



Short communication

## Solventless esterification of fatty acids with trimethylolpropane using sulfonated amorphous carbons derived from wood powder

Dasom Mun<sup>a,b</sup>, Anh Thi Hoang Vo<sup>c</sup>, Bora Kim<sup>a</sup>, Yong-Gun Shul<sup>b</sup>, Jin Ku Cho<sup>a,c,\*</sup><sup>a</sup> Green Material and Process R&D Group, Korea Institute of Industrial Technology (KITECH), Cheonan, Chungnam 31056, Republic of Korea<sup>b</sup> Department of Chemical and Biomolecular Engineering, Yonsei University, Seoul 03722, Republic of Korea<sup>c</sup> Green Process and System Engineering Department, Korea University of Science and Technology (UST), Cheonan, Chungnam 31056, Republic of Korea

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## ABSTRACT

Polyolesters synthesized by an esterification between polyols and fatty acids are value-added oleochemicals widely used as lubricants, cosmetics, and food additives among other applications. However, homogeneous acid catalysts are still preferred in their industrial production, despite their associated energy cost and the environmental issues that they present. In this paper, we describe lignocellulose-derived amorphous carbons with a high loading level of SO<sub>3</sub>H and their application to the synthesis of polyolesters as a biobased heterogeneous acid catalyst. These sulfonated amorphous carbons could be readily prepared via (i) heat treatment at 400°C for 1h and (ii) sulfonation with chlorosulfuric acid. XRD and BET analyses demonstrated that these carbonaceous materials were not crystalline but were amorphous structures with a low surface area. The attachment of SO<sub>3</sub>H groups was confirmed by FT-IR and XPS, and the loading level of SO<sub>3</sub>H was determined by CHNS elemental analysis. Chlorosulfuric acid gave a higher loading level of SO<sub>3</sub>H than other sulfating agents, such as *conc.* sulfuric acid and *fuming* sulfuric acid. The higher SO<sub>3</sub>H-loaded amorphous carbons exhibited a greater catalytic activity for esterification between trimethylolpropane and fatty acids under solventless conditions. Esterification of oleic acid derived from vegetable oil with trimethylolpropane using this catalyst afforded the desired biolubricant at over 93% yield in 3h. The sulfonated amorphous carbons could be reused three times without any significant loss of catalytic activity.

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## 1. Introduction

Polyolesters (POEs) are oleochemicals widely used as lubricants, cosmetics, and food additives among other applications, and they are made by esterification of fatty acids with polyols [1]. Esterification is performed in the presence of Brønsted acids, such as sulfuric acid, phosphoric acid, or *p*-toluenesulfonic acid. Although these homogeneous acid catalysts are preferred in industrial production due to their low cost and strong acidity, (i) they are difficult to separate from reaction mixtures and reuse; (ii) a large amount of acidic waste water is discharged, which causes environmental problems; and (iii) they often cause serious corrosion in process units [2]. To overcome the drawbacks of homogeneous acid catalysts, a variety of heterogeneous acid catalysts were explored. Cation exchange resins with high loading of sufficient sulfonic acid functionalities exhibit good performance in certain cases, but they are expensive and have low thermal stability [3]. Zeolitic solid acids including H-beta and H-ZSM-5 were attempted but the small pore sizes were unsuitable for an effective access of

bulky substrates (fatty acids and polyols) [4]. Esterification of fatty acids using heteropolyacid (HPA) supported on clay K-10 [5] or mesoporous silica [6], an Fe-Zn double-metal cyanide complex [7], and ZrOCl<sub>2</sub>·8H<sub>2</sub>O [8] as catalysts have been reported, but the studies were confined to simple alcohol compounds used primarily to produce the fatty acid methyl esters (FAME) of biodiesel. Additionally, immobilized lipase has been applied to the esterification of fatty acids with long chain alcohols, but there are still economic issues [9]. Currently, amorphous carbons (AC) containing SO<sub>3</sub>H groups attract considerable attention as biobased heterogeneous acid catalysts for esterification due to their physical/chemical stability and high catalytic activity. These carbon materials are typically made from natural carbon sources, such as glucose [10] or cellulose [11], via incomplete carbonization followed by sulfonation. Incomplete carbonization results in AC composed of small polycyclic aromatic carbon sheets in a three-dimensional sp<sup>3</sup>-bonded structure, and these AC can afford highly acidic catalysts by sulfonation because there are numerous reactive sites where SO<sub>3</sub>H groups may attach covalently, compared with crystallized carbon (CC) [12].

In this study, amorphous carbons containing SO<sub>3</sub>H (AC-SO<sub>3</sub>H) were prepared from lignocellulose, the most abundant biomass, and they were applied to the synthesis of polyolesters as biobased heterogeneous acid catalysts. AC-SO<sub>3</sub>H could be readily obtained by the thermal

\* Corresponding author at: Green Material and Process R&D Group, Korea Institute of Industrial Technology (KITECH), Cheonan, Chungnam 31056, Republic of Korea.  
E-mail address: [jkcho@kitech.re.kr](mailto:jkcho@kitech.re.kr) (J.K. Cho).

treatment of wood powder and then sulfonation with sulfonating agents such as *conc.* sulfuric acid ( $\text{H}_2\text{SO}_4$ ), *fuming* sulfuric acid ( $\text{SO}_3\text{-H}_2\text{SO}_4$ ), and chlorosulfonic acid ( $\text{ClSO}_3\text{H}$ ).  $\text{AC-SO}_3\text{H}$  was characterized by XRD, FT-IR, XPS, BET, and elemental analysis. Esterification between trimethylolpropane (TMP), a polyol containing three symmetric alcohol moieties, and fatty acids, including 2-ethylhexanoic acid (2-EHA), isononanoic acid (INA), and oleic acid, was performed without solvent in the presence of as-synthesized  $\text{AC-SO}_3\text{H}$ . The effects of the loading level of  $\text{SO}_3\text{H}$ , the temperature, and the structure of the fatty acids on the synthesis of polyolesters were investigated. The reusability of  $\text{AC-SO}_3\text{H}$  was also tested.

## 2. Experimental procedures

### 2.1. Materials

A wood powder (pine tree, 50–100 $\mu\text{m}$  in diameter) used as a raw material of the lignocellulose was supplied by G·biotech (Korea). The fatty acids 2-ethylhexanoic acid (2-EHA), isononanoic acid, and oleic acid, as well as trimethylolpropane (TMP), a polyol, were provided by Oh Sung Chemical Industry Co., Ltd. (Korea). All other chemicals, including *conc.* sulfuric acid ( $\text{H}_2\text{SO}_4$ , 95.0–98.0%), *fuming* sulfuric acid ( $\text{SO}_3\text{-H}_2\text{SO}_4$ , 28.0–32.0% free  $\text{SO}_3$ ), chlorosulfonic acid ( $\text{ClSO}_3\text{H}$ , >98%), *p*-toluenesulfonic acid monohydrate (PTSA, 99%), and 1,4-dioxane (99.8%), were purchased from Sigma-Aldrich (USA) and directly used without further purification.

### 2.2. Analysis

$\text{AC-SO}_3\text{H}$  was analyzed by XRD (Powder X-ray diffraction, D8 ADVANCE with DAVINCI, BRUKER, Germany), FT-IR (Fourier transform infrared spectroscopy, Nicolet 6700, Thermo Scientific system, USA) and XPS (X-ray photoelectron spectroscopy K-Alpha<sup>TM+</sup>, Thermo Scientific, USA). The loading amounts of sulfur were determined by elemental analysis (Automatic Elemental Analyzer, FLASH 2000 Series, Thermo Scientific, USA), and the surface areas were measured by BET analysis (Brunauer-Emmett-Teller, ASAP2010, Micromeritics, USA), respectively. XRD was conducted at  $2\theta$  from  $2.5^\circ$  to  $30^\circ$ , at a scanning step size of  $0.02^\circ$  and a scan speed per step of 0.5s using  $\text{Cu K}\alpha$  radiation. FT-IR samples were prepared in a pellet form by mixing the catalyst sample with KBr, and spectra were recorded in ATR mode; 126 spectra were accumulated and averaged to improve the signal-to-noise ratio. XPS measurements were performed on a Thermo Scientific K-alpha instrument using monochromatized  $\text{Al K}\alpha$  radiation ( $h\nu=1486.6\text{eV}$ ) and processed using Thermo Avantage software. The calculated spectra represented the transmittance. The specific surface area was determined on a BET surface analyzer using  $\text{N}_2$  as the adsorbent at liquid nitrogen temperature (77K) in the relative pressure ( $P/P_0$ ) range of 0–0.25. The powder samples were degassed in air over 12h at  $100^\circ\text{C}$  prior to analysis.

### 2.3. Procedure

#### 2.3.1. Preparation of $\text{AC-SO}_3\text{H}$

Amorphous carbonaceous materials were prepared directly from wood powder. A wood powder was carbonized by heating at  $400^\circ\text{C}$  under  $\text{N}_2$  for 1h. Fifty grams of wood powder (WP) were placed into a rectangular shaped ceramic alumina crucible ( $10\times 10\times 5\text{cm}^3$ ), and the WP-containing crucible was placed in a chamber-type electric furnace. The furnace was heated to  $400^\circ\text{C}$  over 80min under flowing  $\text{N}_2$ , and the temperature was maintained for 1h to afford approximately 15g of amorphous carbonaceous materials (weight yield: ~30%). For the attachment of  $\text{SO}_3\text{H}$  groups onto the aromatic rings of the amorphous carbonaceous materials, sulfonation proceeded as follows: In the 500mL round bottom flask were placed 10g of amorphous carbonaceous materials, and 100mL of a sulfonating agent such as *conc.* sulfuric acid, *fuming* sulfuric acid, or chlorosulfuric acid were added. The mixtures were

gently stirred at  $80^\circ\text{C}$  in an oil bath for 3h and additionally at room temperature ( $25^\circ\text{C}$ ) for 3h. The resulting sulfonated amorphous carbonaceous materials were washed with hot distilled water ( $70^\circ\text{C}$ ) until pH paper was no longer changed to an acid-indicating color and then washed with 1,4-dioxane. Afterwards, to remove the loosely bonded materials, sulfonated amorphous carbonaceous materials were washed by Soxhlet extraction with 1,4-dioxane for 24h and dried in vacuum oven for one day. The  $\text{AC-SO}_3\text{H}$  species obtained by treatment with *conc.* sulfuric acid, *fuming* sulfuric acid, and chlorosulfuric acid were denoted as  $\text{AC-co-SO}_3\text{H}$ ,  $\text{AC-f-SO}_3\text{H}$ ,  $\text{AC-ch-SO}_3\text{H}$ , respectively.

#### 2.3.2. Esterification between fatty acids and TMP

Into a 250mL two-neck round-bottom flask were placed TMP (3.7mmol, 1equiv) and an excess of fatty acid (12.3mmol, 3.3equiv), and  $\text{AC-SO}_3\text{H}$  (0.123mmol, 1mol% of fatty acid) was added as a catalyst. The reaction mixture was heated to the desired temperature and stirred at 300rpm under  $\text{N}_2$  flow for 24h. Volatile substances formed during the reaction were removed by  $\text{N}_2$ . At intervals of 1h, a small amount of sample was taken out from the reaction mixture using a syringe and then it was diluted with dichloromethane (DCM) and submitted for GC-MS (GCMS-QP2010 Ultra, Shimadzu, Japan) with an  $\text{Rxi-5ms}$  column (50m in length). Helium was used as a carrier gas at  $1\text{mLmin}^{-1}$  of flow rate. Injector temperature was  $150^\circ\text{C}$ . Column temperature was programmed from  $150^\circ\text{C}$  to  $330^\circ\text{C}$  at a rate of  $5^\circ\text{Cmin}^{-1}$  and held isothermal for 14min. The split ratio, ion source temperature, mass scan range were 1:20,  $300^\circ\text{C}$ , 35–1000massunits, respectively.

The yield of polyolester was calculated by the following equation.

$$\text{Yield of polyolester (\%)} = \text{Conversion of TMP} \times \text{Selectivity of polyolesters (T-nF)}$$

where T is an initial letter of trimethylolpropane; F is an initial letter of fatty acid (E, I, O in the cases of 2-EHA, isononanoic acid, oleic acid, respectively); and n is the number of fatty acids coupled with a TMP.

## 3. Results and discussion

### 3.1. Characterization of $\text{AC-SO}_3\text{H}$

According to the previous report by Okamura et al., heat treatment above  $450^\circ\text{C}$  afforded large carbon sheets in a well-crystallized form, which indicated a lack of reactive sites for the attachment of  $\text{SO}_3\text{H}$  groups on the carbon sheets [13]. Therefore, the carbonization process was conducted at a moderate temperature (under  $450^\circ\text{C}$ ) in this study. Wood powders were changed to black carbonaceous materials after heat treatment under  $\text{N}_2$  at  $400^\circ\text{C}$  for 1h. In the XRD patterns of the carbonaceous materials, two broad peaks were observed at  $10\text{--}30^\circ$  and at  $35\text{--}50^\circ$ , corresponding to randomly oriented aromatic carbon sheets [14] (Fig. S1a). The results indicated that the carbonaceous materials formed an amorphous structure due to incomplete carbonization. The BET surface area, under  $100\text{m}^2\text{g}^{-1}$  of the carbonaceous materials, confirmed that they are not crystalline materials. Next,  $\text{SO}_3\text{H}$  groups were attached to the aromatic rings of the amorphous carbon (AC) to impose acidic character. Three sulfonating agents, specifically sulfuric acid, *fuming* sulfuric acid, and chlorosulfuric acid, were examined for efficient sulfonation. Sulfonation of AC was analyzed by FT-IR and XPS. FT-IR spectra of the sulfonated amorphous carbon ( $\text{AC-SO}_3\text{H}$ ) contained bands at  $1377$  and  $1040\text{cm}^{-1}$ , which were assigned as  $\text{O}=\text{S}=\text{O}$  and  $\text{SO}_3^-$  stretching bands, respectively (Fig. S1b) [14]. A peak appearing at  $168.8\text{eV}$  in the XPS spectrum corresponded to the S  $2p$  binding energy of the  $\text{SO}_3\text{H}$  groups [13] (Fig. S1c). The XRD spectra of the  $\text{AC-SO}_3\text{H}$  were similar to that of AC. It was understood that no structural change occurred during sulfonation. The BET surface areas were also sustained after sulfonation, except for  $\text{AC-ch-SO}_3\text{H}$  sulfonated with chlorosulfuric acid ( $286\text{m}^2\text{g}^{-1}$ ). It could be explained that further carbonization occurred during treatment with chlorosulfuric acid, and the crystallinity

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