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Catalytic hydrothermal conversion of macroalgae-derived alginate: effect of pH on production of furfural and valuable organic acids under subcritical water conditions

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ABSTRACT

The hydrothermal decomposition of sodium alginate was analyzed in subcritical water as a function of pH in order to investigate the effects of catalysts on the production of value-added chemicals. A base-catalysed reaction at pH 13 promoted the decomposition of alginate, resulting in the production of lactic acid, fumaric acid and malic acid as major species. At pH 1, monomers (mannuronic acid and guluronic acid), furfural and glycolic acid were predominantly produced by the acid-catalysed hydrothermal decomposition of alginate. Increasing the reaction temperature enhanced both the acid- and base-catalysed reactions, albeit by varying degrees dependent upon the catalyst type. Our results demonstrate that optimizing the reaction temperature and pH is critical for the efficient conversion of seaweed-derived biomass into valuable products.

1. Introduction

Marine algal biomass, composed of microalgae and macroalgae, is emerging as a promising next-generation energy resource due to its inherent advantages including a fast growth rate, ease of cultivation, excellent CO_2 consumption and absence of lignin [1–3]. Alginate, a major component of brown seaweeds, has been widely utilized in various industrial and scientific fields. Alkali metal salts of alginate, such as sodium alginate and calcium alginate, are useful additives for foods that contribute to shape, texture and viscosity [4]. The biocompatibility of alginate has been exploited for various applications, including biological substrate construction and drug delivery [5–8]. In an effort to produce novel biofuels from alginates, the metabolic conversion of alginate has been proposed for the production of ethanol using engineered microorganisms [9,10]. The suggested enzymatic process provides high selectivity for desired products, but involves long reaction times (ca. days), high costs and complex genetic modifications of yeast strains, drawbacks that have hampered its widespread adoption [11]. Hydrothermal treatment with subcritical water produces valuable chemicals from biomass in hot compressed water and has proven itself as a useful alternative, as the reaction can be accomplished within a few hours using a relatively simple procedure [12–16]. In addition, the hydrothermal conversion process is cheap, sustainable and eco-friendly due to its use of subcritical water instead of expensive and toxic organic solvents [17].

Alginate has excellent potential for the generation of value-added chemicals due to its polysaccharide structure of plant-like origin. Alginate is composed of two monomeric subunits containing the carboxylic groups mannuronic acid and guluronic acid [18,19]. The subunits are connected by β-1,4-glycosidic bonds analogous to cellulose [20–23]. Similar to the hydrothermal conversion of cellulose, the linkages in alginate are selectively broken through a β-elimination reaction under hydrothermal reaction conditions, as depicted in Fig. 1 [19,24]. Further hydrothermal decomposition of alginate with the addition of hot compressed water leads to the production of various organic compounds, via breaking of the C—C or C—O bonds within monomeric subunits [25–27].

Hydrothermal conversion of cellulose into valuable organic compounds has been extensively investigated [28–33], but hydrothermal treatment of alginate has only recently been applied to produce useful organic compounds. Aida et al. described the production of monomers and organic acids under subcritical and supercritical water conditions, by investigating the effects of

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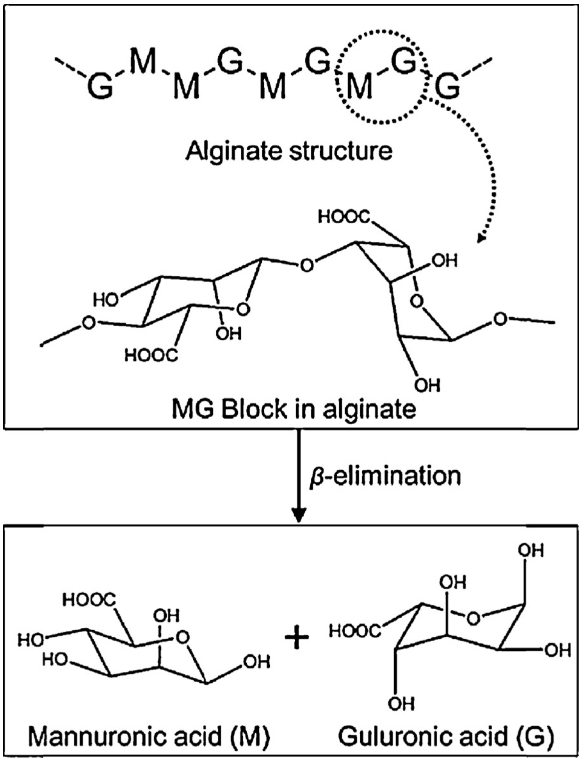


Fig. 1. Decomposition of alginate via the cleavage of 1, 4-glycosidic linkages in a β-elimination pathway.

reaction temperature (150–400 °C) on the conversion of alginate into its monomers and monomer-derived organic acids, such as monocarboxylic and dicarboxylic acids [26,27]. The impact of different catalysts and pH on reactivity at high temperatures, however, remains unknown. We sought to systematically investigate the effects of homogeneous catalysts on hydrothermal reactions as a function of pH for the production of valuable organic acids. The effects of homogeneous catalysts (such as mineral acids and alkali salts) on hydrothermal degradation of alginate were first investigated between the 1960s and 1980s [25,34–36], but the reaction conditions were limited and quantification of the furfural and organic acids was not satisfactory. Furthermore, the rapid decomposition of alginate under conditions with homogeneous catalysts prevented the analysis of the initial reaction states.

In this study, we investigated the effects of varying pH between 1 and 13 in order to better understand acid- and base-catalysed reactions in hydrothermal decomposition of sodium alginate. In addition, reaction temperatures between 150 and 250 °C were used to understand the roles of catalysts and hot compressed water at high temperatures, and to draw a comparison with previous findings conducted at temperatures below 150 °C [25,35–38]. A reaction time of less than 1 h was chosen to investigate the reaction mechanism during the early stage of alginate decomposition. We selected formic acid, acetic acid, glycolic acid, lactic acid, fumaric acid, succinic acid, malic acid and furfural as target products, because these C_1–C_5 organic compounds are considered to be value-added chemicals by industrial chemists. Production of the organic compounds was verified by HPLC equipped with VWD and RID or GC/MS analysis. The production of gaseous products, such CO_2, and solid residues were observed, but a detailed analysis for those products was not performed in this study. The current study characterizes a number of important aspects required for our ongoing efforts to introduce heterogeneous catalysts into the decomposition reaction of sodium alginates to produce value-added organic compounds.

2. Materials and experimental procedures

2.1. Materials

All organic acids were purchased from Sigma–Aldrich, except fumaric acid which was purchased from Tokyo Chemical Industry. Monomers of alginate were also prepared to elucidate the pathways more clearly. Standard chemicals of those monomers, mannuronic and guluronic acid, were purchased from Qingdao BZ Oligo Biotech, China (purity > 98%). Alginic acid sodium salt (sodium alginate) obtained from Sigma–Aldrich was used as a starting material in the hydrothermal depolymerization reaction with no mechanical pretreatment. Cellulose was purchased from Sigma–Aldirich and mechanically treated with a milling machine for 20 h to reduce the particle size and thus enhance the reactivity. Homogeneous catalysts, hydrogen chloride and sodium hydroxide, were purchased from Junsei Chemical and Sigma–Aldrich, respectively. For preparation of the acidic solvents, hydrogen chloride was added to distilled water until the pH of the solvents reached 1 or 3. Likewise, sodium hydroxide and distilled water were used to produce basic solvents of pH 11 and 13.

2.2. Apparatus and experimental procedure

The hydrothermal conversion of sodium alginate was performed using a tubular batch reactor consisting of SUS 316 tubing. A molten salt bath including the mixture of alkali metal nitrates was utilized as a heater. The procedure was comprised of five steps: sample loading, N_2 gas purging, heating, cooling and analysis. As the first step, sodium alginate (60 mg) and solvent (3 mL) were loaded together into the reactor, which had an inner volume of 6 mL. The solvent was prepared using pure distilled water, hydrogen chloride and sodium hydroxide to control pH values between 1 and 13. Existing gases inside the reactor were removed by a vacuum pump and the reactor was filled with N_2 gas (99.999%). Next, the reactor was immersed in the molten salt bath and taken out immediately after the desired reaction time. The reaction time was recorded from the initial time that a temperature sensor in the reactor first detected the desired reaction temperature. After the heating step, and within a few seconds, the reactor was quickly placed into a cold-water bath. Prior to the analysis step, the final products were pretreated using the following methods: dilution, neutralization, centrifugation and filtration.

2.3. Product characterization

Product identification was performed with a GC–MS System (Clarus 680/600T, PerkinElmer) equipped with an Agilent DB-5MS column. Prior to GC–MS analysis, the samples were lyophilized and silylated with a mixture of BSFTA with TMCS (99:1) and pyridine at 65 °C for 2 h. A representative result of GC–MS analysis for major products was shown in Supplementary content Fig. 1S.

Products were quantified with an Agilent 1200 Series HPLC equipped with two Shodex RSpak KC-811 columns in series. Column oven temperature, flow rate of mobile phase and concentration of phosphoric acid aqueous solution were 40 °C, 1 cm^3/min and 5 mM, respectively. Both RI detector (Agilent G1362A) and UV detector (Agilent G1314B) were used to cross-check the HPLC analysis for more precise characterization. The wavelength of UV detector was set to 210 nm for analyzing final products. The separation and detection of each product were effectively conducted as shown in Fig. 2S(a–c). Based on data obtained from HPLC analysis, molar yields of products were calculated as:

$$\mathrm{Yield_i(mol\%)} = 100 \times \frac{nC_i}{6} \times \frac{n_i}{n_{ru}}$$

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 ($C_6H_7O_6Na$) in the sodium alginate, equal to the mass of sodium alginate divided by 198.

The molecular weight distribution of raw alginate and hydrothermally treated alginate was analyzed by a gel permeation chromatography (GPC) technique. The GPC system (Ultimate 3000, Dionex) was configured with three types of Waters Ultrahydrogel columns: 120, 500 and 1000, in series. Sodium azide solution (0.1 M) was used as a mobile phase at 1 mL/min at 40 °C. The GPC calibration was conducted using Pullulan with a molecular weight distribution from 342 to 80,500.

^{1}H NMR analysis for raw alginate and final aqueous products was performed with a 400 MHz spectrometer (JeolJNM-LA400/LFG, JEOL). The ^{1}H NMR spectra were obtained at 80 °C and 128 scans. Liquid products were lyophilized and then dissolved in D_2O (0.6 mL) containing 3-(trimethylsilyl) propionic-2,2,3,3-d_4 acid sodium salt (0.05 wt%) as an internal standard. At a minimum, tests were conducted to ensure reproducibility three times, to obtain reliable results in quantification.

We noticed the production of insoluble aggregates and gaseous compounds during the sample preparation, but they were not further characterized due to their negligible quantities.

3. Results and discussion

Fig. 2 shows the GPC chromatograms of raw alginates and hydrothermally-treated alginates under various reaction conditions. The GPC data were normalized to the intensities of the highest peaks on each chromatogram to compare differences among the chromatograms. The GPC analysis indicated that depolymerization of sodium alginate was very sensitive to the reaction temperature and pH of the solvent. For example, no noticeable peaks were observed for the reaction at pH 7 at 250 °C (Fig. 2(e)), but broad and large peaks appeared for the reaction at pH 7 at 150 °C, which gradually shifted toward longer retention times as the reaction time increased (Fig. 2(b)). This means that the depolymerization of alginate was clearly accelerated by the reaction temperature. As the temperature of reaction medium, neutral water, increased from 150 to 250 °C, the concentrations of hydrogen and hydroxyl ions dissociated from water molecules rose a few times, resulting in the promotion of alginate decomposition via acid- and base-catalysed hydrolysis by hydrogen and hydroxyl ions, respectively. In addition to the reaction temperature, the effects of catalysts on the alginate degradation were observed as shown in Fig. 2(a–c). At 150 °C, the broad and large peaks for the reaction at pH 7 almost disappeared as the pH varied to 1 or 13, which indicates that the initial catalyst addition increased the concentrations of hydrogen or hydroxyl ions, and consequently enhanced the hydrolysis of alginate. Interestingly, any noticeable peaks were not observed within 25 min of retention time when the alginate was degraded with a strong base catalyst at 150 °C (Fig. 2(c)). This demonstrates that a strong base catalyst significantly enhances the rate of depolymerization and shows better catalytic performance than that of a strong acid catalyst. The raw alginate was largely decomposed after catalyst-free hydrothermal treatment at 250 °C, but small broad peaks were observed within 25 minutes of the retention time, as shown in Fig. 2(e), underlining the effect of catalysts on the depolymerization of alginate.

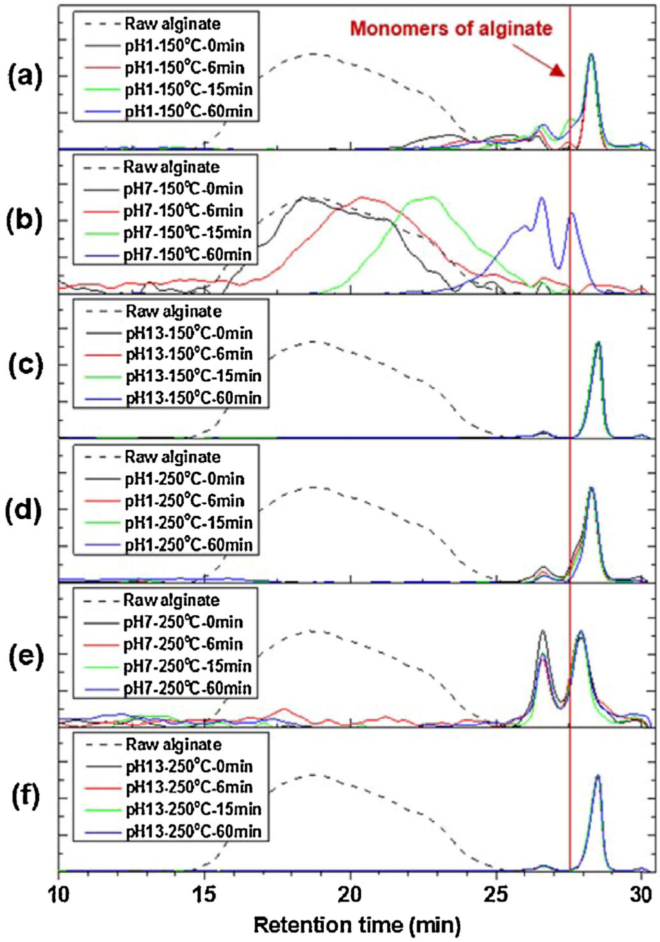


Fig. 2. GPC chromatograms of raw alginate and products obtained by hydrothermal depolymerization of raw alginate: (a) pH 1, 150 °C, (b) pH 7, 150 °C, (c) pH 13, 150 °C, (d) pH 1, 250 °C, (e) pH 7, 250 °C, (f) pH 13, 250 °C.

The average molecular weights (M_w, M_n) of products decreased with increasing reaction temperatures from 150 to 250 °C, as listed in Table 1. Polydispersity index (PDI) values of products also decreased and converged toward 1 at higher temperatures, strongly suggesting that the depolymerization of alginate into small molecules having similar molecular weights was accelerated at higher temperatures due to vigorous hydrolysis triggered by higher concentrations of hydrogens and hydroxyl ions. The increasing thermal energy gives rise to a decrease of relative dielectric permittivity and an increase in ion products in subcritical water systems [17,39], which catalyses the hydrolysis of alginate more effectively. In addition to the reaction temperature, the average molecular weights were drastically reduced when the alginate was depolymerized at 150 °C under acid or base catalysts, as evidenced by GPC chromatograms. The rise of hydrogen and hydroxyl ion concentrations after the addition of catalysts increased the ion products in the subcritical water, promoting hydrolysis, nucleophilic substitution and elimination reactions. In particular, the products that decomposed in the presence of a base catalyst exhibited much lower average molecular weights (M_w, M_n) and polydispersity index values than those with an acid catalyst, suggesting that the base-catalysed elimination (known as a peeling reaction) is more efficient for alginate decomposition. For example, when the hydrothermal reaction occurred under the base catalyst, the values of M_w and M_n immediately converged to approximately 700 and 520, respectively. This means that the base-catalysed reaction accelerated multiple and simultaneous cleavages of overall glycosidic bonds in alginate polymer. However, under the acid catalyst at 150 °C, M_w and M_n gradually decreased and PDI values were higher than those values for base-catalysed reactions, which indicates that the rate of alginate depolymerization was relatively

Table 1
Weight average molecular weight (M_w), number average molecular weight (M_n) and polydispersity index (PDI) values of raw alginate and hydrothermally-treated alginate under different reaction conditions.

Sample		M_w (Da)	M_n (Da)	PDI
Raw alginate		277865	65185	4.26
pH 1–150 °C	0 min	9453	1269	7.45
	6 min	4159	1039	4
	15 min	1396	841	1.66
	60 min	1710	819	2.09
pH 7–150 °C	0 min	268446	107320	2.5
	6 min	129806	50913	2.55
	15 min	36506	15440	2.36
	60 min	3608	1870	1.93
pH 13–150 °C	0 min	704	533	1.32
	6 min	683	521	1.31
	15 min	711	537	1.33
	60 min	699	519	1.35
pH 1–250 °C	0 min	873	703	1.24
	6 min	817	679	1.2
	15 min	753	650	1.16
	60 min	693	607	1.14
pH 7–250 °C	0 min	1367	1009	1.35
	6 min	1171	905	1.29
	15 min	1251	994	1.26
	60 min	1247	962	1.30
pH 13–250 °C	0 min	682	535	1.27
	6 min	678	533	1.27
	15 min	649	524	1.24
	60 min	646	519	1.25

low and the acid-catalysed reaction induced random and partial cleavages of glycosidic linkages.

The presence of GPC peaks after 27.5 min of retention time indicates the breakdown of mannuronic and guluronic acid subunits into smaller molecules due to cleavage of C—C or C—O linkages within the monomer subunits. When sodium alginate decomposed at pH 1 at 150 °C, the GPC peak from the monomer appeared and then perished as reaction time increased (Fig. 2(a)). Coexistence of GPC peaks from the monomer and other smaller products implies that the acid-catalysed hydrolysis of sodium alginates into monomers and the decomposition of monomers into small organic compounds occur simultaneously. As shown in Fig. 2(c), the monomers' peak was not detected within 60 min at pH 13, showing that the decomposition of monomers produced from sodium alginate occurs extremely rapidly in the presence of a strong base catalyst. However, in catalyst-free subcritical water (pH 7), the monomers' peak was observed after 60 min of reaction time. These results were consistent with the ^{1}H NMR analysis, as shown in Fig. 3(a). The unique peaks for alginate between 4.40 and 5.17 ppm were not observed for the reaction at pH 13 at 150 °C, whereas those peaks clearly appeared when alginate was depolymerized at pH 1 and 7 at 150 °C. Instead of those unique peaks, alternative peaks emerged between 1 and 4 ppm only for the sample treated at pH 13 for 0 min. Both NMR and GPC data provide evidence that sodium alginate quickly converts to a complex organic mixture containing hydroxyl and carboxyl groups smaller than monomers at 150 °C under the strong base catalyst.

At 250 °C, the hydrothermal reactions under all pH conditions were accelerated and the raw alginate was immediately degraded as soon as the reaction initiated. As a result, shapes of GPC chromatograms (Fig. 2(d–f)) quickly converged with the average molecular weight values (Table 1). The properties of subcritical water at 250 °C changed significantly as mentioned above and, as a result, strongly promoted the alginate decomposition regardless of the addition of catalysts. The fast degradation of alginate at the higher temperature was also observed in ^{1}H NMR spectra as shown in Fig. 3(b). The characteristic peaks of alginate disappeared completely and, at the same time, numerous other peaks emerged, verifying the production of various organic compounds from alginate decomposition. However, the catalysts were still influential for the molecular distribution of depolymerized alginate. Corresponding with the converged shapes of the chromatograms (Fig. 2(d–f)), the average molecular weights of products obtained by the reaction at 250 °C under acid and base catalysts were lower than those for products generated in neutral subcritical water, as listed in Table 1. This is strong evidence suggesting that the catalyst-assisted hydrothermal treatment is still favorable for depolymerizing sodium alginate at high reaction temperatures (250 °C). It can be expected that the roles of catalysts in reducing the molecular weight of sodium alginate may be relatively weakened if reaction temperatures exceed 250 °C under supercritical water conditions.

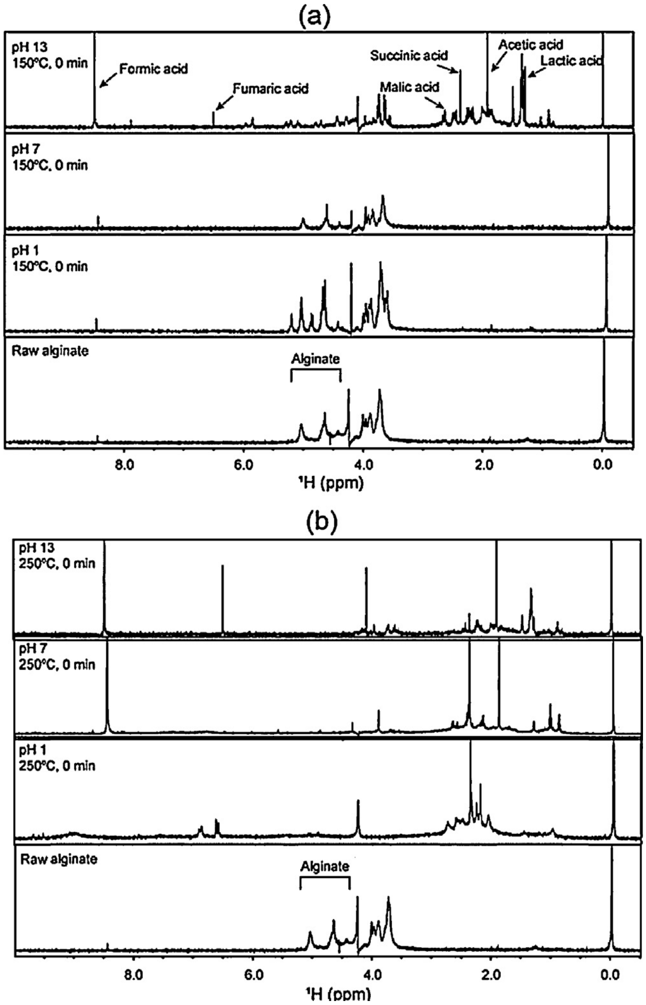


Fig. 3. ^{1}H NMR spectra of raw alginate and hydrothermally treated alginate solutions; H-1 of guluronic acid (δ = 4.95–5.17), H-5 of guluronic acid and H-1 of mannuronic acid (δ = 4.55–4.82), H-5 of guluronic acid (δ = 4.40–4.50).

After the depolymerization of sodium alginate through the selective cleavage of 1,4-glycosidic bonds, the alginate was expected to convert to monomers, followed by decomposition of the monomers to organic products [25,27]. Fig. 4 shows yield distributions of the monomers and organic compounds produced by hydrothermal treatment at 150, 200 and 250 °C. Using a strong acid catalyst (pH 1) at 150 °C, the monomers were instantly generated as the reaction started. This indicates that the selective

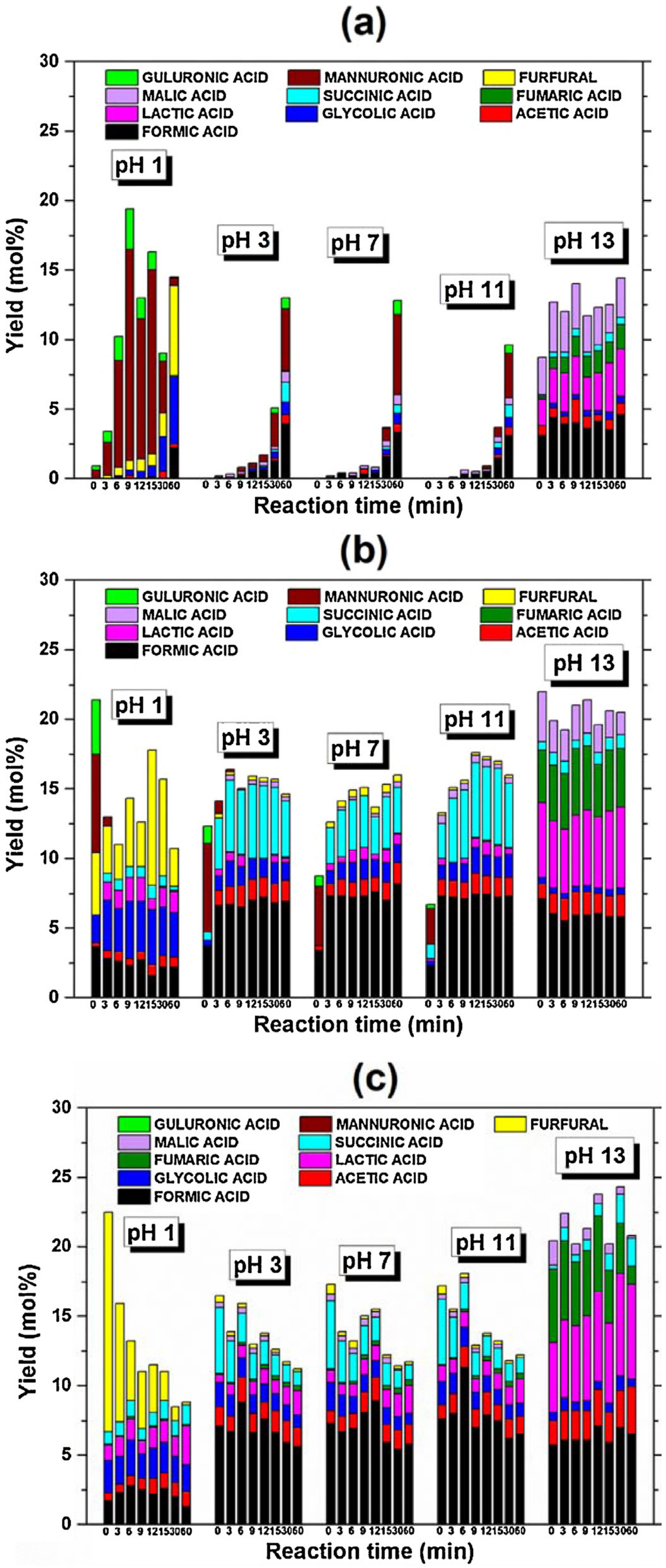


Fig. 4. Molar yields of monomers and organic acids produced by hydrothermal decomposition. (a) 150 °C, (b) 200 °C, (c) 250 °C. Reaction times marked beneath each column are as follows: 0, 3, 6, 9, 12, 15, 30 and 60 min.

cleavage of glycosidic linkages was promoted by acid-catalysed hydrolysis. The production of monomers was also observed in GPC data as shown in Fig. 2(a). The yield of monomers increased and then decreased within a few minutes with the production of furfural, glycolic acid and formic acid. This phenomenon was explained by the further decomposition of monomers through acid-catalysed hydrolysis and dehydration. Another research group reported that mannuronic acid detaches from alginates faster than guluronic acid [26]. Similarly, the quantity of mannuronic acid was higher than that of guluronic acid in acidic and neutral subcritical water at 150 °C in this study. It indicates that the sequence of monomer dissociation in subcritical water remains constant regardless of the addition of an acid catalyst. On the other hand, the rate of monomer production under a strong acid catalyst was remarkably higher than the production rate in catalyst-free alginate hydrothermal depolymerization.

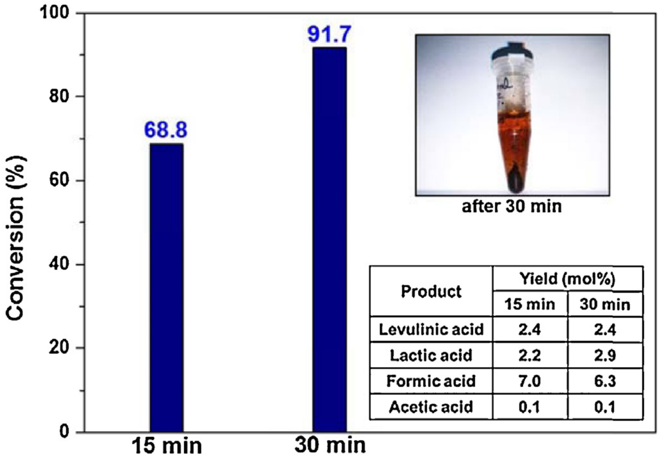
Both monomers were not detected in the hydrothermal treatment of sodium alginate in the presence of a strong base catalyst (pH 13). Instead of monomers, carboxylic and dicarboxylic acids were produced more abundantly, with the amount increasing as reaction time increased. This suggests that a strong base catalyst substantially promotes the decomposition of monomers via the Lorby de Bruyn–Alberta van Ekenstein Transformation (LBET), hydrolysis and dehydration reactions after the peeling reaction of alginate [25]. As a result, the monomers liberated from sodium alginate immediately converted into malic acid, fumaric acid, lactic acid, formic acid, etc., as shown in Fig. 4(a). The production of lactic and dicarboxylic acids was typical for a base-catalysed hydrothermal decomposition of alginate or other hexuronic acids [25,40]. In contrast to the strong acid and base catalysts, at 150 °C, weak acid (pH 3) and weak base (pH 11) catalysts did not show any remarkable difference in performance compared to the catalyst-free reaction (pH 7). Although the hydrothermal treatment of alginate in a pH range from 3 to 11 produced monomers and organic acids, it required at least 60 min to achieve that outcome.

Fig. 4(b) shows the yield distribution of organic compounds produced at 200 °C. Monomers were almost consumed and the production of organic compounds was enhanced in comparison to the reaction at 150 °C. The production of formic acid, acetic acid and glycolic acid is common, and indicates that the reaction temperature (200 °C) is sufficiently high to decompose monomers into smaller organic acids regardless of the presence of an acid or base catalyst. Interestingly, the yield distribution of organic products shows clear differences between hydrothermal reactions under different pH conditions. The strong acid catalyst (pH 1) assisted the production of furfural, glycolic acid and small quantities of other organic acids. Compared with hydrothermal treatment at pH 1, the quantities of succinic acid increased, whereas the quantities of furfural and glycolic acid decreased in the pH range from 3 to 11. This implies that the production of furfural and glycolic acid is a unique feature of acid-catalysed hydrothermal alginate decomposition. On the other hand, malic acid, fumaric acid and lactic acid were generated under a strong base catalyst (pH 13). This indicates that mechanisms of monomer decomposition are completely different, and are dependent upon the acidic or basic nature of the reaction solvents.

As shown in Fig. 4(c), the overall yields of organic products for all pH conditions were reduced as the reaction time increased, in comparison with different reactions at 150 and 200 °C. Such decrease indicates that thermally unstable compounds decomposed at 250 °C. For example, the yield of furfural decreased drastically under the strong acid catalyst (pH 1). This decrease was expected due to its low thermal stability in acidic aqueous media. To ensure the decomposition of furfural in our experimental system, the hydrothermal treatment of furfural in the acidic subcritical water was performed with high-purity furfural

Table 2
Conversion and yields of organic acid products obtained from hydrothermal treatment of dicarboxylic acids in 250 °C of subcritical water at pH 13.

	Starting Material (2 wt% in 3 mL of H_2O)					
	Malic acid			Fumaric acid		
Reaction time (min)	3	15	30	3	15	30
Conversion (%)	63	90.6	93.6	8.8	66.4	90.9
Compound	Yield (mol%)					
Formic acid	0	0	0	0	0	0
Acetic acid	9.2	45.6	88.3	10.7	60.1	82.7
Glycolic acid	0.5	0.2	0.5	0.5	0.9	0.3
Lactic acid	0.1	0.3	0.4	0	0.4	0.8
Succinic acid	0.7	9.2	11.7	1.1	5.4	11.4
Fumaric acid	91.9	23	14.2	–	–	–
Malic acid	–	–	–	35.6	17.0	5.4



Product	Yield (mol%)	
	15 min	30 min
Levulinic acid	2.4	2.4
Lactic acid	2.2	2.9
Formic acid	7.0	6.3
Acetic acid	0.1	0.1

Fig. 5. Conversion of furfural and yields of products after hydrothermal treatment of furfural at pH 1 and 250 °C.

(>99.0%). As expected, the conversion of furfural rapidly proceeded, resulting in the production of small amounts of organic acids and dark solid residues as shown in Fig. 5. The solid residues are considered as humins formed by polymerisation of furfural, known as "furfural resinification", in the acidic hydrothermal conditions. These insoluble particles are observed when hexose or pentose are hydrothermally converted to furan compounds, such as 5-hydroxymethyl furfural or furfural [41,42]. These insoluble particles were also generated in small quantities when alginate was hydrothermally treated in acidic reaction media. The production of humins is a major obstacle to produce furfural from the hydrothermal process, and further investigation for inhibiting the humin formation is required to enhance the yield of furfural.

Yields of malic acid and fumaric acid were also reduced as reaction temperatures increased from 200 to 250 °C at pH 13, as shown in Fig. 4(c). This indicates that these particular acids are unstable in that subcritical water condition. Those two dicarboxylic acids were likely to convert into succinic acid and acetic acid at pH 13 at 250 °C, since it was observed that the yields of succinic acid and acetic acid increased as the reaction time increased. To clarify this, separate hydrothermal treatments of fumaric acid and malic acid was conducted at 250 °C in subcritical water at pH 13, as listed in Table 2. It was observed that malic acid and fumaric acid were consumed as the yields of succinic acid and acetic acid increased. It is believed that malic acid was rapidly transformed to fumaric acid by dehydration reaction and then fumaric acid produced converted to succinic acid and acetic acid. Although fumaric acid was hydrated to form malic acid, the dehydration of malic acid was likely to be more dominant in the reaction condition. To sum up, this high reaction temperature under the strong base catalyst decomposes both malic acid and fumaric acid, and depreciates the final product with the large amount of acetic acid. Therefore, either short reaction times at high temperatures or long reaction times at mild temperatures are favorable for production of hydrothermally unstable compounds, such as furfural, malic acid and fumaric acid.

However, lactic acid was generated under all of the pH conditions at 250 °C without the decrease of yield, since the decomposition of lactic acid is feasible in near critical water (320–400 °C) [43]. The production of lactic acid was typical for the base-catalysed hydrothermal depolymerization of alginate [25], and means that the high reaction temperature induced a base-catalysed reaction by changing the properties of the subcritical water and promoting nucleophilic substitutions and elimination reactions. The high quantities of lactic acid at pH 13 at all of the reaction temperatures indicate that a strong base catalyst is very useful for the production of lactic acid via hydrothermal treatment of alginate in a wide range of temperature.

As summarised in Fig. 6, various organic compounds could be produced by the hydrothermal treatment of alginate over acid and base catalysts in subcritical water. The acid-catalysed reaction promoted the production of furfural and glycolic acid, whereas the base-catalysed reaction induced the production of lactic acid and dicarboxylic acids, such as malic acid and fumaric acid. Catalyst-free reaction at pH 7 showed poor performance in both alginate depolymerization and organic acid production. However, the performance was remarkably enhanced and all of the target products were detected at reaction temperatures higher than 200 °C. This indicates that the high reaction temperature induces both acid- and base-catalysed hydrothermal reactions. Increasing reaction temperature influenced reaction pathways of hydrothermal conversion of alginate and changed the product distributions with the aid of catalysts. For example, lactic acid was produced under the strong acid catalyst at reaction temperatures higher than 200 °C, although it is a typical product from base-catalysed hydrothermal decomposition of carbohydrate biomass including alginate [25,28,44]. Decomposition of furfural in acidic subcritical water is considered as a major factor for the production of lactic acid at pH 1, as shown in Fig. 4(c) and Fig. 5. This means that lactic acid can be produced by acid- or base-catalysed hydrothermal decomposition of alginate at relatively high temperatures via totally different reaction pathways. Namely, in addition to catalysts, the reaction temperature has considerable influence on reaction pathways in hydrothermal conversion of alginate into organic compounds.

We compared the hydrothermal decomposition of cellulose with that of alginate by using acid and base catalysts in our efforts to produce valuable organic compounds. The cellulose was mechanically milled for over 20 h to enhance the susceptibility of crystalline cellulose to hydrothermal conversion, for effective conversion in subcritical water [45]. As shown in Table 3, a monomer of cellulose (glucose) also completely converted during hydrothermal

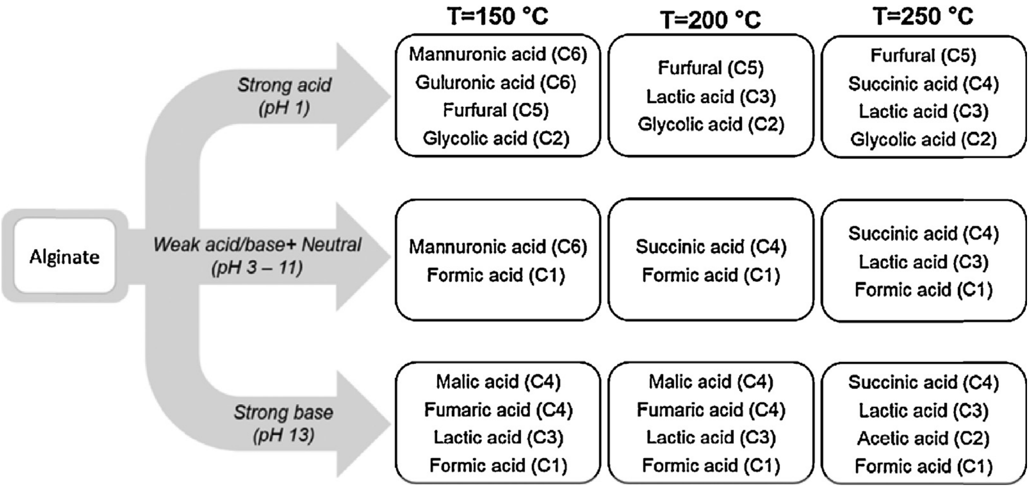


Fig. 6. Reaction pathways of alginate decomposition by catalysts and reaction temperatures.

Table 3
Yields of organic compounds produced by hydrothermal treatment of sodium alginate and cellulose at 150 °C for 30 min in the presence of a strong acid and base catalyst.

Product	Yield (mol%)			
	pH 1		pH 13	
	Alginate	Cellulose	Alginate	Cellulose
Monomer	4.3	6.6	0.0	0.0
Furfural	1.7	3.3	0.0	0.0
Malic acid	0.0	0.0	3.1	0.0
Succinic acid	0.0	0.0	0.4	0.0
Glycolic acid	2.5	0.0	0.6	0.2
Fumaric acid	0.0	0.0	2.8	0.0
Lactic acid	0.0	0.0	3.5	4.8
Acetic acid	0.5	0.6	4.9	0.0
Formic acid	0.0	0.9	1.1	2.8
Total	9.0	13.2	16.4	7.8

treatment at pH 13, similar to the decomposition of mannuronic acid and guluronic acid with a strong base catalyst. In addition, monocarboxylic acids, such as lactic acid and formic acid, were obtained from the hydrothermal conversion of both cellulose and alginate. However, cellulose did not convert into dicarboxylic acids, such as malic acid, succinic acid or fumaric acid. At pH 1, glucose and furfural were produced significantly rather than organic acids. These differences likely arose from an extra carboxylic functional group in an alginate monomer. The acid-catalysed degradation of cellulose showed better performance for production of furfural, compared with alginate. Most final products serve as useful platform chemicals in scientific and industrial fields [46]. Among those products, furfural, lactic acid and succinic acid were selected as important biomass-derived chemicals [47]. Prior to that, malic acid and fumaric acid were also ranked as top value-added chemicals from biomass in 2004, released by the US Department of Energy (DOE) [48]. In that respect, alginate is regarded as a promising and competitive biomass feedstock for production of furfural and value-added organic acids, especially without treating it with mechanical process like cellulose.

4. Conclusions

Alginate represents a promising alternative feedstock to replace cellulose for the production of furfural and organic acids. We found that homogeneous acid and base catalysts accelerate the depolymerization of sodium alginate in subcritical water. A strong acid catalyst promotes the production of mannuronic acid and guluronic acid (monomers of alginate) at 150 °C, whereas the presence of a strong base catalyst immediately converts the monomers to carboxylic acids and dicarboxylic acids after the dissociation of monomers from alginate. As the reaction temperature increases, monomers completely convert to various organic compounds with different acidic and basic distributions for the reaction solvents. Furfural and glycolic acid was mainly produced by acid-catalysed reactions, whereas lactic acid, fumaric acid and malic acid were detected in base-catalysed reactions. Higher reaction temperature and longer reaction time were favorable for hydrothermal decomposition of alginate, but it was observed that a few useful compounds were transformed to less valuable products, such as furfural to humins or C_4 dicarboxylic acids to acetic acid. To sum up, the acid and base catalysts are further influential in determining the distribution of final products, whereas the reaction temperature is a more important factor for reducing the molecular weight of alginate in hydrothermal conditions. Our research demonstrates that an efficient selective production of value-added organic compounds can be achieved by carefully adjusting the reaction conditions such as pH, temperature and time. This will be helpful in understanding the effects of solid catalysts on the hydrothermal depolymerization of alginate, studies of which are now in progress. It is expected that more selective production of valuable organic chemicals will be possible if engineered solid catalysts are applied using this depolymerization reaction.

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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.2015.01.011.

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