



Simultaneously carbonized and sulfonated sugarcane bagasse as solid acid catalyst for the esterification of oleic acid with methanol

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ABSTRACT

Solid acid catalyst was synthesized from sugarcane bagasse, a residue left behind during sugar milling, through a simpler and less energy-intensive one-step process, simultaneous carbonization-sulfonation. A range of synthesis temperature (150, 200, 250 °C) and time (4, 6, 8 h) were investigated in the preparation of the catalyst to determine their effects on the catalytic activity and conversion during esterification of oleic acid and methanol. Extensive washing of the freshly synthesized catalyst have significant influence on the performance of the catalyst, as loosely bound acid sites are removed in the process lowering its activity but improving its stability. The catalyst synthesized at 150 °C for 8 h, having a sulfonic acid density of 0.59 mmol/g, exhibited the best performance during a 4-h esterification assay using oleic acid and methanol, resulting in an FFA conversion of 46.5% and catalytic activity of 4.62 mmol oleic acid/mmol-SO₃H · h. Additionally, the catalyst could be used for at least five 24-h esterification cycles, where an FFA conversion of as high as 87% was achieved. The catalyst retained 76.5 and 86% of its initial catalytic performance and sulfonic acid density, respectively, after the fourth cycle, offering good operational stability.

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1. Introduction

Heterogeneous acid catalysts for biodiesel production have gained increasing attention owing to their significant advantages of eliminating separation, corrosion, toxicity and reduce environmental problems posed by their homogeneous counterparts. In addition, these catalysts can simultaneously catalyze both esterification and transesterification reactions, making them compatible for use with high acid value oils in the production of biodiesel. Traditional solid acid catalysts include zeolites, mesoporous silica, and polystyrene resins. These catalysts generally possess one or more problems of small pore size, low acid density, poor operational stability, bad tolerance to water, and high cost [1–3].

Recently, there has been a growing interest in the use of carbon as the catalyst support material. This led to the emergence of a new class of catalysts derived from natural products having well-defined chemical structures such as sugar, starch, and cellulose. These catalysts can be readily prepared by sulfonation of partially carbonized organic matter using concentrated sulfuric acid. Carbon-based catalysts from glucose [4], sucrose, cellulose, starch [5], and Kraft lignin [6] exhibited high catalytic performance in the esterification of oleic acid (95–96% FFA conversion), outperforming the aforementioned traditional solid acid catalysts. Since these catalysts are derived from major constituents of lignocellulosic biomass, there is a potential for utilizing agricultural residues in the synthesis of such catalysts. In the recent years, several studies have been conducted on using agricultural residues such as coconut shell [7], oil palm trunk [8], rice husk [9], corn straw [10], bamboo [11], spent coffee grounds [12], waste *Jatropha curcas* seed shells [13], and sugarcane bagasse [14] as the starting material for synthesis of solid acid catalyst (SAC). The catalysts prepared from these materials demonstrated good catalytic performance towards

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esterification of high FFA oils, with FFA conversions ranging from 71 to 98%. Esterification reactions involving the use of these catalysts typically require 0.005 to 0.09 w/w of catalyst, a methanol to oil ratio of 1–20, and a reaction time of 2–8 h at 60–110 °C [7–14].

Although catalysts synthesized from different biomass residues as starting material and carbon source may have certain advantages of their own, their potential for later local application is hinged on the availability of the raw material in a given locality. In this regard, sugarcane bagasse (SCB) would be a practical candidate as starting material in the Philippine context as it is available locally (4.45 millions tons/year), given that sugarcane is the top agricultural product of the country (22.7 million tons/year) from 2007 to 2016 [15–17]. The utilization of agricultural residues such as SCB in the synthesis of solid acid catalysts (SAC) is attractive owing to the material's low cost and availability, which could potentially lead to a greener process for the production of biodiesel [18]. Moreover, this could lead to the valorization of these waste materials while at the same time addressing waste management concerns.

Several studies have been conducted on the use of sulfonated activated carbon from sugarcane bagasse (SAC-SCB) for the (*trans*) esterification of oils [5,8,14,19]. The catalysts exhibited desirable catalytic performance ranging from 80 to 96% conversion, depending on the catalyst preparation conditions and reaction parameters. The catalytic activity of a sulfonated activated carbon like that of SAC-SCB is attributed to the presence of sulfonic acid ($-\text{SO}_3\text{H}$) functional groups [20], which are introduced via sulfonation of partially carbonized material.

In view of catalyst synthesis, SAC-SCB is typically synthesized via a two-step process involving partial carbonization of crushed SCB at temperatures of 300–800 °C for about 0.5–20 h and subsequent sulfonation at temperatures of 120–200 °C for a duration of 3–20 h [8,14,19]. Partial carbonization is employed to induce formation of small polycyclic aromatic rings to serve as backbone or support for the active sites [22]. Sulfonation using sulfuric acid is then carried out to introduce the sulfonic acid ($-\text{SO}_3\text{H}$) functional groups into the polycyclic aromatic rings through covalent attachment by substitution of hydrogen in the C–H bonds of the catalyst structure [14]. Another approach in the preparation of SAC-SCB involves carrying out dilute acid hydrothermal pretreatment step prior to carbonization and sulfonation. However, the synthesized catalyst only had minimal improvement in performance (from 90.3 to 93.2% FFA conversion), and required an additional processing time of 10 h at 200 °C for the pretreatment step [21]. Considering the processing conditions (temperature and time) required of the carbonization and sulfonation steps, there are overlaps and could potentially be taken advantage of by combining the two processing steps. An alternative to the above described preparation schemes is the simultaneous carbonization and sulfonation (SCS) of SCB as proposed by Savaliya and Dholakiya [23] in which both carbonization and sulfonation are carried out in one single step.

This approach greatly reduces the preparation time as well as the energy requirements of the synthesis of SAC-SCB. A comparison of the different synthesis schemes in the preparation of SAC-SCB is presented in Table 1.

In the preparation of SAC-SCB through SCS, a mixture of bagasse and sulfuric acid is heated at an elevated temperature under a stream of nitrogen [23]. Through the SCS scheme of synthesizing SAC-SCB the synthesis or preparation could be greatly reduced from almost 30 h to as short as 10 h. Moreover, the main processing steps could be greatly reduced from a synthesis scheme requiring 3 major steps to a one-step synthesis. Furthermore, taking account the fact that sulfuric acid is a dehydrating agent, this would result in the hastening of the carbonization process, whereby removing the inherent hydrogen and oxygen groups present while simultaneously attaching to the carbon backbone. A successful implementation of this approach would result in a cost-effective and more environmentally friendly process, considering the initial investments and capital cost that could be reduced by reducing the required processing steps and the reduction of the energy requirements and emissions entailed in the conventional approach. As of this writing, the effects of time and temperature during SCS on the catalytic activity of SAC-SCB during SCS has not been investigated. Moreover, most of the above mentioned catalyst preparation schemes were typically carried out under oxygen-free atmosphere by continuously purging with nitrogen gas, which would also entail additional cost in the catalyst production. It would be of interest to explore the possibility of preparing SAC-SCB through SCS without the use of purge gas [21,24] to further reduce the preparation cost.

In view of the existing gaps in the conditions for the synthesis of SAC-SCB through SCS, this study aims to determine the effects of time and temperature during SCS under minimized oxidative condition on the catalytic performance (FFA conversion) and activity (sulfonic acid activity) of the SAC-SCB in the esterification of oleic acid. Furthermore, the reusability of SAC-SCB in the esterification of oleic acid was also looked into. Moreover, during the course of this study, the importance of incorporating an extensive washing step to produce catalyst of good stability was also elucidated.

2. Material and methods

Sugarcane bagasse was collected from a local sugarcane juice vendor in Cebu. Ethanol 99.9 %v/v, methanol 99.8%, n-Hexane 96%, Scharlau, Spain and chemical reagents (Sulfuric acid 95–98 %w/w; hydrochloric acid 36–39 %w/w; barium chloride dihydrate 99.0%; anhydrous sodium carbonate 99.8%; oleic acid AV 195–204, Ajax, Sydney, Australia and sodium chloride 99.5%; magnesium oxide 96–100.5%; sodium hydroxide pellets 97%, Scharlau, Spain) used were obtained through local suppliers.

Table 1
Typical operating conditions for different synthesis methods in the preparation of SAC-SCB.

Method of Synthesis	Carbonization-Sulfonation [8,14,21]	Carbonization-Sulfonation with hydrothermal pre-treatment [21]	Simultaneous Carbonization-Sulfonation [23]
No. of steps	2	3	1
Pre-treatment Time	–	10 h	–
Pre-treatment Temperature	–	200 °C	–
Carbonization Time	0.5–20 h	5 h	–
Sulfonation Time	3–20 h	5–15 h	–
Total synthesis time	3.5–23 h	20–30 h	10 h
Carbonization Temperature	300–800 °C	400–800 °C	–
Sulfonation Temperature	100–200 °C	120–200 °C	–
Operating Temperature	100–800 °C	120–800 °C	180 °C

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