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The *C*-Arylcalix[4]pyrogallolarene Sulfonic Acid: A Novel and Efficient Organocatalyst Material for Biodiesel Production

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Abstract

The synthesis of *C*-arylcalix[4]pyrogallolarene sulfonic acid derivatives and their application as the organocatalyst material for biodiesel production were investigated. The *C*-arylcalix[4]pyrogallolarene derivatives were prepared in high yields through a two-step reaction: condensation between pyrogallol and aromatic aldehydes (*i.e.* benzaldehyde, 4-hydroxy-3-methoxybenzaldehyde and 4-ethoxy-3-methoxy benzaldehyde) and then followed by a sulfonation reaction with sulfuric acid. They were evaluated as the organocatalyst for the esterification reaction of palmitic acid with methanol as the representation of biodiesel production. Using 4 mol% of *C*-4-hydroxy-3-methoxyphenylcalix[4]pyrogallolarene sulfonic acid, methyl palmitate was generated in up to 91.9% yield after 4 h at 65°C, making it similarly efficient to sulfuric acid that is used as the catalyst in the conventional reaction under similar conditions. However, different from sulfuric acid, the *C*-4-hydroxy-3-methoxyphenylcalix[4]pyrogallolarene sulfonic acid could be recovered by using a simple filtration technique making it is better than sulfuric acid from the industrial and environmental point of view. These results demonstrating that the *C*-arylcalix[4]pyrogallolarene sulfonic acid derivatives are a novel and potential organocatalyst for methyl palmitate biodiesel production.

Keywords: Calix[4]pyrogallolarene sulfonic acid, organocatalyst, biodiesel.

1. Introduction

Indonesia annually produced 33 million metric tons of palm oil in 2015, which accounted for 54% of global demand. In general, palm oil contains 44% of palmitic acid, 39% of oleic acid, 8% of linoleic acid and 6% of stearic acid.[1] Because of that, palm oil becomes as one of the most important feedstocks for biodiesel production, and it has been widely applied in the food, pharmaceutical and energy industries. Biodiesel is a form of renewable energy that attracts global attention because it is biodegradable, non-toxic, and environmentally friendly.[2] Biodiesel is usually produced by the esterification reaction of fatty acids with alcohol.[3,4]

Many researches have been carried out to develop and optimize biodiesel production. Arbain and Salimon (2011) used sulfuric acid and *p*-toluenesulfonic acid as homogenous catalysts for fatty acid esterification, however, these acids are corrosive and damaging to the environment.[5] Other catalysts, such as enzymes, inorganic polymers and mesoporous materials have been investigated, however, their catalytic performance is still unsatisfied for industrial use.[6-9] For example, Sherkhanov *et al.* (2016) employed the juvenile hormone acid *O*-methyltransferase from the fruitfly *Drosophila melanogaster* to produce fatty acid methyl esters, however, the amount of the produced biodiesel was too low.[6] Pappalardo *et al.* (2017) reported the esterification of palmitic acid with lipase enzyme, however, only 20.7% yield was obtained even after 24 h of reaction at 60°C.[7] Another drawback of enzymes is their high cost as well as low stability to pH and temperature changes. Other catalytic materials have been also been evaluated for biodiesel production. Grigoreva *et al.* (2014) employed H-beta zeolite as a heterogeneous catalyst for the esterification reaction of palmitic acid with methanol, however, the reaction yield was only 54% due to the unsuitable microporous size of the catalyst material for catalytic process.[8] Dang and Chen (2013) utilized Amberlite™ IR-120 (H) for the esterification reaction of palmitic acid with methanol.[10] Even though 98.3% yield of methyl palmitate was attained, the reaction required heating at 61°C at for 10.5 h which is time-consuming. Therefore, the development and optimization of new catalyst materials for biodiesel production are highly required.

Calix[4]arene derivatives have attracted interest for over a century due to their unique characteristics, particularly in the field of host-guest chemistry. The upper and lower rims of calix[4]arene derivatives can be modified to achieve specific purposes and applications.[11] Calix[4]arene derivatives have been exploited for molecular discrimination, as well as their catalytic activity for a wide variety of reactions such as indole and xanthone synthesis, nucleophilic substitution reactions of

alcohol, and heterocyclic coupling reactions.[12-20] Fernandes *et al.* (2012) reported that calix[4]arene sulfonic acid can be used to produce ethyl esters of various carboxylic acids in medium to high yield after 4 h.[21,22] According to Almeida *et al.* (2015), calix[4]arene sulfonic acids can be used as the organocatalysts due to the sulfonic acid group behaving as a Bronsted acid.[23] Calix[4]pyrogallolarenes, as one of the calix[4]arene subfamilies, have been reported for their application as metal ion adsorbents, gas adsorbents, chemosensors, as well as for their drug encapsulation and ion transport properties.[24-29] Therefore, the sulfonation of calix[4]pyrogallolarene was thought to potentially provide a novel organocatalyst material for the esterification of fatty acids for biodiesel production.

In this work, a series of calix[4]pyrogallolarene sulfonic acids were synthesized from pyrogallol and benzaldehyde derivatives, *i.e.* unsubstituted benzaldehyde, 4-hydroxy-3-methoxybenzaldehyde and 4-ethoxy-3-methoxy benzaldehyde. The reaction scheme is shown in Figure 1. The chemical structures of the synthesized products were characterized by FTIR, MS, ^{1}H-NMR and ^{13}C-NMR. The calix[4]pyrogallolarene sulfonic acid derivatives were investigated as organocatalysts for the esterification of palmitic acid, and the effect of the substituent on the benzaldehyde moieties on the catalytic activity was explored. The reaction time, catalyst loading, and temperature were also optimized to identify the best conditions for methyl palmitate production.

2. Experimental

Materials: Used materials in this work were purchased from Merck at analytical grade and used without any further purification.

Instrumentation: FTIR spectra were recorded using a Shimadzu Prestige 21. The purity and mass spectra of the products were determined from either GC-MS using a Shimadzu-QP 2010S with Agilent GC type 6890-MS type 5973 or LC-MS using Acquity HPLC-SQD. NMR spectra were recorded on ^{1}H- (500 MHz) and ^{13}C- (125 MHz) NMR JEOL JNM ECZ500R/S1. Morphological images and elemental analysis were recorded using Scanning Electron Miscrocpoe (SEM) with EDX (Phenom ProX). Particle size analysis was taken by Horiba Laser Scattering Particle Size Distribution Analyzer LA-960.

Synthesis of 4-ethoxy-3-methoxybenzaldehyde. Vanillin (3.8 g, 25 mmol) and sodium hydroxide (3.7 g, 93 mmol, 3.7 equivalents) were dissolved in distilled water (50 mL) and heated to 60°C. Diethyl sulfate (11.6 g, 75 mmol, 3 equivalents) was added dropwise and the mixture was refluxed for 2 h. After the reaction, the mixture was cooled to -15°C and left to stand for 24 h at -15°C. The precipitate formed was filtered to obtain 4-ethoxy-3-methoxybenzaldehyde as a yellow solid (3.3 g, 73% yield). Melting point: 58-60°C. FTIR (ν/cm^{-1}): 3078 (C-H sp^2), 2986 (C-H sp^3), 2855 and 2770 (C-H aldehyde), 1682 (C=O), 1589 and 1512 (C=C aromatic), and 1265 (C-O ether). GC: single peak at retention time (t_R) = 27.09 min. MS: 180 (M^+), 151 (base peak), 137, 123, 109, 95, 81, 65, 51, 29.

Synthesis of *C*-phenylcalix[4]pyrogallolarene (Calix-A). Benzaldehyde (1.6 g, 15 mmol) and pyrogallol (1.9 g, 15 mmol, 1 equivalent) were dissolved in ethanol (30 mL) and the mixture was stirred at room temperature. Concentrated hydrochloric acid (1.5 mL) was added dropwise into the mixture and the mixture was refluxed for 24 h. After the reaction, the mixture was cooled down to room temperature and stored for 24 h. The precipitate formed was filtered and washed with ethanol:distilled water 1:1 to obtain compound Calix-A as a pink solid (3.2 g, 99.7%). Melting point: >280°C. FTIR (ν/cm^{-1}): 3456 (O-H), 2924 (C-H sp^3), 1612 and 1504 (C=C aromatic), and 1285 (C-O ether). ^{1}H-NMR (δ/ppm): 5.62 (s, 4H, C-H methine), 6.19 (s, 4H, aromatic proton of pyrogallol), 6.66 and 6.86 (d and m, 20H, aromatic protons of benzaldehyde), 7.34 and 7.61 (s and s, 12H, OH). ^{13}C-NMR (δ/ppm): 35.20 (C-H methine), 119.04, 121.68 and 133.49 (aromatic carbons of benzaldehyde), 125.52, 128.22, 142.04 and 142.66 (aromatic carbons of pyrogallol). MS: found as 855.57 (M^+) for $C_{52}H_{40}O_{12}$.

Synthesis of *C*-4-hydroxy-3-methoxyphenylcalix[4] pyrogallolarene (Calix-B). Vanillin (2.3 g, 15 mmol) and pyrogallol (1.9 g, 15 mmol, 1 equivalent) were dissolved in ethanol (30 mL) and the mixture was stirred at room temperature. Concentrated hydrochloric acid (1.5 mL) was added dropwise into the mixture and the mixture was refluxed for 24 h. After the reaction, the mixture was cooled down to room temperature and stored for 24 h. The precipitate formed was filtered and washed with ethanol:distilled water 1:1 to obtain compound Calix-B as a pink solid (3.6 g, 93.3%). Melting point: >280°C. FTIR (ν/cm^{-1}): 3395 (O-H), 2924 (C-H sp^3), 1605 and 1512 (C=C aromatic), and 1273 (C-O ether). ^{1}H-NMR (δ/ppm): 3.17 (s, 12 H, OCH_3), 5.54 (s, 4H, C-H methine), 6.04 (s, 4H, aromatic proton of pyrogallol), 6.08-6.30 (m, 12H, aromatic protons of benzaldehyde), 7.76 and 7.95 (s and s, 12H, OH). ^{13}C-NMR (δ/ppm): 39.85 (C-H methine), 55.23 (OCH_3), 113.22, 114.01, 121.13, 121.57, 122.65 and 131.56 (aromatic carbons of benzaldehyde), 134.80, 141.30, 143.56 and 146.37 (aromatic carbons of pyrogallol). MS: found as 1054.09 $[M+14H]^+$ for $C_{56}H_{62}O_{20}$.

Synthesis of *C*-4-ethoxy-3-methoxyphenylcalix[4] pyrogallolarene (Calix-C). 4-Ethoxy-3-methoxybenzaldehyde (2.7 g, 15 mmol) and pyrogallol (1.9 g, 15 mmol, 1 equivalent) were dissolved in ethanol (30 mL) and the mixture was stirred at room temperature. Concentrated hydrochloric acid (1.5 mL) was added dropwise into the mixture and the mixture was refluxed for 24 h. After the reaction, the mixture was cooled down to room temperature and stored for 24 h. The formed precipitation was filtered and washed with ethanol:distilled water 1:1 to obtain compound C as a pink solid (4.3 g, 98.8%). Melting point: >280°C. FTIR (ν/cm^{-1}): 3456 (O-H), 2924 (C-H sp^3), 1628 and 1474 (C=C aromatic), and 1288 (C-O ether). ^{1}H-NMR (δ/ppm): 1.27 (t, 12H, $OCH_2C\mathbf{H}_3$), 3.16 (s, 12 H, OCH_3), 3.88 (q, 8H, $OC\mathbf{H}_2CH_3$), 5.74 (s, 4H, C-H methine), 6.02 (s, 4H, aromatic proton of pyrogallol), 6.19 and 6.28 and 6.41 (d and s and d, 12H, aromatic protons of benzaldehyde), 7.62 and 7.77 (s and s, 12H, OH). ^{13}C-NMR (δ/ppm): 15.05 ($OCH_2\mathbf{C}H_3$), 39.85 (C-H methine), 55.02 (OCH_3), 63.52 ($O\mathbf{C}H_2CH_3$), 111.64, 112.98, 131.65, 145.52 and 148.01 (aromatic carbons of benzaldehyde), 120.45, 121.62, 138.23 and 142.09 (aromatic carbons of pyrogallol).

Synthesis of *C*-phenylcalix[4]pyrogallolarene sulfonic acid (Calix-A-SA). Compound Calix-A (1.7 g, 2.0 mmol) was directly reacted with concentrated sulfuric acid (4.9 g, 50 mmol, 25 equivalent) at 80°C for 4 h. After the reaction, the mixture was cooled down to room temperature and the desired product was triturated from the mixture by using ethyl acetate:methanol 3:2 (50 mL). The precipitate obtained was dried to obtain Calix-A-SA as a black solid (1.9 g, 82.5%). Melting point: >280°C. FTIR (ν/cm^{-1}): 3372 (O-H), 2924 (C-H sp^3), 1597 and 1466 (C=C aromatic), 1157 (C-O ether), 1034 (S=O), 840 (S-O), and 579 (C-S). ^{1}H-NMR (δ/ppm): 4.11 (s, 4H, C-H methine), 6.73 (s, 4H, aromatic proton of pyrogallol), 7.26 and 7.69 (d and d, 16H, aromatic protons of benzaldehyde), 7.44 (q, 12H, C-OH), 8.30 (s, 4H, SO_3H).

Synthesis of *C*-4-hydroxy-3-methoxyphenylcalix[4] pyrogallolarene sulfonic acid (Calix-B-SA). Compound Calix-B (2.1 g, 2.0 mmol) was directly reacted with concentrated sulfuric acid (4.9 g, 50 mmol, 25 equivalent) at 80°C for 4 h.

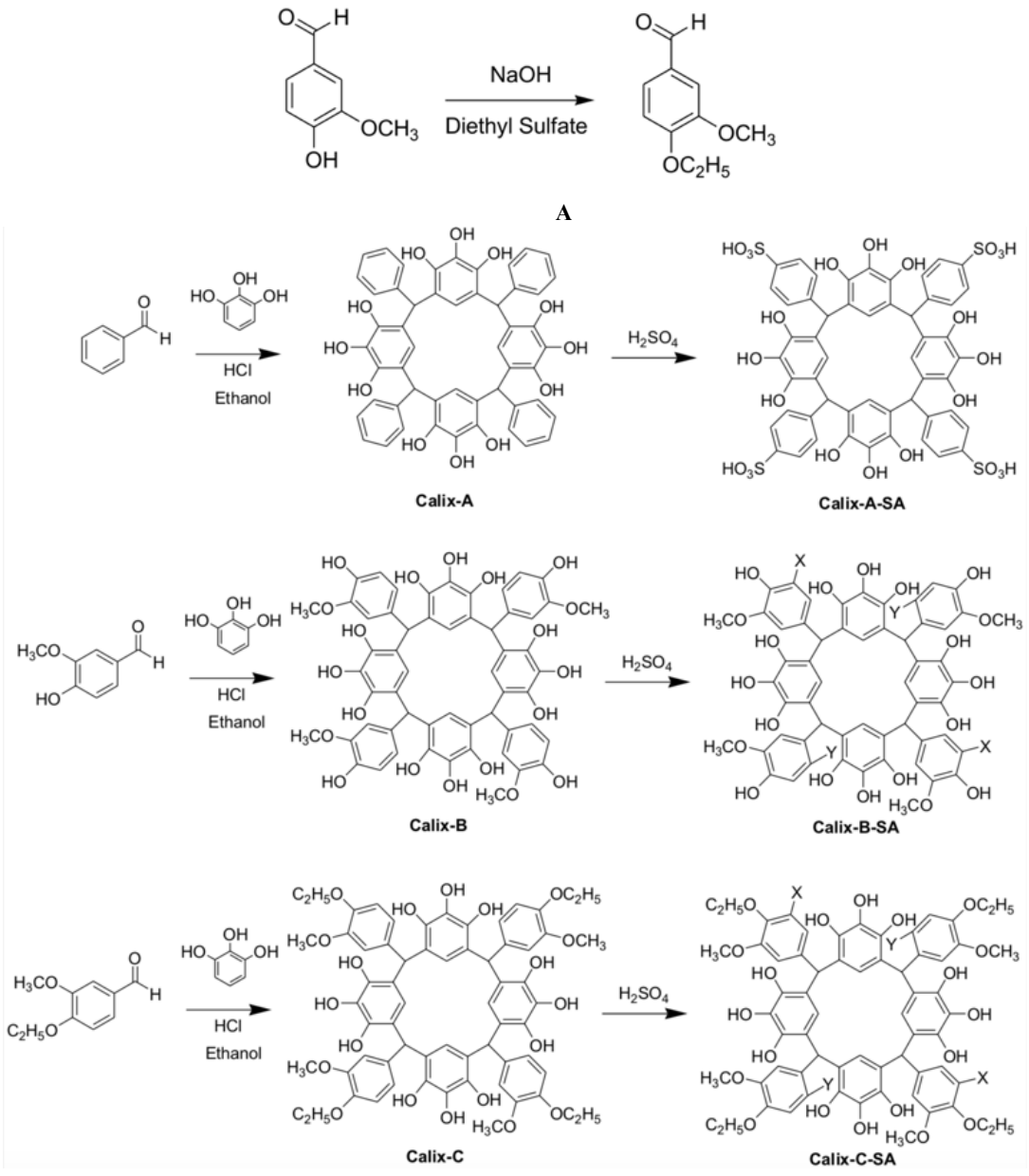


Figure 1. **(A)** Synthesis of 4-ethoxy-3-methoxybenzaldehyde and **(B)** Synthesis of *C*-arylcalix[4]pyrogallolarene sulfonic acid (Calix-A-SA, Calix-B-SA, Calix-C-SA) derivatives.

After the reaction, the mixture was cooled down to room temperature and the desired product was triturated from the mixture by using ethyl acetate:methanol 3:2 (50 mL). The precipitate obtained was dried to obtain B-SA compound as a black solid (2.4 g, 88.9%). Melting point: >280°C. FTIR (ν/cm^{-1}): 3387 (O-H), 2924 (C-H sp^3), 1620 and 1466 (C=C aromatic), 1173 (C-O ether), 1051 (S=O), 880 (S-O), and 579 (C-S). ^{1}H-NMR (δ/ppm): 3.74 (s, 12 H, OCH_3), 3.80-4.03 (broad singlet, 12H, C-H methane and C-OH), 7.01 (s, 4H, aromatic proton of pyrogallol), 7.09-7.41 (s and s and s, 8H, aromatic protons of benzaldehyde), 8.22 and 10.5 (s and s, 4H, SO_3H).

Synthesis of *C*-4-ethoxy-3-methoxyphenylcalix[4] pyrogallolarene sulfonic acid (Calix-C-SA). Compound Calix-C (2.3 g, 2.0 mmol) was directly reacted with concentrated sulfuric acid (4.9 g, 50 mmol, 25 equivalent) at 80°C for 4 h. After the reaction, the mixture was cooled down to room temperature and the desired product was triturated from the mixture by using ethyl acetate:methanol 3:2 (50 mL). The obtained precipitation was dried to obtain C-SA compound as a black solid (2.5 g, 85.3%). Melting point: >280°C. FTIR (ν/cm^{-1}): 3387 (O-H), 2924 (C-H sp^3), 1612 and 1466 (C=C aromatic), 1150 (C-O ether), 1034 (S=O), 856 (S-O), and 584 (C-S). ^{1}H-NMR (δ/ppm): 2.06 (t, 12H, $OCH_2C\mathbf{H}_3$), 3.74 (s, 12 H, OCH_3), 3.77-4.02 (broad singlet, 24H, $OC\mathbf{H}_2CH_3$, C-H methane and C-OH), 7.07 (s, 4H, aromatic proton of pyrogallol), 6.99-7.39 (m, 8H, aromatic proton of benzaldehyde), 8.10 and 10.2 (s and s, 4H, SO_3H). ^{13}C-NMR (δ/ppm): 15.05 ($OCH_2\mathbf{C}H_3$), 39.85 (C-H methine), 55.02 (OCH_3), 63.52 ($O\mathbf{C}H_2CH_3$), 111.64, 112.98, 131.65, 145.52 and 148.01 (aromatic carbons of benzaldehyde), 120.45, 121.62, 138.23 and 142.09 (aromatic carbons of pyrogallol).

Biodiesel production using *C*-arylcalix[4] pyrogallolarene sulfonic acid organocatalysts. Palmitic acid (0.6 g, 2.5 mmol) was dissolved in methanol (8.0 g, 250 mmol, 100 equivalent). Organocatalyst (Calix-A-SA, Calix-B-SA, or Calix-C-SA) (4 mol%) or concentrated sulfuric acid was added, and the mixture was heated at 65°C for 4 h. After the reaction, the mixture was cooled down to the room temperature and the organocatalyst was recovered by using a simple filtration method. The filtrate was neutralized with 10% sodium hydroxide in distilled water, extracted with ethyl acetate (3×10 mL) and the organic phase was washed with distilled water (10 mL) three times. The organic phase was dried over anhydrous sodium sulfate and the solvent was removed in vacuo to obtain methyl palmitate as a yellow liquid.. FTIR (ν/cm^{-1}): 2916 (C-H sp^3), 1743 (C=O), and 1332 (C-O ester). GC: single peak at retention time (t_R) = 39.64 min. MS: 270 (M^+), 239, 227, 199, 185, 171, 157, 143, 129, 115, 101, 87, 74 (base peak). The recovered calix-B-SA organocatalyst was re-used for the esterification of palmitic acid with methanol under the similar condition to afford methyl palmitate.

3. Results and Discussion

Synthesis of 4-ethoxy-3-methoxybenzaldehyde. The 4-Ethoxy-3-methoxybenzaldehyde has been successfully synthesized by the alkylation of vanillin with diethyl sulfate under alkaline condition in 73% yield (Figure 1). The consumption of the starting material was indicated by the absence of the hydroxyl stretching peak at 3600-3300 cm^{-1} in the FTIR spectrum. Furthermore, the FTIR spectrum of 4-ethoxy-3-methoxybenzaldehyde matched the reference spectrum of the standard compound. The purity of the product was confirmed by the appearance of a single peak on GC chromatogram at a retention time of 27.09 min. In the mass spectrum, the molecular ion peak was found at m/z = 180, and it fragmented by loss of an ethyl radical to give the base peak at m/z = 151.

Synthesis of Calix-A, Calix-B and Calix-C. Calix[4]pyrogallolarene A (Calix-A) was obtained in quantitative yield (99.7%) by reacting benzaldehyde and pyrogallol under acidic condition. As a homogenous acid catalyst, HCl protonates the carbonyl group of benzaldehyde to facilitate electrophilic substitution of the electron-rich pyrogallol. In the FTIR spectrum of the product, the C-H aldehyde peaks of benzaldehyde at 2738 and 2820 cm^{-1} disappeared. The existence of the methine bridges ins Calix-A was indicated by the presence of a singlet at 5.62 ppm in the ^{1}H-NMR spectrum and peak at 35.20 ppm in the ^{13}C-NMR spectrum. Further confirmation of the structure was provided by MS, which showed a peak at m/z = 855.57 corresponding to the molecular ion of Calix-A. Moreover, the purity of the product was confirmed using LC which showed a single peak with a retention time of 0.12 min.

Similarly, condensation reaction between vanillin and pyrogallol in the presence of ethanolic HCl produced calix-B as the product. The FTIR spectrum revealed the absence of the vanillin C-H aldehyde peaks at 2742 and 2848 cm^{-1}, indicating that the condensation reaction had occurred. The methine proton appeared at 5.54 ppm on the ^{1}H-NMR spectrum, while the methine carbon appeared at 39.85 ppm on the ^{13}C-NMR spectrum. The MS spectra found the $[M+14H]^+$ ion fragment for calix-B at m/z = 1054.09 at 14.32 minutes as the retention time. Therefore, the chemical structure of calix-B was confirmed from these FTIR, ^{1}H-NMR, ^{13}C-NMR and LC-MS elucidation analyses.

Meanwhile, Calix-C was prepared through a condensation reaction between 4-ethoxy-3-methoxy benzaldehyde and pyrogallol in similar fashion to above. The FTIR spectrum revealed the absence of C-H aldehyde peaks of 4-ethoxy-3-methoxybenzaldehyde at 2770 and 2855 cm^{-1}, while a new peak corresponding to the methine C-H appeared at 1466 cm^{-1}. Moreover, the methine group generated signals at 5.74 ppm in the ^{1}H-NMR spectrum and at 39.85 ppm on the ^{13}C-NMR spectrum. The FTIR, ^{1}H-NMR and ^{13}C-NMR analyses confirmed the chemical structure of either Calix-A or Calix-B or Calix-C in tetrameric macrocyclic structure.

Synthesis of Calix-A-SA, Calix-B-SA and Calix-C-SA. Sulfonation reaction of Calix-A with sulfuric acid gave Calix-A-SA in 82.5% yield. The existence of the sulfonic acid group was indicated by the presence of S=O absorption peaks at 1157 and 1034 cm^{-1}, an S-O absorption peak at 840 cm^{-1} and a C-S absorption peak at 579 cm^{-1} in the FTIR spectrum. Furthermore, a new singlet appeared at 8.30 ppm in the ^{1}H-NMR spectrum with an integration ratio of 4, suggesting that each benzaldehyde ring contained one sulfonic acid group. Moreover, as the other aromatic protons of the benzaldehyde group appeared as a set of two doublets at 7.26 and 7.44 ppm (each 2H), it was deduced that the sulfonic acid group was located at the *para* position.

Calix-B-SA was synthesized from the sulfonation reaction of Calix-B with sulfuric acid. The FTIR spectrum of the product showed S=O peaks at 1173 and 1051 cm^{-1}, an S-O peak at 880 cm^{-1}, and a C-S peak at 579 cm^{-1}. The protons of the -SO_3H group appeared as two distinct signals at 8.22 and 10.45 ppm in the ^{1}H-NMR spectrum, suggesting that the sulfonic group was not located in the same position for each aromatic ring.

Similarly, Calix-C-SA was produced by the sulfonation of Calix-C with sulfuric acid. The FTIR spectrum revealed the appearance of new peaks at 1150 and 1034 (S=O), 856 (S-O) and 584 (C-S) cm^{-1}. Similar to Calix-B-SA, the ^{1}H-NMR spectrum showed two new singlet peaks at 8.10 and 10.2 ppm belonging to the -SO_3H group. Therefore, the spectrometry analysis confirmed the chemical structure of Calix-A-SA, Calix-B-SA and Calix-C-SA, demonstrating that they have been successfully synthesized.

Biodiesel production by using Calix-SA as the novel organocatalyst material. In this work, a preliminary study of biodiesel production was carried out by using palmitic acid as a representative fatty acid as it is found as a major component of palm oil. Hence, the Calix-SA products were evaluated as organocatalysts for the esterification of palmitic acid with methanol. Concentrated sulfuric acid was used as a comparative control. The effect of reaction time (1, 2, 4 or 8 h) on the yield of the esterification reaction of palmitic acid was first investigated. Under these conditions, all catalysts gave the highest yield of methyl palmitate at 4 h reaction time as shown in Figure 2(a). Moreover, the yield did not increase when the reaction was extended to 8 h. At 4 h reaction time, Calix-A-SA, Calix-B-SA, Calix-B-SA, and sulfuric acid gave 80.0, 88.9, 85.9 and 93.3% yield of methyl palmitate respectively, which is remarkable.

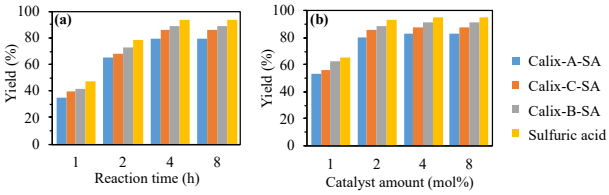


Figure 2. (a) Effect of the reaction time on the yield of methyl palmitate. Catalyst amount: 2 mol%. Reaction temperature: 65°C. (b) Effect of the catalyst loading on the yield of methyl palmitate. Reaction time: 4 h. Reaction temperature: 65°C.

The effect of the catalyst amount in methyl palmitate production was next investigated. It was found that the optimum

amount of all the catalyst materials was 4 mol% at a temperature of 65°C and a reaction time of 4 h as shown in Figure 2(b). Under these conditions, Calix-A-SA, Calix-B-SA, Calix-B-SA, and sulfuric acid gave 83.0, 91.9, 87.4 and 94.8% yields of methyl palmitate, respectively. Furthermore, yields did not improve when the catalyst amount was increased up to 8 mol%. This remarkable catalytic activity reflected the advantages of using calix[4]pyrogallolarene framework, such as preorganized structure with multiple phenolic functional groups and the existence of pKa values enhance the acidity properties of the calix[4]pyrogallolarene.

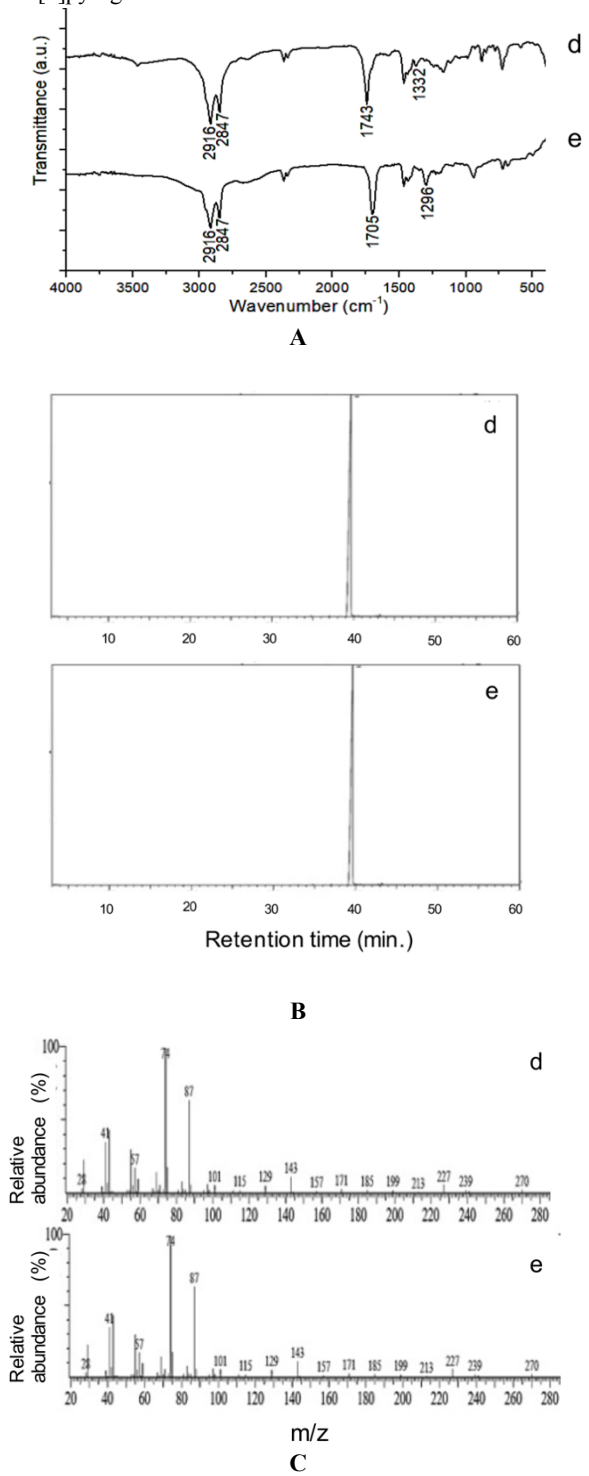


Figure 3. (**A**) The FTIR spectra, (**B**) GC chromatograms and (**C**) MS spectra of the obtained methyl palmitate in the present work (d), and the standard methyl palmitate (e).

The produced methyl palmitate was characterized by FTIR and GC-MS together with the standard methyl palmitate as a comparison. The FTIR and GC-MS spectra of the synthesized methyl palmitate and the standard methyl palmitate are shown in Figure 3. For both the products and the standard, the C-H, C=O and C-O stretching peaks were found at 2916 and 2847, 1705-1745 and 1296-1332 cm^{-1}, respectively, in the FTIR analysis, with only slight differences between both spectra. Furthermore, the purity of the synthesized methyl palmitate was confirmed in 100% purity by the appearance of a single peak in GC chromatogram, which matched the retention time of the standard (39.64 min)[1]. Furthermore, the MS spectra of both compounds gave signals at m/z = 270 for the molecular ion and at m/z = 74 for the base peak. Fragmentation of the molecular ion produced signals at m/z = 227 (loss of ethyl radical) and m/z = 239 (loss of methyl radical). The molecular ion also underwent the McLafferty rearrangement to produce the fragment $C_3H_6O_2^+$ at m/z = 74, which was the base peak.

These results also suggested that the presence of hydroxyl and alkoxy groups on the benzaldehyde scaffold influence the catalytic activity of *C*-arylcalix[4]pyrogallolarene sulfonic acids. Calix-B-SA, with a hydroxy group and a methoxy group on each benzaldehyde ring, exhibited the best catalytic activity out of the three novel organocatalysts synthesized. This could be due to the ability of Calix-B-SA to undergo more hydrogen bonding with either palmitic acid or methanol compared to Calix-A-SA or Calix-C-SA. Moreover, the phenolic group on Calix-B-SA can also function as a Bronsted acid to catalyze the reaction. All of the organocatalysts showed slightly lower (less than 10%) catalytic activity than sulfuric acid. However, it should be noted that the *C*-arylcalix[4]pyrogallolarene sulfonic acids could be easily recovered by filtration after the completion of the esterification reaction, while the sulfuric acid could not and may pollute the environment.

Since Calix-B-SA exhibited the best catalytic activity, the effect of the reaction temperature on the esterification of palmitic acid was further investigated. The yield of methyl palmitate at 50, 55, 60 and 65°C were 32.6, 63.7, 84.4 and 91.9%, respectively. This is likely because esterification reaction is an endothermic process as well as the reaction rate is higher at higher temperature, therefore the yield was increased by increasing reaction temperature. From the overall results of this work, it was concluded that the optimum reaction conditions for the esterification of palmitic acid with methanol are catalyst loading of 4 mol% Calix-B-SA, a temperature of 65°C, and a reaction time for 4 h.

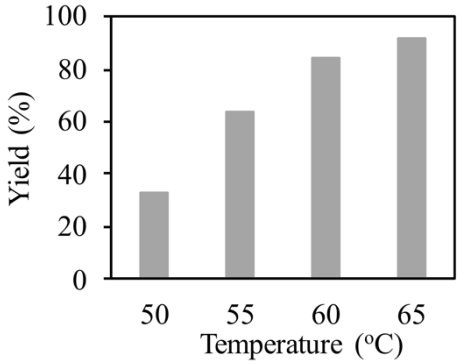


Figure 4. Effect of the reaction temperature on the yield of the esterification of palmitic acid with Calix-B-SA as the catalyst. Catalyst amount: 4 mol%. Reaction time: 4 h.

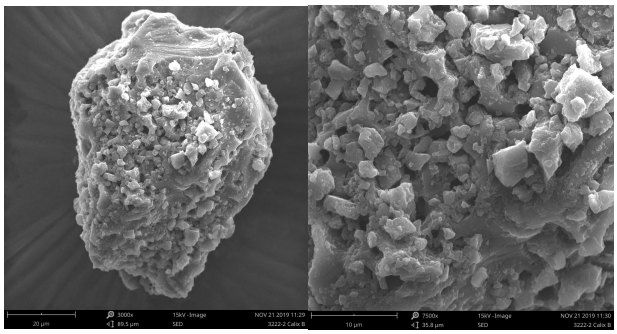
The comparison of catalytic performance for the esterification of palmitic acid with methanol is shown in Table 1. The Calix-B-SA organocatalyst exhibits higher catalytic activity

for methyl palmitate biodiesel production compared with most of the previously reported works. It should be noted that while some reported catalysts showed higher yields of methyl palmitate (Entries 4, 6 and 10), they also needed longer reaction times and/or higher reaction temperature. For example, PW 12/Al-SBA-15 and $[GlyH]_{1.0}H_{2.0}PW_{12}O_{40}$ catalysts gave higher reaction yields of 98.0% and 93.3% respectively, but both required high temperature reactions (≥ 90°C) which is energy-consuming (Entries 6 and 10). Moreover, the Amberlite™ IR-120 catalyst gave 98.3% yield after a long reaction time of 10.5 h, which is undesirable for industrial applications. Notably, Calix-B-SA also gave slightly higher yields than the *p*-sulfonic acid calix[n]arenes reported earlier (Entries 12 and 13).

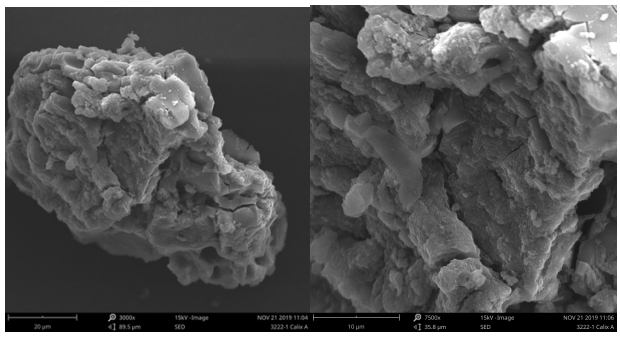
Table 1. Comparison of catalytic methods for methyl palmitate ester biodiesel production.

Catalyst	Temperature (°C)	Reaction Time (h)	Yield (%)	Ref.
Novozym 435	60	24	20.7	7
H-Beta Zeolite	117	3	54.0	8
Zirconia sulphate	60	8	90.7	9
Amberlite™ IR-120	61	10.5	98.3	10
Mesoporous Al-MCM-41	130	2	79.0	30
PW 12/Al-SBA-15	100	8	98.0	31
Phosphotungstic acid-based poly(ionic liquid)	65	8	91.6	32
O.O5SZ	60	6	40.0	33
WO_x/ZrO_2	60	6	30.0	34
$[GlyH]_{1.0}H_{2.0}PW_{12}O_{40}$	90	3	93.3	35
WS_2	60	6	70.0	36
p-Sulfonic acid calix[4]arene	50	6	91.0	22
p-Sulfonic acid calix[6]arene	50	6	90.0	22
p-Hydroxybenzene sulfonic acid	50	6	31.0	22
p-Toluenesulfonic acid	50	6	20.0	22
Sulfuric acid	65	4	94.8	Present
Calix-A-SA	65	4	83.0	Present
Calix-B-SA	65	4	91.9	Present
Calix-C-SA	65	4	87.4	Present

The surface morphology of calix-B-SA and recycled calix-B-SA was measured by SEM (Figure 5). The surface of calix-B-SA and recycled calix-B-SA both exhibited irregular shapes. In addition, the SEM images also showed that the recycled calix-B-SA formed a bigger degree of aggregation in comparison to that of calix-B-SA. In term of particle size, the results of measurement using Static Light Scattering method indicated that the particle size of recycled calix-B-SA (17.08 μm) was smaller than that of calix-B-SA (42.51 μm). This fact is consistent to the result of sulfur content measurement using SEM-EDX which showed that the sulfur content of the recycled calix-B-SA was smaller (2.91%) than that of calix-B-SA (10.25%).



A



B

Figure 5. SEM Image of (A) Calix-B-SA and (B) recycled Calix-B-SA

This findings perhaps showed that some sulfonic acid groups of the calix-B-SA have undergone desulfonation during the esterfication process. Such a phenomenon is not surprising as there have been some reports describing the occurrence of desulfonation reaction of aromatic sulfonic acids under the influence of heat or water.[37] When the recycled calix-B-SA was used for the esterification of palmitic acid with methanol under the same condition as that of calix-B-SA, an 88.8% yield of biodiesel was obtained which was only slightly lower than that of calix-B-SA (92.8%). Again, this finding is perhaps attributed by the lower sulfur content of the recycled calix-B-SA in comparison to that of calix-B-SA. Furthermore, the formation of bigger aggregates of the recycled calix-B-SA in compariosn to those of calix-B-SA was another reason of the slightly lower yield of methyl palmitate catalyzed by recycled calix-B-SA compared to that of calix-B-SA.

4. Conclusion

Three *C*-arylcalix[4]pyrogallolarene derivatives and three *C*-arylcalix[4]pyrogallolarene sulfonic acid derivatives were successfully synthesized in high to quantitative yields (82.5-99.7%). The structure and purity of the products were confirmed by FTIR, GC-MS or LC-MS, ^{1}H-NMR and ^{13}C-NMR. The *C*-arylcalix[4]pyrogallolarene sulfonic acid derivatives were tested as the organocatalyst material for the esterification reaction of palmitic acid and methanol into methyl palmitate. Among these, Calix-B-SA emerged as the most efficient organocatalyst, giving 91.9% yield of methyl palmitate at 65°C for 4 h with a catalyst loading of 4 mol%. Compared with sulfuric acid or other reported catalytic methods in the literature, the prepared calix[4]pyrogallolarenes showed a desirable combination of efficient activity at relatively low temperatures and short reaction times, as well as recoverability. Therefore, these

findings are useful for organocatalyst design from available natural products, and may also provide new scaffolds for large scale biodiesel production process because of their promising catalyst activity.

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