a relatively lower weak acid sites at the T_{max} of 210 ˚C. Moreover, SPSC-SO_3H catalyst

has also demonstrated a moderately desorption peak at the T_{max} of 550 ˚C. Similar sulfonation peaks were reported by Lokman et al. [32] for sugar based solid acid catalyst.

3.2.5. Thermo-gravimetric analysis

The thermal stability of the PSC, SPSC-AC and SPSC-SO_3H catalyst were tested with the thermo-gravimetric analysis (TGA) under a nitrogen flow. As expressed in Fig. 5, each of the samples had an initial weight water loss at around 100 ˚C from the samples. Firstly, the PSC was underwent for early weight loss occurring around 220-400 ˚C where it maintained thermal stability before losing the weight. The H_3PO_4 treatment changed the pattern of thermal decomposition due to which SPSC-AC showed a better stability than PSC. The SPSC-SO_3H catalyst demonstrated a very excellent thermal stability under inert atmosphere. The weight loss of water occurred in the region of 0-100 °C, followed by a steady and gradual loss of weight until 420 °C which could be due to the decomposition of the -SO_3H acid group from the SPSC-SO_3H catalyst. It was thermally stable at temperature close to 300 ˚C before start the decomposition of the -SO_3H group but from 420-800 ˚C there was gradual and steady weight loss. The thermal decomposition reported elsewhere for carbon-based solid acid catalysts is similar to our synthesized bio-based acid catalyst [33].

3.2.6. BET surface area analysis

The BET surface area analysis of PSC, SPSC-AC and SPSC-SO_3H catalyst were analyzed with the relevant nitrogen adsorption/desorption isotherms, and the results are summarized in Table 1. Based on the nitrogen quantity adsorbed at different relative pressures, the surface area was calculated by BET analysis. SPSC-AC (658.34 m^2 g^{-1}) had the highest surface area compared to SPSC-SO_3H (483.07 m^2 g^{-1}) and PSC (89.41 m^2 g^{-1}) and this was clearly as a result of the soaking of the PSC in H_3PO_4. This result also indicates that the presence of -SO_3H acid functional

group had a mild effect on the surface area of SPSC-SO_3H catalyst, which may be due to the partial disturbance of the surface area during sulfonation [17, 34]. The surface area of SPSC-SO_3H catalyst (483.07 m^2 g^{-1}) was a bit lower than the surface area of the Mesua-derived activated carbon sulphonate (MAC- SO_3H) (556 m^2 g^{-1}) [30].

3.3. Chemical properties of crude PFAD

The free fatty acid (FFA) and saponification value of the crude PFAD was determined using the AOCS methods. The FFA content of the PFAD was 85.01 mg KOH/mg of PFAD and the saponification value was 232.8 mg KOH/g, respectively. The fatty acids components were analyzed with GC-FID and it consists of 43.2% palmitic, 30.1% oleic, 7.1% linoleic, 3.6% stearic and 1.0% myristic. It was also contains 10% triglycerides (TG), 3% diglycerides (DG), 1% monoglycerides (MG) and some traces of impurities.

3.4. PFAD esterification process

3.4.1. Effect of methanol/PFAD molar ratio on FFA conversion

An important variable in ensuring a complete reaction that involves the conversion of FFA, is the amount of alcohol utilized. In this case, methanol was used in various molar ratios, ranging from 3:1 to 13:1 as presented in Fig 6a. During the esterification reaction, the following reaction conditions were maintained *i.e.* reaction time 2h, reaction temperature 60 ˚C, and 2 wt. % of the SPSC-SO_3H catalyst. Fig 6a clearly shows that as the methanol-to-PFAD molar ratio increased the FFA conversion also increased. At 9:1 methanol-to-PFAD molar ratio, the highest FFA conversion of 87.7% was achieved. More methanol was added to further increase the methanol-to-PFAD molar ratio to check for possible increments in the FFA conversion, from 11:1 and 13:1, but the FFA conversion reduced to 84.4 and 84.3 %, respectively. This lack of a significant increase in the FFA conversion can be attributed to the fact that excess water may produced during the

esterification reaction, which thus reacted with the PFAD and, therefore pushed the reaction backwards. Although, in principle, an abundant amount of methanol is needed to push the reaction to the product side since esterification is a reversible reaction but this principle was not effective [26-30]. As a result, the 9:1 methanol-to-PFAD molar ratio was chosen as an optimum condition for further study. Zhang and Jiang [35], utilized methanol-to-oil molar ratio of 24:1 in the esterification of *Zanthoxylum bungeanum* seed oil. Whereas, Guldhe et al. optimized 15:1 methanol-to-oil molar ratio to achieved the conversion upto 98.28% [21]. This clearly shows that in the present study less molar ratio of methanol to PFAD was used as compared to other published work.

3.4.2. Effect of the SPSC-SO_3H catalyst dosage on FFA conversion

Fig 6b shows the SPSC-SO_3H catalyst ranges from 0.5 to 3.5 wt.% for the conversion of the FFA. As expected, there was an increase in the FFA conversion as the weight percentage of the catalyst increased. The conversion steadily increased as the amount of catalyst increased until it reached 3 wt. %, where the FFA conversion rose up to 92.1 % before it reduced to 90 % at 3.5 wt. %. The starting conversion of 49.6 % when 0.5 wt. % of SPSC-SO_3H was used, showed a 42.5 % conversion difference when the catalyst weight was increased to 3 wt. %. There was an observed reduction in the conversion when 3.5 wt. % was applied, which indicated that though a sufficient amount of catalyst was needed for the optimum conversion, an excess of the catalyst would not have increased the FFA conversion. This was because there was more than enough mass transfer or contact rate between the catalyst and the methanol, and the feedstock had already reached the equilibrium point [36]. It is as a result of this, that 2.5 wt. % was chosen for further optimization studies as the optimum catalyst concentration. Other operating conditions that were kept constant during the reaction are: reaction time 2h, methanol-to-PFAD molar ratio 9:1, and reaction

temperature 60 ˚C. Acidified soybean soap stock for biodiesel was used by Guo et al [37], for the production of biodiesel using the lignin-derived carbonaceous solid acid catalyst. In their work, an excess of 7 wt. % of their synthesized catalyst was used to convert the FFA up to 96 %.

3.4.3. Effect of reaction temperature on FFA conversion

The role of temperature was studied in the FFA conversion by varying the temperatures from 55 to 75 °C; whilst the following parameters were kept constant all through the reactions; reaction time 2 h, catalyst loading 2.5 wt. % and 9:1 methanol-to-PFAD molar ratio. Activation energy was needed to ensure protonation of the FFA conversion, since the esterification reaction is an exothermic reaction [38]. An increased temperature, as expected, increased the esterification rates. At 60 ˚C, a 98.5 % FFA conversion was observed as seen in Fig 6c, which shows the highest FFA conversion rate. Although the temperature was further increased to 75 ˚C, but there was no significant FFA conversion. Hence, 60 ˚C was chosen as the optimum temperature for further studies. In a similar work done by Leung and Guo [39] and also by Hayyan et al. [40] all showed that higher temperatures above 50 and 60 ˚C, respectively, directly affect the FFA conversions. Guldhe et al. also optimized the biodiesel yield and achieved 98.28% conversion at 80 ˚C of reaction temperature [21].

3.4.4. Effect of reaction time on FFA conversion

Under a continuous methanol single-pot system the effect of the reaction time was investigated and the results have been presented in Fig 6d. Enough contact time was required for all the media involved, for there to be the optimum FFA conversion. During the optimization of reaction time, the optimized reaction conditions; 60 ˚C of reaction temperature, 9:1 methanol-to-PFAD molar ratio and 2.5 wt. % of SPSC-SO_3H catalyst concentration was kept constant. Different reaction times from 1 to 6 h were observed. The FFA conversion progressed smoothly as the

reaction time increased, but early on in the first h to 6 h reaction time, the FFA conversion maintained a steady conversion rate that was above 82 % in the first h and 91 % in the 6 h, although the best FFA conversion was recorded in the second hour with a conversion rate of 97.2 %. It is imperative, therefore, to save energy and to reduce any further reaction time since the transfer rates add no significance in the overall FFA conversion. Dekkhoda et al. [41], produced biochar based solid acid catalyst for biodiesel production and optimized 3 h reaction time. In our present study, we had achieved better reaction time as compared to other published studies [36].

3.5. Yield of the PFAD methyl esters at optimum conditions

The FAME yield (97.8 %) was obtained at following optimized reaction conditions: reaction time of 2 h, reaction temperature of 60 ˚C, 9:1 methanol to PFAD molar ratio and 2.5 wt. % of the SPSC-SO_3H. The predominant ester was methyl palmitate (42.9%), followed by methyl oleate (29.6%), then methyl linoleate (7.0%), methyl stearate (3.5%), and finally methyl myristate (0.9%).

3.6. Catalyst deactivation and reusability analysis

One of the major critical advantages of using the heterogeneous solid acid catalyst is its reusability. A catalyst that has more reusable cycles without reactivation is regarded as more stable. In order to check for the reusability, the CHNS analysis (Table 2) was performed on each of the SPSC-SO_3H catalyst recovered after the esterification reaction. The result has been presented in Fig 8, where the catalyst was able to go up to 8 cycles having a final FAME yield of 68.2 % and FFA conversion of 69.8 % at optimum reaction conditions as presented in Fig 7. In a related work by Alhassan et al. [11] where they used hydrogen sulphate as a heterogeneous solid acid catalyst to produce biodiesel, they were only able to reuse their catalyst for five cycles and similarly, Guldhe et al. [21] also reused the sulfonated catalyst for four catalytic batches.

4. Conclusions

The synthesis of sulfonated soaked palm seed cake has been demonstrated for the production of biodiesel. In this study, SPSC-SO_3H catalyst has been efficiently used for highly acidic PFAD, which contained around 85 wt.% of FFA, for biodiesel production. The synthesized SPSC-SO_3H catalyst showed good thermal stability, better acid density, sufficient porosity and reusability. The SPSC-SO_3H catalyst illustrated the high catalytic activity during esterification reaction. The attached sulfonic group largely affected the FFA conversion rates as compared to PSC and SPSC-AC. The FFA conversion of 98.2 % and the FAME yield of 97.8% were achieved under the optimized reaction conditions of 9:1 methanol-PFAD molar ratio, 2 h reaction time, 60 °C reaction temperature and 2.5 wt. % of SPSC-SO_3H catalyst loading. The SPSC-SO_3H catalyst was successfully reused for esterification cycles (8 times) due to the stable attachment of the –SO_3H functional group. Moreover, the leached sulfur content was insignificant for the first five reaction runs, but it gradually decreases across the sixth through the eighth runs. In this study, the SPSC-SO_3H catalyst maintained good reusability and better catalyst activity for PFAD to produce higher biodiesel yield, which indicated that some other waste biomass could be utilized to produce efficient solid acid catalyst for waste oils.

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Figure captures:

Fig. 1 XRD patterns of (a) palm seed cake (PSC) (b) soaked palm seed cake – activated carbon (SPSC-AC) and (c) sulphonated soaked palm seed cake (SPSC-SO_3H) catalyst

Fig. 2 FT-IR spectra of (a) palm seed cake (PSC) (b) soaked palm seed cake – activated carbon (SPSC-AC) and (c) sulphonated soaked palm seed cake (SPSC-SO_3H) catalyst

Fig. 3 FESEM images of (a) palm seed cake (PSC) (b) soaked palm seed cake – activated carbon (SPSC-AC) and (c) sulphonated soaked palm seed cake (SPSC-SO_3H) catalyst

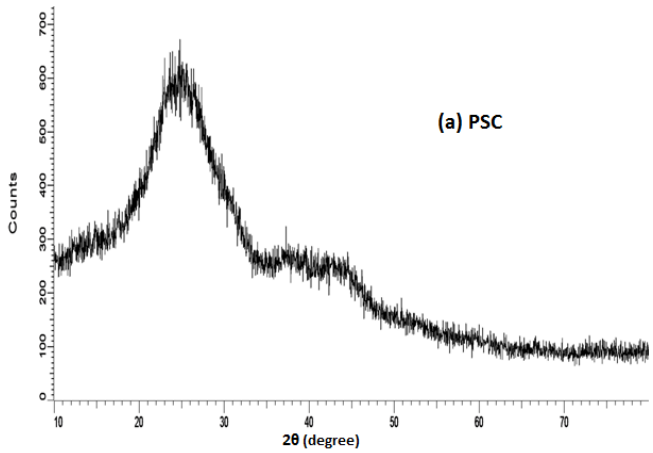
Fig. 4 NH_3-TPD of (a) palm seed cake (PSC) (b) soaked palm seed cake – activated carbon (SPSC-AC) and (c) sulphonated soaked palm seed cake (SPSC-SO_3H) catalyst

Fig. 5 Depiction of TGA analysis of (a) palm seed cake (PSC) (b) soaked palm seed cake – activated carbon (SPSC-AC) and (c) sulphonated soaked palm seed cake (SPSC-SO_3H) catalyst

Fig. 6 Optimized reaction parameters; (a) methanol-to-PFAD molar ratio; (b) SPSC-SO_3H catalyst concentration (c) reaction temperature; and (d) reaction time for conversion of FFA from PFAD.

Fig. 7 FFA conversion, FAME yield and leached sulfur ion during reusability study at optimized reaction conditions: reaction time = 2 h, reaction temperature = 60 ˚C, methanol-to-PFAD molar ratio = 9:1 and catalyst loading = 2.5wt. %.

Scheme 1 Experimental set up diagram for esterification reaction.



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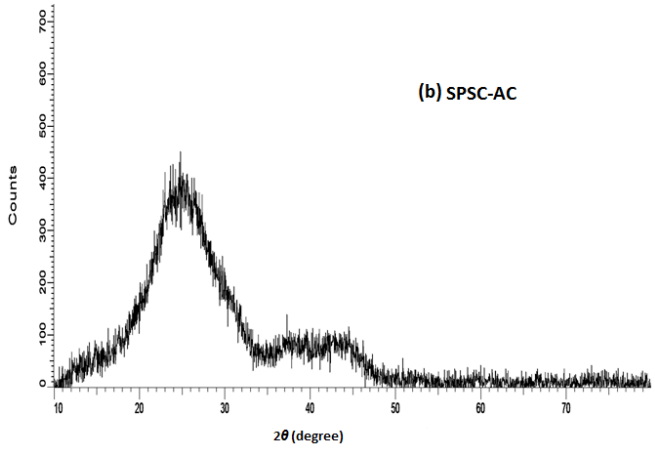

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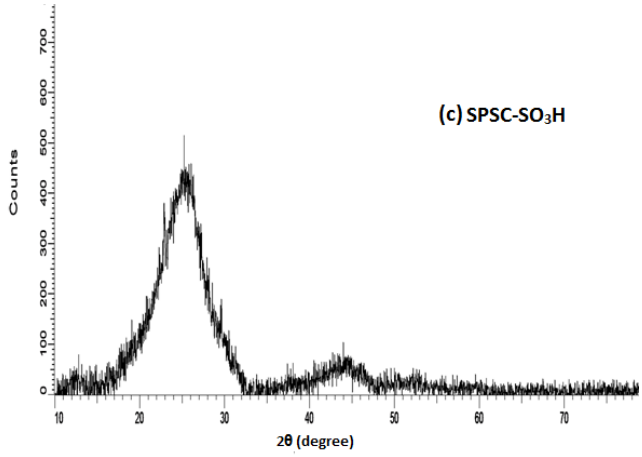

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571 **Fig. 1**

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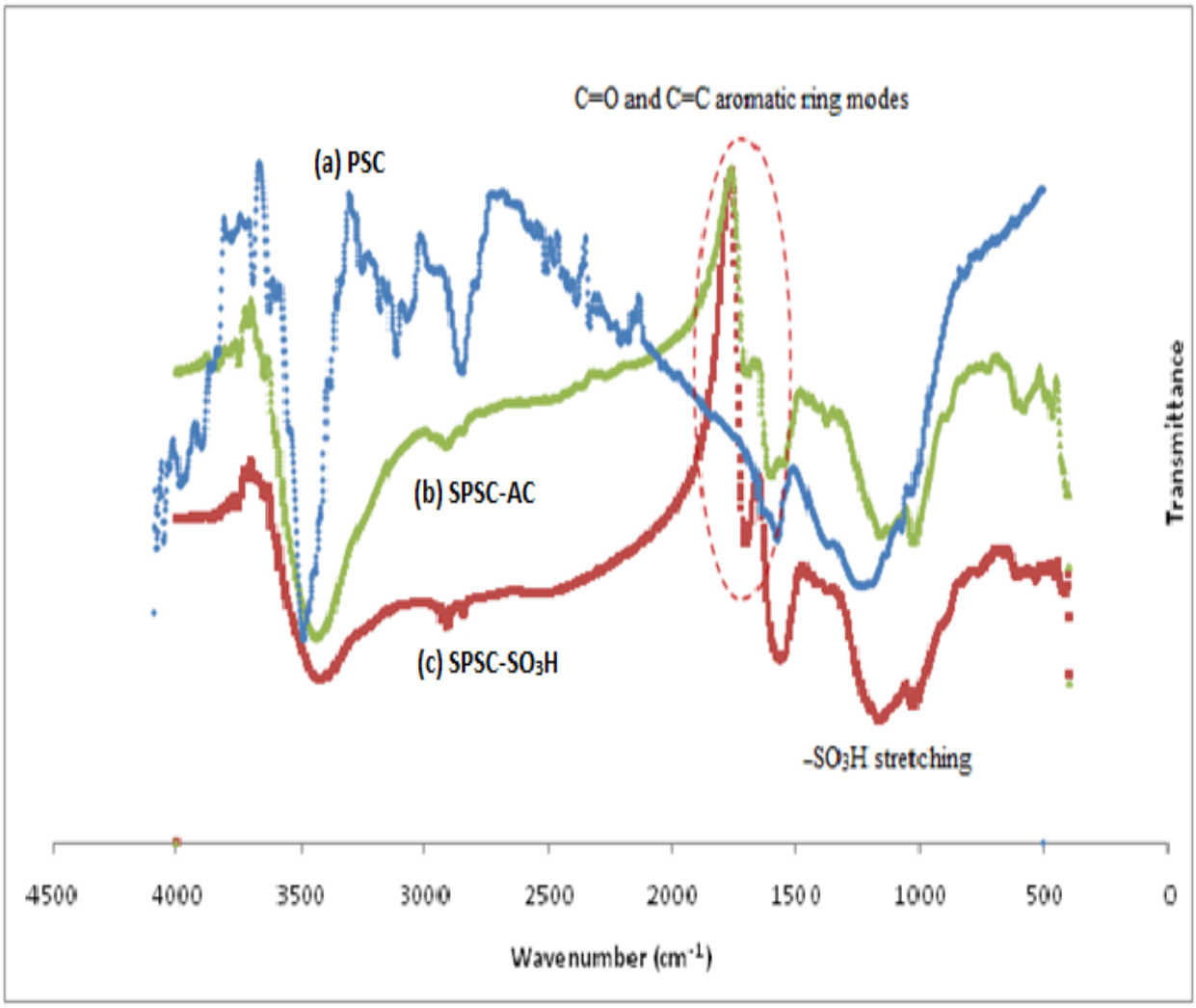

Fig. 2

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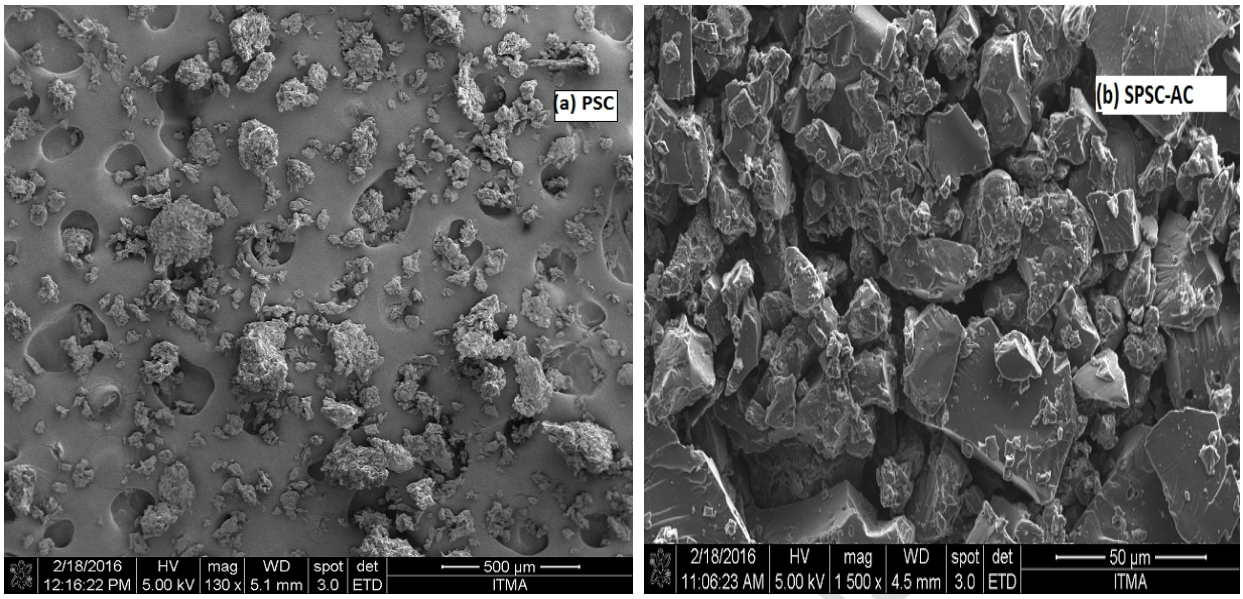

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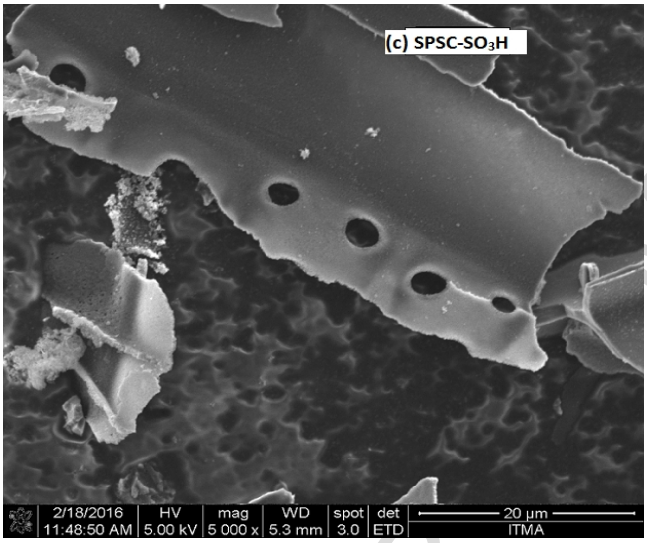

586 **Fig. 3**

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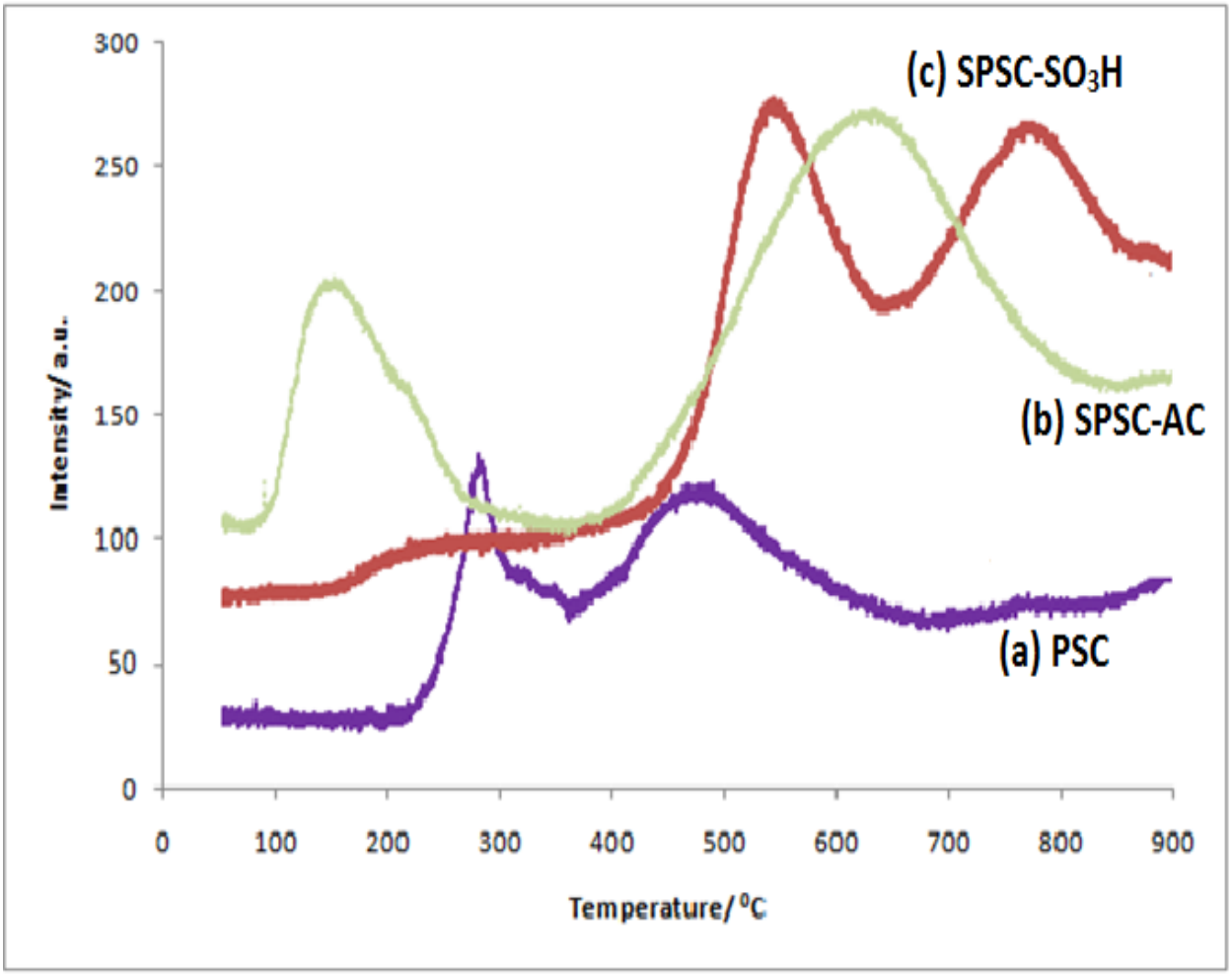


Fig. 4

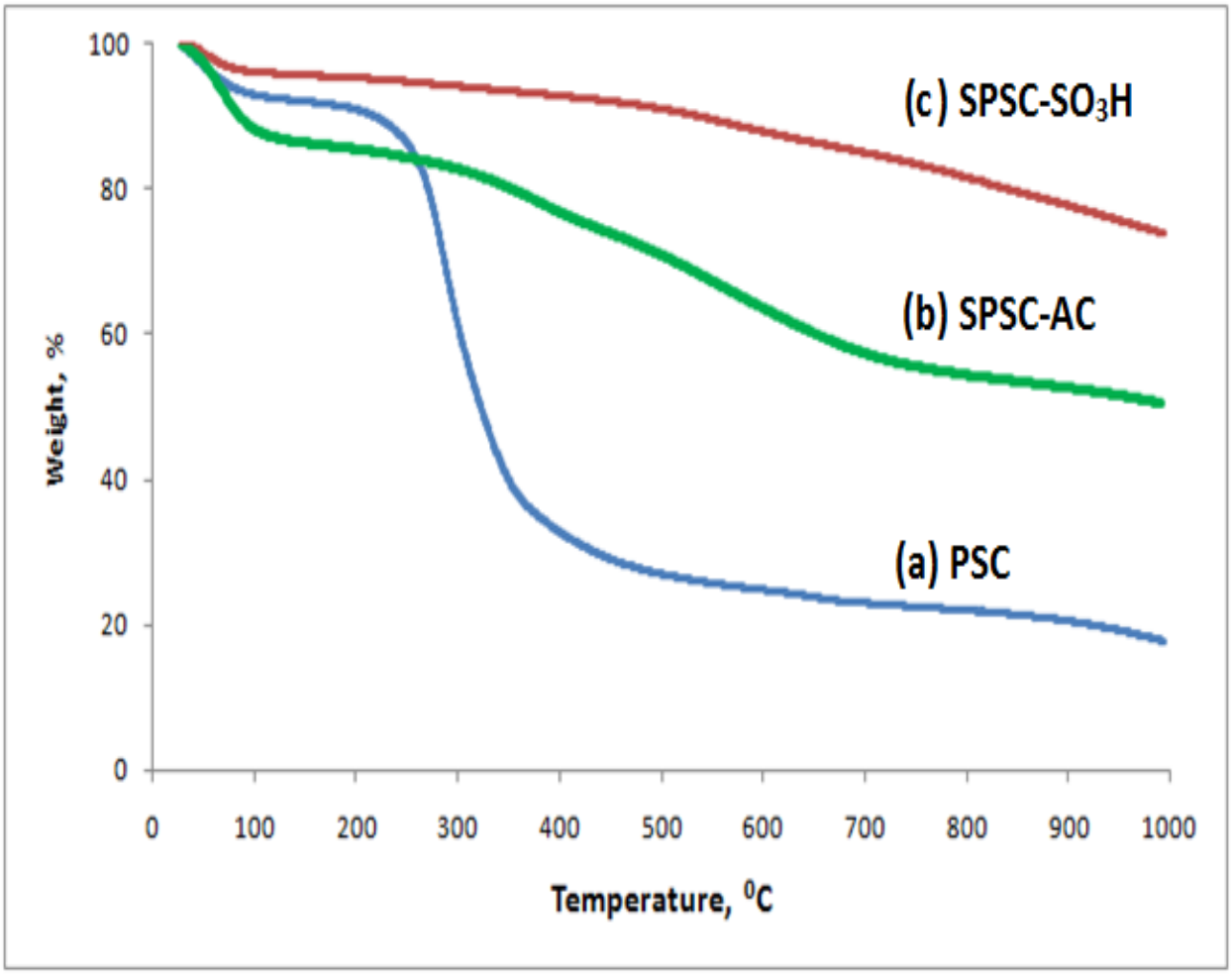
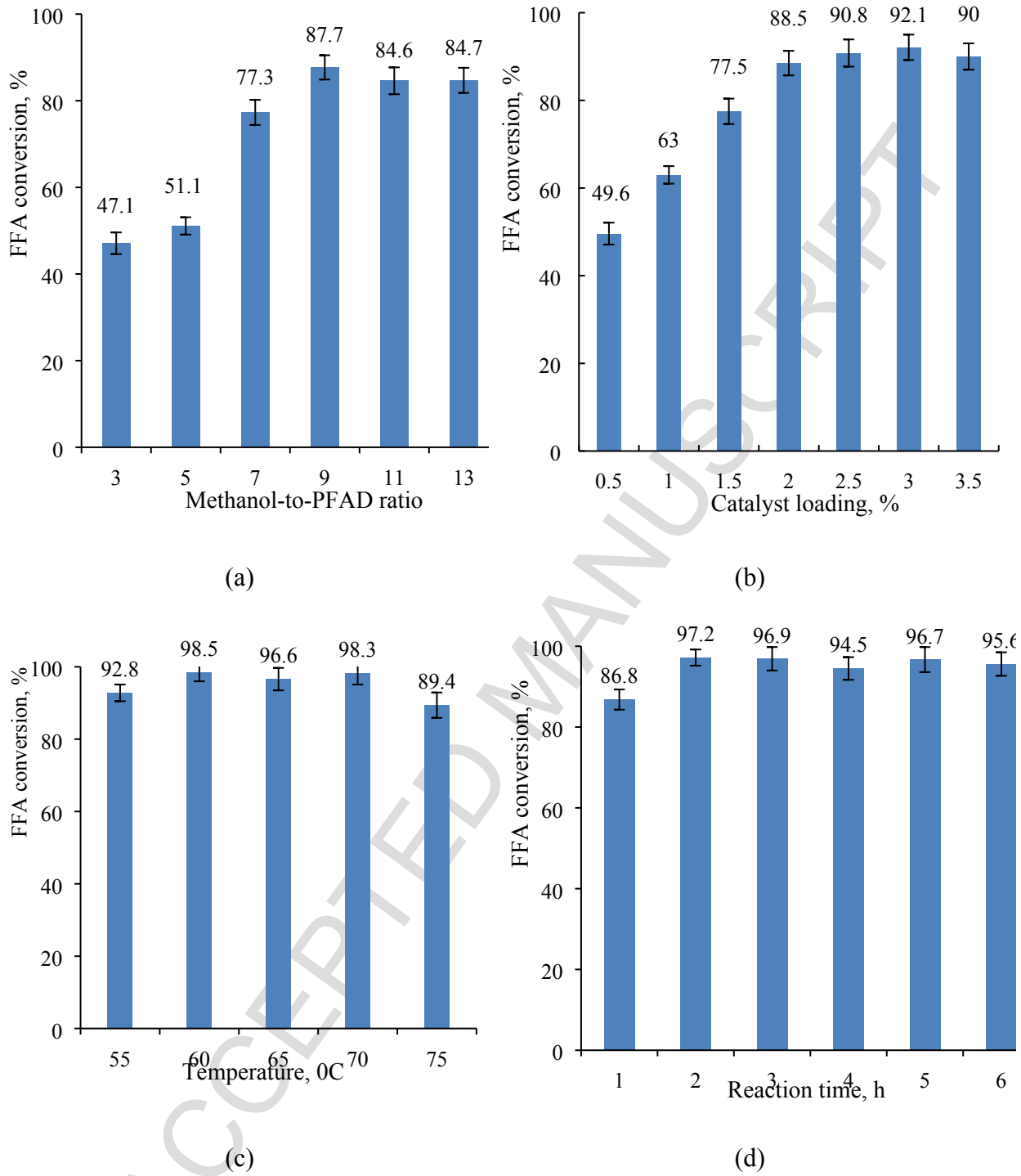


Fig. 5



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615 **Fig. 6**

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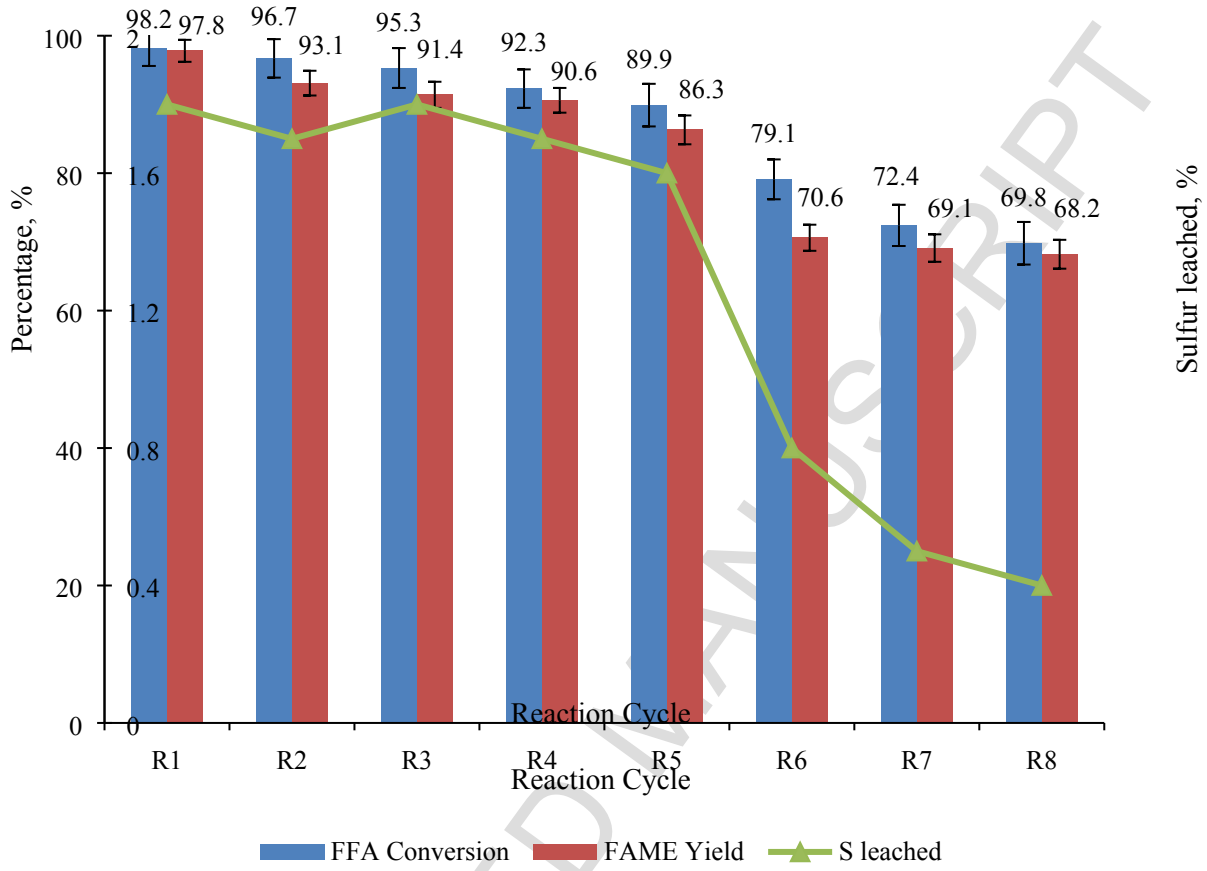
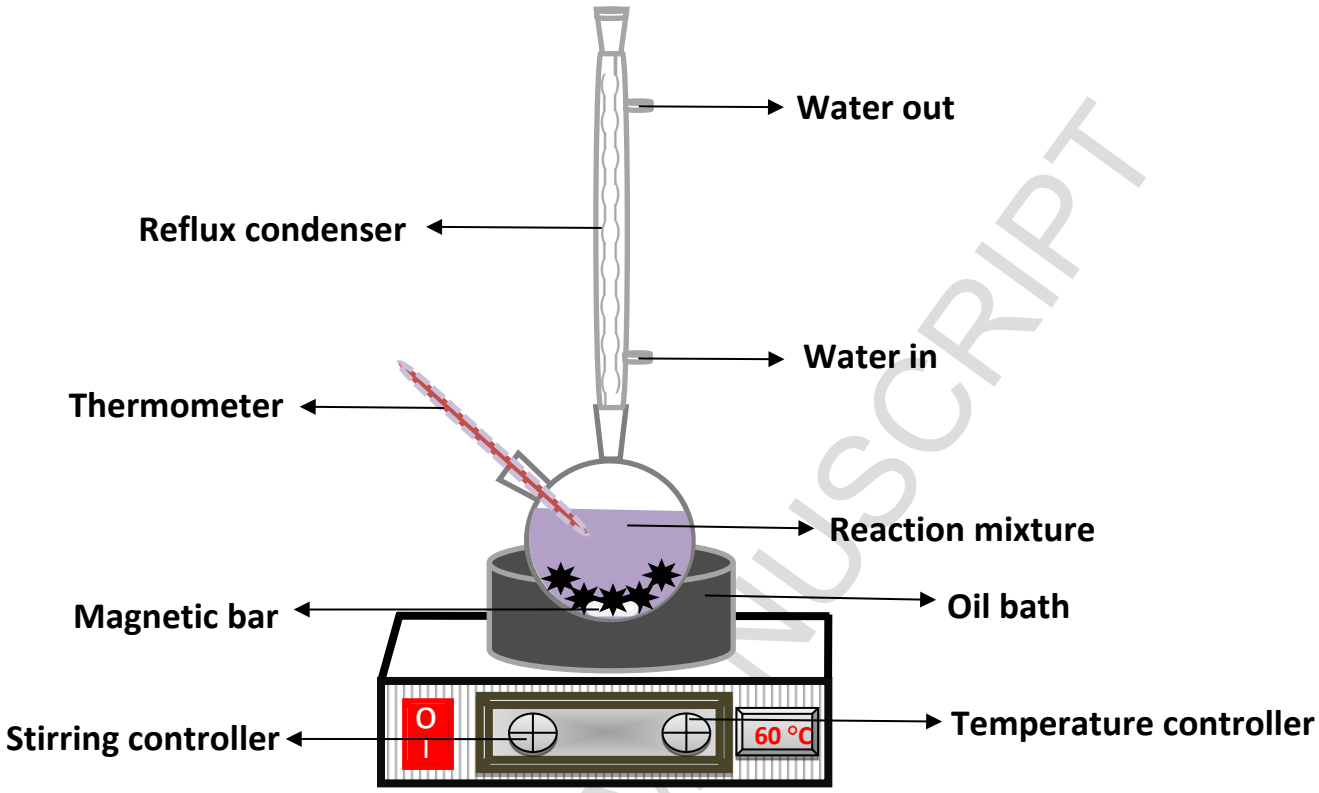


Fig. 7



Scheme 1

664 **Table 1**. BET analysis of palm seed cake (PSC), palm seed cake- activated carbon (PSC-AC),
665 soaked palm seed cake – activated carbon (SPSC-AC) and sulfoonated soaked palm seed cake
666 (SPSC-SO_3H) catalyst
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Sample	Specific surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Pore diameter (nm)
PSC	89.41	0.11	0.32
PSC-AC	107.05	0.15	0.95
SPSC-AC	658.34	1.18	5.09
SPSC-SO_3H	483.07	0.84	4.13

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687 **Table 2**. Elemental and acid site density analysis of palm seed cake (PSC), soaked palm seed cake
688 – activated carbon (SPSC-AC) and sulphonated soaked palm seed cake (SPSC-SO_3H) catalyst
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Sample	C		O		S		Total acidity (mmol g^{-1})
	[a]Weight (g)	[b]Atomicity	[a]Weight (g)	[b]Atomicity	[a]Weight (g)	[b]Atomicity	
PSC	52.11	59.18	47.89	40.82	-	-	5.44
SPSC-AC	86.31	89.36	13.69	10.64	-	-	8.35
SPSC-SO_3H	66.65	73.65	30.19	25.02	3.16	1.31	12.08

690 [a]Measured by using EDS analysis
691 [b]Measured by using CHNS elementally analysis
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