Catalytic hydrolysis of cellulose and oil palm biomass in ionic liquid to reducing sugar for levulinic acid production

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ABSTRACT

Biomass is now regarded as a potential feedstock to produce renewable valuable chemicals that can be derived from sugar. In this study, it was demonstrated that Fe/HY catalyst was able to promote the hydrolysis in ionic liquid of oil palm biomass to reducing sugar without a prior pretreatment step. Initially, cellulose was utilized as a model compound and the effects of several variables including temperature, time, catalyst loading, cellulose loading, and 1-butyl-3-methylimidazolium bromide (BMIMBr) purity on the hydrolysis process were evaluated. A total reducing sugar (TRS) yield of 60.8% was obtained using Fe/HY catalyst in BMIMBr at 120 °C within 3 h. Next, the same catalyst was applied for direct hydrolysis of oil palm frond (OPF) and empty fruit bunch (EFB). The TRS yields obtained were 27.4% and 24.8%, respectively, while the efficiencies were 54.6% and 58.5% for OPF and EFB, respectively. The catalyst, tested for five runs, exhibited a minimal loss in the catalytic activity signifying its potential recyclability ability. Further conversion of the cellulosic hydrolysate led to promising levulinic acid yield and process efficiency. The experimental results confirmed that Fe/HY catalyst and BMIMBr have the potential to be used in a lignocellulosic biorefinery at mild process conditions for processing renewable feedstocks.

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1. Introduction

Concerns about increasing petroleum oil prices compel the chemical industry to explore alternatives to fossil resources for basic chemical productions [1]. Biomass is more favorable as compared to other resources since biomass does not compete with food chain [2]. The hydrolysis of cellulose, major component of biomass, to produce reducing sugars is important in the utilization of biomass in the chemical industrial processes. The reducing sugars can be converted into a wide range of valuable chemicals such as ethanol, 5-hydroxymethylfurfural, and levulinic acid [3–5]. Cellulose is a crystalline polymer of D-anhydroglucopyranose units bonded together in long chains by β-1,4-glycosidic bonds [5]. The extensive networks of inter- and intramolecular hydrogen bonding and Van der Waals interactions make cellulose insoluble in water and most conventional organic solvents. The insoluble property is the cause of biomass recalcitrant in the hydrolysis process. The cellulose dissolution is important to make cellulose more accessible for catalytic processes [6].

Biomass feedstocks have been used extensively in the productions of biofuels and other bio-based chemicals. Oil palm residues are the most abundant biomass wastes in Malaysia. Malaysia is one of the largest palm oil producers in the world with a large area of plantation around 5 million ha [7]. The oil palm industries in Malaysia alone generate 30 million tons per year of palm oil residues in the form of empty fruit bunch (EFB), trunks and oil palm fronds (OPF). These biomasses contain a large amount of cellulose, which can be fractionated to release sugars that can be further converted to biobased products [8,9]. Biobased products are produced in biorefinery that incorporates biomass conversion processes [10].

There are many ways to extract sugars from biomass materials including by the use of ionic liquids [11,12]. In recent times, efforts have been made to hydrolyse cellulose and biomass in ionic liquids [5, 13–15]. Among various types of ionic liquids, imidazolium ion based ionic liquids such as 1-butyl-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium bromide and 1-allyl-3-methylimidazolium chloride are well acknowledged for their cellulose dissolution competency [5,14,16].

In order to further enhance the hydrolysis of cellulosic biomass, homogeneous acid catalyst was utilized [17–20]. The system was effective but caused many problems such as equipment corrosion, environmental pollution, and acid recovery. Heterogeneous catalyst could overcome the problems associated with the hydrolysis of cellulosic biomass in the homogeneous system. Early studies on the hydrolysis of cellulose over heterogeneous catalysts have been reported in 2008 [21–23] followed by more recent extensive studies [24–27]. Product separation is more convenient in a heterogeneous catalytic system and the catalyst can be recycled for repeated use [25–27]. Besides, thorough reviews on cellulose hydrolysis using both homogeneous and heterogeneous catalysts can be found elsewhere [28,29].

Several studies have reported that metal salts can catalytically hydrolyse carbohydrates effectively into useful feedstock chemicals. Peng et al. have applied metal chlorides as catalyst for cellulose hydrolysis [30]. Earlier researchers have mostly used chromium chlorides as catalyst for the cellulose and biomass hydrolysis [1,31–33]. However, considering the toxicity and environmental pollution caused by chromium chlorides, we envisage that commercially available Lewis acid FeCl$_3$ is able to act as an eco-friendly catalyst for the catalytic hydrolysis of cellulose. Fe-zeolite based catalyst is expected to demonstrate a high catalytic activity for the hydrolysis of cellulose and biomass to sugars, with the additional possibility of being easy to be separated from the reaction products by impregnating the metal on a zeolite as support.

Currently, extensive study on the conversion of sugars into biofuels and other feedstock chemicals [34] is being carried out. Among these explorations, one attractive approach is the production of levulinic acid. Levulinic acid is a versatile building block containing a ketone carbonyl group and an acidic carboxyl group, which can be used for the preparation of various high-value added organic chemicals, polymers, resin, flavor substances, and fuel additives with numerous potential industrial applications [35]. Some levulinic acid derivatives can be used as fuel additives. Esterification of levulinic acid with alcohols produces levulinic esters which can be used as diesel additives [36]. Levulinic acid can also undergo hydrogenation to produce γ-valerolactone (GVL), with a potential to be blended with gasoline as well as to serve as a precursor of polymers and fine chemicals [37].

In this study, the production of total reducing sugars (TRSs) through the cellulose hydrolysis process using Fe/HY as the solid catalyst has been demonstrated in 1-butyl-3-methylimidazolium bromide (BMIMBr) ionic liquid. The Fe/HY catalyst and BMIMBr are combined to afford a good performance for cellulose hydrolysis since Fe/HY is a solid catalyst with acidic sites and BMIMBr favors the cellulose dissolution. Fe/HY and parent HY zeolite were characterized to evaluate the effect of physicochemical properties of the catalysts on the hydrolysis process. The factors influencing the cellulose hydrolysis involving temperature, time, catalyst loading, cellulose loading, and BMIMBr purity were examined. Next, the potential of oil palm frond (OPF) and empty fruit bunch (EFB) for TRS production using the same catalyst were evaluated. The reusability and leaching of Fe/HY catalyst were also investigated. Subsequently, the production of levulinic acid was inspected from the cellulosic hydrolysate containing reducing sugars generated from cellulose, OPF, and EFB hydrolysis. Direct conversion of the feedstocks to levulinic acid was also tested for comparing and determining the role of ionic liquid in the hydrolysis process. The findings from this study are expected to improve the knowledge of catalytic transformation to renewable feedstocks.

2. Methods

2.1. Materials

1-Butyl-3-methylimidazolium bromide (BMIMBr), iron chloride (FeCl$_3$), levulinic acid, 5-hydroxymethylfurfural (5-HMF), formic acid, and furfural were purchased from Merck, Germany. NaY zeolite (SiO$_2$/Al$_2$O$_3$ = 5) was obtained from Zeolyst International. Cellulose was supplied by Sigma Aldrich, USA while NH$_4$Cl was from Qrec, New Zealand. Meanwhile, OPF and EFB were supplied by Malaysia Palm Oil Board (MPOB), Kuala Lumpur, Malaysia.

2.2. Catalyst preparation

The acidic form of NaY zeolite was prepared by ion exchanging the Na$^+$ from NaY zeolite with NH$_4$Cl. NaY zeolite was stirred with 2 M of NH$_4$Cl at room temperature for 2 h. The solution was washed with distilled water before being dried overnight at 120 °C. The material was calcined at 500 °C for 5 h resulting in the acidic form of zeolite, HY zeolite. The Fe/HY catalyst was prepared according to the wetness impregnation method. FeCl$_3$ aqueous solution (10 w/v%) and HY zeolite powder (10 g) were mixed and stirred at room temperature for 2 h and the mixture was dried overnight at 120 °C. Finally, the Fe/HY catalyst was calcined at 500 °C for 5 h.

2.3. Catalyst characterization

As for catalyst characterization, the FTIR spectra were recorded using a Perkin Elmer equipment in the range of 400–4000 cm^{-1}. The morphology of the catalyst was evaluated using field emission scanning electron microscopy (FESEM, Hitachi SU8020). Meanwhile, the catalyst crystallinity was analyzed by using a Bruker D8 advance diffractometer system (Cu Kα radiation, 40 kV, 30 mA) and the 2θ angle between 5 and 80°. N$_2$ physisorption method was applied to determine the surface area and pore volume of the catalysts using a Micromeritics ASAP2020 instrument. The acid properties of the catalyst samples were determined using temperature-programmed desorption (TPDRO 1100 series, Thermo Finnigan) with ammonia as the probe molecule (NH$_3$-TPD). Initially, a catalyst sample (500 mg) was degassed at 150 °C for 0.5 h under constant nitrogen flow (20 ml/min). Then, the sample was cooled to 50 °C and ammonia was adsorbed for 1 h. After saturation, nitrogen was purged for 0.5 h at 20 ml/min to remove excess ammonia on the catalyst surface. Finally, the catalyst sample was heated from 50 °C to 800 °C under constant helium flow (20 ml/min). The concentration of desorbed ammonia was quantified by a thermal conductivity detector (TCD).

2.4. Procedure for hydrolysis

An amount of 0.1 g of cellulose was dissolved in 2 g of BMIMBr by heating and stirring at 100 °C until a transparent solution was formed. Next, distilled water and catalyst, 0.1 g each, were added to the solution. The reaction mixture was heated and stirred at a specified reaction temperature and time in a closed batch reactor in the oil bath. Product samples were diluted with 10 ml distilled water and filtrated before being subjected to TRS analysis. Randomly selected experimental runs were repeated to test the reproducibility of the data. The same steps were further applied to the hydrolysis of OPF and EFB.

2.5. Analysis of cellulose hydrolysis product

The amount of TRS in the product sample was measured using the DNS method. 1 ml of supernatant from the product sample was mixed with 4 ml of DNS reagent. The resulting solution was heated in boiling water for 5 min. The absorbance of the mixture was measured at 540 nm using a UV–vis spectrophotometer. The TRS concentration was calculated by using a calibration curve of the standard glucose solution. Meanwhile, the TRS yield, theoretical TRS yield and efficiency were calculated according to Eqs. (1), (2), and (3), respectively.

$$\text{TRS yield } (\%) = \frac{\text{amount of TRS}}{\text{amount of feedstock}} \times 100\% \quad (1)$$

$$\text{Theoretical TRS yield } (\%) = \frac{\text{cellulose content in biomass} \times 1.11}{\text{amount of biomass}} \quad (2)$$

where the value of 1.11 is the molecular weight of sugar divided by the molecular weight of cellulose (MW of sugar, C$_6$H$_{12}$O$_6$ = 180, MW of cellulose, C$_6$H$_{10}$O$_5$ = 162).

$$\text{TRS efficiency } (\%) = \frac{\text{TRS yield}}{\text{theoretical TRS yield}} \times 100\% \quad (3)$$