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Production of furfural from macroalgae-derived alginic acid over Amberlyst-15

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ABSTRACT

Alginic acid derived from macroalgae was evaluated as a renewable biomass feedstock for the hydrothermal production of furfural over Amberlyst-15 as a solid acid catalyst. The maximum yield of furfural (18.5 mol%) was attained when 0.5 wt% of alginic acid was hydrothermally treated with 600 mg of Amberlyst-15 at 180 °C for 30 min. Although the production of furfural over the catalyst was enhanced with increasing temperature and reaction time, elongated time-on-stream gave rise to the decrease in the yield of furfural due to the generation of humin originating from the side reactions of furfural. Higher catalyst loading resulted in the increased furfural production, however, the acid-catalyzed polymerization of furfural with other organic products was simultaneously accelerated with increasing the catalyst amount, leading to the decrease in the overall yield of furfural. Amberlyst-15 showed considerable catalytic performance in the production of furfural from alginic acid and it could be reused 5 times without significant deactivation.

1. Introduction

Alginic acid, a major carbohydrate compound contained in macroalgae such as brown seaweeds, is composed of two kinds of hexuronic acids, such as β-D-mannuronic acid and α-L-guluronic acid, via 1,4-glycosidic linkage, as shown in Scheme 1 [1,2]. The glycosidic bond between monomer of alginic acid is almost same with that of cellulose, except a carboxylic group of alginic acid monomer. Celllulose-like structure of alginic acid implies that the hydrothermal reaction of alginic acid over catalyst can give rise to similar product distribution with that from cellulose. In our previous study, homogeneous acid and base catalysts were employed to the hydrothermal reaction of alginic acid sodium salt at temperature between 150 and 250 °C, in order to study the effects of acidity and basicity of catalysts on the product distribution [3]. It was found that the homogeneous acid catalyst (HCl) promotes the conversion of alginate to furfural and glycolic acid, whereas the homogeneous base catalyst (NaOH) enhances the production of lactic acid and dicarboxylic acids. Especially, the yield of furfural reached approximately 10 mol% at 200 °C within 60 min over HCl catalyst, suggesting that alginic acid has a potential as a biomass feedstock for the production of furfural over acid catalysts.

Furfural is a promising platform chemical for the production of fuels and high value-added chemicals in industry. The useful furan compound can be utilized in a wide range of applications, such as plastics, agrochemicals, pharmaceuticals, fragrances and fuel additives [4,5]. Unfortunately, it is known that the conversion of hemicellulose is the only way to synthesize furfural, leading to the high dependence on hemicellulosic biomass feedstocks for the production of furfural [6]. Hemicellulose, mainly composed of pentose such as xylose or arabinose, has been known as the most promising renewable feedstock for the production of furfural, since pentose is easily converted to furfural via acid-catalyzed hydrothermal reactions [7–11]. Contrary to the intensive studies on the production of furfural from hemicellulosic biomass, macroalgae-derived carbohydrates such as alginic acid were out of the picture.

In this research, macroalgae-derived alginic acid was evaluated as an alternative feedstock to hemicellulose for the production of furfural via acid-catalyzed hydrothermal reaction, based on our previous study [3]. We used Amberlyst-15, an ion exchange resin catalyst functionalized with sulfonic acid groups, as a solid acid catalyst in this research. Amberlyst-15 has been widely used as an efficient and reusable catalyst since the solid catalyst is cheap and suitable for the separation of used catalysts in liquid phase reactions [12,13]. This resin catalyst has been widely used for catalytic

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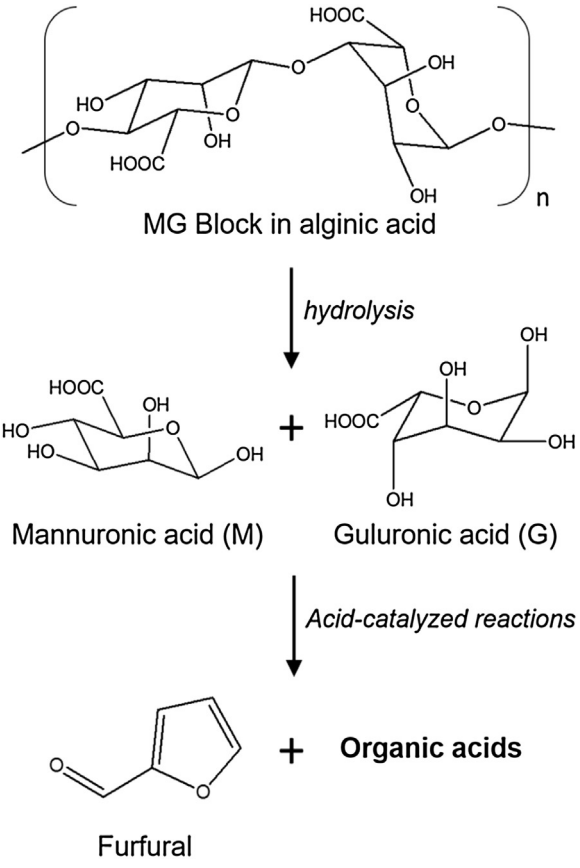

Scheme 1. Decomposition of alginic acid to its monomer via the cleavage of 1,4-glycosidic bond.

biomass conversion in liquid phases due to its abundant active sites (-SO_3H) that promote the acid-catalyzed reaction. Dias et al. [14] employed Amberlyst-15 as a solid acid catalyst for the dehydration of xylose to furfural, which yielded high xylose conversion (100%) and furfural selectivity (78%) in dimethyl sulfoxide (DMSO) at 170 °C. In addition, Amberlyst-15 showed reliable catalytic activity for the hydrothermal conversion of cellulose to glucose and other valuable chemicals, such as hydroxymethylfurfural (HMF), at 190 °C [15]. In this work, four main reaction parameters, such as temperature, reaction time, amount of catalyst and concentration of alginic acid as a reactant, were systematically controlled to understand the fundamental nature of the hydrothermal conversion of alginic acid to furfural over the solid acid catalyst. In addition to the use of the separable solid acid catalyst, pure water was used as a reaction medium in order to perform an economic and environmentally benign one-pot processing for the production of furfural from alginic acid.

2. Experimental

2.1. Materials

Amberlyst-15 (H) was purchased from Alfa Aesar. Alginic acid from brown algae and formic acid (>95%) were obtained from Sigma-Aldrich. This product is comprised of mannuronic acid (61%) and guluronic acid (39%), and its molecular weight is approximately 240 kDa. Furfural (>98%) was purchased from Tokyo Chemical Industry (TCI). Monomers of alginic acid, mannuronic acid and guluronic acid, were obtained from Qingdao BZ Oligo Biotech, China (purity > 98%).

2.2. Activity test

Alginic acid was hydrothermally treated in a stainless steel batch reactor (50 mL) lined with Teflon. The aqueous mixture containing alginic acid and Amberlyst-15 was stirred by a built-in impeller at 600 rpm, leading to an effective contact between insoluble alginic acid and Amberlyst-15 in water. The amount of water as a reaction solvent was fixed at 30 mL with varying amounts of catalyst and alginic acid. Before heating step, the sealed reactor was purged with nitrogen gas and then mounted in a heater. It took approximately 30 min to reach the target temperatures as plotted in Fig. S1. The ramping time was excluded in counting the reaction time. After heating the reactor for a certain length of time, the reactor was immediately cooled down with a cold-water. Amberlyst-15 could be easily separated by a steel sieve (80 mesh) after reactions. After the separation of used catalysts, final products were filtered and centrifuged in order to separate liquid products from solid-liquid mixtures before analysis. For the regeneration of deactivated catalysts, sulfuric acid was used to provide sulfonic acid groups on the catalyst surface. After a recycling test, the used catalyst was separated and washed with 500 mL of distilled water. Finally, the used catalyst was treated with 5 wt% of H_2SO_4 solution overnight at room temperature. The conversion of alginic acid was qualitatively determined by a gel permeation chromatography (GPC) analytical method, not by directly measuring weights of unreacted alginic acid due to the difficulty in separating the remaining reactant from other water-insoluble residues like humin.

2.3. Product analysis

The degree of depolymerization of alginic acid was measured by a gel permeation chromatography (GPC) method. The GPC system (Ultimate 3000, Dionex) was composed of three types of columns (Waters Ultrahydrogel column: 120, 500 and 1000) in series. A mobile phase, 0.1 M of sodium azide solution, run through the column (40 °C) at a flow rate of 1.0 mL min^{-1}. Pullulan with a molecular weight distribution from 342 to 80,500 was used as a standard compound in the GPC system.

The liquid products were identified using a LC–MS system (Surveyor, Thermo Finnigan) in combination with a mass spectrometer (LCQ Deca XP Plus, Thermo Finnigan) equipped with an electrospray ionization (ESI) module. The ionization was operated in negative modes at a capillary temperature of 275 °C. Three types of mobile phases (0.1% of formic acid dissolved in distilled water, acetonitrile or methanol) were delivered to a column (Synergi^{TM} 4 μm Polar-RP 80 Å, LC Column 150 × 2 mm, Phenomenex) at a flow rate of 0.25 mL min^{-1}.

The main liquid products, such as furfural, mannuronic acid, guluronic acid and formic acid, were quantified with an Agilent 1200 Series HPLC system equipped with two Shodex RSpak KC-811 columns in series. Other organic acids like acetic acid, glycolic acid and succinic acid were also detected, however, the amounts were insignificant (≤1 mol%). A mobile phase, 5 mM of phosphoric acid aqueous solution, was flowed through the column (40 °C) at a flow rate of 1.0 mL min^{-1}. Both RI detector (Agilent G1362A) and UV detector (Agilent G1314B) were used to crosscheck the quantification. The wavelength of the UV detector was set to 210 nm for simultaneous detection of furfural and organic acids. Based on data obtained from HPLC analysis, molar yields of products were calculated as:

$$Yield_i = 100 \times \frac{nC_i}{6} \times \frac{n_i}{n_{ru}}$$

where nC_i = the number of carbon atoms in the organic acid i, n_i = the number of moles of the organic acid i as determined by HPLC analysis, n_{ru} = the initial number of moles of repeating units