

Effect of Sulfonating Agent on Esterification Reaction Using Aerogel Carbon Based Support Material

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Abstract. The effect of sulfonic agents on the performance of solid acid catalysts in esterification reactions of long-chain fatty acids has been studied. Herein, sulfonated activated carbon with sulfanilic acid (SAC-SA) and sulfuric acid (SAC-SO₄) as a sulfonic agent were prepared and used for esterification reaction to convert long-chain fatty acids into methyl esters within 5 h at 65°C. The obtained SAC-SA has a higher surface area than SAC-SO₄ of 1301.981 and 1182.096 m²/g, respectively. When SAC-SO₄ and SAC-SA catalysts were applied to the esterification reaction, the FAME product conversion results were 74.47 and 46.98 %, respectively. The physical property of SAC-SO₄ has more macropores size distribution than mesopores size based on the BJH method. Large pore size on the catalyst will support the diffusion of large organic molecules to improve catalytic ability. The pore size determines the performance of solid acid catalysts, especially in long-chain fatty acid reactants for biodiesel production.

Introduction

Biodiesel is a monoalkyl ester composed of lipids (C₁₂, C₁₄, C₁₆, C₁₈, and C₂₂) such as vegetable oil, waste cooking oil, microalgae, and animal fat [1]. The cetane number, energy content, viscosity, and phase change of biodiesel are like those of fossil diesel so that biodiesel can be mixed with a specific composition with petroleum (diesel) to become a biofuel that can be used as an alternative fuel for diesel engines. Biodiesel is produced through a transesterification reaction between triglycerides contained in fats or oils and alcohol. Oil as biodiesel feedstock with an FFA content of more than 5% will react with base catalysts in the transesterification reaction, causing a saponification reaction, so it is necessary to carry out an esterification reaction to reduce the FFA content of the raw material [2], [3]. Thus, an esterification reaction is necessary to reduce the FFA content below 5%w/w as a pretreatment step of the transesterification process. In esterification reactions, homogeneous catalysts such as phosphoric acid (H₃PO₄) and sulfuric acid (H₂SO₄) are often used. However, homogeneous catalysts have drawbacks, such as toxic and environmentally harmful properties, as well as corrosion of metal industrial equipment. They are also difficult to recycle because they have the same physical form as the products and reactants [4].

Previous research has been conducted on using support materials in heterogeneous catalysts to improve the stability of the catalyst structure and expand the surface area through high porosity. Some materials that are commonly used as catalyst supports are Al₂O₃, ZrO₂, zeolite, and biochar [5]. Recently, biochar has been the focus of research in heterogeneous catalysis. Biochar has advantages in terms of easy availability from biomass waste at low cost, large surface area, controllable pore size, and good stability [6]. For acid catalysis, under severe reaction conditions, SO₃H groups can be successfully grafted on biochar by direct sulfonation methods, such as the direct sulfonation of H₂SO₄ and -SO₃ [4], [7], [8]. Previous research by Fauziyah et al. (2020) reported the synthesis of carbon aerogel-based heterogeneous acid catalyst derived from coir fiber through the carbonization method

and continued sulfonation with sulfuric acid as a sulfonic agent and catalytic activity test through the esterification of acetic acid with ethanol. This catalyst can provide an 81-83% esterification conversion with a molar ratio of ethanol to acetic acid of 2:1, adding 1%wt heterogeneous acid catalyst, esterification temperature of 80°C, and esterification time for 3 hours [4]. However, the biochar-based sulfonic acidic catalyst can not have hydrophobicity due to the hydrophilicity of SO₃H.

On the other hand, esterification reactions for biodiesel production produce by-products in the form of water; the water will cover with the active side of the catalyst, resulting in poor catalytic activity. In addition, hydrophobic and non-polar reactants will find it challenging to approach the hydrophilic surface to interact with the active sites of the catalyst and consequently decrease the catalytic activity. [9]. Therefore, solid catalysts with strong hydrophobicity and acidity are exciting topics to be researched for enhancing catalytic activity in esterification or transesterification reactions [10]. Recently, sulfonation with 4-benzenediazoniumsulfonate (sulfanilic acid) as the sulfonating agent has more efficient results than its sulfonating agent H₂SO₄ due to the high sulfonation rate and increased catalyst reuse due to the stable C-SO₃H bond due to the benzene structure in sulfanilic acid which causes the hydrophobic properties of the catalyst to increase [11].

Furthermore, sulfonated carbons generated by direct sulfonation are prone to substantial deactivation, with a loss of 30-40% of initial activity, primarily due to SO₃H group leaching, limiting their effectiveness [11]. The present work focused on using coir fiber waste as a raw material for preparing sulfonated hydrophobic carbon aerogels applied as solid acid catalysts in the esterification reaction of long-chain fatty acids. The characteristics of the solid acid catalyst were studied by varying the sulfonating agent used in the sulfonation process. Catalysts with hydrophobic characteristics are expected to increase the conversion of long-chain fatty acid esterification reaction.

Experimental Method

Materials

The materials used in this study were: Coir fiber was collected from a coconut milling facility in Tulungagung, Indonesia. sodium hydroxide (NaOH; 99% p.a.), sulfanilic acid (H₃NC₆H₄SO₃, p.a.), and sodium nitrite (NaNO₂, p.a.), were obtained from Merck. Urea (CON₂H₄) was obtained from PT Petrokimia Gresik Indonesia. 4-tert-Butylaniline ((CH₃)₃C₆H₄NH₂; p.a.), ethanol (C₂H₅OH; 99.9%), and oleic acid (C₁₈H₃₄O₂; 90%) were obtained from Sigma Aldrich. Sulfuric acid (H₂SO₄; 98%, reagent grade) and hydrochloric acid (HCl; 37%, reagent grade) were purchased from Mallinckrodt. Hydrogen peroxide (H₂O₂; 50%) was obtained from PT Peroksida Indonesia Pratama. All chemicals/materials were used as received without further purification.

Catalyst preparation

In the present study, carbon aerogel was used as catalyst support; the preparation of carbon aerogel itself consists of two main steps, the preparation of cellulose aerogel from coir fiber and carbonization. Coir fiber was ground and sieved with a 150-mesh sieve and then digested in 17.5% NaOH at 20 mL/g coir fiber under atmospheric reflux for 2 h. Then the coir pulp was bleached with a solution of 3% H₂O₂ at 20 mL/g pulp at 90°C for 1 h. Two grams of pulp (dry basis) was mixed into a solution containing 4 g urea and 1 g NaOH in 10 mL demineralized water using a stirrer in an ice bath for 30 minutes. The mixture was then refrigerated at -14°C for 24 h to form a gel and continued thawing at room temperature. It was then immersed in ethanol for 24 h for coagulation. The ethanol in the gel was then exchanged with demineralized water and frozen at -20 °C for 24 h prior to freeze-drying. The freeze-drying (FDU-1200, EYELA) was carried out at a temperature of -49°C under a vacuum pressure of 20 Pa for 24 h to obtain the cellulose aerogel. The cellulose aerogel was carbonized by pyrolyzing in a furnace under flowing nitrogen at 100 mL/min. The pyrolysis temperature was initially set at 150 °C for 30 min to remove the moisture content and then increased to 400°C for 30 min to decompose the cellulose compound and evaporate any other volatile matter. The temperature was increased to 700°C and held for 2 h to allow carbonization to occur, increasing the temperature at rate of 10°C min⁻¹. Next, the carbon aerogel was neutralized using 0.5 M HCl

solution. Then the carbon aerogel was crushed and sieved with a 45-mesh sieve. The sulfonation process with two different methods:

Sulfonation method 1

Sulfonic acid was used for sulfonated by immersed carbon aerogel under a nitrogen atmosphere. 1 gram of carbon aerogel was spread in 25 mL of 98% H_2SO_4 , and the resulting mixture was then heated with continuous stirring for 5 hours at 100°C . After cooling to room temperature, the mixture was diluted with demineralized water and filtered, and the sulfonated carbon aerogel product was thoroughly washed with demineralized water to remove any remaining H_2SO_4 . The successful removal of H_2SO_4 was indicated by the absence of white precipitates upon introducing the washing solution to a BaCl_2 solution. The material was subsequently dried in an 80°C oven for 3 hours [4]. The sample of activated carbon aerogel with sulfuric acid will be referred to as SAC- SO_4 .

Sulfonation method 2

4-Benzenediazoniumsulfonate was synthesized by diazotization using sulfanilic acid. Sulfanilic acid (5.2 g, 0.03 mol) was dispersed within a three-necked round-bottom flask containing 300 mL of 1 M HCl aqueous solution. The flask was transferred to an ice water bath, and the temperature was carefully maintained between $3\text{--}5^\circ\text{C}$ while continuously stirring the mixture. Subsequently, a 10% excess of NaNO_2 (33 mL, aqueous solution) was incrementally introduced, resulting in the formation of a clear solution once all the NaNO_2 had been added. Following an additional 1-hour stirring at the same temperature, the ensuing white precipitate of 4-benzenediazoniumsulfonate was separated through filtration. Then, the isolated precipitate was transferred to another three-necked round-bottom flask containing 200 mL of deionized water and 120 mL of ethanol. At a temperature of $3\text{--}5^\circ\text{C}$, 3 g of aerogel carbon was introduced. Subsequently, a 30–32% aqueous solution of H_3PO_2 (100 mL) was added into the mixture. After stirring for 30 minutes, an additional 50 mL of H_3PO_2 aqueous solution was added, and the mixture was allowed to stand for an additional hour with occasional stirring. The resulting sulfonated aerogel carbon was washed with acetone and distilled water before being dried overnight [11]. The sample of activated carbon aerogel with sulfanilic acid will be referred to as SAC-SA.

Catalyst characterization

The density (ρ_b) of the cellulose aerogel and carbon aerogel was determined by dividing the mass of the measured sample by the volume of the measured aerogel. The porosity of the aerogels was calculated by equation :

$$\phi = 1 - \frac{\rho_b}{\rho_t} \quad (1)$$

where ρ_t is the original density of cellulose and carbon particle are 1.528 g/cm and 1.4 g/cm, respectively [12], [13]. Fourier Transform Infra-Red spectra (FTIR spectroscopy; Thermo Scientific Nicolet iS10) recorded in the wavelength range of $400 - 4000 \text{ cm}^{-1}$ were used to identify the formation of $\text{C}=\text{C}$ groups on carbon aerogels and sulfonate functional groups on solid acid catalyst samples. Specific Surface Area (SSA) was measured quantitatively with an N_2 adsorption-desorption instrument (Nova 1200, Quantachrome). Previously, the samples were degassed at 80°C for 5 hours for cellulose aerogel samples and 300°C for 3 hours for carbon aerogel samples before analysis. SSA was calculated using the Bruanuer-Emmet-Teller (BET) method at relative pressure (P/P_0) < 0.3 . The pore size distribution was quantitatively investigated using the Barret-Joyner-Halenda (BJH) method. Sample morphology was analysed by scanning electron microscope (SEM; Hitachi FlexSEM 1000). The hydrophobicity of the samples has been characterised by measuring the contact angle to water droplets on the catalyst surface and dispersed into water.

The acid-base titration method was used to calculate the total acid density 0.05 g of catalyst was mixed with 30 mL of 0.02 M NaOH solution and ultrasonicated for 1 hour to replace hydron with sodion. Then the sample was filtered and titrated with 0.01 M HCl solution with phenolphthalin

indicator. The concentration of OH^- ions remaining from the NaOH solution is identified from the amount of H^+ ions supplied from HCl equivalent to the amount of OH^- ions consumed from the NaOH solution. Thus, acid density is calculated as the amount of OH^- consumed (mmol) divided by the weight of the catalyst sample (grams) [14].

Catalytic test

An evaluation was made of the catalytic performance of the sulfonated carbon aerogel in the esterification of oleic acid with methanol to produce methyl oleat. The esterification was performed in a three neck flask with a volumetric ratio of oleic acid to methanol of 1:9 and catalyst loading of 0.05 g/g of oleic acid. The temperature was set at a constant of 65 °C and the reaction was carried out for 5 hours. The methyl oleate concentration was quantitatively analyzed using gas chromatography (GC Trace 1310; Thermo Scientific). The GC instrument was equipped with a flame ionization detector (FID), and the column of Thermo Scientific TG-5MS type (30m; 0.25 μm ; 330/350°C). Helium gas as a carrier gas constantly flowed at a 1 mL/minute flow rate during analysis with an injector inlet temperature of 240°C with a split ratio of 1:150. Sample analysis began at 100°C, then the temperature was held for 3 minutes, then increased to 240°C with a heating rate of 5 °C/minute. The sample was then cooled to 100°C. The mass of amyl alcohol and methyl oleate was determined using an internal calibration, where the calibration curve was made by dissolving methyl oleate into amyl alcohol at various concentrations.

Result and Discussion

Characterization of carbon aerogels

Carbon aerogel produced from the pyrolysis treatment of cellulose aerogel made from coconut fiber, cellulose aerogel has a light brown color, bulk density, and porosity of 0.1734 g.cm^{-3} and 92.91%, respectively, as show in Fig. 1(a). In comparison, the carbon aerogel produced has bulk density and porosity of 0.1177 g.cm^{-3} and 91.59%, respectively. Pyrolysis treatment produced carbon aerogel with a yield of $30\% \pm 0.0194$. Fig. 1(b) shows the FTIR data of cellulose aerogels and carbon aerogels. Wavenumber peak values on cellulose aerogel show the characteristics of the functional groups of cellulose aerogels; the peak at wavenumber 3330 cm^{-1} shows the O-H stretch functional group. The group comes from intramolecular hydroxyl cellulose. The wavenumber 2891 cm^{-1} peak shows a C-H stretch group derived from C-H in cellulose. The C=O functional group at the peak of wavenumber 1634 cm^{-1} shows an amide group that binds to the carbon atom in the carbonyl group; this comes from urea which acts as a crosslinking. At the peak of wavenumber 1018 cm^{-1} , there is a C-O stretch functional group that overlaps with the C-N group; the C-O functional group can come from the C-OH bond in cellulose, while the C-N functional group comes from the C-N bond in urea. However, wavenumber 3330 cm^{-1} was previously an O-H stretch functional group, strengthening the conjecture that wavenumber 1018 cm^{-1} is a C-O functional group derived from cellulose [12], [15]. Pyrolysis treatment at 700°C significantly impacts the characterization of the resulting carbon aerogel; there are two aromatic groups, C=C and C-H, at wavenumbers 1428 and 878 cm^{-1} , respectively. Pyrolysis treatment on aerogel causes dehydration and dissociation of carbonyls. It triggers the formation of aromatic groups on cellulose aerogel so that O-H and C-H groups on cellulose aerogel are lost due to the heating effect during pyrolysis treatment, and C=O stretch and C-O stretch groups on cellulose aerogel turn into aromatic C=C and C-H groups on carbon aerogel [15].

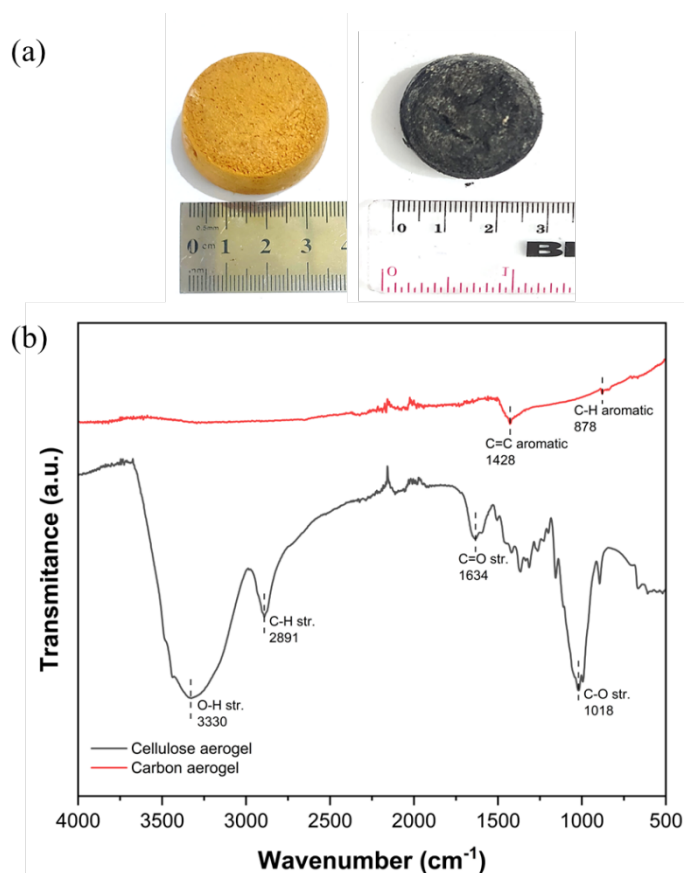


Fig. 1. (a) Picture of cellulose aerogel (left) and aerogel carbon (right); (b) FTIR Spectra of cellulose aerogel and aerogel carbon

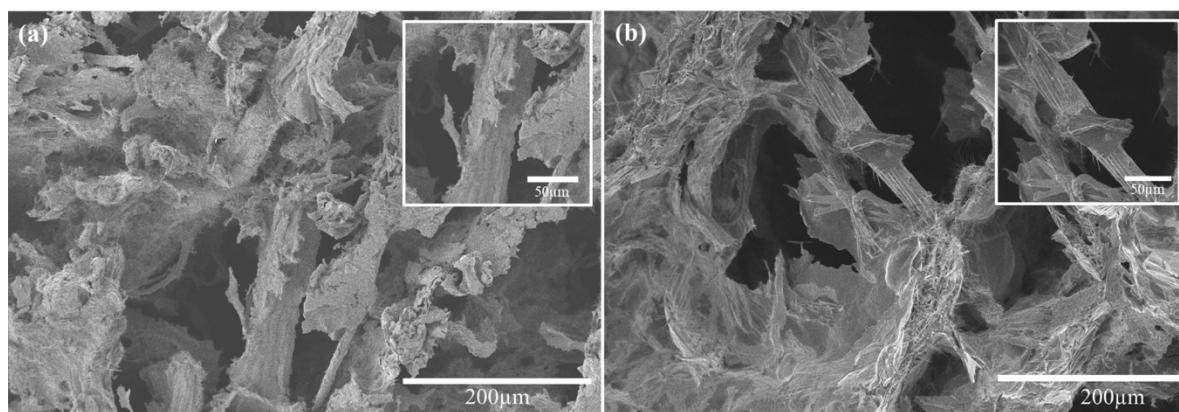


Fig. 2. SEM Image of (a) cellulose aerogel and (b) carbon aerogel

Figure 2 shows cellulose aerogel and carbon aerogel SEM images after pyrolysis. The SEM image results show that the aerogels have fibers in the form of thick lines and open pores. The cavity and pore size produced in carbon aerogels is more significant than in cellulose aerogels due to the pyrolysis treatment. The increase was also proven by the surface area analyzer (SAA) using the BET method. Table 1 shows cellulose aerogel and carbon aerogel BET SSA and pore volume. The surface area of aerogel increased from 430.522 to 1655.099 m²/g; pyrolysis treatment can increase the surface area of carbon aerogel more than three times. The increase in surface area is due to the decomposition of cellulose compounds and the evaporation of volatile matter contained in cellulose aerogels [16]. Pyrolysis treatment also increased total pore volume of aerogel carbon from 0.367 to 1.449 cm³/g, the increase is due to the accelerated release of volatile matter, as depicted in the SEM image (Fig. 2) [17].

Table 1. Specific surface areas of cellulose aerogel and carbon aerogel.

Sample	S_{BET} (m^2/g)	V_{total} (cm^3/g)
Cellulose aerogel	430.522	0.367
Carbon aerogel	1655.099	1.449

Characterization of sulfonated carbon aerogels

From the results of the FTIR analysis shown in Fig. 3, information was obtained about the constituent groups of sulfonated carbon aerogel from the sulfonation method previously described. The vibration peaks near 668 and 1100 cm^{-1} are assigned to the C-S stretching and S-O asymmetric stretching, respectively, of the SO_3H group. The functional groups read from the analysis indicate that the sulfonate process was successful due to the presence of C groups bonding with $-\text{SO}_3\text{H}$ and S groups bonding with O [4], [18]. The characteristics of the carbon aerogel content were indicated by the presence of C=C aromatic, which appeared at 1437 cm^{-1} . Acid density analysis was performed on SAC-SA and SAC-SO4 with acid density values of 2.30 and 3.58 mmol/gr, respectively (Table 2). The two analyses showed that although the peak of the $-\text{SO}_3\text{H}$ group was less sharp in the FTIR analysis, the acid density analysis showed the successful grafting of the SO_3H group on the carbon aerogel. The nature of sulfonate has an effect on the acid density value of sulfonated carbon aerogel catalyst, where sulfuric acid as a strong acid has a higher acid density value compared to SAC-SA which uses sulfanilic acid which is a weak acid, this indicates the use of sulfuric acid as a strong acid that has high reactivity so that it is able to form sulfonate ions ($\text{R}-\text{SO}_3\text{H}$) by replacing hydrogen groups from carbon aerogel better than using sulfanilic acid. It also shows the use of sulfuric acid as an effective sulfonating agent and validates the efficiency of the sulfonation process by producing high acid density values [19].

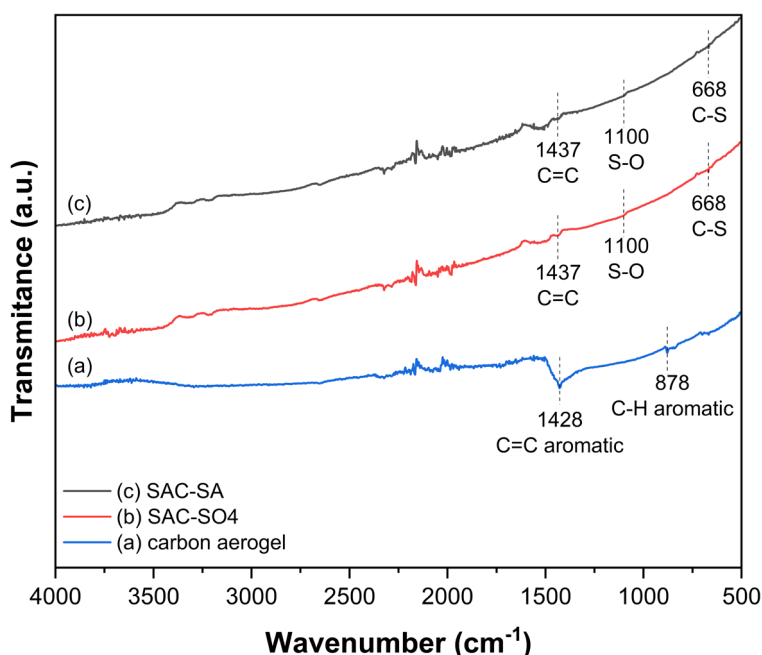


Fig. 3. FTIR spectra of (a) carbon aerogel and sulfonated carbon prepared using (b) sulfuric acid and (c) sulfanilic acid.

Table 2. Specific surface areas of solid acid catalyst with sulfuric acid and sulfanilic agent.

Sample Code	Surface area (m^2/g)	Acid density (mmol/g)
SAC-SA	1301.981	2.30
SAC-SO4	1182.096	3.58

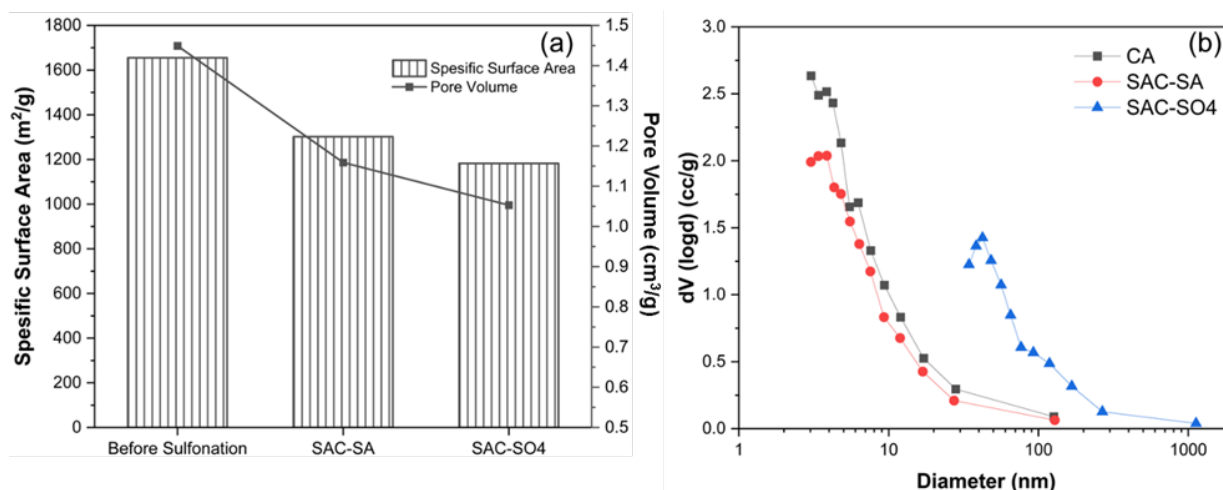


Fig. 4. (a) Effect of sulfonation agent on specific surface area and pore volume; and (b) pore size distribution of carbon aerogel and sulfonated carbon with variation of sulfonate agent.

After the sulfonation process, the BET surface area and pore volume for the solid acid catalyst samples with sulfonic agents sulfanilic acid and sulfuric acid decreased from the values in the initial carbon aerogel from 1655.099 m²/g to 1301.981 and 1182.096 m²/g, 1.449 cm³/g to 1.159 and 1.053 cm³/g, respectively. The decrease in surface area is due to the -SO₃H groups grafted on the cellulose groups in the carbon aerogel, as shown in Fig. 4(a). Fig. 4(b) about pore distribution analysis with the BJH method provides information on the pore size distribution before and after sulfonation. Using sulfanilic acid as a sulfonating agent resulted in the particle size distribution in SAC-SA being more dominantly mesoporous than macroporous, as seen from the graph with diameters less than 50 nm. However, when sulfonation uses sulfuric acid as a sulfonic agent, the particle size of SAC-SO4 is distributed towards macropores, as seen from the diameter produced in BJH analysis, which is more dominant above 50 nm. Apart from being a sulfonating agent, high concentrations of sulfuric acid are corrosive so that they can erode and damage the pore structure of carbon aerogels. Erosion or physical changes to the pore structure can increase overall pore size, including forming larger or combining tiny pores into larger pores [20], [21].

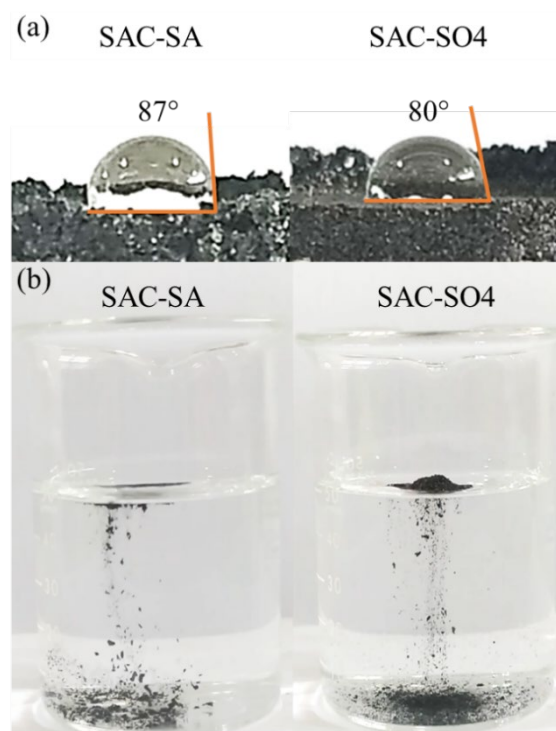


Fig. 5. (a) water contact angles of catalysts and (b) dispersion of prepared catalysts into water.

The hydrophobicity of the catalyst was evaluated by dripping water on the catalyst surface; the result of the contact angle of the two catalysts was still below 90° , which indicated that the catalyst was still hydrophilic, as shown in Fig. 4(a). The catalyst is hydrophobic when water drips on the catalyst and forms a contact angle of more than 90° [4]. A small amount of sulfonated catalyst was dispersed into water to test the hydrophilicity of the catalyst; both catalysts would eventually sink to the bottom of the beaker. This indicates the catalyst hydrophilic characteristics, shown in Fig. 4(b).

Catalyst application in esterification reaction

In our study, the performance of sulfonated carbon catalyst has been tested for the under-reflux esterification reaction between oleic acid and methanol to produce fatty acid methyl ester (FAME) and water. As the result, SAC-SO₄ produced higher conversion than SAC-SA after the esterification reaction for 5 hours under reflux, as seen in Fig. 6. Although SAC-SA contains a non-polar sulfonic group, causing the catalyst to be more hydrophobic than SAC-SO₄ after the contact angle test, SAC-SA still produces a small conversion compared to SAC-SO₄. Pore size is another factor for the catalytic application of mesoporous materials in reactions using solid catalysts, especially when synthesizing biodiesel with large organic molecules. Although the surface area and acid density values of SAC-SO₄ used in the catalytic reaction were lower than those of SAC-SA, the significantly different conversion results between SAC-SO₄ and SAC-SA after the esterification reaction can be attributed to the fact that the SAC-SO₄ catalyst has a material with a micropore size that is more dominant than the mesopore size, Fig. 3(b). The influence of pore size on catalytic performance suggests that factors favoring the diffusion of large organic molecules contribute to improving catalytic properties.

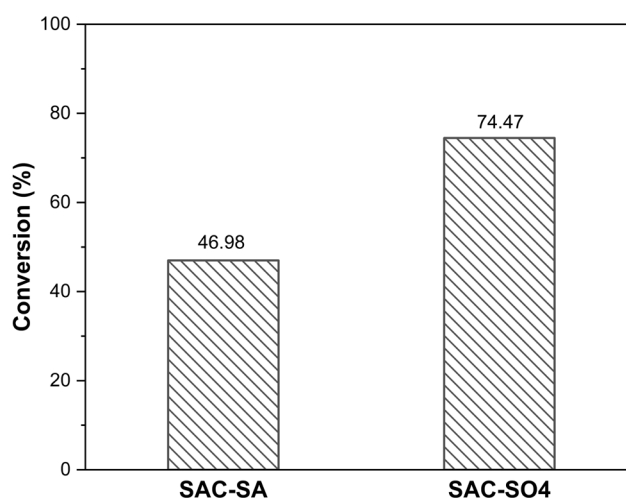


Fig. 6. Catalytic performance of sulfonated carbon aerogel in esterification reaction

Conclusion

Preparation of solid acid catalysts for esterification reaction has been reported in long-chain fatty acids. Heterogeneous solid acid catalysts have been successfully prepared from coir fiber using different sulfonic agents, with sulfanilic acid and sulfuric acid. Surprisingly, although SAC-SA has higher surface area than SAC-SO₄, it was found that the conversion of FAME products was higher when SAC-SO₄ was applied as a catalyst in esterification reaction with the property that SAC-SO₄ has more macropore size distribution than mesopores. The large pore size (macropores) on the catalyst will support the diffusion of large organic molecules to improve catalytic ability.

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