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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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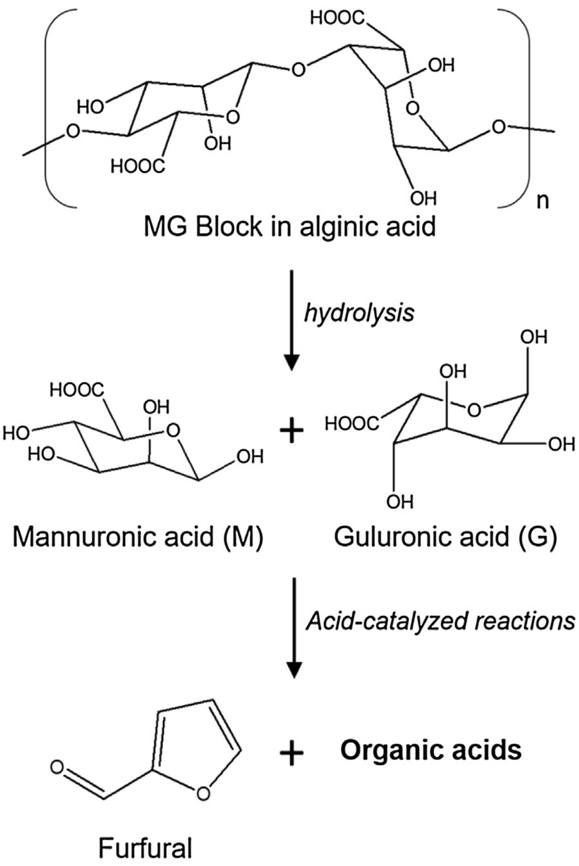

Scheme 1. Decomposition of alginic acid to its monomer via the cleavage of 1,4-glycosidic bond.

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™ 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

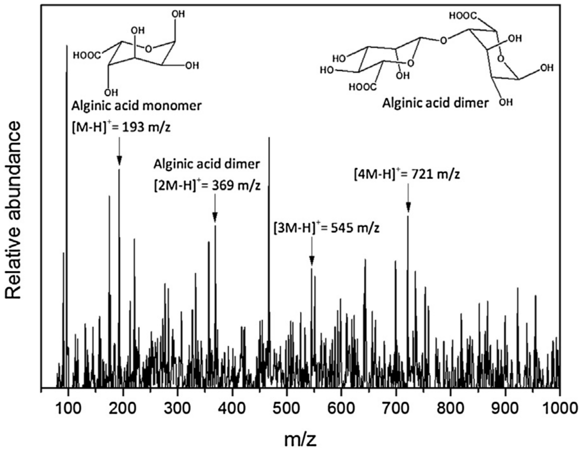

Fig. 1. LC–MS spectrum of hydrothermally treated alginic acid. Reaction condition: alginic acid concentration (2 wt%), catalyst loading (600 mg), stirring speed (600 rpm), reaction time (30 min).

($C_6H_8O_6$) in alginic acid, equal to the mass of alginic acid divided by 176.

3. Results and discussion

3.1. Decomposition of alginic acid over Amberlyst-15

Effective cleavage of 1,4-glycosidic linkages in alginic acid is essential to enhance the yield of furfural since it was observed that mannuronic acid and guluronic acid produced by hydrolysis of alginic acid were converted to furfural over acid catalysts according to our previous work [16]. Fig. 1 exhibits the formation of various organic compounds with the wide range of molecular weight via the hydrothermal reaction of alginic acid at 180 °C for 30 min over Amberlyst-15. Based on the LC–MS spectrum, it was found that both alginic acid monomer and oligomers were produced by the selective cleavage of the ether bonds in alginic acid over the acid catalyst. On the other hand, the other numerous compounds were also produced with the wide range of molecular weight, which implies that undesired reactions, such as random C—C cleavages or polymerization of products, simultaneously occurred under the reaction condition. To investigate the effects of reaction temperature and the acid catalyst on the hydrothermal depolymerization of alginic acid, the molecular weight distributions of liquid products were analyzed by a GPC method.

Fig. 2 shows the effect of reaction temperature on the molecular weight distributions of hydrothermally treated alginic acid. A peak for raw alginic acid disappeared almost completely after the hydrothermal treatment in the temperature ranging from 140 to 220 °C for 30 min, and two representative peaks were shown at 26.5 and 27.5 min. Such change in the chromatogram demonstrates that raw alginic acid is hydrothermally decomposed to smaller molecules with specific molecular weight distributions. In particular, the peak at 27.5 min indicates the production of organic compounds having similar molecular weights to alginic acid monomer. By the way, the intensity of peak at 26.5 min decreases significantly when the reaction temperature increases from 140 to 160 °C, followed by the gradual increase in the peak intensity with elevating reaction temperature from 180 to 220 °C. This peak variation implies that the higher reaction temperature is favorable for the depolymerization of alginic acid, however, the polymerization of products is simultaneously accelerated with increasing the reaction temperature over Amberlyst-15, as evidenced by the formation of dark water-insoluble residues like humin after the reactions above 180 °C, as shown in Fig. S2. It is known that humin is produced by the polymerization of furan compounds like furfural or hydroxymethylfurfural with other organic compounds like xylose or glucose, respectively, over acid catalysts [17,18]. Similarly, the monomeric units of alginic acid, such as mannuronic acid and guluronic acid, would be polymerized with furfural produced by the acid-catalyzed hydrothermal reaction of alginic acid.

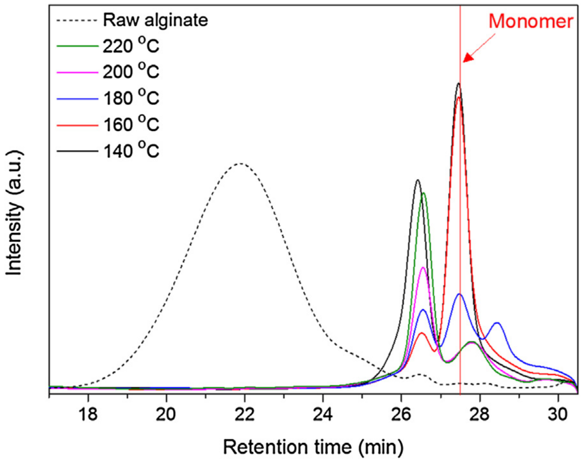

Fig. 2. GPC chromatograms of hydrothermally treated alginic acid at different temperatures. Reaction condition: alginic acid concentration (2 wt%), catalyst loading (600 mg), stirring speed (600 rpm), reaction time (30 min).

Table 1
Molecular weight distribution of raw alginic acid and hydrothermally treated alginic acid at 180 °C for 30 min over different amounts of Amberlyst-15.

Catalyst loading (mg)	M_w (Da)	M_n (Da)	PDI
Raw alginic acid[a]	54972	20134	2.73
0	1603	1128	1.42
150	1258	840	1.50
300	1319	839	1.57
600	1331	888	1.50
900	1442	1021	1.41
1200	1440	1024	1.41

M_w = Weight average molecular weight.
M_n = Number average molecular weight.
PDI = Polydispersity index (M_w/M_n).

[a] Raw alginic acid solution was prepared by dissolving alginic acid in 0.2 M of NaOH.

Table 1 exhibits the effect of a catalyst amount on the molecular weight distribution of hydrothermally treated alginic acid at 180 °C for 30 min. Compared to a catalyst-free reaction, 150 mg of Amberlyst-15 clearly accelerated the degradation of alginic acid within 30 min, as confirmed by the decrease of M_w from 1603 to 1258. However, the M_w value gradually increased from 1258 to 1440 as the larger amounts of the catalyst were employed than 150 mg, implying that more acid catalyst also promoted the polymerization between furfural and alginic acid-derived by-products like organic acids. In summary, the hydrothermal depolymerization of alginic acid was enhanced with 150 mg of Amberlyst-15, leading to almost complete decomposition of alginic acid. However, it was revealed that the higher catalyst loading than 150 mg is detrimental to the depolymerization of alginic acid due to the acid-catalyzed polymerization of the organic products.

3.2. Production of furfural as a function of reaction temperature and time

The yields of furfural, alginic acid monomer and formic acid obtained by hydrothermal treatment of alginic acid over Amberlyst-15 are presented in Fig. 3. The yield of the monomer is

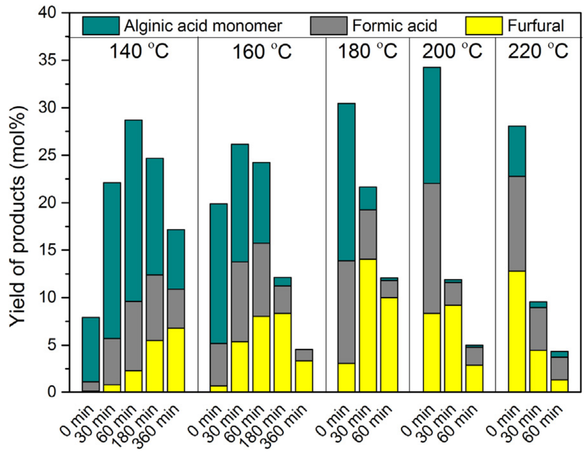

Fig. 3. Yields of alginic acid monomer, furfural and formic acid obtained by hydrothermal reaction of alginic acid at different reaction temperatures and times. Reaction condition: alginic acid concentration (2 wt%), catalyst loading (600 mg), and stirring speed (600 rpm).

defined as the sum of yields of mannuronic acid and guluronic acid. At 140 and 160 °C, the production of the monomer was noticeable during the initial stages of reaction, which demonstrates that the cleavage of 1,4-glycosidic linkage of alginic acid by acid-catalyzed hydrolysis was dominant at the mild reaction temperature. This is well corresponding with the higher intensities of GPC peaks at 27.5 min for the monomer-sized molecules produced at 140 and 160 °C for 30 min, as discussed in Fig. 2. However, the yield of the monomer decreased with the time-on-stream whereas the yield of furfural gradually increased at 140 °C due to the acid-catalyzed conversion of the monomer to furfural. Moreover, the increase in reaction temperature also caused the enhanced production of furfural at the expense of monomer yield. For example, the furfural yield significantly increased from 3.1 to 14.1 mol% at 180 °C for 30 min while the monomer yield decreased from 7.7 to 1.3 mol%, implying that the monomer produced by hydrolysis of alginic acid was rapidly converted to furfural by the acid-catalyzed reactions like decarboxylation and dehydration [16]. In addition to the alginic acid monomer and furfural, formic acid was produced by the hydrothermal reaction of alginic acid over Amberlyst-15. The yield of formic acid was also strongly dependent on reaction temperature and time with the maximum of 13.7 mol% at 200 °C. A feasible reaction pathway for the formic acid production would be the hydrothermal conversion of alginic acid and its monomer, since formic acid is commonly produced by the hydrothermal reaction of alginic acid regardless of the kinds of catalysts [3,19,20]. According to previous study, formic acid can be also produced from furfural due to the hydrothermal instability of furfural over acid catalysts, which is regarded as another possible route to yield formic acid [21]. Based on the product distribution at 140 °C within 30 min, the former possibility would be more reasonable since formic acid was already produced before furfural began to form. In addition, it seems that the variation in the yield of formic acid is well matched with that of the monomer whereas the furfural yield increases independently, supporting the hypothesis about the production of formic acid primarily from alginic acid monomer.

At higher reaction temperatures than 140 °C, it was observed that the yields of alginic acid monomer, furfural and formic acid significantly decreased, suggesting that all the products were unstable under the hydrothermal condition at the reaction temperatures over Amberlyst-15. After the acid-catalyzed reactions over 160 °C, humin was generated as shown in Fig. S2. The production of humin is expected to cause the decrease in the yields of the monomer, furfural and formic acid. In addition to the production of humin, the acid-catalyzed decomposition of furfural to formic acid at relatively high reaction temperatures would be also ascribed to the consumption of furfural. Therefore, it is essential to optimize the reaction temperature and time in order to maximize the production of furfural from alginic acid while suppressing the side reaction of furfural to humin or formic acid.

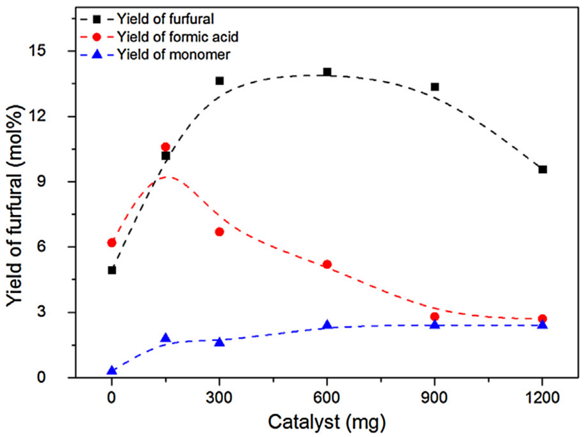

Fig. 4. Effect of catalyst amounts on productions of alginic acid monomer, furfural and formic acid from alginic acid. Reaction condition: alginic acid concentration (2 wt%), temperature (180 °C), reaction time (30 min), and stirring speed (600 rpm).

3.3. *Effects of catalyst amounts and reactant concentrations on production of furfural*

Fig. 4 shows the yields of alginic acid monomer, furfural and formic acid produced by hydrothermal treatment of alginic acid at 180 °C for 30 min with different amounts of Amberlyst-15. In a blank test without the acid catalyst, 4.9 and 0.3 mol% of furfural and alginic acid monomer were produced, respectively, demonstrating that the acid catalyst is essential for both hydrolysis of alginic acid and production of furfural from alginic acid. Although there is no acid catalyst initially loaded in the reactor, protons (H^+), the Brønsted acid catalyst, can be produced by the dissociative ionization of water molecule at 180 °C, which catalyzed the hydrothermal conversion of alginic acid to furfural to some extent [22]. When 150 mg of Amberlyst-15 was added to the hydrothermal reaction, the yield of furfural almost doubled from 4.9 to 10.2 mol%. The increase in the furfural yield can be explained by the fact that Amberlyst-15 has sulfonic acid groups grafted on the catalyst surface, which play a role as an active site to promote the acid-catalyzed hydrothermal reactions, such as hydrolysis and dehydration [23–26]. In addition to furfural, other products were produced more abundantly over the doubled amount of the catalyst. In particular, formic acid showed the maximum yield (10.6 mol%) over 150 mg of Amberlyst-15. However, as the amount of the catalyst increased from 150 to 300 mg, the formic acid yield began to decrease whereas the furfural yield increased remarkably, which implies that Amberlyst-15 is a more selective catalyst to furfural than formic acid under the hydrothermal conditions. However, it was observed that the furfural yield was almost constant (ca. 14 mol%) although the amount of Amberlyst-15 increased from 300 to 900 mg, which demonstrates that the optimum ratios of catalyst to reactant lie in between 0.5 and 1.5. On the other hand, the yield of furfural significantly decreased over 1200 mg of the catalyst with the production of humin, implying that the excess amount of the acid catalyst more accelerated the polymerization of furfural to humin than the production of furfural from alginic acid. The decrease in the yields of both furfural and formic acid at the higher catalyst loading is likely related to the increase in the average molecular weights of hydrothermally treated alginic acid

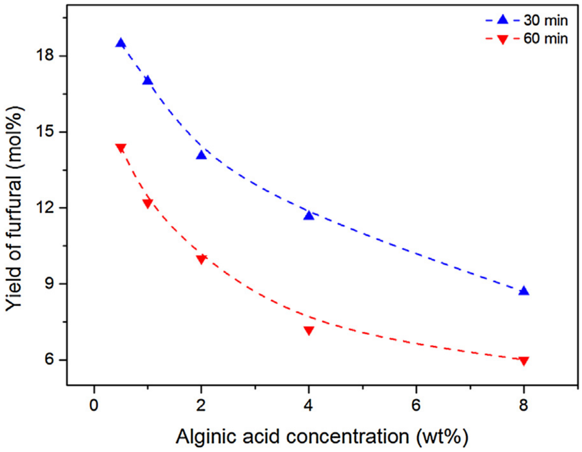

Fig. 5. Effect of alginic acid concentration on furfural production. Reaction condition: catalyst loading (600 mg), temperature (180 °C), reaction time (30 and 60 min), stirring speed (600 rpm).

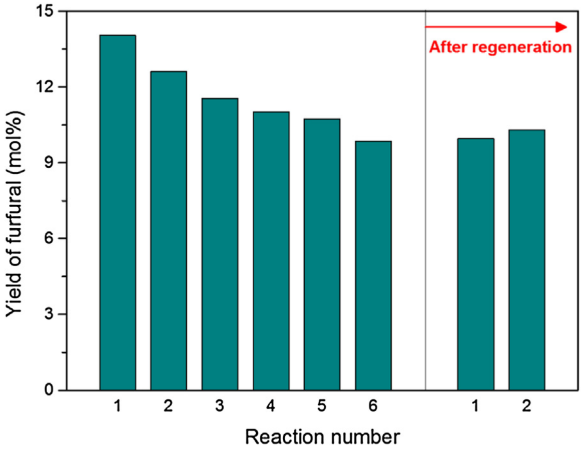

Fig. 6. Yields of furfural obtained by hydrothermal reaction of alginic acid over repeatedly used Amberlyst-15 and regenerated catalyst. Reaction condition: alginic acid concentration (2 wt%), catalyst loading (600 mg), temperature (180 °C), reaction time (30 min), stirring speed (600 rpm).

as discussed in Table 1. The activity test with various amounts of Amberlyst-15 suggests the existence of an optimum amount of catalyst loading for the selective conversion of alginic acid to furfural in the hydrothermal conditions that prevent the loss of the target product.

The concentration of alginic acid is also one of important reaction parameters influencing the production of furfural in hydrothermal reaction of alginic acid, as shown in Fig. 5. Notably, lower alginic acid concentration seems to be more favorable for higher yield of furfural. For example, when 0.5 wt% of alginic acid was hydrothermally treated at 180 °C for 30 min, a maximum furfural yield (18.5 mol%) was obtained. On the other hand, the yield of furfural gradually decreased as the alginic acid concentration doubled, which demonstrates that the larger amount of reactant lessened reaction efficiency for the production of furfural over the fixed amount of Amberlyst-15 catalyst (600 mg) due to the limited quantity of active sites on the acid catalyst with increasing reactant concentration. Another reason for the decrease of the furfural yield might be insufficient reaction time (30 min) considering the high reactant concentration. In order to prove the hypothesis, the reaction time was doubled at the same reaction condition. As a result, the yields of furfural for all the alginic acid concentrations decreased to about 70% of the furfural yields obtained for 30 min, which demonstrates that the longer reaction time accelerated the decomposition or polymerization of furfural produced from alginic acid.

3.4. *Reusability of Amberlyst-15 in hydrothermal conditions*

Major advantages of using heterogeneous catalysts for aqueous phase reactions are easy separation and recycling of used catalysts. Amberlyst-15 is composed of regular size of spherical resin particles, thus the solid acid catalyst could be easily separated with an 80-mesh steel sieve. To evaluate the reusability of Amberlyst-15 in hydrothermal reaction of alginic acid, it was repeatedly used at 180 °C for 30 min after a simple washing step with water. As a result, the yield of furfural slightly decreased during the repeated cycles as described in Fig. 6. Approximately 70% of initial furfural yield was obtained after the 6th recycling test. However, the yields of other products, such as formic acid, were almost constant with increasing recycling time, which implies that the active sites on Amberlyst-15 are more sensitive to the production of furfural. The deactivation of Amberlyst-15 in the liquid-phase reaction can be explained by the adsorption of by-products onto the catalyst surface, collapse of catalyst structure or leaching of active sites [27,28]. Among these possibilities, the adsorption of by-products seems to be most relevant in our case since a color of used catalyst changed to that of dark liquid product and a weight of the used catalyst continuously increased as the recycling test proceeded. For example, the grey color of fresh Amberlyst-15 gradually changed to almost black color after the 6th run, as shown in Fig. S3. Moreover, the weight of Amberlyst-15 rose from 600 to 641 mg after the first run, followed by additional increase of the catalyst weight from 641 to 696 mg after the second run. Both the gain in the catalyst weight and the apparent color change during the hydrothermal reaction of alginic acid were also observed in our previous study [29]. In order to recover the catalytic performance of Amberlyst-15 used six times, the used catalyst was treated with 5 wt% of sulfuric acid to regenerate sulfonic acid groups on the catalyst surface [30]. However, the catalytic activity of Amberlyst-15 was not recovered to that of the fresh one, which suggests that the unsuccessful recovery of the used catalyst is attributed to the coverage of byproducts on the resin surface of Amberlyst-15. In other words, the byproducts adsorbed on the catalyst surface prevented from grafting sulfonic acid groups on the catalyst surface during the regeneration process.

4. Conclusions

Macroalgae-derived alginic acid was used for the production of furfural under hydrothermal conditions. Amberlyst-15 as a solid acid catalyst improved the selective conversion of alginic acid to furfural with easy separation and reliable reusability. As a maximum, 18.5 mol% of furfural was produced by the catalytic hydrothermal reaction of alginic acid. The catalyst could be reused 5 times with approximately 30% of loss in furfural yield. Based on color variations of the catalyst during the recycling test, the catalytic deactivation would be caused by the adsorption of alginic acid-derived by-products on the catalyst surface, leading to the blockage of active sites on the catalyst. Higher catalyst loading and reaction temperature enhanced the production of furfural from alginic acid, however, the polymerization of alginic acid-derived products, such as alginic acid monomer, furfural and formic acid, were also accelerated. Therefore, the optimization of reaction condition or the development of anti-polymerization reagents would be helpful to facilitate the furfural production. In conclusion, macroalgae-derived alginic acid exhibited a promising potential as a renewable biomass feedstock for the production of furfural. Moreover, the utilization of the cheap and recyclable solid catalyst and the aqueous reaction medium is favorable for an eco-friendly catalytic process.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2016.07.020.

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