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Kinetic study on the dilute acid catalyzed hydrolysis of waste mushroom medium

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ABSTRACT

In this study, kinetic modeling for the acid hydrolysis of waste mushroom medium was investigated. Sulfuric and oxalic acid were used as catalyst, under 140–160 °C at 50 mM acid concentration for 80 min. Glucose was the most abundant sugar in the hydrolysate for both acid catalysts. The production of glucose and xylose increased in proportion to reaction time until 150 °C. However, the sugar concentration increased in the initial stages at 160 °C and it has not increased after 10 min of reaction time, due to the degradation of sugars to furfural and 5-hydroxymethylfurfural (HMF) at high temperature and long reaction time. The activation energies for the degradation of xylan and glucan to xylose and glucose on oxalic acid catalyst were 59.1 and 38.7 kJ/mol, respectively, which were lower values than that of sulfuric acid. The degradation reactions of xylose (105.4 kJ/mol) and glucose (128.2 kJ/mol) to furfural and HMF have high activation energies, compared to those of xylan (69.1 kJ/mol) and glucan (50.0 kJ/mol) degradation on sulfuric acid catalyst.

Introduction

Biomass conversion promises to be an efficient and environmentally responsible process for producing renewable fuels and chemicals alternatives to petroleum. In particular, lignocellulosic biomass is an attractive biomass to produce fuels and chemicals, due to its abundance, and low price [1]. Lignocellulosic biomass consists of cellulose, hemicellulose and lignin, and their relative abundances depend on the type of biomass. Among those, cellulose and hemicelluloses can be converted to monosaccharide, such as glucose, xylose, arabinose, galactose and mannose, by thermochemical or enzymatic hydrolysis. These monosaccharides are widely known as basic chemicals for high value added chemical production [2].

The waste mushroom medium is a lignocellulosic byproduct of the commercial mushroom industry, and the total production was approximately 1670,000 t annually in Korea [3]. Most mushroom is cultivated artificially, using plastic pots filled with medium material, such as lignocellulosic biomass and some additives. After mushroom harvest, most of the waste mushroom medium is usually discarded, as solid waste. Therefore, it has advantageous terms to monosaccharide conversion for bio-based chemical production, since the waste mushroom still contains most of the carbohydrate, after mushroom harvest.

In this study, waste mushroom medium of cauliflower (*Sparassis crispa*) was used as lignocellulosic biomass. Cauliflower mushroom is well known as a brown-rot fungus, which selectively degrades the heartwood of wood. The production of cauliflower mushroom is increasing in Korea, because of its anticancer and immune activity [4]. Many researchers have reported the utilization of waste mushroom medium as lignocellulosic biomass, for value added chemicals production by hydrothermal treatment [5–7]. Generally, dilute acid pretreatment has been widely used for the monosaccharide production from lignocellulosic biomass. However, monosaccharide is easy to degrade during acid pretreatment, to produce some undesirable byproducts, such as furfural, 5-hydroxymethylfurfural, formic acid, and levulinic acid [8]. Those are widely known as fermentation inhibitors. Therefore, an appropriate pretreatment condition is required, to increase monosaccharide production, with low concentration of fermentation inhibitors.

In this study, we studied properties of the glucan and xylan hydrolysis of waste mushroom medium, with two acid catalysts, at different temperature. Based on those data, the reaction kinetic was investigated, to obtain the maximum yield of glucose and xylose.

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Experimental

Biomass

Waste medium after cauliflower (*Sparassis crispa*) cultivation was used as biomass in this study. The medium for the cultivation of cauliflower mushroom consisted of douglas fir sawdust 80%, wheat powder 10%, corn powder 10% and oligosaccharide 16 Brix. The biomass was provided from Jeonnam Forest Resources Research Institute (Naju, Jeonnam, South Korea). Prior to hydrolysis, the biomass was milled to pass a 40 mesh, using a Wiley mill J-NCM (JISICO, Korea), and stored at 4 °C, with less than 10% moisture content.

Dilute acid hydrolysis of biomass

The hydrolysis was performed in oil bath, with temperature and time control system. Each biomass (0.4 g/dry weight basis) and acid solutions (50 mM) was placed in the glass reactor tube with a screw cap then heated to the desired temperature. The biomass/acid solution ratio was 1:10 (w/w). The reaction temperature and time ranged from 140 to 160 °C, and 0 to 80 min, respectively [9,10]. Oxalic and sulfuric acid were used as the acid catalyst in this study.

Analysis of hydrolysate

The sugars, furfural, and 5-hydroxymethylfurfural (HMF) concentrations in the hydrolysate were determined, using HPLC (Waters 2695 system; Alliance, MA, USA), outfitted with an Aminex HPX-87H column (300 × 7.8 mm, Bio-Rad, Hercules, CA, USA), and a refractive index detector (Waters 2414 system; Alliance, MA, USA). The analysis was performed with 5 mM H_2SO_4 as the mobile phase at an isocratic flow rate of 0.3 mL/min, for 55 min. All samples were properly diluted and filtered through a 0.45 μm spin-filter before analysis, to remove particles. All analyses were carried out in triplicate.

Waste mushroom medium hydrolysis kinetic model

The kinetic study of lignocellulosic biomass hydrolysis on acid catalysts is difficult because the xylose, arabinose, glucose, furfural, HMF, acetic acid, etc is produced by hydrolysis reaction. For this reason, pseudo homogeneous kinetic models are used to overcome the problem of the heterogeneity of the hydrolysate [9,10]. Lignocellulosic biomass hydrolysis by acid catalysts was on the hypothesis of pseudo homogeneous irreversible first-order reactions. In this study, xylose and glucose oligomers were negligible during xylose and glucose formation. The model can be generalized as follows:

$$\underset{\text{Oligomers}}{\text{Xylan, Glucan}} \xrightarrow{k_1} \text{Xylose, Glucose} \xrightarrow{k_2} \text{Degradation products}$$

Where, k_1 is the rate constant of xylose and glucose formation (min^{-1}), and k_2 is the reaction rate constant of xylose and glucose degradation to furfural and HMF (min^{-1}).

The reaction rate constants (k_1, k_2) in the kinetic model were assumed by Arrhenius equation:

$$k = A\ \exp\left(\frac{-E}{RT}\right)$$

where A is the pre-exponential factor for lignocellulosic biomass hydrolysis (min^{-1}), E is the activation energy (kJ/mol), T is the reaction temperature (K), and R is the universal gas constant (8.314 kJ/mol/K).

Results and discussion

Hydrolysis of biomass

The hydrolysis was performed at a temperature range of 140–160 °C, to investigate the different catalytic behavior on lignocellulosic biomass degradation. The raw material contained 28.8% lignin, 51.3% glucan and 11.2% xylan [11].

Glucose was the most abundant sugar in the hydrolysate obtained, under all experimental conditions. However, the xylose released from hemicelluloses was relatively low. The waste medium after cauliflower mushroom cultivation contained mostly cellulose and lignin, since *S. crispa* as brown rot fungi secreted various hemicellulases during cultivation, unlike other waste mushroom medium [5,6]. Also, waste mushroom medium contained rich glucan, such as mycelium of *S. crispa* and oligosaccharide. Therefore, high glucose concentration was detected in hydrolysate in this study.

Fig. 1 shows the effect of reaction time and temperature on the glucose and xylose production. The total sugar concentration depended on both the reaction temperature and time. At 140 °C, the glucose concentration increased with reaction time, on both acid catalysts. On the other hand, the glucose concentration did not increase, after reaching a maximum value at 160 °C. This was due to the degradation of glucose to HMF at high temperature. The highest glucose concentration was 17.9 g/l, which was achieved after 80 min of hydrolysis, at 150 °C with 50 mM sulfuric acid. The behavior of glucan hydrolysis slightly differed, depending on the acid catalyst.

The xylose concentration gradually increased, during hydrolysis at 140 °C and 150 °C with sulfuric acid. However, the trend of xylose production was similar to that of glucose, when the reaction temperature was 160 °C. The reason was that the high reaction temperature easily induced the degradation of xylose to furfural [2].

Fig. 2 shows the effect of reaction time and temperature on furfural and HMF production, during dilute acid hydrolysis. Furfural and HMF, which are generated from hemicelluloses, were detected over all pretreatment conditions, in parallel to the

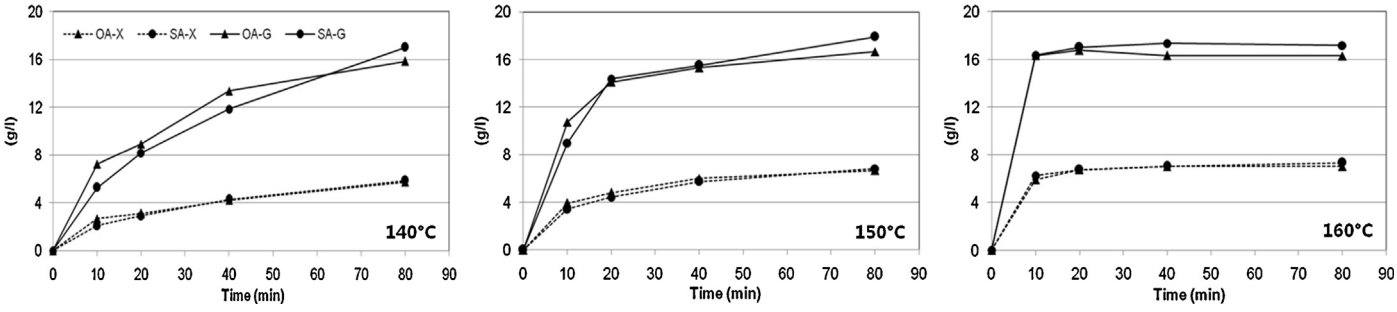

Fig. 1. Effect of temperature and reaction time on xylose and glucose production at different acid catalyst (OA: oxalic acid, SA: sulfuric acid, X: xylose, G: glucose).