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Development of Carbon-Based Solid Acid Catalysts Using a Lipid-Extracted Alga, *Dunaliella tertiolecta*, for Esterification

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This paper is dedicated to the memory of Dr. Dong-Ho Seong, who devoted his life to developing microalgal biodiesel at National Marine Bioenergy R&D Consortium.

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Novel carbon-based solid acid catalysts were synthesized through a sustainable route from lipid-extracted microalgal residue of *Dunaliella tertiolecta*, for biodiesel production. Two carbon-based solid acid catalysts were prepared by surface modification of bio-char with sulfuric acid (H_2SO_4) and sulfuryl chloride (SO_2Cl_2), respectively. The treated catalysts were characterized and their catalytic activities were evaluated by esterification of oleic acid. The esterification catalytic activity of the SO_2Cl_2-treated bio-char was higher (11.5 mmol Prod.·h^{-1}·g Cat.$^{-1}$) than that of commercial catalyst silica-supported Nafion SAC-13 (2.3 mmol Prod.·h^{-1}·g Cat.$^{-1}$) and H_2SO_4-treated bio-char (5.7 mmol Prod.·h^{-1}·g Cat.$^{-1}$). Reusability of the catalysts was examined. The catalytic activity of the SO_2Cl_2-modified catalyst was sustained from the second run after the initial activity dropped after the first run and kept the same activity until the fifth run. It was higher than that of first-used Nafion. These experimental results demonstrate that catalysts from lipid-extracted algae have great potential for the economic and environment-friendly production of biodiesel.

Keywords: Bio-char catalyst, biodiesel, microalgae, lipid-extracted algae, esterification

Introduction

The development of clean and alternative renewable energy resources, capable of fulfilling increasing energy demands, has been extensively investigated owing to increased concern about depleted fossil fuels and elevated CO_2 levels in the atmosphere [1, 2]. Among various alternative energies, biodiesel is one of the most promising and readily available alternatives because of its chemical similarities to petroleum diesel, indicating applicability to current diesel engines without major engine modification [3]. Currently, most of the biodiesel has been produced from edible vegetable and animal oils, but they possess serious concerns and drawbacks, including ethical issues, land use, and environmental degradation [4, 5]. In this regard, microalgae have been recognized as a promising bioresource for biodiesel feedstock owing to its superior characteristics, such as fast growth rate, high lipid content, *etc*. [6–9].

Although some microalgae are capable of accumulating biodiesel-convertible lipid up to 70% within their body, some fatty acids exist in the form of free fatty acid (FFA) [10]. It possibly interferes with the transesterification process. Thus, currently used base catalysts such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) are unsuitable for transesterification of microalgal oils, because their use may cause undesired soap (saponification), indicating the requirement of an additional separation process [11–13]. Acid catalysts like sulfuric acid, capable of simultaneously catalyzing esterification and transesterification, would be preferable and better than base catalysts [14, 15] since acid catalysts do not reveal measurable susceptibility to FFA. However, the problem is that acid catalysts are less active than base catalysts, especially in transesterification.

Moreover, use of homogeneous acid catalysts requires a downstream process for separation and neutralization of the acid [16, 17].

Heterogeneous catalysts (*i.e.*, solid catalysts) act in a different phase with the reaction mixture, unlike homogeneous ones [17, 18]. They are more environmentally friendly for the biodiesel conversion process owing to easy separation, possibility of recycling, and low toxicity. There are several reported heterogeneous catalysts for biodiesel production, such as zeolites (La/zeolite beta), MCM-41, Amberlyst-15, Nafion, and niobic acids [19, 20]. However, their high cost has hampered their commercial and wide applications [21, 22].

Sulfonated carbon-based solid acid catalysts using various waste materials have received much attention recently owing to their good performance in active site stability and esterification activity as well as low costs [21, 23–25]. The carbon-based catalysts are prepared by incomplete carbonization using various rigid carbon materials (*e.g.*, sugar, starch, wood powder, bio-char, *etc*.) that are composed of small polycyclic aromatic carbon sheets with carbonyl groups and phenolic groups [20]. These materials form stable solids with a high density of active sites by oxidizing the aliphatic CH_3/CH_2 groups to carboxylic acid and introducing an SO_3H group via sulfonation [14, 20, 25]. These materials have lower production cost compared with other solid acid catalysts, such as strong acidic cation-exchangeable resins, (*e.g.*, Nafion). Furthermore, their esterification of oleic acid is comparable to that with sulfuric acid and they are easily recycled via a simple washing process [26].

In this study, we developed solid acid catalysts prepared by residual microalgal biomass after lipid extraction for acid esterification of microalgal oils, because using microalgal residue as a biodiesel production catalyst would add environmental and economic value to microalgal biodiesel production. Two reagents (sulfuric acid (H_2SO_4) and sulfuryl chloride (SO_2Cl_2)), with different surface modification mechanisms, were used to introduce desirable functional groups to the bio-char. The properties of prepared catalysts were characterized and then compared. Their reusability as well as catalytic activities were determined for esterification of oleic acid and compared with a commercial sulfonated tetrafluoroethylene catalyst, Nafion SAC-13. The catalyst reusability was investigated through five consecutive runs.

Materials and Methods

Preparation of Solid Acid Catalysts

Dunaliella tertiolecta LB 999 used in this study was purchased from the Culture Collection of Algae at the University of Texas at Austin (USA). Cells were incubated in a 0.5 L bubble column photobioreactor containing 0.4 L of 3-fold f/2-Si medium at 20°C, under continuous illumination from fluorescent lamps at 100 $\mu E \cdot m^{-2} \cdot s^{-1}$, at 0.1 VVM aeration with 2% CO_2 enriched air.

Solid acid catalysts were prepared as follows: (i) 500 g of dried *D. tertiolecta* was mixed with 1.5 L of a mixture of methanol-chloroform (2:1 (v/v)) in a 2-L round flask and incubated at 60°C for 2 h to extract lipids. (ii) Lipid-extracted algal (LEA) cells were obtained after vacuum filtration. (iii) The LEA cells pyrolized in a 100-ml round flask at 400°C under a nitrogen stream for 2.5 h to make bio-char (refer to Fig. 1). (iv) The bio-char was ground to powder using a mortar and pestle. (v) Surface modifications of the bio-char were conducted using two different sulfonating agents, H_2SO_4 and SO_2Cl_2, respectively.

For sulfonation of the bio-char, 40 ml of H_2SO_4 (98%) and 40 ml of SO_2Cl_2 (97%) were added to a 100-ml round flask containing 4 g of bio-char and the mixture was kept at 150°C under a nitrogen

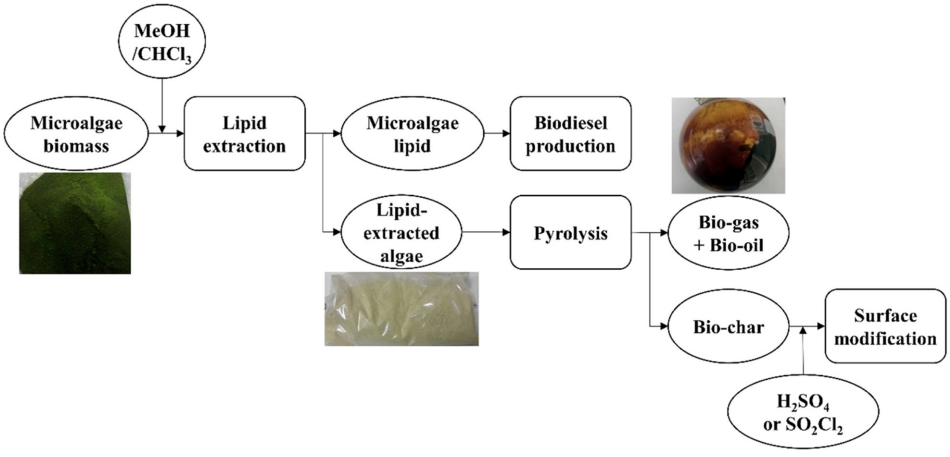

Fig. 1. Scheme of the preparation of sulfonated microalgae residue-based catalysts using H_2SO_4 and SO_2Cl_2.

stream for 1.5 h, respectively. After adding 50 ml of methanol to the suspension, it was centrifuged at 3,000 ×*g* for removing acidic residue. After the sulfonation, the suspension was washed with methanol to remove acidic residue. The product was collected and oven-dried at 40°C overnight to obtain the sulfonated microalgae residue-based catalyst. The resulting bio-chars sulfonated by H_2SO_4 and SO_2Cl_2 were named as CAT_H and CAT_S. Nafion SAC-13, a commercially available catalyst, was used as a control to compare catalytic activity and reusability with the CATs. Reagents used in this study were of analytical grade and purchased from Sigma-Aldrich (USA).

Analytical Studies

The physical and chemical characteristics of the solid acid catalysts were investigated. The LEA cell-derived solid acid catalysts were analyzed using X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform-infrared spectroscopy (FT-IR), elementary analysis, and an acid-base back titration method [11, 13, 17].

XRD is one of the most commonly used techniques for crystalline phase identification [25]. The CAT powders were characterized by XRD analysis (D/MAX-2500, Rigaku Co., Japan) using Cu/Kα radiation with a 1.54 Å wavelength. Diffractograms were recorded in the 2θ range of 10° to 90° (20 kV, 20 mA).

Visual observation of CAT_H and CAT_S via SEM (Hitachi S-4200, Hitachi Co., Japan) was conducted to gain insight into the catalyst morphology and particle size. Samples were observed with the same acceleration voltage of 20 kV.

The presence of functional groups on the surface of each catalyst was analyzed using FT-IR spectroscopy, conducted using a Bruker VERTEX 80V FT-IR vacuum spectrometer (Bruker Co., USA) equipped with attenuated total reflectance in the range of 400–4,000 cm^{-1}.

Carbon, hydrogen, nitrogen, sulfur, and oxygen contents of the bio-char-based catalysts were determined by an elemental analyzer (Thermo Fisher Scientific Inc., USA).

The total acid density of CAT_H and CAT_S was determined using the standard acid-base back titration method. The CATs were oven-dried at 40°C overnight prior to analysis, and then 50 mg of catalyst was placed in 30 ml of 0.1 N NaOH and stirred for 30 min before back titration with 0.1 N HCl. The titration was conducted three times independently. The main contributed acids to the total acid density in a bio-char are groups of sulfur-containing carboxylic and phenolic groups. As reported by Mo *et al*. [20], the SO_3H group strongly contributes to the esterification reaction of fatty acids compared with the other acidic groups (*i.e.*, carboxyl (-COOH) and phenolic (-OH)). To measure the density of groups containing sulfur in each catalyst as well as the total acid density, catalyst samples were subjected to elemental analysis.

Catalytic Activity

The catalytic activity was examined through esterification of oleic acid using methanol. Esterification was conducted at 65°C using a 10% (w/v) oleic acid/methanol mixture with a catalyst concentration of 5% (w/w) for 30 min. The performance of Nafion, a commercial acid catalyst, was measured as a control under the same reaction condition. Samples drawn from the reaction mixture were centrifuged to separate catalyst traces, and the product was analyzed using a gas chromatograph equipped with a flame ionized detector (YL6500 GC, Young Lin Instrument Co., Ltd., Korea). The catalytic activity was defined as the rate of methyl oleate formation per gram of catalyst. The following equation was used to calculate the catalytic activity.

$$\text{Catalyst activity (mmol Prod.}\cdot h^{-1}\cdot\text{g Cat.}^{-1}) = \frac{\text{Produced methyl oleate (mmol)}}{\text{Reaction time (h)}} \times \frac{1}{\text{Catalyst (g)}}$$

Catalyst Reusability

Recycling catalyst is crucial as it reduces the overall cost of biodiesel production. The economic efficiency of the catalyst depends on its reusability. To evaluate the reusability of the CATs and Nafion, the used catalysts were collected and washed with methanol and *n*-hexane without regeneration by an acid agent.

Results and Discussion

Catalyst Synthesis and Refinement

In this study, we used two different reagents (sulfuric acid and sulfuryl chloride) to functionalize the bio-char for esterification of fatty acids. Through synthesis and refinement of the catalysts, we obtained 0.18 g of CAT_H and 0.30 g of CAT_S from 1 g of lipid-extracted algal biomass, respectively. The obtained catalysts were characterized to establish their physical and chemical characteristics as described below.

Characteristics of the Carbon-Based Acid Catalysts

The structure and morphology of the catalysts (CAT_H and CAT_S) were determined by X-ray diffraction. As shown in Fig. 2, the catalysts exhibited one broad C (002) diffraction peak at the 2θ angle of 15–30°, attributable to amorphous carbon composed of aromatic carbon sheets oriented in a considerably unordered form [27]. The major pattern of CAT_H and CAT_S was similar, but the intensity was different depending on the surface modification reagents used. The diffraction peak of CAT_S presented a further disrupted structure with a large surface area compared with that of CAT_H [28].

SEM images for CAT_H and CAT_S after being sulfonated at 150°C for 1.5 h using two different chemical agents are shown in Fig. 3. The images reveal the irregular surface of the acid catalysts and different morphology. The SEM

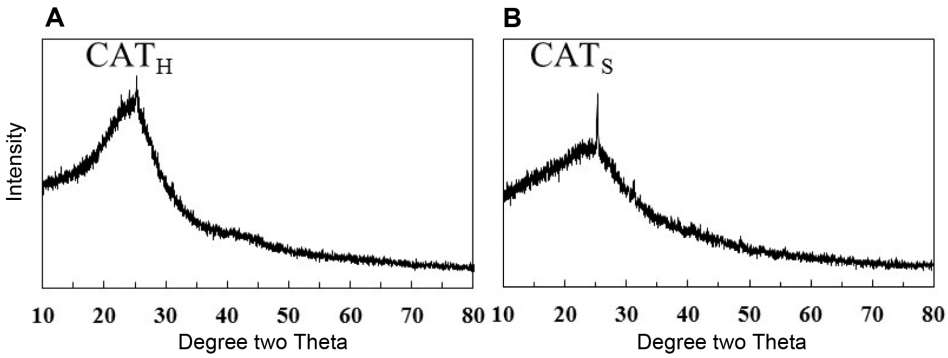

Fig. 2. X-ray diffraction patterns of catalysts CAT_H (**A**) and CAT_S (**B**).
The diffractograms were recorded in the 2θ range of 10° to 90° (20 kV, 20 mA).

image of CAT_S exhibited well-developed cubic crystals compared with those of CAT_H, which corresponded to the XRD analysis. It indicates that the smaller particle sizes (*i.e.*, large surface area) could improve intraparticle diffusion of the reactants, contributable to higher catalytic activities [30].

Corresponding FT-IR absorption spectra of the bio-char, CAT_H, and CAT_S are shown in Fig. 4. These can be related to the spectra library or from published literature to identify the functional group or structure of the sample being analyzed [30]. The formation of the sulfonated complex was confirmed by the FT-IR spectrum of CAT_H. As can be seen in Fig. 4, peaks at 1,122 cm^{-1}, and 1,200 and 1,363 cm^{-1}, corresponding to sulfone and sulfonate stretching, respectively, were detected, indicating that the bio-char was successfully sulfonated through sulfuric acid treatment. Peaks at 1,060, 1,161, and 1,202 cm^{-1}, corresponding to sulfate stretching, were detected in CAT_S. The result indicates that a bidentate sulfate complex was formed by sulfuryl chloride treatment. It seems that the sulfate complex could be formed by elimination of HCl between the SO_2Cl_2 and OH groups of the bio-char surface [29].

The prepared carbon-based acid catalysts and bio-char were characterized by elemental analysis and total acid density. Total acid density, constituting the Brönsted acid site, was measured using an acid-base back titration method. According to reports [22, 31], only sulfur-containing groups have sufficient acid strength to contribute significantly to the reaction. Carboxyl and hydroxyl groups do not have sufficient acid strength to catalyze the esterification reaction. Thus, the density of groups containing sulfur

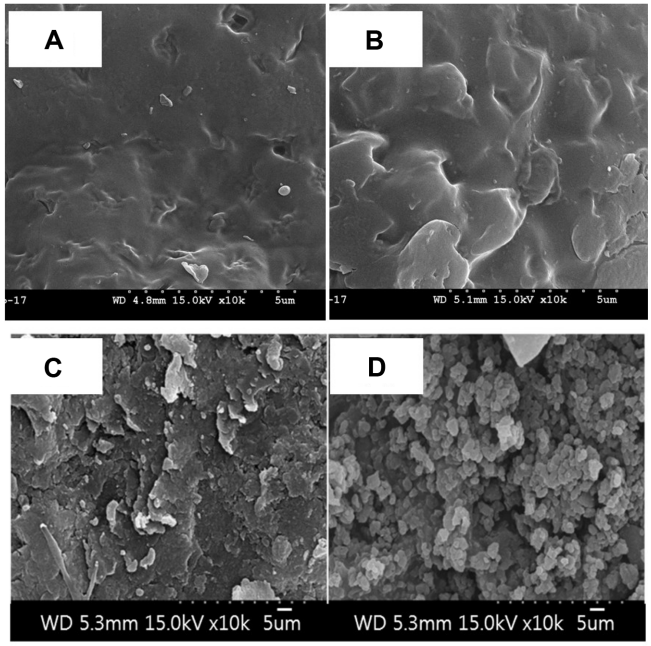

Fig. 3. SEM micrographs of lipid-extracted algal cells (**A**), bio-char (**B**), CAT_H (**C**), and CAT_S (**D**).
Samples were observed with the same acceleration voltage of 20 kV. Scale bars present 5 μm.

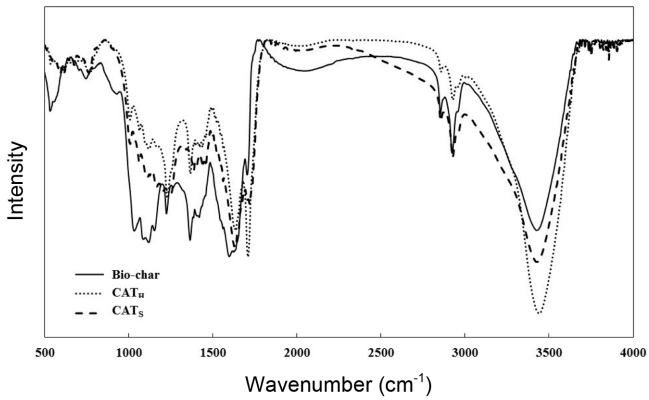

Fig. 4. FT-IR spectra of microalgal bio-char, CAT_H, and CAT_S.

Table 1. Elemental composition (%, w/w) of bio-char, CAT_H, and CAT_S.

	Elemental composition (%, w/w)				
	C	H	O	N	S
Bio-char	60.8 ± 0.9	4.7 ± 0.1	14.0 ± 1.7	11.4 ± 0.2	0.2 ± 0.2
CAT_H	54.1 ± 1.2	2.9 ± 0.2	21.1 ± 0.9	8.1 ± 0.5	1.5 ± 0.2
CAT_S	49.7 ± 0.7	3.0 ± 0.2	14.5 ± 1.2	7.8 ± 0.4	1.5 ± 0.1

could be considered as a main contributor to determine the catalytic activity of CATs. Additionally, as shown in Table 1, the sulfur (S) contents in bio-char and CAT_H (before and after sulfonation) were 0.24% and 1.50% respectively. The total acid density of CAT_H (Fig. 5) increased from 0.7 ± 0.2 mmol·g^{-1} to 4.2 ± 0.1 mmol·g^{-1}. Likewise, the S content of CAT_S increased from 0.24% to 1.54% after sulfation. The total acid density of CAT_S increased from 0.7 ± 0.2 mmol·g^{-1} to 4.6 ± 0.1 mmol·g^{-1}. These results are much higher than that of Nafion (1.2 ± 0.1 mmol·g^{-1}). This indicates the increased S content in CATs was closely related to the total acid density. The results exhibit successful formation of active sites on the CATs by the surface modification process.

Catalyst Activity

To evaluate the catalytic activity of CAT_H and CAT_S, esterification of oleic acid in the presence of methanol was examined. As mentioned in the Materials and Methods section, the catalytic activity of CATs was defined as the rate of formation of methyl oleate per gram of catalyst. To exclude contributions from potential non-catalytic reactions, blank esterification reactions of oleic acid with methanol were conducted at 65°C in the absence of the catalyst. Negligible activity was observed in all cases (data not shown). To provide a better comparison of the catalytic performance of these catalysts, a commercial acid catalyst, Nafion SAC-13, was tested under the same reaction condition. As shown in Fig. 6, CAT_S revealed the highest esterification activity of oleic acid (11.5 ± 1.3 mmol Prod.·h^{-1}·g Cat.$^{-1}$) in comparison with Nafion (2.3 ± 0.1 mmol Prod.·h^{-1}·g Cat.$^{-1}$) and CAT_H (5.7 ± 0.3 mmol Prod.·h^{-1}·g Cat.$^{-1}$). Although CAT_H and CAT_S have similar acid density (4.2 mmol·g^{-1} and 4.6 mmol·g^{-1}, respectively), CAT_S exhibited approximately 2 times higher catalytic activity than CAT_H due to super acid sites of the CAT_S (*i.e.*, bidentate sulfate complex on the surface of bio-char) [29]. Thus, the difference in catalytic activity between CAT_H and CAT_S is mainly attributed to the acid strength of the catalysts [29, 31].

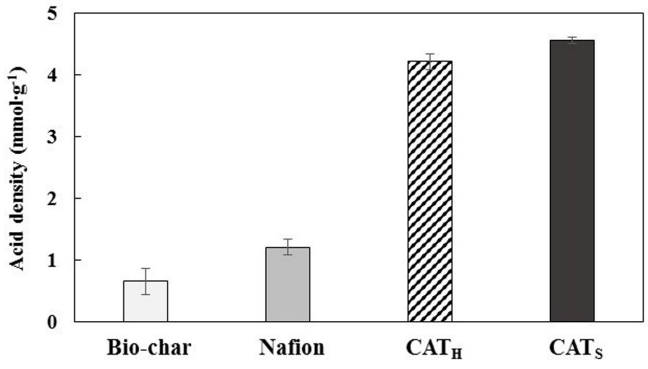

Fig. 5. Total acid density of Nafion, bio-char, CAT_H, and CAT_S.

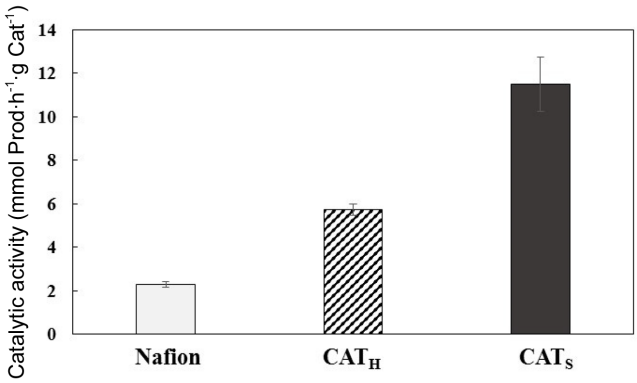

Fig. 6. A comparison of the catalytic activity of oleic acid with methanol by Nafion, CAT_H, and CAT_S.

The catalytic activity was examined through esterification of oleic acid using methanol. Esterification was conducted at 65°C using a 10% (w/v) oleic acid/methanol mixture with a catalyst concentration of 5% (w/w) for 30 min.

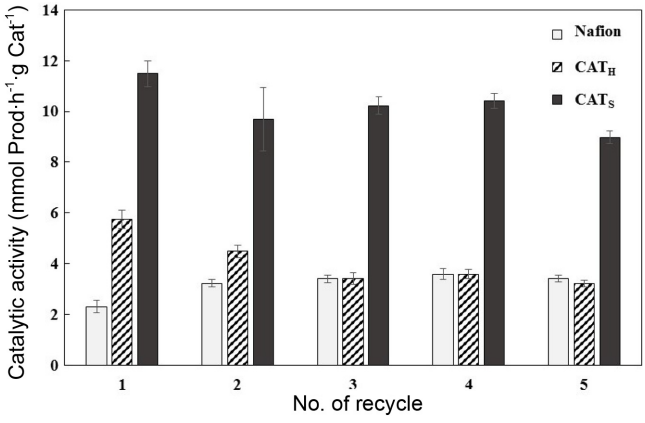

Fig. 7. Reusability of the lipid-extracted algae-derived solid catalysts.

Catalyst Reusability

One of the distinctive advantages of heterogeneous acid catalysts over liquid acids is that the used catalyst can be easily recovered from the reaction mixture and can be potentially regenerated and reused [28]. Catalyst recycling is a crucial step as it reduces the cost of biodiesel production. The efficiency of the catalyst depends on its reusability. To evaluate reusability, the prepared catalysts and Nafion were used in the esterification of oleic acid for five consecutive runs without regeneration. Results are presented in Fig. 7. The catalytic activity of both CATs was decreased and that of Nafion revealed a similar pattern. The deactivation of CAT_H was mainly caused by leaching of SO_3^{2-} groups. It has been pointed out that leaching of SO_3H groups is a common problem for sulfonated catalysts [31]. Likewise, the catalytic activity of CAT_S was 11.5 ± 1.3 mmol Prod.·h^{-1}·g Cat.$^{-1}$ but activity in the second run decreased slightly to 9.7 ± 0.4 mmol Prod.·h^{-1}·g Cat.$^{-1}$. This activity loss of the recycled catalyst could be due to the dissolution of active sites and structural changes during the first run process. Interestingly, after the second run, the reused catalyst sustained similar activity as with the second run (approximately 9 mmol Prod.·h^{-1}·g Cat.$^{-1}$), higher than that of first used Nafion and CAT_H (Fig. 7). Collectively, SO_2Cl_2 is a better reagent for surface modification of microalgal bio-char than H_2SO_4, considering the catalytic activity and reusability. The deactivation of solid catalysts in this study has been found in other solid catalysts with the same reasons. This limitation could be overcome or improved via process optimization regarding regeneration process, reaction temperature, esterification time, reagent type or amount, *etc*. [32–34], because the solid catalysts developed in this study were synthesized under fixed condition to exploit LEA cells as a raw material of solid catalysts for the first time.

In this study, a novel carbon-based solid acid catalyst has been synthesized via a sustainable route, by using microalgae residue, LEA, obtained after lipid extraction from microalgae, as a starting raw material. The successfully synthesized solid acid catalysts have higher activity and stability than a commercial solid acid catalyst (Nafion). The synthesized carbon-based solid acid catalyst is amorphous, with irregular morphology and high acid density. The catalyst treated with SO_2Cl_2 revealed higher recycling performance in the esterification of oleic acid in comparison with that modified with H_2SO_4. The developed solid acid catalysts have great potential not only for use as a catalyst in biodiesel production from high FFA-containing oils, including microalgal lipid, but also for economic and environment-friendly production of biodiesel by reducing homogeneous catalyst use and waste products. It would provide a sustainable way for biodiesel production by recycling LEA. Therefore, currently, an in-depth study on our developed bio-char based catalyst is being carried out including catalyst characterization and reaction optimization. Subsequently, LEA-based catalysts would be applied to the microalgal biodiesel production process after the optimizing process for preparation of the catalyst.

Acknowledgments

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Conflict of Interest

The authors have no financial conflicts of interest to declare.

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