Identification of the Soluble Byproducts Formed during the Hydrothermal Conversion of Cellulose Catalyzed by Solid Tungstated Alumina

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ABSTRACT: The soluble byproducts formed during the hydrothermal conversion of cellulose catalyzed by solid tungstated alumina (AIW) were analyzed by LC−MS and LC−MS² to determine their formulas and possible structures. These identified soluble compounds could be roughly divided into four species of carboxylic acids, α-carbonyl aldehydes, carbocyclic compounds, and furanic compounds with molecular mass in the range of 90−220 Da. Compared with the noncatalytic condition, the addition of AIW could increase the selectivity of carboxylic acids (especially α-hydroxy acid) from cellulose and suppress the formation of furanic compounds, carbocyclic compounds, and hydrochar. Based on the product distribution, the hydrothermal conversion route of glucose was proposed by regarding the formed α-carbonyl aldehydes as the key intermediates for formation of carboxylic acids, carbocyclic compounds, and furanic compounds.

1. INTRODUCTION

The catalytic hydrothermal biorefinery process is one efficient method to produce value-added chemicals and liquid fuels from renewable lignocellulosic biomass and has gained considerable attention.1 Because cellulose is the main component of lignocellulosic biomass, great efforts are devoted to developing efficient catalysts for conversion of cellulose into valuable platform chemicals such as 5-hydroxymethylfurfural (HMF), levulinic acid, and lactic acid. During the past decades, researchers have found that multiple catalysts such as HCl, H₂SO₄, H₃(PO₄)₃, CrCl₃, AlCl₃, and Al₂(SO₄)₃ are efficient in converting cellulose into 5-hydroxymethylfurfural (HMF) and levulinic acid,1−11 while Al-Sn salts, Er³⁺ salts, Pb²⁺ salts, Sn-beta, and solid tungstated alumina (AIW) are efficient in converting cellulose into lactic acid and derived esters12−18. Previously, our study showed that NaHSO₄−ZnSO₄ could catalyze the conversion of cellulose into HMF in biphasic systems,4 and AIW could catalyze the conversion of cellulose into lactic acid.13 However, the formation of hydrochar and other soluble byproducts blocked the further improvement of the selectivity to these desired platform chemicals from cellulose.

Nowadays, most studies on the catalytic biorefinery process are focused on the development of efficient catalysts, but relatively fewer studies are carried out on byproduct analysis. To reveal the formation mechanism of hydrochar, previously, we studied the hydrothermal conversion behavior of various biomass-derived organics including carbohydrates and furanic compounds and found that the α-carbonyl aldehydes such as 3-deoxyglucosone, 2,5-dioxo-6-hydroxyhexanal, and pyruvaldehyde formed during the hydrothermal conversion of carbohydrates should be the key intermediates for hydrochar formation, while aldol condensation should be the key step for hydrochar formation.19−21

In addition to the well-known compounds of glucose, 3-deoxyglucosone, HMF, levulinic acid, lactic acid, and formic acid, a certain amount of unknown byproducts was also formed during the catalytic hydrothermal conversion of cellulose. Identification of these byproducts could benefit the hydrothermal biorefinery process through several aspects. On the one hand, the identification of these byproducts could shed light on their formation mechanism, thus helping to develop methods to suppress their formation. On the other hand, identification of the byproducts could help to develop methods for their utilization, making the catalytic biorefinery process more economical. Thus, identification of the soluble byproducts is necessary for a comprehensive hydrothermal biorefinery process. However, the study on the identification of the byproducts formed during the hydrothermal biorefinery
process is far from satisfactory. Due to the low volatility and high polarity of the byproducts formed during the hydrothermal conversion of carbohydrates, most of those compounds could not be detected by GC−MS, which is one common method to identify the unknown volatile organic compounds. By improving the volatility of the formed compounds through a variety of derivatization reactions including silylation, methylation, and acylation, Poerschmann et al. employed GC−MS to identify multiple furanic compounds and hydroxylated benzofuran derivatives with the molecular mass range between 120 and 300 Da formed during the hydrothermal carbonization of glucose. On the other hand, LC−MS is one efficient method to identify soluble organic compounds in mixtures, and multiple researchers have employed LC−MS to analyze the soluble products formed during the hydrothermal biorefinery process. By using the LC−MS method, Maruani et al. identified some water-soluble oligomers of glucose formed during the acidic hydrothermal dehydration of glucose, while Rasmussen et al. identified some pentose dimers with bicyclic moieties formed during the pretreatment of biomass. Previously, we analyzed the soluble products formed during the hydrothermal carbonization of

Figure 1. Yields of the solid residue and soluble fraction with and without AlW.

Figure 2. Yields of the soluble compounds formed during the hydrothermal conversion of cellulose.
glucose by using LC−MS and LC−MS² to identify multiple furanic compounds and carbocyclic compounds with molecular mass in the range of 170−260 Da.²⁸ Among those reported catalysts for the hydrothermal biorefinery process, the solid AlW shows good catalytic activity in converting cellulose into lactic acid and could be easily prepared and recycled, making it one promising catalyst for the hydrothermal biorefinery process.¹³,¹⁵ However, little information about the byproducts formed during the hydrothermal conversion of cellulose catalyzed by AlW is known. Hence, we analyzed the soluble byproducts formed during the catalytic hydrothermal conversion of cellulose by using LC−MS and LC−MS² to identify multiple furanic compounds and carbocyclic compounds with molecular mass in the range of 170−260 Da.²⁸

Figure 3. LC-MS total ion chromatogram of the sample obtained from the noncatalytic conversion of cellulose.
LC−MS$^2$ here and identified multiple $\alpha$-carbonyl aldehydes, carboxylic acids, carboxyclic compounds, and furanic compounds with molecular mass in the range of 90−220 Da. Based on the product distribution, the hydrothermal conversion route of glucose was proposed.

2. RESULTS AND DISCUSSION

2.1. Overview of Product Distribution of the Hydrothermal Conversion of Cellulose. Few gaseous products were formed during the catalytic conversion of cellulose here, which was in accord with the previous studies; thus, the formed products could be roughly divided into two fractions of a water-soluble fraction and a solid residue. Figure 1 shows the yield of the solid residue and soluble compounds obtained from hydrothermal decomposition of cellulose with and without AlW. With a short reaction time of 0.5 h, the yield of the solid residue has already decreased to only 40.9% with the presence of AlW, while the yield of the solid residue (mainly containing unreacted cellulose) was still as high as 82.9% for the noncatalytic condition, indicating that AlW could catalyze the hydrolysis of cellulose. Under the noncatalytic condition, the yield of the solid residue slowly decreased to 54% in 3 h and remained constant after 3 h, indicating that noncatalytic conversion of cellulose could generate around 54% hydrochar and 46% soluble compounds. On the contrary, when AlW was used, the yield of the solid residue sharply decreased to only around 21%, indicating that only below 21% of the cellulose was converted to hydrochar and over 79% of the cellulose was converted to soluble compounds. The above results confirmed that AlW could catalyze the conversion of cellulose into soluble compounds and suppress the formation of hydrochar during the hydrothermal conversion of cellulose.

Among the soluble compounds formed during the hydrothermal conversion of cellulose, the yield of glucose, HMF, levulinic acid (LEA), and lactic acid (LCA) could be quantified by HPLC, but the yield of the unknown soluble compounds could only be determined by the difference between the feedstock and the identified compounds. Figure 2 shows the yields of those compounds. For the noncatalytic condition, the yield of glucose, HMF, LEA, and LCA were all below 10%, indicating that cellulose could not be selectively converted under the noncatalytic condition. On the contrary, addition of AlW could obviously increase the yield of LCA to over 27%, which was in accord with previous studies. The total yields of the unknown byproducts obtained after 3 h were around 27 and 41% for the noncatalytic and catalytic condition, respectively, indicating that considerable cellulose was converted into unknown compounds for both conditions. Obviously, the yield of unknown compounds formed with the presence of AlW was higher than that formed under the noncatalytic condition, which was ascribed to the fact that AlW could suppress the formation of hydrochar.

2.2. Identification of the Soluble Products Formed during the Conversion of Cellulose. Considering that identification and suitable utilization of these soluble unknown byproducts could improve the economy of the hydrothermal biorefinery process, we tried to determine the formulas and the structures of the soluble compounds formed during the hydrothermal conversion of cellulose by using the LC−MS and LC−MS$^2$ method.

2.2.1. Identification of the Soluble Products Formed under the Noncatalytic Condition. The LC−MS chromatograms and the formulas of these detected soluble compounds formed under the noncatalytic condition are shown in Figure 3. Obviously, the compounds C$_{6}$H$_{12}$O$_{6}$ (4.27 min), C$_{6}$H$_{10}$O$_{5}$ (4.93 min), C$_{6}$H$_{12}$O$_{5}$ (13.02 min), C$_{6}$H$_{10}$O$_{4}$ (14.63 min), C$_{7}$H$_{12}$O$_{5}$ (17.13 min), C$_{6}$H$_{12}$O$_{5}$ (18.13 min), C$_{7}$H$_{12}$O$_{6}$ (18.72 min), C$_{7}$H$_{12}$O$_{5}$ (19.09 min), C$_{7}$H$_{12}$O$_{5}$ (19.90 min), C$_{7}$H$_{12}$O$_{5}$ (21.52 min), C$_{7}$H$_{12}$O$_{5}$ (22.50 min), and C$_{7}$H$_{12}$O$_{5}$ (25.47 min) were detected in the positive ionization mode, while the compounds C$_{6}$H$_{10}$O$_{6}$ (4.38 min), C$_{6}$H$_{10}$O$_{6}$ (4.95 min), C$_{6}$H$_{12}$O$_{7}$ (7.35 min), C$_{7}$H$_{12}$O$_{5}$ (10.27 min), C$_{7}$H$_{12}$O$_{5}$ (10.56 min), C$_{6}$H$_{12}$O$_{4}$ (13.00 min), C$_{6}$H$_{12}$O$_{4}$ (14.65 min), C$_{7}$H$_{12}$O$_{5}$ (15.51 min), C$_{7}$H$_{12}$O$_{5}$ (16.09 min), C$_{7}$H$_{12}$O$_{5}$ (18.13 min), C$_{12}$H$_{15}$O$_{4}$ (19.72 min), and C$_{7}$H$_{12}$O$_{5}$ (20.12 min),

| $t_f$ (min) | formula | molecular mass | core structure | functional group | DBE | DBE/C | (H−2O)/C |
|------------|---------|----------------|----------------|------------------|-----|-------|-----------|
| 4.27−4.38  | C$_{6}$H$_{12}$O$_{6}$ | 180.06 | noncyclic | hydroxy, carbonyl | 1   | 0.17  | 0         |
| 4.93−4.95  | C$_{6}$H$_{12}$O$_{6}$ | 162.05 | noncyclic | hydroxy, carbonyl | 2   | 0.33  | 0         |
| 7.35       | C$_{6}$H$_{12}$O$_{5}$ | 90.03 | noncyclic | hydroxy, carbonyl | 1   | 0.33  | 0         |
| 10.27      | C$_{6}$H$_{12}$O$_{5}$ | 126.03 | furanic  | hydroxy, carbonyl | 4   | 0.67  | 0         |
| 10.56      | C$_{6}$H$_{12}$O$_{5}$ | 118.03 | noncyclic | hydroxy, carbonyl | 2   | 0.5   | −0.50     |
| 13.00−13.02| C$_{6}$H$_{12}$O$_{5}$ | 116.05 | noncyclic | carbonyl, carbonyl | 2   | 0.4   | 0.40      |
| 14.63      | C$_{6}$H$_{12}$O$_{5}$ | 144.04 | furanic  | hydroxy, carbonyl | 3   | 0.5   | 0         |
| 15.51      | C$_{6}$H$_{12}$O$_{5}$ | 234.05 | furanic  | hydroxy, carbonyl | 8   | 0.67  | 0         |
| 16.09      | C$_{6}$H$_{12}$O$_{5}$ | 132.04 | noncyclic | hydroxy, carbonyl | 2   | 0.4   | 0         |
| 16.56      | C$_{6}$H$_{12}$O$_{5}$ | 154.06 | carboxyclic | hydroxy, carbonyl | 4   | 0.5   | 0.50      |
| 17.13      | C$_{6}$H$_{12}$O$_{5}$ | 190.06 | carboxyclic | hydroxy, carbonyl | 7   | 0.64  | 0.36      |
| 18.13−18.15| C$_{6}$H$_{12}$O$_{5}$ | 192.08 | carboxyclic | hydroxy, carbonyl | 6   | 0.55  | 0.55      |
| 18.72      | C$_{6}$H$_{12}$O$_{5}$ | 170.09 | carboxyclic | hydroxy         | 3   | 0.33  | 0.89      |
| 19.09      | C$_{6}$H$_{12}$O$_{5}$ | 210.09 | carboxyclic | hydroxy, carbonyl | 5   | 0.45  | 0.55      |
| 19.72      | C$_{6}$H$_{12}$O$_{5}$ | 220.07 | carboxyclic | hydroxy, carbonyl | 7   | 0.58  | 0.33      |
| 20.12      | C$_{6}$H$_{12}$O$_{5}$ | 206.06 | carboxyclic | hydroxy, carbonyl | 7   | 0.64  | 0.18      |
| 21.54      | C$_{6}$H$_{12}$O$_{5}$ | 234.05 | furanic  | hydroxy, carbonyl | 8   | 0.67  | 0         |
| 22.50      | C$_{6}$H$_{12}$O$_{5}$ | 192.08 | carboxyclic | hydroxy, carbonyl | 6   | 0.55  | 0.55      |
| 24.92      | C$_{6}$H$_{12}$O$_{5}$ | 224.07 | furanic  | hydroxy, carbonyl | 6   | 0.55  | 0.18      |
| 25.47      | C$_{6}$H$_{12}$O$_{5}$ | 180.08 | carboxyclic | hydroxy, carbonyl | 5   | 0.5   | 0.60      |
| 25.61      | C$_{6}$H$_{12}$O$_{5}$ | 220.07 | carboxyclic | hydroxy, carbonyl | 7   | 0.58  | 0.33      |

Table 1. Structural Information of the Detected Soluble Compounds Formed under the Noncatalytic Condition
C12H10O5 (21.54 min), C11H12O5 (24.92 min), and C12H12O4 (25.61 min) were detected in the negative ionization mode. Among these detected compounds, the compound C6H8O4 (14.63 min) was present as the main product in the positive ionization mode, while the compounds C6H12O6 (4.38 min) and C6H10O5 (4.95 min) were present as the main products in the negative ionization mode. The C atoms of these detected compounds were in the range of 3−12, and the O atoms were in the range of 3−6, quite similar to the soluble compounds formed during the hydrothermal carbonization of glucose.22,28

Table 1 shows the core structure and the functional groups of these detected compounds according to the MS2 data of these compounds (shown in Table S1). Among all those compounds, the compounds C6H12O6 (4.27 min), C6H10O5 (4.93 min), C 3H6O3 (7.35 min), C 4H6O4 (10.56 min), C5H8O3 (13.00 min), and C5H8O4 (16.09 min) all contained noncyclic structures, the compounds C6H6O3 (10.27 min), C6H8O4 (14.63 min), C12H10O5 (15.51 min), C12H10O5 (21.54 min), and C11H12O5 (24.92 min) all contained furanic structures, while the other compounds all contained carbocyclic structures. Thus, the detected soluble compounds could be roughly divided into three species of chain compounds, furanic compounds, and carbocyclic compounds. Hydroxy groups and carbonyl groups were proven to be present in most of these compounds, while the carboxylic group was only present in the compounds C6H4O3 (7.35 min), C6H8O4 (10.56 min), C6H10O5 (13.00 min), and C6H12O4 (16.09 min). Thus, the compounds C6H9O3 (7.35 min), C6H10O4 (10.56 min), C6H10O5 (13.00 min), and C6H12O4 (16.09 min) were all proposed to be chain carboxylic acids.

The double-bond equivalents (DBEs) and the DBE/C of these detected compounds could be determined through the formulas of these compounds, and the results are also shown in Table 1. The DBEs of the detected chain compounds were no more than 2, while the DBEs of these furanic compounds and carbocyclic compounds were in the range of 3−8, which was in accord with the fact that the furanic compounds and carbocyclic compounds contained more unsaturated structures. The DBE/C denotes the value of DBE per carbon atom of the identified compounds. Under the hydrothermal condition, the water addition reactions could decrease the DBE/C of the formed compounds from the reactant, while the water removal reactions were reverse. For example, the DBE/C values of glucose, HMF, and levulinic acid are 0.17, 0.67, and 0.4, respectively, and formation of HMF from glucose involves dehydration, while formation of levulinic acid from HMF involves rehydration. The DBE/C of these detected carbocyclic compounds was in the range of 0.33−0.64, suggesting that the formation of these compounds should involve dehydration of glucose or rehydration of HMF.

Figure 4. Proposed molecular structure of the compounds formed during the noncatalytic hydrothermal conversion of cellulose. (Note that ring substitution positions are given for clarity, but isomerism was not determined.)

C12H10O5 (21.54 min), C11H12O5 (24.92 min), and C12H12O4 (25.61 min) were detected in the negative ionization mode. Among these detected compounds, the compound C6H4O3 (14.63 min) was present as the main product in the positive ionization mode, while the compounds C6H12O6 (4.38 min) and C6H10O5 (4.95 min) were present as the main products in the negative ionization mode. The C atoms of these detected compounds were in the range of 3−12, and the O atoms were in the range of 3−6, quite similar to the soluble compounds formed during the hydrothermal carbonization of glucose.22,28

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Figure 4. Proposed molecular structure of the compounds formed during the noncatalytic hydrothermal conversion of cellulose. (Note that ring substitution positions are given for clarity, but isomerism was not determined.)
(H-2O)/C indicates the neat H atom per carbon atom of the organic compounds, and this parameter could not change under the hydrothermal condition unless the redox reactions occurred. The water addition/removal reactions could not change the (H-2O)/C of the product from the reactant because those reactions were not redox reactions. On the contrary, the hydrolytic C−C cleavage reaction is one intramolecular redox reaction of organic compounds, leading to formation of one oxidation product with (H-2O)/C lower than the reactant and one reduction product with (H-2O)/C higher than the reactant. Thus, the (H-2O)/C could show whether the hydrolytic C−C cleavage reaction occurred during the formation of those compounds from cellulose under the hydrothermal condition.26 As shown in Table 1, among these

Figure 5. LC-MS total ion chromatograms of the sample obtained from the conversion of cellulose catalyzed by AlW.
identified compounds, the \((\text{H}-2\text{O})/\text{C}\) values of \(\text{C}_9\text{H}_{10}\text{O}_2\) (4.89 min), \(\text{C}_9\text{H}_{10}\text{O}_3\) (7.35 min), \(\text{C}_9\text{H}_{10}\text{O}_4\) (10.27 min), \(\text{C}_9\text{H}_{10}\text{O}_5\) (14.65 min), \(\text{C}_{12}\text{H}_{12}\text{O}_4\) (15.51 min), and \(\text{C}_{12}\text{H}_{10}\text{O}_5\) (21.54 min) were all equal to 0, which was the same as that of glucose, indicating that the formation of these compounds did not involve the hydrolytic C–C cleavage reaction. On the contrary, the \((\text{H}-2\text{O})/\text{C}\) values of the detected carboxylic compounds were all not equal to that of glucose, indicating that the formation of these compounds should involve the hydrolytic C–C cleavage reaction.

Figure 4 shows the possible molecular structures of these compounds determined according to the structural information of these detected compounds. The compounds \(\text{C}_6\text{H}_{12}\text{O}_5\) (4.27 min), \(\text{C}_6\text{H}_{12}\text{O}_3\) (7.35 min), \(\text{C}_6\text{H}_{12}\text{O}_5\) (10.27 min), and \(\text{C}_6\text{H}_{12}\text{O}_4\) (13.00 min) are well known to be glucose, lactic acid, HMF, and levulinic acid, respectively. The compound \(\text{C}_5\text{H}_8\text{O}_5\) (4.89 min) should be 3-deoxyglucosone formed by dehydration of glucose, while the compound \(\text{C}_8\text{H}_{10}\text{O}_5\) (14.65 min) containing a furanic structure should be the intermediate formed from glucose by losing two water molecules. Multiple carboxylic compounds containing a hydroxy group and a carbonyl group were also identified, with a carbon chain length of 8–12. Among those detected compounds, glucose and 3-deoxyglucosone were detected as the main compounds in positive ionization mode while \(\text{C}_6\text{H}_{10}\text{O}_5\) (4.91 min), \(\text{C}_3\text{H}_6\text{O}_3\) (7.29 min), \(\text{C}_6\text{H}_{10}\text{O}_3\) (12.07 min), \(\text{C}_6\text{H}_{10}\text{O}_4\) (12.44 min), \(\text{C}_9\text{H}_{12}\text{O}_4\) (16.00 min), \(\text{C}_9\text{H}_{8}\text{O}_3\) (16.53 min) \(\text{C}_{12}\text{H}_{12}\text{O}_4\) (19.81 min), and \(\text{C}_{12}\text{H}_{10}\text{O}_5\) (21.26 min) were detected in the negative ionization mode. The formulas of some detected peaks were not determined due to the lack of MS information. According to the above analysis, the compounds with retention times of 4.91 min \((\text{C}_9\text{H}_{10}\text{O}_5)\), 7.29 min \((\text{C}_9\text{H}_{10}\text{O}_3)\), and 12.95 min \((\text{C}_9\text{H}_{10}\text{O}_4)\) should be 3-deoxyglucosone, lactic acid, and levulinic acid, respectively. Levulinic acid and lactic acid were present as the dominant compounds detected in positive and negative ionization modes, respectively, indicating that AlW could catalyze the conversion of cellulose into these carboxylic acids, in accord with the above results shown in Figure 2. The molecular mass of all those detected compounds were all below 170 Da except for \(\text{C}_9\text{H}_{12}\text{O}_4\) (19.81 min), indicating that AlW could catalyze the C–C cleavage of the formed soluble polymers into smaller compounds.

Table 2 shows the core structure and the functional groups of these detected compounds according to the MS data of these compounds (shown in Table S2). Among these detected compounds, the compounds \(\text{C}_9\text{H}_{10}\text{O}_3\) (4.91 min), \(\text{C}_9\text{H}_{10}\text{O}_3\) (7.29 min), \(\text{C}_9\text{H}_{10}\text{O}_3\) (10.51 min), \(\text{C}_9\text{H}_{10}\text{O}_3\) (12.44 min), \(\text{C}_9\text{H}_{12}\text{O}_4\) (12.95 min), \(\text{C}_9\text{H}_{12}\text{O}_4\) (16.00 min), \(\text{C}_9\text{H}_{12}\text{O}_4\) (16.53 min) \(\text{C}_{12}\text{H}_{12}\text{O}_4\) (19.81 min), and \(\text{C}_{12}\text{H}_{10}\text{O}_5\) (21.26 min) were all noncyclic compounds, and only the compounds \(\text{C}_9\text{H}_{10}\text{O}_3\) (11.92 min) and \(\text{C}_9\text{H}_{10}\text{O}_4\) (12.07 min) were furanic compounds, while the compounds \(\text{C}_9\text{H}_{10}\text{O}_5\) (15.53 min), \(\text{C}_9\text{H}_{10}\text{O}_5\) (16.51 min), \(\text{C}_9\text{H}_{12}\text{O}_3\) (19.14 min), \(\text{C}_9\text{H}_{12}\text{O}_4\) (19.81 min), \(\text{C}_9\text{H}_{12}\text{O}_5\) (20.52 min), and \(\text{C}_9\text{H}_{12}\text{O}_5\) (21.26 min) were all carboxylic compounds. Obviously, the species of chain compounds were more than that of the noncatalytic condition, while the species of furanic compounds and carboxylic compounds were less than that of the noncatalytic condition, suggesting that the AlW could increase the selectivity of the chain compounds and suppress the formation of furanic compounds and carboxylic compounds. Similar to the compounds formed under the noncatalytic condition, the hydroxy group and carbonyl group were present in most of those detected compounds. Interestingly, all these noncyclic compounds all
contained the carboxylic group except 3-deoxyglucosone, indicating that these compounds were chain carboxylic acids. The values of DBE, DBE/C, and \((\text{H} - 2\text{O})/\text{C}\) of these compounds are also shown in Table 2. Except for the compounds \(\text{C}_{12}\text{H}_{12}\text{O}_{4}\) (19.81 min), \(\text{C}_{9}\text{H}_{8}\text{O}_{3}\) (20.52 min), and \(\text{C}_{8}\text{H}_{8}\text{O}_{3}\) (21.26 min), the DBEs of those compounds were no more than 4, indicating that the compounds detected here contained less unsaturated structures. The DBE/C of these chain compounds was in the range of 0.33−0.67, suggesting that the formation of these compounds involved dehydration of glucose. The \((\text{H} - 2\text{O})/\text{C}\) values of \(\text{C}_{6}\text{H}_{10}\text{O}_{5}\) (4.91 min), \(\text{C}_{6}\text{H}_{5}\text{O}_{3}\) (7.29 min), \(\text{C}_{4}\text{H}_{4}\text{O}_{2}\) (16.00 min), and \(\text{C}_{6}\text{H}_{10}\text{O}_{5}\) (16.53 min) were all equal to that of glucose, indicating that the formation of these compounds did not involve the hydrolytic C−C cleavage reaction, while the formation of other compounds should involve the hydrolytic C−C cleavage reaction.

Figure 6. Proposed structure of the compounds during the catalytic conversion of cellulose with AlW as the catalyst. (Note that ring substitution positions are given for clarity, but isomerism was not determined).

Figure 7. Proposed routes of conversion of glucose into various compounds.

The values of DBE, DBE/C, and \((\text{H} - 2\text{O})/\text{C}\) of these compounds are also shown in Table 2. Except for the compounds \(\text{C}_{12}\text{H}_{12}\text{O}_{4}\) (19.81 min), \(\text{C}_{9}\text{H}_{8}\text{O}_{3}\) (20.52 min), and \(\text{C}_{8}\text{H}_{8}\text{O}_{3}\) (21.26 min), the DBEs of those compounds were no more than 4, indicating that the compounds detected here contained less unsaturated structures. The DBE/C of these chain compounds was in the range of 0.33−0.67, suggesting that the formation of these compounds involved dehydration of glucose. The \((\text{H} - 2\text{O})/\text{C}\) values of \(\text{C}_{6}\text{H}_{10}\text{O}_{5}\) (4.91 min), \(\text{C}_{6}\text{H}_{5}\text{O}_{3}\) (7.29 min), \(\text{C}_{4}\text{H}_{4}\text{O}_{2}\) (16.00 min), and \(\text{C}_{6}\text{H}_{10}\text{O}_{5}\) (16.53 min) were all equal to that of glucose, indicating that the formation of these compounds did not involve the hydrolytic C−C cleavage reaction, while the formation of other compounds should involve the hydrolytic C−C cleavage reaction.
According to the structural information, the proposed structures of these compounds were shown in Figure 6. Similar to the noncatalytic condition, the detected soluble compounds formed during the catalytic conversion of cellulose could be roughly divided into four species of chain α-carbonyl aldehydes, chain carboxylic acids, furanic compounds, and carbocyclic compounds. Among these detected carboxylic acids, the compounds C₂H₄O₂ (7.29 min), C₃H₆O₂ (12.44 min), C₄H₈O₂ (16.00 min), and C₅H₁₀O₅ (16.53 min) were all proposed to be α-hydroxy acids because the fragment ion at m/z 89.02 (corresponding to the formula [C₄H₈O₂]) was presented in the MS² data of these compounds (shown in Table S2). C₅H₁₀O₅ (16.53 min) was proposed to be 2,4,5,6-tetrahydroxyhexanoic acid formed during the conversion of glucose.  

In brief, AlW could catalyze the hydrothermal conversion of cellulose into carboxylic acids and suppress the formation of furanic compounds, carbocyclic compounds, and hydrochar.

### 2.3. Hydrothermal Conversion Route of Glucose

The above results confirmed that hydrothermal conversion of cellulose could generate multiple carboxylic acids, furanic compounds, carbocyclic compounds, and hydrochar. Based on the identified byproduct distribution, the hydrothermal conversion route of glucose was proposed, as shown in Figure 7.

Generally, the α-hydroxy acids are formed by an intramolecular Cannizaro reaction of α-carbonyl aldehydes.  

For example, the formation of 2,4,5,6-tetrahydroxyhexanoic acid from glucose involves the intramolecular Cannizaro reaction of the α-carbonyl aldehyde 3-deoxyglucosone, and the formation of 2,4,5-trihydroxypentanoic acid from xylose involves the intramolecular Cannizaro reaction of 3-deoxyxylosone, while the formation of lactic acid from glucose involves the intramolecular Cannizaro reaction of β-carbonyl aldehyde 3-deoxyglucosone, which was also one α-carbonyl aldehyde. Thus, the identification of multiple carboxylic acids (especially the α-hydroxy acids) suggested that multiple α-carbonyl aldehydes were formed during the hydrothermal conversion of glucose. On the other hand, our previous studies suggested that the hydrochar and carbocyclic compounds were also formed by condensation/polymerization of the α-carbonyl aldehydes. Thus, α-carbonyl aldehydes were proposed to be the key intermediate for the formation of the carboxylic acids, the carbocyclic compounds, and the hydrochar.

In fact, multiple previous studies have reported that hydrothermal decomposition of glucose could generate several kinds of α-carbonyl aldehydes such as 3-deoxyglucosone, 2,5-dioxo-3-hexenal, 2,5-dioxohex-3-enal, and pyruvaldehyde. According to the previous studies, α-carbonyl aldehydes could be formed from glucose through three routes: (1) glucose could undergo acetalization and dehydration to generate HMF, which could undergo hydrolytic ring opening to generate 2,5-dioxo-6-hydroxyhexanal (DH2) and 2,5-dioxo-3-hexenal; (2) glucose could directly undergo β-elimination and keto-enol tautomerism to generate 3-deoxyglucosone; (3) glucose could undergo retro-aldol condensation to generate C₃-C₄ carbohydrates, which further undergo β-elimination and keto-enol tautomerism to generate α-carbonyl aldehydes such as pyruvaldehyde. Those α-carbonyl aldehydes were not detected here except for 3-deoxyglucosone, maybe because these α-carbonyl aldehydes were too unstable under the hydrothermal condition.

Then, those formed α-carbonyl aldehydes could be converted through three main routes: (1) the α-carbonyl aldehydes could undergo a Cannizaro reaction to generate C₃-C₄ α-hydroxy acids, such as lactic acid and 2,5,6-trihydroxyhex-3-enoic acid; (2) the α-carbonyl aldehydes could undergo hydrolytic C=C cleavage to release carboxylic acid; (3) the α-carbonyl aldehydes could undergo aldol condensation to generate initial polymers, which then further undergo polymerization/condensation to hydrochar or undergo a C=C cleavage reaction to release some carboxylic compounds containing hydroxy groups and carboxyl groups.

### 3. Conclusions

The soluble compounds formed during the hydrothermal conversion of cellulose with and without AlW were analyzed by LC–MS and LC–MS² to identify multiple compounds including carboxylic acids, α-carbonyl aldehydes, furanic compounds, and carbocyclic compounds with molecular mass in the range of 90–220 Da. The addition of AlW could catalyze the conversion of cellulose into carboxylic acids (especially the lactic acid) and suppress the formation of furanic compounds, carbocyclic compounds, and hydrochar. The α-carbonyl aldehydes formed during the hydrothermal conversion of glucose were proposed to be the key intermediates for the formation of α-hydroxy acids, carbocyclic compounds, and hydrochar. Comprehensive utilization of these identified soluble compounds could improve the economics of the hydrothermal biorefinery process.

### 4. Materials and Methods

#### 4.1. Materials

NaWO₄·2H₂O and Al₂(SO₄)₃·18H₂O were all of analytically pure grade. Microcrystalline cellulose was purchased from Aladdin Reagent Co. (Shanghai, China) and used without further treatment.

#### 4.2. Preparation of Solid Catalyst AlW

The preparation of solid catalyst AlW was reported previously. In brief, 3.29 g of NaWO₄·2H₂O and 2.22 g of Al₂(SO₄)₃·18H₂O were accurately weighed and dissolved into two 30 mL solutions of deionized water. Under a stirring state, the Al₂(SO₄)₃ solution was added to the Na₂WO₄ solution to obtain milky white precipitates. After aging for 2 h, the above precipitates were separated by filtration, washed with 2 L of deionized water, and dried at 105 °C. Then, the powders are calcined at 700 °C for 3 h to form a solid AlW catalyst.

### 4.3. Hydrothermal Conversion of Cellulose

All catalytic reactions were performed in a magnetic stirring stainless steel high-pressure reactor (50 mL). In a typical experiment, 3.0 g of microcrystalline cellulose, 25 mL of deionized water, and 0.3 g of AlW catalyst were added to the reactor, and the reactor was heated to the specified temperature and kept for a period of time under stirring. After the catalytic hydrothermal conversion process, the solid products were separated by filtration, washed with distilled water, and finally dried at 378 K and weighed, while the filtrates were analyzed by HPLC, LC–MS, and LC–MS². The yield of the hydrochar was calculated by dividing the total mass of solid residues by the feedstock. The yields of the unidentified soluble products were calculated by 100% minus the yield of the solid residue and the yield of the identified compounds.
4.4. Quantitative Analysis of the Products by HPCL.

The concentrations of sugars, organic acids (i.e., lactic acid and levulinic acid), and 5-hydroxymethylfurfural were analyzed on an Agilent 1200 series HPLC (Bio-Rad HPX-87H) with an RI and UV detector (210 nm) using a 5 mM aqueous sulfuric acid solution as the eluent at a flow rate of 0.5 mL/min. The column and RI detector temperatures were set at 55 and 45 °C, respectively.4,13

4.5. Identification of the Soluble Products by LC–MS and LC–MS². LC–MS and LC–MS² analyses were performed on an ultrahigh-performance liquid chromatography (UHPLC–Q) instrument (Dionex Ultimate 3000, USA) equipped with a mass spectrometer (Thermo Scientific Q Exactive, USA) with heated electrospray ionization (HESI) in both positive and negative ionization. Accurate mass spectra were recorded across the range from m/z 50 to 5000 by mass spectrometry. The mass axis was calibrated using the mixture provided by the manufacturer in the 4.0 and 3.2 kV for positive and negative modes, respectively.

The column was an Eclipse Plus C₁₈ 250 mm × 4.6 mm, 5 μm particle size. The column temperature was maintained at 25 °C. Mobile phases A and B were water with 0.1% formic acid and methanol, respectively. The system was equilibrated with 95% mobile phase A solution for 3 min, and then a linear gradient progressed from 95% A to 50% A in 17 min after which the mobile phase composition was linearly changed to 5% A and 95% B in the following 5 min and maintained at 5% A for 5 min. The flow rate was 0.6 mL/min, and 5.0 μL of the samples was injected.

4.6. Analysis Process of the LC–MS and LC–MS² Data. The corresponding ion formula of the ion peaks in the MS and MS² spectra were determined by software developed in our lab, and the core structures and the functional groups of the detected compounds were determined through the ion formula.28 The corresponding formulas of ions with m/z at 95.01, 97.03, 107.01, 123.01, and 125.02 were [C₆H₇O₂], [C₇H₇O₂], [C₆H₇O₃], [C₇H₈O₃], and [C₈H₉O₃], respectively, all of which were proposed to contain furanic structures because the DBEs of these ions were no less than 3 and the number of oxygen atoms of those ions was no less than 2. The formulas of ions with m/z at 79.05, 91.05, 93.07, 95.05, 105.07, 107.05, 133.06, and 147.08 were [C₆H₉], [C₇H₇], [C₇H₈], [C₆H₆O], [C₆H₅], [C₆H₄O], and [C₇H₅], respectively, all of which were proposed to contain carbocyclic structures because the DBEs of those ions were no less than 3 and the number of oxygen atoms of those ions was no more than 1. These characteristic ion peaks were used to determine the core structure of the detected compounds. The mass losses of 14.02, 18.01, 26.02, 27.99, 28.03, 30.01, and 43.99 between the ion peaks were ascribed to the losses of CH₂, H₂O, C₆H₅, CO, C₆H₆O, CH₃O, and CO₂, respectively, which were used to determine the functional groups in the detected compounds.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02491.

MS and MS² data of the detected compounds (PDF)

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Notes

The authors declare no competing financial interest.

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