Production of lactic acid from C6-polyols by alkaline hydrothermal reactions

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ABSTRACT. Production of lactic acid from C6-polyols (Mannitol) under alkaline hydrothermal conditions was investigated. Experiments were performed to examine the difference in the production of lactic acid between C6-polyols and C3-polyols (glycerine), as well as C6-aldoses (glucose). Results showed that the yield of lactic acid from C6-polyols was lower than that from both glycerine and glucose. It indicated that long chain polyols might follow a different reaction pathway from that of glycerine. Further investigation is needed to clarify the reaction mechanism and improve the relatively low lactic acid acid yield from C6-polyols.

1. Introduction
Lactic acid is nowadays attracting more attention to be a raw material for the production of biodegradable polymers. At present, the production of lactic acid is dominated by fermentation of starch. But fermentation is a time-consuming process and can not directly convert cellulose and lignocellulos. On the other hand, the outstanding properties⁴ owned by high temperature water made hydrothermal reaction one of the most promising ways for biomass conversion.

Our previous studies showed that lactic acid could be obtained from glucose in subcritical water at 300 °C and reaction time of 60 s[⁵], yet the yield was maintained at a low level of about 27%. Additionally, our studies also showed that glycerin could be converted into lactic acid at a high yield of 90%[⁶], so it was reasonable to propose that hydrothermal conversion of polyols may be more effective than that of aldoses. However, few studies have examined the generation of lactic
acid from C6-polyols under hydrothermal conditions. In this study, the generation of lactic acid from mannitol in subcritical water was investigated, and comparisons between the products from mannitol and those from glucose were conducted to explore the mechanisms of the hydrothermal reactions.

2. Experiments
Mannitol was selected as a model compound of C6-polyols and NaOH as a basic catalyst. Glucose, xylose and xylitol (reagent grade) were used as test materials. All experiments were performed in a batch reactor made of stainless steel 316 tubing providing an internal volume of 5.7 cm$^3$. Details of the reactor were described elsewhere$^{[4]}$. When the desired amount of test materials and alkaline-water mixture were loaded, the reactor was sealed and put into a salt bath preheated to a preset temperature. After reaction, the reactor was removed from the salt bath and put into a cold water bath to quench the reaction. In this study, all experiments were performed at 300$^\circ$C. Yield was reported in mole percent of carbon atoms of lactic acid to that of the reactant. Liquid products were analyzed by Waters 600E HPLC equipped with a Waters 486 UV detector and RsparK KC-811 column.

3. Results and Discussion
3.1. Production of lactic acid from mannitol
3.1.1. Effect of alkali concentration on the yield of lactic acid
To investigate the influence of alkali concentration on the generation of lactic acid from mannitol, experiments were carried out by varying NaOH concentration from 0 to 6 M at reaction time of 30 min. As shown in Fig. 1, the yield of lactic acid increased remarkably as the concentration of NaOH increased from 0 to 1.75 M. The yield reached a maximum value of 23.34% at a NaOH concentration of 1.75 M, and decreased slightly with the further increase of NaOH from 1.75 to 6 M.

![Fig. 1 Yield of lactic acid at different NaOH concentrations (Temperature: 300$^\circ$C, reaction time: 30min).](image1)

![Fig. 2 Yield of lactic acid at different reaction time (Temperature: 300$^\circ$C, NaOH concentration: 1.75M).](image2)
Apparently, alkali had a significant effect on the production of lactic acid. The optimum NaOH concentration to achieve the maximum lactic acid yield from mannitol was 1.75 M, lower than that from glucose which is about 2.5 M\(^2\).

3.1.2. Effect of reaction time on the yield of lactic acid
Fig. 2 shows the effect of reaction time on the yield of lactic acid at 300°C and a NaOH concentration of 1.75 M. The yield increased rapidly from 1 to 60 min, and levelled off at a value of 25.61% after 60 min. Our previous research showed that the optimal reaction time required by glucose is 1 min\(^2\). Obviously, the reaction time required by mannitol was much longer than that of glucose. It could be attributed to the better stability of mannitol compared with glucose, which leads to a longer time for the conversion.

3.2. Comparison between C6-polyols and aldose
Fig. 3 shows the products of mannitol and glucose identified by HPLC, which mostly involve one to three carbon carboxylic acids. Lactic acid was the major product for both reactants. Other products were formic acid, acetic acid and acrylic acid. Peak 2 and 3 could not be identified and labeled as “unknown”.

**Fig. 3** HPLC chromatograph for products of glucose and mannitol.
A: glucose at 300°C, reaction time of 1 min, NaOH of 2.5 M.
B: mannitol at 300°C, reaction time of 60 min, NaOH of 1.75 M.

It should be noted that there was a high similarity between the reaction products from mannitol and glucose, suggesting that both of them might share the same reaction mechanism. In sugar chemistry, it is generally known that lactic acid could be generated through reverse aldol condensation of hexoses\(^2\), which might also account for the mannitol conversion. The yield of
25.61% from mannitol (Fig. 3 B) was not high as expected, lower than that of 27% from glucose (Fig. 3 A).

3.3. Comparison between C5-polyols and aldose
Experiments on C5-polyols were performed to investigate the effect of carbon chain length on the production of lactic acid. Products identified as illustrated in Fig. 4 are same as those shown in Fig. 3, indicating that the mechanism of reverse aldol condensation as discussed above might also be responsible for the C5-polyols conversion. The major reaction products still included C1 to C3 carboxylic acids as shown in Fig. 4. The highest yield of lactic acid from xylitol reached 24.92%, being slightly lower than that of 31.08% from xylose.

4. Conclusions
Production of lactic acid could be achieved through C6-polyols conversion under alkaline hydrothermal conditions. Alkali concentration had a significant effect on the lactic acid generation, and a reaction time of 60 min seems to be sufficient for the conversion under the current conditions. The similarity in products between C6-polyols and aldose implies that lactic acid might be generated through the reverse aldol condensation. Additionally, the fact that the yields from both C6 and C5-polyols were markedly lower than that from glycerine suggested long chain polyols might follow a different reaction pathway from that of glycerine.

5. References
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