Hydrothermal Process for Increasing Acetic Acid Yield from Lignocellulosic Wastes

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(Received January 25, 2002; CL-020097)

To increase the acetic acid yield in a wet oxidation of lignocellulosic wastes, a new two-step reaction process is proposed. The first step produces 5-hydroxymethyl-2-furaldehyde (HMF) and 2-furaldehyde (2-FA) by dehydration of monosaccharides which are formed by hydrolysis of polysaccharides under the condition of non-supply of oxygen. In the second step, HMF and 2-FA are oxidized to acetic acid with oxygen newly added. The yield increased about twofold.

Acetic acid production by wet oxidation (WO) of various food wastes and lignocellulosic wastes had been investigated to produce calcium/magnesium acetate (CMA)[1] known as an environmentally friendly deicer.[2,3] Results indicate that the yield of acetic acid is limited to only 12–13% on a TOC/TOC basis at most, by a usual wet oxidation procedure.[1] In order to improve the conversion efficiency to acetic acid, other reaction pathways of lignocellulosic wastes in hydrothermal reaction including WO were investigated.

Rice hulls, as a representative of lignocellulosic wastes, and cellulose, as a representative of the main component of lignocellulosic wastes, were used as test materials, as well as glucose as an intermediate product of cellulose by hydrolysis. A 0.07 g (dry base) of test material was used in each run. As an oxidant, liquid H_2O_2 was used. A 100% oxygen supply was defined on the basis of the stoichiometric demand of oxygen for complete oxidation of carbon in the test material to carbon dioxide. Previous studies revealed that an oxygen supply of 100% was sufficient for complete oxidation of lignocellulosic wastes.[4]

All experiments were carried out with a batch reactor system described earlier.[5] For WO, the experimental procedure was as follows: a desired amount of test material and H_2O_2-water were added into a microreactor, and then the reactor was put into a salt bath that had been preheated to a desired temperature. After a certain reaction time, the reactor was removed from the salt bath, and then put into a cold-water bath to quench the reaction.

In a two-step reaction process, which is a new process proposed in this study, the procedure described above was repeated twice. That is, in the first step, only the test material and water were put into the reactor for reaction. After this reaction, H_2O_2 was added to the cooled reactor, and the second step took place.

Experimental conditions are as follows: temperature 280–350 °, reaction time 0.5–6 min, oxygen supply 0–150%, and water fill 30% (70% was also used in the two step reaction of rice hulls). After the reaction was quenched, a solution sample was collected and analyzed by HPLC, GC/MS and ^{1}H-NMR.

Intermediate products in the WO of rice hulls, cellulose and glucose were identified to see the main WO pathway of lignocellulosic wastes. Results of HPLC analysis are shown in Figure 1. Rice hulls, cellulose and glucose show similar results to each other, i.e., many low molecular weight carboxylic acids including acetic acid were identified. These results may suggest the main WO pathways of cellulose/lignocellulosic wastes as shown in Figure 2(A). That is to say, cellulose and lignocellulosic wastes are first hydrolyzed to monosaccharides (mainly glucose) and then the oxidation of monosaccharides takes place. Oxidation of monosaccharides leads to the formation of both monocarboxylic acids and dicarboxylic acids, because the treatment of monosaccharides with a more vigorous oxidizing agent brings about the oxidation of not only the –CHO group but also the –CH_2OH group.

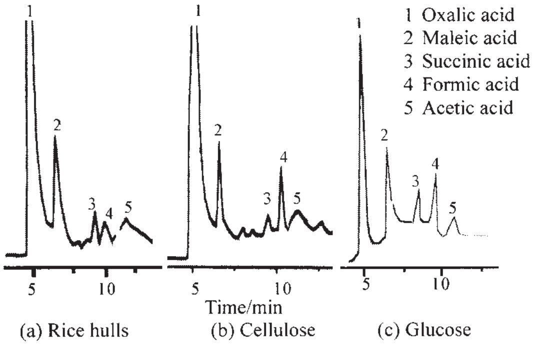

Figure 1. HPLC chromatograms of intermediate products for oxidation of rice hulls, cellulose and glucose at 300 °C, 1 min of reaction time and 100% oxygen supply (UV detection at 210 nm).

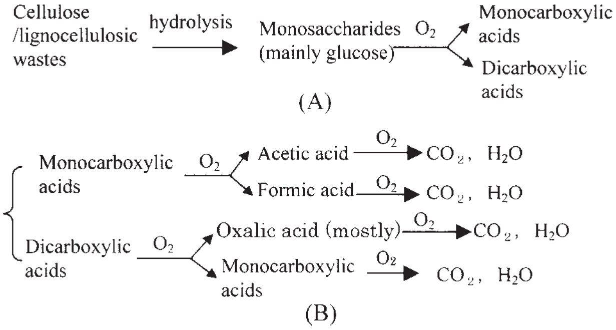

Figure 2. Reaction pathways for oxidation of cellulose/lignocellulosic wastes.

The oxidation of monocarboxylic acids and dicarboxylic acids may proceed as shown in Figure 2(B). When the oxidation of monocarboxylic acids takes place, acetic acid and formic acid are formed as final organics, while for the oxidation of dicarboxylic acids, either lower molecular weight monocarboxylic acids or dicarboxylic acids are formed. Our quantitative analysis showed that the concentration of oxalic acid was overwhelmingly high, and additional experiments also showed that oxalic acid was easily decomposed to CO_2 and H_2O by WO, so that the total amount of oxalic acid produced could be much more than that we expected from the analytical data. This indicates that the formation of dicarboxylic acid takes precedence over the formation of monocarboxylic acids.

From the discussion above, it is understandable that the conversion efficiency of acetic acid from cellulose/lignocellulosic wastes is hardly improved by changing the reaction condition in conventional WO, because WO of cellulose and lignocellulosic wastes easily forms dicarboxylic acids, only a little of which is decomposed to form monocarboxylic acids by further oxidation. Therefore, in order to increase the acetic acid yield, oxidative decomposition pathways via dicarboxylic acids should be avoided. In other words, direct oxidation of monosaccharides should be inhibited.

In order to find some intermediate products, which can form a large amount of monocarboxylic acids rather than dicarboxylic acids by their oxidation, decomposition experiments were performed with a lower oxygen supply. Large quantities of 5-hydroxymethyl-2-furaldehyde (HMF) and 2-furaldehyde (2-FA) were detected in all cases (Figure 3). It was also found that the oxidation of HMF and 2-FA forms acetic acid as well as formic acid, and oxalic acid was not detected in their oxidation reaction (Figure 4).

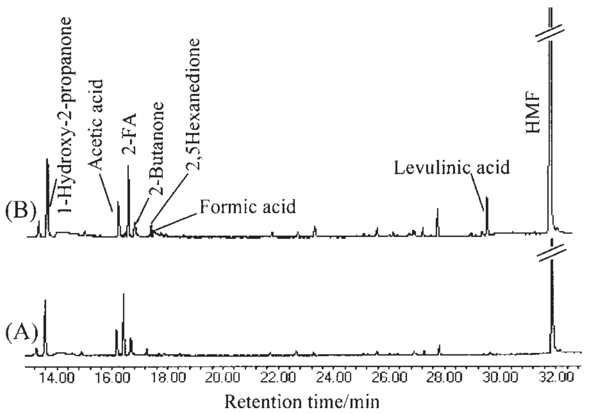

Figure 3. GC/MS chromatograms for glucose (A) and cellulose (B) after reaction at 300 °C and 1 min for glucose, 2 min for cellulose.

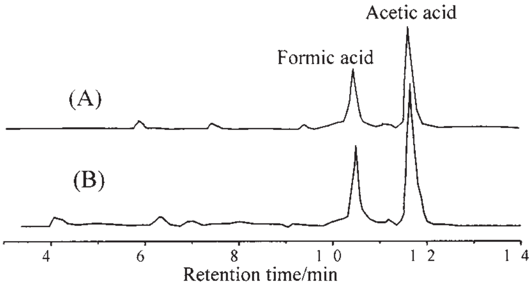

Figure 4. HPLC chromatograms of liquid samples after oxidation of HMF (A) and 2-FA (B) at 300 °C for 1 min and with 100% oxygen supply (UV detection at 210 nm).

It is generally known that, on heating with or without acid, hexoses undergo dehydration and cyclization to form HMF while pentoses form 2-FA. But 2-FA, as well as HMF, has been reported as a product of dehydration of glucose, although the amount of 2-FA is less.[6] In the present study, a relatively large amount of 2-FA, about a half of HMF, was produced.

Other products such as 1-hydroxy-2-propanone, which is a thermal decomposition product of glucose, levulinic acid, which is a rehydration product of HMF, 2-butanone and 2,5-hexanedione were also detected as shown in Figure 3. They also form monocarboxylic acids by oxidation, although their amounts are small.

On the basis of these results, a new two-step reaction process for promoting acetic acid production is proposed, as shown in Figure 5. In the first step, cellulose/lignocellulosic wastes are hydrolyzed to monosaccharides, which subsequently undergo dehydration to form HMF and 2-FA under the condition of nonsupply of oxygen. In the second step, the HMF and 2-FA produced are further converted to acetic acid by oxidation with newly added oxygen.

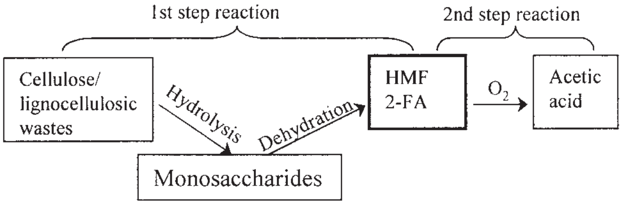

Figure 5. Two-step reaction process proposed for production of more acetic acid.

To obtained better conditions for producing HMF and 2-FA from cellulose in the first step and then converting the HMF and 2-FA into acetic acid in the second step, the first step experiments were performed using cellulose at temperatures between 280 and 370 °C and reaction time from 30 s to 6 min, and the second step experiments with HMF and 2-FA as test material at temperatures between 280 and 370 °C, reaction time from 30 s to 6 min and oxygen supply from 50 to 130%. Conditions so far obtained as optimum are as follows: temperature 300 °C and reaction time 2 min for the first step, and temperature 300 °C, reaction time 1 min and oxygen supply 70% for the second step.

Under the conditions mentioned above, rice hulls were treated in the two-step reaction process. Results showed that the acetic acid yield obtained in the two-step reaction was approximately twice that obtained by the usual WO procedure (Table 1).

Table 1. Comparison of acetic acid yields[a] by a conventional wet oxidation (WO) and a two-step reaction proposed in this study

		Conventional WO	Two-step reaction	
			1[#]	2[#]
Cellulose/%		8.6	16.2	
Rice hulls/%		12.7	21.2	20.1
Reaction condition	Temp./°C	300	*300*[b], **300**	*300*[b], **300**
	Time/min	1	*2*[b], **1**	*2*[b], **1**
	O_2 supply/%	70	*0*[b], **70**	*0*[b], **70**
	Water fill/%	30	*30*[b], **70**	*70*[b], **70**

[a]TOC/TOC from starting material. [b]Italic and bold figures correspond to conditions in the first and second steps, respectively.

References and Notes

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