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Hydrothermal conversion of alginic acid to furfural catalyzed by Cu(II) ion

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ABSTRACT

Alginic acid, a major carbohydrate material of macroalgae, was hydrothermally treated to produce furfural over various metal cations as catalysts. Among the metal cations, Cu(II) ions showed the highest furfural yield (13.19 mol%) at 200 °C for 30 min. In the hydrothermal reaction of alginic acid catalyzed by Cu(II) ion at reaction temperatures from 160 to 220 °C, the yields of furfural were proportional to reaction time, however, the maximum furfural yields decreased after certain reaction times due to the conversion of furfural to humins or organic acids. The catalyst concentration was significantly influential on the yield of furfural, the optimal concentration of Cu(II) ions was 0.01 M for the most effective production of furfural. In addition to furfural, lactic acid, glycolic acid and formic acid were produced in different amounts depending on the metal cations. The effect of Cu(II) ion on the depolymerization of alginate was studied with gel permeation chromatography (GPC) analysis in various reaction conditions. A plausible reaction pathway of furfural production catalyzed by Cu(II) ions was suggested.

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1. Introduction

Alginic acid is one of major carbohydrate compounds contained in macroalgae like brown seaweeds [1]. This biopolymer comprises two kinds of hexuronic acids, such as β -D-mannuronic acid and α -L-guluronic acid, with 1,4-glycosidic linkages [2], as shown in Scheme 1. Recently, this biopolymer is extensively used in biochemical processes in order to produce high value-added chemicals like bioethanol or volatile fatty acids (VFAs) [3–6]. Unlike cellulose, alginate is composed of monomers containing a carboxyl group. ascribed to the production of organic acids in hydrothermal decomposition of alginate. Niemela and Sjostrom [7] used NaOH and Ca(OH)₂ as a base catalyst for the hydrothermal decomposition of alginate. As a result, numerous di- and mono-carboxylic acids were produced at relatively low reaction temperatures, 95 and 135 °C. Main products in the base-catalyzed hydrothermal reaction were lactic acid, α -hydroxyglutaric acid and glucoisosaccharinaric acid. In the absence of catalysts, the hot-compressed water can act as acid and base catalysts itself [8]. Aida et al. [9] treated alginate in suband super-critical water with a view to producing organic acids. In their study, main products were formic acid and malic acid at

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http://dx.doi.org/10.1016/j.cattod.2015.12.001 0920-5861/© 2015 Elsevier B.V. All rights reserved. 150 °C, however, lactic acid was produced by the base-catalyzed reaction at 350 and 450 °C without adding any base catalysts. In our previous study, the effect of pH on the product distribution of organic acids was studied with using HCl and NaOH as acid and base catalysts, respectively [10]. We found that acid-catalyzed hydrothermal treatment of alginate yielded the furan compounds, such as furfural and 2-furoic acid, in addition to various organic acids. Especially, the production of furfural with considerable yields (ca. 10 mol%) at 200 °C within 60 min showed the potential of the alginic acid to be used as a biomass feedstock for the production of furfural via the catalyst-aided hydrothermal reaction.

Furfural is an important renewable and non-petroleum-derived chemical for sustainable production of fuels and other valuable chemicals. This useful platform chemical can be utilized in a wide range of applications, such as plastics, agrochemicals, pharmaceuticals, fragrances and fuel additives [11,12]. In spite of the wide spectrum of applications, it is known that there is no synthetic route available to produce furfural except the conversion of lignocellulosic biomass [13]. A representative process for the furfural production from lignocellulosic biomass is the acid-catalyzed hydrolysis and dehydration of hemicellulose [14–16]. Unlike cellulose and lignin, hemicellulose is mainly composed of C5 sugars like xylose or arabinose. This structure of hemicellulose is favorable for the selective production of furfural, since pentose tends to convert to furfural over acid catalysts in aqueous reaction medium.

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Scheme 1. The basic structure of alginic acid and its depolymerization by the cleavage of 1,4-glycosidic bonds.

For example, Choudhary et al. [17] reported that the yield of furfural was 23.5% when xylose was reacted at 110°C for 60 min over Amberlyst-15, as a solid acid catalyst, in an aqueous medium. Sahu and Dhepe [18] studied the effect of biphasic reaction system on the hydrothermal conversion of hemicellulose to furfural using solid acid catalysts. The addition of organic solvents into the aqueous medium in order to establish the biphasic reaction system significantly enhanced the production of furfural while inhibiting the degradation of furfural. Recently, the catalytic hydrothermal production of furfural from lignocellulosic biomass has been extensively investigated in order to obtain high furfural yields [19,20]. In particular, metal cations have been widely used as catalysts in the valorization of biomass feedstocks. Mao et al. [21] reported that metal cations (Fe³⁺) in FeCl₃ enhanced the seawater-based production of furfural via hydrolysis of corncob in acetic acid steam. They found that the metal cations catalyzed the swelling of corncob

particles and the oligomerization of swelled corncob by the penetration effect. Yu et al. [22] studied the influences of metal salts on the hydrothermal decomposition of sweet sorghum bagasse in a flowing liquid system. In the previous study, various metal salts containing transition, alkaline and alkaline earth metal cations promoted the hydrolysis of the carbohydrates. In addition, the metal cations enhanced the recovery of sugars produced by the hydrothermal decomposition via the formation of saccharide-sugar complex.

In this work, we evaluated the macroalgae-derived alginate as an alternative feedstock to hemicellulose for the furfural production in hydrothermal conditions. As catalysts, various metal cations were used to investigate the effect of metal cations on the hydrothermal decomposition of alginate. The effect of experimental conditions, such as temperature, time and catalyst concentration, was also studied. In our experiments, alginic acid, not a salt form, was used as a reactant in order to analyze the function of metal cations in the hydrothermal reaction excluding interference with other metal cations, since general alginic acid metal salts contain Na⁺, Ca²⁺ or K⁺, which may influence the catalytic reaction.

2. Materials and methods

2.1. Materials

Alginic acid obtained from brown algae was purchased from Sigma-Aldrich. This product was composed of mannuronic acid (61%) and guluronic acid (39%) approximately. The metal cation solutions were prepared with various metal nitrate compounds. The metal nitrate compounds used in this research are the following: Cr(NO₃)₃·9H₂O (99%), Mn(NO₃)₂·4H₂O (>97%), Fe(NO₃)₃·9H₂O (>98%), Co(NO₃)₂·6H₂O (>98%), Ni(NO₃)₂·6H₂O (98%), $Cu(NO_3)_2 \cdot 3H_2O$ (99–104%), $Zn(NO_3)_2 \cdot 6H_2O$ (99%), Y(NO₃)₃·6H₂O (99.9%), ZrO(NO₃)₂·xH₂O (99%), La(NO₃)₃·6H₂O (99.99%), $Ce(NO_3)_3 \cdot 6H_2O$ (99%), $Pr(NO_3)_3 \cdot 6H_2O$ (99.9%), Nd(NO₃)₃·6H₂O (99.9%), Gd(NO₃)₃·6H₂O (99.9%), Pb(NO₃)₂ (>99%), Al(NO₃)₃·9H₂O (98–102%), Ga(NO)₃·xH₂O (99.9%). The nitrates were added into distilled water at the target concentrations, followed by stirring for 3 h at room temperature.



Fig. 1. Temperature profiles of a batch reactor during a heating step at different reaction temperatures.

2.2. Reaction procedure

A stainless steel batch reactor (50 mL) lined with Teflon was used for hydrothermal treatment of alginic acid. A stirrer was located inside the reactor for an effective contact between insoluble alginic acid and metal cations in water (600 rpm). Alginic acid (0.6 g) and metal cation solution (30 mL) were added to the reactor. The sealed reactor was purged with nitrogen gas and mounted in a heater. The heating time to different target temperatures varied as shown in Fig. 1. The heating time, approximately 30 min, was excluded in counting reaction time. For example, 61 min of reaction time was actually needed to complete the hydrothermal reaction of alginic acid at 180 °C for 30 min, since it took 31 min for heating the reactor to the reaction temperature. After dwelling at the target temperatures, the reactor was immediately guenched with a cold-water. The final products obtained were filtered and centrifuge in order to separate liquid products from solid-liquid mixtures before analysis.

2.3. Product analysis

The furfural and organic acids in liquid products were quantified with an Agilent 1200 Series HPLC equipped with two Shodex RSpak KC-811 columns in series. RI detector (Agilent G1362A) and UV detector (Agilent G1314B) were used together for crosschecking the data. The wavelength of the UV detector was set to 210 nm in order to observe furfural and organic acids simultaneously. Phosphoric acid aqueous solution (5 mM), as a mobile phase, was run through the column (40 $^{\circ}$ C) at a flow rate of 1.0 mL min⁻¹.

Based on data obtained from HPLC analysis, molar yields of products were calculated as:

$$\text{Yield}_i(\text{mol}\%) = 100 \times \frac{nC_i}{6} \times \frac{n_i}{n_{\text{ru}}}$$

where nC_i = the number of carbon atoms in the organic product *i*, n_i = the number of moles of the organic product i as determined by HPLC analysis, n_{ru} = the initial number of moles of repeating units $(C_6H_8O_6)$ in alginic acid, equal to the mass of alginic acid divided bv 176.

The molecular weight distribution of products was analyzed by gel permeation chromatography (GPC). The GPC system (Ultimate 3000, Dionex) was composed of three types of columns (Waters Ultrahydrogel column: 120, 500 and 1000) in series. Sodium azide solution (0.1 M), as a mobile phase, flowed through the colum $(40 \circ C)$ at a flow rate of 1.0 mLmin⁻¹. Pullulan with a molecular weight distribution from 342 to 80,500 was used to calibrate the GPC system.

Furfural and intermediates of the hydrothermal reaction were identified 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 and working in positive or negative mode with a capillary temperature of 275 °C. Three types of mobile phases (0.1% of formic acid dissolved in distilled water, acetonitrile or methanol) were run through 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 UV wavelength was set from 210 to 280 nm.

3. Results and discussion

3.1. Effect of different metal cations on the conversion of alginic acid to furfural

The various metal cations were used as catalysts in the hydrothermal conversion of alginic acid to furfural at 200 °C for 30 min. It should be noticed that the reaction condition was determined based on the results of our previous research in order to compare the catalytic activity of metal ion catalysts. The determination of the reaction condition is important since the production of furfural from alginate over catalysts is greatly influenced by reaction temperature and time [10]. For example, the catalytic hydrothermal conversion of alginate to furfural is promoted by increasing the reaction temperature and time, however, the yield of furfural suddenly decreases in the reaction condition due to side reactions of furfural produced. Therefore, the reaction temperature (200 °C) and time (30 min) were selected as an optimal reaction condition in the evaluation of catalytic activity of various metal ions, in order to minimize the loss of furfural produced by the hydrothermal reaction of alginic acid. As shown in Fig. 2, Cu(II) ions shows the highest furfural yield (13.19 mol%) higher than two times the furfural yield obtained in a blank test (5.14 mol%). Based on the furfural yield of the blank test, Cu(II), Fe(III) and Pb(II) ions promoted the conversion of alginic acid to furfural. In the hydrothermal reaction under Zn(II), Co(II) and Ni(II) ions, there was little or no catalytic effect. Other metal cations except the six metal cations mentioned above inhibited the production of furfural rather than catalyzing it. In particular, the yield of furfural decreased from 5.14 to 2.5 mol% when Y(III) ions participated in the reaction. Generally, xylose obtained by hydrolysis of hemicellulose is sequentially dehydrated to furfural in the hydrothermal conversion of hemicellulose [23,24]. In contrast, glucose, a monomer of cellulose, tends to convert to hydroxymethylfufrual (HMF) rather than furfural, since glucose has an extra alcohol functional group compared to xylose [25]. The conversion of HMF to furfural was feasible via the loss of formaldehyde in HMF, but it is not favorable [26]. In the same manner, the carboxylic functional group of mannuronic acid and guluronic acid should be eliminated to produce furfural from alginic acid. In other words, both decarboxylation and dehydration are important steps for the conversion of alginic acid to furfural, which would be influenced by metal cations.

In order to explain the effect of metal cations on the production of furfural from alginic acid, the physical or chemical properties of the metal ions were correlated with the yields of furfural. Fig. 3(a)shows the correlation between the furfural yield and ionic radius of metal ions. For lanthanide metal ions, the yield of furfural linearly increases with the ionic radius of the metal ions. However, the lanthanide metal cations shows poor catalytic performance in the production of furfural, showing lower furfural yields than that of the blank test. The yields of furfural for post-transition metal ions are also proportional to the size of metal ions. The largest metal ions, Pb(II) (119 pm), exhibits the highest furfural yield (7.12 mol%) among the post-transition metal ions. On the other hand, there was no clear relation between the furfural yield and the ionic radius of transition metal cations. Overall, the yields of furfural produced by the hydrothermal reaction of alginic acid catalyzed by those two groups of metal ions are lower than by transition metal ions.

The yields of furfural under post-transition or transition metal ions are almost proportional to the electronegativity as shown in Fig. 3(b). The strong electronegativity of metal cations suggests that the metal ions can play a role of Lewis acid catalysts in the hydrothermal conversion of alginic acid, since the electronegative metal ions attract electrons towards itself, promoting the electron transfer in the reaction. Lewis acidity is proportional to the electronegativity of metal cations [27], which may lead to the acidcatalyzed dehydration in the conversion of alginic acid to furfural. On the other hand, the yield of furfural increases with decreasing electronegativity under the lanthanide metal ions, implying that these metal ions likely participate in the hydrothermal reaction through different pathways, compared to the transition metal ions.

In addition to furfural, a few organic acids were produced in the hydrothermal reaction of alginic acid. As listed in Table 1, glycolic acid, lactic acid and formic acid were mainly produced with furfural in the conversion of alginic acid at 200 °C for 30 min. In the blank

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Fig. 2. Catalytic performance of metal cations for the conversion of alginic acid to furfural at 200 °C for 30 min.

Fable 1
Effect of metal cations on the production of furfural and organic acids at 200 $^\circ$ C for 30 m

Catalyst (0.01 M)	Yield (mol%)				
	Furfural	Glycoic acid	Lactic acid	Formic acid	
Blank	5.14	0.32	_	2.36	
Zn (II)	5.77	3.19	-	2.24	
Cr (III)	3.75	5.87	3.34	1.96	
Mn (II)	3.44	0.88	-	3.03	
Co (II)	5.64	1.85	-	2.42	
Ni (II)	5.02	2.44	0.95	2.79	
Cu (II)	13.19	0.99	-	1.68	
Fe (III)	9.43	1.61	-	1.72	
Y (III)	2.5	2.15	-	4.8	
Pb (II)	7.12	2.91	2.24	2.31	
Ga (III)	3.49	3.76	5.63	3.33	
Al (III)	3.24	4.52	6.73	3.08	
Ce (III)	3.92	2.53	-	3.73	
Pr (III)	3.77	1.54	-	3.97	
La (III)	4.31	1.56	1.24	3.6	
Nd (III)	3.66	2.60	-	4.24	
Gd (III)	2.92	2.67	-	5.37	

test, 0.32 mol% of glycolic acid and 2.36 mol% of formic acid were formed with 5.14 mol% of furfural. The Cu(II) ions yielded relatively small amounts of organic acids compared to other metal cations, while the Cu(II) ions exhibited the best catalytic performance in the production of furfural. This indicates that Cu(II) ions can convert alginic acid to furfural more selectively than different metal ions. The highest yield of glycolic acid was achieved in the reaction under Cr(III) ions. The production of both furfural and glycolic acid is an evidence of which the acid-catalyzed reaction took place in the conversion of alginic acid due to Brønsted acid (H⁺) provided from alginic acid in the aqueous reaction medium [10]. However, relatively high amounts of lactic acid were produced under Pb(II), Ga(III) and Al(III) ions, implying that the post-transition metal cations seem to activate both the acid- and base-catalyzed hydrothermal reactions of alginic acid.

As demonstrated in Fig. 4, the yield of formic acid is reversely proportional to that of furfural. In our previous research, it was observed that furfural mainly concerted to formic acid and water-insoluble humins in hydrothermal conditions [10]. Therefore, the high yield of formic acid with the low yield of furfural can be explained by the decomposition of furfural under metal cations,

such as Gd(III) and Y(III) ions. However, Cu(II) and Fe(III) ions seem to make furfural produced stable in the acidic hydrothermal condition. Otherwise, more formic acid should be produced from more furfural produced under Cu(II) and Fe(III) ions.

3.2. Influence of reaction conditions on production of furfural

In order to study the effect of reaction conditions on the production of furfural, the hydrothermal treatment of alginic acid was performed at different reaction temperatures and times. As shown in Fig. 5, the reaction temperature and time strongly influenced the production of furfural. When Cu(II) ions were used as a catalyst, the yield of furfural significantly increased compared to the blank test at 200 °C. The maximum furfural yield (13.19 mol%) was obtained at 200 °C in 30 min, however, it rapidly decreased to 5.34 mol% for next 30 min. The decreasing furfural yield after 30 min seems to be ascribed to the hydrothermal conversion of furfural to formic acid or humin compounds. At 220 °C, the maximum value of furfural yield could not be observed, which can be explained as furfural produced began to be degraded or polymerized prior to reaching to the target temperature due to a sufficiently long ramping

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Fig. 3. Effects of physical or chemical properties of metal cations on the yield of furfural produced at 200 °C for 30 min. (a) ionic radius of metal ions, (b) electronegativity of metal ions.

period, approximately 30 min. At lower temperatures than 200 °C, both the maximum furfural yields and the production rates of furfural were lower than at 200 °C. For instance, the yield of furfural reached to the maximum value, 9.53 mol%, at 160 °C after 180 min and it was constant after next 180 min, indicating that furfural is hydrothermally stable at 160 °C.

In addition to the reaction temperature and time, the concentration of metal ions significantly influenced the yield of furfural, as plotted in Fig. 6. Interestingly, there was an optimal concentration of Cu(II) ions for the highest furfural yield. When the hydrothermal treatment of alginic acid was conducted at 200 °C under 0.01 M of Cu(II) ions, 13.19 mol% of furfural was produced. As the Cu(II) concentration increased from 0.0025 to 0.01 M, the yield of furfural rose from 7.39 to 13.19 mol%, which means that the increasing Cu(II) ions further catalyzed the conversion of alginic acid to furfural as Lewis acid catalysts. On the other hand, higher concentrations of Cu(II) ions than 0.01 M was likely to inhibit the conversion of alginic acid to furfural rather than catalyzing it. The excess Cu(II) ions seems to unselectively react with oxygen atoms of alginic acid, leading to side reactions. For example, the metal ions can interact with oxygen atoms of each carboxyl group of alginic acid and thus bidentate chelate compounds are formed [28], which might hinder the decarboxylation of alginic acid monomers.

3.3. Effect of metal cations on hydrothermal depolymerization of alginic acid

Fig. 7 shows the effect of metal ions on the depolymerization of alginic acid. Compared to the blank test, Y (III) ions catalyzed the degradation of alginic acid, while the catalytic effect by Cu(II)

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Fig. 4. The correlation between yields of furfural and formic acid produced in the conversion of alginic acid under various metal cations at 200 °C for 30 min.



Fig. 5. Effect of reaction temperature and time on the conversion of alginic acid to furfural catalyzed by Cu (II) ions.

ions were insignificant. As mentioned above, Cu(II) and Y(III) ions exhibited the highest and lowest furfural yield in the conversion of alginic acid, respectively. Based on the peak of monomer, Y(III) ions promoted the production of smaller molecules than monomers, mannuronic acid and guluronic acid. Y(III) ions are effective for the hydrothermal decomposition of alginic acid, but not for the production of furfural. On the contrary, Cu(II) ions are favorable for the conversion of alginic acid to furfural in spite of the relatively low catalytic performance for degrading alginic acid. The concentration of metal ions also influences the depolymerization of alginic acid as listed in Table 2. The sample produced in 0.01 M of Cu(II) ion solution has the highest weight average molecular weight (M_w) with the highest polydispersity index (PDI) value, indicating that the Cu(II) concentration shows relatively low catalytic performance in the depolymerization of alginic acid with a wide molecular weight

Table 2

Effect of Cu (II) ion concentration on the depolymerization of alginic acid at 200 $^\circ\text{C}$ for 30 min.

Sample	$M_{ m w}$ (Da)	M _n (Da)	PDI
Raw alginic acid	240,000	-	-
Cu (II)-0.0025 M	1482	658	2.25
Cu (II)-0.05 M	1452	666	2.18
Cu (II)-0.01 M	1711	712	2.40
Cu (II)-0.02 M	1470	937	1.57
Cu (II)-0.04 M	1613	1148	1.40

distribution of liquid product, compared to different Cu(II) concentrations. The relation between the Cu(II) concentration and the PDI value is similar with that between the Cu(II) concentration and the furfural yield as shown in Fig. 6. This suggests that furfural is pro-

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Fig. 6. The yield of furfural produced by the hydrothermal reaction of alginic acid under Cu (II) ions with different concentrations.



Fig. 7. GPC chromatograms of liquid products obtained by the hydrothermal treatment of alginic acid under Cu (II) and Y (III) ions at 200 °C for 30 min.

duced more abundantly when alginic acid is decomposed to various sizes of molecules rather than similar sizes of molecules.

3.4. Reaction pathway of furfural production from alginic acid

As mentioned above, a monomeric unit of alginic acid has a carboxyl group, providing Brønsted acid (H^+) to the aqueous reaction medium. The acidic reaction medium can act as an acid catalyst in the conversion of alginic acid to furfural, via catalyzing hydrolysis and dehydration reactions. In the hydrothermal conversion of xylose to furfural, Brønsted acid significantly enhances the acid-catalyzed dehydration of xylose, a key reaction for the furfural production [29,30]. Based on the structural differences between the monomers of alginic acid and xylose, the removal of the carboxyl group is necessary for the production of furfural from alginic acid. As shown in Fig. 8(a), a plausible reaction pathway for the catalytic conversion of alginic acid to furfural involves both decarboxylation and dehydration. As an evidence, carbon dioxide generated in all reactions performed as a main gaseous product, simply checked by gas chromatography equipment. Furfural and intermediates in a product sample were also detected by LC–MS analysis, as shown in Fig. 8(b–f). Prior to the decarboxylation, the dehydration of monomer at C-3 position is necessary, since a carbonyl group near the carboxyl group is favorable for the

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Fig. 8. Proposed reaction pathway of the furfural production from monomer of alginic acid catalyzed by Cu (II) ions. (a) reaction network, (b–e) mass spectrum of monomer and intermediates at negative ionization mode, (f) mass spectrum of furfural at positive ionization mode.

cleavage of the linkage between C-1 and C-2 positions. The carbonyl group can be formed by keto-enol tautomerization. Metal cations can play a role of catalyst promoting keto-enol tautomerization in hydrothermal conditions [31,32]. In the hydrothermal reaction of alginic acid, Cu(II) ions likely catalyze the tautomerization, leading to the formation of the carbonyl group at C-2 position. After the decarboxylation, the intermediate is transformed to a ring type of compound, followed by sequential dehydration of the ring compound to furfural. In the conversion of alginic acid to furfural, the tautomerization catalyzed by metal ions is likely a key reaction determining the yield of furfural. Based on the correlation between the electronegativity and the furfural yield, it is strongly suggested that the high electronegativity is favorable for the ketoenol tautomerization since electrons of an oxygen atom can be easily attracted to electronegative metal cations.

4. Conclusions

The hydrothermal treatment of alginic acid under metal cations was performed in order to study the effect of metal cations on the production of furfural. Among many metal ions, Cu(II) ions exhibited the best catalytic performance for the conversion of alginic acid to furfural. The yield of furfural was proportional to the electronegativity of metal ions, however, there was no clear relationship between the furfural yield and the size of metal ions. Experimental conditions, such as temperature, time and concentration of metal ions, are significantly influential on the production of furfural from alginic acid. From the results of GPC analysis, it was found that the high degree of depolymerization did not guarantee the high furfural yield in our reaction conditions. The proposed reaction pathway suggests that the tautomerization catalyzed by metal ions is important for the conversion of alginic acid to furfural via decarboxylation and dehydration.

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