

Activity of Carbon-Based Solid Acid Catalyst Derived from Palm Empty Fruit Bunch for Esterification of Palmitic Acid

Indika Thushari and Sandhya Babel*

Sirindhorn International Institute of Technology, Thammasat University, Pathum Thani 12120, Thailand

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* Corresponding author:

E-mail: sandhya@siit.tu.ac.th

ABSTRACT

The activity of a heterogeneous solid acid catalyst derived from palm empty fruit bunch, synthesized through the direct in-situ H_2SO_4 impregnation was investigated for the esterification of palmitic acid. The prepared catalyst was characterized by scanning electron microscopy (SEM), Nitrogen adsorption and desorption isotherm, Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), and thermogravimetric analysis (TGA). It was also analyzed for acid density and elemental composition. The results revealed that the esterification efficiency increases with increasing reaction time, temperature, and methanol loading up to an optimum value. The catalyst showed an excellent activity resulting in >98% esterification efficiency using 5 wt% catalyst, a 6:1 methanol to palmitic acid molar ratio, at 80°C for 5 h in an open reflux reactor, for the reaction conditions. The catalyst was employed in three consecutive runs without considerable loss of the activity. The obtained high catalytic activity is attributed to the high acid density due to the presence of strong (SO_3H) and weak ($COOH$, OH) acid sites in the hydrophobic carbon structure.

1. INTRODUCTION

Biodiesel can be produced from the transesterification of triglycerides and esterification of fatty acids with alcohols using acid or alkaline catalysts. However, alkaline catalyzed transesterification is challenging in the presence of a high free fatty acids (FFA) content in feedstocks. An alkaline catalyst produces soap with FFA, making the biodiesel production more complex and expensive (Su and Guo, 2014). Therefore, it is necessary to neutralize the FFA in the acidic feedstocks for conventional biodiesel production.

Homogeneous acid catalysts have been widely used in acid catalyzed reactions, such as the esterification or pre-treatment of acidic feedstocks. However, difficulty in catalyst separation, recycling, and waste treatment has encouraged researchers to use solid acid catalysts (SACs) for the esterification or pre-treatment of acidic feedstocks (Su and Guo, 2014). Commercially available SACs, such as sulfated metal oxides (Zhang et al., 2017), ion exchange resin (Fu et al., 2015), and heteropolyacid (Han et al., 2016) are favorable for biodiesel production. However, the activity of these SACs is very low compared to the homogeneous acid catalysts. In addition, low stability, high cost, and the possible environmental damage make their use less

popular in biodiesel production (Dehkhoda, 2010). Therefore, the demand for the development of novel, economical, and sustainable SACs with high activity and stability is increasing. Carbon-based SACs have gained much interest in esterification due to various advantages; they can eliminate further washing and neutralization steps while increasing the catalyst reusability (Nakajima et al., 2007; Su and Guo, 2014). Also, they can be derived from various types of low-cost carbon precursors, such as agricultural and industrial wastes (Bennett et al., 2016; Fu et al., 2013; Konwar et al., 2014; Ngaosuwan et al., 2016; Savaliya and Dholakiya, 2015) via economical and sustainable methods. Various types of carbon-based SACs have been developed and successfully employed for esterification. A coffee residue based SAC was used by Ngaosuwan et al. (2016) for the esterification of caprylic acid. Bamboo (Zhou et al., 2016), banana peel (Liu et al., 2015), rice husk (Zeng et al., 2016) derived SACs were used for the esterification of oleic acid. Thailand produces an extensive amount of agricultural waste biomass (Visvanathan and Chiemchaisri, 2008). Therefore, this study attempts to develop a promising SAC from the abundant agricultural waste biomass in Thailand for the esterification of palmitic acid.

Palm empty fruit bunch (PEFB), which is an easily obtainable agricultural waste biomass in Thailand, was used for the preparation of a SAC via a simple and economical method (Thushari and Babel, 2018). In this study, the activity of the prepared PEFB-based SAC was investigated for the esterification of palmitic acid. The effects of reaction time, temperature, and methanol loading on the esterification efficiency and the reusability of the catalyst were explored.

2. METHODOLOGY

2.1 Materials

All chemicals were of analytical grade. Ethanol (C_2H_6O , Wako), methanol (CH_3OH , Wako), palmitic acid ($CH_3(CH_2)_{14}COOH$, Wako), potassium hydroxide (KOH, Wako), and sulfuric acid (H_2SO_4 , Wako) were used as received.

2.2 Preparation of PEFB-DS- SO_3H catalyst

The PEFB-based SAC was prepared by the direct in-situ concentrated H_2SO_4 acid impregnation method, as reported in Thushari and Babel (2018). In a typical procedure, the ground PEFB powder (average particle size <500 microns) was dried in an oven (FED 115, BINDER) at $110^\circ C$ for 5 h. The oven dried PEFB powder (10 g) and concentrated H_2SO_4 acid (50 g) were then mixed in a flat glass beaker on a hot plate (C-MAG HS7, IKA) at $100^\circ C$ for 1 h to facilitate in-situ incomplete sulfuric carbonization. After 24 h following the sulfuric carbonization, the reaction mixture was diluted, filtered, and repeatedly washed with hot distilled water using vacuum filtration until the pH of the filtrate was neutral. Then, the obtained black residue was dried in an oven at $120^\circ C$ for 2 h and denoted as PEFB-DS- SO_3H . The prepared PEFB-DS- SO_3H catalyst was stored in an airtight container before using for esterification.

2.3 Characterization of PEFB-DS- SO_3H catalyst

Properties of the prepared catalyst were investigated using the standard methods, as reported in Thushari and Babel (2018). The total acid density was measured by standard acid-base back titration, following Dehkhoda (2010). The elemental composition of the catalyst was determined by energy dispersive X-ray spectroscopy (EDS) (S-3400 N, HITACHI) using EDAX Genesis software and a CHNS/O analyzer (628 series, Leco

Corporation). N_2 adsorption and desorption isotherm data at $-196^\circ C$ (BELSORP miniII, Japan) were used to investigate the surface area, pore volume, and pore size distribution of the catalyst. Surface morphology of the PEFB-DS- SO_3H catalyst was examined by a scanning electron microscope (SEM) (VE-8800, Keyence, Japan). Fourier transform infrared spectroscopy (FT-IR) (610, Jasco) with attenuated total reflectance technique was used to investigate the functional groups present on the surface of the catalyst. The chemical states of the functional groups were analyzed by X-ray photoelectron spectroscopy (XPS) (PHI5000 Versa Probe II @ Ulvac- PHI Inc, Japan) with Al Ka radiation. The thermal stability of the catalyst was analyzed by thermogravimetric analysis (TGA/DSC3 +HT/1600/219) under an N_2 flow (25 mL/min) at $25-900^\circ C$.

2.4 Evaluation of catalytic activity

The activity of the PEFB-DS- SO_3H was investigated for the esterification of palmitic acid with methanol, in a 250-mL round bottom flask equipped with a reflux condenser and a thermometer on a hot plate with a magnetic stirrer. Palmitic acid (10 g), PEFB-DS- SO_3H catalyst (0.5 g), and methanol were loaded into the reactor. The esterification efficiency was investigated using a different reaction temperature (40, 60, and $80^\circ C$), time (1, 2, 3, 4, and 5 h), and methanol:palmitic acid molar ratio (2:1, 4:1, 6:1, and 8:1). Upon completion of the reaction after the desired time, used catalysts were separated for reuse by vacuum filtration using a suction filtration kit, washed with ethanol, and oven dried for 2 h at $105^\circ C$. Excess methanol in the final product was removed by evaporation at $80^\circ C$ in a water bath. All of the experiments were conducted in duplicate, and the average values were reported and discussed.

The esterification efficiency of the catalysts was determined using the following equation:

$$\text{Esterification efficiency (\%)} = \frac{(AV_0 - AV_1)}{AV_1} \times 100 \quad (1)$$

Where, AV_0 and AV_1 are the acid values (mg KOH/g) of the feedstock and the final product, respectively.

The acid value of the reaction medium was measured by titration following the Guabiao (GB) standard test method (The National Standard of the

People's Republic of China, 2005). In a typical procedure, about 0.5 g of the sample was vigorously dissolved in 50 mL of ethanol by heating the mixture for 10 min. Then, the resultant mixture was titrated against 0.1 M KOH solution.

3. RESULTS AND DISCUSSION

3.1 Characterization of PEFB-DS-SO₃H catalyst

As found from the CHNS/O analyzer, the elemental analysis reveals the presence of carbon, hydrogen, nitrogen, oxygen, and sulfur in the PEFB-

DS-SO₃H catalyst (Table 1). Results showed that the elemental composition changes in the catalyst, compared to the original PEFB. Carbonization and activation of biomass in the presence of concentrated H₂SO₄ increase the carbon and sulfur content of the catalyst. Dehydration and de-oxygenation during carbonization decrease the hydrogen and oxygen contents of the catalyst. Similar phenomena are reported by Zhou et al. (2016) and Malins et al. (2016) during the preparation of a carbon-based SAC using bamboo and cellulose.

Table 1. Elemental composition of PEFB-DS-SO₃H catalyst

| | C (wt%) | H (wt%) | N (wt%) | O (wt%) | S (wt%) | O:C |
|---------------------------|---------|---------|---------|---------|---------|------|
| Raw PEFB | 44.18 | 5.08 | 0.58 | 39.75 | 0.21 | 0.89 |
| PEFB-DS-SO ₃ H | 58.20 | 2.23 | 0.37 | 31.02 | 1.10 | 0.53 |

The total acid density of the PEFB-DS-SO₃H catalyst was found to be 5.4 mmol/g (Thushari and Babel, 2018). Three acid groups, SO₃H, COOH, and OH, contributed to the total acid density of the biomass-derived SACs (Nakajima et al., 2007; Su and Guo, 2014). The presence of a large amount of sulfonic acid groups is important as they are directly involved in catalyzing the esterification. As mentioned by Hara (2010), the hydrophilic COOH and OH groups present in the carbon framework enhance the catalytic activity by acting as the anchoring sites for the reactants. Therefore, the presence of a high density of both strong (SO₃H) and weak (COOH and OH) acid groups promotes the catalytic activity.

Figure 1 shows the FT-IR spectra of raw PEFB, PEFB-DS-SO₃H, and the used catalyst after the first run. The presence of functional groups (on the surface of the catalyst), which are responsible for esterification, was confirmed by FT-IR analysis (Thushari and Babel, 2018). As shown in Figure 1, the strong and broad peak at 3,600-2,800 cm⁻¹ is attributed to the alcoholic or phenolic OH (Coates, 2000) in the raw PEFB, PEFB-DS-SO₃H, and the used catalyst. FT-IR spectra showed that the intensity of the peak decreases with the activation of biomass due to deoxygenation and dehydration. The

decrease of the peak intensity after the first run may be due to the hydration of the catalyst. The peak present at around 1,800-1,500 cm⁻¹ is attributed to the carbonyl/carboxyl region of COOH (Allen et al., 2007). According to Coates (2000), the peak at around 1,700 cm⁻¹ may be assigned to SO₃H (1712 cm⁻¹). As can be seen in Figure 1, this peak is only conspicuous in the catalysts, confirming the presence of SO₃H after the activation. The intensity of the peak at around 1,700 cm⁻¹ remains unchanged after the first run, showing the stability of the active SO₃H groups in the catalyst. The sharp and strong stretching peak at around 1,230-1,120 cm⁻¹ is attributed to the S=O group which is from the sulfonic acid or sulfonate ion or O=S=O symmetric and asymmetric stretching vibrations of SO₃H, which is conspicuous in the catalysts produced after the sulfonation of incompletely carbonized biomass (Fu et al., 2012).

The XPS of PEFB-DS-SO₃H clearly reveals the peaks corresponding to the S2p, C1s, and O1s at 168 eV, 284 eV, and 530 eV binding energy, respectively (Russo et al., 2014; Thushari and Babel, 2018), confirming the presence of chemically bound SO₃H, COOH, and OH functional groups in line with the FT-IR results.

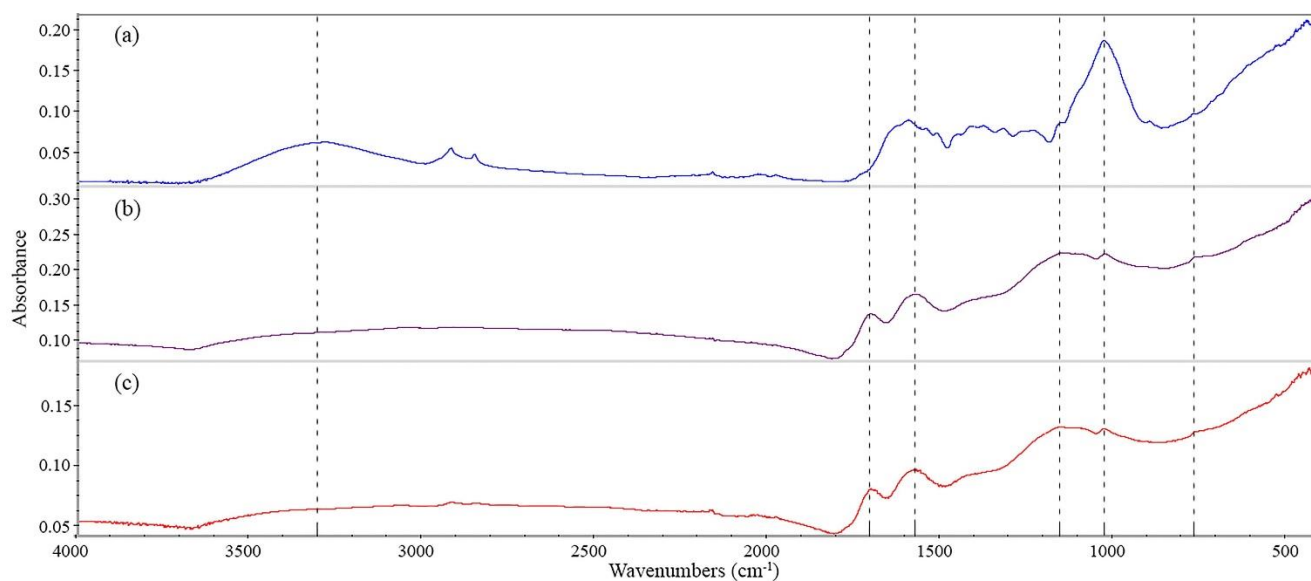


Figure 1. FT-IR spectrum of (a) Raw PEFB, (b) PEFB-DS-SO₃H catalyst, and (c) used catalyst after the 1st run (remark: (a) and (b) were taken from Thushari and Babel (2018))

Table 2 shows the surface area, pore volume, and diameter of the fresh catalyst and used catalyst after the third run. Results showed that the surface area of the catalyst decreases from 5.5 to 3.0 m²/g after the third run. The relatively small surface area

and pore volume of PEFB-DS-SO₃H catalysts may be due to the accumulation of SO₃H groups. Accumulation of products, by-products, and intermediates in the pores decreases the surface area and volume in the reused catalysts.

Table 2. Microstructural properties of PEFB-DS-SO₃H

| | Surface area (m ² /g) | Mean pore volume (cm ³ /g) | Pore diameter (nm) |
|---|----------------------------------|---------------------------------------|--------------------|
| PEFB-DS-SO ₃ H catalyst | 5.5 | 0.13 | 17.0 |
| Used catalyst (after 3 rd run) | 3.0 | 0.07 | 17.5 |

The nitrogen adsorption and desorption isotherms of the catalyst were found to be type III and/or type IV. This indicates the presence of nonporous and mesoporous phases of the catalyst, as confirmed by SEM (Brunauer et al., 1938; Thushari and Babel, 2018).

The TGA spectrum of PEFB-DS-SO₃H is shown in Figure 2. The low-temperature weight loss is below 200°C and the high-temperature weight loss is from 200 to 900°C. The small weight loss in the low-temperature range is due to the evaporation of absorbed water from the catalyst (Fu et al., 2012). Since the thermal degradation of the catalyst starts after 200°C, the reaction temperature should be below 200°C to achieve a maximum catalytic activity.

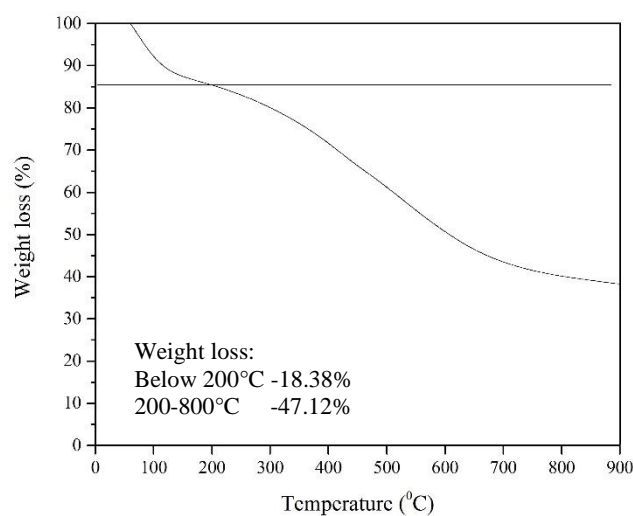


Figure 2. TGA of PEFB-DS-SO₃H catalyst

3.2 Evaluation of catalytic activity

The activity of the PEFB-DS-SO₃H catalyst for esterification is shown by a decrease in the acid

value of the palmitic acid feedstock. The reaction scheme of the esterification of palmitic acid with methanol is depicted in Figure 3.

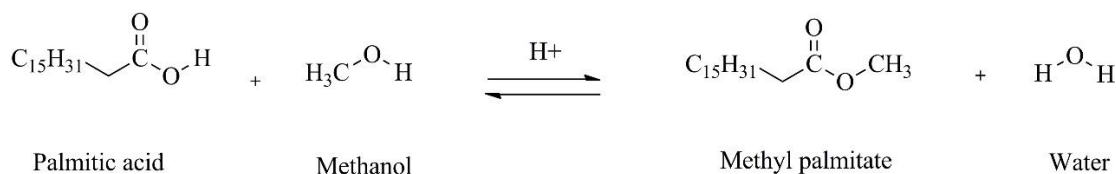


Figure 3. Acid-catalyzed esterification of palmitic acid

3.2.1 Effect of reaction time and temperature on catalytic activity

The reaction medium for the esterification of palmitic acid with methanol using PEFB-DS-SO₃H is a heterogeneous system. It is necessary to have sufficient time to complete the esterification reaction. Therefore, the effect of reaction time on esterification efficiency was investigated. Since the esterification of palmitic acid is an endothermic reaction, high temperatures shift the reaction equilibrium towards methyl palmitate formation. Therefore, the effect of temperature on the palmitic acid esterification efficiency was investigated. The results are shown in Figure 4. It is found that the catalytic activity increases with increasing reaction time and temperature up to an optimum value. The highest esterification efficiency of 98.5% was obtained using 5 wt% of catalyst, a 6:1 methanol to palmitic acid molar ratio, at 80°C after 5 h. Among the three selected reaction temperatures used in this study, more than 70% esterification efficiency is obtained at both 60°C and 80°C after 3 h. An increase of reaction temperature increases the solubility of palmitic acid in methanol and promotes the rapid diffusion of catalyst and reactants in the liquid mixture. In addition, an increase of molecular motion due to the increased temperature increases the mass transfer, increasing the catalytic activity (Zhou et al., 2016). Also, methanol starts to boil and the methanol vapor can effectively contact with the palmitic acid, providing higher esterification efficiency at 80°C. However, Saravanan et al. (2016) reported a 90% yield of methyl palmitate at 60°C while Zhou et al. (2016) reported 98.4% oleic acid esterification efficiency at 90°C.

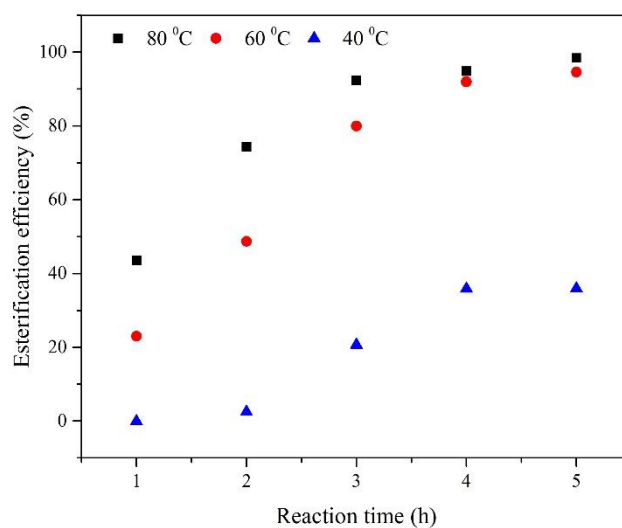


Figure 4. Effect of reaction time and temperature on esterification efficiency of palmitic acid with 5 wt% PEFB-DS-SO₃H and 6:1 methanol to palmitic acid molar ratio.

3.2.2 Effect of methanol loading on catalytic activity

The effect of methanol loading on the esterification of palmitic acid is shown in Figure 5. The esterification reaction stoichiometrically requires a 1:1 methanol:fatty acid molar ratio. It is found that the esterification efficiency increases with increasing methanol:palmitic acid molar ratio up to an optimum value. Esterification is a reversible reaction, and thus, it requires more methanol than the theoretical amount to shift the reaction equilibrium towards product formation. Nevertheless, the presence of excess methanol can deactivate the catalyst by inundating the active acid sites (Saravanan et al., 2016), decreasing the esterification efficiency.

However, a further increase of the methanol: palmitic acid molar ratio beyond 6:1 did not significantly affect the esterification efficiency. Saravanan et al. (2016), reported an increase of the methyl palmitate yield from 32% to 60% when increasing the methanol:palmitic acid molar ratio from 5:1 to 20:1 using 1 wt% of sulfated zirconia catalyst, at 60°C for 7 h.

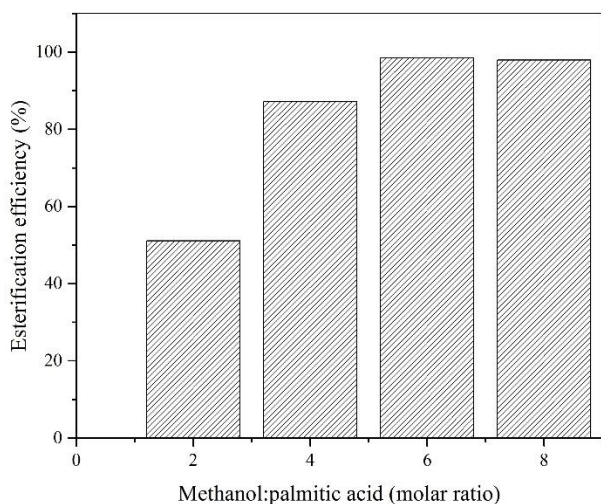


Figure 5. Effect of methanol loading on esterification efficiency of palmitic acid using 5 wt% PEFB-DS-SO₃H at 80°C for 5 h

3.2.3 Reusability of PEFB-DS-SO₃H catalyst

Reusability is important in measuring the performance of a SAC. The used catalyst after each run was easily recovered by vacuum filtration. Results showed that the esterification efficiency of the PEFB-DS-SO₃H catalyst decreases from 98.5% to 90.8% after the third run (Figure 6). This decrease of esterification efficiency during reuse is due to various reasons. Deactivation of catalyst active sites, such as SO₃H, due to the accumulated water and methanol decreases the esterification efficiency (Fraile et al., 2012). Deposition of reactants, intermediates, and products on the surface and the pores of the catalyst also decreases the activity due to the hindrance of active sites (Ngaosuwan et al., 2016).

This study reveals the capability of using PEFB as an abundant lignocellulose waste biomass for SAC preparation through a simple and one-step protocol for the esterification of palmitic acids. Table 3 shows that the esterification efficiency of a SAC varies according to the type and amount of catalyst used. This variation is also due to the other conditions, such as reaction temperature, time,

methanol loading, and the reactor type. However, as can be seen in Table 3, it can be concluded that the PEFB-DS-SO₃H catalyst shows appreciable activity, compared to the reported carbon-based SACs in the literature for esterification. Since the PEFB-DS-SO₃H can be reused, it is an environmentally friendly catalyst and is a promising alternative for a homogeneous acid catalyst.

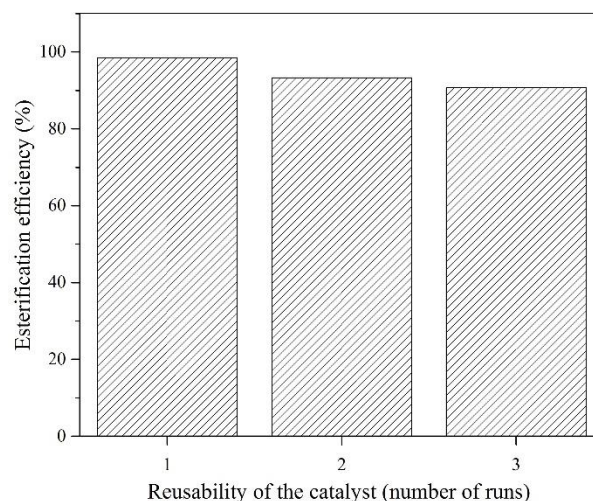


Figure 6. Reusability of PEFB-DS-SO₃H for esterification of palmitic acid using 5 wt% catalyst and 6:1 methanol to oil molar ratio at 80°C for 5 h

4 Conclusions

The PEFB derived SAC, prepared through the one-step concentrated sulfuric acid impregnation, was successfully used for the esterification of palmitic acid with methanol. XPS and FT-IR analysis confirmed the activation of the PEFB-DS-SO₃H catalyst. As found from TGA, the catalyst can be employed at temperatures of up to 200°C without decomposition of the active functional groups. The high acid density, despite a relatively small surface area, may be attributed to the obtained high catalytic activity. A maximum esterification efficiency of 98.5% was achieved using 5 wt% catalyst, a 6:1 methanol to palmitic acid molar ratio, at 80°C for 5 h, for the reaction conditions. The catalyst had good stability and was used for three consecutive runs without considerable loss of the activity. In addition to the high activity, facile and economical synthesis using waste biomass makes the PEFB-DS-SO₃H a promising catalyst for esterification. However, a further improvement of the porous structure and the stability of the functional groups will increase the activity and the reusability of the catalyst.

Table 3. Comparison on usage of carbon-based SAC for esterification

| Catalyst | Catalyst preparation | Catalyst characterization | | Catalytic activity | | Reference |
|----------------------------|--|--|--|---|---------------------------------------|-------------------------------|
| | | Total acid density (mmol/g)/sulfonic acid density (mmol/g or wt%)/surface area (m ² /g)/pore size (nm)/pore volume (cm ³) | | Feedstock/methanol loading (molar ratio)/catalyst loading (wt%)/reaction temperature (°C)/reaction time (h) | Conversion or yield (%) / reusability | |
| PEFB based SAC | Simultaneous carbonization and sulfonation: Conc. H ₂ SO ₄ (1:5 wt%), 100°C, 1 h | 5.4/1.1/5.5/17/0.13 | | Palmitic acid/6:1/5/80/5 in a reflux reactor | 98.5/2 cycles | This study |
| Glycerol based SAC | Simultaneous carbonization and sulfonation: Conc. H ₂ SO ₄ (1:4 wt%), 180°C, 20 min | 1.6/-/1.0 /-/- | | Palmitic acid/25 mL for 2.56 g/10/65/4 in a reflux reactor | 99%/8 cycles | Devi et al. (2009) |
| Banana peel derived SAC | Activation: Fragments of banana peel (1.2 kg) submerged in an aqueous FeCl ₃ (1.8 L, 80°C, 1 week) Carbonization: 650°C, 3 h under N ₂ environment | 1.43-2.68/0.9-4.8%/156-1097/6.1-11.4/0.17-0.74 | | Oleic acid/150 mg: 5 g/150 mg/80/2 in a reflux reactor | 63-94%/4 cycles | Liu et al. (2015) |
| Bagasse based SAC | Simultaneous carbonization and sulfonation: Conc. H ₂ SO ₄ (5 g:30 mL), 180°C, 10 h | 1.9/-/1.27/-/0.003 | | Soap stock oil/15:1/5/65/11 in a reflux reactor | 97.2%/3 cycles | Savaliya and Dholakiya (2015) |
| Rice husk derived SAC | Activation: calcined for 450°C, 15 h under N ₂ environment (leaching with NaOH, 100°C, 5 h) Sulfonation: Conc. H ₂ SO ₄ (98%), 150°C, 12 h under N ₂ environment | 5.25/-/1233/38.9/0.74 | | Oleic acid/5:1/0.015 g catalyst (20 mmol oleic acid)/80/9 in a reflux reactor | 91%/10 cycles | Zeng et al. (2016) |
| Coffee residue derived SAC | Activation: mixed with ZnCl ₂ (1:3 wt/wt) at 110°C for 12 h Carbonization: 600°C, 4 h under CO ₂ atmosphere Sulfonation: Conc. H ₂ SO ₄ (1 g: 20 mL), 200°C for 18 h | 0.99/0.45/1091/3.5/3.5 | | Caprylic acid/3:1/5/60/4 in an autoclave reactor | 71.4%/4 cycles (very low reusability) | Ngaosuwan et al. (2016) |

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