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Note

Impact of phenolic compounds on hydrothermal oxidation of cellulose

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Abstract—The effect of phenolic compounds on hydrothermal oxidation of cellulose was studied using a batch reactor at 300 °C with H_2O_2 as oxidant. Intermediate products, as well as the yields of acetic acid produced in the oxidation of cellulose, phenolic compounds, and cellulose–phenolic compound mixtures were examined. Phenolic compounds used were phenol, 1,4-benzenediol, 2-methoxy-4-methylphenol, and 2,6-di-*tert*-butyl-4-methylphenol. In the case of oxidation of cellulose–phenolic compound mixtures, (1) formic acid, a basic oxidation product from carbohydrates, decreased considerably, (2) 5-hydroxymethyl-2-furaldehyde and 2-furaldehyde, acid-catalyzed dehydration products from carbohydrates, appeared, and (3) the yield of acetic acid increased compared to that in the oxidation of cellulose. From these results, phenolic compounds seem to inhibit the oxidation of cellulose under hydrothermal conditions. The inhibition of the oxidation of cellulose by phenolic compounds seems to be related closer to the stability of phenolic compounds under oxidation conditions rather than the ease to remove phenolic hydrogen on the OH group.

Keywords: Cellulose; Lignocellulosic biomass; Rice hulls; Sawdust; Oxidation inhibitor; Hydrogen peroxide; Acetic acid; Formic acid

There have been extensive studies on the application of high temperature water, particularly near-critical water at temperatures from 200 to 374 °C, as a reaction medium for biomass recycling and organic waste destruction.[1,2] Few studies have examined the interaction between the main components of natural materials, such as cellulose and lignin in lignocellulosic biomass. Our study[3] on the conversion of lignocellulosic biomass into acetic acid by hydrothermal oxidation showed that acetic acid yields by partial oxidation of lignocellulosic biomass of rice hulls and sawdust were higher than those for cellulose or lignin itself, indicating that there were interactions between cellulose and lignin.

Lignin is a complex phenylpropane polymer that can be easily broken down into phenol and phenol derivatives (phenolic compounds) in hydrothermal oxidation. Phenolic compounds are widely used as oxidation inhibitors in food chemistry. Phenolic compounds act as inhibitors in the oxidation of many organic compounds in low temperatures.[4–8] Therefore, phenolic compounds could have an inhibiting role in the oxidation of cellulose in hydrothermal oxidation of lignocellulosic biomass. The inhibiting role of phenolic compounds in the oxidation of organics, however, remains poorly understood under hydrothermal conditions.

In the present study, intermediate products were identified in the oxidation of cellulose, phenolic compounds and cellulose–phenolic compound mixtures. In preparing the mixtures, the mixing ratio of a phenolic compound is defined as the weight percent of the phenolic compound against the sum of cellulose and phenolic compound.

Figures 1 and 2 show the GC/MS chromatograms for experiments at 300 °C for 2 min with a 70% oxygen

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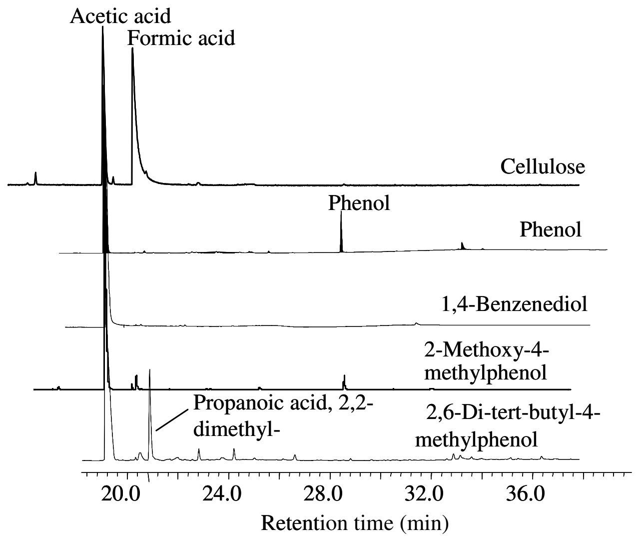

Figure 1. GC/MS chromatograms for solutions after oxidation for cellulose and phenolic compounds at 300 °C for 120 s with 70% oxygen supply.

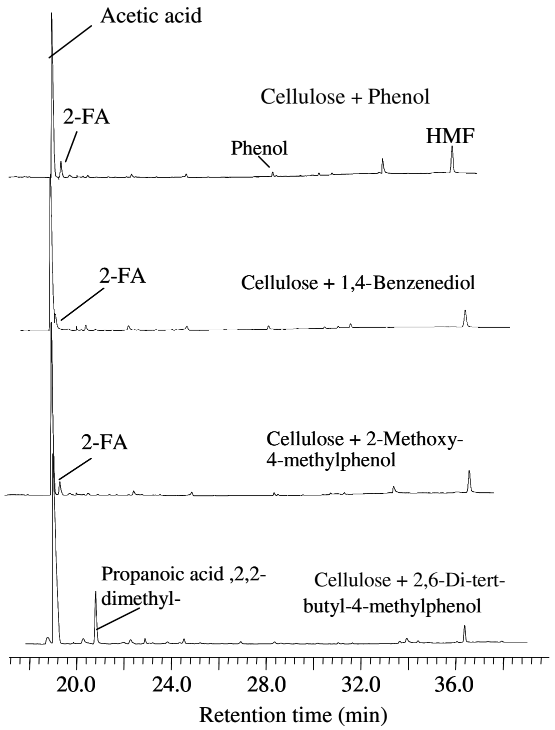

Figure 2. GC/MS chromatograms for the solutions after oxidation for the mixtures with the mixing ratio of phenolic compounds of 20% at 300 °C for 120 s with 70% oxygen supply. (The mixing ratio of phenolic compounds: the weight percent of phenolic compounds against the sum of cellulose and phenolic compounds.)

supply. It is seen in Figure 1 that the oxidation of cellulose gave formic and acetic acids and the oxidation of four phenolic compounds gave acetic acid as the major product(s). However, in the case of oxidation of the mixtures shown in Figure 2, two differences can be noticeably seen compared with the case shown in Figure 1. First, the amount of formic acid decreased considerably and second, two new products of 5-hydroxymethyl-2-furaldehyde (HMF) and 2-furaldehyde (2-FA) were detected. Because formic acid is a basic oxidation product from carbohydrates[3,9] and it is generally known that HMF and 2-FA are typical acid-catalyzed dehydration products from carbohydrates but are seen in the solution after hydrothermal treatment of carbohydrates without any catalyst,[3,9] the decrease of formic acid and the appearance of HMF and 2-FA may provide evidence that phenolic compounds could have a inhibiting role in the oxidation of cellulose. The formation of HMF and 2-FA would lead to an increase in acetic acid production because direct oxidation of carbohydrates yields little acetic acid,[3] while the oxidation of HMF and 2-FA can produce a large amount of acetic acid.

A series of oxidation experiments were performed for varying the mixing ratio between 0% and 100%. Figure 3 shows the yield of acetic acid from the mixtures against the mixing ratio of phenolic compounds. The acetic acid yield is defined as the percentage of the amount of carbon in the acetic acid produced against that in the starting material. As shown in Figure 3, the acetic acid yield from the mixtures obtained experimentally lies above the straight-dashed line AB discussed below. The increment of acetic acid yield is the largest when the mixing ratio of phenolic compounds is around 20%, and is very small when the mixing ratio becomes larger than 50%, and shows the possibility that phenolic compounds may have a inhibiting role in the hydrothermal oxidation of cellulose and the hydrothermal oxidation of phenolic compounds may not be affected by cellulose. If these phenolic compounds have no influence on the oxidation of cellulose, the acetic acid yield from the mixtures should lie on a straight-dashed line connecting both points at the mixing ratio of 0% and 100% (dashed line AB).

Another possibility for the increase in acetic acid yield is supposed to be due to the inhibiting effect of phenolic compounds on the oxidative destruction of acetic acid. To examine this possibility, oxidation experiments using CD_3COOD with and without phenol were performed at the same reaction conditions as that mentioned above but with a 30% oxygen supply. The oxygen supply of 30% was chosen because the oxidation of acetic acid occurred at a later stage of the oxidation of cellulose, where the remaining oxygen became less. The amount of residual CD_3COOD after the oxidation of CD_3COOD when mixed with phenol was determined by the difference between the total amount of CH_3COOH and CD_3COOD measured by GC/FID and the amount of CH_3COOH measured by ^1H NMR analyses. CH_3COOH is thought to be the product from phenol. Results showed that the remaining CD_3COOD when mixed with phenol was 90.7%, while 88.2% remained without phenol. From these results, phenolic

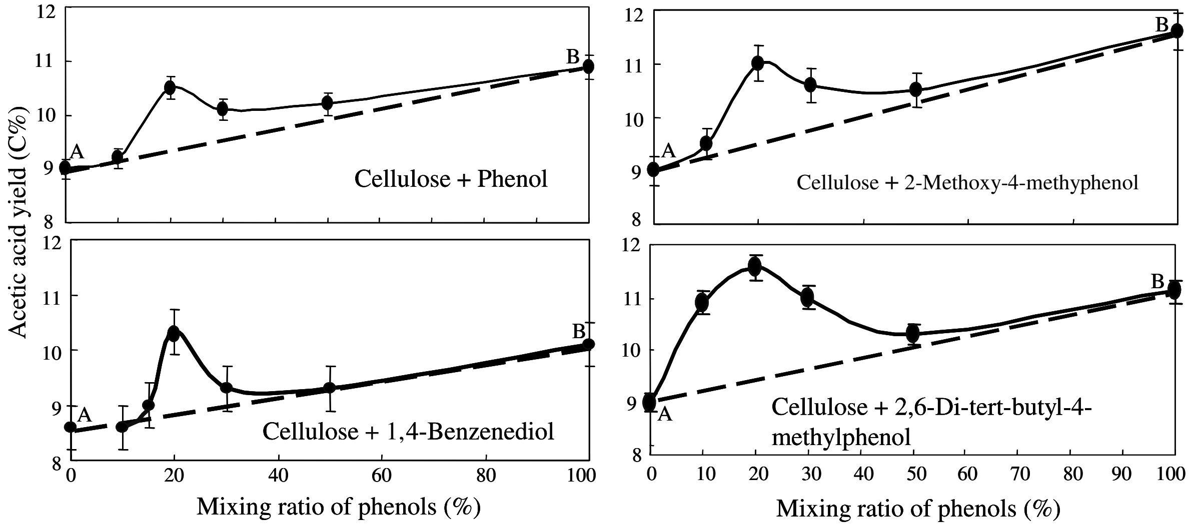

Figure 3. Acetic acid yield against the mixing ratio of phenolic compounds in the case of the oxidation of cellulose–phenolic compounds mixtures at 300 °C for 120 s with 70% oxygen supply. (The definition of the mixing ratio of phenolic compounds is same as that in Fig. 2.)

compounds may also have an inhibiting role in the oxidation of acetic acid. However, the inhibiting effect for acetic acid is not obvious, possibly due to its stability. Therefore, it can be concluded that an increase in acetic acid yield when adding phenolic compounds to cellulose is mainly attributed to the action of phenolic compound inhibiting the direct oxidation of cellulose.

The inhibiting effect of phenolic compounds is discussed by examining the acetic acid yield in the oxidation of mixtures. As can be seen in Table 1, the order of magnitude for both the area surrounded by the dashed line AB and the solid line experimentally obtained and the highest acetic acid yield follows the sequence of 2,6-di-*tert*-butyl-4-methylphenol, **4** > 2-methoxy-4-methylphenol, **3** > phenol, **1** > 1,4-benzenediol, **2**. This means that the inhibiting effect of **4** is probably the strongest, followed by **3** with **2** being the weakest. It is generally known that the mechanism of oxidation inhibition by phenolic compounds at low temperatures is mainly because phenolic compounds react very rapidly with peroxy radicals because of the low energy requirement to remove the hydrogen of ArO–H. Thus, substituents raising the electron density of the aryl ring generally decrease the energy of rupture of the ArO–H bond, making the phenolic compounds a more effective inhibitor. If the mechanism of inhibition by phenolic compounds in hydrothermal oxidation is similar to that at low temperatures, the order of retarding effectiveness among them would be expected to follow the sequence of **4** > **3** > **2** > **1**. Similar trends have been reported in the oxidation of some organics at low temperature.[4–8] The order of **4** and **3** in our experiments is the same as that reported for oxidation at low temperatures, but the order of **2** and **1** is difference from that observed at low temperatures. A possible explanation would be as follows.

In hydrothermal oxidation, the inhibiting effect of phenolic compounds on the oxidation of cellulose should be also critically dependent upon the stability against their oxidative decomposition, because phenolic compounds themselves are rather easily decomposed to yield open-ring products which play no inhibiting role any more. Our experiments showed that the order of the remaining amount of four phenolic compounds after their reaction was **4** > **3** > **1** > **2** with the remaining ratio being 5.9:3.5:2.4:1.0. This order was the same as that observed for inhibition effect. The order of instability of **2** > **1** is most likely caused by the fact that **2** has one more OH group of electron donation than **1**.

On the basis of these result and general radical oxidation mechanism of organics at low and high temperatures,[3,4,10] it may be expected that the oxidative destruction of 1,2,3-benzenetriol, **5**, would be easier than **2**, thus, leading to its low retarding effectiveness at high temperatures, although **5** is a strong inhibitor in liquid oxidation of many organics at low temperatures. Further experiments using **5** and **2** at 300 °C for 30 s with a 50% oxygen supply showed that the decomposition of **5** and **2** were 93% and 86%, respectively, and the inhibiting effect of **5** was not observed in the oxidation

Table 1. Relative area surrounded by the dashed line AB and the solid line, and the highest yield of acetic acid shown in Figure 3

	Phenol	1,4-Benzenediol	2-Methoxy-4-methylphenol	2,6-Di-*tert*-butyl-4-methylphenol
Area	1.4	1.0	2.0	3.3
Yield[a] (%)	10.7	10.7	11.0	11.6

[a] Percentage on carbon base.

of a mixture of cellulose and **5** at the same oxidation condition described above.

From these results, in hydrothermal oxidation, the inhibiting effect of phenolic compounds is probably dependent predominantly upon their stability against their oxidative decomposition rather than the ease to remove phenolic hydrogen on the OH group.

1. Experimental

1.1. Chemicals and materials

Phenol **1**, 1,4-benzenediol **2**, 2-methoxy-4-methylphenol **3**, 2,6-di-*tert*-butyl-4-methylphenol **4**, and 1,2,3-benzenetriol **5** of reagent grade (99.9% purity) were used. All chemicals used were obtained from Wako Pure Chemicals Industries Ltd, Tokyo. Cellulose was a filter paper powder (under 200-mesh, Toyo Roshi Kaisha, Ltd.). A H_2O_2 solution was used as the oxidant for experimental convenience. The stoichiometric demand of oxygen for complete oxidation of carbon in the starting material(s) to CO_2 was defined as a 100% oxygen supply.

1.2. General procedures

All experiments were performed using a batch reactor consisting of SUS 316 tubing.[10,11] The typical reaction procedure was as follows.[10,11] The desired amount of test material and a H_2O_2–water mixture of 3.4 cm^3 providing a 60% water fill were put into the reactor, which was then put into a salt bath preheated to 300 °C. After the desired reaction time, the reactor was quickly cooled in a cold water bath.

1.3. Products analyses

1.3.1. GC/MS/FID analysis. A Hewlett-Packard model 5890 Series II Gas Chromatograph with a HP-INNOWAX column equipped with a model 5890B Mass Selective Detector was used. Quantitative data of acetic acid were obtained with a GC/FID and were the average of 5 sample analyses.

1.3.2. ^1H NMR analysis. ^1H NMR measurement was limited to only the samples after the oxidation of CD_3COOD with the addition of phenol. The solution sample after reaction and a capillary tube filled with benzene as an external reference for determining the concentration of acetic acid were put into a 5 mm i.d. NMR tube for ^1H NMR analyses. NMR spectra were recorded on a JEOL JNM-LA300 spectrometer. More details about the conditions for GC/MS and NMR analyses are available elsewhere.[10,11]

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