



Preparation of hydrothermal carbon acid catalyst from defatted rice bran

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ABSTRACT

In this study, the effects of carbonization conditions: temperature (180–250 °C) and time (1–8 h) on the yield and the chemical characteristics of hydrothermal carbon derived from defatted rice bran (HTCDBR) were determined. The morphological and chemical characteristics of the sulfonated HTCDBR catalyst were also examined. In addition, the stability of the catalyst was evaluated based on the amounts of biomass conversion products (5-hydroxymethylfurfural (HMF), furfural, levulinic acid and formic acid) leached into water at a specified biomass conversion condition. Since no HMF and furfural, and only small amounts of levulinic acid (1.75 wt.%), and formic acid (0.42 wt.%), were leached from the catalyst synthesized from HTCDBR prepared at the carbonization condition of 220 °C for 3 h, this condition was suggested to be a suitable carbonization condition. Despite having similar structural and chemical characteristics, the leaching test suggested that the DRB-based hydrothermal carbon catalyst was found to be more stable than the glucose-based hydrothermal carbon catalyst, prepared at the same condition. The catalytic activity for cellulose hydrolysis of the catalyst was higher than that of the commercial Amberlyst 16 WET catalyst.

1. Introduction

Owing to the increased world population, the rising energy demand for transportation and industries to produce various consumer products has inevitably become an important societal issue. Consequently, research on development of technology for effective processing and utilization of non-petroleum feedstocks for production of biomaterials, fine chemicals and alternative fuels has now been under attention globally. Taking rice, the major food crop of Asian countries including Thailand, as an example, other than the edible milled rice, all other parts of rice are being extensively researched to provide the maximal benefits to human. Rice straws and rice husks are generally burned to produce heat (Kataki et al., 2017; Quispe et al., 2017). More recent research has been focusing on their conversion into other high energy-density fuels and valuable chemicals such as production of ethanol, methane, acetic acid, sugar (glucose and xylose), 5-hydroxymethylfurfural (HMF), and furfural (Das et al., 2013; de Assis Castro et al., 2016). Given its high silica content, rice husks have been processed in silica synthesis, amine-modified SiO₂ aerogel preparation,

synthesis of belite cement, and development of refractory ceramics materials (Sinyoung et al., 2017; Sobrosa et al., 2017). Rice bran, due to the high oil content, is extracted for edible oil (Capellini et al., 2017; Lakkakula et al., 2004; Mamidipally and Liu, 2004). Defatted rice bran (DRB), the residue from the rice bran oil industry, have been researched for extraction of protein (Bandyopadhyay et al., 2012; Jongjareonrak et al., 2015) and phenolic compounds (Chiou et al., 2012; Devi and Arumughan, 2007; Wataniyakul et al., 2012) through various processes ranging from enzymatic extraction/hydrolysis to subcritical water extraction/hydrolysis by a number of research groups (Hata et al., 2008; Sereewatthanawut et al., 2008; Sunphorka et al., 2012; Viriya-Empikul et al., 2012).

In most industrial processes including those of bio-based nature, catalysts have for a long time played a key role. Research studies are being conducted to develop heterogeneous catalysts to replace the conventionally used homogeneous catalysts, due to their ease of separation and reusability. Owing to the low cost of raw materials, carbon-based acid catalyst, has recently been developed from various carbon sources such as sugars, polycyclic aromatic compounds,

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polystyrene resins, activated biochar, and lignin (Mo et al., 2008; Toda et al., 2005; Yao et al., 2017; Yu et al., 2010), and have been applied to processes involving biofuel and biochemical production. Such catalysts can be produced via rather simple synthesis route, either by carbonization of sulfopolycyclic aromatic carbons or sulfonation of carbonized inorganic/organic compounds (Boonnoun et al., 2010; Gao et al., 2007; Shu et al., 2009). Other advantages of this class of catalyst include high acid density and high thermal stability. Carbon-based solid catalysts synthesized from various carbon sources such as glucose and biomass have been tested for the production of biodiesel by esterification and transesterification (Han et al., 2016; Yu et al., 2010) and biomass conversion via processes in hot compressed water, particularly, hydrolysis of biomass to monomer sugars, and dehydration of the monomer sugars to furan compounds such as HMF and furfural (Daengprasert et al., 2011; Li et al., 2015). These furan compounds are, not only the key intermediates for liquid fuels, but also important platform chemicals for production of various chemicals and polymers.

Although various types of carbon sources such as glucose (Zong et al., 2007) and cellulose (Suganuma et al., 2010) can be used for the preparation of carbon-based catalysts, the biomass derived carbon source offers additional advantages of being renewable and being available in abundance at extremely low cost. When biomass is used, the first few catalyst synthesis steps resemble those of the activated carbon preparation. These involve water removal (dehydration) and conversion of organic matter to elemental carbon by driving off the non-carbon portion with heat (carbonization), and optionally, followed by pore enlargement (activation). To further make the carbon more suitable for catalysing a specified reaction, the surface chemical properties of the carbon may be modified by means of physical or chemical functionalization. Nevertheless, a major bottleneck of this preparation process is the use of high carbonization/pyrolysis temperatures (400–800 °C) (Jindo et al., 2014). The energy requirement becomes even more consuming, particularly when additional heat is needed to remove water from biomass with high moisture content.

A new method for preparation of carbonaceous materials has recently been developed, in which carbonization of the carbon sources takes place in hot compressed water at moderate temperature (180–250 °C) under self-generated pressure (Fiori et al., 2014; Libra et al., 2011). This process results in hydrothermal carbon (HTC) that could be further functionalized to perform specific catalytic activity. It should be noted that, the hydrothermal carbonization process resembles that of biomass conversion to produce HMF, furfural, and other valuable products such as glucose, levulinic acid, and formic acid. The main difference is that the HTC production from biomass requires much longer time from one to several hours (Libra et al., 2011). For this reason, biomass residues (i.e. DRB) that have been extracted for high value products (amino acids (Sereewatthanawut et al., 2008), phenolic compounds (Wataniyakul et al., 2012), and etc.), could potentially be a very attractive carbon source for HTC production.

This study therefore aims to investigate the possibility for synthesizing a HTC from DRB, with a specific objective to understand the effect of hydrothermal conditions on the characteristics of DRB derived HTC. The thermal stability of the catalyst obtained by functionalization of the HTC with sulfuric acid, a strong acid commonly used for carbon-based acid catalyst preparation, was also evaluated based on the Thermogravimetric Analyzer (TGA) results. Furthermore, the catalytic activity of the HTC catalyst on cellulose hydrolysis was investigated. In addition, if the catalyst is to be used in biomass conversion, due to the similar chemical nature of the carbon catalyst and the starting biomass, the stability of the prepared catalyst should also be evaluated based on the leaching of biomass conversion products (i.e. HMF, furfural, levulinic acid and formic acid) from the catalyst itself at a specified biomass conversion condition.

2. Materials and methods

2.1. Materials

Defatted rice bran used in this study was obtained from Thai Edible Oil Co., Ltd., Thailand. The chemical compositions (percent lignin, cellulose, hemicelluloses, and ash) of defatted rice bran were analysed using the standard NREL's method (Sluiter et al., 2008). The defatted rice bran was found to comprise of cellulose (25.48 wt.%), hemicellulose (9.35 wt.%), lignin (25.63 wt.%), ash (9.89 wt.%), and others (29.65 wt.%). D-Glucose anhydrous was of analytical grade and was purchased from Ajax Finechem Pty Ltd (Thailand). Sulfuric acid was of analytical grade and was purchased from Fluka (Singapore). Cellulose powdered, HMF, furfural, levulinic acid, formic acid, and perchloric acid (HClO₄) were of analytical grade and were purchased from Wako Pure Chemical Company (Osaka, Japan). The commercial grade sulfonated solid catalyst-Amerlyst 16 WET was purchased from Fluka (Singapore).

2.2. Preparation of hydrothermal carbon

The HTC was prepared in an 8.8 ml SUS-316 stainless steel closed batch reactor (AKICO Co., Japan) by hydrothermally carbonizing 1 g of carbon materials (DRB or glucose) in 5 ml of deionized water. The closed batch reactor containing water and the carbon source was heated with an electric heater to the desired temperature, 180–250 °C. This generally took approximately 15–25 min depending on the setpoint temperature. After a holding period of 1–8 h at the desired reaction temperature, the reactor was cooled to room temperature by submerging it into a water bath. The resulting solid HTC was separated from the liquid carbonization portion by a filter paper (Whatman no.1), and it was then washed with deionized water until the pH of the washed water was neutral. After drying overnight at 110 °C, the resulted HTC was stored in a sealed plastic bag for further analysis. The DRB and glucose derived HTC are called HTCDRB and HTCG, respectively.

2.3. Preparation of sulfonated hydrothermal carbon-based catalyst

The HTC-based catalyst (HTC-SO₃H) was prepared by sulfonation of the HTC following the method described by Yu et al. (2010). Briefly, 5 g of HTC was heated in 50 ml of concentrated H₂SO₄ (> 96%) using a 3-neck round bottom flask at 150 °C for 15 h under N₂ flow. The condenser was connected to 3-neck round bottom flask to condense the acid vapor. A 1-l flask containing activated carbon was connected to the condenser to trap the condensed acid. The remaining acid vapor was then trapped by water in another 1-l flask connected to the system. The obtained solid acid catalyst was washed with deionized water (1000 ml) before being separated with a vacuum filter. The solid was repeatedly washed with boiling distilled water until no change in water pH was observed. After drying overnight at 110 °C, the HTC-SO₃H catalyst was obtained. The DRB and glucose derived HTC-based catalysts are called HTCDRB-SO₃H and HTCG-SO₃H, respectively.

2.4. Analysis and characterizations

The HTC yield was determined as the percentage of weight ratio (dry basis) of the produced HTC and raw materials (DRB and glucose). The elemental compositions (C, H, and N) of raw material and HTC samples were determined by a CHN analyzer (LECO CHN628 elemental analyzer). The sulphur content (S) of samples was determined by a TruSpec Sulphur (LECO Corporation, USA). The oxygen (O) was calculated by subtraction of C, H, N, and S content from 100%. Furthermore, the surface morphologies of HTC were observed by Field Emission Scanning Electron Microscopy (FESEM) using a FEI Quanta 200 microscope (Eindhoven, Netherlands) operated at 2 kV.

The structural analysis of HTC and HTC-SO₃H was examined by X-

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