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Production of lactic acid from glucose by alkaline hydrothermal reaction

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Abstract In this paper, alkaline hydrothermal conversion of glucose, a model compound of carbohydrate biomass, into lactic acid was discussed. Results showed that both NaOH and $Ca(OH)_2$, can promote the formation of lactic acid in a hydrothermal reaction of glucose. In the case of the addition of NaOH, lactic acid was obtained with a yield of 27% based on a starting carbon mass of glucose at 300 °C for 60 s with a NaOH concentration of 2.5 M. In the case of the addition of $Ca(OH)_2$, the highest yield of lactic acid is 20%, which occurred at 300 °C for 60 s with a $Ca(OH)_2$ concentration of 0.32 M. The formation mechanisms of lactic acid from glucose were also discussed according to intermediate products identified, to examine if lactic acid is also formed via the aldose having one and two carbon atoms besides via the aldose having three carbon atoms. Result showed that lactic acid may be generated via formaldehyde, glycolaldehyde besides via the aldose having three carbon atoms in hydrothermal reaction which all formed by the reverse aldol condensation of hexoses.

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Introduction

Lactic acid is receiving attention as a material for producing biodegradable lactic acid polymers [1]. At present, fermentation of starch is a dominant method for producing lactic acid. However, bioconversion (bacterial fermentation) is not directly available to cellulose and lignocelluloses.

The hydrothermal process is one of the most promising processes for the conversion of biomass to recycled resources among the several biomass conversion processes, because water at high temperature and pressure behaves as a reaction medium with outstanding properties. It is well-known in sugar chemistry that lactic acid is a typical base-catalyzed product from carbohydrates [2, 3]. Our past studies on the conversion of carbohydrate biomass into useful substances showed that lactic acid can be formed by hydrothermal reaction of carbohydrates without the addition of any catalyst, possibly because water in the subcritical region acts as an effective alkaline catalyst [4]. Therefore, it is quite possible that lactic acid can be formed in a considerable amount under a hydrothermal condition by adding alkali. However, there are few studies involving the conversion carbohydrate biomass to lactic acid by alkaline hydrothermal reaction.

In this study, the production of lactic acid by alkaline hydrothermal reaction of carbohydrate biomass is investigated. Formation mechanisms of lactic acid were also discussed according to intermediate products identified.

Experimental

Glucose (99.9%) was used as a test material because it is a primary intermediate compound during the conversion of carbohydrates. Lactic acid (98%) and some intermediate compounds in reaction such as formaldehyde (36–38% solution), glycolaldehyde (Aldrich), and glyceraldehydes (99%) were also used as test materials. 1.0 N standardized solution lactic acid (Alfa Aesar company) was used for the quantitative analysis of lactic acid. NaOH (99%) and $Ca(OH)_2$ (99%) were selected as an alkaline catalyst, which were obtained from Wako Pure chemicals Industries Ltd.

All experiments were carried out with a batch micro-reactor made of SUS 316, with an internal volume of 5.7 cm^3 [5]. The typical experimental procedure was as follows: The desired amount of test material, and the desired pH alkaline solution prepared in advance were put into the batch reactor, which was then sealed. The reactor was put into a salt bath preheated to a desired temperature. After a desired reaction time, the reactor was quickly moved from the salt bath 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. The defined reaction time is shorter than the apparent reaction time, because the time required to raise the temperature of reaction medium from 20 to 300 °C was about 15 s. A 0.07 g test material was used in all experiments. The desired concentration ranged from 0.16 to 7.0 M in the case of alkaline catalyst of NaOH. In comparison, the desired concentration was from 0.08 to 0.4 M in the case of $Ca(OH)_2$.

After the reaction was quenched, solution samples were collected and analyzed by HPLC and GC-MS. HPLC analysis was performed with a Waters HPLC system equipped with a tunable absorbance detector (UV/VIS detector) (Waters 486) and a differential refractometer (RI detector) (Waters 410). KC-811 (Shodex) column was used to separate samples for the analysis of lactic acid with 2 mM $HClO_4$ solvent using UV detector. SH1011 (Shodex) column was used to separate samples for the analysis of aldose with 5 mM H_2SO_4 solution using RI detector. For GC-MS analyses, a Hewlett-Packard model 5890 Series II Gas Chromatograph equipped with a model 5890B Mass Selective Detector was used. The samples were separated on a HP-INNOWAX capillary column (Cross-Linked Polyethylene Glycol) using helium as the carrier. Details on the conditions of HPLC and GC-MS analyses are available elsewhere [5].

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

Results and discussion

Influence of NaOH on the production of lactic acid

First of all, the influence of NaOH concentration on the production of lactic acid from glucose was investigated using NaOH as an alkali catalyst. Experiments were carried out with the concentration of NaOH varying from 0.16 to 7.0 M at 300 °C for 60 s. As shown in Fig. 1, an increase in the concentration of NaOH from 0.16 to 2.5 M led to a remarkable increase in the lactic acid yield. When NaOH increased to 2.5 M, lactic acid yield was up to 27%. The results that the lactic acid yield increased to 27% at only 60 s means that the addition of alkali is very effective to promote the formation of lactic acid in a hydrothermal reaction. As can also be seen in Fig. 1, a further increase of NaOH from 3 up to 7 M had no significant effect on the yield of lactic acid. All yields are reported in a carbon percent to a carbon of the initial reactant.

Comparison of NaOH and $Ca(OH)_2$ catalysts in the lactic acid production

In low temperatures, NaOH is often selected as an alkaline catalyst. But in high temperatures and high pressures conditions, effectiveness of NaOH and $Ca(OH)_2$ for the production of lactic acid remains poorly understood. A series of experiments were carried out with $Ca(OH)_2$ concentration varying from 0.08 to 0.4 M at a reaction temperature of 300 °C, reaction time of 60 s. Figure 2 shows the comparison of NaOH and $Ca(OH)_2$ in the lactic acid production. To compare the effect between $Ca(OH)_2$ and NaOH, alkaline concentration was presented using OH^- concentration. As shown in Fig. 2, when alkaline concentration was lower, $Ca(OH)_2$ for promoting the production of lactic acid is much more effective than NaOH in the same OH^- concentration. When OH^- concentration of $Ca(OH)_2$ increased to 0.64 M, the lactic acid yield of 20% was obtained. However, the further increase of $Ca(OH)_2$ from 0.64 (OH^-) to 0.8 M (OH^-) did not lead to the increase in the yield of lactic acid. As shown in Fig. 1, on the other hand, the increase in the concentration of OH^- from 0.8 to 2.5 M led to a further increase in lactic acid yield to 27% in the case of NaOH. The phenomenon that a high concentration of $Ca(OH)_2$ did not lead to the increase in lactic acid yield is probable due to a low solubility of

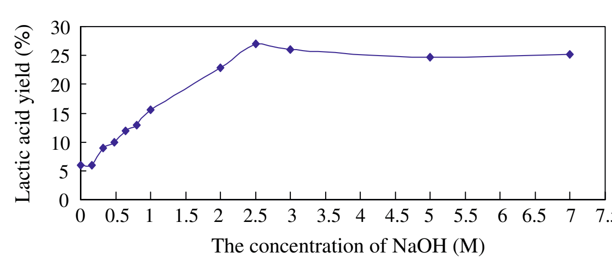


Fig. 1 Influence of NaOH concentration on the yield of lactic acid (300 °C, 60 s)

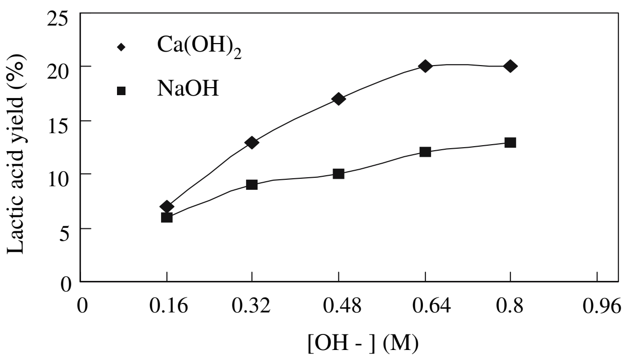


Fig. 2 Comparison of $Ca(OH)_2$ and NaOH in the production of lactic acid (300 °C, 60 s)

$Ca(OH)_2$. In general, saturated solubility of $Ca(OH)_2$ is 0.185 g/100 g (0.025 M)in room temperature.

While a higher lactic acid yield of 27% was obtained when NaOH concentration increased to 2.5 M, serious corrosion of reactor was observed. This will increase the cost for conversion of biomass to lactic acid in industry scale. Therefore, from the viewpoint of economic production of lactic acid, $Ca(OH)_2$ as a alkaline catalyst should be more suitable than NaOH in the hydrothermal treatment of biomasses.

The effect of reaction temperature and time on the production of lactic acid

As mentioned above, the selection of $Ca(OH)_2$ as a alkaline catalyst should be more suitable than NaOH. So, in discussing the effect of reaction temperature and time on the production of lactic acid, alkaline catalysts was only limited to $Ca(OH)_2$, and $Ca(OH)_2$ concentration was fixed on 0.32 M (OH^- 0.64 M) which is a better condition for producing lactic acid as shown in Fig. 2. As shown in

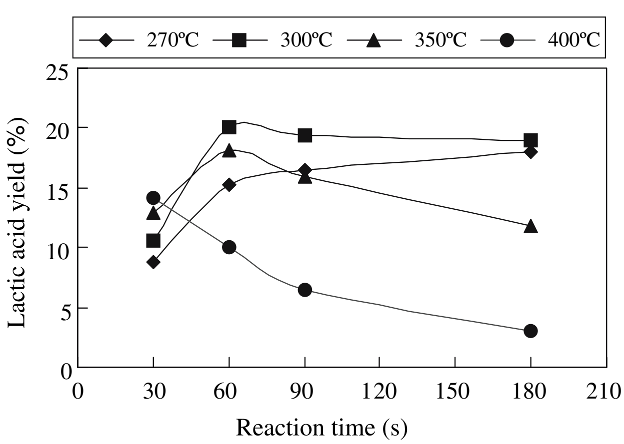


Fig. 3 Influence of reaction time and temperature on the yield of lactic acid in the case of $Ca(OH)_2$

Fig. 3, the lactic acid yield initially increased then decreased as the reaction time increased. The highest yield occurred at 60 s for all reaction temperatures except 400 °C. The decrease after 60 s was not critical at 270 and 300 °C, but the decrease became critical at 350 °C. From these observations, the use of the reaction temperature above 350 °C should be avoided to obtain a high yield of lactic acid.

From the discussion above, it can be seen that the highest yield of lactic acid is 20% in case of use $Ca(OH)_2$ as a alkaline catalyst, which occurred at the reaction temperature of 300 °C, the reaction time of 1 min, and a $Ca(OH)_2$ concentration of 0.32 M.

Other intermediate products

Intermediate products other than lactic acid were also identified in detail by GC/MS and HPLC. As shown in Table 1, many intermediate products were identified. Among these products, except for acetic acid and formic acid, their amount was quite low. So, we examined the yields of acetic acid and formic acid obtained at 300 °C for 60 s. As shown in Fig. 4, although when NaOH concentration was lower, the yields of acetic acid and formic acid were lower, when NaOH concentration increased to 2.5 M, the optimum condition for the formation of lactic acid, the

Table 1 Identified intermediate products in the alkali hydrothermal reaction of glucose

Group	Chemical substances detected
Aldoses	1. Fomaldehyde
	2. Glycolaldehyd
	3. Glyceraldehyde
	4. Fructose
	5. Formic acid
Organic acids	6. Lactic acid
	7. Acetic acid
	8. Propanoic acid
	9. Acylic acid
	10. 2-Hydroxy,Butanoic acid
	11. Glycolic acid
	12. 2,3-2Hydroxy,-2methyl,Propanoic acid
	13. 2,4-2Hydroxy,Butanoic acid
	14. Metasaccharinic acid
Ketones	15. Acetone
	16. 3-Hydroxy,2-Btanone
	17. 1-Hydroxy,2-Propanone
	18. 2-Cyclopenten,-1-one
	19. 3-Ethyl,-2-hydroxy,-2-cyclopenten,-1-one
	20. 3-Methy,-2-cyclopenten,-1-one

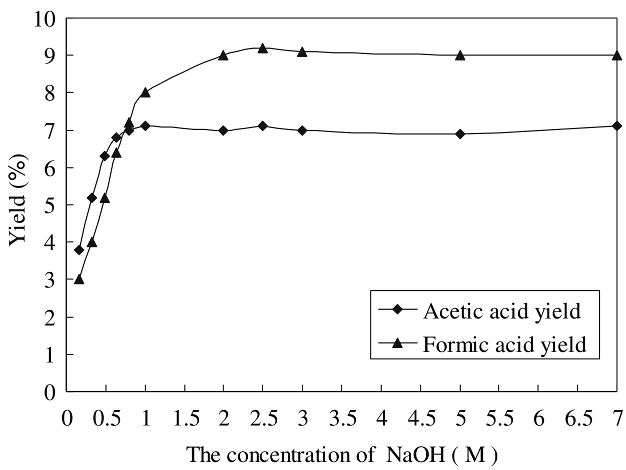


Fig. 4 Influence of NaOH concentration on the yield of acetic acid and formic acid (300 °C, 60 s)

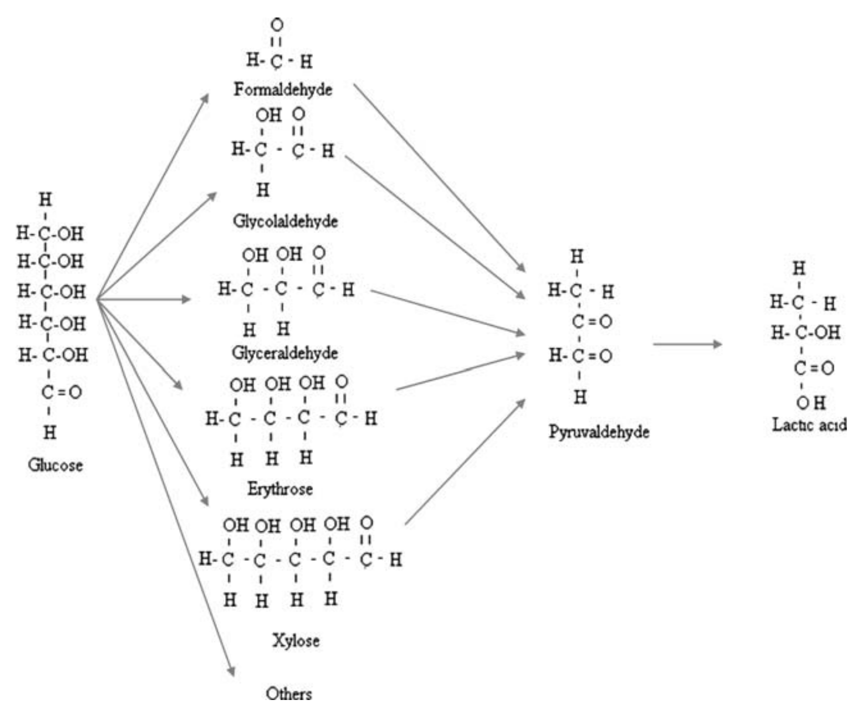
yields of acetic acid and formic acid increased to about 9 and 7, respectively. Under this condition, the decomposition rate of glucose was 90%. So, 50% of glucose was converted into lactic acid, acetic acid and formic acid.

Formation mechanisms of lactic acid from glucose

It is generally known in sugar chemistry that lactic acid 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 such mechanism appeared to follow the same pathway that was elucidated in the conversion of sugar to lactic acid in an alkaline solution [4]. Few studies reported, however, if lactic acid is generated via the aldose having one and two carbon atoms besides the aldose having three carbon atoms, which formed by the reverse aldol condensation of glucose. Jin et al. reported that lactic acid can be generated via glycolaldehyde besides the aldose having three carbon atoms in hydrothermal reactions which all formed by the reverse aldol condensation of hexoses [6]. To investigate the mechanism of lactic acid formation from glucose in alkaline hydrothermal reaction, the identification of aldose from alkaline hydrothermal reaction was identified by HPLC. As shown in Table 1, formaldehyde, glycolaldehyde, glyceraldehyde were identified.

Since formaldehyde and glycolaldehyde were identified, and our previous study showed that glycolaldehyde can produce lactic acid via pyruvadehyde, the formation mechanism of lactic acid from glucose could be proposed as shown in the Fig. 5. That is, lactic acid can be generated via the formaldehyde, glycolaldehyde besides the aldose having three carbon atoms in hydrothermal reaction. More precisely, carbon–carbon break by the reverse aldol condensation of hexoses occurred also at C_1–C_5 and C_2–C_4 besides C_3–C_3. Arai et al. [7] also reported that erythrose, being an aldose having four carbon atoms, was produced from glucose by the reverse aldol condensation of glucose at C_2–C_4 at 400 °C and 30 MPa without the addition of any alkaline catalyst.

Fig. 5 The proposed pathway for converting glucose into lactic acid



Conclusions

Both NaOH and $Ca(OH)_2$ can promote the formation of lactic acid in a hydrothermal reaction of glucose. Lactic acid was obtained with a yield of 27% based on a carbon base, which occurred at a reaction temperature of 300 °C, reaction time of 1 min, and a NaOH concentration of 2.5 M. In the case of $Ca(OH)_2$, the highest yield of lactic acid was 20%, which occurred at a reaction temperature of 300 °C, reaction time of 1 min, and a $Ca(OH)_2$ concentration of 0.32 M.

Although NaOH concentration increased to 2.5 M, a higher lactic acid yield of 27% was obtained, from the viewpoint of economic production of lactic acid from hydrothermal treatment of biomass, $Ca(OH)_2$ as a alkaline catalyst should be more suitable than NaOH.

The formation mechanisms of lactic acid from glucose were also discussed according to intermediate products identified. Lactic acid maybe generated via formaldehyde, glycolaldehyde besides via the aldose having three carbon atoms in hydrothermal reaction which all formed by the reverse aldol condensation of hexoses.

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