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Optimization of levulinic acid from lignocellulosic biomass using a new hybrid catalyst

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ABSTRACT

Conversion of glucose, empty fruit bunch (efb) and kenaf to levulinic acid over a new hybrid catalyst has been investigated in this study. The characterization and catalytic performance results revealed that the physico–chemical properties of the new hybrid catalyst comprised of chromium chloride and HY zeolite increased the levulinic acid production from glucose compared to the parent catalysts. Optimization of the glucose conversion process using two level full factorial designs (2^3) with two center points reported 55.2% of levulinic acid yield at 145.2 °C, 146.7 min and 12.0% of reaction temperature, reaction time and catalyst loading, respectively. Subsequently, the potential of efb and kenaf for producing levulinic acid at the optimum conditions was established after 53.2% and 66.1% of efficiencies were reported. The observation suggests that the hybrid catalyst has a potential to be used in biomass conversion to levulinic acid.

1. Introduction

Due to depleting fossil resources, more attentions have been devoted for future transition of chemical industry from fossil raw materials to renewable feedstocks (Hongzhang et al., 2011). Lignocellulosic biomass feedstocks have been used widely in the biofuel and bio-based chemicals productions. Efb and kenaf are examples of the lignocellulosic wastes in Malaysia. Earlier, efb has been utilized for the biofuel production while kenaf has been used for the fiber board, particle board, textile and fuel productions (Abdullah and Gerhauser, 2008; Abdul Khalil et al., 2010;). Efb and kenaf seem to be potential feedstocks for the levulinic acid production. These biomass contain a large amount of cellulose and they can be fractionated to release the sugars before they can be further converted to produce levulinic acid (Rackemann and Doherty, 2011).

Biomass transformation to chemical products has a potential to replace those presently derived from petrochemical. Based on screening results for the top value added chemicals from biomass by Werpy and Petersen (2004), levulinic acid is one of the more recognized building blocks available from carbohydrates and has frequently been suggested as a starting material for a wide number of compounds. Levulinic acid can be produced from glucose, fructose, starch and lignocellulosic biomass (Hongzhang et al., 2011). Levulinic acid ($C_5H_8O_3$) is also known as 4-oxopentanoic acid, β-acetylpropionic acid and γ-ketovaleric acid. This compound is soluble in water, alcohol, ether and organic solvents with a ketone (CO) and carboxylic acid (COOH) groups giving it a wide range of functionality and reactivity (Fang and Hanna, 2002; Chang et al., 2007; Girisuta, 2007; Rackemann and Doherty, 2011). Extraction of levulinic acid from lignocellulosic biomass can be enhanced in presence of catalyst such as homogenous and heterogenous in the reaction system.

Homogeneous acids (H_2SO_4, HCl, etc.) were the popular methods for a long time to synthesize levulinic acid. These methods have been used in the first commercial-scale plant for the conversion of lignocellulosic biomass to levulinic acid. This plant was built in Caserta, Italy through a process developed by Biofine Renewables (Girisuta et al., 2008). Although these hydrolysis reactions were effective, the use of the mineral acid causes serious pollution and promotes equipment corrosion. Besides, it is difficult to recover acid from the reaction products for recycling purpose (Peng et al., 2010; Rackemann and Doherty, 2011). As an alternative, heterogeneous acid catalysts have been promoted since these catalysts can overcome the problems occurred in homogeneous catalysts (Hongzhang et al., 2011).

Heterogeneous acid catalysts such as LZY, HY and MFI type zeolites and $CrCl_3$ have been used previously for the synthesis of levulinic acid from fructose, glucose and cellulose (Jow et al., 1987; Lourvanij and Rorrer, 1993; Peng et al., 2010; Zeng et al., 2010). Performance testing over faujasite (LZY and HY) and mordenite (MFI) type zeolites revealed that acid sites, acidity, porosity and shape selectivity of the catalysts have significantly influenced the levulinic acid production. Peng et al., 2010 screened the catalytic performance of metal halides and they found that $CrCl_3$ effectively

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catalyzed the cellulose by producing 67 mol% of levulinic acid. Solid superacid catalyst, $S_2O_8^{2-}/ZrO_2–SiO_2–Sm_2O_3$ has also been used for levulinic acid production from rice straw (Hongzhang et al., 2011). These previous studies have mainly focused on the effect of the various feedstocks over solid catalysts for the levulinic acid production process. Recently, the hydrolysis of cellulose to levulinic acid by Nafion and alkali metal halide salts were reported by Hegner et al. (2010) and Potvin et al. (2011). The metal halide salts were physically incorporated with the Nafion supported on amorphous silica. These studies reported low yields, slow reaction rates and prolonged reaction times for producing levulinic acid. Therefore, further studies are required to comprehend the catalytic activities in the formation of levulinic acid. The search continues for more reactive catalysts by investigating the performance and physico–chemical properties of the catalysts.

Hybrid catalyst comprising of zeolite and metal halide salt is rarely utilized in biomass processing especially in levulinic acid production. Hybrid catalysts have been used widely in the chemical processes especially for synthesis of high quality fuel (Xiao and Mao, 1995). The hybrid catalysts were prepared by constituting the mixture of two or more components and the intention was to catalyze more than one reaction at once (Flores and Silva, 2008). Presently, HY zeolite (Brönsted type acid site) showed high catalytic reactivity through porosity and shape-selective properties while $CrCl_3$ (Lewis type acid site) could facilitate the mutarotation and isomerization processes of glucose and cellulose towards fructose and simultaneously dehydrated to HMF (hydroxymethyl furfural) before further rehydrated to levulinic acid and formic acid (Lourvanij and Rorrer, 1993; Peng et al., 2010; Pidko et al., 2010; Tan et al., 2011b). In addition, very low HMF yield was reported over zeolite and chromium catalysts alone in the reaction systems (Zhang and Zhao, 2009). Low levulinic acid yield could also be expected in these reaction systems since HMF is the intermediate compound before levulinic acid is formed. Therefore, modification of HY zeolite by introducing the $CrCl_3$ to form a hybrid catalyst is expected to improve the catalytic properties and possibly enhance the levulinic acid yield from glucose and lignocellulosic biomass.

Optimization studies have been conducted in this study by applying central composite design (CCD) under the response surface methodology (RSM). RSM is one of the methods to analyze the significance or the influence of the factors on the response (Tanyildizi et al., 2006). Central composite design (CCD) was chosen to obtain the optimum process conditions by developing a second order model for the response. In the previous study, this method has been successfully applied to optimize the levulinic acid production from wheat straw and gelidium amansii (Chang et al., 2007; Jeong and Park, 2010). Thus, this method is useful and it can reduce the number of experiments and consequently can reduce the cost and time consumed.

Accordingly, the purpose of this work was to determine the effects of physico–chemical properties of hybrid catalyst on the levulinic acid production from glucose followed by optimization of levulinic acid production. The variation of process conditions (reaction temperature, reaction time and catalyst loading) which could affect the responses (levulinic acid yield and glucose conversion) were evaluated within the range. Subsequently, the potential of efb and kenaf to produce levulinic acid at the optimum conditions were also evaluated in this study.

2. Methods

2.1. Materials

HY zeolite (SiO_2/Al_2O_3 = 30) was purchased from Zeolyst International Inc. Chromium Chloride, $CrCl_3$ was supplied from Merck, Germany. Meanwhile D(+)-glucose monohydrate and sulfuric acid (H_2SO_4) 95–97% were purchased from QRec, New Zealand. Standard analytical grade of levulinic acid 98% (Sigma Aldrich) was used for analysis of the desired products. Deionized water was used for the solution reactions. Empty fruit bunch was supplied by Malaysia Palm Oil Board (MPOB), Kuala Lumpur, Malaysia. Meanwhile, kenaf was supplied by the Polymer Engineering Department, Faculty of Chemical Engineering, Universiti Teknologi Malaysia, Malaysia. The samples were dried overnight at 105 °C in an oven. Then the dried samples were grinded and reduced to small size particles (less than 1.0 mm).

2.2. Biomass feedstock characterization

The chemical compositions of efb and kenaf were determined by thermal gravimetric analyzer (TGA) using a Mettler Toledo Thermogravimetric (TGA/SDTA 851) instrument. Samples (5.0 mg) were heated in a platinum cell with heating rate of 10 °C/min in a compressed air. The characterization and analytical assays for the sugars and ash content of the oven dried efb and kenaf were performed according to the standard laboratory analytical procedures (LAP 002 and LAP 005) provided by the National Renewable Energy Laboratory (NREL) (NREL, 1996). The experiments were carried out in duplicate for all samples and the values were treated statistically and presented as mean value.

2.3. Preparation and characterization of hybrid catalyst

Hybrid catalyst was prepared according to the wetness impregnation method. Aqueous solution $CrCl_3$ (10 w/v%) with HY zeolite powder (10 g) were mixed and stirred at room temperature for two hours. The mixture was dried overnight in an oven at 120 °C. Finally, the hybrid catalyst was calcined at 400 °C in 24 h for the activation of the catalyst (Xiao and Mao, 1995).

As for catalyst characterization, Brunauer–Emmet–Teller (BET) method was applied to determine the surface area, pores volume and size distribution in hybrid catalyst using Quantachrome Autosorb-1 instrument isotherm nitrogen adsorption at 77 K. The acidity of hybrid catalyst was determined using temperature programmed desorption of ammonia (NH_3–TPD). The N_2 (20 ml/min) was flowed for 1 h over 20 mg catalyst at 250 °C. NH_3 in N_2 was ramped at 10 K/min for 1 h. After adsorption, NH_3 was removed by purged N_2 at room temperature for 30 min. Then, the sample was heated from room temperature to 900 °C at rate of 10 K/min.

2.4. Hybrid catalyst testing

One pot catalytic reaction was carried out by dissolving glucose in deionized water (1.0%) and mixed with hybrid catalyst at various catalyst loading in a closed 150 ml Scott bottle (batch reactor). Then, the batch reaction system was immersed in the preheated silicon oil at the desired temperature and atmosphere pressure with stirring speed, 300 rpm. Immediately, after the reaction was completed, 10 ml of deionized water was added in the solution at room temperature. The reaction mixture was briskly stirred to rehydrate and dissolve the water-soluble reaction products away from the solid hybrid catalyst and humin. These steps were further applied in hydrolysis of efb and kenaf at the optimum conditions. All the samples were filtered through a 0.45 μm membrane syringe filter and the liquid phase was further analyzed using high performance liquid chromatography (HPLC).

2.5. Product analysis

The concentration of liquid phase samples were determined by using a model of Perkin Elmer Series 200 instrument (HPLC) under