



Direct catalytic conversion of brown seaweed-derived alginic acid to furfural using 12-tungstophosphoric acid catalyst in tetrahydrofuran/water co-solvent



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ABSTRACT

Furfural, a biomass-derived platform chemical, was produced by acid-catalyzed reaction of alginic acid extracted from brown seaweed. Three acid catalysts, H₂SO₄, Amberlyst15 and 12-tungstophosphoric acid (H₃PW₁₂O₄₀), were compared to evaluate their catalytic performance for the alginic acid conversion. The H₃PW₁₂O₄₀ catalyst showed the highest catalytic activity, yielding the maximum furfural yield (33.8%) at 180 °C for 30 min in tetrahydrofuran/water co-solvent. Higher reaction temperature promoted the conversion of alginic acid to furfural, but the transformation of furfural to humin was also accelerated. To our knowledge, this is the highest furfural yield among studies about the direct catalytic conversion of alginic acid. Furthermore, products distribution with time-on-stream was investigated in detail, which led us to propose a reaction pathway.

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1. Introduction

Marine algae biomass has a great potential as a promising renewable energy resource since it has inherent advantages such as fast growth rate, easy cultivation, and lignin free composition [1,2]. The aquatic biomass is divided into two groups, micro- and macroalgae, depending on its compositions, such as proteins, lipids and carbohydrates. Microalgae has been widely utilized for biodiesel production via bio- or thermochemical conversion processes like chemical liquefaction, pyrolysis, gasification or alcoholic fermentation [3,4]. On the other hand, macroalgae is mainly composed of carbohydrate compounds like alginic acid, instead of lipids, which makes it being promising for biomass valorization via catalytic conversion processes in various reaction media [5,6]. Alginic acid, predominant constituent of brown seaweed, is a carbohydrate polymer comprised of two monomers (mannuronic acid (MnA) and guluronic acid (GIA)) via β-1,4-glycosidic bond similar to cellulose [7,8]. Such structural similarity implies that the reaction conditions used in lignocellulosic biomass conversion can be applied to marine algae biomass. However, alginic acid has a carboxyl group at the C5 position of the monomeric unit in the polymer structure whereas cellulose has a hydroxymethyl group

at the same position, leading to different product distributions between alginic acid and cellulose. The main products of alginic acid decomposition under hydrothermal conditions are two monomers (MnA and GIA) and C1–C5 organic acids (carboxylic acid and dicarboxylic acid), due to the extra carboxylic acid group [9–12]. On the other hand, hydrothermal conversion of cellulose produces its monomer, glucose, and carboxylic acids, such as levulinic acid and lactic acid, depending on catalysts [13–15]. In addition, furfural is produced from alginic acid over acid catalysts whereas hydroxymethylfurfural (HMF) is predominantly produced from cellulose and its monomeric unit [16–18].

Furfural is one of important platform chemicals obtained from biomass conversion processes listed by US Department of Energy (DOE) [19]. The worldwide demand for furfural is expected to steadily increase, because furfural can be used as a starting compound in production of furan-derivatives such as a polymer unit (furfuryl alcohol), organic solvents like tetrahydrofuran and various liquid fuel additives [20–24]. Therefore, the production of furfural from lignocellulosic biomass has been intensively investigated with the development of catalysts [22,25]. On the other hand, the production of furfural has been heavily dependent on hemicellulosic biomass despite the increasing demand for furfural, suggesting that diversification of feedstock is necessary for reliable supply of furfural in the future [26]. In our previous research, alginic acid sodium salt was hydrothermally treated with homogeneous acid catalyst, hydrochloric acid, resulting in

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13% of furfural yield [12]. This result shows a possibility that alginic acid can be used as an alternative raw material to hemi-cellulose for the furfural production. Based on the previous study, we attempt to enhance the production of furfural from alginic acid by applying strong acid catalysts and a polar aprotic reaction media.

Heteropolyacid, a cluster of polyoxometalates and hetero atom, has been widely used as an acid catalyst in many organic reactions because the acid strength and redox properties of heteropolyacid could be controlled by various combinations of its hetero- and addenda atoms [27]. Heteropolyacid is more advantageous than mineral acids in liquid-phase reaction systems due to those lower volatility, less corrosiveness and better safety of handling [28]. It has been steadily attempted to convert lignocellulosic biomass into useful compounds by using heteropolyacids [8]. Ogasawara et al. reported that negatively charged heteropolyacids ($H_5BW_{12}O_{40}$) showed a 77% of glucose yield in the saccharification of cellulose at 60 °C [29]. Dias et al. studied the dehydration of xylose to furfural using tungsten-based heteropolyacids in dimethylsulfoxide (DMSO), resulting in about 60% of furfural yield at 140 °C for 4 h [28]. Herein, the acid-catalyzed decomposition of alginic acid is conducted using commercial $H_3PW_{12}O_{40}$ to enhance the production of furfural from alginic acid.

A reaction medium is known to highly influence the product distribution and selectivity of platform chemicals in biomass conversion [30,31]. It has been reported that hydrothermal treatment using water as a reaction medium gave rise to the poor yield of furfural because of many side reactions [32]. Ionic liquids have been regarded as functional reaction media since they can attenuate the recalcitrant cellulose structure through lowering the strength of hydrogen bond in cellulose, however, the high prices and unknown toxicity of ionic liquids are still controversial [33]. Recent researches have attempted to improve the production of furfural with polar aprotic solvents [34–36]. Hu et al. studied the conversion of xylose into furfural over Amberlyst70 in various organic solvents, such as water, alcohol, ketones, furans, ethers, esters, hydrocarbons, and aromatics, which showed that tetrahydrofuran significantly accelerated the acid-catalyzed production of furfural compared to water [37]. The tetrahydrofuran solvent has an advantage of reducing energy input required for the separation of products, since it has lower boiling point and heat of vaporization than water [38,39]. For those reasons, tetrahydrofuran/water co-solvent was selected as a reaction medium to examine the effect of tetrahydrofuran and water on the furfural production in this study.

2. Experimental section

2.1. Materials

Tetrahydrofuran purchased from Sigma–Aldrich was used as a reaction medium. Alginic acid obtained from FMC Biopolymer was used as a starting material with no further purification. Standard chemicals of alginic acid monomers, mannuronic acid (MnA) and guluronic acid (GIA) were purchased from Qingdao BZ Olig Biotech, China (Purity > 98%). However, the monomers could not be used as reactants since the amounts of the monomers were significantly small (<10 mg). Furfural and triethylamine (TEA) were purchased from Tokyo Chemical Industry. Glucuronic acid (GcA) and glucuronolactone (GcL) were obtained from Alfa Aesar. Sulfuric acid (H_2SO_4), Amberlyst15 and 12-tungstophosphoric acid hydrate ($H_3PW_{12}O_{40} \cdot xH_2O$) were purchased from Junsei Chemical, Alfa Aesar and Sigma–Aldrich, respectively. All chemicals were reagent grade and used as received.

2.2. Catalytic conversion of alginic acid

All batch reactions were conducted in a SUS316 tubular reactor (Swagelok) with inner volume of 4 mL. 10 mg of reactants (alginic acid, GcA, GcL or furfural), catalysts (H_2SO_4 , Amberlyst15 or $H_3PW_{12}O_{40}$) and 1 mL of tetrahydrofuran/water co-solvent were loaded into the reactor with a magnetic stirrer (400 rpm). Amount of the solid catalyst loading was 10 and 20 mg, and the proton concentration of H_2SO_4 solution was adjusted to 0.05 M and 0.1 M. The concentrations of H_2SO_4 solution indicate final concentrations after being mixed with reactants. Before reaction, the reactor was purged with pure N_2 (99.999%) gas in order to remove air in the reactor. The reactor was then soaked into an oil bath at different temperatures (150–190 °C). The heating time (ca. 2 min) was not considered for determination of reaction time. After the reaction, the reactor was quenched with cold water to prevent further reaction. Final products were separated to solid and liquid parts via centrifugation and filtration prior to characterization. At least three experiments were performed for each reaction condition and the standard deviation of the yields are less than 5% for each data point. The conversion of alginic acid was qualitatively determined by a gel permeation chromatography (GPC) analytical method, not by measuring weights of unreacted alginic acid, since alginic acid remained after reactions was unable to be separated from final products containing different solid residues like humin. It should be noticed that alginic acid was almost completely decomposed above 170 °C (see Fig. S1) while uncertain amounts of unreacted alginic acid remained at 150 and 160 °C.

2.3. Analytical methods

CO_2 produced during the catalytic conversion of alginic acid was quantified by gas chromatography (Agilent GC 6890N) equipped with a thermal conductivity detector (TCD) and a 60/80 Carboxen-1000 packed column. Gas phase products were collected with using a gas-tight syringe and the collected products were injected to GC by a manual injection method. The column flow rate was 30 mL min^{-1} with a He carrier gas. The GC oven temperature was initially held at 35 °C for 5 min and then ramped to 225 °C at 20 °C min^{-1} .

The molecular weight distribution of products was measured by GPC analysis. The GPC system (Ultimate 3000, Dionex) was comprised of three types of columns (Waters Ultrahydrogel column: 120, 500 and 1000) in series. The flow rate of a mobile phase, sodium azide solution (0.1 M), was 1 mL min^{-1} and the column temperature was maintained at 40 °C. The GPC system was calibrated using pullulan with a molecular weight distribution from 342 to 80,500.

Hexuronic acids were identified with liquid chromatography–mass spectrometry (LC–MS). The LC–MS analysis was performed with a LC–MS system (Surveyor, Thermo Finnigan) in combination with a mass spectrometer (LCQ Deca XP Plus, Thermo Finnigan) equipped with an electrospray ionization module. Capillary temperature and spray voltage of the ionization module were 250 °C and 5000 V, respectively. 0.1% (v/v) formic acid solution was used as a mobile phase and delivered to a column (Phenomenex Synergi 4 μm Fusion-RP 80 Å) at a flow rate of 250 $\mu L min^{-1}$.

All the products were quantified with HPLC equipped with two Shodex RSpak KC-811 columns in series. Column oven temperature was 40 °C and 5 mM of phosphoric acid aqueous solution was used as mobile phase at a flow rate of 1 mL min^{-1} . Prior to the quantification, the samples were pretreated with 1% (v/v) TEA in order to convert lactones to hexuronic acids for reliable quantification of alginic acid monomers [40,41]. The amounts of MnA and GIA were measured with a UV detector (Agilent G1314B) at 210 nm, while furfural was quantified with a RI detector (Agilent G1362A).

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