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Degradation of Cellulose to Organic Acids in its Homogeneous Alkaline Aqueous Solution

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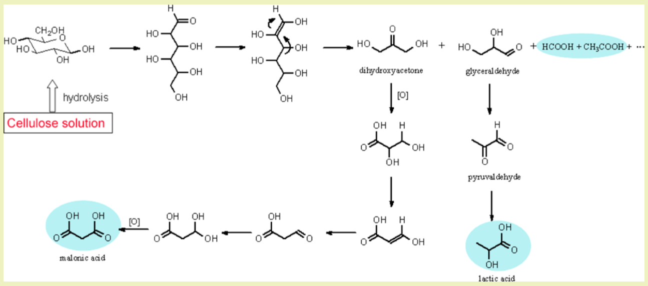

ABSTRACT: Conversion of cellulose to chemicals or fuels is the key point for the utilization of biomass to substitute for fossil resources. Here, a simple method has been developed to degrade the cellulose chains in its homogeneous solution in free of any noble or transition metal catalysts. The homogeneous alkaline aqueous solution of cellulose was prepared at first, and then it was hydrothermally degraded at 160−300 °C . Malonic acid (MA), lactic acid (LA), formic acid (FA), and acetic acid (AA) are the major valuable products, among them MA and LA are the top valuable platform molecules for synthesis of bulk chemicals and fuels. The maximum yield of MA is 39.7%, and the maximum total yield of the four kinds of organic acid is 81.2%. In addition, it is the first report that cellulose can be directly degraded to MA in a simple chemical route.

KEYWORDS: *Cellulose, Degradation, Malonic acid, Lactic acid, Aqueous solution, Hydrothermal reaction*

■ INTRODUCTION

Conversion of biomass to chemicals or liquid fuels are attracting topic today for the shortage of oil and coal.[1−4] The key points of the conversion include the degradation of cellulose into top valuable platform molecules with multifunctional groups, such as lactic acid, malonic acid, etc.[5−7] Among them, lactic acid has attracted much attention for it has potential application in various fields, especially as monomer for synthesis of biodegradable polymers.[8] The conversion of cellulose or glucose into lactic acid is usually carried out by fermentation of sugar or polysaccharides, and this process has some disadvantages such as small space-time yields and the production of plenty of salt.[9] Subcritical or supercritical water had been employed to convert glucose into lactic acid, but the process is high-cost.[10] Recently, alkaline hydrothermal reaction has been widely used to prepare lactic acid from glucose, fructose, cellulose, and even lignocelluloses.[11−13] To further improve the yield of lactic acid, various metal catalysts had been studied, such as Zn, Ni, Sn, CuO, Pd^{2+}, etc.[6,14−19] However, the processes usually are heterogeneous, and cellulose crystalline had been directly used during the process. The degradation of the cellulose aggregations is step-by-step from the surface to inner, resulting a slow degradation rate. Solving of cellulose will help to the degradation in its homogeneous solution while the cellulose chains are free approached. Conversion of cellulose in its homogeneous solution requires suitable solvents, especial green solvents.[20]

It is well-known that cellulose is difficult to be dissolved in a simple solvent for the existence of crystalline structure of complex hydrogen-bonding network. Recently, two kinds of green solvents for cellulose had been reported: room temperature ionic liquids and alkaline aqueous solution.[21−24] Plenty of research has been reported using ionic liquid as solvent to convert cellulose in its homogeneous solution over solid or liquid catalysts, such as conversion of cellulose to 5-hydroxymethylfurfural (HMF) or lactic acid, etc.[25−27] However, the high-cost of ionic liquids and the difficult in recovery and the difficult in reutilization of ionic liquid limit their application in large scale by now. In addition, the biotoxicity of ionic liquids in long-term is still a problem that has not been resolved. On the other hand, alkaline aqueous solution such as NaOH and urea/PEG/thiourea are also the green solvents for cellulose, and it is easy to form a homogeneous cellulose aqueous solution by a freezing−thawing process.[23] So it provides a chance to prepare lactic acid in the homogeneous cellulose solution by an alkaline hydrothermal reaction in a weak catalysis condition, especially in the absence of noble or transition metal catalysts. However, the conversion of cellulose in its homogeneous aqueous solution has scarce reports because cellulose was usually degraded by acidic catalysts, while the aqueous solution of cellulose is an alkaline environment.

In addition, as one of the degraded product of glucose, malonic acid (propanedioic acid), is a dicarboxylic acid with structure of $CH_2(COOH)_2$ and a bulk chemical molecule for preparation of malonates, barbituric acid, or meldrum's acid, and it is also a feedstock to prepare 1,3-propanediol, one of the chemical precursors of polytrimethylene terephthalate (PTT),[1]

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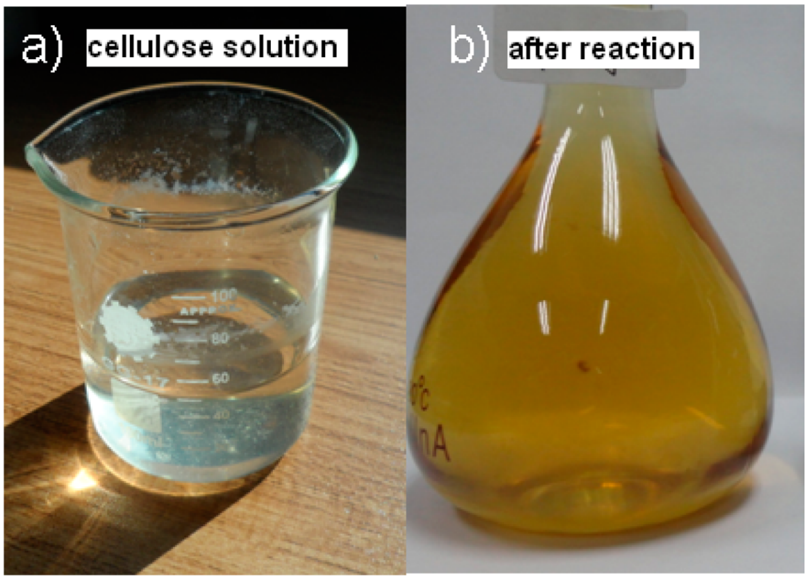


Figure 1. Photographs of cellulose aqueous solution (4.3 wt %) at room temperature (a) and the products diluted by water after hydrothermal reaction at 200 °C for 60 min (b).

an alternative to polyethylene terephthalate (PET) in the future. Malonic acid is also prepared mainly by fermentation of glucose or starch, and there is less reports on the conversion of malonic acid from cellulose directly, especially by a chemical route.[28]

Here, we developed a simple method to degrade cellulose to organic acids in its homogeneous solution free of any noble or transition metal catalysts. An alkaline aqueous solution of cellulose was prepared by a well-known freezing−thawing process at first, and then the well-dispersed cellulose chains were degraded under hydrothermal conditions, and a high yield of organic acid was obtained.

EXPERIMENTAL SECTION

Materials. Microcrystalline cellulose powder ($M_w = 1.08 \times 10^5$ g/mol by an Ubbelohde viscometer using DMAc/LiCl as solvent) was purchased from Shanghai Hengxin Chemical Reagent Co. Ltd. Sodium hydroxide and urea were all analytical grade, and standard samples of malonic acid, lactic acid, formic acid, and acetic acid were all purchased from Sinopharm Chemical Reagent Co. Ltd. Deionized water with resistivity of 18 MΩ·cm was produced by a Milli-Q (Millipore, USA) and was used for solution preparation.

Alkaline Hydrothermal Reaction of Cellulose in Its Aqueous Solution. A 3 g portion of NaOH, 1.0 g urea, and 45 g deionized water were added into a flask, and a mixture was obtained under stirring. Then, the mixture was precooled at 4 °C for 2 h, and next, 0.2−2.5 g microcrystalline cellulose was added under stirring. The as-formed suspension was cooled at −20 °C for 12 h, and then, it was thawed under strong stir at room temperature. At the end, homogeneous cellulose solutions with concentration of 0.004−0.06 g/mL were obtained.[29] Then 10 mL of the solution was added into an autoclave for the hydrothermal reaction. The reaction temperature changed from 160 to 300 °C, and reaction time changed from 10 to 80 min. In some case, Zn powder or Ni powder were added as catalysts for the hydrothermal reaction.

Characteristics of the Product. After reaction, the reactor was cooled down to room temperature, and the solution was neutralized by 10% phosphatic acid. The products were analysis by means of a high-performance liquid chromatography (HPLC, LC-20AD, Shimadzu) using a C-18 column, 0.1% H_3PO_4 works as the mobile phase with a flow rate of 0.8 mL/min, and the injection conditions is 40 °C.

RESULTS AND DISCUSSION

Here, microcrystalline cellulose was used as feedstock and it was dissolved in the aqueous solution of NaOH and urea to form a homogeneous aqueous solution with high viscosity (Figure 1a), and then, it was added into an autoclave for the hydrothermal reaction at 160−300 °C for the organic acids preparation. After reaction, a clear yellow solution was obtained as shown in Figure 1b, and the solution is in low viscosity, indicating the efficient degradation of cellulose chains.

The as-obtained product is a mixture of salts of organic acids, and after neutralization by phosphatic acid, the organic acids were formed and can be directly detected by means of HPLC. Figure 2 shows the typical HPLC curve of the product, and clearly four main organic acids were obtained in the product: lactic acid, malonic acid, formic acid, and acetic acid. Table 1 shows the yield of different small molecular organic acids and their total yield at various hydrothermal reaction temperatures from 160 to 280 °C.

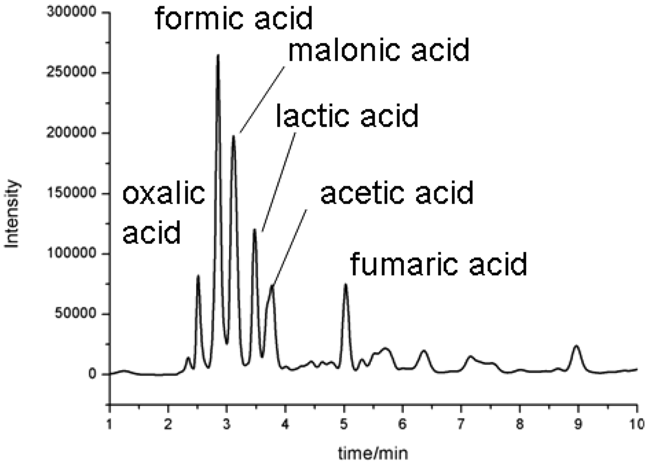


Figure 2. Typical HPLC curve of the product of cellulose after alkaline hydrothermal reaction in its aqueous solution.

Table 1. Yield of Organic Acids in the Products of Hydrothermal Degradation of Cellulose in Its Homogeneous Aqueous Solution at Different Temperature[a]

temperature (°C)	formic acid (%)	malonic acid (%)	lactic acid (%)	acetic acid (%)	yield of the four kinds of acids (%)
160	5.18	15.85	5.81	5.56	32.4
180	9.64	14.11	5.85	4.53	34.13
200	12.27	20.91	11.81	9.47	54.46
220	16.55	20.16	15.74	11.52	63.97
260	35.07	9.32	10.13	10.00	64.52
280	37.37	12.1	15.06	16.57	81.2

[a] Cellulose concentration 0.04 g/mL, reaction time 60 min, NaOH 0.07 g/mL.

In addition, trace amounts of oxalic acid and fumaric acid were also detected. At 160 °C, malonic acid is the major product with yield of 15.85%, and the yields of formic acid, acetic acid, and lactic acid are 5.18%, 5.56%, and 5.81%, respectively, while the total yield of the four acids is 32.4%, indicating the successful conversion of cellulose in its alkaline aqueous solution. Increasing the reaction temperature could promote the conversion rate of cellulose as expected. The yield of malonic acid reaches 20.91% with 11.81% of lactic acid, 12.27% of formic acid, and 9.47% of acetic acid at 200 °C, and the total yield of the four kinds of acids is 54.46%. Interestingly, further increasing the reaction temperature should result in high yield of formic acid, such as 35.07% or 37.37% at temperature of 260 or 280 °C, with the total yields of the four kinds of acids being 64.52% or 81.2%, respectively. However, the yields of malonic acid decrease to 9.32% or 12.1%, indicating the excess degradation of cellulose molecules. The results also reveal that at high temperature cellulose can be converted to organic acids efficiently, and much formic acid will be obtained when the concentrations of cellulose and NaOH are 0.04 and 0.07 g/mL, respectively, when the reaction was carried out for 60 min.

The conversion route of cellulose in its alkaline aqueous solution can be described as a systemic degradation of cellulose chains as shown in Scheme 1. At first, cellulose chains was hydrolyses to glucose while the chains is in molecular state, and then the as-formed glucose was degraded through dihydroxyacetone or glyceraldehyde routes respectively, and results in the formation of malonic acid or lactic acid.[18] At the same time, glucose can also be directly degraded into formic acid or acetic acid, etc., and the efficiency of this chemical conversion is higher than that of a traditional fermentation.[30]

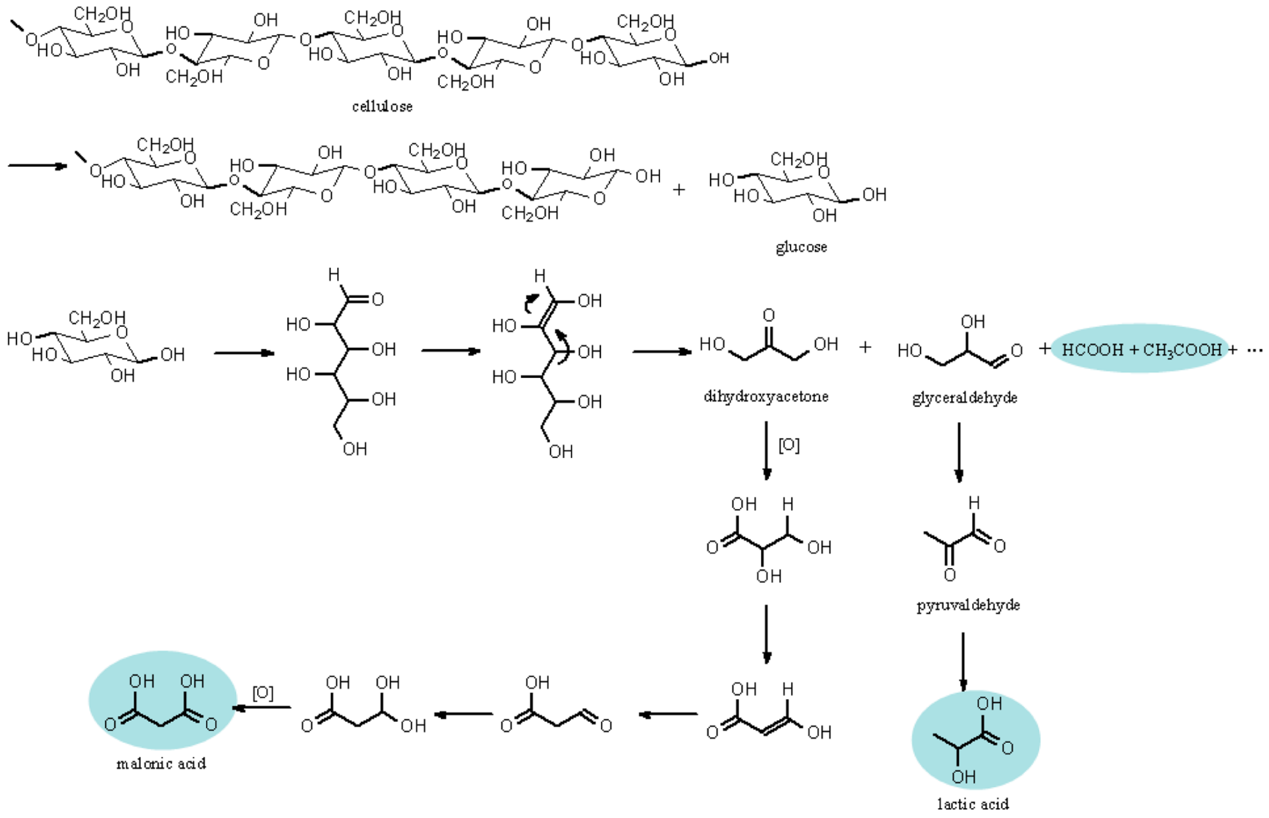
The conversion efficiency of cellulose also depends on its concentration in aqueous solution, and Table 2 lists the results

Table 2. Yield of Organic Acids in the Products of Hydrothermal Degradation of Cellulose in Its Homogeneous Aqueous Solution at Different Cellulose Concentration[a]

concentration of cellulose (g/mL)	formic acid (%)	malonic acid (%)	lactic acid (%)	acetic acid (%)	yield of the four kinds of acids (%)
0.02	5.14	23.72	15.27	9.93	54.06
0.03	10.83	24.19	12.20	12.14	59.36
0.04	16.55	20.16	15.74	11.52	63.97
0.06	24.38	16.52	16.96	14.98	72.84

[a] Reaction temperature 200 °C, reaction time 60 min, NaOH 0.07 g/mL.

Scheme 1. Proposed Mechanism for the Formation of Malonic Acid, Lactic Acid, Formic Acid, and Acetic Acid from Cellulose by an Alkaline Hydrothermal Reaction in Its Homogeneously Aqueous Solution



of conversion of cellulose at various concentrations from 0.02 to 0.06 g/mL. Clearly, higher concentration of cellulose favors the higher yields of the total four kinds of acids, and it reaches 72.94% when 0.06 g/mL of cellulose was used. However, it seems that malonic acid easily formed at low concentration of cellulose while formic acid and lactic acid can be easily obtained at higher concentration of cellulose.

Interestingly, further decreasing the concentration of cellulose and increasing the amount of NaOH in its aqueous solution could increase the yield of malonic acid, as shown in Table 3. The yield of malonic acid can reach 39.7% when the concentrations of cellulose and NaOH are about 0.004 and 0.1 g/mL, indicating the process is a potential way to prepare malonic acid by chemical conversion instead of traditional fermentation route.

Table 3. Yield of Organic Acids in the Products of Hydrothermal Degradation of Cellulose in Its Homogeneous Aqueous Solution Free of Zn Catalysis[a]

concentration of cellulose (g/mL)	formic acid (%)	malonic acid (%)	lactic acid (%)	acetic acid (%)	yield of the four kinds of acids (%)
0.004	6.71	39.70	9.51	7.86	63.78

[a] Reaction temperature 300 °C, reaction time 60 min, NaOH 0.1 g/mL.

Traditionally, hydrothermal reaction of cellulose was carried out under metal catalysis, such as Zn, Ni, or CuO powders while cellulose is in aggregated state. What will happen if such kinds of catalysts were added into the homogeneous alkaline aqueous solution under hydrothermal reaction? Here, Zn was used as a metal catalysis, and different amounts of Zn powder (0.03−0.06 g/mL) were added into the cellulose solution to the catalytic degradation of cellulose, and the results were list in Table 4. Formic acid is the major product while the total yields of the four kinds of acids are about 53−58%, lower than that of metal-free catalysis in homogeneous solution. In addition, the yields of lactic acid and malonic acid are also low, indicating the presence of Zn catalyst promote the oxidation of cellulose.

Table 4. Yield of Organic Acids in the Products of Hydrothermal Degradation of Cellulose in Its Homogeneous Aqueous Solution in the Presence of Zn Catalyst[a]

Zn content (g/mL)	formic acid (%)	malonic acid (%)	lactic acid (%)	acetic acid (%)	yield of the four kinds of acids (%)
0.03	31.11	7.14	9.23	9.50	56.98
0.04	28.59	8.59	10.77	9.75	57.70
0.05	28.23	8.07	10.44	10.45	57.19
0.06	27.60	7.69	8.53	9.46	53.28

[a] Reaction temperature 200 °C, reaction time 60 min, NaOH 0.07 g/mL.

Ni powder was also used as catalyst for the hydrothermal reaction of cellulose in its homogeneous solution, and Table 5 lists the main products of the reaction. Clearly, Ni powder can also be used to catalysis the degradation of cellulose at this condition. However, the yields of malonic acid, lactic acid, formic acid and acetic acid are 24.14%, 6.76%, 24.31%, and 6.65%, while the total yield of the four kinds of organic acid is 61.86%. The result is similar to that of Zn catalysis with a high yield of formic acid, but the yield of malonic acid is higher than that of Zn catalysis while it is still lower than that of the yield in free of Zn/Ni catalysts.

Table 5. Yield of Organic Acids in the Products of Hydrothermal Degradation of Cellulose in Its Homogeneous Aqueous Solution in the Presence of Ni Catalyst[a]

formic acid (%)	malonic acid (%)	lactic acid (%)	acetic acid (%)	yield of the four kinds of acids (%)
24.31	24.14	6.76	6.65	61.86

[a] Reaction temperature 200 °C, reaction time 60 min, NaOH 0.07 g/mL, Ni content 0.04 g/mL.

■ CONCLUSIONS

In conclusion, it was found that cellulose dissolved in alkaline aqueous solution make it easy to convert the polysaccharide to organic acids, such as malonic acid, lactic acid, formic acid, and acetic acid. Among them, malonic acid and lactic acid are especially important for they are the top valuable plenty molecules that can be widely used for production of bulk chemicals and fuels. In addition, the conversion can be carried out in the absence of noble or transition metals or their compounds as catalysts, which makes the conversion more environmental benign. The systemic studies also reveal that cellulose concentration, reaction temperature, and the amount of sodium hydroxide are the key factors to affect the products and the total yield of the four kinds of organic acid.

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Notes

The authors declare no competing financial interest.

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