# Effect of Lignin on Acetic Acid Production in Wet Oxidation of Lignocellulosic Wastes

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The role of lignin in acetic acid production in wet oxidation (WO) of lignocellulosic biomass was discussed. It was found that lignin was indirectly attributed to the increase of acetic acid production in WO of lignocellulosic waste. A possible mechanism for this is that decomposition intermediates of lignin would act as a retardant in WO of cellulose, leading to the formation of HMF and 2-FA which are dehydration products from monosaccharides and can produce a large amount of acetic acid by their oxidation.

Our study[1] on the conversion of lignocellulosic biomass into acetic acid by wet oxidation (WO) showed that the acetic acid yields by partial WO of rice hulls and Japan cedar sawdust were higher than those of cellulose and lignin, which were their main components (see Table 1). It was also shown that the acetic acid yield from the rice hulls, in which the content of lignin was lower, was the highest. These may imply that lignin most likely affects the reaction of cellulose to produce acetic acid. In this study, the effect of lignin on the acetic acid production in WO treatment of lignocellulosic waste was investigated.

The cellulose used was a filter paper powder (larger than 200 mesh in size) obtained from Wako Chemicals, and the lignin was a reagent lignin, alkali ($M_w = 28000$, $M_n = 5000$) obtained from Aldrich Chemical Co. A $H_2O_2$ solution was used as the oxidant. The stoichiometric demand of oxygen for complete oxidation of carbon in the raw material(s) to $CO_2$ was defined as the 100% oxygen supply. All experiments were carried out with a batch reactor made of SUS 316 with an internal volume of 5.7 $cm^3$, described earlier.[2] Briefly, the desired amount of test material and $H_2O_2$–water mixture of 3.4 $cm^3$ (60% water fill) were added into the reactor, and the sealed 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 put into a cold-water bath to quench the reaction. The definition of reaction temperature and reaction time was described earlier.[2,3] After the reaction, a solution sample was collected and analyzed by GC/MS, $^1$H NMR and $^2$H NMR.

To investigate whether or not and/or how lignin affects the production of acetic acid in WO of lignocellulosic biomass, WO experiments of cellulose with lignin as a mixture were carried out under the condition where the highest acetic acid yield was obtained for all of rice hulls, sawdust and cellulose, that is, the reaction temperature of 300 °C, reaction time of 2 min and oxygen supply of 70% (see Table 1). The mixing ratio of cellulose and lignin was set at 8:2 and 5:5. The ratio of cellulose and lignin in rice hulls was approximately 8:2. The results are shown in Table 2. Here, acetic acid yield is defined as the carbon percent based on that of initial material(s). By comparing with the results shown in Table 1, it can be seen that in the case of a mixture of lignin and cellulose, the acetic acid yield became higher than that in the cases of cellulose and lignin, and that the acetic acid yield with mixing ratios of 8:2 and 5:5 are almost the same as those with rice hulls and sawdust, respectively. These results clearly indicate that lignin plays an important role in the production of acetic acid increasing in WO of cellulose. Lower acetic acid yields in both cases of sawdust and a mixture with a mixing ratio of 5:5 are possibly due to the lower acetic acid yield by WO of lignin itself.

**Table 1.** Acetic acid yield from lignocellulosic biomass, cellulose and lignin

| Material | Acetic acid yield/%[a] |
|---|---|
| Cellulose | 9.0 |
| Lignin | 6.3 |
| Rice hulls | 11.7 |
| Sawdust | 9.7 |

[a] Carbon in acetic acid/Carbon in initial material Reaction temp.: 300 °C, Reaction time: 2 min, Oxygen supply: 70%

Next, intermediate products of solution samples after WO for cellulose, lignin, and a mixture of cellulose and lignin with a mixing ratio of 8:2 were analyzed by GC/MS, to study how lignin works to increase the acetic acid yield. From Figure 1A, it can be seen that the intermediate products were mainly acetic and formic acids in the case of cellulose. A small amount of phenol was formed in the case of lignin as well as acetic and formic acids. However, in addition to acetic acid, formic acid and phenol, 5-hydroxymethyl-2-furaldehyde (HMF) and 2-furaldehyde (2-FA) were formed in the case of the mixture. The peaks of HMF were very high. It is generally known that HMF and 2-FA are not oxidation products but are typical dehydration products of mono-

**Table 2.** Acetic acid yield by WO of mixture of cellulose and lignin

| Mixing rate | Acetic acid yield/%[a] |
|---|---|
| 8:2 (cellulose:lignin) | 11.1 |
| 5:5 (cellulose:lignin) | 10.7 |

[a] Carbon in Acetic acid/Carbon in initial material
Reaction temp.: 300 °C, Reaction time: 2 min, Oxygen supply: 70%

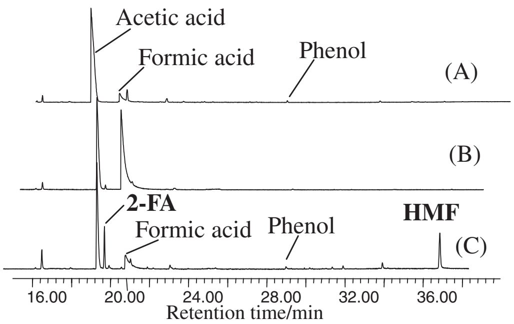


**Figure 1.** GC/MS chromatograms of samples after reaction at 300 °C, 2 min and 70% oxygen supply for lignin (A), cellulose (B) and a mixture of cellulose and lignin with the mixing ratio of 8:2 (C) (Column:HP-INWAX(30 m × 0.25 mm × 0.25 μm)).

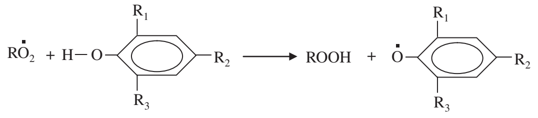
saccharides in a hydrothermal reaction. Our previous study[4] indicated that HMF and 2-FA were intermediates that could produce a large amount of acetic acid by their oxidation. It may be considered that adding lignin to cellulose could result in the formation of HMF and 2-FA, leading to the higher yield of acetic acid.

The mechanism of the formation of HMF and 2-FA, when adding lignin to cellulose, was discussed. Lignin is a complex phenylpropanoid polymer, which is easily broken down into phenol derivatives by WO. Phenols are widely used as oxidation inhibitors in the food chemistry. Emanuel et al.[5] reported that phenols also acted as an inhibitor in the oxidation of hydrocarbons in the liquid phase. The mechanism of inhibition by phenols is described as follows:

The oxidation of organic compounds takes place with the participation of peroxy radicals. The rate of oxidation, $r = k [RH] [ROO^{\bullet}]$, is determined by the concentration of peroxy radicals, $ROO^{\bullet}$. If AH added to the system reacts with the peroxy radicals forming radicals of low activity $A^{\bullet}$, the compound AH will inhibit the oxidation process of organic compounds.

$$ROO^{\bullet} + AH \rightarrow ROOH + A^{\bullet}$$

The retarding action of an inhibitor added to a substance undergoing oxidation is dependent on two factors: (1) the rate of reaction of the peroxide radicals with the inhibitor and (2) the activity of the radicals $A^{\bullet}$ (the lower the activity of $A^{\bullet}$, the greater the inhibiting effect). For phenols, (1) it reacts very rapidly with peroxy radicals because of the low energy required to remove the hydrogen located at the alpha position to a double bond and (2) the phenoxy radical generated is much less active than peroxy radicals because of resonance stabilization, so, phenols are considered to be an effective inhibitor against oxidation. As shown below, the mechanism of inhibition by phenols consists of the abstraction of a hydrogen atom from the phenol molecule by the peroxy radical to form a phenoxy radical that hardly propagates the chain.



As mentioned above, although it is known well that phenols play an inhibiting role in the oxidation of hydrocarbons in the liquid phase in a relatively lower temperature range of 50 to 200 °C, it is not well understood how actively phenols play the inhibiting role in WO of organic waste at high temperatures and pressures, and whether or not decomposition intermediates of lignin can work as a retardant. Considering that lignin is easily decomposed into a large number of phenols in WO, and assuming that phenols also can play the retarding role in WO of cellulose, an addition of lignin to cellulose would result in the formation of HMF and 2-FA. The mechanism may be explained as follows:

In general, in the WO reaction of cellulose, there are various competing reaction pathways, each of which is favored by different conditions. When the oxygen supply is sufficient, oxidation reaction takes place over other reactions such as hydration and dehydration, because the rate of oxidation reaction is much more rapid than other reactions. However, when decomposition intermediates of lignin as oxidation retardants exist with cellulose, the rate of oxidation reaction of cellulose will decrease, while other reactions will proceed. Because cellulose easily forms HMF and 2-FA, which are dehydration products of monosaccharides by hydrothermal treatment without an oxygen supply as reported in our previous study,[4] they would be easily formed when adding lignin to cellulose. In other words, the formation of HMF and 2-FA may indicate that decomposition intermediates of lignin makes peroxide radicals transfer to inactive radicals in WO of cellulose when adding lignin to cellulose. Supplemental experiments with phenylpropane, *p*-phenoxyphenol, and 2-methoxy-4-methylphenol, as well as phenol, showed the similar result to that with lignin (data not shown). This means that decomposition intermediates of lignin would play a retarding role for the oxidation of cellulose in WO at a high temperature and pressure and the retarding mechanism would be the same as the known-inhibition mechanism in the liquid oxidation of hydrocarbons at a lower temperature.

Moreover, if decomposition intermediates of lignin plays a retarding role in WO of lignocellulosic waste, lignin may also retard the oxidation of acetic acid, which also leads to an increase in acetic acid yield to some extent. To investigate whether lignin retards the oxidation of acetic acid, WO experiments of deuterated acetic acid $C_3DCOOD$ with and without lignin were performed at the same reaction temperature and time described above but with a 30% oxygen supply. Considering that the oxidation of acetic acid takes place at the later stage of the oxidation reaction of cellulose, where the remaining oxygen becomes much less, a 30% oxygen supply on the basis of oxidation of both cellulose and lignin was used. Use of $C_3DCOOD$ can possibly help to estimate the degree of decomposition of acetic acid in the case of adding lignin because WO of lignin also produces acetic acid. The residual concentration of $C_3DCOOD$ and $CH_3COOH$ after WO of $C_3DCOOD$ with and without the addition of lignin was determined by $^1$H NMR and $^2$H NMR analyses. Results showed that the decomposition efficiency of $C_3DCOOD$ when adding lignin was about 10.2%, which is slightly lower than that (11.8%) without lignin. Slightly lower acetic acid decomposition may also occur if most of the oxygen is consumed in the oxidation of lignin. However, this is unlikely since the acetic acid concentration obtained by $^1$H NMR analysis, that is, acetic acid produced by the oxidation of lignin, was quite low. These results may indicate that decomposition intermediates of lignin also plays a retarding role in the oxidation of acetic acid, though the retarding action for acetic acid is not very obvious, possibly because acetic acid is a stable compound against oxidation. Therefore, it may be concluded that the high yield of acetic acid with a lignocellulosic biomass and an increase in acetic acid yield when adding lignin to cellulose are mainly attributed to the formation of HMF and 2-FA resulting from the retardant action of decomposition intermediates of lignin in WO. In addition, lignin itself as a chemical could also act as an oxidation retardant, because there is no evidence which denies this act, as so far discussed.

These results may also imply that lignin plays an important role in WO treatment for complete oxidative destruction of organic mixtures with a lignocellulosic biomass.

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