Catalytic conversion of alginic acid to furfural using 12-tungstophosphoric acid catalyst in tetrahydrofuran/water co-solvent

테트라하이드로퓨란/물 공용매에서 헤테로폴리산을
이용한 알긴산으로부터 푸르푸랄 생성

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박건우

Abstract

Catalytic conversion of alginic acid to furfural using 12-tungstophosphoric acid catalyst in tetrahydrofuran/water co-solvent

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Furfural is one of platform chemicals from biomass conversion processes listed by the US Department of Energy (DOE). The world wide demand for furfural is expected to steadily increase, because furfural can be used as a starting compound in production of furan-derivates such as a polymer unit, organic solvent and various

liquid fuel additives. Until now, furfural has been exclusively obtained from hemicelluloses despite increasing demand for furfural, suggesting that diversification of feedstock is necessary for stable supply of furfural. In view of this, we attempted to produce furfural using alginic acid derived from brown seaweeds, and considered a possibility whether alginic acid could be used as an alternative feedstock for furfural production. Alginic acid, main constituent of brown seaweed, is a bio-polymer comprised of hexuronic acid monomers (mannuronic acid and guluronic acid) via β-1,4-glycosidic bond. Notably, the direct conversion of alginic acid to furfural is a somewhat different approach for utilization of the marine algae biomass. In the present work, the decomposition of alginic acid was performed in tetrahydrofuran (THF)/water co-solvent over Brønsted acid catalysts, such as H_2SO_4, Amberlyst15 and 12-tunstophosphoric acid ($H_3PW_{12}O_{40}$) in order to investigate the effect of the different acid catalysts on the furfural production. Among the catalysts, $H_3PW_{12}O_{40}$ exhibited a higher catalytic performance than other acid catalysts by suppressing the formation of by-product such as an insoluble black precipitate (humin). The maximum furfural yield from alginic acid was 33.8% under the reaction conditions of 180 ^{o}C for 30 min in THF/water co-solvent containing 5% (v/v) water over $H_3PW_{12}O_{40}$. To our knowledge, this is the highest furfural yield among the studies about the alginic acid decomposition. In this reaction, THF was a more effective reaction medium than water for furfural production. In particular, addition of small amounts of water to THF drastically enhanced the furfural yield. Furthermore, products distribution with time-stream was investigated to elucidate the reaction pathway. This result

showed that alginic acid was initially hydrolyzed to hexronic acid, and then it converted to furfural by removing carbon dioxide and water molecules from the hexuronic acid in presence of acid catalyst. In the reaction pathway, subsequent reaction comprised of decarboxylation and dehydration occurred slower than hydrolysis, which led us to determine rate-limiting steps in the proposed reaction pathway.

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Chapter 1. Introduction

1.1. Background

Rapid consumption of limited fossil fuels causes a imbalance problem between supply and demand of energy, and accelerates the global warming due to carbon dioxide emission by combustion of the fossil fuels.[1] To ease off these energy and environmental problems, biomass has attracted attention as an alternative energy source that can replace the fossil fuel.[2] Since the biomass consists of carbon, hydrogen, and oxygen, which are the basis of organic compound, it has a potential to be applied to the conventional petrochemical process. In addition, biomass has an advantage of carbon neutral which means that carbon is not accumulated in the air, because biomass is requires the carbon dioxide to grow through photosynthesis.[1, 3] The current research efforts of utilization of lignocellulosic biomass in fuels and chemicals are being focused on the production of building block chemicals, such as hydroxymethylfurfural (HMF) and furfural, for bio-based products. These furanic aldehydes have been obtained via dehydration of monosaccharides (hexose and pentose) prepared by acid hydrolysis of carbohydrate polymers (cellulose and hemicelluloses).[4-7] Furfural, the latter of these furanic aldehydes, is one of platform chemicals of biomass conversion processes specified in the U.S. Department of energy (DOE).[8] The world wide demand for furfural is expected to steadily increase, because furfural can be used as a starting compound for furan-derivates such as polymer unit (furfuryl alcohol),

organic solvent (THF) and various liquid fuel additives.[9-11]

To date, although the interest in valorization of marine algae biomass resources has not been as much as that of ligonocellulosic biomass, macroalgae is thought to promising renewable energy resource since it has inherent advantages such as fast growth rate, ease of cultivation, and lignin free.[3, 12-14] Alginic acid, main constituents of brown seaweed,[15-17] is a carbohydrate polymer comprised of mannuronic acids and guluronic acids via β-1,4-glycosidic bonding similar with glucose linkages in cellulose, as shown in Figure 1.[18-21] This structure similarity tells us that reaction conditions used in lignocellulosic biomass conversion can be applied to the marine algae biomass utilization. However, because alginic acid has carboxyl group at the C5 position in monomeric unit of polymer structure in contrast to cellulose, decomposition products distributions of those carbohydrates are thought to be different from each other. It has been demonstrated that main products of alginic acid degradation in hydrothermal conditions are its monomers (mannuronic acid, guluronic acid) and C1-C5 organic acids (formic acid, glycolic acid, lactic acid, etc.), and furfural is considered as a byproduct due to its low selectivity.[22-24] To our knowledge, there have been few studies attempting to produce the furfural as target compound in alginic acid conversion. In previous our research, hydrothermal decomposition of alginic acid sodium salt under concentrated acid conditions were studied and enhancement of furfural production was observed, but the carbon yield of furfural still remained at a low level (13%).[25]

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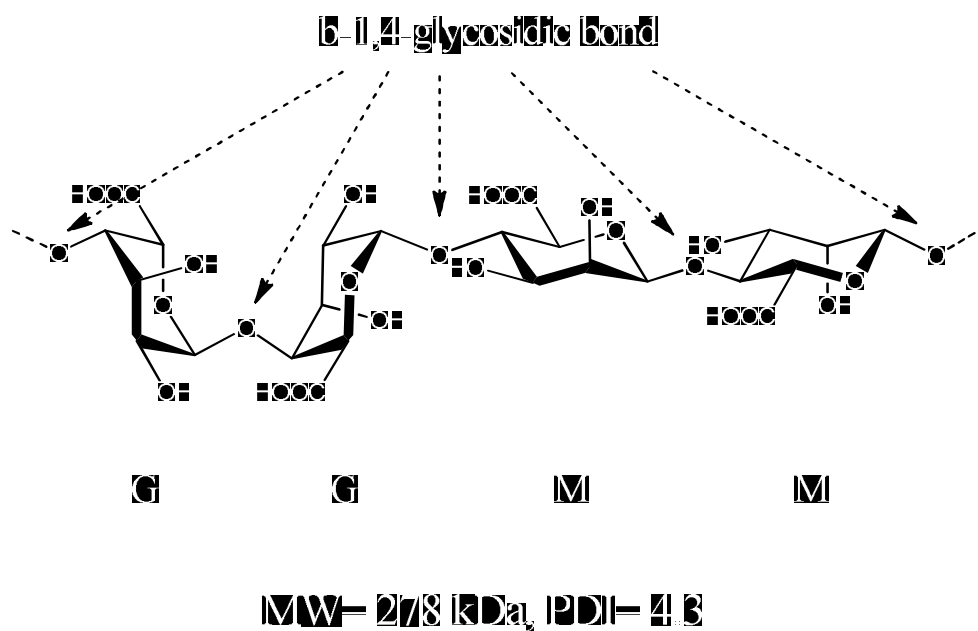
Figure 1. Structure of alginic acid derived from brown-seaweed

1.2. Objective

Two important factors in this study applied to obtain the higher furfural yield are introductions of (i) Keggin-type heteropolyacid and (ii) THF solvent. Firstly, suitable Brønsted acid catalyst should be used to produce the furfural from alginic acid because this reaction involves the hydrolysis and the dehydration similar to hemicellulose conversion.[26] It has been steadily attempt to convert the biomass into useful compounds by using heteropolyacids,[20, 27-29] which is stronger in solution than usual mineral acids such as H_2SO_4 and HCl.[30] For example, Mizno et al. found that negatively charged heteropolyacids showed a good performance for the hydrolysis of cellulose,[31] and Valente et al. studied the dehydration of xylose using heteropolyacids.[32] Herein, we attempted to enhance the furfural yield using commercial $H_3PW_{12}O_{40}$, Keggin-type heteropolyacid. Secondly, reaction medium is known to highly influence the product distribution and selectivity of platform chemical on biomass conversion.[33-35] It has been reported that hydrothermal treatment, the most basic form, using water as the reaction medium is poor for furfurals production because of the low selectivity causing many side reactions.[36] In addition, many studies have been carried out using ionic liquid to reduce the effect of hydrogen bond causing the rigid cellulose structure,[37-39] but this solvent has a problem in economic terms due to its expensive price.[33] Recent researches have been attempted to increase the yield of furfurals introducing the organic solvent such as polar aprotic solvent.[40-42] Recently, Huber et al. reported conversion of cellulose into HMF using acid catalyst in polar aprotic solvents; when THF solvent was used, HMF yield was

higher than that of other solvents, and the maximum yield was 44%.[43] THF is advantageous to reduce energy input required for the separation of products, because it has a low boiling point, specific heat and heat of vaporization than water.[40, 43] For those reasons, we chose THF solvent as a reaction medium to increase the furfural yield and process operating effectiveness.

In the present work, the catalytic conversion of alginic acid to furfural with different Brønsted acids (H_2SO_4, Amberlyst15, and $H_3PW_{12}O_{40}$) in THF solvent has been studied and activities of the catalysts are compared. Reaction conditions such as temperature, time, water content in the reaction medium and catalyst concentration were systematically investigated and optimized to obtain highest furfural yield. Thermal and water effect on furfural production are discussed in detail. In addition, we examine the products distribution as a function of time-stream to clarify the transformation pathway of alginic acid to furfural under acidic conditions and consider a rate-limiting step of the reaction.
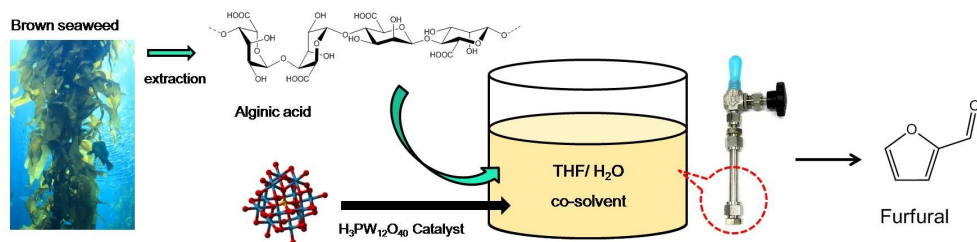
Scheme 1. Graphical outline of this work

Chapter 2. Experimental

2.1. Materials

Tetrahydrofuran (THF) was purchased from Sigma-Aldrich and used as 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 (GlA) were purchased from Qingdao BZ Olig Biotech, China (Purity > 98%). Furfural, triethylamine (TEA), glucuronic acid (GcA) and glucuronolactone (GcL) were purchased from Tokyo Chemical Industry and Alfa Aesar. Brønsted acid catalysts, sulfuric acid (H_2SO_4), Amberlyst15 and phosphotungstic acid hydrate ($H_3PW_{12}O_{40} \cdot xH_2O$) were purchased from Junsei Chemical, Alfa Aesar and Sigma-Aldrich, respectively. Unless otherwise indicated, all chemicals were reagent grade and used as received.

2.2. Catalytic reaction of alginic acid.

All batch reactions were conducted in SUS316 tubular reactors (Swagelok) with inner volume of 4mL. 10mg of substrate (alginic acid, GcA, GcL or furfural), Brønsted acid catalyst (H_2SO_4, Amberlyst15 or $H_3PW_{12}O_{40}$) and 1mL of x% (v/v) THF/Water mixture, denoted by x is the water contents in reaction medium, were charged into the reactor with a magnetic stirrer. Amount of the solid catalyst

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loading was 10 and 20 mg, and the proton concentration of H_2SO_4 solution was adjusted to 0.05 and 0.10 M. The reactor is then soaked into an oil bath maintained at different temperatures (150–190 °C) for desired reaction times with stirring at 400 rpm. Time zero was defined by excepting the heating time (2 min in average). After the reaction, the reactor was quenched with cool water to prevent further degradation. Obtained products were centrifuged and filtered, followed by diluted with water before the analysis.

2.3. Analytical methods

2.3.1. Gas chromatography (GC)

CO_2 produced by decarboxylation of alginic acid was measured 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 by using gas-tight syringe and the samples were injected to GC by 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, ramped to 225 °C at 20 °C min^{-1}.

2.3.2. Liquid chromatography-mass spectroscopy (LC-MS)

Hexuronic acids, intermediates of the reaction, were identified by liquid

chromatography–mass spectrometry (LC-MS). LC-MS was performed using a Thermo Scientific LCQ Deca XP Plus and Surveyor high performance liquid chromatograph (HPLC) system equipped with A Phenomenex Synergi 4 μm Fusion-RP 80 Å column. 0.1% (v/v) formic acid solution was used as mobile phase at a flow rate of 250 μL min^{-1}. On the MS analysis, capillary temperature and spray voltage was 250 °C and 5000 V.

2.3.3. High performance liquid chromatography (HPLC)

All the products were analyzed by 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}. The samples were adjusted to a final concentration of 1% (v/v) TEA 10 min prior to analysis, in order to facilitate the hexuronic acid detection.[44, 45] Concentrations of MnA and GlA were measured by the UV detector (Agilent G1314B) at 210 nm, while furfural was quantified on RI detector (Agilent G1362A). The separation of each product was effectively achieved as shown in Figure S1. Based on data obtained from HPLC analysis, carbon yields of products and turnover frequency (TOF) were calculated as follows:

$$[\text{Carbon Yield}]_i \ (\%) \ = \ 100 \ \times \ \frac{\text{moles of carbon of product i}}{\text{initial moles of carbon in feed}}$$

$$\text{Turnover frequency (s}^{-1}) \ = \ \frac{\text{d(moles of furfural produced)}}{\text{dt} \cdot \text{moles of protons}}$$
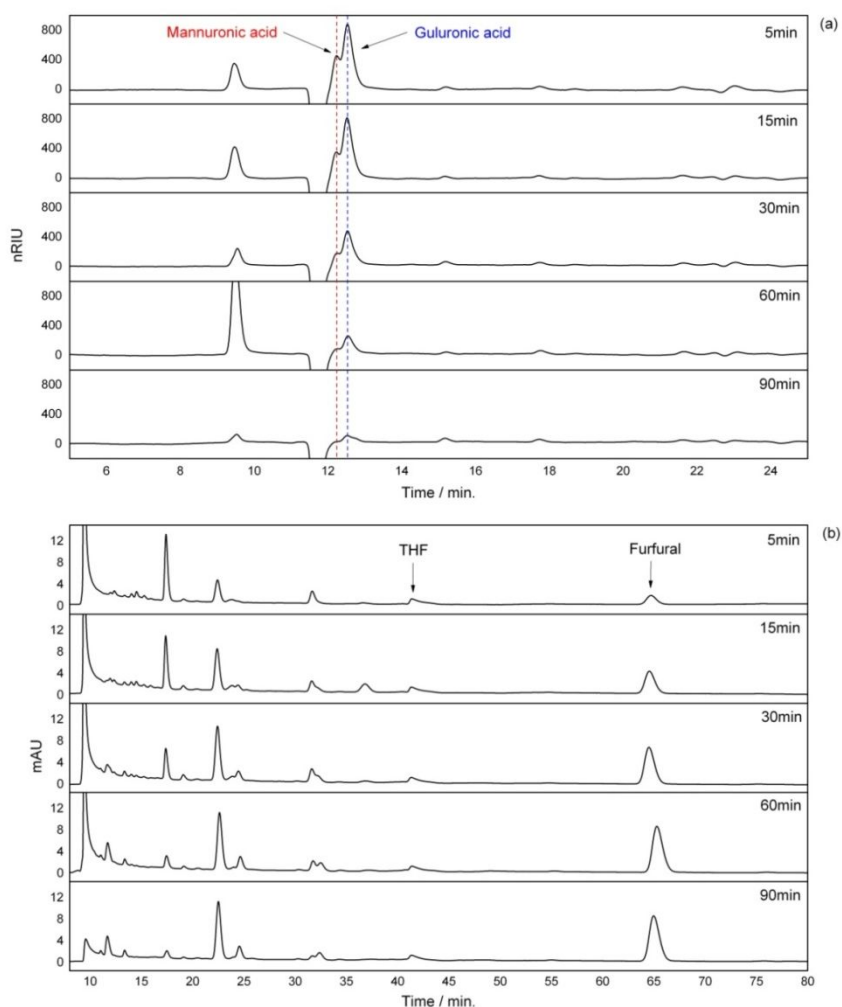
Figure 2. HPLC chromatograms of product samples during the decomposition of alginic acid

The chromatogram (a), the signal of RI detector, was obtained after treating the product with TEA (1% (v/v)) before HPLC analysis to transform uronic acid lactone to uronic acid. The chromatogram (b), the signal of UV detector, was obtained without treating the product with TEA. Reaction conditions: alginic acid (10 mg), $H_3PW_{12}O_{40}$ catalyst (10 mg), THF/water co-solvent (1 mL, 5% (v/v) water ratio), 170 °C, and stirring speed of 400 rpm.

Chapter 3. Result and discussion

3.1. Acid catalyzed reaction of alginic acid to furfural

We initially investigated the decomposition of alginic acid to furfural in THF containing 5 % (v/v) water, by using the three types of Brønsted acid and varying the amount of catalyst at 170 °C (Table 1, Figure 3). The acid catalyzed reactions were carried out with H_2SO_4, Amberlyst15, and $H_3PW_{12}O_{40}$ as Brønsted acid catalysts. In order to determine the yield of furfural according to the amount of catalyst, the experiments were performed with different catalyst loadings (the concentration of H_2SO_4 was adjusted as equal to the proton concentration of Amberlytst15). To verify the effect of THF on furfural production, the reaction medium used to entry 1-7 was small amounts of water added THF and entry 8 was pure water.

The catalytic activity of Brønsted acids for the reaction could be confirmed by comparing the blank test (without acid catalyst) with other experiments (Table 1, entry 7 versus 1–6). As can be seen from entries 1–6 in Table 1, when employing the $H_3PW_{12}O_{40}$ catalyst, the furfural yield was higher than using the H_2SO_4 or Amberlyst15. As listed in Table 1, the catalytic performance of each catalyst is evaluated by the TOF values, since the concentration of Brønsted acid (H^+) can be a reliable standard in the evaluation for the different catalysts.[46] In particular, TOF values for furfural production demonstrates a significant activity difference

between the catalysts. The catalytic activities based on TOF values of the $H_3PW_{12}O_{40}$ are about 10–12 times higher than those of H_2SO_4 and Amberlyst15, showing that the proton reactivity of $H_3PW_{12}O_{40}$ is superior to those of the other catalysts (Table1, entry 1-6). A.S Dias et al. reported xylose dehydration over heteropolyacids in DMSO, giving 40.2 ($\times 10^{-5}$ /s) maximum TOF value of $H_3PW_{12}O_{40}$ catalyst at 140 °C for 4h.[32] Although different biomass resources were used as reagent for production of furfural, the TOF values for $H_3PW_{12}O_{40}$ using alginic acid or xylose were of the same order of magnitude, suggesting that alginic acid can be used as a feedstock for furfural synthesis as well. The effect of catalyst loading on furfural production can be determined with comparison of entry 1–3 and 4–6 in Table 1. It demonstrates that the increase of catalyst loading enhances furfural yield. However, there is a non-linear relation between the catalyst loading and the furfural yield, and thereby TOF values of catalysts decrease. As shown in entry 3 and 8 in Table 1, the furfural yield in small amounts of water added THF is 5 times higher than that in pure water (only 4.3%), which indicates THF solvent is effective reaction medium for the alginic acid conversion. The high furfural yield in THF is attributed that the heteropolyanion and furfural are more stable in organic solvents than in aqueous medium.[47, 48] In addition, it is probable that the heteropolyanion stabilizes reaction intermediates due to its high affinity to organic molecules, leading to a high activity of $H_3PW_{12}O_{40}$.[49]

Figure 3 shows activities of the catalysts depending on the amount of catalyst and reaction time. The activity of $H_3PW_{12}O_{40}$ was higher than that of H_2SO_4 and Amberlyst15 in whole reaction time range. In all the three acid catalysts, the

maximum yields of furfural were obtained at 60 min regardless of catalyst loadings, followed by the furfural production was decreased. The furfural yields slightly increased if the catalyst loading was increased from 10 to 20 mg. When the amount of catalyst was doubled, the slope of furfural production with time was steeper in initial reaction time (from 5 to 15 min), whereas after 60 min the furfural yields decreased faster from the maximum yield. It appears that the more Brønsted acid loading elevates the further degradation of furfural as well as the production rate. As catalyst loading increased, the maximum furfural yield using H_2SO_4 (from 11.7 to 16.5%) and Amberlyst15 (from 13.1 to 17.7%) was increased, but there was a little variation of the maximum yield in case of $H_3PW_{12}O_{40}$ (from 29.7 to 30.3%). These results point out that the $H_3PW_{12}O_{40}$ loading do not significantly impact the maximum furfural yield in this reaction condition.

The higher catalytic performance of $H_3PW_{12}O_{40}$ than H_2SO_4 and Amberlyst15 was proved by the relatively high furfural yields obtained via the acid-catalyzed conversion of alginic acid in THF co-solvent. The superior catalytic activity of $H_3PW_{12}O_{40}$ can be deduced by observing the products samples. It can be seen that a higher conversion of alginic acid was attained when using $H_3PW_{12}O_{40}$ (85%) than H_2SO_4 (63%). The external oxygen atoms in heteropolyanion seems to be more favorable for accepting hydrogen bonds in carbohydrate polymers, leading to the decrease of the interaction between the polymer chains.[31] This unique property of $H_3PW_{12}O_{40}$ might promote the decomposition of alginic acid more effectively. Furfural, commonly, is polymerized into humin, being insoluble solid residue, and also decomposes to organic acids such as formic acid in hot acid aqueous

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medium.[50-52] Figure 4 shows the formation of humin as a by-product in alginic acid decomposition. Relatively more humin was formed over H_2SO_4 than $H_3PW_{12}O_{40}$. This indicates that $H_3PW_{12}O_{40}$ has higher selectivity for furfural production by work inhibiting the undesired side reactions.

Apart from the high activity of $H_3PW_{12}O_{40}$ for furfural production, because heteropolyacids have high solubility in polar solvents and particularly are more expensive than mineral acids, the recovery and recycling of heteropolyacids are key issue for practical applications.[53] A solution to this challenge can be deduced from the performance of H_2SO_4 and Amberlyst15 which are homo- and heterogeneous catalyst, respectively. Both the H_2SO_4 and the Amberlyst15 have a same sulfuric acid group as Brønsted acid site, and the TOF values of these catalysts were comparable, as shown in entries 2-3 and 4-5 of Table 1. This result indicates that mass-transport limitation of alginic acid molecules do not occur at macropore channel in Amberlyst15. Therefore, this implies that other solid acid catalysts, such as heteropolyacid immobilized to support, having meso- and macropore like Amberlyst15, might be also applicable to the alginic acid conversion.

Table 1. Decomposition of alginic acid to furfural using Brønsted acid catalysts with different catalyst loadings and conditions[a]

Entry	Acid catalyst	Catalyst loading	Furfural carbon yield [%]	TOF [$s^{-1} \times 10^{-5}$]
1	H_2SO_4	0.05 M[c]	8.9	7.0
2	Amberlyst15	10 mg	6.3	4.6[d]
3	$H_3PW_{12}O_{40}$	10 mg	22.8	75.5
4	H_2SO_4	0.10 M[c]	15.0	5.5
5	Amberlyst15	20 mg	12.5	4.6[d]
6	$H_3PW_{12}O_{40}$	20 mg	28.8	47.5
7	none	-	1.8	-
8[b]	$H_3PW_{12}O_{40}$	10 mg	4.3	14.4

[a] Reaction conditions: Alginic acid (10 mg), THF/Water reaction medium (1 mL, 5 % (v/v) water ratio in mixture), 170 °C, 30 min, and stirring at 400 rpm.

[b] The reaction was performed in pure water without THF and other conditions were same.

[c] Proton concentration in reaction medium.

[d] TOF calculation of Amberlyst15 was based on the acid density as specified by Rohm and Hass Company (5.0 mmol/g).
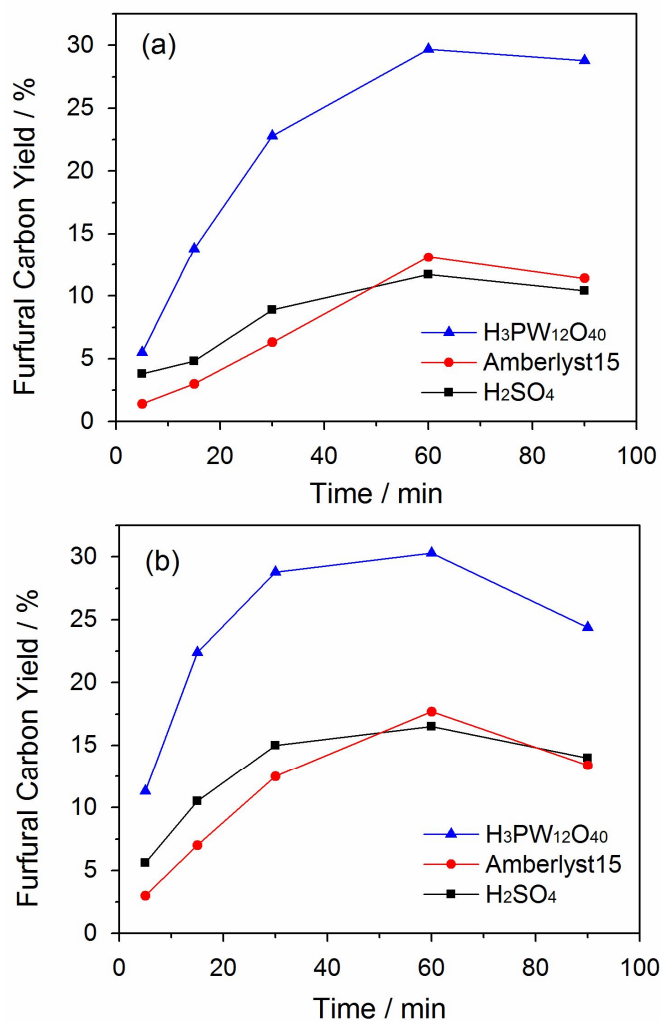
Figure 3. Yield of furfural from alginic acid with time-on-stream using Brønsted acid catalyst

Reaction conditions: Alginic acid 10 (mg), catalyst loading ((a) 10 mg (or 0.05 M) and (b) 20 mg (or 0.1 M)), THF/water co-solvent (1 mL, 5% (v/v) water ratio), 170 ^{o}C, and stirring speed of 400 rpm.
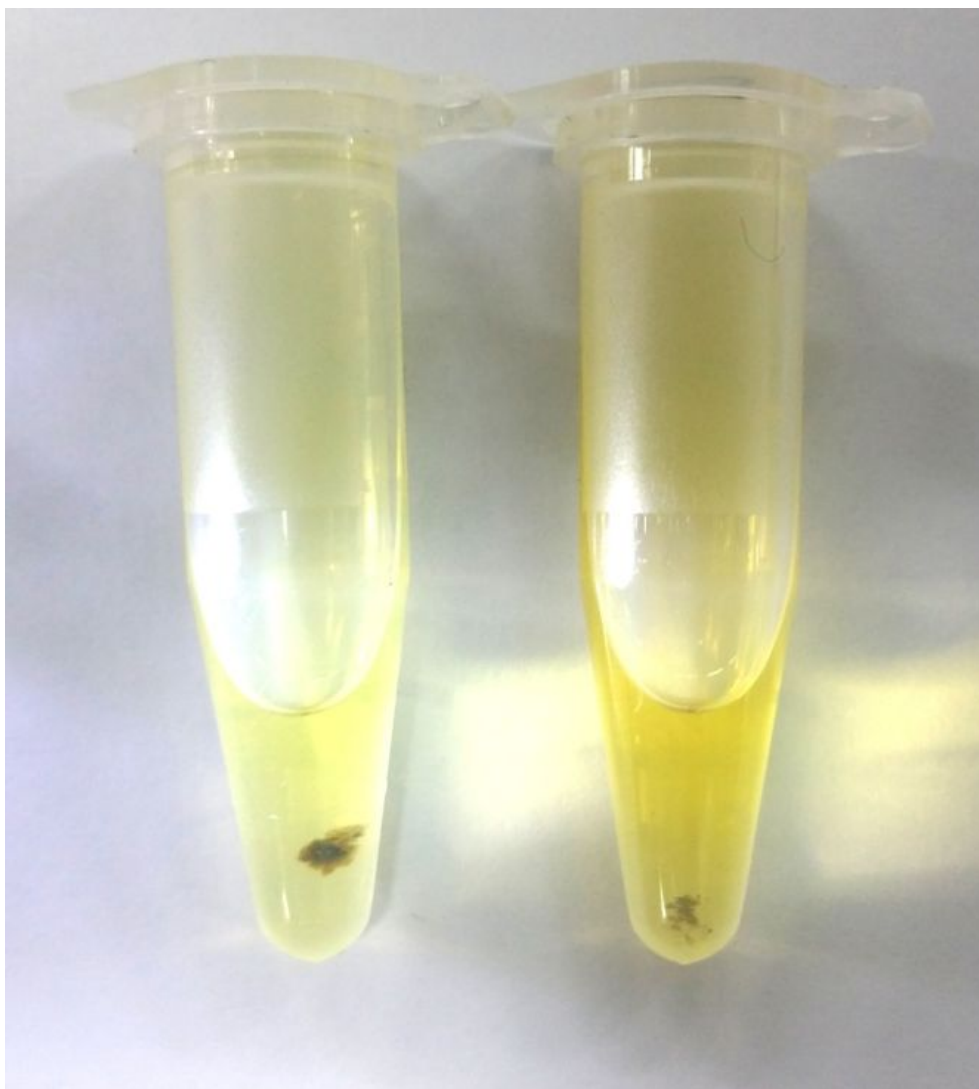
Figure 4. Formation of humin in alginic acid decomposition using H_2SO_4 (left) or $H_3PW_{12}O_{40}$ (right)

Reaction conditions: alginic acid (10 mg), H_2SO_4 (0.05 M) or $H_3PW_{12}O_{40}$ (10 mg), THF/water co-solvent (1 mL, 5% (v/v) water ratio), 170 °C, 15 min, and stirring speed of 400 rpm.

3.2. Thermal effect on furfural production

The effect of reaction temperature on the production of furfural from alginic acid was investigated, as shown in Figure 5. The reaction was conducted in the range of 150 °C to 190 °C. The trend of furfural production is rather different despite of the small temperature changes (10 °C), indicating that temperature significantly affects the furfural production. As the reaction temperature increased, the initial rate of furfural production also increased. At 5 min of the reaction, furfural yield was 0.8% at 150 °C, while the yield was increased to 24.4% at 190 °C. The maximum yield of furfural was obtained with less reaction time at higher temperature. More notably, the highest furfural yield in this study reaches 33.8% at 180 °C for 30 min. Such relationships between temperature and furfural yield might be associated with the conversion of alginic acid. It was observed that alginic acid was completely converted within 5 min of reaction time at 190 °C, whereas the unreacted alginic acid remained after reaction at 150 °C for 30 min. Thus, the enhancement of furfural production at high temperature is attributed to the thermal energy which facilitates the depolymerization of alginic acid.

Meanwhile, the maximum furfural yield decreased when the temperature increased further from 180 to 190 °C. Furthermore, as the reaction proceeded, the furfural yield decreased more rapidly after point of the maximum yield. Such behavior can be explained by two reasons; (i) thermal degradation of THF solvent and (ii) further decomposition of produced furfural. THF is regarded as stable and acid-resistant solvent because identifiable degradation products of the solvent were

not detected in hot sulfuric acid solution (170 °C). However, it was reported that low reaction temperature below 180 °C was recommended when THF was used as reaction medium, since THF performed poorly by its thermal degradation above 180 °C.[43] Figure 6 shows decomposition behavior of furfural as a function of temperature to determine the stability of furfural under the same reaction condition. Furfural unreacted decreased linearly from 97 to 50% when the temperature increased from 150 to 190 °C. In addition, the production of formic acid increased with elevating temperature as shown in Figure 7, where the yield of formic acid was about 2 times higher at 190 °C than at 150 °C. These results demonstrate that furfural is destabilized more significantly due to the thermal decomposition under acidic condition at the elevated reaction temperature.[48]
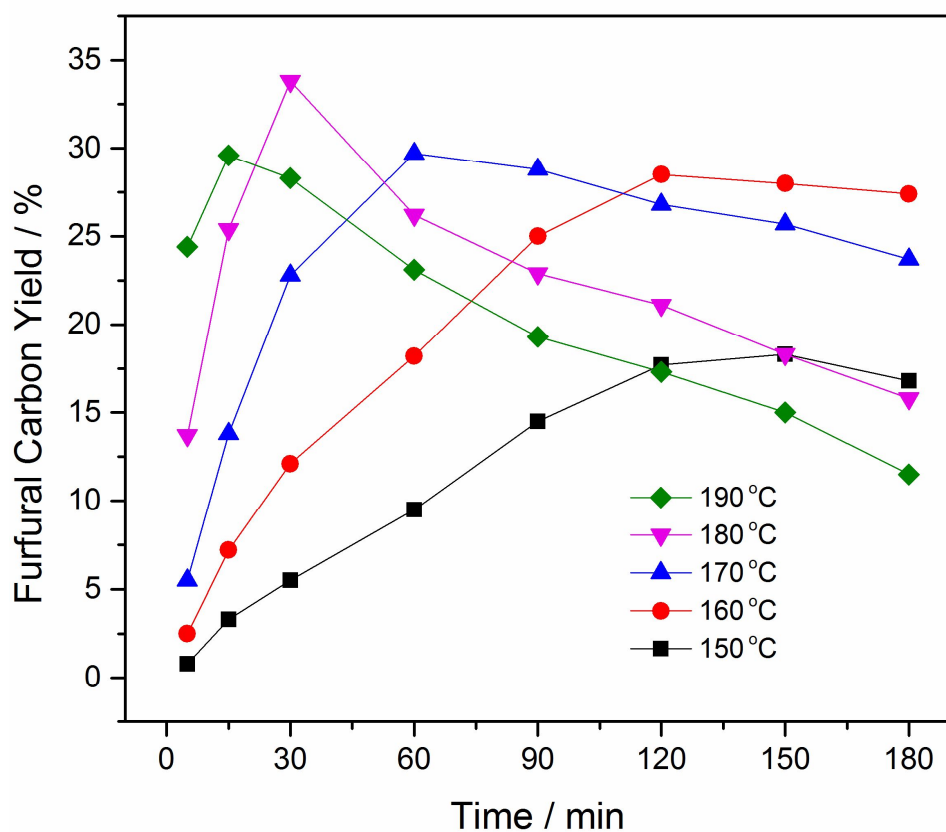
Figure 5. Yield of furfural with time-on-stream as a function of temperature

Reaction conditions: Alginic acid 10 (mg), $H_3PW_{12}O_{40}$ catalyst (10 mg), THF/water co-solvent (1 mL, 5% (v/v) water ratio), and stirring speed of 400 rpm.
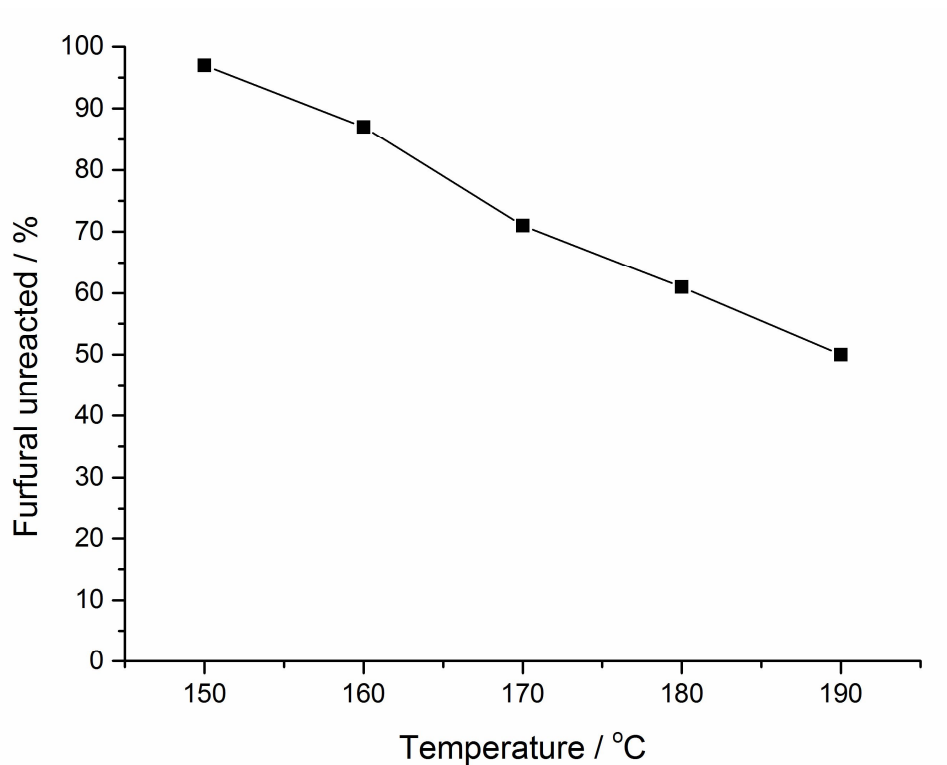
Figure 6. Decomposition of furfural by acid catalyzed reaction at different temperatures

Reaction conditions: Furfural (10 μL), $H_3PW_{12}O_{40}$ catalyst (10 mg), THF (1 mL), 60 min, and stirring speed of 400 rpm.
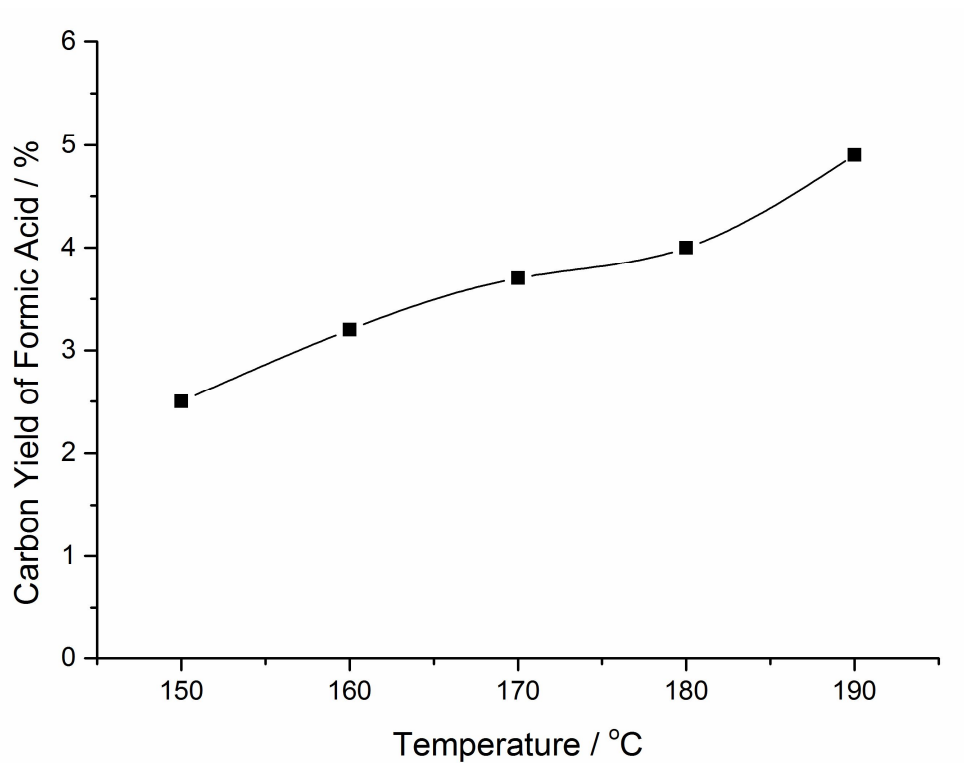
Figure 7. Production of formic acid from alginic acid decomposition by acid catalyzed reaction at different temperatures

Reaction conditions: alginic acid (10 mg), $H_3PW_{12}O_{40}$ catalyst (10 mg), THF/water co-solvent (1 mL, 5% (v/v) water ratio), 30 min, and stirring speed of 400 rpm.

3.3. Water effect on furfural production

To investigate the effect of water in reaction medium on furfural production, alginic acid was decomposed by varying amounts of water added to THF. According to Figure 8, the furfural yield in THF (14.8%) is higher than that in water (6.7%). Table 2 shows the decomposition of furfural over $H_3PW_{12}O_{40}$ in THF or water. Furfural was decomposed in THF and water with a conversion of 28.2 and 38.6%, respectively. In addition, formic acid, main degradation product of furfural, is produced with a yield of 13.8% in THF, whereas, the yield increases to 28.7% when water is used as a reaction medium, suggesting that furfural is more stable in THF than in water. Meanwhile, organic solvents can reduce structural changes of heteropolyanions during the reactions,[47] in contrast to aqueous solution, which is thought to contribute to the higher catalytic performance of heteropolyacid. Therefore, these results indicate that THF is more advantageous reaction medium to the conversion of alginic acid than water.

By the way, the furfural yield increases dramatically with the water ratio from 0 (only THF) to 5%, whereas it decreases if the water content is more than 5%. Notably, the maximum furfural yield was obtained at the 5% water added THF mixture, suggesting that this reaction system should contain certain amounts of water necessarily. Water requirement for enhancing the furfural yield is attributed to hydrolysis of alginic acid into hexuronic acid which should be occurred initially to produce the furfural. It indicates that water content in reaction medium is highly important factor on furfural production. On the other hand, Figure 8 shows that

furfural was produced as well, although the reaction was performed in only THF (without water). This results is supposed that the reaction medium is not completely anhydrous because water is formed as a byproduct and is also existed in the hydrated heteropolyacid.[32] Previous work on selective conversion of cellulose into HMF using polar aprotic solvents reported that the HMF yield was enhanced by using THF solvent.[43] Furthermore, adding small amounts of water (< 2-3 vol%) to THF was advantageous for the HMF production. Although different reactants are used, it is notable that the tendency of previous results is consistent with that of our results in terms of the solvent effect. The authors explained that the proton catalyst was more reactive in THF since the Gibbs free energy for solvation of a proton was more positive in the aprotic solvent than in the water, which led the proton destabilized. Based on this assertion, it seems that the significant decrease of furfural yield with increasing the water content above 5% is correlated with solvation of the proton by water molecules. The proton is more stabilized by solvation with increasing the water content in mixed solvent, and which could lead to the lower reactivity.[54]
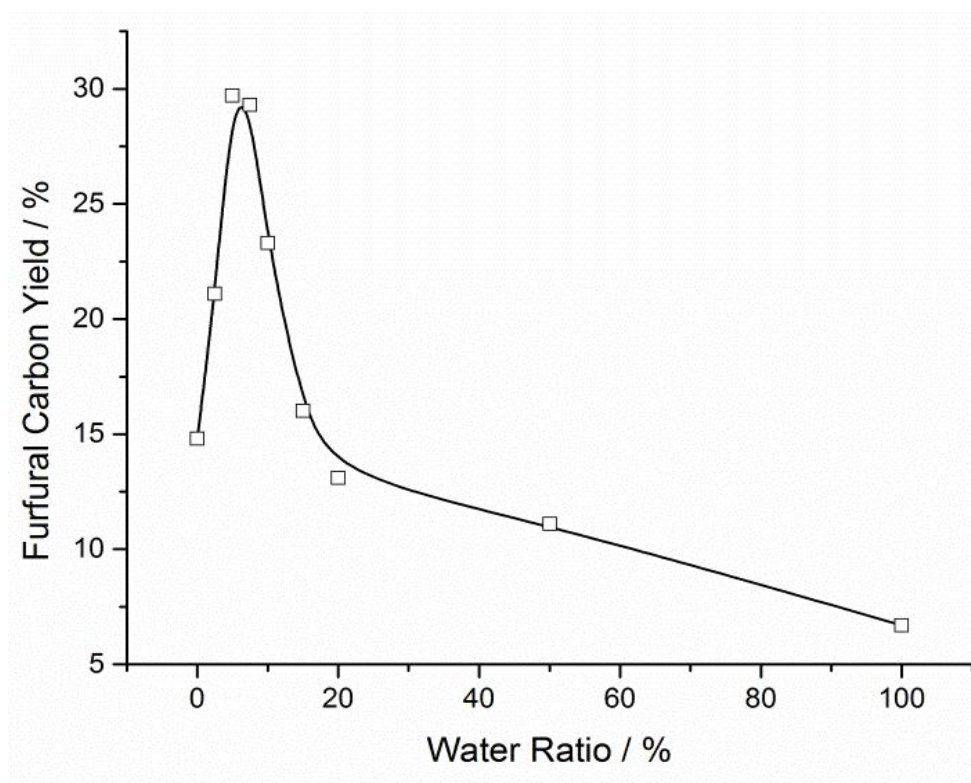
Figure 8. Effect of water ratio in THF/water co-solvent on furfural yield

Reaction conditions: Alginic acid (10 mg), $H_3PW_{12}O_{40}$ catalyst (10mg), reaction medium (1 mL), 170 ^{o}C, 60min, and stirring speed of 400 rpm.

Table 2 Decomposition of furfural by acid catalyzed reaction [a]

Entry	Solvent	Formic acid yield [mol%]	Furfural conversion [%]
1	THF	13.8	28.2
2	H_2O	28.7	38.6

[a] Reaction conditions: Furfural (0.01 mL), $H_3PW_{12}O_{40}$ catalyst (10 mg), solvent (1 mL),170 °C, 60 min, and stirring at 400 rpm.

3.4. Reaction pathway of alginic acid to furfural

A reaction pathway of direct conversion of alginic acid to furfural is unclear because furfural had not been considered as a target compound in alginic acid decomposition. In particular, there have been few studies that have attempted to examine the pathway. In order to elucidate how alginic acid converts to furfural, products distribution was investigated. As shown in Figure 9–(a), the LC-MS chromatogram indicates that hexuronic acid (HxA, m/z=193.2) was produced by hydrolysis of alginic acid at the beginning of the reaction (5min). In addition, hexuronic acid lactone (HxL, m/z=175.1) was also detected because some HxAs converted to HxLs by chemical equilibrium in presence of strong acids.[55, 56] Previous works reported that HxLs interfere with detection of HxAs on HPLC analysis, so TEA treatment was needed to hydrolyze the HxLs to HxAs with breaking the equilibrium.[44, 45] Thus, we treated the products with 1% TEA before the analysis to facilitate the detection of HxA considered as intermediates, which chromatograms is shown in Figure 9–(b).

The carbon yields of monomers and furfural quantified by HPLC are shown in Figure 10. Through the identification of precipitates in liquid products, we observed the white alginic acid powder disappeared within 5 min, which indicates that complete conversion of the reactant take place in the initial time. In early stages of the reaction, MnA and GlA were produced by the hydrolysis of alginic acid, reaching a maximum monomers yield of 58.3% in 3min. The ratio of MnA to GlA decreased with time because MnA was decomposed faster than GlA.[22]

Products distribution shows the yields of monomers steadily decrease, whereas the yield of furfural increase as the reaction time proceeded. This trend indicates that MnA and GlA, monomers of alginic acid, are intermediates in the furfural production. Although a few papers have been reported that HxA could be converted into furfural by acid catalyzed reaction,[55, 56] a mechanism for this reaction has not yet been fully understood. In the present system, in order to clarify the transformation pathway of alginic acid, it was essential to find out whether the furfural was derived from the monomers produced by hydrolysis, and so we did experiment using HxA and HxL as reactants. It should be noted that GcA (and GcL), more affordable isomer of HxA, was used as a surrogate reactant of MnA and GlA. The result is given in Figure 11, which shows the fact that the GcA and GcL could convert into furfural in the present reaction conditions. In addition, it has been known that conversion of HxA into furfural accompanied with decarboxylation and dehydration.[57, 58] In this reaction, one carbon dioxide and three water molecules were removed from an HxA. Thereby, carbon dioxide and furfural should be produced as equal number of molecules theoretically. In order to check for this, we analyzed the gas products by GC. A quantitative relationship between carbon dioxide and furfural produced as a function of time stream is given in Figure 12. The amounts of carbon dioxide released to gas phase corresponded closely with that of furfural produced in liquid phase, and the mutual trend were analogous. This result is consistent with that found in previous studies.[57, 58] Meanwhile, small differences in the number of carbon dioxide and furfural molecules were attributed to additional carbon dioxide associated with complex

side reactions, such as a further decomposition.

To our best knowledge, some studies about decomposition of alginic to its monomers have been demonstrates that total monomer yield is not exceeded 30%. For example, MnA yield was 30% if solid-state alginic acid pretreated using concentrated sulfuric acid at 4 °C for 18 hr, followed by added water and reacted at 100 °C for 16 hr.[59] Decomposition of Alginate (Na salt of alginic acid) using hydrothermal condition,[22] and acid aqueous solution was reported,[25] in which the total monomer yield was 17% and 18%, respectively. Consequently, high furfural yield could be obtained in this work, because $H_3PW_{12}O_{40}$ catalysts and THF solvent promoted the production of monomers (58.3%) compared to previous studies.

Based on the results obtained in this work, a reaction pathway can be proposed for the acid catalyzed conversion of alginic acid to furfural in THF/Water reaction medium. As shown in Scheme 2, alginic acid initially undergoes the hydrolysis of glycosidic bond to produce HxAs (MnA and GlA) under acidic conditions. Produced HxAs are in the equilibrium with HxLs by the removal or addition of water. After that, the decarboxylation and the dehydration occur with the formation of carbon dioxide and water, which these reactions transform HxA and HxL into furfural. When the HxA and HxL, intermediates of reaction, were used as a starting compound, the furfural yield was 32% and 35.4%, whereas the yield was 29.7% with alginic acid (see Figure 11). Although the reaction intermediates were used, a significant difference in furfural production was not

seen. It seems that the hydrolysis of alginic aicd to HxA occurs faster than the transformation of HxA to furfural in the reaction network. According to previous report on conversion of hemicellulose to furfural over acid catalyst, the dehydration of xylose to furfural is evaluated to be five times slower than the hydrolysis of xylan to xylose.[50] Furthermore, it is known that the dehydration step is rate-limiting in the conversion of hemicelllulose.[26, 60] Similarly, in case of alginic acid conversion, it would be expected that the subsequent reaction step (decarboxylation and dehydration) act as a reaction barrier and also have higher activation energy than hydrolysis. Considering these results, future studies have to focus on finding catalysts that particularly can promote the subsequent reaction while enhancing the activity on hydrolysis.
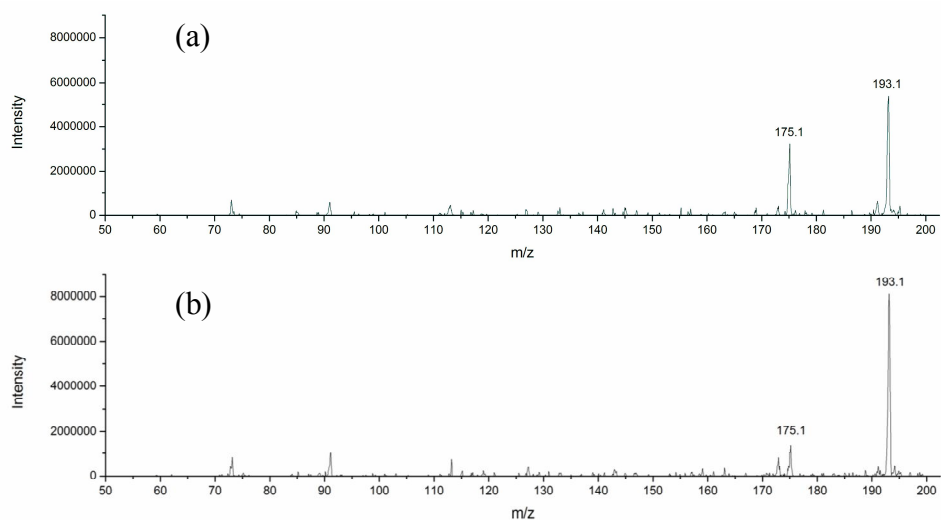
Figure 9. Determination of alginic acid decomposition products using liquid chromatography-tandem mass spectrometry (LC-MS).

(a): reaction product, (b): reaction product treated with 1% (v/v) TEA. Reaction conditions: alginic acid (10 mg), $H_3PW_{12}O_{40}$ catalyst (10 mg), THF/water co-solvent (1 mL, 5% (v/v) water ratio), 170 °C, 5 min, and stirring speed of 400 rpm.
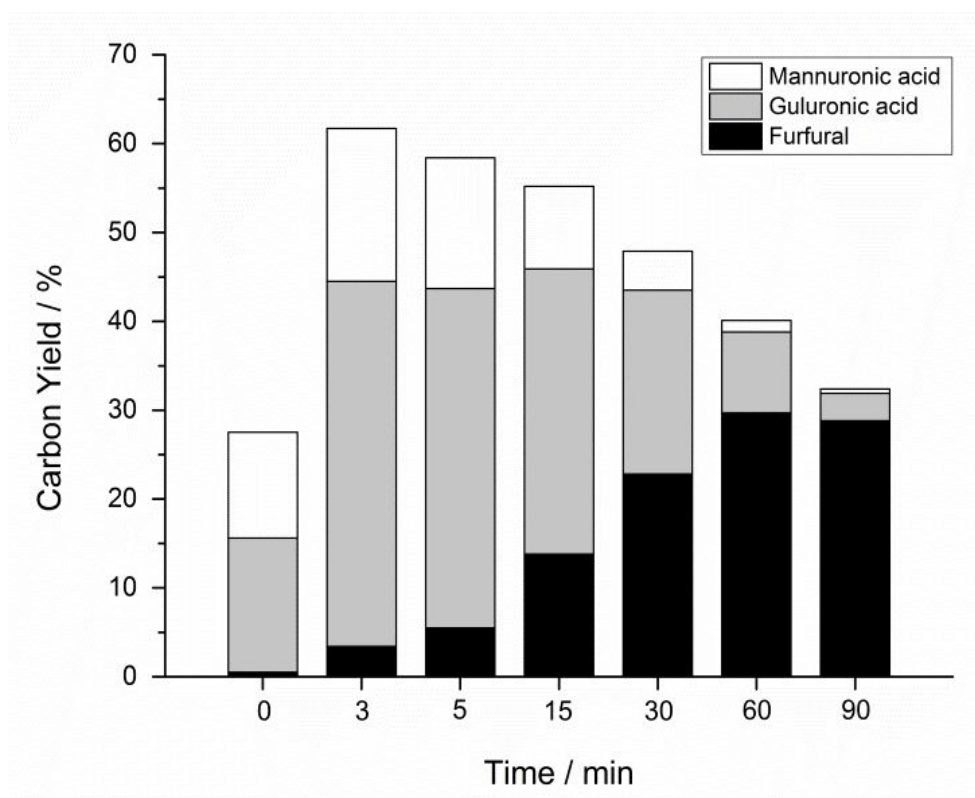
Figure 10. Product distribution during the decomposition of alginic acid

Reaction conditions: Alginic acid (10 mg), $H_3PW_{12}O_{40}$ catalyst (10mg), THF/water co-solvent (1 mL, 5% (v/v) water ratio), 170 ^{o}C, and stirring speed of 400 rpm.

Figure 11. Production of furfural from different reactants such as alginic acid, glucuronic acid and glucurono lactone

Reaction conditions: Substrate (10 mg), $H_3PW_{12}O_{40}$ catalyst (10 mg), THF/water co-solvent

(1 mL, 5% (v/v) water ratio), 170 °C, and stirring speed of 400 rpm.

Figure 12. Furfural and CO_2 Produced from alginic acid decomposition.

Reaction conditions: Alginic acid (10 mg), $H_3PW_{12}O_{40}$ catalyst (10mg), THF/water co-solvent (1 mL, 5% (v/v) water ratio), 170 ^oC, and stirring speed of 400 rpm.

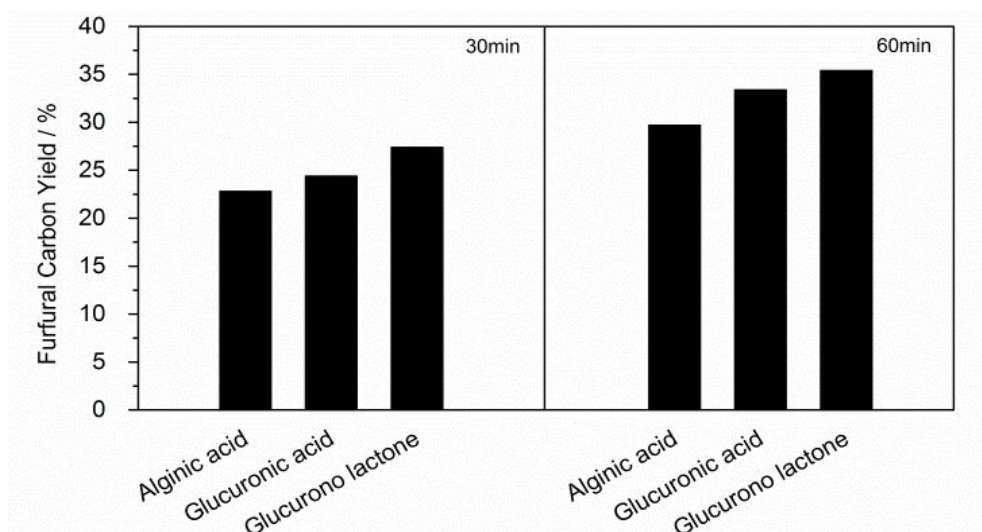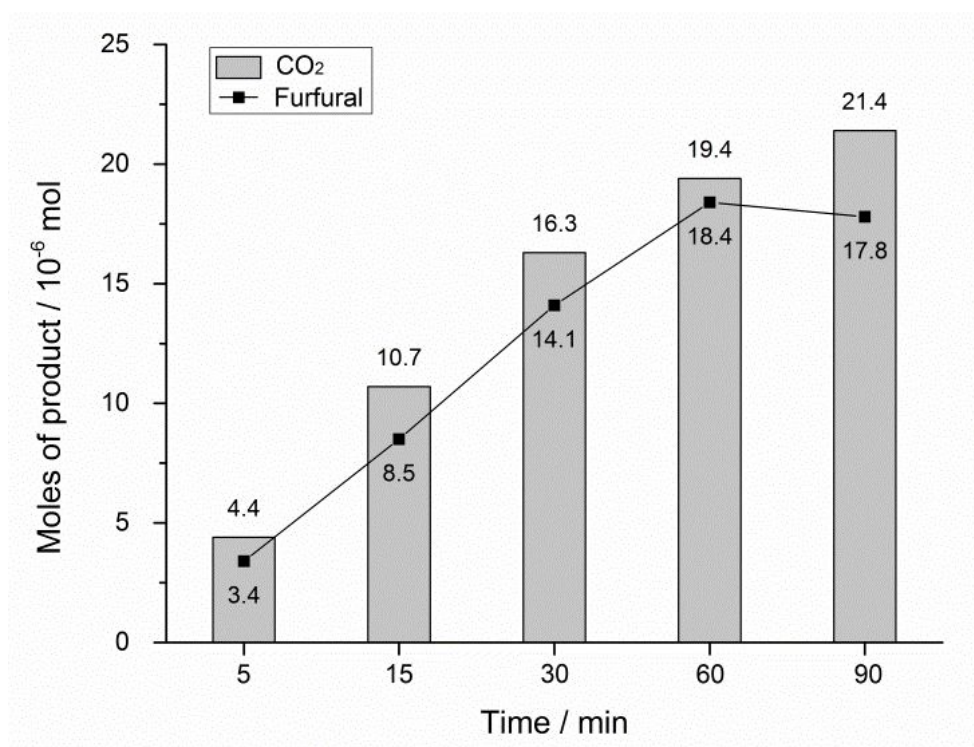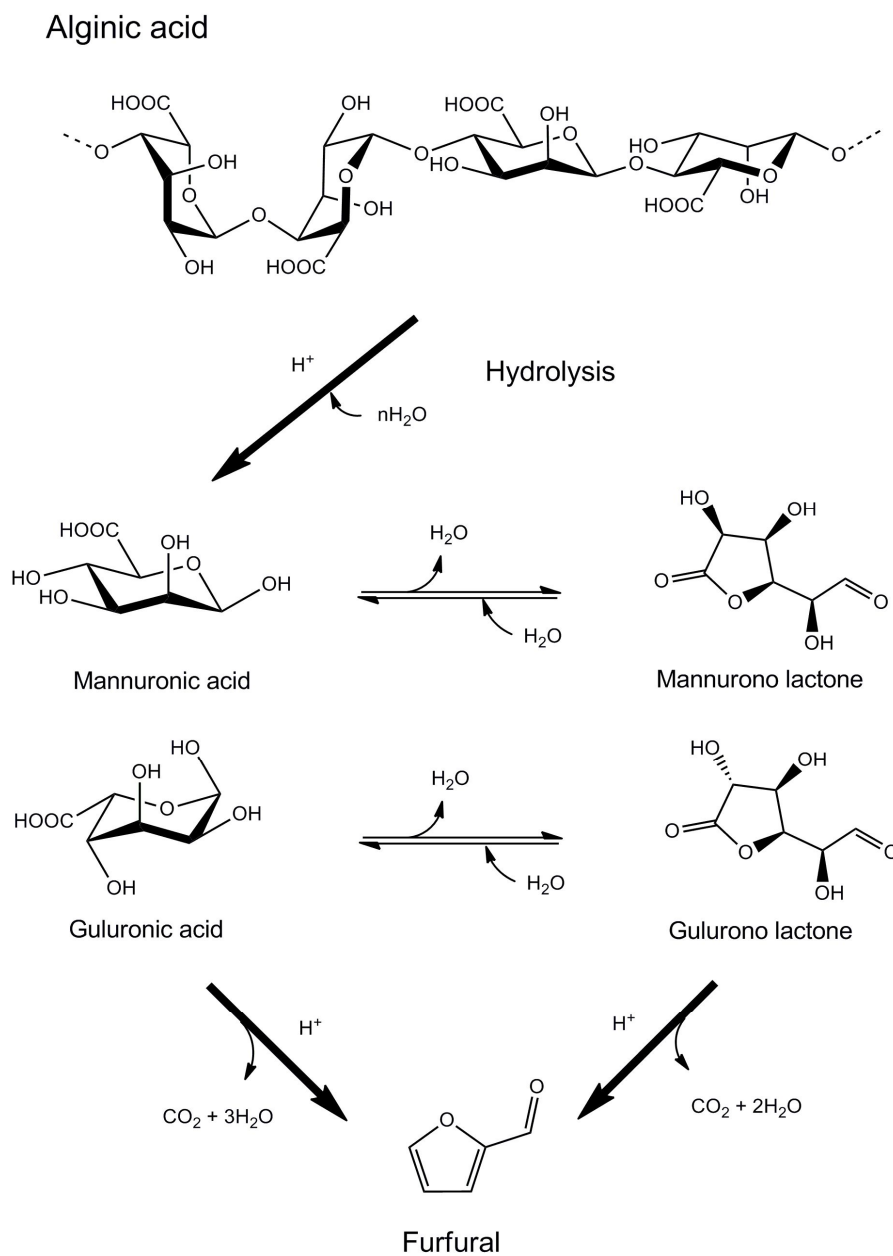Scheme 2. Proposed reaction pathway from alginic acid to furfural over acid catalyst

Chapter 4. Conclusion

In this research, we have demonstrated a possibility that brown seaweed-derived alginic acid could be used as a feedstock for furfural production. In particular, synthesis of furfural from alginic acid is a new approach for utilization of marine algae biomass. In this study, reaction conditions such as temperature, water content in reaction medium and time were explored to obtain a highest furfural yield, and which reached 33.8% by using $H_3PW_{12}O_{40}$ catalyst under the conditions of 180 °C, 5% water added THF mixture for 60 min. $H_3PW_{12}O_{40}$ was more active than H_2SO_4 and Ambelyst15 by suppressing the side reaction such as a formation of humin. It was found that the mixture of H_2O and THF solvent demonstrated the significant synergistic effect on the furfural production. Especially, this reaction was enhanced in presence of small amounts of water in THF because the decomposition of alginic acid involves the hydrolysis. Products distribution with time-on-stream indicated that the hydrolysis of alginic acid to hexuronic acid monomers proceeded initially, followed by the subsequent reactions (decarboxylation and dehydration) to produce furfural in series. In the reaction network, the hydrolysis was faster than subsequent reactions, suggesting that the latter reactions were rate-limiting. As a result, a future direction of this study will be focus on promoting the subsequent reactions.

References

1. Ragauskas, A.J., et al., *The path forward for biofuels and biomaterials.* Science, 2006. **311**(5760): p. 484.

2. Klass, D.L., *Biomass for Renewable Energy, Fuels and Chemicals*. 1998, San Diego: Academic Press.

3. Kerton, F.M., et al., *Green chemistry and the ocean-based biorefinery.* Green Chem., 2013. **15**(4): p. 860.

4. Chheda, J.N., Y. Román-Leshkov, and J.A. Dumesic, *Production of 5-hydroxymethylfurfural and furfural by dehydration of biomass-derived mono- and poly-saccharides.* Green Chem., 2007. **9**(4): p. 342.

5. Dutta, S., et al., *Advances in conversion of hemicellulosic biomass to furfural and upgrading to biofuels.* Catal. Sci. Technol., 2012. **2**(10): p. 2025.

6. Corma, A., S. Iborra, and A. Velty, *Chemical routes for the transformation of biomass into chemicals.* Chem. Rev., 2007. **107**: p. 2144.

7. Li, H., et al., *Catalytic hydrothermal pretreatment of corncob into xylose and furfural via solid acid catalyst.* Bioresour Technol, 2014. **158C**: p. 313.

8. Werpy, T. and G. Peterson, Top Value Added Chemicals from Biomass, Pacific Northwestern National Laboratory, 2004: p. vol. 1.

9. Climent, M.J., A. Corma, and S. Iborra, *Conversion of biomass platform molecules into fuel additives and liquid hydrocarbon fuels.* Green Chem., 2014. **16**(2): p. 516.

10.   Zeitsch, K.J., *The chemistry and technology of furfural and its many by-products*. 2000, Amsterdam: Elsevier.

11.   Wegenhart, B.L., et al., *From Furfural to Fuel: Synthesis of Furoins by Organocatalysis and their Hydrodeoxygenation by Cascade Catalysis.* ChemSusChem, 2014: p. n/a.

12.   Williams, P.J.l.B. and L.M.L. Laurens, *Microalgae as biodiesel & biomass feedstocks: Review & analysis of the biochemistry, energetics & economics.* Energy Environ. Sci., 2010. **3**(5): p. 554.

13.   Yuan, Y. and D.J. Macquarrie, *Microwave Assisted Acid Hydrolysis of Brown SeaweedAscophyllum nodosumfor Bioethanol Production and Characterization of Alga Residue.* ACS Sustainable Chem. Eng., 2015. **3**: p. 1359.

14.   Gao, K. and K.R. McKinley, *Use of macroalgae for marine biomass production and CO2 remediation.* J. Appl. Phycol., 1994. **6**: p. 45.

15.   Haug, A. and B. Larsen, *Quantitative determination of the uronic acid composition of alginates.* Acta Chem. Scand., 1962. **16**: p. 1908.

16.   Grasdalen, H., B. Larsen, and O. Smidsrød, *A P.M.R study of the composition and sequence of uronate residues in alginates.* Carbohydr. Res., 1979. **68**: p. 23.

17.   Sanchez-Machado, D.I., et al., *Determination of the uronic acid composition of seaweed dietary fibre by HPLC.* Biomed Chromatogr, 2004. **18**(2): p. 90.

18.   Dhepe, P.L. and A. Fukuoka, *Cellulose conversion under heterogeneous*

catalysis. ChemSusChem, 2008. **1**(12): p. 969.

19. Suganuma, S., et al., *Hydrolysis of cellulose by amorphous carbon bearing SO3H, COOH, and OH groups.* J. Am. Chem. Soc., 2008. **130**: p. 12787.

20. Huang, Y.-B. and Y. Fu, *Hydrolysis of cellulose to glucose by solid acid catalysts.* Green Chem., 2013. **15**(5): p. 1095.

21. Annison, G., N.W.H. Cheetham, and I. Couperwhite, *Determination of the uronic acid composition of alginates by high-performance liquid chromatography.* Journal of Chromatography A, 1983. **264**(0): p. 137.

22. Aida, T.M., et al., *Depolymerization of sodium alginate under hydrothermal conditions.* Carbohydr. Polym., 2010. **80**(1): p. 296.

23. Aida, T.M., et al., *Production of organic acids from alginate in high temperature water.* J. Supercrit. Fluids, 2012. **65**: p. 39.

24. Jeon, W., et al., *Hydrothermal conversion of macroalgae-derived alginate to lactic acid catalyzed by metal oxides.* Catal. Sci. Technol., 2015.

25. Jeon, W., et al., *Catalytic hydrothermal conversion of macroalgae-derived alginate: effect of pH on production of furfural and valuable organic acids under subcritical water conditions.* J. Mol. Catal. A: Chem., 2015. **399**: p. 106.

26. Mamman, A.S., et al., *Furfural: Hemicellulose/xylosederived biochemical.* Biofuels, Bioprod. Biorefin., 2008. **2**(5): p. 438.

27. Su, F. and Y. Guo, *Advancements in solid acid catalysts for biodiesel production.* Green Chem., 2014. **16**(6): p. 2934.

28. Vilcocq, L., et al., *Hydrolysis of Oligosaccharides Over Solid Acid*

Catalysts: A Review. ChemSusChem, 2014. **7**: p. 1010.

29.   Tian, J., et al., *Hydrolysis of cellulose by the heteropoly acid H3PW12O40.* Cellulose, 2010. **17**(3): p. 587.

30.   Kozhevnikov, I.V., *2015 03 16 Catalysis by heteropoly acids and multicomponent polyoxometalates in liquids-phase reactions.* Chem. Rev., 1998. **98**: p. 171.

31.   Ogasawara, Y., et al., *Saccharification of natural lignocellulose biomass and polysaccharides by highly negatively charged heteropolyacids in concentrated aqueous solution.* ChemSusChem, 2011. **4**(4): p. 519.

32.   Dias, A.S., M. Pillinger, and A.A. Valente, *Liquid phase dehydration of d-xylose in the presence of Keggin-type heteropolyacids.* Appl. Catal., A, 2005. **285**(1–2): p. 126.

33.   Rinaldi, R. and F. Schüth, *Design of solid catalysts for the conversion of biomass.* Energy Environ. Sci., 2009. **2**(6): p. 610.

34.   Rinaldi, R. and F. Schüth, *Acid hydrolysis of cellulose as the entry point into biorefinery schemes.* ChemSusChem, 2009. **2**(12): p. 1096.

35.   Román-Leshkov, Y., J.N. Chheda, and J.A. Dumesic, *Phase Modifiers Promote Efficient Production of Hydroxymethylfurfural from Fructose.* Science, 2006. **312**(5782): p. 1933.

36.   Saha, B. and M.M. Abu-Omar, *Advances in 5-hydroxymethylfurfural production from biomass in biphasic solvents.* Green Chem., 2014. **16**(1): p. 24.

37.   Swatloski, R.P., et al., *Dissolution of Cellose with Ionic Liquids.* J. Am.

Chem. Soc., 2002. **124**(18): p. 4974.

38.   Li, C., Q. Wang, and Z.K. Zhao, *Acid in ionic liquid: An efficient system for hydrolysis of lignocellulose.* Green Chem., 2008. **10**(2): p. 177.

39.   Rinaldi, R., R. Palkovits, and F. Schüth, *Depolymerization of Cellulose Using Solid Catalysts in Ionic Liquids.* Angew. Chem., Int. Ed., 2008. **47**(42): p. 8047.

40.   Cai, C.M., et al., *THF co-solvent enhances hydrocarbon fuel precursor yields from lignocellulosic biomass.* Green Chem., 2013. **15**(11): p. 3140.

41.   Román-Leshkov, Y. and J.A. Dumesic, *Solvent Effects on Fructose Dehydration to 5-Hydroxymethylfurfural in Biphasic Systems Saturated with Inorganic Salts.* Top. Catal., 2009. **52**(3): p. 297.

42.   Qi, L., et al., *Catalytic Conversion of Fructose, Glucose, and Sucrose to 5-(Hydroxymethyl)furfural and Levulinic and Formic Acids in γ-Valerolactone As a Green Solvent.* ACS Catal., 2014. **4**: p. 1470.

43.   Weingarten, R., et al., *Selective Conversion of Cellulose to Hydroxymethylfurfural in Polar Aprotic Solvents.* ChemCatChem, 2014. **6**(8): p. 2229.

44.   Miyamoto, I. and S.A. Nagase, *A simple and rapid electrophoretic method for the separation of glucuronic acid and induronic acid.* Anal. Biochem., 1981. **115**: p. 308.

45.   P. Gacesa, A.S. and P.J. Winterburn, *The determination of the uronic acid composition.* Carbohydr. Res., 1983. **118**: p. 1.

46.   Alsalme, A., E.F. Kozhevnikova, and I.V. Kozhevnikov, *Heteropoly acids*

as catalysts for liquid-phase esterification and transesterification. Appl. Catal., A, 2008. **349**(1-2): p. 170.

47.   Timofeeva, M.N., *Acid catalysis by heteropoly acids.* Appl. Catal., A, 2003. **256**(1-2): p. 19.

48.   Weingarten, R., et al., *Kinetics of furfural production by dehydration of xylose in a biphasic reactor with microwave heating.* Green Chem., 2010. **12**(8): p. 1423.

49.   Misono, M., *Catalysis of Heteropoly Compounds (Polyoxometalates).* 2013. **176**: p. 97.

50.   Möller, M. and U. Schröder, *Hydrothermal production of furfural from xylose and xylan as model compounds for hemicelluloses.* RSC Adv., 2013. **3**(44): p. 22253.

51.   Oefner, P.J., et al., *Quantitative studies on furfural and organic acid formation during hydrothermal, acidic and alkaline degradation of D-xylose.* Monatsh. Chem., 1992. **123**(6-7): p. 547.

52.   G. Marcotullio, M.A.T.C., W. De Jong and and A.H.M. Verkooijen, *Bioenergy II: Furfural destruction kinetics during sulphuric acid-catalyzed production from biomass.* Int. J. Chem. Reactor Eng., 2009. **7**: p. A67.

53.   Patel, A., *Environmentally Benign Catalysts - for Clean Organic reactions*, 2013, Springer: Netherlands.

54.   Mellmer, M.A., et al., *Solvent effects in acid-catalyzed biomass conversion reactions.* Angew. Chem., Int. Ed., 2014. **53**(44): p. 11872.

55.   Beljanin, M.L., et al., *US Patent: method of obtainging D-glucuronic acid*,

2009: U. S.

56.   Marsh, C.A., in *Glucuronic acid Free and Combined: Chemistry,*
        Biochemistry, Pharmacology and Medicine, G. Dutton, Editor. 1966,
        Academic Press: New York. p. 4.

57.   Koshelev, L.P., G.Y. Ilchenko, and L.I. Glebko, *Uronic acid content in*
        polysaccharides: Estimation by decarboxylation involving use of gas
        chromatography. Anal. Biochem., 1976. **73**: p. 115.

58.   Perlin, A.S., *Thermal decarboxylation of uronic acids.* Can. J. Chem., 1952.
        30: p. 278.

59.   Frush, H.L. and H.S. Isbell, *Preparation of mannuronic lactone from algin.*
        Journal of research of the national bureau of standards, 1946. **37**: p. 312.

60.   Shen, J. and C.E. Wyman, *A novel mechanism and kinetic model to explain*
        enhanced xylose yields from dilute sulfuric acid compared to hydrothermal
        pretreatment of corn stover. Bioresour. Technol., 2011. **102**(19): p. 9111.

요약 (국문초록)

　　푸르푸랄은 미국 에너지부 (U.S. Department of Energy)에서 지정한 바이오매스 전환 공정의 플랫폼 화합물 중 하나로써 수소화 또는 축합 반응 등으로 고분자의 단량체 및 유기용매, 액체연료의 첨가제 등 다양한 퓨란 유도체들의 시작물질로 사용될 수 있기 때문에 푸르푸랄의 전 세계 수요는 앞으로 지속적으로 증가할 것으로 예상되고 있다. 하지만 증가하는 수요에도 불구하고 현재까지 푸르푸랄은 목질계 바이오매스를 구성하고 있는 물질 중에 하나인 헤미셀룰로오즈에서만 전적으로 얻어지고 있는 실정이다. 이러한 사실은 안정적인 푸르푸랄의 공급을 위해서 원료물질의 다양화가 필요하다는 것을 대변한다. 따라서 본 연구에서는 제 3세대 바이오매스 자원인 갈조류로부터 유래된 알긴산을 사용하여 푸르푸랄의 제조를 시도하였고, 알긴산이 푸르푸랄 생산의 대체 원료로 사용될 수 있는지에 대한 가능성을 알아보았다.

　　알긴산은 갈조류를 구성하고 있는 주된 물질로써 우론산 단량체들(만누론산 및 굴루론산)이 β-1,4-글리코시딕 결합으로 이루어진 탄수화물 고분자이다. 알긴산의 분해반응의 주요 생성물은 단량체인 만누론산과 굴루론산 및 C1-C5의 탄소 수를 가지는 여러 유기산들 (젖산, 호박산, 말산 등)로 알려져 있다. 반면, 푸르푸랄은 알긴산 분해반응에서 낮은 수율로 인해 부산물로 여겨져 왔다. 본 연구에서 주목할 점은 해조

류 바이오매스의 활용에서 알긴산으로부터 푸르푸랄을 생산하는 것은 다소 새로운 접근이라 할 수 있다. 알긴산 분해반응에서 부산물로 여겨지는 푸르푸랄의 낮은 수율을 높이기 위해 본 연구에서는 Keggin 형의 헤테로폴리산 ($H_3PW_{12}O_{40}$) 촉매와 테트라하이드로퓨란/물 공용매를 반응에 도입하였다. 헤테로폴리산 촉매의 활성을 비교하기 위한 대조군으로는 대표적인 무기산인 황산과 고체 산촉매인 Amberlyst15을 사용하였다. 그 결과, $H_3PW_{12}O_{40}$ 촉매의 활성이 다른 산 촉매들에 비해 우수하였고 휴민 생성과 같은 부반응을 억제하는 것을 확인하였다. 테트라하이드로퓨란은 물에 비해 푸르푸랄 생성에 유리한 용매로 작용하였고, 특히 소량의 물(5%)이 첨가된 테트라하이드로퓨란/물 공용매에서 푸르푸랄의 수율이 높게 나타났다. 본 연구에서 푸르푸랄의 최고수율은 33.8%였고, 이는 현재까지 보고된 알긴산 분해반응 연구 중에서 가장 높은 수율로 여겨진다.

한편, 알긴산으로부터 푸르푸랄이 형성되는 반응 경로를 알아보기 위해서 시간에 따른 생성물들의 분포를 알아보았다. 본 반응시스템에서 탄수화물 고분자인 알긴산은 우론산 단량체들로 먼저 가수분해가 되고, 그 이후에 단량체로부터 이산화탄소와 물 분자들이 제거되는 탈카복실화 반응과 탈수반응을 거치면서 최종적으로 푸르푸랄이 생성되는 반응경로를 제안하였다. 또한, 시작물질인 알긴산과 중간생성물인 단량체를 이용한 반응 결과를 바탕으로 단량체가 형성되는 가수분해 반응이 탈카복실

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화 및 탈수 반응에 비해 빠르게 일어나는 것을 확인하였고, 이로부터 푸르푸랄이 생성되는 경로에서 단량체가 푸르푸랄로 전환되는 반응이 전체 반응의 속도를 결정하는 단계임을 유추할 수 있었다. 결과적으로는 알긴산이 푸르푸랄의 생산에서 헤미셀룰로오즈의 대안의 원료로써 활용될 수 있는 가능성을 확인할 수 있었다.

주요어 : 알긴산, 우론산, 푸르푸랄, 헤테로폴리산, 공용매

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