J Mater Sci (2008) 43:2463–2471
DOI 10.1007/s10853-007-2013-z

NOVEL ROUTES OF ADVANCED MATERIALS PROCESSING AND APPLICATIONS

Application of hydrothermal reaction to conversion of plant-origin biomasses into acetic and lactic acids

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Received: 27 October 2006 / Accepted: 20 July 2007 / Published online: 29 September 2007

Abstract In this paper, some recent advances in our research on hydrothermal conversion of biomass into useful substances are presented. Here, we mainly focus on the production of acetic acid and lactic acid from carbohydrates including aldose, lignocellulosic biomass, and glycerin along with the discussion of some reaction mechanisms and the interaction between the main components of natural material, such as cellulose and lignin in lignocellulosic biomass. A large-scale continuous flow reactor system was also presented.

Introduction

Dependence on fossil fuels as the main energy sources has led to serious energy crisis and environmental problems. Utilization of energy and chemicals from renewable biomass resources would reduce atmospheric CO_2 increase associated with fossil fuel use and our dependence on petroleum-derived feedstock. Hydrothermal process has a promising potential for environmentally friendly conversion of biomass into useful chemicals and energy, because high-temperature water (HTW) is an environmentally benign solvent against less desirable organic solvents, and has remarkable properties as a reaction medium [1, 2]. For example, HTW has a lower dielectric constant, fewer and weaker hydrogen bonds, and a higher isothermal compressibility than ambient liquid water [3]. Moreover, the ion product (K_w) for HTW is about 3 orders of magnitude higher than that of ambient liquid water [4]. The natural abundance of hydronium and hydroxide ions suggests that some acid and base-catalyzed reaction may proceed in HTW in the absence of an added catalyst.

There has been much previous research on the application of HTW as a reaction medium for chemical syntheses [5–8], waste destruction [9–11], plastics recycling [12–13], coal liquefaction [14] and biomass processing [15–19]. We have also been carrying out studies for biomass recycling by HTW [20–26].

In this paper, some recent advances in our research involving hydrothermal conversion of biomass into useful substances are presented, mainly including (1) the conversion of carbohydrate biomass into acetic acid, which is followed by conversion of the acetic acid into an environmentally friendly road deicer of calcium/magnesium acetate (CMA); (2) the conversion of carbohydrate biomass into lactic acid by alkali hydrothermal reaction; (3) the conversion of glycerin, a by-product of manufacturing biodiesel fuel, into lactic acid by alkali hydrothermal reaction, and (4) the discussion of some hydrothermal reaction mechanisms.

Experimental

Materials

Glucose, as a model compound of carbohydrate, and cellulose and potato starch, as the main components of carbohydrate biomass, were used as test materials. Rice

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hulls and sawdust as representatives of lignocellulosic biomass and potato as a representative of carbohydrate biomass were also selected as test materials. Starch and glucose were of reagent grade. Cellulose used in this study is a filter paper powder for chromatograph column (under 200-mesh in size, Toyo Roshi Kaisha, Ltd.). Rice hulls used in this study were obtained from a local harvest, and sawdust (Japanese cedar) from a local sawmill. Their components are shown in Table 1. The rice hulls and sawdust were ground to pass a 100-mesh size screen in a cross-beater mill.

Amounts of starting materials were limited to 0.07 g (dry base) in all batch experiments. Hydrogen peroxide was used as an oxidant for experimental convenience. The oxygen supply was defined as the ratio of the amount of oxygen supplied by H_2O_2 to the stoichiometric demand of oxygen for complete oxidation of carbon, calculated from the carbon content of test material, to carbon dioxide.

Experimental procedure

All batch experiments were conducted with a batch reactor consisting of SUS 316 tubing [21]. The typical experimental procedure was as follows [21, 27]. A 0.07 g test material and deionized water (for hydrothermal reaction) or a mixture of deionized water and hydrogen peroxide (for hydrothermal or wet oxidation, WO) of 3.4 cm^3 in volume, providing a 60% water fill, were put into a batch reactor, which was then sealed and put into a salt bath preheated to the desired temperature. In the salt bath, the reactor was shaken, keeping it horizontally, to enhance mixing and heat transfer. After the desired reaction time, the reactor was taken out of the salt bath and was immediately put into a cold water bath to quench the reaction. The reaction time was defined as the time that the reactor was kept in the salt bath.

In a two-step process treatment, the two-step procedure was taken: one is a hydrothermal reaction without an oxygen supply (the first step reaction) and the other WO (the second step reaction). That is, at the first step reaction, only the test material and water were added to the reactor for the reaction. After the first step, H_2O_2 was added to the reactor cooled down, and then the second step reaction took place.

Table 1 Acetic acid yields by wet oxidation of various carbohydrate and lignocellulosic biomasses

	Yield[a] (%)	Conditions		
		Temp. (°C)	Time (s)	Oxygen supply (%)
Carbohydrate biomass				
Carrots	13.0	400	30	50
Welsh onion	12.9	400	30	50
Mixture[b]	13.2	400	30	50
Potato	11.1	300	60	70
Lignocellulosic biomasses				
Rice hulls	11.7	300	120	70
Sawdust	9.7	300	120	80
Main components in carbohydrate and lingollulosic biomasses				
Cellulose	9.0	300	120	70
Starch	9.6	300	60	70
Lignin	6.3	300	120	70

[a] The carbon percent based on that of initial material(s)

[b] The mixture of six kinds of vegetables (carrots, white radish, potato, burdock, cabbage and eggplant)

Composition of rice hulls: cellusoe: 37.7%, hemicellulose: 18.8, lignin: 12%, SiO_2: 22.5, soluble extracts: 6.9

Composition of sawdust: cellusoe: 48.8%, hemicellulose: 15.9, lignin: 33.7%, SiO_2: 0.5, soluble extracts: 5.5

Product analysis

After the reaction, liquid samples were collected and intermediate products were identified and quantified by GC/MS and/or HPLC. Details on the conditions for GC/MS and HPLC are available elsewhere [21, 28]. All yields reported in this paper are defined as the carbon percent based on that of initial material(s). The yields obtained are the average of analyses on three samples and the deviation was within 1% in all cases. The residual organic carbon concentration (TOC) in liquid samples was also measured with a TOC analyzer.

Results and discussion

Conversion of carbohydrate and lignocellulosic biomasses into acetic acid by conventional wet oxidation (WO)

Acetic acid production

First of all, in order to test whether acetic acid can be produced in large quantities by WO, experiments with various biomass wastes and their main components were performed over a wide range of conditions, with temperature varying from 250 °C to 450 °C, H_2O_2 supply varying from 10% to 150 %, and reaction time varying from 10 s to 300 s. Results have indicated that acetic acid can be obtained and can be increased by optimizing the reaction condition of WO of organic waste (see Table 1). However, there is a limit to acetic acid production, i.e., only 11–13% of acetic acid yield at most for all test materials selected. It also can be seen that, in Table 1, the acetic acid yields from lignocellulosic biomasses of rice hulls and sawdust were higher than those from their main components of cellulose and lignin.

Retarding role of phenols and lignin in the WO of cellulose

As mentioned above, acetic acid yields by the oxidation of ligocellulosic biomass of rice hulls and sawdust were higher than those for cellulose or lignin itself, indicating that there was some interaction between cellulose and lignin. Although there have been extensive studies on the application of HTW for biomass recycling and organic waste destruction, few studies have examined the interaction between the main components of a natural material, such as cellulose and lignin in lignocellulosic biomass.

Lignin is a complex phenylpropane polymer that can be easily broken down into phenol and phenol derivatives in WO. Phenols are widely used as oxidation inhibitors in the food chemistry. Emanuel et al. [29, 30] has reported that phenols also acted as an inhibitor in the oxidation of hydrocarbons in the liquid phase. Therefore, phenols could have an inhibiting role in the oxidation of cellulose in WO of lignocellulosic biomass. However, besides our past study [31], few studies have reported the inhibiting role of phenols and lignin in the oxidation of organics in WO.

In order to test the effect of lignin and/or phenols on WO of cellulose, intermediate products were identified in the oxidation of cellulose, phenol, cellulose–phenol mixture, and cellulose–lignin mixture. As shown in Fig. 1, two new products of 5-hydroxymethyl-2-furaldehyde (HMF) and 2-furaldehyde (2-FA) were formed in the oxidation of the mixtures. In addition, the amount of formic acid decreased greatly compared to that in WO of cellulose. Formic acid is a basic oxidation product from carbohydrates [21], and it is generally known that HMF and 2-FA are typical acid-catalyzed dehydration products from carbohydrates. In general, in the WO reaction of cellulose, there are various competing reaction pathways, each of which is favored by different conditions. When the oxygen supply is sufficient, oxidation reaction takes place over other reactions such as hydration and dehydration, because the rate of oxidation reaction is much more rapid than other reactions. However, when lignin or phenols as oxidation retardants exist with cellulose, the rate of oxidation reaction of cellulose will decrease, while other reactions will proceed. Because cellulose easily forms HMF and 2-FA, they would be easily formed when adding lignin or phenols to cellulose. In other words, the formation of HMF and 2-FA suggests that reactions other than oxidation increased, and a decrease in formic acid in the oxidation of the mixtures indicate that the oxidation reaction rate of cellulose decreased. From these results, lignin and phenols seem to have a retarding role in WO of cellulose.

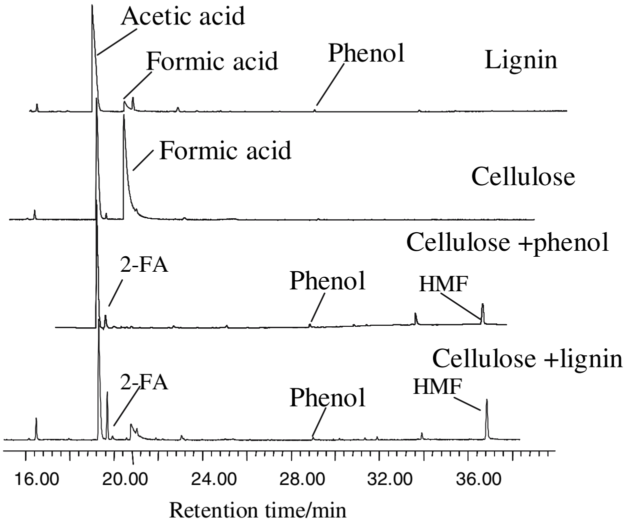


Fig. 1 GC/MS chromatograms of samples after reaction at 300 °C, 2 min and 70% oxygen supply for lignin, cellulose and a mixture of cellulose and lignin or phenol (mixing ratio 8:2)

Improvement of the acetic acid production by a two-step reaction

As described before, the yield of acetic acid from carbohydrate biomass is limited to only 11–13% by the conventional WO (the direct oxidation). These results suggest that the direct oxidation reaction of carbohydrate biomass should be inhibited to improve the acetic acid yield. Therefore, a new two-step process for improving the yield of acetic acid was proposed.

Improvement of acetic acid production by the two-step reaction without the addition of any catalyst

The two-step process without the addition of any catalyst for improving acetic acid production is shown in Fig. 2 [21, 32]. The two-step process consists of both a hydrothermal reaction process without the supply of oxygen (the first step reaction) and a subsequent oxidation reaction process (the second step reaction). The first step is to convert carbohydrates mainly to HMF, 2-FA and lactic acid, and the second step is to further convert HMF, 2-FA and lactic acid produced in the first step to acetic acid by the oxidation with newly supplied oxygen. HMF, 2-FA and lactic acid can produce a large amount of acetic acid by their oxidation.

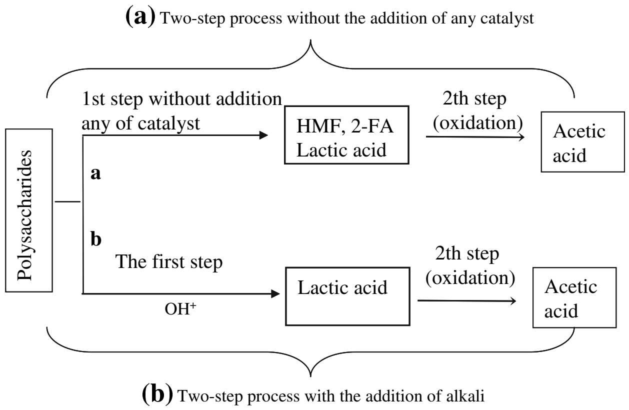


Fig. 2 Proposed two-step process for enhancing acetic acid yield

Experiments were performed to obtain respective favorable conditions for producing HMF, 2-FA and lactic acid by hydrothermal reaction of cellulose and starch, and for producing acetic acid by the oxidation reaction of HMF, 2-FA and lactic acid. Conditions so far obtained as optimum are as follows: temperature and reaction time of 300 °C and 2 min, respectively for the first step, and temperature, reaction time and oxygen supply of 300 °C, 1 min and 70% respectively for the second step. Under respective optimum conditions, cellulose and starch as well as rice hulls were treated in the two-step process. As shown in Table 2, the acetic acid yield obtained in the two-step process became approximately twice as much as those obtained by the usual WO procedure for all test materials. From Table 2, it is also seen that, besides the yield of acetic acid, the purity of acetic acid was also improved greatly. It should be noted that most of the components in the liquid phase other than acetic acid is formic acid. Since our purpose of generating acetic acid is to produce CMA as a noncorrosive road deicer, and calcium formate ($Ca(HCOO)_2$) as well as other carbonic acids of lower molecular weight than oxalic acid can also have the deicing effect, formic acid and other carboxylic acids except for oxalic acid could be also useful products. In this case, total purity of all carboxylic acids were over 99%, indicating that a separation of acetic acid from other residual products in the solution after the two-step reaction process would not be necessary.

Improvement of acetic acid production by alkali two-step reaction

Although, in the first step, a considerable amount of lactic acid, as well as HMF and 2-FA was formed, it could be expected that the yield of lactic acid would be selectively increased by adding an alkali in the first step, because it is generally known in sugar chemistry that lactic acid is a product of alkaline degradation of sugar. Since the acetic acid yield by the oxidation of lactic acid was much higher than that by the oxidation of furans in a previous report [21], it could be expected that the acetic acid yield would be further improved by adding an alkali in the first step. Therefore, a new alkali two-step process was proposed by modifying the previously developed two-step process using an alkali in the first step reaction (see Fig. 2b). In this study, glucose was used as a test material. $Ca(OH)_2$ was used as an alkali catalyst, because $Ca(OH)_2$ has the benefit of obtaining calcium acetate as the final product. Results showed that the addition of an alkali promoted the formation of lactic acid in a hydrothermal reaction of glucose. A good acetic acid yield of 27% on the carbon base was obtained by alkali two-step process. The purity of the acetic acid on carbon basis was about 90%.

Oxidation pathways of carbohydrates

The oxidation pathways of carbohydrates was discussed, to study why the direct oxidation of carbohydrate can not produce a large amount of acetic acid. On the basis of the oxidation mechanism of high molecular weight carboxylic acids in supercritical water [28], the oxidation mechanism of secondary alcohols in a liquid phase [29, 30], and experimental results of the oxidation of all of cellulose,

Table 2 The acetic acid yields[a] and purity[b] by two-step process

Materials	Yield (%)	Purity (%)	Conditions				
			1st step		2nd step		O_2 supply (%)
			Temp. (°C)	Time (min)	Temp. (°C)	Time (min)	
Rice hulls	21.7 (11.7)	75.5 (33.4)	300	2	300	1	70
Cellulose	16.3 (9.0)	68.5 (26.0)	300	2	300	1	70
Starch	17.5 (9.6)	70.0 (28.2)	300	1	300	1	70

[a] The percentage of TOC of acetic acid and starting material

[b] The percentage of TOC of acetic acid and the all residual remaining in the liquid after reaction

The yield and purity in parentheses correspond to those obtained by usual WO starch and glucose which yielded a considerably high quantity of formic acid, the oxidation pathways of hexoses was proposed as shown in Fig. 3 [21].

It can be seen in Fig. 3 that basic product is formic acid for both of the rupture of C-1–C-2 (α-scission) and C-2–C-3 (β-scission). α-Scission may directly yield formic acid and β-scission may give formic acid via oxalic acid. This may be the reason why direct oxidation of carbohydrates produces little acetic acid. A possible source of acetic acid in the WO of carbohydrate may be due to intermediates in other reactions like dehydration products of aldose, because dehydration of aldose occurs easily. These discussions seem to imply that if aldose does not eliminate the –OH group, little acetic acid is formed.

The two-step process proposed in Fig. 4 does express such a mechanism. That is, the first direct dehydration makes hexoses form HMF or first hexoses are cleaved at a middle (C-3 and C-4), and then there is dehydration and rearrangement to form lactic acid. A reason why HMF and lactic acid can yield a large amount of acetic acid is probably due to the elimination of three water molecules from glucose for HMF and two water molecules for lactic acid.

Lactic acid production by alkali hydrothermal reaction

Lactic acid production from carbohydrate biomass

In this study, glucose was used as a test material because it is a primary intermediate compound formed during the conversion of carbohydrates. A series of experiments were carried out at reaction temperatures varying from 200 °C to 400 °C, reaction times varying from 30 s to 5 min and the

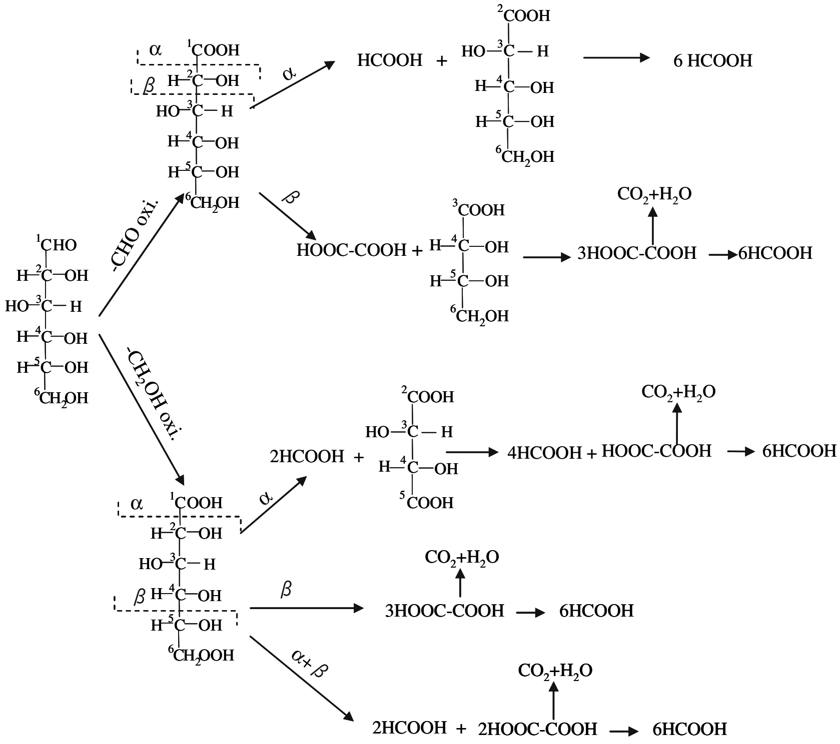


Fig. 3 Proposed oxidation pathways (direct oxidation) of glucose

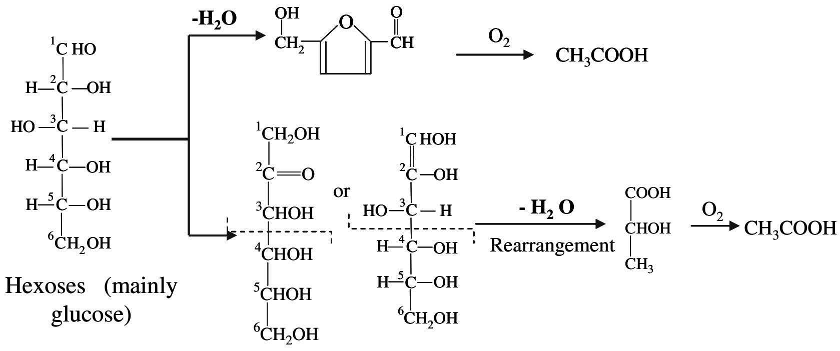


Fig. 4 Mechanism of the two-step process for carbohydrates

concentrations of $Ca(OH)_2$ varying from 0.08 M to 0.4 M, to obtain a high yield of lactic acid. Results showed that a good lactic acid yield of 28 % was obtained, which occurred at a condition of reaction temperature of 300 °C, reaction time of 1 min, and $Ca(OH)_2$ concentration of 0.32 M.

It is generally known in sugar chemistry that lactic acid is a typical base-catalyzed product and is generated via the aldose having three carbon atoms formed by the reverse aldol condensation of hexoses. Our previous study on the conversion mechanism of glucose to lactic acid in hydrothermal reaction also showed that the conversion mechanism appeared to follow the same pathway that was elucidated in the conversion of sugar to lactic acid in an alkaline solution [33]. Few studies report, however, if the aldose containing two carbon atoms, that is glycolaldehyde, can form lactic acid, although glycolaldehyde is also generated by the reverse aldol condensation of hexoses. So, a study was carried out [34], to examine the formation of lactic acid in alkali hydrothermal reaction from the aldose which contains less carbon number than 3.

An experiment with glycolaldehyde was conducted at 300 °C, for 10 min, with 0.75 M NaOH, to examine if lactic acid can be formed from glycolaldehyde. HPLC analyses of solution after the reaction (Fig. 5) showed a large lactic acid peak, indicating that glycolaldehyde can produce lactic acid. In Fig. 5, there are peaks corresponding to formic, acetic and acrylic acids. Acrylic acid is most likely a dehydration product of lactic acid and acetic acid is a decarbonylation product of lactic acid. Therefore, formic acid would be a product involved in the formation of lactic acid from glycolaldehyde. Further, γ-butyrolactone, which contains four-carbon atoms, was also detected by GC/MS analyses, suggesting that a condensation reaction occurred in alkali hydrothermal reaction of glycolaldehyde. Further, an experiment with glycolaldehyde was performed at a short reaction time (1 min), erythrose, pyruvaldehyde and glyceraldehyde were detected.

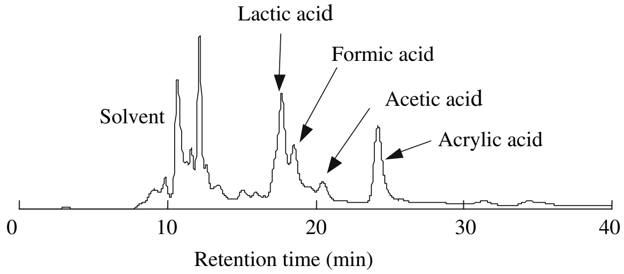
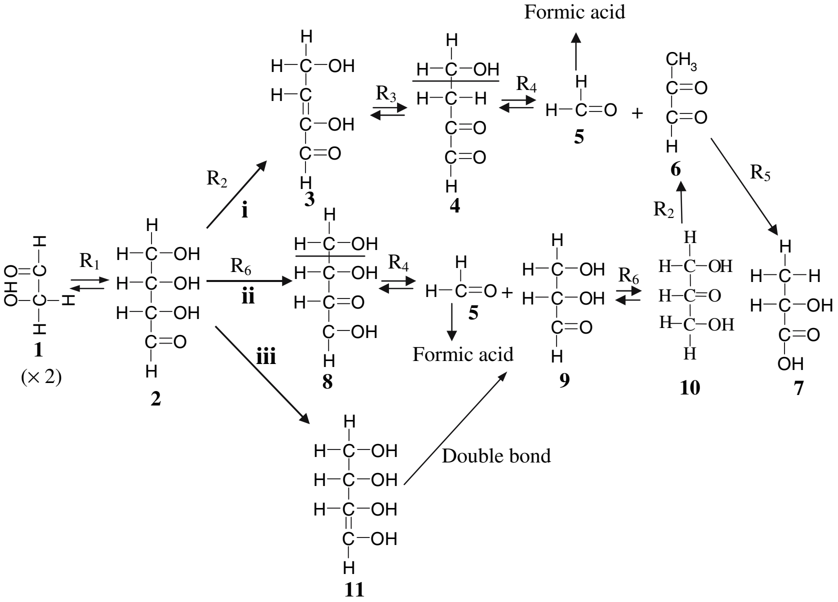


Fig. 5 HPLC chromatogram of the sample after alkali hydrothermal treatment of glycolaldehyde (Temp.: 300 °C, reaction time: 10 min, NaOH: 0.75 M)

On the basis of these experimental findings and the basic theories in alkaline degradation of monosaccharide, a pathway for the formation of lactic acid from glycolaldehyde in alkali hydrothermal reaction was proposed as shown in Fig. 6. Because erythrose was identified, glycolaldehyde **1**, may undergo aldol condensation to give erythrose **2**. Lactic acid may be produced from 2 by one of the three pathways. First (pathway **i**), considering that the dehydration easily occur under hydrothermal conditions, erythrose may lose water to form a carbon-carbon double bond between the α- and β-carbon atoms, yielding 2,4-dihydroxybutanal **3**. At the same time, **3** may undergo the keto-enol tautomerization to give **4,** which may be decomposed subsequently into formaldehyde and pyruvaldehyde **5** by a reverse aldol condensation. Finally, **5** may

Fig. 6 Proposed pathway for converting glycolaldehyde into lactic acid. (R_1: Aldol condensation, R_2; Elimination of H_2O, R_3; Keto-enol tautomerization, R_4; Reverse aldol condensation R_5: Benzilic acid rearrangement, R_6: Lobry de Bruyn-Albeda van Ekenstein transformation (LBAE)



undergo the benzilic acid rearrangement to lactic acid **7**. A possible second pathway **(ii)** is based not only on the traditional theory of the conversion of carbohydrates to lactic acid in alkaline solution but also on recent studies on hydrothermal reaction pathways of monosaccharide model compounds. In pathway **ii**, erythrose **2** may be rearranged into **8** by a Lobry de Bruyn-Albeda van Ekenstein transformation (LBAE). Subsequent cleavage by a reverse aldol condensation results in formic acid and a glyceraldehyde **9**, which then undergoes isomerization to dihydroxyacetone **10**. Both glyceraldehyde and dihydroxyacetone can undergo the dehydration to give pyruvaldehyde **6,** which subsequently undergoes the benzilic acid rearrangement to lactic acid. The identification of glyceraldehyde may provide a support of the presence of pathway **ii**. A possible co-product with **8,** if LBAE transformation occurs, would be 1,2-enediol **11**. Glyceraldehyde could also be formed by cleavage of erythrose (pathway **iii**), because the formation of double bond between carbon 1 and carbon 2 in erythrose would be expected to weaken the single bond between carbon 3 and carbon 4.

Lactic acid production from glycerin

In recent years, bio-diesel fuel (BDF) derived from the transesterification of vegetable oil and fat with alcohols in the presence of an alkaline catalyst has been gathering attention, because BDF has a good potential as an alternative diesel fuel. As the production of BDF increases, an effective and acceptable conversion of glycerin, which is a by-product of the BDF manufacturing process, to useful substances is becoming increasingly important. Since the glycerin of the by-product from BDF production process contains a large amount of alkali, a study on the hydrothermal conversion of glycerin with an alkali was performed. Results presented in Fig. 7 showed that glycerin could be converted into lactic acid with a high yield of about 90 mol% based on the glycerin used. The pathway for the conversion of glycerin to lactic acid was also proposed as shown in Fig. 8 [23].

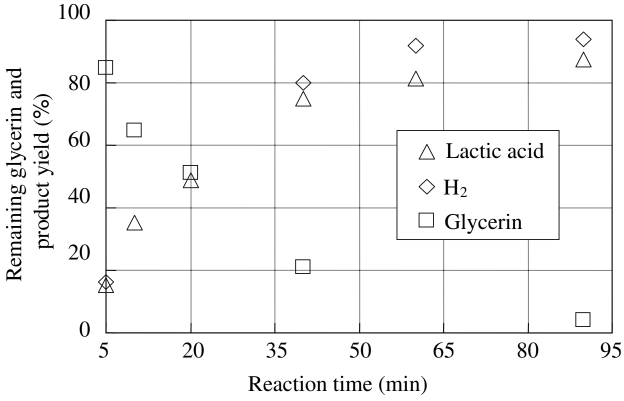


Fig. 7 Variation of lactic acid yield, remaining glycerin and H_2 yield with reaction time (Temp.; 300 °C, NaOH; 1.25 M)

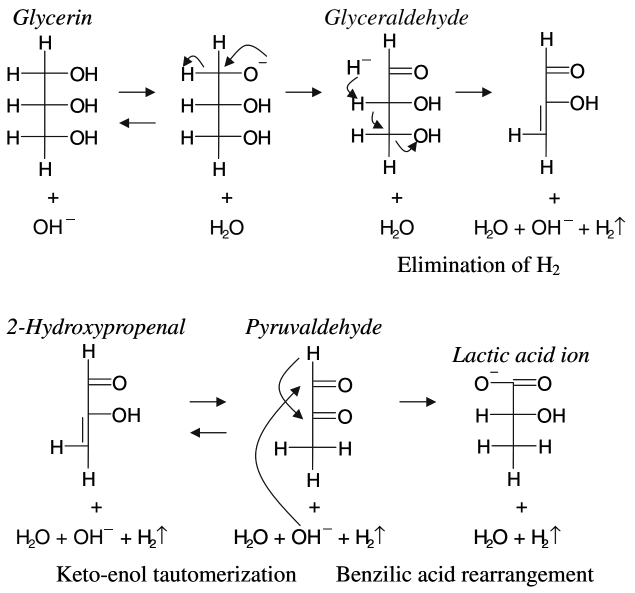


Fig. 8 Proposed reaction pathway for conversion of glycerin into lactic acid

Development of a continuous-flow reaction system for producing acetic acid from biomass by hydrothermal reaction

Based on the results with the batch reactor, a continuous flow reaction system to produce acetic acid and then convert the acetic acid produced to CMA was developed. As shown in Fig. 9, the major components of the system comprised of tanks for slurry and H_2O_2-water solution, feed pump for slurry, H_2O_2 supply pump, preheater, WO reactor, cooler, solid-liquid separator, pressure regulator, gas-liquid separator, and reactor for producing CMA. The section before the pressure regulator along the flow line is maintained at a high temperature (250–300 °C) and a high pressure (12–20 MPa) for producing acetic acid. The section after the pressure regulator is for converting the acetic acid into CMA by reacting with oyster shells at normal temperature and pressure. The treatment capacity and specification of the main compositions of the continuous flow reaction system are summarized in Table 3.

Considering that the optimum conditions for producing acetic acid with batch experiments were at temperature, reaction time and oxygen supply of 300 °C, 1–2 min and 70%, respectively, (see Tables 1 and 2), experiments with rice hulls and starch were conducted with this continuous-flow system with a temperature varying from 280 °C to

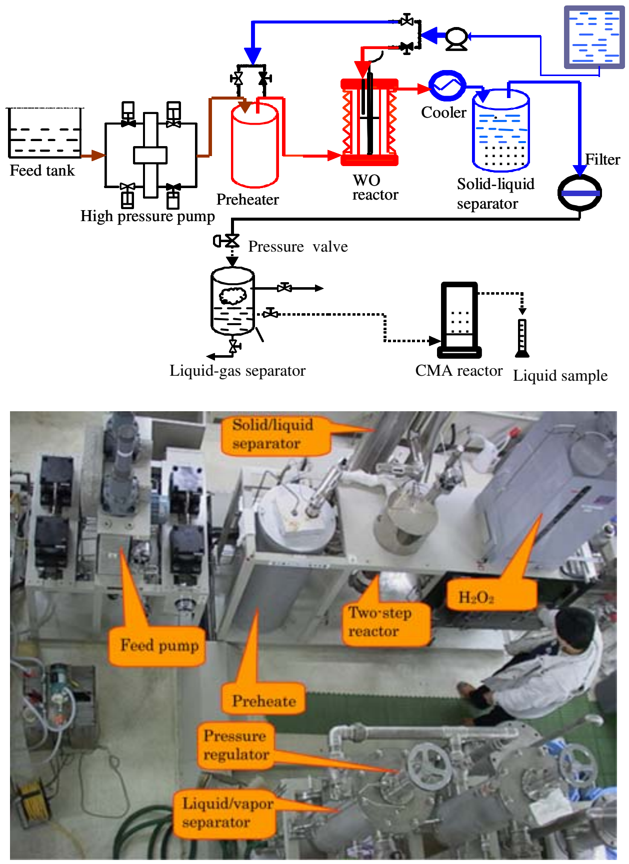


Fig. 9 Flow diagram and photograph of continuous flow reactor system

320 °C, an oxygen supply varying from 70% to 120%, and a reaction time varying from 1 to 3 min. In most cases, each experiment was carried out three times, and the yield was obtained as the average of three runs. As shown in Table 4, the highest acetic acid yields obtained in the continuous-flow system and their operation conditions

Table 3 Treatment capacity and specification of the main components of the continuous flow reaction system

	Specification
Treatment capacity	2 kg/h (dry base)
Feed pump	Flow rate: 7.5–20 L/h
	Pressure: 40 MPa max.
	Slurry Concentration: 10 wt% max.
Preheater	Temperature: 200–250 °C
	Pressure: 40 MPa, max.
Reactor	Temperature: 430 °C max.
	Pressure: 40 MPa, max.
	Size: $\varphi 50 \times 660$ mm
	Volume: 1.3 L (HC-276)
Pressure valve	Temperature: 40 °C, max.
	Pressure: 40 MPa, max.

Table 4 Comparison of the highest acetic acid yields and their respective experimental conditions by batch and continuous flow experiments

	Batch experiment								Continuous flow experiment							
	Usual WO				Two-step reaction				Usual WO				Two-step reaction			
	Yeild* (%)	Condition			Yeild (%)	Condition			Yeild (%)	Condition			Yeild (%)	Condition		
		Temp. (°C)	Time (min)	O_2 (%)		Temp. (°C)	Time (min)	O_2 (%)		Temp. (°C)	Time (min)	O_2 (%)		Temp. (°C)	Time (min)	O_2 (%)
Starch	9.6	300	1	70	17.5	300 (300)	1 (1)	0 (70)	9.0	300	1	80	17.5	300 (300)	1 (1)	0 (75)
Rice hulls	11.7	300	2	70	21.7	300 (300)	2 (1)	0 (70)	12.2	300	2	80	–			

* The carbon percent based on that of initial material(s)

The values in parentheses correspond to the second step reaction

For continuous flow experiments: slurry concentration of 2 wt% (dry base), system pressure of 20 MPa, the flow rate of 10–15 L/h were almost the same as those obtained in the batch study for both usual WO and the two-step reaction process. These results indicate that the continuous flow reaction system developed has the expected fundamental performance to produce acetic acid for both usual WO and a new two-step process. Also, many know-hows and important data were obtained for designing and operating a full-scale system.

Conclusions

This report describes some recent advances in our research regarding the application of hydrothermal reaction to conversion of biomass into resources, which mainly include (1) acetic acid production, (2) lactic acid production from carbohydrate biomasses by alkali hydrothermal reaction, (3) lactic acid production from glycerin by alkali hydrothermal reaction, and (4) discussions on some reaction mechanisms and the interaction between the main components of a natural material, such as cellulose and lignin in lignocellulosic biomass. Results indicate that hydrothermal reaction can easily and directly convert a biomass into acetic acid or lactic acid in just a few minutes, indicating that the hydrothermal process possesses a high potential for converting a wide range of biomass into useful materials.

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