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Hydrolysis of delignified sugarcane bagasse using hydrothermal technique catalyzed by carbonaceous acid catalysts

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HIGHLIGHTS

- Carbon-based catalysts were active for hydrolysis of lignocellulose and starch.
- Direct sulfonated catalyst had similar efficiency as pyrolyzed/sulfonated ones.
- Higher glucose yield was achieved from more severe condition compared with xylose.

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ABSTRACT

Carbonaceous catalysts derived from sugarcane bagasse (SCB), cellulose and lignin were synthesized by three different methods using slow pyrolysis and subsequent sulfonation. The synthesized catalysts were used for hydrolysis of lignocellulose and cassava starch. The catalysts synthesized from SCB 100 mesh (type I) and lignin (type II) were highly active for hydrolysis of SCB (70 mesh), cellulose and starch at 140 °C for 3 h yielding 18.0%, 27.6%, 87.6% and 65.0%, 46.0%, 96.5% total reducing sugar (TRS) yields, respectively. Box–Behnken design was applied to investigate the influence of reaction temperature, amount of catalyst and reaction time on hydrolysis yield of delignified SCB in the presence of these two catalysts. The finding demonstrated that the lignin catalyst (type II) prepared by direct sulfonation without pyrolysis had equal or higher catalytic performance than catalysts prepared by pyrolysis and sulfonation.

1. Introduction

Lignocellulosic materials which contain mainly cellulose, hemicellulose and lignin have become attractive precursors for production of energy and building block chemicals as they are plentiful, renewable resources and not competitive to human and animal consumption. Conventionally, lignocellulose conversion to produce C5 and C6 sugars for biorefinery processes requires homogeneous acid catalyst to hydrolyze hemicellulose and cellulose. This process needs high energy input, produces high volume of effluent and thus requires difficult practices for wastewater treatment. Moreover, these liquid acid catalysts used in the process cannot be reused [1,2].

Using heterogeneous acid catalyst is a way to protect the environment and makes the lignocellulosic pretreatment economically efficient as the solid acid catalyst is reusable and easily separated from reaction solution by filtration. In addition, amount of wastewater from the hydrolysis process is significantly reduced. Due to these advantages, researchers have initiated many approaches to synthesize different types of solid catalysts such as H-form zeolites [3–5], cation-exchange resins [6–9] and transition metal oxide [9]. However, the catalytic performances of those catalysts were still lower than that of liquid acid catalyst. Recently, carbon catalyst was synthesized by Suganuma and coworkers [10] using incomplete carbonization by fast pyrolysis of cellulose followed by sulfonation in fuming sulfuric acid (15 wt% SO_3) [10]. The apparent activation energy for hydrolysis of crystalline cellulose to glucose in the presence of carbon catalyst is approximately 110 kJ/mol at 343–373 K which is smaller than that of the reaction in the presence of sulfuric acid under optimal conditions (170 kJ/mol) [11]. However, the former required longer reaction time (24 h) and higher reaction temperature (>200 °C) to achieve over 50% for hydrolysis of cellulose [12]. This carbon catalyst additionally yielded rather low glucose product (4% glucose yield) [10]. After that, Guo and colleagues [13] synthesized solid acid catalyst by hydrothermal carbonization of glucose and subsequent sulfonation [13]. The hydrolysis of cellulose catalyzed by this kind of catalyst was performed at 110 °C for 4 h and required to use [BMIm][Cl], an ionic liquid, for better swelling of cellulose. Although the TRS yield of cellulose hydrolysis with sulfonated carbon material in [BMIm][Cl] was high (72.7% TRS yield), there was no report of

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glucose yield and cellulose conversion of the hydrolysis. Since the cost of ionic liquid was extremely high, thus it is not feasible to use for industrial application. From the previous reports, the researchers found that the amorphous carbon bearing —SO_3H, —COOH and phenolic —OH groups from sulfonation of pyrolytic carbon materials can catalyze the hydrolysis of crystalline cellulose indicated as either TRS yield or glucose yield [10,13,14]. However, all the earlier research concerning heterogeneous acid catalysts for lignocellulose model compounds, i.e. crystalline cellulose, cellobiose, xylan has been still in the catalyst screening stage [3,6,14–17]. Moreover, the catalytic performance of synthesized carbon-based catalysts on hydrolysis of lignocellulose material such as sugarcane bagasse has not been tested before.

In the present study, solid acid catalysts were synthesized from cellulose, lignin and sugarcane bagasse. Subsequently, their performances on hydrolysis of cellulose, cassava starch and delignified sugarcane bagasse were investigated. Three methods of catalyst synthesis by different carbonization (dry and hydrothermal) and sulfonation techniques using concentrated sulfuric acid and fuming sulfuric acid were proposed. The aim of the study was to improve the catalytic performance of carbonaceous solid acid catalyst by enhancing —SO_3H functional groups attached to amorphous carbon support as well as increasing of acid site, surface area and porosity of synthesized carbon catalyst. Catalyst from lignin which has polycyclic aromatic structure was first time used as catalyst precursor by direct sulfonation without pyrolysis in order to optimize the energy consumption during synthesis process. In particular, hydrophobic groups of aromatic lignin were suggested to prevent catalyst deactivation by the water during the hydrolysis reaction [18]. Moreover, introduction of hydrophobic lignin for synthesis of carbonaceous catalyst was proposed to increase the affinity of lignin catalyst toward lignin–carbohydrate compound (LCC) in bagasse. The subsequent polysaccharide hydrolysis apparently enhanced by attack of SO_3H groups toward β,1–4 glycosidic linkages. Additionally, performances of all catalysts synthesized were compared with commercial acid catalysts namely Amberlyst 15 and phosphotungstic acid.

2. Materials and methods

2.1. Materials

Cellulose powder (20 μm in particle size) was purchased from Hi-Media Laboratories Pvt. Ltd. Fuming sulfuric acid was purchased from Merck chemical and concentrated sulfuric acid (H_2SO_4) was purchased QREC Chemical Co. Ltd. Lignin (alkali lignin, low sulfonate content with 150–200 μm in particle size, 100 mesh), Amberlyst-15 (600–850 μm in particle size, 18–23 mesh), phosphotungstic acid ($H_3PW_{12}O_{40}$), standard glucose and xylose were purchased from Sigma–Aldrich. Sugarcane bagasse was obtained from Khonburi Sugar Public Co., Ltd. Cassava starch (9–15 μm in particle size) was supplied from Chuthin Company.

2.2. Characterization of SCB

For compositional analysis of SCB, dry sample was milled to 80 μm particles using an ultracentrifugal mill (Retsch GmbH-5657, Germany) for analyses of extractives, Klason lignin, acid-soluble lignin, and ash [19]. For extractive determination, 3.5 g milled sample was sequentially extracted using (1) cyclohexane–ethanol (2:1 v/v) for 6 h, (2) ethanol (95%v/v) for 1 h, and (3) water for 24 h according to TAPPI T 264 om-88. Klason lignin was determined after acid hydrolysis (72 wt% H_2SO_4, 20 °C, 2 h and subsequent 3 wt% H_2SO_4, 100 °C, 4 h) [20]. Amount of acid-soluble lignin in 3 wt% H_2SO_4 supernatant was measured by spectrophotometry at 205 nm according to TAPPI T250 [21]. Total lignin content refers to the sum of Klason and acid-soluble lignin contents. Ash content was the residue after ignition of a known dry weight sample at 550 ± 5 °C for 2 h [22]. Total polysaccharide content is calculated by subtraction of weight loss, total lignin, extractives, and ash contents from 100 wt% untreated SCB.

2.3. Preparation of carbon-based solid acid catalyst

In the present study, three types of carbon-based solid acid catalysts were synthesized. The catalyst type I was prepared by sulfonation of pyrolyzed SCB (100 and 50 mesh) and cellulose. SCB and cellulose were heated at 400 °C for 1.5 h in a pyrolysis reactor with N_2 flow at 30 mL min^{-1}. The pyrolyzed substances were ground to black powder, and then boiled in concentrated sulfuric acid (98 wt% H_2SO_4) using 1:10 of solid to liquid ratio at 170 °C for 18 h with N_2 flow at 30 mL min^{-1}. After that, sulfonated catalysts were cooled at room temperature and washed repeatedly with deionized water until neutral pH and no released sulfate ions. Second type of catalyst (type II) was synthesized by pyrolysis and subsequent sulfonation in fuming sulfuric acid (15 wt% SO_3) at 100 °C for 18 h. For the third type of catalyst (type III), 10 g of SCB (100 mesh and 50 mesh) and cellulose were boiled in 100 mL of distilled water at 100 °C for 4 h. Sequentially, the solid phase was filtered and washed repeatedly with ethanol and deionized water. Then, solid catalyst was dried at 60 °C overnight and sulfonated by the same procedure as the catalyst type I. It was noted that lignin catalyst was prepared by direct sulfonation according to the procedures of catalysts type I and II without any prior pyrolysis step.

2.4. Catalyst characterization

The crystalline structure of carbon-based solid acid catalyst was analyzed by X-ray diffractometry (XRD) (Bruker D8-Discover, Germany) at 2°/min scan rate, in the range of $2\theta = 5–80°$. The functional groups of pyrolytic SCB, pyrolytic cellulose, lignin and sulfonated carbon were determined by Fourier transform infrared (FT-IR) spectroscopy (Thermo Scientific Nicolet 6700, USA) from 4000–400 cm^{-1} with 4 cm^{-1} resolution and 100 number of scans. The acid density (mmol g^{-1} catalyst) of catalysts was estimated by titration when 0.1 g of catalyst was mixed with 100 mL of a 0.1 M NaOH solution and stirred at 145 rpm at room temperature overnight. Afterward, 10 mL of solution was back titrated with 0.5 M HCl until the pH was neutral (3 replicates) [23]. Surface area of solid acid catalyst was analyzed by 11-point BET analysis equation (Quantachrome AUTOSORB 1-AG, USA). Pore size and pore volume were calculated by HK method.

2.5. Screening of active catalysts on hydrolysis of SCB, cellulose and cassava starch

The objective of this methodology was to determine the most active catalysts for hydrolysis of SCB (70 mesh and 100 mesh), cellulose and cassava starch. Comparison study was performed using commercial catalysts, Amberlyst 15 and phosphotungstic acid ($H_3PW_{12}O_{40}$). In catalytic hydrolysis reaction, 0.05 g of substrate was placed in a Pyrex tube, then 0.03 g of synthesized catalyst and 5 mL of deionized water were added. The mixture was heated at 140 °C in a pressurized hydrothermal reactor for 3 h. When the hydrolysis reaction stopped, the liquid phase was obtained by filtration. Total reducing sugars released into the liquid phase was measured by modified DNS method [24] and the amount of glucose and xylose in supernatant was measured by high performance liquid chromatography (HPLC) (Perkin Elmer Series 200, USA) equipped with 300 mm × 7.8 mm Aminex HPX-87H Ion Exclusion Column (BioRad) at column temperature of 65 °C. The