

Activity of a Sulfonated Carbon-Based Catalyst Derived from Organosolv Lignin toward Esterification of Stearic Acid under Near-Critical Alcohol Conditions

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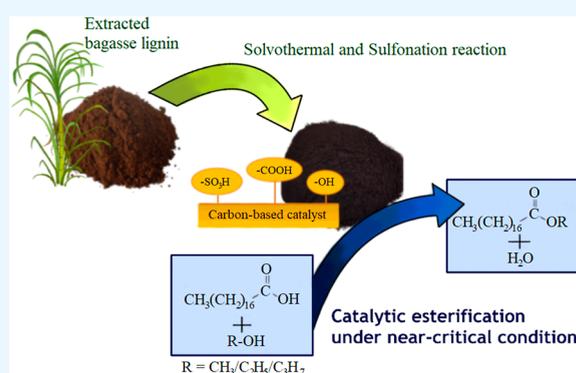
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ABSTRACT: In this study, an environmentally benign carbon-based catalyst derived from extracted bagasse lignin (EL) was successfully synthesized by solvothermal carbonization and sulfonation with methane sulfonic acid (MSA). Interestingly, the results indicated that the use of MSA as a sulfonation agent made a catalyst with higher thermal stability than conventional sulfuric acid. Thus, in comparison to the catalyst prepared by using sulfuric acid, the catalyst prepared by using MSA (EL–MSA) exhibited higher catalytic activity in the esterification of stearic acid under near-critical methanol conditions. Under optimum conditions (260 °C for 5 min, a 9:1 methanol-to-stearic-acid molar ratio, 5 wt % catalyst loading, and 10% v/v toluene), the esterification over the EL–MSA catalyst promoted a 91.1% methyl stearate yield. Moreover, the results also revealed that the high thermal stability of the EL–MSA catalyst not only affects its great catalytic activity, but it also prevents damage to the porous structure and decomposition of acidic surface oxygen-containing functional groups. It contributes to the excellent reusability of the catalyst. After the fifth run, a high yield of 82.8% was obtained. The effect of alcohol type on the catalyst performance was also studied. It was found that the EL–MSA catalyst also presented good performance toward esterification with ethanol and propanol, from which ethyl stearate and propyl stearate with a more than 80% ester yield can be achieved.



1. INTRODUCTION

Nowadays, the concept of efficient production of biodiesel has been widely investigated globally to overcome the depletion of fossil fuels and global environmental problems. The esterification of free fatty acid with short-chain alcohols was typically used for biodiesel production. Recently, several reports presented that esterification in supercritical alcohol is an efficient method to produce biodiesel in a short time.^{1,2} For instance, Alenezi et al. (2010) reported that 97% of fatty acid methyl ester (FAME) was achieved by the esterification of free fatty acid with methanol at 320 °C within 5 min, a methanol-to-free-fatty-acid molar ratio of 7:1, and a pressure of 10 MPa.³ However, the major disadvantage of this method is high energy consumption and cost of production due to the severe conditions (high reaction temperature, pressure, and alcohol-to-reactant ratio). Consequently, the appropriate catalyst which allows the supercritical reaction to be carried out under milder conditions has been investigated.

Among various types of catalysts, the functionalized carbonaceous catalysts are interesting, economically eco-friendly, and potentially substituted for a homogeneous sulfuric acid (SA) catalyst for esterification in industries.^{4,5} Syazwani et al. (2017) prepared an efficient sulfated calcined angel wing

shell catalyst for the esterification of palm fatty acid distillate (PFAD).⁶ A high FAME yield of 98% was obtained at a temperature of 290 °C, a reaction time of 15 min, a molar ratio of methanol to PFAD of 6:1, and a catalyst loading of 2 wt %. Another report by Lokman et al. (2016) presented the use of D-glucose and starch to produce solid acid catalysts for the esterification of PFAD.⁷ Under optimum reaction conditions (290 °C for 5 min, a molar ratio of methanol to PFAD of 6:1, and a catalyst amount of 1 wt %), a high FAME yield of higher than 95% was obtained. Although many carbon sources and methods have been investigated to develop functionalized carbonaceous catalysts, the main acid used for functionalization was still SA.⁸ This might result in environmental threats and corrosion problems. Thus, alternative acids for catalyst preparation should be investigated.

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Methanesulfonic acid (MSA), which is one of the sulfonic acid derivatives, presents a potential green catalyst for several reactions including esterification as its strong acid and less corrosive and toxic.^{9,10} In our previous work, we developed an efficient sulfonated carbon-based catalyst prepared by using MSA as the functionalized agent [extracted bagasse lignin (EL)–MSA] to promote the esterification of stearic acid with methanol to produce methyl stearate, which has attractive for use as biodiesel because of its high combustion efficiency.¹¹ The studied reaction was performed at 240 °C for 10 min, with a molar ratio of methanol-to-stearic-acid of 9:1, and a catalyst loading of 5 wt %, which provided 89.2% of ester yield. This work indicates that MSA is an efficient functionalized agent to produce an environmentally benign catalyst for esterification. However, the obtained methyl stearate yield of 89.2% was slightly lower than that reported in the literature.^{6,7}

Despite the addition of a catalyst, the improvement of the esterification reaction can be achieved by the addition of a cosolvent in the esterification process. As reported by our research group, the enhanced performance of the esterification reaction of PFAD was observed when benzene and toluene were added to the process.¹² Furthermore, the operating conditions including reaction temperature, reaction time, catalyst dosage, and the molar ratio of alcohol to feedstock significantly impacted the esterification process.^{13,14} Therefore, this work aims to find an appropriate esterification condition for the synthesized EL–MSA catalyst to maximize the methyl stearate yield. The esterification conditions, including temperature, time, methanol-to-stearic-acid molar ratio, catalyst loading, and the presence of toluene, were varied. The stability and reusability of synthesized catalysts were also investigated. Besides the esterification of stearic acid with methanol, the catalytic activity of the synthesized catalyst was also tested in reaction with ethanol and propanol. Ethyl ester and propyl ester can be also used instead of methyl ester because of their low-temperature flow performance.¹⁵

2. EXPERIMENTAL SECTION

2.1. Chemicals. EL containing 78.56 wt % of Klason lignin was obtained by our developed fractionation procedure. In brief, bagasse was pulped in a mixture of water/ethanol (30%:70%) with SA at 175 °C for 40 min. The liquid product was placed into a separatory funnel, in which deionized water was then added for phase separation. The extracted lignin was recovered from the separated organic phase by drying at 105 °C.

Methanol (99.9%), ethanol (99.9%), propanol (99%), stearic acid (99%), SA (98%), and methane sulfonic acid (99%) were analytical reagent grade and purchased from Sigma-Aldrich (Singapore). The analytical standard of methyl stearate was obtained from Sigma-Aldrich (Singapore).

2.2. Catalyst Preparation. Initially, solvothermal carbonization of EL was performed in a 300 mL stainless-steel tubular reactor. The reaction mixture containing 7.5 g of EL and 150 mL of ethanol was heated at 240 °C for 6 h with an initial pressure of 50 bar in a N₂ atmosphere. After heating under the desired condition, the reaction was stopped by immediately quenching the reactor in a water bath. The lignin char was filtered, washed with ethanol until the filtrate was nearly colorless, and dried in an oven.

Then, sulfonation of the lignin char was carried out to prepare sulfonated carbon-based catalysts. 10 mL of concentrated acid (SA or MSA) and 1 g of the lignin char were

mixed in a three-neck round-bottom flask. The mixture was then heated at 150 °C under an N₂ atmosphere. After sulfonation for 14 h, hot distilled water (>80 °C) was added to the mixture. Then, the catalyst samples were obtained by filtration, washed with hot water until the pH of the washing liquid was neutral, and dried in an oven at 105 °C. According to the types of acids, the catalysts were named EL–SA and EL–MSA.

2.3. Catalyst Characterization. The scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM–EDS) test was performed using a JEOL JSM-6610 LV instrument to characterize the morphological and elemental compositions of the lignin char and the synthesized catalysts. Prior to the measurements, the specimens were coated with Au by sputter coating (Cressington, 108 Auto). The measurement of Brunauer–Emmett–Teller (BET) surface area was performed by the N₂ physisorption technique using Belsorp-max Bel Japan equipment. In addition, thermogravimetric analysis (TGA, Pyris 1TGA, Perkin Elmer) was carried out to investigate the thermal stability of catalysts. TGA was conducted by heating a sample from 50 to 900 °C with a heating rate of 10 °C/min under He. Fourier-transform infrared (FT-IR) spectra were recorded on a Spectrum 2000, PerkinElmer FT-IR spectrometer in the range of 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹. The acid density of the synthesized catalysts was measured by the acid–base titration method. About 0.1 g of the catalyst was mixed with 50 mL of sodium hydroxide solution (20 mmol/L). Then, the mixture was treated under ultrasonic oscillation for 30 min. After filtration, 20 mL of the supernatant was titrated with a hydrochloric acid solution (20 mmol/L). In addition, transmission electron microscopy (TEM) images were captured using a JEOL JEM-2010 (Japan) and operated at an accelerating voltage of 200 kV.

2.4. Catalytic Test. A batch-type stainless-steel reactor with a vertical shaker has been employed for methyl stearate production. First, a mixture of methanol, stearic acid, and catalyst was added to the reactor. The molar ratios of methanol and stearic acid mixtures were varied to be 3:1, 6:1, 9:1, and 12:1. Before running the experiments, the furnace was heated to desired reaction temperature, which varied from 200 to 280 °C. The reactor was then placed in the furnace. After the inside temperature of the reactor reached the desired reaction temperature, the reaction was allowed to continue for 1–20 min. Then, the system was immediately cooled down by quenching in a water bath. Finally, the product was separated into three phases, namely, the phase of catalyst, the phase of water, and the phase of methyl stearate. The effect of cosolvent on the reaction performance was investigated by adding toluene (10% v/v) along with the reactants. Ester analysis was carried out in a Shimadzu 2010 model gas chromatograph equipped with a flame ionization detector and a DB-WAX column (30 m, 0.32 mm ID, 0.25 μm). The formula for calculating the percentages of the ester yield is given in the equation below.

$$\% \text{ Yield} = \frac{\text{Moles of ester product (mol)}}{\text{Moles of stearic acid (mol)}} \times 100 \quad (1)$$

3. RESULTS AND DISCUSSION

3.1. Characterization of the Synthesized Catalysts. The catalytic activity of catalysts is significantly affected by

their physicochemical properties. Several analytical techniques were carried out to characterize the lignin char and the catalysts such as N_2 physisorption, SEM–EDS, TGA, and FT-IR. Overall, it was found that the BET surface area of EL–SA (4.31 m^2/g) is almost the same as the surface area of lignin char (3.04 m^2/g). This trend is consistent with SEM images, which are shown in Figure 1a,b. Both the char and EL–SA

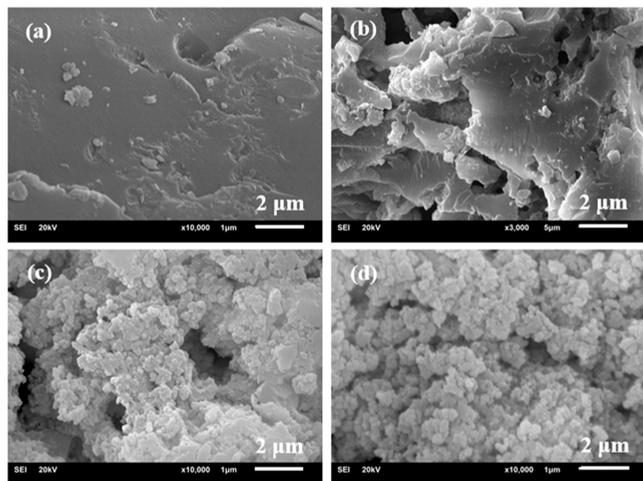


Figure 1. SEM images of (a) lignin char, (b) EL–SA, (c) EL–MSA, and (d) spent EL–MSA.

present a plate structure with no internal pore. In contrast, the solvothermal method using MSA caused the development of the pore structure on the surface of the catalyst (see Figure 1c). As a result, the BET surface area of EL–MSA of 19.00 m^2/g was about 6 times as high as that of lignin char. In addition, the nanoscale morphologies of the catalysts were investigated using TEM.

As shown in Figure 2, it can be seen that both EL–SA and EL–MSA catalysts present a sheet-like morphology. In detail, the TEM images of EL–SA exhibited aggregation in the sheets. Chhabra et al. (2021) indicated that the interaction between carbon catalyst and sulfonic functional groups led to an increase in the stacking of sheets.¹⁶ Therefore, the stacked sheets in EL–SA confirm the successful sulfonation.

EDS analysis was employed to characterize the surface elemental composition of the lignin char and the catalysts. As shown in Table 1, the characteristic peak of the S element was not observed in the EDS analysis of lignin char, while the S content of EL–SA and EL–MSA was 2.90 and 0.23%, respectively. These results confirm the incorporation of sulfonic acid groups on the surface of the catalysts.

Table 1. Textural Properties of Lignin Char and Catalysts^a

samples	elemental composition (%)			acid density (mmol/g)
	C	O	S	
lignin char	67.71	29.05	N.D.	0.20
EL–SA	56.28	40.82	2.90	2.27
EL–MSA	68.00	31.77	0.23	1.63
EL–MSA after the fifth cycle	64.36	35.64	N.D.	1.53

^aN.D. = not detected.

The state of S incorporated in the surface of EL–SA and EL–MSA was analyzed by X-ray photoelectron spectroscopy, and the results indicated that S existed in the forms of SO_3H groups.¹¹ In our previous work, the chemical bonds in molecules and the thermal stability of the lignin chars and the catalysts were identified by FT-IR spectroscopy and TGA, respectively.¹¹ The FT-IR spectroscopy results which were reported in ref 11 indicated that there were several functional groups such as carbonyl ($C=O$), carboxyl ($-COOH$), and hydroxyl ($-OH$) groups on the surface of lignin char. Jain et al. (2016) indicated that the density of the oxygenated functional group in the precursor used for catalyst preparation is an important indicator of the effectiveness of chemical activation in the synthesized catalyst.¹⁷ Therefore, it can be concluded that the prepared lignin char is an effective precursor for the synthesis of the catalyst as its highly oxygenated functional group. After sulfonation with MSA, the EL–MSA exhibited a significant increase in the aromatic carbon and hydroxyl groups. It might have resulted from the further carbonization by the recondensation of aromatic units during sulfonation.¹⁸ This high cross-linking between the carbon might hinder reactant access to SO_3H groups, resulting in the low SO_3H groups on the surface of EL–MSA.¹⁷ In addition, the acid–base titration was carried out to determine the acid density of lignin char and the catalysts. As shown in Table 1, the acid densities of lignin char, EL–SA, and EL–MSA were 0.20, 2.27, and 1.63 mmol/g, respectively. Compared with lignin char, the sulfonated carbon-based catalysts exhibited higher acidity. The result confirms successful sulfonation. It can be concluded that after sulfonation with SA, the acid density of EL–SA was significantly increased due to the successful incorporation of sulfonic acid groups on its surface. In contrast, an increase in the acid density of EL–MSA was mainly due to the increase in surface area and oxygenated functional groups, which are known to have a weak acidic nature.¹⁹ Moreover, the TGA results reported in our previous work indicated that the

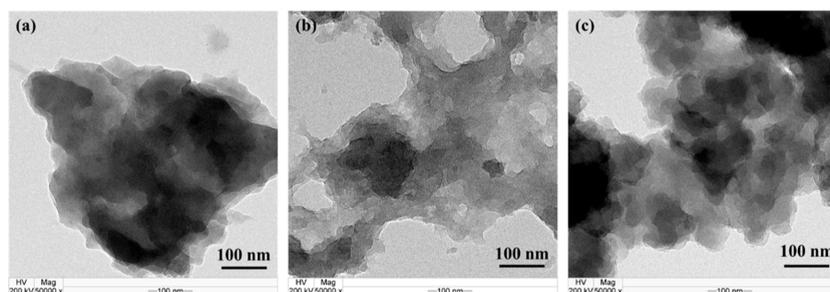


Figure 2. TEM images of (a) EL–SA, (b) EL–MSA, and (c) spent EL–MSA.

thermal stability of the synthesized catalyst was improved by sulfonation with MSA.¹¹ The lignin char showed the highest weight loss at the broad temperature range of 200–600 °C, while EL–MSA showed the highest weight loss at the temperature range of 400–800 °C. The weight loss at high temperatures (>500 °C) is caused by the decomposition of the aromatic network.²⁰ Therefore, the improvement of thermal stability of the EL–MSA catalyst may be caused by the increase in aromatic carbon after sulfonation with MSA. For comparison, EL–SA exhibited high decomposition of the catalyst surface sulfonic groups at 200–300 °C. The low thermal stability of EL–SA might be caused by the partial oxidation of the carbon-based EL structure during sulfonation.²¹ It should be noted that in this study, esterification was performed at 200–280 °C. On the other hand, a huge weight loss of EL–MSA was observed at 400–800 °C, corresponding to the decomposition of oxygenated functional groups.

3.2. Catalyst Performance on the Esterification of Stearic Acid with Methanol. 3.2.1. Effect of Catalyst Types.

The lignin char, EL–SA, and EL–MSA catalysts were evaluated for the esterification of stearic acid with methanol at 200 °C for 5 min and a methanol-to-stearic-acid molar ratio of 3:1. As shown in Figure 3, compared with the reaction

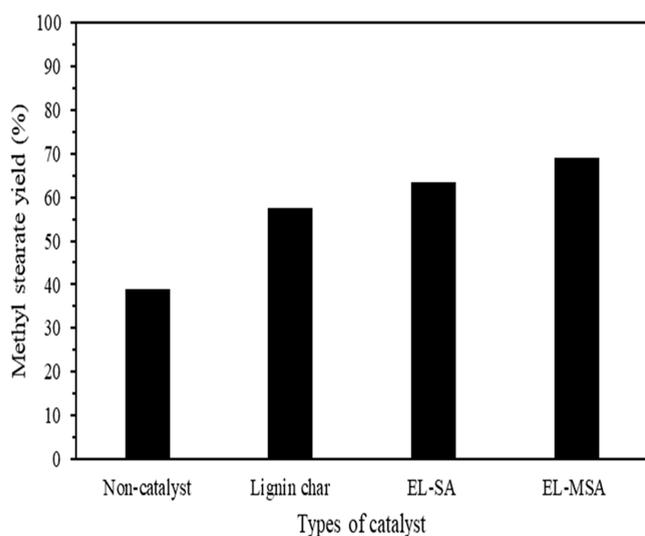


Figure 3. Effect of different catalysts on methyl stearate yield from the esterification at 200 °C for 5 min with a methanol-to-stearic-acid molar ratio of 3:1.

without the catalyst, an increase in methyl stearate yield from 39.0 to 57.6% was observed when the lignin char was added to the reactor. The catalytic activity of lignin char might be caused by the presence of oxygenated functional groups (–COOH and –OH) on its surface. However, the 57.6% methyl stearate yield was still low. This indicated that only the acidic functional groups on the char surface might be not enough for this reaction. Ma et al. (2014) indicated that the main influence for the high catalytic activity of a solid acid catalyst was the amounts of three different surface functional groups (–SO₃H, –COOH, and –OH groups) with proper proportions.²² Consequently, lignin char was sulfonated to incorporate the sulfonic acid groups on its surface, obtaining sulfonated carbon-based catalysts. The methyl stearate yield of EL–SA and EL–MSA was 63.4 and 69.1%, respectively. It should be noted that even though EL–SA contains higher

surface sulfonic acid groups than EL–MSA, it presented lower catalytic activity. It might be caused by the thermal deactivation of EL–SA, leading to the loss of active phase-support reactions.²³ In contrast, EL–MSA presented the highest catalytic activity due to its properties such as large surface area, high acidic surface oxygen-containing functional groups, and high thermal stability.

The Eley–Rideal mechanism with chemisorption on the active sites was introduced to elucidate the esterification catalyzed by solid catalysts.^{14,24} In this study, it is clear that the interaction between reactants with the active sites of the catalyst was a significant factor in the catalytic activity of the reaction. It confirms that the esterification of stearic acid with methanol over sulfonated carbon-based catalysts followed the Eley–Rideal mechanism, as demonstrated in Figure 4. The

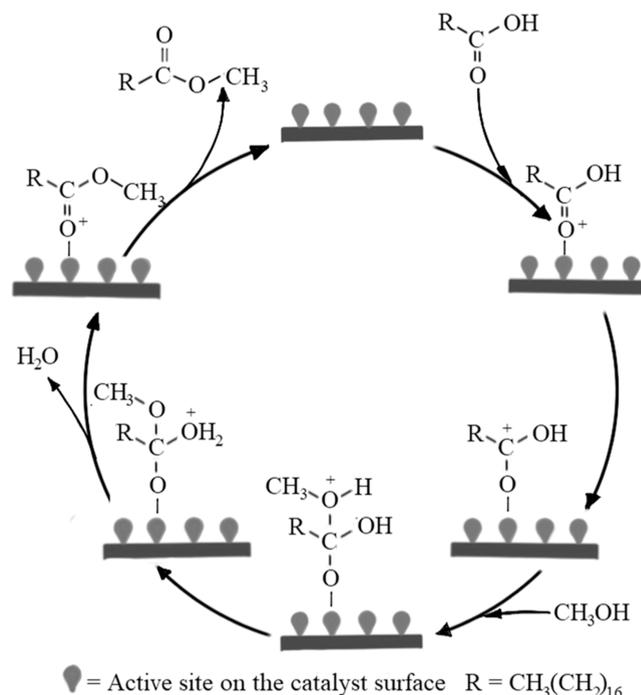


Figure 4. Proposed reaction mechanism of stearic acid esterification over the sulfonated carbon-based catalyst.

stearic acid molecule adsorbs on the active acid sites of catalysts. It increases the electrophilicity of the carbonyl carbon atom of stearic acid, causing a nucleophilic attack of methanol on the adsorbed stearic acid. Then, a tetrahedral intermediate is formed by transferring a proton from ethanol to the hydroxyl group of stearic acid. A water molecule eliminates from the intermediate, resulting in a methyl oleate molecule on the catalyst surface. Finally, the methyl oleate molecule is desorbed from the surface of the catalyst. The obtained highest product yield in this condition (200 °C and 5 min) was only 69.1%. This obtained yield was too low compared with the ester yields reported in other studies, which were within the range of 90–98%.^{3,6,25} Consequently, the reaction conditions should be optimized.

3.2.2. Effect of Reaction Temperature. It is well known that various operating factors such as temperature, time, and the molar ratio of reactants influence the rate of the esterification of fatty acid to ester and the performance of catalysts, affecting the productivity of ester products.²⁶ In this study, the reaction temperature, time, reactants' mole ratio, and catalyst loading

were optimized in the esterification of stearic acid to maximize methyl stearate yield. First, the esterification was conducted in the temperature range of 200–280 °C for 5 min with a methanol-to-stearic-acid molar ratio of 3:1 and EL–MSA catalyst loading of 5 wt % to study the effect of temperature on the esterification reaction. As shown in Figure 5, the

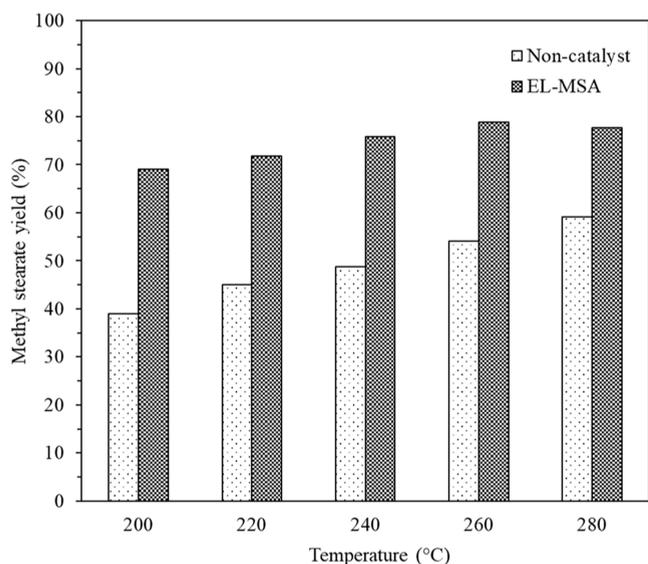


Figure 5. Effect of reaction temperature on the methyl stearate yield from the esterification with and without the presence of the EL–MSA catalyst at the reaction time of 5 min and a methanol-to-stearic-acid molar ratio of 3:1.

esterification without a catalyst exhibited a representative behavior of a linear increase in yield with the reaction temperature. It was known that the internal energy of molecules increases with rising temperature, increasing the number of collisions that have enough energy to break the bonds and reform new bonds.²⁶ Another reason could be that the solubility of stearic acid in methanol is improved at high temperatures and the mass transfer limitation between the reactants and the catalyst is reduced, resulting in a fast reaction rate.^{7,27}

As shown in Figure 5, methyl stearate yield was promoted by adding the EL–MSA catalyst when compared with the noncatalytic test. An uncatalyzed reaction gave a maximum yield of only 59.2% at 280 °C. In contrast, a 69.1% yield was achieved when the reaction temperature was only 200 °C in a catalyzed reaction. This indicates that the presence of a catalyst helps to reduce the requirement of energy by providing an alternative way with low activation energy.²⁸ The different energy requirement between esterification with and without a catalyst leads to a different tendency of product yield when the temperature changes. For esterification over EL–MSA, the yield rose steadily from 69.1 to 78.9% upon an increase in temperature from 200 to 260 °C before declining slightly when the temperature further went up. Lokman et al. (2015) and Ning and Niu (2017) also found a similar trend in their work, where a decrease in biodiesel production was observed when the temperature increased above the optimum reaction temperature depending on the viscosity of the feedstock.^{29,30} In addition, Syazwani and co-workers indicated that the tar formation at high temperatures might be the reason for the

decrease in product yield.⁶ As a result, 260 °C was taken as the optimal reaction temperature.

3.2.3. Effect of Reaction Time. In order to investigate the effect of reaction time, esterification was studied at different times ranging from 1 to 20 min with a 260 °C reaction temperature and a methanol-to-stearic-acid molar ratio of 3:1. The results are shown in Figure 6. Similar to the effect of

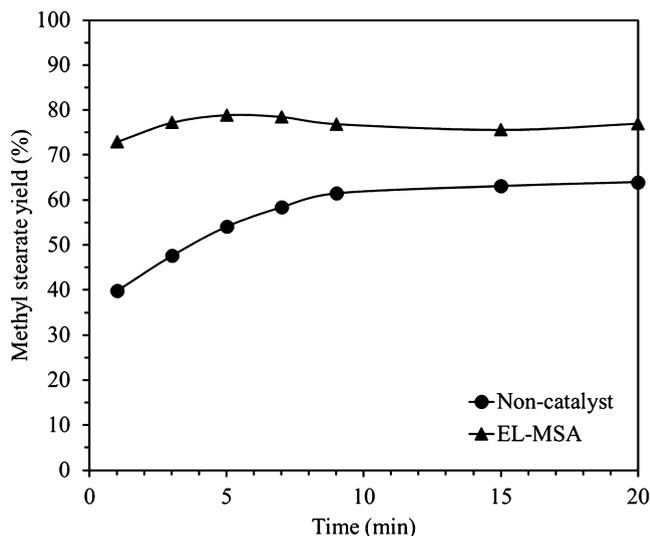


Figure 6. Effect of reaction time on the methyl stearate yield from the esterification with and without the presence of the EL–MSA catalyst at 260 °C and a methanol-to-stearic-acid molar ratio of 3:1.

temperature, the reaction without a catalyst requires severe conditions to promote the reaction. In the case of the absence of a catalyst, the highest product yield of 64.0% was obtained within 20 min of reaction time. In contrast, a methyl stearate yield of 72.9% was obtained at only 1 min of reaction with the EL–MSA catalyst. It was due to the decrease in activation energy when the catalyst was added to the reaction mixture, as mentioned above.

As shown in Figure 6, the reaction without a catalyst presented a substantial increase in product yield from 39.8 to 61.5% with an increase in reaction time from 1 to 9 min. Then, the product yield was increased slowly to 64.0% when the reaction time further increased. This low reaction rate was caused by the low concentrations of reactions at a long time of reaction and closing to reach the chemical equilibrium of the reaction. A study by Pan and co-workers (2016), which investigated the esterification of oleic acid in methanol under subcritical conditions, showed that the high acid value of oleic acid was reduced by 85% within a 20 min esterification time using a 12:1 molar ratio of methanol to oleic acid, and then slowed before remaining unchanged within 100 min which the reaction reached equilibrium.³¹ There was a different tendency of product yield between the esterification with and without a catalyst. The reaction over EL–MSA presents a moderate increase in methyl stearate yield from 72.9 to 78.9% when the reaction time went up from 1 to 5 min. However, a further increase in time affected a slight decrease in methyl stearate yield. The downward trend might be due to methyl ester decomposition that occurred after reaction equilibration.³² These results indicate that the synthesized EL–MSA has an effective performance to accelerate the esterification reaction

rate. Consequently, the esterification was completed in only 5 min.

3.2.4. Effect of the Methanol-to-Stearic-Acid Molar Ratio.

The effect of the methanol-to-stearic-acid molar ratio was determined by varying this ratio between 3:1 and 12:1 for the esterification of stearic acid at 260 °C for 5 min. As shown in Figure 7, both the absence and presence of the EL-MSA

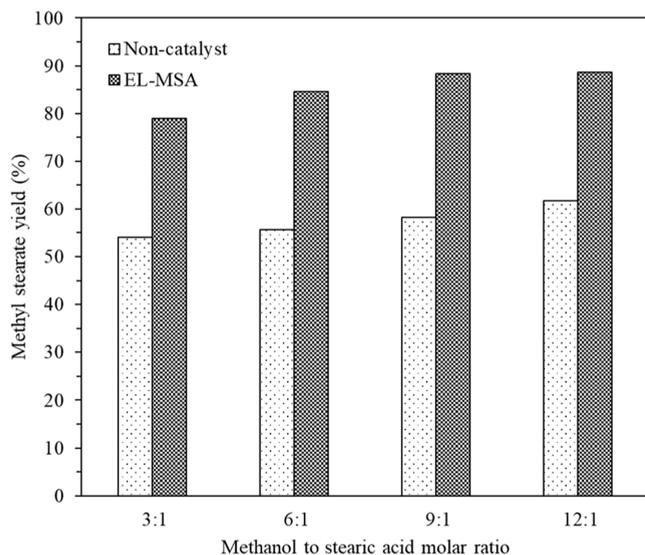


Figure 7. Effect of the methanol-to-stearic-acid molar ratio on the methyl stearate yield upon esterification with and without the presence of the EL-MSA catalyst at 260 °C with a reaction time of 5 min.

catalyst presented an increase in methyl stearate yield with the methanol-to-stearic-acid molar ratio. When the methanol-to-stearic-acid molar ratio increased from 3:1 to 12:1, the methyl stearate yields rose moderately from 54.1 to 61.7% and from 78.9 to 88.7% for esterification with and without the EL-MSA catalyst, respectively. It is well known that esterification is a reversible reaction. Therefore, an excess amount of methanol is required to force the equilibrium toward methyl stearate production. In addition, the high methanol concentration in the reaction mixture makes a complete dissolution of stearic acid in methanol. This causes a change in the reaction mixture from a heterogeneous to a homogeneous state, which helps to easily make contact between reactants and leads to a high product yield.³³ However, when the methanol-to-stearic-acid molar ratio is sufficient to change the reaction mixture into a homogeneous state, further addition of methanol cannot promote the product yield. Therefore, it was found that in the case of the presence of EL-MSA catalysts, there was no significant difference in the methyl stearate yield obtained by using methanol-to-stearic-acid molar ratios of 9:1 and 12:1. Thus, 9:1 was taken as the optimal methanol-to-stearic-acid molar ratio.

3.2.5. Effect of Catalyst Loading. The EL-MSA catalyst loading in the reaction was varied from 0 to 10 wt % to study the effect of catalyst loading on the methyl stearate yield from the esterification at 260 °C for 5 min with a methanol-to-stearic-acid molar ratio of 9:1. The results are presented in Figure 8. It can be seen that the ethyl stearate yield significantly increased from 58.2 to 88.3% when the catalyst loading increased from 0 to 5 wt %. It is well known that the increase in catalyst loading caused an increase in available

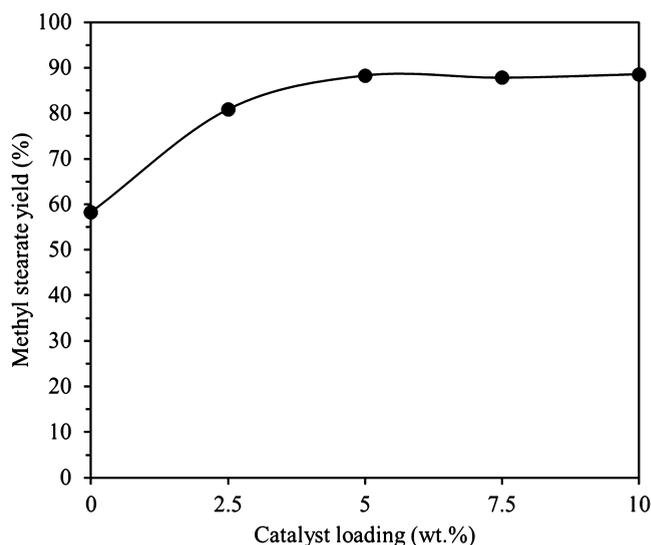


Figure 8. Effect of catalyst loading on the methyl stearate yield from esterification at 260 °C for 5 min with a methanol-to-stearic-acid molar ratio of 9:1.

active sites, which led to an increase in the rate of reaction.³⁴ The methyl stearate yield remained reasonably steady when the catalyst loading was further increased to 10 wt % as the reaction reached equilibrium at a high catalyst loading. As the result, the esterification of stearic acid with near-critical methanol over EL-MSA catalysts was optimized at 260 °C for 5 min, a 9:1 molar ratio of methanol to stearic acid, and a 5 wt % catalyst loading with a high methyl stearate yield of 88.3%.

3.2.6. Effect of the Cosolvent. Furthermore, the effect of the cosolvent on esterification was also evaluated by adding toluene to the reactor. The toluene amount was varied from 0 to 20% v/v, and esterification was conducted at 260 °C for 5 min, a methanol-to-stearic-acid molar ratio of 9:1, and a catalyst loading of 5 wt %. The results are presented in Figure 9. It was found that the addition of toluene promotes the

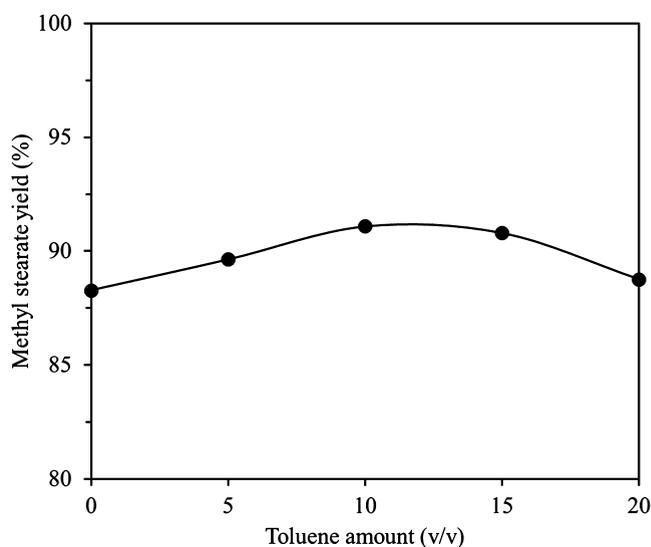


Figure 9. Effect of the toluene amount on the methyl stearate yield upon esterification at 260 °C for 5 min, a methanol-to-stearic-acid molar ratio of 9:1, and an EL-MSA catalyst loading of 5 wt %.

reaction. The methyl stearate yields slightly increased from 88.3 to 91.1% with an increase in toluene from 0 to 10% v/v. The reaction enhancement by adding toluene might be because of the good solubility of stearic acid in toluene that helps the mixing of methanol with stearic acid in the reactor.³⁵ However, the yield slightly decreased to 88.8% when the toluene amount was further increased to 20% v/v. This might be due to a decrease in reactant concentration with an increase in toluene amount.

3.2.7. Catalyst Reusability. A good solid catalyst must not only present a relatively high catalytic activity but also exhibit high reusability. Therefore, the reusability of the EL–MSA catalyst was tested in five consecutive runs without any intermediate treatment under optimal reaction conditions with and without the cosolvent. As shown in Figure 10, it can be

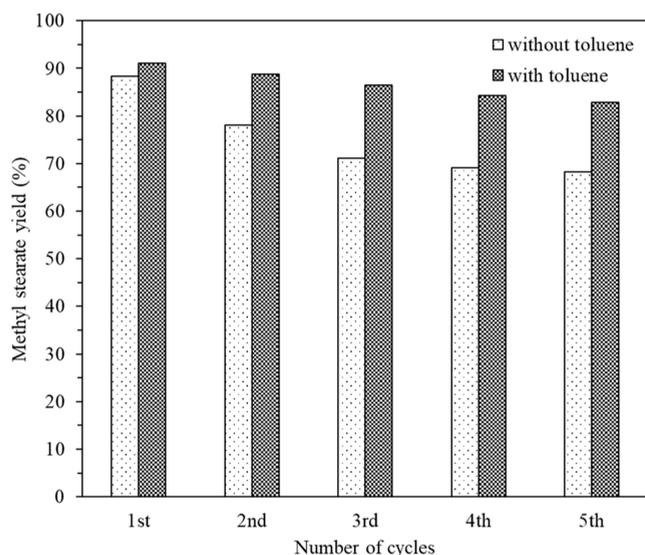


Figure 10. Effect of reusability and the cosolvent on product yield in five consecutive runs over EL–MSA at 260 °C for 5 min and methanol-to-stearic-acid molar ratios of 9:1.

seen that for the reaction without the cosolvent, the catalytic activity of the EL–MSA catalyst decreased significantly only in the first three runs. The methyl stearate yields decreased dramatically from 88.3 to 71.1% after the third run. In contrast, when the EL–MSA catalyst was repeatedly used in the fourth and fifth runs, the product yield decreased slightly. Methyl stearate yields of 69.1 and 68.3% were obtained in the fourth and fifth catalyst cycles, respectively. The deactivation of the catalyst might be due to a decrease in sulfonic acid groups on the surface of carbonaceous materials through the formation of sulfonic esters and the leaching of sulfur on the surface of catalysts.^{36,37}

Moreover, it is noted that the reusability of the EL–MSA catalyst was also improved by the addition of toluene. As shown in Figure 10, there was a slight decrease in the product yield following the number of runs. After the fifth run, a high methyl stearate yield of 82.8% was obtained. It might be caused by the nonpolar property of toluene which helps to reduce the leaching of sulfonic acid in methanol. Nakhate and Yadav (2016) also found a similar result in their work, in which compared with the first run, there was only an 8% conversion drop in the fifth run of the esterification of levulinic acid with benzyl alcohol in the toluene solvent.³⁴

3.2.8. Characterization of the Spent Catalyst. The spent EL–MSA catalyst was characterized by several analytical techniques including SEM–EDS, TEM, N₂ physisorption, and FT-IR spectroscopy and compared with the fresh one. As shown in Figure 1c,d, the spent EL–MSA catalyst presented slightly higher particle packing than the fresh catalyst. The result is in agreement with the TEM images, which show that the carbon particles of the catalyst tend to aggregate after esterification (see Figure 2). This particle aggregation was due to the self-aggregation of carbon at high temperatures. The aggregation of the spent EL–MSA catalyst (0.05 cm³/g) made it exhibit a slightly lower total pore volume than the fresh EL–MSA catalyst (0.07 cm³/g), as shown in Table 2. However,

Table 2. Textural Properties of Fresh and Spent EL–MSA Catalysts

catalysts	BET surface area (m ² /g)	total pore volume (cm ³ /g)	mean pore diameter (nm)
EL–MSA	19.00	0.07	13.94
EL–MSA after the fifth cycle	20.44	0.05	10.42

overall, the fresh and the spent EL–MSA catalysts have the morphology in common, in which they have a stacking structure of numerous particles. Therefore, there was no significant difference between the surface area of the fresh and spent EL–MSA. The results indicate good physical stability of the synthesized EL–MSA catalyst.

In addition to physical properties, the chemical properties of the spent catalyst were also characterized. Table 1 presents the elemental compositions of fresh and spent EL–MSA catalysts obtained by EDS analysis. Both fresh and spent EL–MSA catalysts were similar in the characteristic peaks of C, O, and S elements. Indeed, the S content decreased from 0.23 wt % and then was not detected. Consequently, it might be concluded that the decrease in methyl stearate yield was mainly due to the leaching of sulfur on the surface of the catalyst. In addition, the FT-IR spectroscopy analytical technique was employed to characterize chemical bonds in molecules of fresh and spent EL–MSA catalysts. The result is presented in Figure 11. It is clear that the fresh and spent EL–MSA had FT-IR spectra in

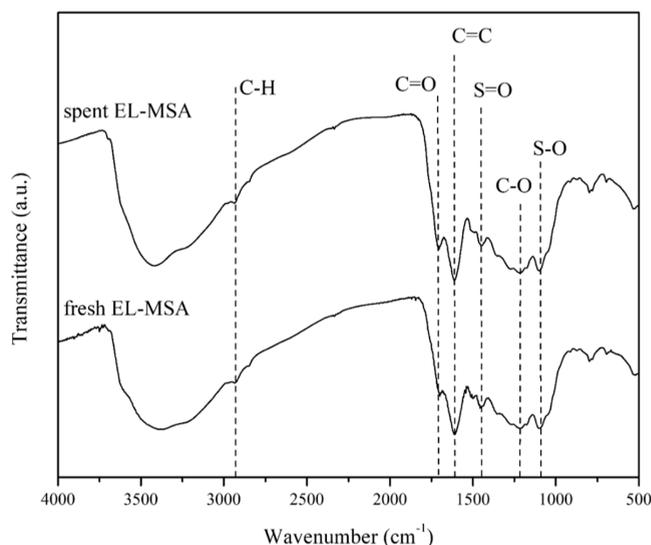


Figure 11. FT-IR spectra of fresh and spent EL–MSA catalysts.

common. In detail, the characteristic peaks of the O–H bond at 3400 cm^{-1} , C–H bond of hydrocarbons at 2910 and 2839 cm^{-1} , C=O bond at 1710 cm^{-1} , C=C bond at 1600 , 1507 , 1455 , and 1426 cm^{-1} , and C–O bond at 1210 cm^{-1} still appeared in the FT-IR spectra of the spent EL–MSA catalyst. In addition, these peaks were almost of the same intensity as that of the fresh catalyst. The acid density of the spent EL–MSA catalyst was also determined. As shown in Table 1, the acid density of reused EL–MSA (1.53 mmol/g) was slightly lower than that of fresh EL–MSA (1.63 mmol/g). It was due to the maintenance of the acidic functional groups on the surface of the spent catalyst, as mentioned above. The results confirm the good chemical stability of the synthesized EL–MSA catalyst, resulting in its great reusability. In light of the aforementioned results, the good physical and chemical stability of the synthesized EL–MSA catalyst might be due to its high thermal stability, which prevents damage to the porous structure and decomposition of acidic surface oxygen-containing functional groups.

3.3. Catalyst Performance upon the Esterification of Stearic Acid with Different Alcohols. The esterification of stearic acid with different alcohols (e.g. methanol, ethanol, and propanol) over the EL–MSA catalyst was also studied. The reaction was conducted under the optimal condition of $260\text{ }^{\circ}\text{C}$ for 5 min, a methanol-to-stearic-acid molar ratio of 9:1, and a catalyst loading of 5 wt %. It should be noted that the reaction was tested without toluene to avoid the effect of cosolvent upon esterification with different alcohols. The results are presented in Figure 12. Overall, it is clear that the EL–MSA

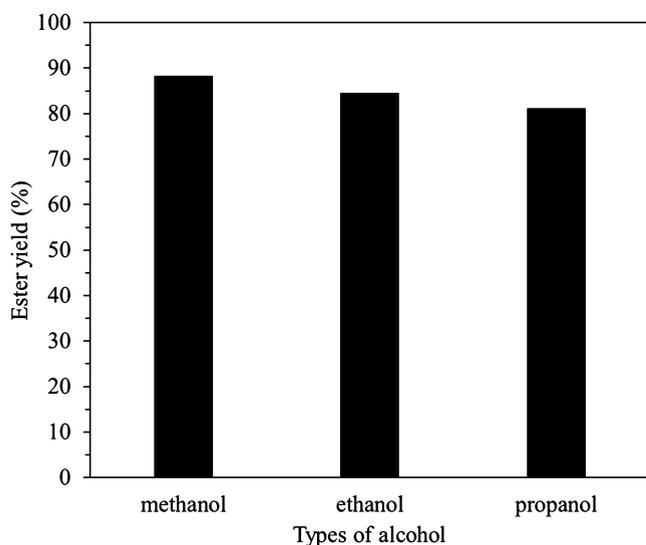


Figure 12. Ester yield obtained from the esterification of stearic acid with different types of alcohol at $260\text{ }^{\circ}\text{C}$ for 5 min, a methanol-to-stearic-acid molar ratio of 9:1, and an EL–MSA catalyst loading of 5 wt %.

catalyst has a good ability to promote esterification with different alcohols with high ester yields ($>80\%$). The obtained ester yields were 88.3, 84.5, and 81.2% for the esterification of stearic acid with methanol, ethanol, and propanol, respectively. This result is in agreement with the results reported by Sahu et al. (2019), in which at low catalyst loading, the ester yield decreased with the increase in branch and chain lengths of the alcohols.²⁶

4. CONCLUSIONS

The EL–MSA catalyst was successfully prepared by sulfonation of carbon derived from lignin in MSA. Its high thermal stability caused an efficient catalytic activity for the esterification of stearic acid in near-critical alcohol. In addition, the reaction conditions including reaction temperature, reaction time, and the molar ratio of reactants were the significant factors affecting esterification. The reaction was optimized at a $260\text{ }^{\circ}\text{C}$ reaction temperature within 5 min, a 9:1 methanol-to-stearic-acid molar ratio, and a 5 wt % catalyst loading. Moreover, methyl stearate production and the catalyst reusability can be improved by the addition of toluene in the reactor due to its nonpolar property, which helps to increase the solubility of stearic acid in the reactant mixture and reduce the leaching of sulfonic acid in methanol. Under the optimal condition with the presence of toluene, an 82.8% methyl stearate yield was obtained in the fifth run with the EL–MSA catalyst.

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Notes

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