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Simultaneously carbonized and sulfonated mango seed husk as a solid acid catalyst for the esterification of oleic acid with methanol

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SIMULTANEOUSLY CARBONIZED AND SULFONATED MANGO SEED HUSK AS A SOLID ACID CATALYST FOR THE ESTERIFICATION OF OLEIC ACID WITH METHANOL

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Abstract

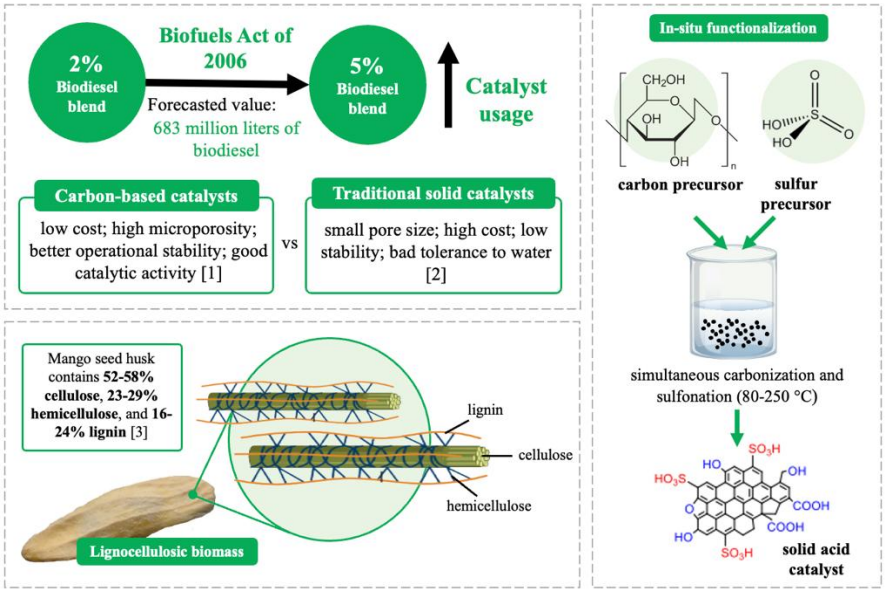
The Philippines has mandated an increase in biodiesel blending from B2 (2%) to B5 (5%) under the Biofuels Act of 2006, increasing the demand for efficient and sustainable catalysts for biodiesel production. Although homogeneous catalysts are widely used, they are economically impractical since it is difficult to recover, expensive, and not reusable. This study investigated mango seed husk (MSH) as a carbon-based precursor for a solid acid catalyst (MSH-SAC) for biodiesel production through heterogeneous esterification. Nine MSH-SAC samples were synthesized using a full factorial design with varying synthesis temperatures (100, 150, and 200 °C) and times (4, 5, and 6 h) through simultaneous sulfonation and carbonization. Catalytic performance was evaluated in the esterification of oleic acid with methanol at 65 °C for 6 h, using a 10:1 methanol-to-oil molar ratio and 8 wt% catalyst loading. Esterification conversions ranged from approximately 61% to 84%. Catalysts synthesized at 150 °C for 4 and 5 h achieved the highest conversion of 84%. The 150 °C, 4 h catalyst retained approximately 78% of its initial activity after four reuse cycles, demonstrating promising stability and reusability.

Keywords: waste valorization, mango seed husk, solid acid catalyst, esterification, simultaneous carbonization and sulfonation, biodiesel production

Statement of Novelty

This study introduces mango seed husk, an underutilized waste, as a precursor for a solid acid catalyst produced through simultaneous carbonization and sulfonation. Unlike conventional approaches that prepare carbon materials and subsequently modify them through separate treatment steps, the proposed process combines these transformations into a single preparation route. The resulting catalyst provides acidic functional groups capable of promoting the esterification of oleic acid with methanol, offering a potential alternative to conventional homogeneous acid catalysts. By converting mango seed husk into a value-added catalytic material, this work links agricultural waste valorization with catalyst development and biodiesel-related applications. The study provides a basis for utilizing locally available biomass residues as low-cost solid acid catalysts.

Graphical abstract



1. Introduction

Most of the energy sources utilized by modern society come from fossil fuels which are not only large contributors to global climate change [1] but are also a non-renewable resource. Hence, renewable energy sources such as biodiesel are being considered as alternatives to non-renewable options [2]. The mandate to raise biodiesel blend in the Philippines from B2 (2 %) to B5 (5 %) as stipulated in the Biofuels Act of 2006 (Republic Act 9367) necessitates an increase in the production of biodiesel to meet the biodiesel growing demand, consequently leading to an increase in the use of catalysts [2].

Esterification is the reaction that produces biodiesel or fatty acid alkyl esters (FAAEs), a family of natural neutral lipids such as methyl (FAMEs) esters, and water via reversible catalyzed chemical reaction of oils with an alcohol, usually short-chain anhydrous alcohols like methanol or ethanol [3], [4]. The former is often utilized for being cost-efficient and physically and chemically advantageous (polar and shortest chain alcohol), such that it quickly reacts with fatty acids and provides better conversions under the same reaction time [5]. The esterification reaction is carried out either via catalytic (homogeneous or heterogeneous) processes such as in **Fig 1**.

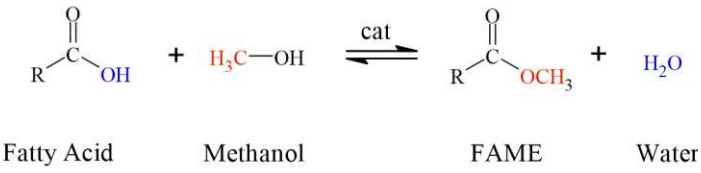


Fig 1 Esterification of a fatty acid with methanol (Rendered using ACD/Chemsketch Freeware)

In the absence of a catalyst, esterification reactions occur slowly and require several days to attain equilibrium. To enhance reaction rate and yield, homogeneous catalysts such as mineral acids (H_2SO_4, HCl, and HF) and strong organic acids (HCOOH) are often utilized. However, homogeneous catalysts are corrosive at higher concentrations and are difficult to separate from the reaction medium due to their miscibility. In addition, they cannot be reused nor regenerated, making them labor-intensive and uneconomical in the long run [6]. These brought the attention to the usage of heterogeneous catalysts as they can be tailored to match specific esterification requirements and can be reused for multiple cycles. Their solid form also allows easier separation as opposed to homogeneous catalysts. Owing to their simplicity [7] and environmentally benign nature [8], heterogeneous catalysts are currently the best alternative to conventional homogeneous catalysts [9].

Under the major classification of heterogeneous catalysts are solid acid catalysts (SACs) which are utilized in a wide range of applications [10]. However, traditional solid acid catalysts (e.g., zirconium sulfate, Smopex-101, and Amberlyst-15) possess poor microporosity, poor acid site, high cost of catalyst synthesis, and low stability [11], [12], [13]. Hence, a new class of catalysts derived from biomass (e.g., lignocellulose, sugars, aromatic, biochar) are being studied.

Lignocellulosic biomasses are commonly characterized by their high carbon content from cellulose (20-51%), hemicellulose (9-28%), and lignin (10-26%) [14], [15], [16], [17], [18], [19], [20]. These organic materials, when subjected to a partial carbonization, would yield a highly disorganized form of carbon with a wide range of pore sizes, cracks, and crevices [21]. This results in a high porosity matrix, making these biomasses a promising choice as a carbon precursor for sulfonated carbon-based solid acid catalyst [22]. Apart from that, these catalyst sources address the limitations of their traditional counterparts since they are cost-effective, have larger surface area, and increased microporosity. As a result, the utilization of these biomass sources as solid acid catalysts is widely investigated including sugarcane bagasse [15], cacao shells [23], peanut shells [24], and spent coffee grounds [25]. Mango seed husk, containing approximately 52-58% cellulose, 23-29% hemicellulose, and 16-24% lignin is yet to be explored for its potential as raw material for solid acid catalyst synthesis. Although different catalyst sources offer different advantages, the potential of the mango seed husk is hinged on that fact that mango is abundant in the Philippines as it is one of the top agricultural products of the country [26].

A carbon-based solid acid catalyst can be synthesized by a two-step carbonization-sulfonation process or by direct sulfonation. An in-situ functionalization approach is illustrated in **Fig 2** where both carbonization and sulfonation steps occur simultaneously through direct sulfonation (A) and has a direct impact on the structure, surface chemistry, stability, and cost of sulfonated carbon materials [21]. A carbon precursor and a sulfur precursor (e.g., H_2SO_4, isethionic acid, 2-hydroxy-5-sulfobenzoic acid) are mixed and heated to induce both sulfonation and carbonization [14], where the former refers to the introduction of a sulfonating agent on the surface of the carbonaceous material or biomass, whereas the latter refers to a thermal decomposition technique [15], [27].

Unlike direct sulfonation, however, the two-step carbonization-sulfonation method (B) is a post grafting functionalization approach where pre-carbonized materials or carbon supports are treated with different sulfonating reagents to create covalently bonded $–SO_3H$ sites. In simpler terms, the biomass has undergone carbonization step prior to sulfonation [21].

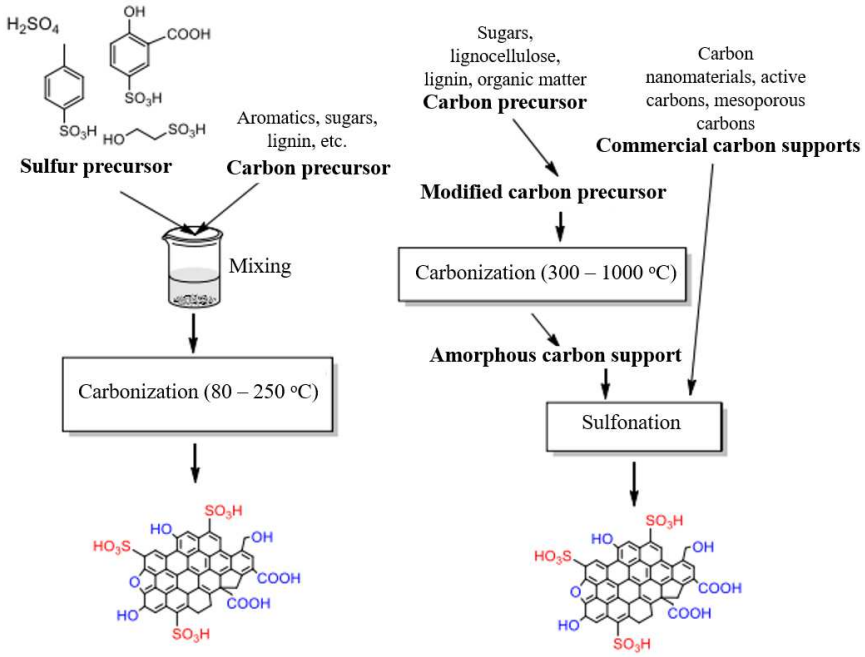


Fig 2 Different methods for functionalizing carbon materials with SO3H sites: (a) Direct Sulfonation or Simultaneous Carbonization-Sulfonation Process; (b) Two-step Carbonization-Sulfonation Process [21]

As presented in **Fig 3**, the first stage of solid acid catalyst synthesis for any lignocellulosic biomass source is a partial carbonization (A) of the carbon material. This step is accompanied by dehydration which results in the liberation of water from the molecule and the dissociation (B) of the C–O–C bond, forming polycyclic aromatic carbon sheets at temperatures typically ranging between 300 °C to 800 °C for approximately 0.5 h to 20 h [28], [29], [30]. The carbonized material then undergoes sulfonation process (C) using sulfuric acid [31]. The $–SO_3H$ is introduced along with the –COOH and –OH groups at the edge of the aromatic carbon rings, resulting in the 3D structure of the sulfonated carbon-based acid solid. Formation of layers of larger sheets of polycyclic aromatic carbon rings (D) will continually form [9] during sulfonation process subjected at a temperature of 100 °C to 200 °C for 3 h to 20 h [28], [29], [30]. The total synthesis time of the two-step synthesis is around 3.5 h to 23 h at operating temperatures of 100 °C to 800 °C. Considering the synthesis conditions of the two-step synthesis, the overlaps of time and temperature

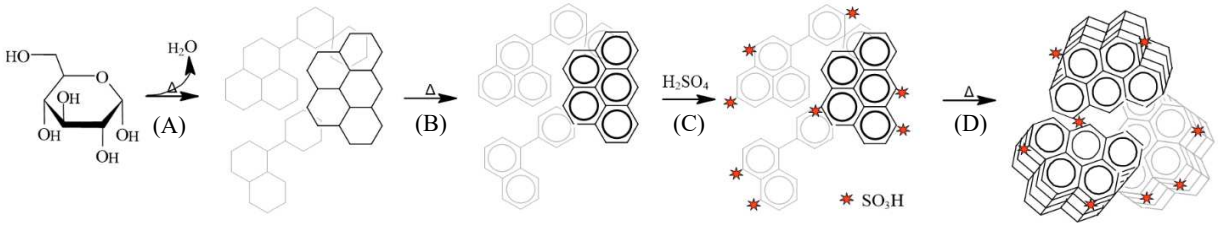


Fig 3 Mechanism of sulfonated carbon-based acid solids (CBAS) synthesis as adapted from Okamura et al. [31] (Rendered using ACD/Chemsketch Freeware)

during carbonization and sulfonation can be integrated and utilized to shorten synthesis time and to lessen energy requirements. This alternative preparation step **[32]**, as previously mentioned, is simultaneously carbonizing the lignocellulosic material while functionalizing the carbon structure with acid groups at given process conditions.

This study investigated the potential of mango seed husk-derived solid acid catalyst as a new solid acid catalyst source via simultaneous carbonization-sulfonation process to meet the expected rise in catalyst usage. Synthesis temperature (100 °C, 150 °C, and 200 °C) and synthesis time (4 h, 5 h, and 6 h) were varied to determine the effects of synthesis conditions on catalytic activity. The best synthesis temperature and time for the catalyst were determined to be the conditions that produced the catalyst with the highest conversion under the tested reaction conditions.

2. Material and Methods

2.1 Collection and preparation of materials

2.1.1 Reagents and chemicals

The chemicals used during the synthesis and characterization of the solid acid catalyst include concentrated sulfuric acid (AR grade 98.0%, Ajax, Sydney, Australia), barium chloride dihydrate (AR grade 99.0%, Ajax, Sydney, Australia), magnesium oxide (extra pure 96.0-100.5%, Scharlau, Spain), anhydrous sodium carbonate (AR grade 99.8%, Ajax, Sydney, Australia), sodium chloride (99.7%, Ajax, Sydney, Australia), sodium hydroxide pellets (97.0%, HiMedia, India), and hydrochloric acid (AR grade 36.0%, Ajax, Sydney, Australia). Other main chemicals used for esterification, analysis, and separation include oleic acid (purity 99.0%, Ajax, Sydney, Australia), methanol (HPLC grade 99.9%, RCI Labscan, Thailand), n-hexane (AR grade 95-96%, RCI Labscan, Thailand), undenatured ethanol (AR grade 99.5%, ChemSupply, Australia), ethyl acetate (AR grade 99.8%, RCI Labscan, Thailand), and fatty acid methyl (FAME) standards SMB00937-1ML fatty acid methyl ester mixture (≥ 95%, Merck, Germany).

2.1.2 Mango seed husks

The mango seed wastes were sourced from ProFood International Corporation located in Mandaue City, Cebu. The collected mango seeds were soaked in tap water (5:1 v/v water-to-biomass ratio) at room temperature for about 1 hour to soften the remaining flesh for easier cleaning. The mango flesh on the seed husk was removed through brushing, while the fibrous part was trimmed using scissors. The samples were sun-dried for about 3 days. The dried mango seeds were cracked opened to remove the kernels inside by hand. Dried husks were obtained and cut before undergoing a 2-mm mesh milling process in the Wiley mill (Model 4, Thomas Scientific, USA). The milled husks were further dried in a convective oven (UM500, Memmert, USA) at 60–80 °C for 12 h. These were stored in tightly sealed plastic containers at room temperature for later characterization.

2.2 Characterization of mango seed husks

2.2.1 Particle size distribution

Milled mango seed husks were subjected to sieve analysis for the determination of average particle diameter. The mean particle size determination was based on ASTM C136-01 [33]. About 100 g of milled MSH were placed on pre-weighed standard Tyler sieves stacked in decreasing screen opening (2 mm, 850 µm, 450 µm, 250 µm, and 180 µm). The sieves containing the sample were transferred to a mechanical sieve shaker (Model A5911, Intertest Benelux,

Netherlands) and shaken for 15 minutes. The remaining samples on every sieve were weighed and recorded. The mean particle size ($\overline{d_m}$) of the milled mango seed husk was calculated using **Equation 1.**

$$\overline{\boldsymbol{d_m}} = \sum \boldsymbol{x_i d_i} \ [=] \ \boldsymbol{mm} \qquad \textbf{Equation 1}$$

where $\boldsymbol{x_i}$ is the mass fraction of the retained particles on a corresponding sieve and $\boldsymbol{d_i}$ is the average screen opening of the retaining sieve and the adjacent top sieve.

2.2.2 Proximate composition analysis

The proximate analysis of the milled mango seed husk was carried out based on ASTM D1762-84 [34]. Three crucibles were dried in a muffle furnace (PF3/SPEC, Vecstar, UK) for 10 minutes at 750 ℃ and cooled in a desiccator for 1 hour. The pre-fired crucibles excluding the lids were weighed using an analytical balance (572 KP, Kern, Germany). For the moisture analysis, about 1 g of powdered MSH was weighed (to the nearest 0.1 mg) into the pre-fired and pre-weighed crucible. The crucibles containing the dried samples were heated in the muffle furnace at 105 ℃ for 2 hours followed by another cooling in a desiccator 1 hour prior to weighing. The process was repeated at one-hour intervals until the change in weight was constant (±0.0005 g). The moisture content (%$\boldsymbol{MC}$) of the MSH was calculated using **Equation 2**.

$$\%\boldsymbol{MC} \ = \frac{\boldsymbol{m_i} - \left(\boldsymbol{m_{cs,105°C}} - \boldsymbol{m_c}\right)}{\boldsymbol{m_i}} \times \mathbf{100}\% \ [=] \ \%\frac{\boldsymbol{w}}{\boldsymbol{w}} \qquad \textbf{Equation 2}$$

where $\boldsymbol{m_i}$ is the initial mass of the MSH sample, $\boldsymbol{m_c}$ is the mass of the pre-fired crucible, and $\boldsymbol{m_{cs,105°C}}$ is the mass of the crucible containing the MSH sample after drying at 105 ℃.

For the determination of the volatile matter component, the crucibles containing the dried MSH samples were covered with pre-fired crucible lids before undergoing drying in the muffle furnace to remove volatile matter. The crucibles were positioned on the outer ledge of the furnace for 2 minutes with the muffle door open at 300 ℃. They were moved to the edge of the furnace for 3 minutes at 500 ℃, and then to the rear of the furnace with the muffle door closed for 6 minutes at 950 ℃. The samples were transferred to a desiccator and were allowed to cool for an hour before weighing. The volatile matter content (%$\boldsymbol{VMC}$) was calculated using **Equation 3.**

$$\%\boldsymbol{VMC} \ = \frac{\boldsymbol{m_{cs,105°C}} - \boldsymbol{m_{cs,950°C}}}{\boldsymbol{m_i}} \times \mathbf{100}\% \ [=] \ \%\frac{\boldsymbol{w}}{\boldsymbol{w}} \qquad \textbf{Equation 3}$$

where $\boldsymbol{m_{cs,950°C}}$ is the mass of the covered crucible containing the MSH sample after drying at 950 ℃.

For the determination of the ash content and fixed carbon, the crucibles without the lids were placed again in the furnace at 750 ℃ for 6 hours. The crucibles were transferred to the desiccator for an hour before weighing the samples.

The procedure was repeated at one-hour intervals until the mass was constant. The ash content (%$\boldsymbol{AC}$) and fixed carbon (%$\boldsymbol{FC}$) were calculated using **Equation 4** and **Equation 5**, respectively.

$$\%\boldsymbol{AC} = \frac{\boldsymbol{m_{cs,750°C} - m_c}}{\boldsymbol{m_i}} \times \mathbf{100}\% \; [=] \; \% \frac{\boldsymbol{w}}{\boldsymbol{w}} \qquad \textbf{Equation 4}$$

$$\%\boldsymbol{FC} = \mathbf{100}\% - \%\boldsymbol{M} - \%\boldsymbol{VMC} - \%\boldsymbol{AC} \; [=] \; \% \frac{\boldsymbol{w}}{\boldsymbol{w}} \qquad \textbf{Equation 5}$$

where $\boldsymbol{m_{cs,750°C}}$ is the mass of the crucible containing the MSH sample after firing at 750 ℃.

2.3 Simultaneous carbonization and sulfonation (SCS) of dried mango seed husk

The SCS of mango seed husks was carried out in duplicates based on the methodology of the studies by Flores et al. [15] and Mendaros et al. [14]. Nine samples of approximately 3.5 g of milled mango seed husk (912.27 μm) with a moisture content of 3.86 ± 0.20 %w/w were transferred into Kjeldahl digestion flasks fully immersed in a 55 mL concentrated sulfuric acid (biomass to acid ratio of 1:30). Nine flasks containing the sample-acid mixture were mounted in the Kjeldahl digester (DK-8S Heating Digester, VELP 241 Scientifica, Italy) and heated at a rate of 10 ℃/min until the temperature reached the desired synthesis temperature (100 ℃, 150 ℃, and 200 ℃). Every temperature was maintained for a particular time (4 h, 5 h, and 6 h) where direct sulfonation process took place. The reaction mixtures were cooled for few minutes before slowly diluting with 1 L of distilled water and transferred to a 1 L reagent bottle with screwed cap. The reagent bottles were allowed to cool overnight in a water bath. The reaction mixtures were filtered using filter paper (Whatman Grade No. 2). Upon the recovery of the solid acid catalyst derived from mango seed husk (MSH-SAC), further washing using hot distilled water (~90 ℃) was done to remove the unbound acids. The washing was continued until the pH value of the washing solution was near or equal to that of the distilled water used for washing.

To qualitatively test the presence of sulfate ions, about three to four drops of 0.48 M of barium chloride were added into the washing solution after every washing. A neutral washing solution when added with barium chloride will not react to form barium sulfate precipitates in the solution. A pH strip was also soaked into the solution to check if the pH value was near or equal to that of the distilled water used for washing. The recovered solids were heated in an oven at 60 ℃ for approximately 10 hours to ease handling of the solids. The solids were weighed. The catalyst yield ($\boldsymbol{Y_{MSH-SAC}}$) was calculated using **Equation 6.**

$$\boldsymbol{Y_{MSH-SAC}} \; (\boldsymbol{w/w}) = \frac{\boldsymbol{total\ MSH - SAC}}{\boldsymbol{total\ MSH}} = \frac{\sum \boldsymbol{m_{MSH-SAC}}}{\sum \boldsymbol{m_{MSH}}} \; [=] \; \frac{\boldsymbol{g\ MSH - SAC}}{\boldsymbol{g\ MSH}} \qquad \textbf{Equation 6}$$

where $\boldsymbol{m_{MSH}}$ is the total mass of mango seed husk subjected to direct sulfonation in each condition, $\boldsymbol{m_{MSHSAC}}$ is the total mass of solid acid catalyst recovered after direct sulfonation in each condition.

2.4 Characterization of the mango seed husk-derived catalyst

2.4.1 Sulfur content and sulfonic acid density

The recovered solid acid catalyst was characterized for its total sulfur content, total acid density ($\boldsymbol{\rho_{TAD}}$), and sulfonic acid density ($\boldsymbol{\rho_{SO3H}}$). The total sulfur content analysis was carried out according to Eschka method as described by ASTM D3177-02 [35]. About 1 g of MSH-SAC was mixed with 3 g of Eschka mixture which is composed of 2 parts by weight of magnesium oxide and 1 part of anhydrous sodium carbonate in a 30 mL porcelain crucible. The resulting mixture was covered with another 1 g of Eschka mixture on the top and was heated in a muffle furnace at 800 ℃ with a heating rate of 10 ℃/min for 4 hours. This allowed complete oxidation of MSH-SAC. The crucible was cooled for an hour. After cooling, the contents of the crucible were transferred into a 250 mL beaker. The contents were mixed with 100 mL hot water with continuous stirring conditions. The mixture was allowed to heat in a hot plate (420D, Corning, USA) at 90 ℃ for 45 minutes and was stirred at 5-minute intervals. The solids in the mixture were separated through settling process and the liquid was decanted to a 600 mL beaker passing through a filter paper (Whatman Grade No.4). The remaining residue in the filter paper was washed four times with 50 mL hot water. The collected filtrate was added with 30 mL of 1 M hydrochloric acid. It was heated to 90 ℃ through the hot plate. A 15 mL of 100 g/L barium chloride solution was added dropwise to the filtrate to precipitate the dissolved sulfates. The solution was allowed to heat in the hot plate for 2.5 hours. The settled solids were filtered using a fine ashless filter paper (Whatman Grade No. 42) with the aid of a vacuum pump. After filtration, washing was done using hot water until 10 mL of the collected filtrate resulted in a clear solution when reacted with a 1 drop of 0.1 M $AgNO_3$ solution. The ashless filter paper was folded and placed into the porcelain crucible. The crucible was heated inside the furnace from room temperature to 800±50 ℃ with a heating rate of 15 ℃/min. Upon reaching the 800±50 ℃ mark, the temperature was maintained for 30 minutes to burn the filter paper inside the crucible. The crucible was weighed until a 0.01 g difference of the crucibles with samples was obtained. The sulfur content (%$\boldsymbol{S}$), acid density ($\boldsymbol{\rho_{SO3H}}$)**,** and extent of sulfonation ($\boldsymbol{\xi_S}$) was calculated using the equations below, respectively.

$$\%\boldsymbol{S} = \frac{(\boldsymbol{m_{c,BaSO4}} - \boldsymbol{m_c})\frac{\boldsymbol{MW_S}}{\boldsymbol{MW_{BaSO4}}}}{\boldsymbol{m_{SAC}}} \times \mathbf{100}\% \; [=]\% \frac{\boldsymbol{w}}{\boldsymbol{w}} \qquad \textbf{Equation 7}$$

$$\boldsymbol{\rho_{SO3H}} = \frac{\%\boldsymbol{S}}{\mathbf{100}} \times \frac{\mathbf{1000}}{\boldsymbol{MW_S}} \; [=] \frac{\boldsymbol{mmol\ H^+}}{\boldsymbol{g\ SAC}} \qquad \textbf{Equation 8}$$

$$\boldsymbol{\xi_S} = \frac{\%\boldsymbol{S_{SAC}}}{\%\boldsymbol{S_{MSH}}} \qquad \textbf{Equation 9}$$

where $\boldsymbol{m_{SAC}}$ is the mass of the MSH-SAC sample, $\boldsymbol{m_c}$ is the mass of the pre-fired crucible, $\boldsymbol{m_{c,BaSO4}}$ is the mass of the crucible containing the barium sulfate precipitates, $\boldsymbol{MW}$ are the molecular weights of sulfur and barium sulfate, and $\%\boldsymbol{S_{SAC}}$ and $\%\boldsymbol{S_{MSH}}$ is the sulfur content of MSH-SAC and mango seed husk, respectively.

2.4.2 Total acid density

The determination of the total acid density was adapted from the study of Dhokaliya & Savaliya [32]. About 0.5 g of MSH-SAC was mixed with a 50 mL of 2 N sodium chloride solution in a 125 mL Erlenmeyer flask. The mixture was shaken at 200 rpm for 24 hours in an incubator shaker (Model-G25, New Brunswick Scientific Co. Inc, USA) and was filtered using a filter paper (Whatman Grade No. 4) to separate the solids. A 15 mL filtrate aliquot with 3 drops of phenolphthalein indicator was titrated with a standardized 0.01 M NaOH solution until the endpoint is reached. The total acid density of the catalyst ($\boldsymbol{\rho_{TAD}}$) was calculated using **Equation 10** and the weak acid density ($\boldsymbol{\rho_{WAD}}$) was calculated using **Equation 11**.

$$\boldsymbol{\rho_{TAD}} = \frac{\boldsymbol{V_{NaOH} C_{NaOH} \frac{V_{NaCl}}{V_{aliquot}}}}{\boldsymbol{m_{SAC}}} [=] \frac{\boldsymbol{mmol\ H^+}}{\boldsymbol{g\ SAC}} \qquad \textbf{Equation 10}$$

$$\boldsymbol{\rho_{WAD}} = \boldsymbol{\rho_{TAD} - \rho_{SO3H}} [=] \frac{\boldsymbol{mmol}}{\boldsymbol{g\ SAC}} \qquad \textbf{Equation 11}$$

where $\boldsymbol{V_{NaOH}}$ is the volume of the sodium hydroxide solution titrated, $\boldsymbol{C_{NaOH}}$ is the concentration of the titrant, $\boldsymbol{V_{NaCl}}$ is the volume of the sodium chloride solution added to the MSH-SAC, and $\boldsymbol{V_{aliquot}}$ is the volume of the aliquot titrated with the NaOH solution.

2.5 Esterification of oleic acid and methanol with MSH-SAC

2.5.1 Catalytic activity and sulfonic acid activity determination

The process in producing methyl oleate from the esterification of oleic acid with methanol was conducted based on the study of Flores et al. [15]. Approximately 30 g of oleic acid was mixed with 43 mL methanol (methanol to oleic acid molar ratio of 10:1) in a 250 mL screw-capped Erlenmeyer flask. The flask containing the mixture was loaded in a pre-warmed incubator shaker with a 200 rpm and 65 °C settings for incubation for 30 minutes. The esterification reaction was facilitated by adding 2.5 g of catalyst into the mixture in the flask (approx. 8 %w/w catalyst loading based on oleic acid). The reaction was kept at the set temperature for 6 hours. After the set reaction time, the flasks were removed from the shaker and allowed to be cooled in the refrigerator (NR-BY552XS, Panasonic, Japan) for 6 h to stop the reaction from proceeding further. The resulting cooled mixtures were filtered using a filter paper (Whatman Grade No. 4) into a 250 mL separation funnel to separate the solid catalyst from the mixture. The filtrate in the separation funnel was dissolved in a 50 mL n-hexane. The spent MSH-SAC on the filter paper was also rinsed thrice with 15 mL n-hexane to thoroughly remove the methyl oleate and unreacted oleic acid from the surfaces of the catalyst. The collected catalyst was dried and analyzed for its sulfur content and total acid density.

In the separation funnel, the mixture was added with 20 mL of 5 %w/w aqueous NaCl solution to induce the liquid-liquid separation for oil recovery. The mixture was gradually swirled and settled, forming two layers: the organic layer (containing n-hexane, unreacted free fatty acids, and methyl esters) and the aqueous layer (containing methanol and water). The bottom layer was discarded, and the remaining mixture (organic layer) was further washed with 5 %w/w

NaCl solution twice to ensure that the methanol and leached acids were removed from the catalyst. The upper layer was transferred into a pre-weighed evaporation flask. To recover the oil sample, a Soxhlet extractor (EME30500/CEB, Electrothermal, USA) was used. Further heating was done until 0.01 g difference of the samples was obtained. The conversion ($\boldsymbol{X_{OA}}$) was determined using **Equation 12**, respectively. Moreover, the catalytic activity ($\boldsymbol{A_C}$) was calculated using **Equation 13**.

$$X_{OA} = \frac{AV_i - AV_f}{AV_i} \qquad \textbf{Equation 12}$$

$$A_C = \frac{m_{OA} X_{OA}}{m_{SAC} \frac{MW_{OA}}{1000} t} [=] \frac{mmol\ OA}{g\ SAC \cdot h} \qquad \textbf{Equation 13}$$

where $\boldsymbol{m_{MO}}$ and $\boldsymbol{m_{OA}}$ are the masses of the concentrated product (methyl oleate) and initial oleic acid, respectively; $\boldsymbol{AV}$ is the acid value of the oil pre- and post-esterification; $\boldsymbol{MW_{MO}}$ and $\boldsymbol{MW_{OA}}$ are the molecular weights of the product methyl oleate and the oleic acid, respectively; and t is the esterification time.

2.5.2 Fatty acid content and acid value determination

Fatty acid content of oil samples was determined via titration as described in ISO 660:2020 [36]. To analyze the FA content of the oil samples, about 0.5 g of recovered sample was placed inside the 125 mL Erlenmeyer flask. A 25 mL of neutralized ethanol and three drops of phenolphthalein indicator were added to the flask using a dropper. The mixture was titrated against a standardized 0.075 M ethanolic NaOH solution until endpoint was reached. The acid value ($\boldsymbol{AV}$) and fatty acid content ($\boldsymbol{FA}$) were calculated using **Equation 14** and **Equation 15**, respectively.

$$AV = \frac{C_{NaOH} V_{NaOH} MW_{KOH}}{m_{oil}} [=] \frac{mg\ KOH}{g\ oil\ sample} \qquad \textbf{Equation 14}$$

$$FA = \frac{AV}{AV_{OA}} [=] \frac{g\ OA}{g\ oil\ sample} \qquad \textbf{Equation 15}$$

where $\boldsymbol{C_{NaOH}}$ is the concentration of the NaOH solution used in the titration, $\boldsymbol{V_{NaOH}}$ is the volume of the titrant used, $\boldsymbol{m_{oil}}$ is mass of oil sample, $\boldsymbol{MW_{KOH}}$ is the molar mass of potassium hydroxide, and $\boldsymbol{AV_{OA}}$ is the acid value of oleic acid.

2.6 Reusability of MSH-SAC

The reusability of the carbon-based derived catalyst was done using the method established in the study of Mendaros et al. [14]. The best synthesis temperature and time was based on the combination setting with the highest catalytic activity. The esterification setting of oleic acid with methanol was set to 6 hours at 65 °C and 200 rpm. The reaction was done in duplicates. These same conditions were used for the reusability tests in which the catalyst was reused up to 4 cycles. For the first cycle, eight sets of reactant mixture were loaded in the incubator shaker to be esterified. The same process was done for the recovery of catalyst and oil samples as presented in this study. The methanol-to-oil

ratio and catalyst loading was proportioned to the actual recovered mass of the MSH-SAC after every cycle. The recovered MSH-SAC was washed with n-hexane, dried, and pooled to undergo the succeeding cycles. The excess spent catalyst was analyzed for their acid density after every cycle and the retention of the catalytic activity ($\boldsymbol{R}_{\%}$) relative to the first cycle was calculated using **Equation 16**.

$$\boldsymbol{R}_{\%} = \frac{\boldsymbol{A_{Cn}}}{\boldsymbol{A_{C1}}} \times \mathbf{100\%} \qquad \textbf{Equation 16}$$

where $\boldsymbol{A_{Cn}}$ is the catalytic activity of the nth cycle, and $\boldsymbol{A_{C1}}$ is the catalytic activity of the first cycle.

2. 7 Data analyses

To understand the possible relationship between catalyst characteristics and acid densities to the catalytic activity, a Pearson correlation was done. To determine the influence of synthesis conditions, time and temperature, on the acid densities and to the catalytic activity, a two-way ANOVA with replication was employed. The Tukey's HSD test was also conducted to have a pair-wise comparison of the responses to identify which set of responses were statistically different from one another. This was used as basis for selecting the best synthesis conditions to be adopted for subsequent reusability experiments.

3. Results and Discussion

3.1 Characterization of mango seed husk

The collected mango seed husks were dried, milled, and characterized in terms of particle size distribution, proximate composition, sulfur content, and total acid density. It was found out that the mean particle size of dried MSH is 912.27 µm. Meanwhile, the proximate composition of the collected mango seed husks is shown in **Table 1.**

Table 1 Characteristics of collected mango seed husk

Characterization	**This Study**	**Siacor et al.** [39]
Proximate composition[a] (%w/w)		
Moisture	3.86 ± 0.20	5.57 ± 0.17
Volatile matter	82.12 ± 0.23	75.14 ± 0.11
Ash	0.65 ± 0.10	1.04 ± 0.06
Fixed carbon	13.37 ± 0.24	18.24 ± 0.13
Sulfur content[a] (%w/w)	0.13	n.d.
Total acid density (mmol H^+/g)	0.06 ± 0.01	n.d.
Particle size mean (µm)	912.27	≤ 1000

[a]calculated based on dry-matter basis, n.d. – not determined

The results of the proximate analysis of MSH in **Table 1** are close to the reported values in literature [39]. The mango seed husk must have a low moisture content as having this in excess could lead to sample contamination, and mold growth that could compromise the characteristics of the biomass source. It is also observed that most of the proximate composition of MSH is volatile matter (%VMC). This is expected since biomass like MSH typically contains high amounts of %VMC (up to 87%) that influences its combustion characteristics and ignition temperature [40], [41]. Despite the high %VMC, in terms of catalytic synthesis application, the focus is given to fixed carbon (FC) because

it quantifies the remaining carbon content of the biomass after undergoing carbonization. The fixed carbon content of MSH used in the study is within the range of values of other lignocellulosic biomass used in catalyst synthesis (13.33–24.46%) [14], [15], [16], [17], [18], [19], [20], [42]. This suggests that mango seed husk is a suitable carbon support for the synthesis of solid acid catalyst.

Moreover, the sulfur content of the raw biomass is characterized to determine whether there is already a significant amount of active sites (sulfonic acid groups) in the synthesized solid acid catalyst. The sulfur content of the raw MSH was found to be 0.13 %w/w (dry basis), comparable to the reported values of other biomass residues used in solid acid catalyst synthesis (<1%) [14], [15], [24], [43]. Aside from the sulfur content, the total acid density of raw MSH was found to be 0.061 ± 0.01 mmol H^+/g. The total acid density is comprised of main acid sites, namely weak (–COOH and –OH) and sulfonic ($–SO_3H$) functional groups. The determination of the densities of these three functional groups is vital in catalytic synthesis because these quantities directly affect the catalytic activity of the synthesized catalyst in the esterification of oils. The results suggest that the initial amounts of sulfur and acid densities present in the raw MSH are considerably low and will not be sufficient for an effective solid acid catalyst, hence a functionalization step is required to incorporate more sulfonic acid groups to the carbon matrix of the catalyst.

3.2 Characterization of catalyst samples

In this study, a full factorial of nine MSH-SAC samples with varying synthesis time (4, 5, 6 h) and temperature (100, 150, 200 °C) were prepared via simultaneous carbonization and sulfonation. The highest catalyst yield of ~68% was obtained at direct sulfonation conditions of 100 °C and 6 h, while the lowest yield of ~40% was obtained at 200 °C and 6 h. In general, a 30% to 40% decrease in catalyst yield were observed as the sulfonation temperature increased from 100 °C to 200 °C. Analysis of variance revealed that the sulfonation temperature has a significant effect on the resulting catalyst yield ($p < 0.05$). The decrease in catalyst yield as the carbonization temperature is increased suggests that more of the larger chemical constituents of MSH (lignin, hemicellulose, and cellulose) were either depolymerized into smaller units or fragmented into light organic molecules (e.g., CO_2 and H_2O), and released as volatiles during the carbonization step [41]. Furthermore, higher catalyst yield at lower direct sulfonation temperature is due to a reduced rate of carbonization related reactions (e.g., dehydration and charring) at lower temperatures during direct sulfonation, resulting to lower weight loss and higher yield [24].

On the other hand, it was found that there is no significant difference between sulfonation time and catalyst yield ($p = 0.283$). The varying trend of sulfonation time against catalyst yield may be due to mass losses incurred during the recovery and washing of catalysts. The variability in the texture and size of catalyst particles affected the rate and yield of recovered catalyst via filtration.

In terms of the multifunctional carbon structure of catalyst, the properties are typically determined by its total acid and sulfonic acid densities. Strong and weak acid groups are expected to attach to the carbon matrix after functionalization, which are responsible for the total acid density of a solid acid catalyst. However, only the strong acid sites ($–SO_3H$) are responsible for catalyzing the reaction (e.g., esterification). The $–SO_3H$ groups can be quantified according to the sulfonic density. This can be calculated from the determined sulfur content of the catalyst assuming

that all S atoms were present in the carbon surface as $–SO_3H$ [44], [45]. The nine synthesized MSH-SAC with their corresponding sulfur contents and acid densities are shown in **Table 2.**

The sulfur content of the synthesized MSH-SAC at different synthesis temperature and time ranges from 2.05 %w/w to 2.53 %w/w, corresponding to a ~16-fold to ~20-fold increase in sulfur content with respect to the initial sulfur content of raw MSH (0.13 %w/w). The increase in sulfur content in the synthesized MSH-SAC solidifies the idea that sulfonic acid groups have successfully linked to the carbon layer of the catalyst, hence giving its acidic nature expressed by its acid density [46].

Table 2 Characteristics of catalyst samples derived from mango seed husks in terms of sulfur content and acid densities prepared under different conditions.

MSH solid acid catalyst		S content (%w/w)	Acid density (mmol H^+/g)	
T[a] (°C)	t[b] (h)		Total acid	Sulfonic group[c]
100	4	2.27	1.20	0.71
	5	2.22	1.36	0.69
	6	2.36	1.20	0.74
150	4	2.40	1.20	0.75
	5	2.53	1.35	0.79
	6	2.48	1.19	0.77
200	4	2.05	1.22	0.64
	5	2.09	1.31	0.65
	6	2.07	1.23	0.65

[a]direct sulfonation temperature, [b]direct sulfonation time, [c]calculated from the S content

The sulfur content increases with temperature from 100 °C to 150 °C but decreases at 200 °C for all synthesis times (4, 5, and 6 h). This suggests that the maximum sulfur content is observed in MSH-SACs synthesized at 150 °C across every sulfonation time. Statistical analysis of the results highlighted the significant difference ($p = 0.002$) between the sulfonation temperature and the sulfur content of the synthesized MSH-SAC. In contrast, sulfonation time has no significant effect ($p = 0.468$) on sulfur content.

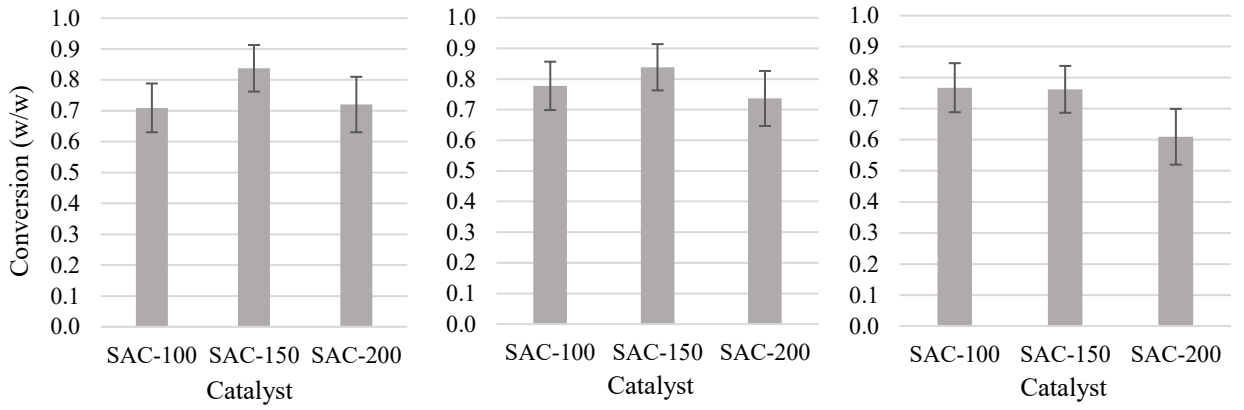
In terms of $–SO_3H$ density, high sulfonic acid densities (≥ 0.75 mmol H^+/g) were achieved when the catalyst was synthesized at 150 °C across every sulfonation time being investigated. Similar to the sulfur content, increasing the sulfonation temperature further to 200 °C resulted in a decrease in sulfonic acid density of the catalysts. These findings were also observed in related studies by Flores et al. [15] and Lou et al. [30] using sugar cane bagasse as the carbon precursor for the synthesis of SAC-SCB. Flores et al. [15] found out that higher $–SO_3H$ densities of around 0.57–0.67 mmol H^+/g SAC-SCB were obtained after synthesis was carried out at 150 °C, which generally decreases as temperature is increased up to 250 °C. Similarly, Lou et al. [30] determined that 150 °C is the optimum sulfonation temperature in a two-step preparation of SAC-SCB with a sulfonic acid density of 1.06 mmol H^+/g SAC-SCB. It can be inferred that to achieve a high sulfonic acid density of MSH-SAC, the simultaneous carbonization sulfonation temperature should not go beyond 150 °C. The sulfonation temperature has a significant effect ($p = 0.002$) on the $–SO_3H$ density. The dependency of sulfonic acid density on the carbonization temperature is largely based on the fact that at higher temperatures, polycyclic aromatic rings form after the dissociation of C–O–C bonds of the biomass [9],

[47]. The increase in temperature leads to graphitization of the biomass, forming a rigid structure of cross-linking carbons. This carbon structure becomes harder with increasing carbonization temperature due to plane growth and stacking of the carbon sheets. In effect, it hinders the attachment of $–SO_3H$ to the carbon matrix, lowering the density of $–SO_3H$ groups, along with other weak acid groups (–COOH and –OH). Instead of attaching to the matrix, the $-SO_3H$ would likely undergo thermal degradation or decomposition. This occurs because sulfur-containing compounds are heat sensitive and can break down with other components within the carbon matrix at high temperatures [48]. On the other hand, catalysts carbonized at lower temperatures have smaller carbon sheets and therefore have higher $–SO_3H$ densities because the $–SO_3H$ groups are attached only to the edges of the carbon sheets [31]. Varying the sulfonation time from 4 h to 6 h did not significantly influence ($p = 0.468$) the sulfonic acid density. However, the differences in the sulfonic density at these sulfonation times are relatively close to each other. These variances can be influenced by factors such as devolatilization, thermal decomposition, and changes in morphology.

In view of the influence on total acid density, only the sulfonation time ($p < 0.05$) has a significant effect compared to the sulfonation temperature ($p = 0.790$). The total acid density of the catalyst was highest at a sulfonation time of 5 h (1.31–1.35 mmol H^+/g) at constant sulfonation temperature (100 °C, 150 °C, and 200 °C). It is also worth noting that highest total acid density of 1.36 mmol H^+/g was obtained at synthesis conditions of 100°C and 5 h, followed closely by MSH-SAC carbonized and sulfonated at 150 ℃ for 5 h with a total acid density of 1.35 mmol H^+/g. However, between the two catalysts and among all the samples, MSH-SAC carbonized and sulfonated at 150 ℃ for 5 h possessed the highest sulfonic acid density of 0.7897 mmol H^+/g while the remaining 42% are composed of the weak acid groups (–COOH and –OH). On the other hand, in terms of weak acid density to sulfonic acid density ratio, MSH-SAC produced at 150 ℃ for 4 h arguably has the lowest ratio of 0.60 and therefore its structure is more concentrated in sulfonic acid groups (0.75 mmol H^+/g) rather than weaker acid groups (0.45 mmol H^+/g). The presence of more sulfonic acid groups inherently increases the catalytic activity of the synthesized SAC as it provides more catalytic active sites [49], which directly catalyzes a reaction [50].

3.3 Catalytic activity of MSH-SAC

Although it is known that the sulfonic acid density greatly influences the inherent catalytic activity of a solid acid catalyst, the actual activity and effectiveness of the synthesized SAC is best determined through its performance in its intended application (i.e., model reaction). As a response to the catalytic activity, the conversion of fatty acids in the esterification reaction of oleic acid (OA) with methanol (MeOH) using MSH-SAC as the catalyst is evaluated as shown in **Figure 4.**



(a) Direct sulfonation for 4 h (b) Direct sulfonation for 5 h (c) Direct sulfonation for 6 h

Fig 4 The effect of direct sulfonation temperature and time on the catalyst performance expressed as conversion during esterification with methanol at 65 °C, methanol-to-oil ratio of 10:1 mol/mol, approx. 8 %w/w catalyst loading based on oleic acid, for 6 h, using the mango seed husk-derived solid acid catalyst at a dry biomass-to-acid ratio of 1:30 w/w, and stirred at 200 rpm

Generally, high conversions ranging from ~61% to ~84% were attained when MSH-SAC was used in the esterification of OA with MeOH compared to uncatalyzed esterification with only 6.9% conversion. da Luz Corrêa et al. [43] shared similar results when they compared the performance, in terms of conversion, of murumuru kernel shell-derived SAC in the esterification of OA with MeOH in the presence of catalyst (96%–99%) and without catalyst (6.8%). The huge increase in conversion when using MSH-SAC in the esterification of OA with MeOH indicates the catalyst's effectivity in increasing the conversion of oleic acid.

Moreover, the high conversion of fatty acids obtained can be attributed to the sulfonic acid density of each catalyst synthesized at these conditions. Through Pearson Correlation Test, it was found out that conversion is positively correlated ($r = 0.7390$) with the sulfonic acid densities of the catalysts. The highest fatty acid conversion (0.8384 w/w) corresponds to MSH-SAC carbonated and sulfonated at 150 °C for 5 h, which also had the highest sulfonic acid density. However, some other combinations of synthesis temperature and time (e.g., MSH-SAC synthesized at 100 °C for 5 h) with slightly lower sulfonic acid density than other catalysts (e.g., MSH-SAC synthesized at 100 °C for 6 h) yielded a higher conversion than the latter. This finding suggests that other factors beside the acidic properties of the SAC may have affected the conversion, such as morphology, porosity, and surface hydrophobicity [51]. Nevertheless, the conversions obtained by the synthesized catalysts are still in agreement with their sulfonic acid densities, whereby the higher the sulfonic acid density (>0.70 mmol H^+/g) translates to a higher conversion (>70%). This is because the high number of $–SO_3H$ group increases the hydrophilicity of the catalyst. The polar nature of $–SO_3H$ and other polar acidic or basic functional groups incorporated in the polymeric structure impart a certain hydrophilicity to the catalytic surface. This allows more hydrophilic MeOH molecules to enter the carbon bulk, leading to reactions with hydrophobic reactants (fatty acids and triglyceride) to occur on the interior of the catalyst as well as on the surface [49]. However, as consequence to its hydrophilicity, $–SO_3H$ can also attract more polar water molecules produced in

the reaction, which adsorbs onto the surface of the catalyst, hindering the access of both more hydrophobic fatty acid molecules and the less polar methanol [52], [53]. Consequently, this could impact the stability of the catalyst.

Meanwhile, in terms of weak acid density, no strong correlation could be observed between the weak functional groups (r = –0.2571) and the amount of OA converted, as also observed by Mendaros et al. [14].

In view of the influence of sulfonation temperature on conversion, higher conversions of 0.77–0.84 w/w were consistently achieved when MSH-SAC was simultaneously carbonized and sulfonated at 150 °C throughout 4 h, 5 h, and 6 h of synthesis period. When the sulfonation temperature was increased from 100 °C to 150 °C, there was a steady increase of 9.62% for MSH-SAC carbonized and sulfonated at 4 h; however, for MSH-SAC carbonized and sulfonated for 6 h, the conversions at 100 °C and 150 °C have comparable values (76%–77%). In a related study, Bureros et al. [23] observed a similar trend when they used cacao shell-derived SAC in the esterification reaction using the same reactants, OA and MeOH, as in this study. There was a significant increase from 63% to 78% as the sulfonation temperature was increased from 80 °C to 120 °C for the catalysts obtained at sulfonation time of 4 h. Similarly, the conversion increased from 69% to 79% for CS-SAC carbonized and sulfonated for 6 h as the temperature was increased from 80 °C to 120 °C. On the other hand, increasing the temperature from 150 °C to 200 °C reduced the oleic acid conversion during esterification by ~28% for MSH-SAC synthesized for 4 h to as high as ~39% for MSH-SAC synthesized for 6 h. Similar results were found in other biomass-derived solid acid catalyst studies involving sugar cane bagasse [15] and murumuru kernel shell [43], whereby they observed a reduction in fatty acid conversion at a higher temperature (200–250 °C). This could imply that the optimum synthesis temperature and time to attain high conversions are within ranges of conditions varied.

With regard to the influence of sulfonation time on conversion, the MSH-SAC that was simultaneously carbonized and sulfonated for 5 h showed the most promising catalytic activities at constant sulfonation temperature (100, 150, and 200 °C). Prolonging the sulfonation time from 4 h to 5 h increases the catalytic activity of the catalyst, while increasing the sulfonation time to 6 h significantly decreased the catalytic activity. Despite these observations, results show that sulfonation time (p = 0.387) did not significantly influence conversion.

3.4 Reusability of MSH-SAC

Aside from the catalytic efficiency in terms of conversion as the response parameters in assessing the catalysts for their potential applications, the stability of these catalysts must also be considered. The synthesized heterogenous catalysts should also exhibit a stable activity throughout their reusability cycles. To evaluate the stability, the spent catalysts were subjected to the same characterization process performed on the fresh catalysts. It was observed that the total acid sites and sulfonic groups in all the MSH-SAC decreased after their first esterification cycles. This could be attributed to the leaching out of the loosely bound active sites due to the several washing steps of n-hexane and the deactivating nature of the sulfonated solids. When used in water participating reactions such as esterification and hydrolysis [54], [55], carbon-based SAC normally loses their catalytic activity due to leaching of $–SO_3H$ in aqueous suspensions [49]. However, the stability of sulfonated SAC under these harsh conditions can be enhanced by the abundance of electron-withdrawing –COOH groups [47]. In electrophilic substitution reaction like that of sulfonation

of polycyclic aromatic compounds, the weak acid (–COOH) is supposed to increase the electron density between C and S atoms, resulting in the tight attachment of $–SO_3H$ groups to the carbon framework and consequently, lesser leaching of $–SO_3H$ group [56], [57]. This concept was demonstrated in the current study when a leaching of only 5–13% $–SO_3H$ was observed for catalysts with higher density of weaker functional groups (0.64–0.67 mmol H^+/g) after first reuse. Despite the MSH-SACs with higher weak acid densities having better stability than MSH-SACs with higher sulfonic acid densities, the latter have higher catalytic performance than the former. Hence, a good balance between catalytic performance and stability should be taken into consideration when choosing the best MSH-SAC.

Although the catalytic activities of MSH-SACs synthesized at 150 ℃ for 4 h and 5 h were comparable ($p > 0.05$), the catalyst obtained at 4 h was chosen for the reusability tests because it was achieved at a lesser time. In addition, MSH-SAC synthesized at 150 °C for 4 had lower percent reductions in sulfonic acid and total acid densities (23.43%, 16.74%) after reuse compared to MSH-SAC synthesized at 150 °C for 5 h (25.84%, 22.43%), indicating a better stability and more acid sites are still available for the next cycle.

It can be observed in **Figure 5** that there was a decrease in conversion from approximately 0.87 w/w to around 0.68 w/w after four cycles. During the first cycle, approximately 0.87 w/w was achieved using the fresh catalyst. Upon the second cycle or the first reuse of the catalyst, the conversion decreased to 0.79 w/w. The third and fourth cycle then decreased the conversion to 0.75 w/w and 0.68 w/w, respectively. After four esterification cycles, the catalyst has retained its activity up to 78% retention. Although the decrease in catalytic activity, the catalyst still demonstrates satisfactory results when compared to literature (42-89% activity retention) [14], [15], [23], [24], [30], [58].

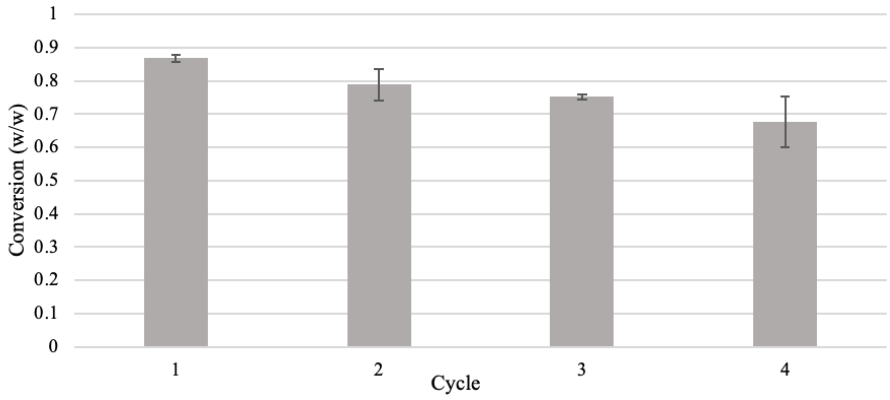


Fig 5 Reusability of MSH-SAC directly sulfonated at 150 ℃ for 4 h and resulting catalyst used in the esterification of oleic acid with methanol at a methanol-to-oil ratio of 10:1 mol/mol, approx. 8 %w/w catalyst loading based on oleic acid at a reaction temperature of 65 ℃ for 6 h, and stirred at 200 rpm

Aside from the conversion, a decrease in active sites can also be observed as indicated by the decrease in total acid density of the spent catalyst after the fourth cycle from 0.91 mmol H+/g to 0.66 mmol H+/g. The total acid sites present in the catalyst have retained ~72% from its original active sites. Such observation supports the concept, wherein as the catalyst was continuously reused, the functional groups responsible for catalyzing the reaction, particularly those that are weakly attached, were leached out, thereby resulting in a decrease in conversion. A constant

catalytic activity may possibly be achieved after running more than 4 cycles considering that all loosely attached active sites in the catalyst are removed, leaving active sites that are sturdily attached to the carbon matrix. This linear conversion after reusability cycles could become an attribution to the catalyst's inherent stability which could indicate that the mango-seed husk derived solid acid catalyst is effective in catalyzing reactions over multiple uses.

4. Conclusions and Recommendation

A solid acid catalyst from mango seed husk (MSH-SAC) was successfully prepared through functionalization of acid groups (i.e., sulfonic groups) using concentrated sulfuric acid at 100-200 °C for 4-6 h. Mango seed husks that were simultaneously sulfonated and carbonized at 150 °C for 4 h and 5 h achieved higher conversions of approximately 84%, compared to other synthesized MSH catalysts, when an esterification reaction of oleic acid and methanol was carried out at of 65 °C, methanol-to-oil ratio of 10:1 mol/mol, approx. 8 %w/w catalyst loading based on oleic acid, for 6 h, and stirred at 200 rpm analyzed through acid-base titration. The activity of the synthesized catalyst was largely dependent on the sulfonic acid density rather than the total acid. Moreover, catalyst reusability test was done using the best synthesis condition (150 °C for 4 h) under the same esterification conditions. After 4 esterification cycles, there was a consistent decrease in both conversion and total acid density, retaining about 78% of its original activity. A constant catalytic activity may possibly be achieved after running more than 4 cycles. Future researchers could focus on optimizing the catalyst synthesis temperature and time and other parameters involved in the esterification process (methanol-to-oil ratio, reaction temperature and time, catalyst loading) for maximum conversion, increasing the number of esterification cycles to determine the extent at which the catalyst could retain its activity, investigating the effect of morphology on the attachment of acid sites, quantifying other functional groups (-COOH and –OH acid groups) attached to the surface of the catalyst, investigating the catalyst performance with crude feedstocks (e.g., waste cooking oils and COFAD), and conducting kinetic studies to obtain kinetic models and parameters in the design of chemical reactors for large-scale production of biodiesel.

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Statements & Declarations

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Competing interests

The authors declare that they have no competing interest.

Data availability

Data will be available upon reasonable request to the authors of the manuscripts.

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