Hydrothermal Conversion of Carbohydrate Biomass to Lactic Acid

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We investigated the hydrothermal conversion of the carbohydrates including glucose, cellulose, and starch to lactic acid using NaOH and $Ca(OH)_2$ as alkaline catalysts. Both catalysts significantly promoted the lactic acid formation. The highest yield of lactic acid from glucose was 27% with 2.5 M NaOH and 20% with 0.32 M $Ca(OH)_2$ at 300°C for 60 s. The lactic acid yields from cellulose and starch were comparable with the yield from glucose with 0.32 M $Ca(OH)_2$ at 300°C, but the reaction time in the case of cellulose was 90 s. The mechanism of lactic acid formation from glucose was discussed by identifying the intermediate products. Lactic acid may be formed via the formation of aldoses of two to four carbons including aldose of three carbons, which are all formed by reverse aldol condensation and double bond rule of hexose. This implies that carbon–carbon cleavage occurs at not only C_3—C_4 but also at C_2—C_3. © 2010 American Institute of Chemical Engineers *AIChE J*, 56: 2727–2733, 2010
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Introduction

Over the last two decades, the conversion of cellulosic biomass (materials such as wood wastes, bagasse, and straw) to high-value products, particularly fuels, has attracted considerable attention.[1] Lactic acid has particularly gained interest for use in producing biodegradable lactic acid polymer.[2–4] Currently, the fermentation of starch is the most common method for producing lactic acid. However, such bioconversion (bacterial fermentation) cannot be directly applied to cellulose and lignocelluloses.[5,6]

Among the several biomass conversion processes, hydrothermal process is one of the most promising methods for the conversion of biomass to recycled resources; the hydrothermal process is superior to others because at high temperature and pressure, water serves as a reaction medium with unique properties.[7–11] It is well known in sugar chemistry

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that lactic acid is a typical base-catalyzed product of carbohydrates.[12,13] Our previous studies on the conversion of carbohydrate biomass to high-value products have demonstrated that lactic acid can be formed by the hydrothermal reaction of carbohydrates without the addition of a catalyst.[14] Many other researches also have reported similar results.[15,16] Recently, Bicker et al.[17] have reported that Zn(II) as catalyst can promote the formation of lactic acid from glucose and fructose in subcritical water and proposed that the pathway of lactic acid formation almost agreed with the conventional base-catalyzed conversion of carbohydrates in sugar chemistry. The formation of lactic acid without the addition of a catalyst is probably because in subcritical region, water acts as an effective alkaline catalyst.[14] Therefore, it is expected that lactic acid can be obtained in high yields under hydrothermal conditions by the addition of an alkali. However, the mechanism of the conversion of glucose to lactic acid in alkaline hydrothermal conditions has not been clearly explained. For example, Kishida et al.[18] have reported that lactic acid can be formed using glycolaldehyde (an aldose of two carbons), but no discussion was made whether this kind of pathway exists in the conversation of glucose to lactic acid, or is there any other pathways exist except for the conventional pathway that the lactic acid is formed via the formation of an aldose of three carbons by the reverse aldol condensation of a hexose.

The purpose of this study is to investigate the production of lactic acid by the alkaline hydrothermal treatment of carbohydrates and determine the optimum conditions for obtaining lactic acid in high yields. The possible mechanisms of the formation of lactic acid from glucose are also discussed on the basis of the identified intermediate products.

Experimental

Glucose (99.9%) was used as the test material because it is the primary intermediate formed during the conversion of carbohydrates. Cellulose and starch were also used as the test materials as representatives of the main component of lignocellulosic wastes and carbohydrate wastes, respectively. A standardized solution of 1.0 N lactic acid (Alfa Aesar Company) was used to carry out the quantitative analysis of lactic acid. NaOH (99%) and $Ca(OH)_2$ (99%) were selected as the alkaline catalysts, which were purchased from Wako Pure Chemicals Industries. Erythrose was also used as test material, which was purchased from Sigma-Aldrich.

Two kinds of batch reactors with internal volume of 5.7 cm^3 were used in this research. One is made of SUS-316 stainless steel, and the other is made of Hastelloy C-276. In most cases, experiments were carried out in SUS-316 stainless steel microreactor. In the case of high concentration of NaOH (from 1 to 7 M), the experiments were carried out in Hastelloy C-276. The general experimental procedure was as follows. The desired amount of test material and the desired high-pH alkaline solution prepared in advance were put into the batch microreactor, and the reactor was sealed. The reactor was placed into a salt bath preheated to the desired temperature. After a desired reaction time had passed, the reactor was removed from the salt bath and immediately placed in a cold water bath to quench the reaction. Hereafter, the duration for which the reactor was placed in the salt bath will be referred to as the reaction time. It should be noted that the typical heat-up period of the reactor to raise its temperature from 20 to 300°C was approximately 15 s. The amount of test materials used was 0.07 g in all experiments.

In this study, water fill rate was fixed at 30%, but temperature was changed from 270 to 400°C. The pressure in the reactor was the saturated vapor pressure of water in the corresponding temperature in the case of subcritical condition ($<$374°C). That is, the pressure was 5.5 MPa at 270°C, 8.6 MPa at 300°C, 16.5 MPa at 350°C, respectively. At 400°C, the pressure was 28.8 MPa.

After the reaction was quenched, reacted solution samples were collected and analyzed by HPLC and GC-MS. In some cases, the collected solution samples were treated by silylation method before being analyzed, while in most cases, the samples were directly analyzed by HPLC and GC-MS. The silylation method is described as follows. First, the collected liquid sample was dried in a freeze dryer at –54°C for 24 h. Then, 1 mL of pyridine was mixed with the dried residues in a vial, after which 1 mL of the silylation reagent BSTFA-TMCS (BSTFA:TMCS = 99:1) was added to it and stirred for 30 min. After stirring, the sample was made to stand for 12 h with its temperature maintained at 20°C before carrying out the GC-MS analysis.

The HPLC analyses were performed using a Waters HPLC system equipped with a tunable absorbance detector (UV-VIS detector, Waters 486) and a differential refractometer (RI detector, Waters 410). For analysis of organic acid, the samples were separated by a Shodex KC-811 column using 2 mM $HClO_4$ as the solvent and the UV–Vis detector. For analysis of aldose, the samples were separated by a SH1011 Shodex column using 5 mM H_2SO_4 as the solvent and the RI detector. The GC-MS analyses were carried out on a Hewlett-Packard Model 5890 Series II gas chromatograph equipped with a Model 5890B mass selective detector. The samples were separated by a HP-Innowax capillary (crosslinked polyethylene glycol) column using helium as the carrier gas. The silylated samples were separated on a HP-1 capillary column. Details on the experimental conditions during HPLC and GC-MS analyses are provided elsewhere.[19]

The total residual organic carbon (TOC) in the liquid samples was also measured using a TOC analyzer (Shimadzu TOC 5000A).

Results and Discussion

Production of lactic acid in the presence of NaOH

For carrying out alkaline degradation of carbohydrates at low temperatures, NaOH is often selected as the alkaline catalyst. However, the effect of NaOH on the formation of lactic acid at higher temperature and pressure conditions remains relatively unexplored. Therefore, a series of experiments were first carried out using glucose at a reaction temperature of 300°C with NaOH concentration varying from 0.16 to 7 M and a reaction time of 60 s. As shown in Figure 1a, the lactic acid yield increased with an increase in the initial OH^- concentration of the reaction medium from 0.16 to 2.5 M. At the initial OH^- concentration of 2.5 M, the lactic acid yield was 27%. This result shows that the formation of lactic acid is facilitated by the addition of an alkali in a hydrothermal reaction. However, further increase in NaOH concentration from 3 to 7 M did not significantly change the yield of lactic acid. All yields were measured in terms of the percentage of carbon in the product to the carbon in the reactant.

Production of lactic acid in the presence of $Ca(OH)_2$

After the aforementioned experiments, a series of experiments using $Ca(OH)_2$ as the catalyst were carried out to investigate the effect of the cation on the conversion of glucose to lactic acid. As shown in Figure 1b, the lactic acid yield increased with an increase in the initial OH^- concentration from 0.16 to 0.64 M. At the initial OH^- concentration of 0.64 M, the lactic acid was obtained in a 20% yield. However, further increase in $Ca(OH)_2$ concentration, i.e., from 0.64 to 0.8 M of OH^- concentration, did not increase the yield of lactic acid above 20%. These results indicate that lactic acid can be obtained in a yield of 20% even by using $Ca(OH)_2$ as the alkaline catalyst. However, the highest yield of lactic acid in the presence of $Ca(OH)_2$ is slightly lower than that in the presence of NaOH. This difference can be attributed to the fact that the saturated solubility of $Ca(OH)_2$ is lower than that of NaOH.

On comparing Figures 1a, b, it is observed that at low alkali concentrations, the lactic acid formation is facilitated by $Ca(OH)_2$ to a greater extent than it is by NaOH at the same initial OH^- concentration. According to some literatures,[20–23] in aqueous solution, the use of divalent cations favors the formation of lactic acid. It is well known in sugar chemistry that lactic acid is generally formed via the formation of an aldose of three carbons by the reverse aldol condensation of a hexose.[12,13] A study by Jin et al.[14] on the conversion mechanism of glucose to lactic acid by hydrothermal reaction also demonstrated that the mechanism of this conversion followed the same pathway as that of the conversion of sugar to lactic acid in an alkaline solution; that is, it proceeded via a carbon–carbon bond cleavage by reverse aldol condensation of hexoses at C_3—C_4. On the basis of the aforementioned results, a possible explanation was proposed for the effectiveness of $Ca(OH)_2$ for promoting the lactic acid formation as compared with that of NaOH in hydrothermal conditions, which is as follows:

Ca^{2+} is a divalent cation, and its radius is larger than that of Na^+; therefore, it is speculated that Ca^{2+} has a greater tendency to combine with two oxygen atoms to form complexes (Figure 2) than Na^+. These complexes may promote the C_3—C_4 bond fission by reverse aldol condensation.

Effect of reaction temperature and time on yield of lactic acid

The effect of reaction temperature and time on the yield of lactic acid was investigated to find the optimum conditions to obtain lactic acid in high yields. Although the highest yield of lactic acid formed in the presence of NaOH was slightly higher than that formed in the presence of $Ca(OH)_2$, it was observed that the reactor walls were corroded to some extent by using NaOH at high concentrations (above 1 M). Thus, to study the effect of reaction temperature and time on the formation of lactic acid, the alkaline catalyst used was $Ca(OH)_2$, and the $Ca(OH)_2$ concentration was fixed at 0.32 M (0.64 M OH^-); these conditions were suitable for the formation of lactic acid without the

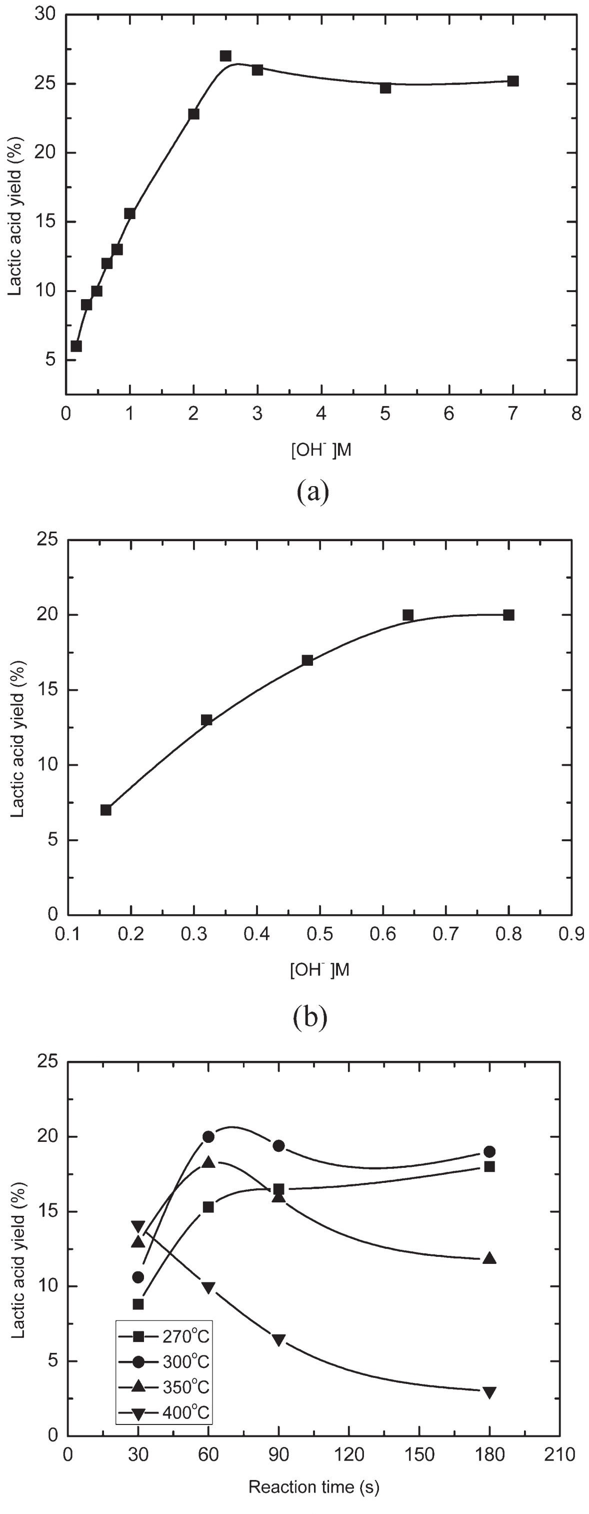


Figure 1. **(a) Influence of NaOH concentration on yield of lactic acid produced from glucose (300°C, 60 s), (b) influence of $Ca(OH)_2$ concentration on lactic acid yield (300°C, 60 s), and (c) influence of reaction time and temperature on lactic acid yield with $Ca(OH)_2$ as the catalyst.**

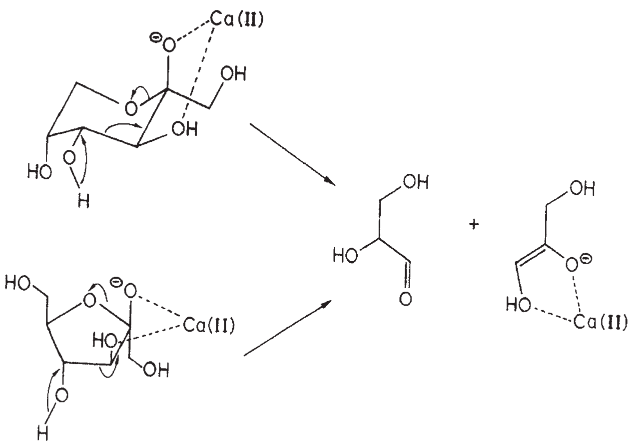


Figure 2. Proposed retro aldolization of D-glucose and D-fructose by complexation with divalent calcium.

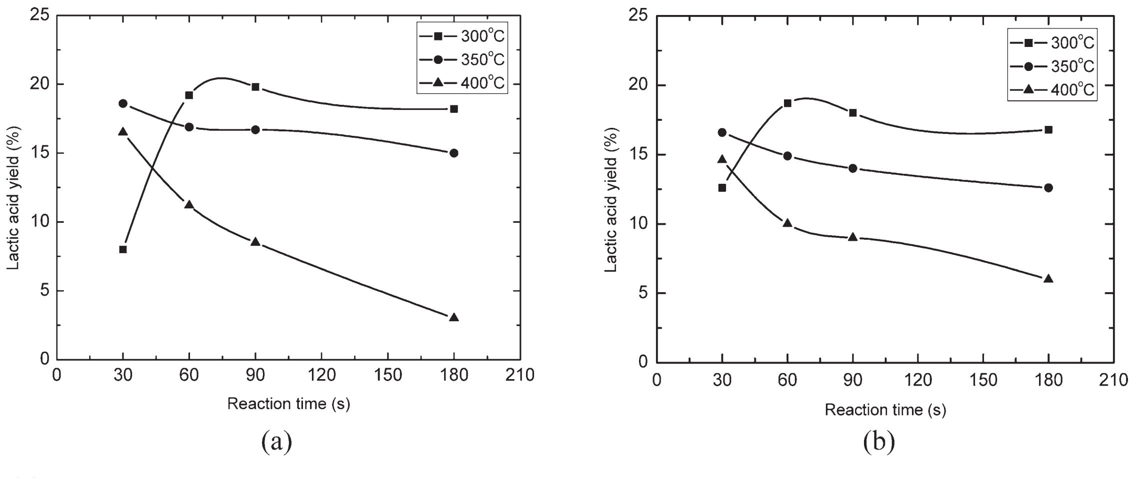
corrosion of the reactor vessel. As shown in Figure 1c, at all reaction temperatures except 400°C, the lactic acid yield initially increases and then decreases with an increase in the reaction time. The highest yield was observed at the reaction time of 60 s. It implies that lactic acid should be both formed and decomposed with increasing reaction time. Although we did not measure the rates of formation and decomposition of lactic acid, the decrease in lactic acid after 60 s indicates that the rate of decomposition of lactic acid is faster than the rate of formation of lactic acid. As shown in Figure 1c, the lactic acid yield after 60 s did not decrease significantly at either 270 or 300°C, but at 350°C. Such observation indicates that lactic acid was relatively stable at 270 and 300°C. At 400°C, the yield of lactic acid drastically decreased with increasing reaction time, suggesting that the rate of decomposition of lactic acid was obviously faster than the formation of lactic acid. It is suggested that the reaction temperatures should be maintained below 350°C to ensure a high yield of lactic acid. To examine the decomposition of lactic acid at these temperatures, supplementary experiments with lactic acid at 300°C and 350°C at reaction time of 60 s using 0.32 M $Ca(OH)_2$ were conducted. Results showed that lactic acid did not decompose at 300°C, but approximately 10% decomposition was observed at 350°C.

Production of lactic acid from cellulose and starch by alkaline hydrothermal reaction

On the basis of the results obtained using glucose, we attempted to produce lactic acid from cellulose and starch. We carried out these experiments at reaction temperatures that varied from 300 to 400°C and reaction times of 30–180 s with the $Ca(OH)_2$ concentration of 0.32 M (OH^- concentration of 0.64 M), to find the optimum conditions to obtain lactic acid in high yields from cellulose and starch. As shown in Figures 3a, b, the lactic acid yield from both cellulose and starch increased initially and then decreased with increasing reaction time at 300°C. It is similar to the case of glucose. However, at 350 and 400°C, the lactic acid yield decreased with increasing reaction time in both cases. The phenomena suggested that lactic acid was both formed and decomposed with increasing reaction time, the decomposition of lactic acid become obvious above 350°C. It indicates that the cases of cellulose and starch are similar to the one of glucose. The highest lactic acid yield from cellulose was 19.2%, which was obtained at the reaction temperature of 300°C and the reaction time of 90 s; the highest lactic acid yield from starch was 18.7%, which was obtained at the reaction temperature of 300°C and reaction time of 60 s. From these results, it is clear that the variation in the lactic acid yield with reaction time, temperature, the highest lactic acid yield, and the corresponding optimum conditions found in the case of cellulose and starch are almost the same as those found in the case of glucose. These results suggest that cellulose, whose direct bioconversion has not been widely used, can be used to produce lactic acid in high yields by its direct alkaline hydrothermal reaction.

Mechanism of conversion of glucose to lactic acid

To investigate the mechanism of lactic acid formation from glucose by alkaline hydrothermal reaction, the intermediate products were identified in detail by GC-MS and HPLC.



(a) (b)

Figure 3. (a) Influence of reaction time and temperature on yield of lactic acid produced from cellulose using $Ca(OH)_2$ and (b) influence of reaction time and temperature on yield of lactic acid produced from starch using $Ca(OH)_2$.

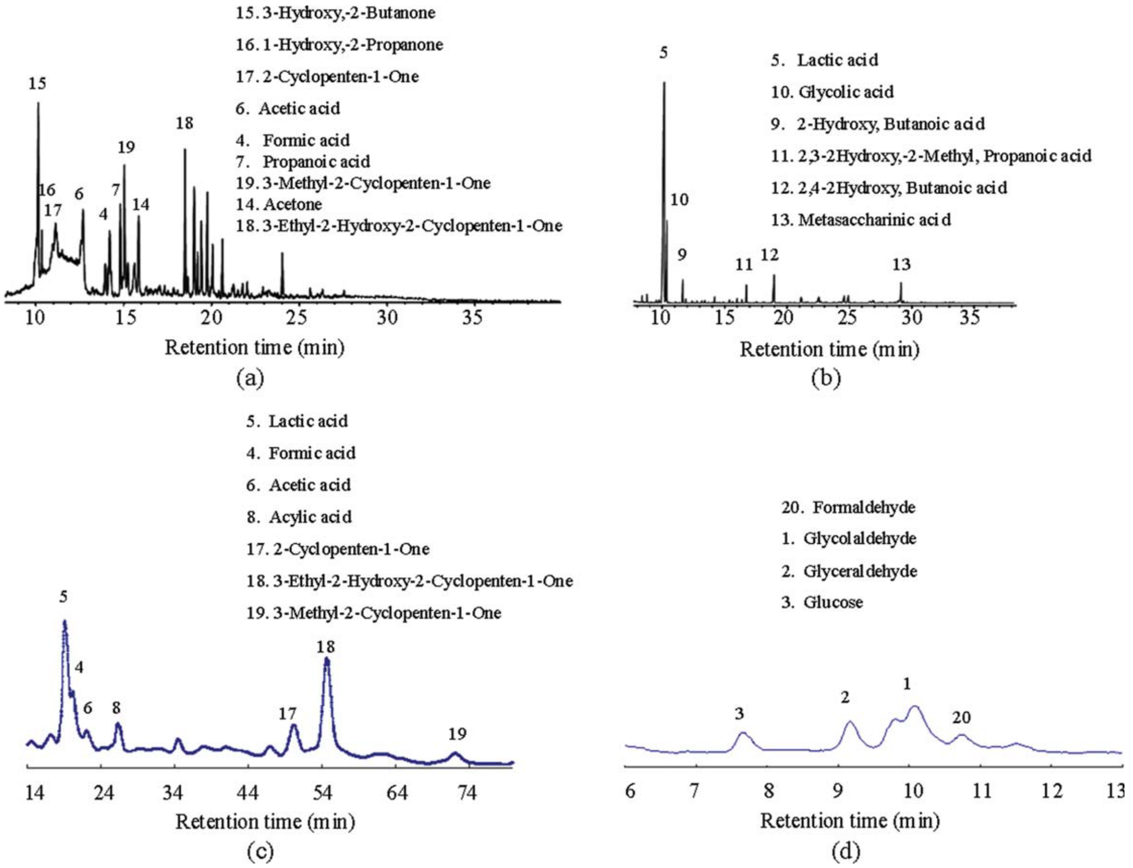


Figure 4. (a) GC-MS chromatogram of sample obtained after alkaline hydrothermal reaction of glucose, (b) GC-MS chromatogram of silylated sample, (c) HPLC chromatogram of sample (KC-811 Shodex column, UV detector, 2 mM $HClO_4$ solvent), and (d) HPLC chromatogram of sample (SH1011 Shodex column, RI detector, 5 mM H_2SO_4 solvent).

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Figure 4a shows a GC-MS total ion chromatogram in the 10–35 min region, of the sample obtained by the hydrothermal reaction of glucose at 300°C for 1 min using 0.32 M $Ca(OH)_2$. The other time regions were not included in this chromatogram because those regions did not show clear or significant peaks. From the chromatogram, it is observed that many compounds were detected in the sample. Among all the peaks observed, the ones that are labeled with numbers, as shown in Figure 4a, correspond to the compounds that were identified. The compounds were identified by matching both the observed mass spectrum and the GC retention time of each compound with those of the corresponding standard compounds.

Figure 4b shows a GC-MS total ion chromatogram in the 10–35 min region of a silylated sample obtained by the hydrothermal reaction of glucose under the same conditions as the sample whose chromatogram is shown in Figure 4a. In this chromatogram, six different compounds were identified and labeled with numbers. Notably, these compounds are labeled as the substance before treated by silylation method. The compounds were identified by matching the mass spectrum of the corresponding silylated compounds.

Further identifications were performed by HPLC analysis. As shown in Figure 4c, in addition to formic acid and acetic acid which were detected by GC/MS, lactic acid and acrylic acid were detected in the HPLC chromatogram using a column

Table 1. Intermediate Products Identified During Alkaline Hydrothermal Reaction of Glucose

Group	Chemical substances detected	Analysis method
Aldose	1. Glycolaldehyde	HPLC*
	2. Glyceraldehyde	HPLC*
	3. Glucose	HPLC*
Organic acids	4. Formic acid	HPLC, GC/MS
	5. Lactic acid	HPLC, GC/MS*
	6. Acetic acid	HPLC, GC/MS
	7. Propanoic acid	GC/MS
	8. Acrylic acid	HPLC
	9. 2-Hydroxybutanoic acid	GC/MS*
	10. Glycolic acid	GC/MS*
	11. 2,3-2-Hydroxy-2-methylpropanoic acid	GC/MS*
	12. 2,4-2-Hydroxybutanoic acid	GC/MS*
	13. Metasaccharinic acid	GC/MS*
Ketones	14. Acetone	GC/MS
	15. 3-Hydroxy-2-butanone	GC/MS
	16. 1-Hydroxy-2-propanone	GC/MS
	17. 2-Cyclopenten-1-one	HPLC, GC/MS
	18. 3-Ethyl-2-hydroxy-2-cyclopenten-1-one	HPLC, GC/MS
	19. 3-Methyl-2-cyclopenten-1-one	HPLC, GC/MS
Others	20. Formaldehyde	HPLC*

HPLC, HPLC system equipped with KC-811 (Shodex) column; HPLC*, HPLC system equipped with SH1011 (Shodex) column; GC/MS, gas chromatograph equipped with HP-INNOWAX capillary column; GC/MS*, gas chromatograph equipped with HP-1 capillary column.

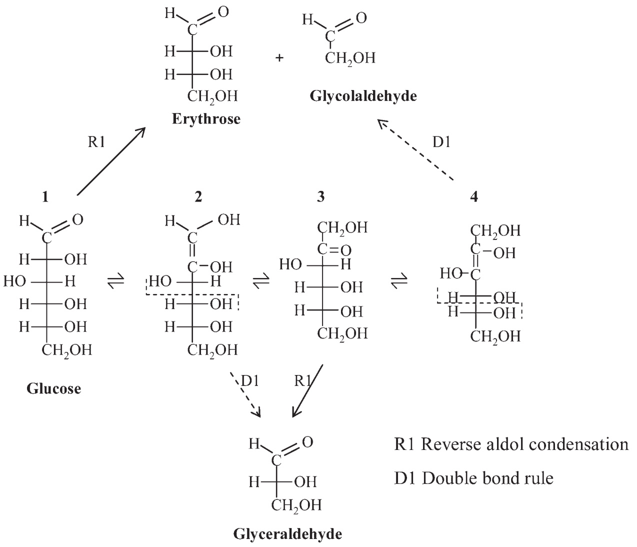

Figure 5. Proposed pathways of formation of glycolaldehye, glyceraldehyde, and erythrose from glucose by alkaline hydrothermal reaction.

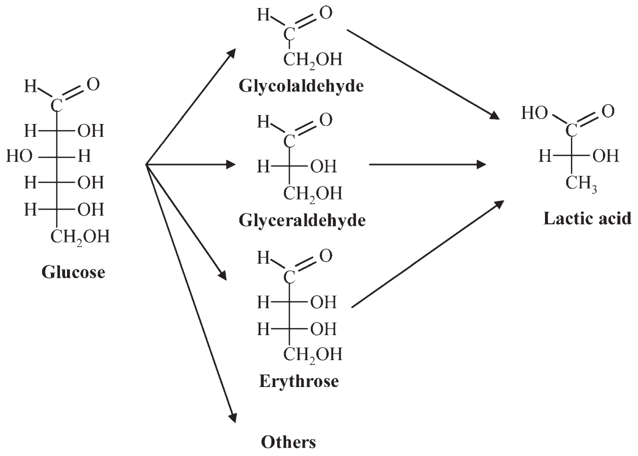

Figure 7. Proposed pathway of formation of lactic acid from glucose by alkaline hydrothermal reaction.

of KC-811. The analytical results obtained using a column of Sugar SH1011 are shown in Figure 4d; in this chromatogram, glucose, formaldehyde, glycolaldehye, and glyceraldehyde were detected.

All the identified intermediate products can be roughly classified into four groups as shown in Table 1. That is, aldoses, organic acids, ketones, and other products. The mechanism of the conversion of glucose to lactic acid was elucidated on the basis of these intermediate products and the basic knowledge of carbohydrate chemistry. First, the degradation of glucose results in the formation of several kinds of isomers of glucose via the Lobry de Bruyn-Alberda van Ekenstein transformation, as shown in Figure 5.[24] Next is the formation of aldoses of two to four carbon atoms, i.e., glycolaldehye, glyceraldehyde, and erythrose via the reverse aldol condensation and double bond rule. Kabyemela et al.[25] had also reported that the treatment of glucose with supercritical and subcritical water results in the formation of glycolaldehye, glyceraldehyde, and erythrose, via the reverse aldol condensation and double bond rule. As shown in Table 1, erythrose was not detected by GC-MS or HPLC analysis of our samples. This could be explained by the fact that erythrose is unstable in alkaline hydrothermal conditions. Supplementary stability experiment of erythrose (0.34 M) was carried out at 300°C with 0.32 M $Ca(OH)_2$; even after a reaction time of only 30 s, the sample did not show the presence of erythrose confirming the aforementioned instability assumption of this compound.

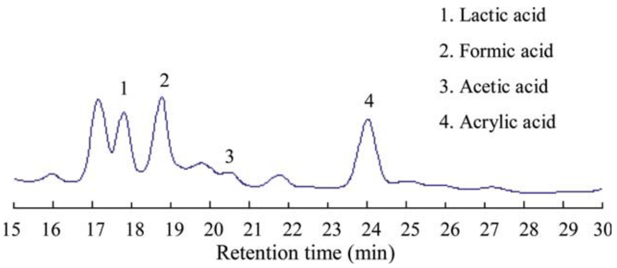

Figure 6. HPLC chromatogram of samples obtained by alkaline hydrothermal treatment of erythrose (KC-811 Shodex column, UV detector, 2 mM $HClO_4$ solvent).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

These aldoses formed as described earlier may subsequently yield lactic acid. Among glyceraldehyde, glycolaldehye, and erythrose, glyceraldehyde is well known to produce lactic acid via the formation of pyruvaldehyde by elimination of water and benzilic acid rearrangement,[12–14] and glycolaldehyde is known to produce lactic acid via the formation of pyruvaldehyde by aldol condensation, elimination of water, keto-enol tautomerism, reverse aldol condensation, and benzilic acid rearrangement, as reported by Kishida et al.[18] To confirm if lactic acid can be formed from erythrose, we performed experiment using erythrose at 300°C for 60 s using 0.75 M NaOH. Figure 6 shows the HPLC chromatogram of the samples obtained after the reaction of erythrose. In chromatogram, lactic acid, formic acid, acetic acid, and acrylic acid were detected. Therefore, this result suggests that erythrose can also form lactic acid by alkaline hydrothermal reaction. On the basis of these findings, the proposed pathway of the formation of lactic acid from glucose is illustrated in Figure 7. Glucose can produce aldoses of two to four carbon atoms via the reverse aldol condensation and double bond rule. All these aldoses can further result in the formation of lactic acid in hydrothermal conditions. In other words, the carbon–carbon cleavage during the reverse aldol condensation of hexoses occurs not only at the C_3—C_4 bond but also at C_2—C_3. Arai et al.[26] also reported that erythrose and glycolaldehyde are produced from glucose by the carbon–carbon cleavage at C_2—C_3 at 400°C and 30 MPa without the addition of a catalyst. Although glycolaldehye, glyceraldehyde, and erythrose can produce lactic acid, glyceraldehyde can produce a relatively large amount of lactic acid. Thus, the fact that carbon–carbon cleavage occurs at C_2—C_3 positions in addition to the C_3—C_4 position may be one of the reasons for the highest yield of lactic acid from glucose to be only 27%. Conversely, if the bond cleavage at C_2—C_3 is avoided, then the yield of lactic acid could be improved.

Conclusion

Both NaOH and $Ca(OH)_2$ act as effective catalysts in the formation of lactic acid by hydrothermal reaction of glucose. Lactic acid was obtained with the highest yield of 27% in terms of carbon percent at a reaction temperature of 300°C and reaction time of 1 min using 2.5 M NaOH. In the case of $Ca(OH)_2$, the highest yield of lactic acid was 20%, which was obtained at the reaction temperature of 300°C and reaction time of 1 min using 0.32 M $Ca(OH)_2$.

Lactic acid was obtained from cellulose and starch in almost the same yield that obtained from glucose under the same reaction conditions of 300°C and 0.32 M $Ca(OH)_2$), but in the case of cellulose, a slightly longer reaction time of 90 s was required.

The formation mechanism of lactic acid from glucose was also discussed on the basis of the intermediate products identified. Lactic acid can be formed via the formation of aldoses with 2–4 carbons in addition to that of glyceraldehyde (the aldose with three carbons) by hydrothermal reactions. In other words, the carbon–carbon cleavage by the reverse aldol condensation of hexoses occurs not only at $C_3—C_4$ but also at $C_2—C_3$. This fact may be one of the reasons for the highest yield of lactic acid from glucose to be limited to 27% because the conversion efficiency of glycolaldehye and erythrose to lactic acid is lower than that of glyceraldehyde.

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