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Wet oxidation of lignin model compounds and acetic acid production

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To investigate the wet oxidation (WO) pathways of acetic acid production from lignin, 2-methoxyphenol, 2,6-dimethoxyphenol, and phenol, as lignin model compounds were oxidized in a batch reactor at a temperature of 300°C, residence times of 10–60 seconds and oxygen supplies of 50–100%. Oxidation experiments using major intermediate products in WO of lignin model compounds, as reactants were also performed.
Based on the intermediate products identified by GC/MS and HPLC, WO pathways of lignin model compounds are discussed. Acetic acid production by WO of lignin model compounds is also discussed. It was found that the yield of acetic acid for lignin model compounds was lower, at about 9%. The reason that lignin model compounds cannot produce a large amount of acetic acid may be contributed to the fact that the oxidation of phenols easily forms unsaturated dicarboxylic acids with 4 carbon atoms, which cannot produce a large amount of acetic acid. However, saturated dicarboxylic acids and glutaconic acid can produce a higher yield of acetic acid. Therefore, it is possible to increase the yield of acetic acid from lignin by controlling reaction pathways to increase the formation of saturated dicarboxylic acids and glutaconic acid.

1. Introduction

The potential to use biomass as a source of useful chemicals and fuel has been a subject of renewed interest recently in response to depletion of fossil resources. In order to realize the use of biomass, various ways to convert biomass have been used such as pyrolysis, acid hydrolysis, and enzymatic hydrolysis. Beside these ways, wet oxidation (WO) is receiving increased attention in the use of biomass wastes. WO is a process in which organics in aqueous solution or as a suspension are oxidized by oxygen under high temperature (about 150–350°C) and pressure (about 6–17MPa) conditions. Because water under these conditions possnesses outstanding properties as a reaction medium, WO treatment has been recognized as being most effective. The conversion of a variety of organics to chemicals by WO has been examined by a number of investigators. We also have carried out investigations on the conversion of biomass to acetic acid. Some of the reasons why the conversion of biomass to acetic acid is targeted are that acetic acid is a useful chemical for production of an environmentally friendly deicer and our previous results showed that acetic acid was a stable and highly recoverable intermediate product for almost all organic wastes [1–3].

In our previous studies on the conversion of biomass to acetic acid, the conversion of cellulosic biomass to acetic acid was mainly investigated [3, 4]. In this paper, lingo-cellulosic biomass, consisting mainly of cellulose and lignin, is the target material to be converted to acetic acid. Lignin is not only a main composite of lignocellulosic biomass but also the second most abundant natural product after cellulose. To get a high yield of acetic acid, studies on the mechanism of acetic acid production from lignin are needed. The purposes of this study are to study the WO mechanism of lignin, and to get a high yield of acetic acid by WO of lignin.

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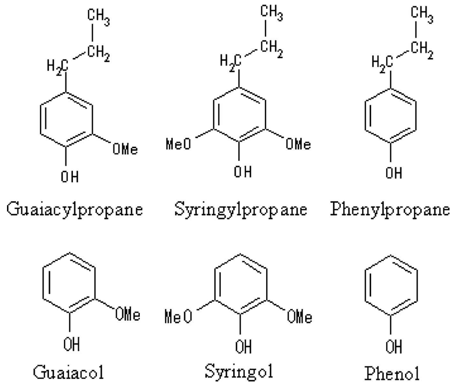


Figure 1 Basic structures of lignin and the adopted lignin model compounds in this study.

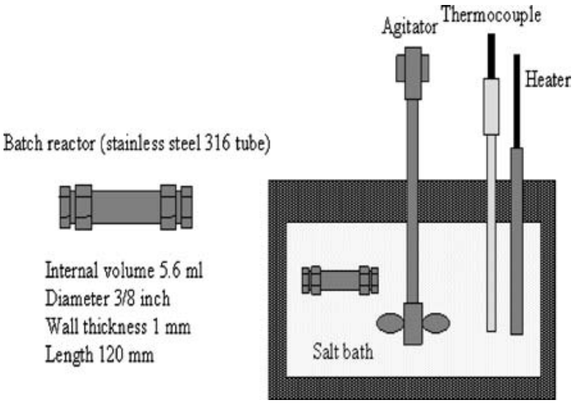


Figure 2 Experimental apparatus.

Lignin is a complex phenylpropanoid polymer, and the structure of lignin varies with the kind and locality of the biomass. Therefore, using lignin as a reactant may not be appropriate [5, 6]. In this work, we used phenol and substituted phenols as model compounds of lignin.

2. Experimental methods

2.1. Materials

Lignin is a highly cross-linked hydroxylated and methoxylated phenylpropane polymer, and mainly consists of guaiacyl propane, syringyl propane, and phenyl propane structures. Therefore, guaiacol (2-methoxyphenol), syringol (2,6-dimethoxyphenol) and phenol were selected as lignin model compounds. Their structures are shown Fig. 1. Besides the three lignin model compounds, some materials which are intermediate products in WO of guaiacol, syringol, and phenol were also used as test materials.

2.2. Experimental procedure

All test materials were oxidized in a batch reactor with an internal volume of 5.6 mL, constructed of a piece of stainless steel 316 tubing (3/8 inch diameter, 1 mm wall thickness, and 120 mm length) at a temperature of 300°C, reaction times of 10–60 s, and oxygen supplies of 50–100%. The experimental apparatus is shown in Fig. 2.

H_2O_2 diluted with water was used as an oxidant. The stoichiometric demand of oxygen for complete oxidation for each test material to CO_2 and H_2O was defined as the 100% oxygen supply. To keep the reaction can be carried out in one phase, water fill was fixed at 60%, which was defined as the ratio of the volume of water and H_2O_2 put into the reactor and the inner volume of the reactor.

The typical reaction procedure was as follows: The desired amount of a test material and H_2O_2-water mixture was put into the reactor, which was then sealed. The reactor was heated up to a desired temperature in a preheated salt bath and was shaken during reaction. After the desired reaction time elapsed, the reactor was removed from the salt bath and put into a cold water bath to quench the reaction. The reaction time was defined as the time at which the reactor was maintained in the salt bath. A detailed description is available elsewhere [1].

2.3. Analytical methods

Liquid samples after reaction were analyzed by high-performance liquid chromatography (HPLC) and gas chromato-graphy/mass spectroscopy (GC/MS). Details on the conditions for GC/MS and HPLC analyses are available elsewhere [2]. For HPLC analysis, peak identification was accomplished by comparing sample peak retention times with those of standard solutions of pure compounds. For GC/MS analysis, identification of intermediate products was made with the total and selected ion chromatograms with the aid of a computer library as well as the GC retention times.

3. Results and discussion

3.1. Identification of intermediate products

3.1.1. Intermediate products from lignin model compounds

Identification of the intermediate products is an essential prerequisite in an investigation of any reaction mechanism of organics. Thus, intermediate products after reaction for three lignin model compounds were identified in detail by GC/MS, HPLC. Fig. 3 displays the GC/MS chromatograms of liquid samples obtained at a temperature of 300°C, a reaction time of 60 s, and an oxygen supply of 50%. A lower oxygen supply is helpful to easily get the initial oxidation products. As shown in Fig. 3, in the case of guaiacol, 1,2-benzenediol and 2-methoxy-1,4-benzenediol were identified as major intermediate products. In the case of syringol, 3-methoxy-1,2-benzenediol and 2,6-dimethoxy-1,4-benzenediol were detected as major intermediate products. With phenol, major products detected were 1,2-benzenediol and 1,4-benzenediol.

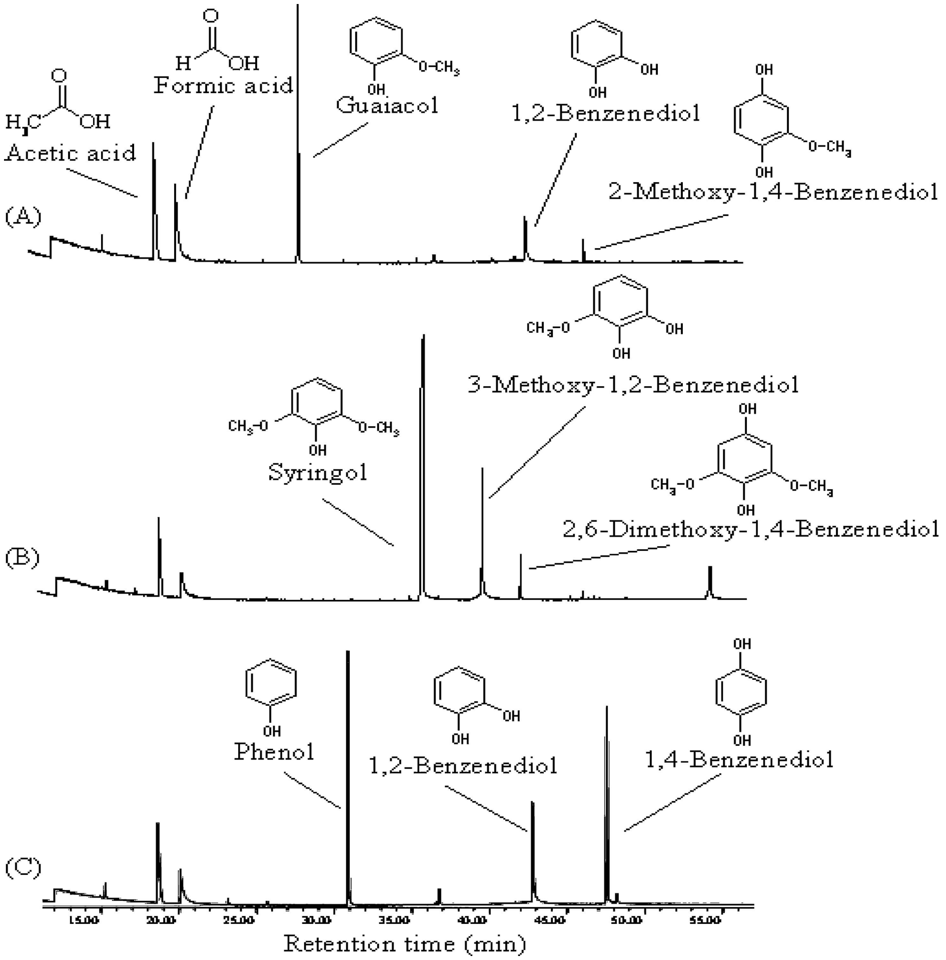


Figure 3 HPLC chromatograms of the oxidation products for lignin model compounds at a temperature of 300%C reaction time 60 s, and oxygen supply 70%. (A: Guaiacol, B: Syringol, C: Phenol)

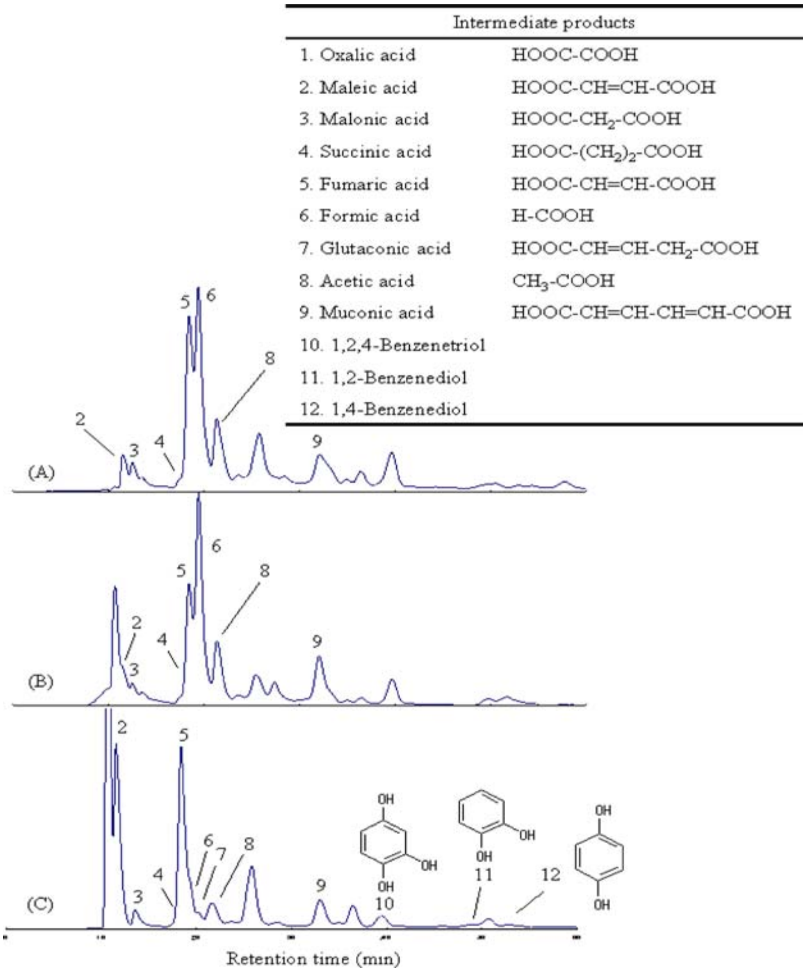
Beside theses substituted phenols, acetic acid and formic acid were identified in all cases. Identification of 1,2-benzenediol, 1,4-benzenediol, acetic acid and formic acid was obtained by matching both the mass spectrum and the GC retention time for each compound with those of the authentic compounds. Identification of other intermediate products was performed only by matching the mass spectrum, because authentic standards were not commercially available. In these cases, a good match between the mass spectra of a product and reference spectra stored in the computer library was obtained.

Fig. 4 shows HPLC chromatograms for liquid samples after reaction of guaiacol, syringol and phenol at 300°C and for 60 s, with a 70% oxygen supply. Selection of an oxygen supply at 70% was helpful to detect further oxidation products such as low molecular weight carboxylic acids. Many of the compounds formed are seen in Fig. 4. Among these compounds, peaks labeled 1–12 represent compounds identified as shown in Fig. 4. These compounds were mainly a variety of low molecular weight carboxylic acids with 1–6 carbon atom(s), including unsaturated dicarboxylic acids (muconic acid, glutaconic acid, maleic acid, fumaric acid), saturated dicarboxylic acids (succinic acid, malonic acid, oxalic acid) and saturated monocarboxylic acids (acetic acid, formic acid). Although the peaks of glutaconic acid and oxalic acid are not clearly seen in Fig. 4, they were clearly identified with a shorter reaction time of 10 s for all three model compounds (data not shown). Besides the low molecular weight carboxylic acids, substituted phenols of 1,2-benzenediol, 1,4-benzenediol and 1,2,4-benzenetriol were detected in the case of phenol.

Most of the intermediate products described above have also been reported as major products in the WO or SCWO of phenol and/or substituted phenols [7–10]. However, the formation of glutaconic acid as an intermediate product in WO or SCWO of phenol or substituted phenols has not yet been reported.

3.1.2. Oxidation of ring-opening products

To get more and precise information for an investigation of the oxidation mechanisms of lignin model compounds, identifying not only the intermediate products obtained



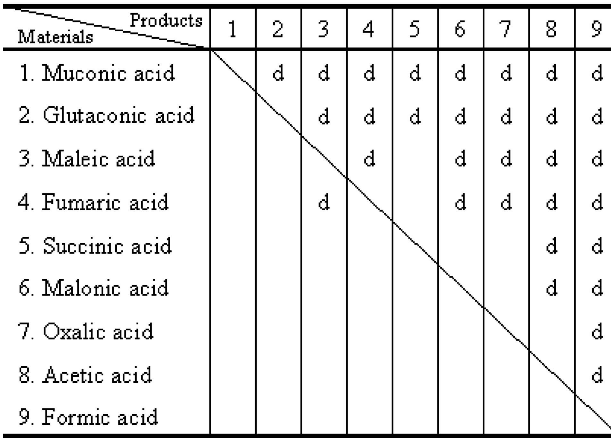
Intermediate products	
1. Oxalic acid	HOOC-COOH
2. Maleic acid	HOOC-CH=CH-COOH
3. Malonic acid	$HOOC-CH_2-COOH$
4. Succinic acid	$HOOC-(CH_2)_2-COOH$
5. Fumaric acid	HOOC-CH=CH-COOH
6. Formic acid	H-COOH
7. Glutaconic acid	$HOOC-CH=CH-CH_2-COOH$
8. Acetic acid	CH_3-COOH
9. Muconic acid	HOOC-CH=CH-CH=CH-COOH
10. 1,2,4-Benzenetriol	
11. 1,2-Benzenediol	
12. 1,4-Benzenediol	

Figure 4 HPLC chromatograms of the oxidation products for lignin model compounds at a temperature of 300°C reaction time 60 s, and oxygen supply 70%. (A: Guaiacol, B: Syringol, C: Phenol)

directly from the oxidation of lignin model compounds but also further oxidation products of the intermediate products from the lignin model compounds is important. So, a series of oxidation experiments with 1,2-benzenediol, 1,4-benzenediol, and 1,2,4-benzenetriol as well as all low molecular weight carboxylic acids identified (see Fig. 4) were performed at a temperature of 300°C, a reaction time of 60 s and an oxygen supply of 70%.

The intermediate products from 1,2-benzenediol, 1,4-benzenediol and 1,2,4-benzenetriol were almost the same as those from phenol. The intermediate products from ring-opening products or low molecular weight carboxylic acids are summarized clearly in Table I.

Table Ⅰ. WO products of ring-opening products for lignin model compounds(d: detected).



Materials \ Products	1	2	3	4	5	6	7	8	9
1. Muconic acid		d	d	d	d	d	d	d	d
2. Glutaconic acid			d	d	d	d	d	d	d
3. Maleic acid				d		d	d	d	d
4. Fumaric acid			d			d	d	d	d
5. Succinic acid								d	d
6. Malonic acid								d	d
7. Oxalic acid									d
8. Acetic acid									d
9. Formic acid									

3.2. WO pathways of lignin model compounds

Although there are many studies on the mechanism of the oxidation of phenol and substituted phenols, the mechanism of the oxidation of phenols is extremely complex and is not yet fully understood. In this study, on the basis of the products obtained in the oxidation reaction of model compounds and further oxidation products of the intermediate products from model compounds, WO pathways of lignin model compounds are discussed. Figs. 5 and 6 summarize the proposed pathways before

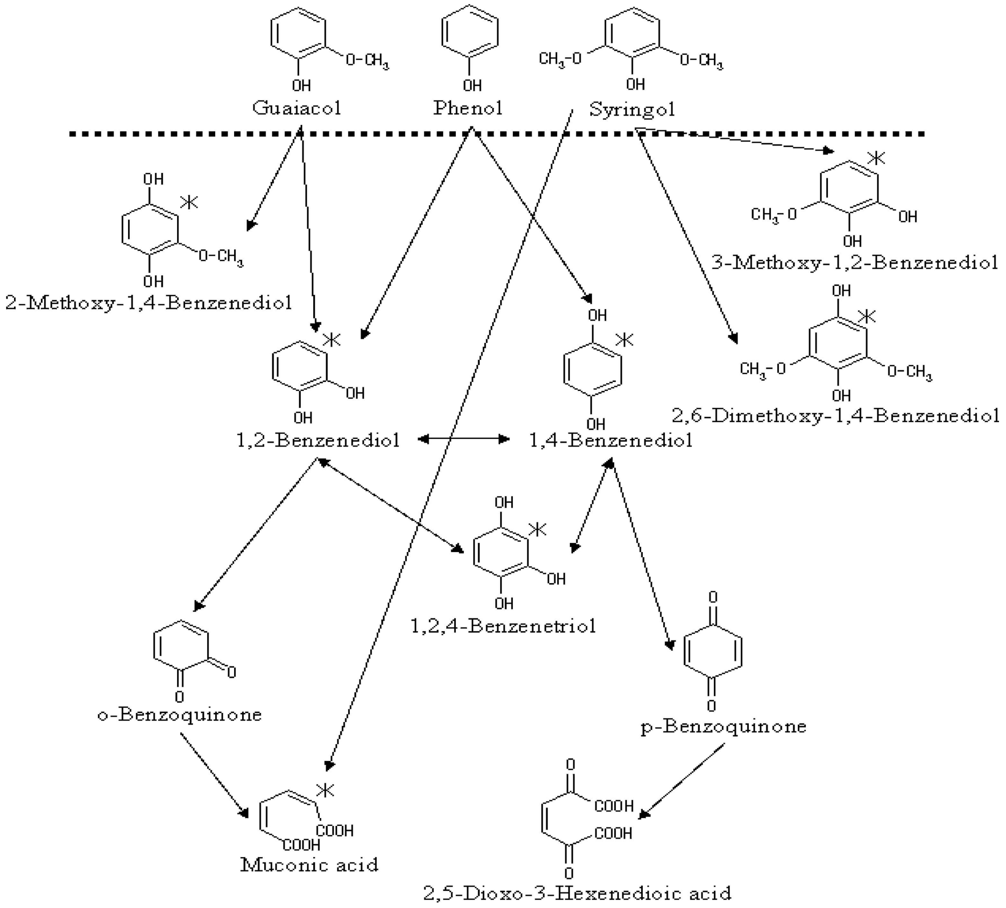


Figure 5 Proposed pathway to ring-opening reactions for lignin model compounds. (*:compounds identified in this study)

and after ring-opening reactions for three lignin model compounds. For the pathways before ring-opening reactions, it was assumed that firstly phenol, guaiacol and syringol were oxidized into their *ortho* and *para* compounds, because *ortho* and *para* compounds were identified for all phenol, guaiacol and syringol as shown in Fig. 3. It should be noted that for guaiacol and syringol, oxidation occurred only at the *para* position, and 1,2-benzenediol from guaiacol and 3-methoxy-1,2-benzenediol from syringol could be hydrolysis products rather than oxidation products, because 3-methoxy-1,2-benzenediol was not found as an intermediate product in the oxidation of guaiacol. That the oxidation of guaiacol and syringol hardly occurs at the *ortho* position would probably be because they have a substituent group at the *ortho* position.

The 1,2-benzenediol and 1,4-benzenediol produced may be further oxidized to *o*-benzoquinone and *p*-benzoquinone, which are subsequently oxidized to the corresponding unsaturated dicarboxylic acids, muconic acid and 2,5-dioxo-3-hexenedioic acid, by ring-opening reactions. However, in our experiments, both *o*-benzoquinone in particular and *p*-benzoquinone were hardly identified. A possible reason would be that benzoquinone is highly unstable when it is in contact with a strong oxidant like H_2O_2 and is easily cleaved into carboxylic acids. Additionally, 1,2,4-benzenetriol was found in the oxidation experiments with 1,2-benzenediol and 1,4-benzenediol, which implies that 1,2-benzenediol and 1,4-benzenediol was also oxidized to 1,2,4-benzenetriol. However, a further oxidation mechanism of 1,2,4-benzenetriol and OCH_3-substituted benzenediols such as 2-methoxy-1,4-benzenediol, 3-methoxy-1,2-benzenediol and 2,6-di-methoxy-1,4-benzenediol is still unclear.

To the best of our knowledge, there are no reports concerning the oxidation mechanism of OCH_3-substituted benzenediols and phenol attached at more than two sites.

Subsequently, pathways after ring-opening reactions were assumed on the basis of the identification of intermediate products from lignin model compounds and further oxidation products from ring-opening products (shown in Table I). As shown in Fig. 6, unsaturated dicarboxylic acids with 6 carbon atoms, muconic acid and 2,5-dioxo-3-hxenedioic acid, may be directly oxidized to unsaturated dicarboxylic acids with two less carbon atoms, maleic and fumaric acids, and with four less carbon atoms, oxalic acid. The formation of maleic and fumaric acids probably happened in an oxidation process with hydroxyl radicals at a double bond of the unsaturated dicarboxylic

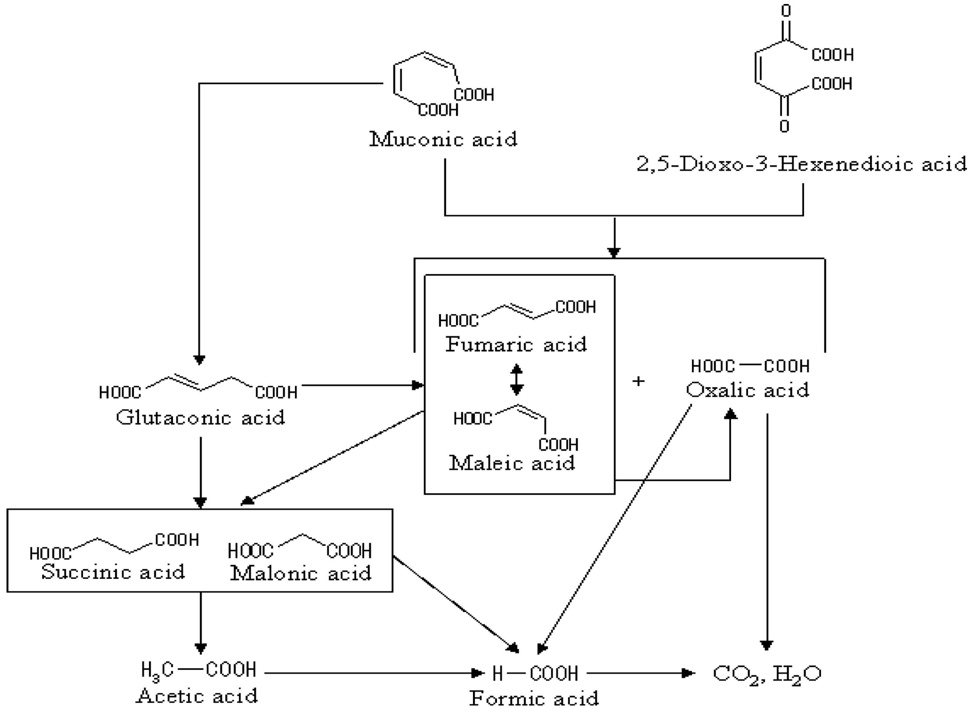


Figure 6 Proposed pathways after ring-opening reactions for lignin model compounds.

acids having 6 carbon atoms. Some studies also reported that the formation of maleic and fumaric acids comes from the direct oxidation of muconic acid or 2,5-dioxo-3-hexenedioic acid [10, 11].

In addition to the pathway described above, glutaconic acid was formed in the oxidation of muconic acid, and further oxidation of glutaconic acid would form maleic and fumaric acids so that muconic acid may also be converted to maleic and fumaric acids via glutaconic acid. Subsequently, maleic and fumaric acids were further oxidized to oxalic acid. Oxalic acid may be oxidized either directly or via formic acid into CO_2 and H_2O. Additionally, a little saturated dicarboxylic acid with 3, 4 carbon atoms, succinic and malonic acids, was found in the oxidation of unsaturated dicarboxylic acids, maleic acid, fumaric acid and glutaconic acid. The possibility of the formation these saturated dicarboxylic acids is supposed to be hydrogenation of unsaturated dicarboxylic acids. An experiment with maleic acid at 300°C without oxygen showed that succinic acid was not formed. These results indicated that succinic and malonic acids were not come from reduction of unsaturated dicarboxylic acids. A further investigation on the formation mechanism of saturated carboxylic acids in the oxidation of unsaturated carboxylic acids is needed.

3.3. Acetic acid production

Acetic acid production by the oxidation of three lignin model compounds was investigated. Table II shows the results obtained at a temperature of 300°C, a reaction time of 60 s and an oxygen supply of 70%, which were the conditions in which the highest acetic acid yield was obtained. Here, the acetic acid yield is reported in carbon percent against carbon of the initial reactant. As shown in Table II, the yield of acetic acid from three lignin model compounds was not high, about 9%, indicating that the oxidation of phenols does not produce a large amount of acetic acid. This may be the reason why lignin did not produce a large amount of acetic acid. To explain this, the

TABLE II Yield of acetic acid in WO of lignin model compounds, products before ring-opening reaction of phenol, and products after ring-opening reaction of guaiacol, syringol and phenol

Material	Yield (%)
Guaiacol	9.6
Syringol	8.5
Phenol	8.8
1,2- Benzenediol	9.5
1,4- Benzenediol	9.7
1,2,4-Benzenetriol	9.9
Muconic acid	9.2
Glutaconic acid	21.1
Maleic acid	6.4
Fumaric acid	7.1
Succinic acid	13.9
Malonic acid	50.4
Oxalic acid	0
Formic acid	0

acetic acid production by the oxidation of the products before and after ring-opening reactions was also investigated. Results are shown in Table II. For the oxidation of products before ring-opening reactions, the acetic acid yield was almost the same for all three model compounds, only about 9%. For the oxidation of the unsaturated dicarboxylic acids except glutaconic acid, the yield of acetic acid was low, only 6–9%. In the oxidation of the saturated dicarboxylic acids except oxalic acid, the acetic acid yield was higher and, especially for malonic acid, the acetic acid yield reached about 50%. Quantitative analyses for the oxidation samples of three model compounds showed that the amount of maleic and fumaric acids was much higher than that of saturated carboxylic acids, succinic and malonic acids. This may be the reason why lignin model compounds or lignin cannot produce a large amount of acetic acid.

However, the above results may give us some suggestion of how to improve the yield of acetic acid. That is, increasing the formation of saturated dicarboxylic acids and glutaconic acid would enhance the acetic acid yield.

4. Conclusions

Based on the intermediate products identified for the samples obtained not only from direct oxidation of lignin model compounds but also further oxidation of intermediate products of lignin model compounds, WO pathways of lignin model compounds were discussed.

Subsequently, acetic acid production by WO of lignin model compounds was discussed. It was found that the yield of acetic acid from WO of lignin model compounds was low, about 9%. The reason why lignin model compounds cannot produce a large amount of acetic acid may be attributed to the fact that the oxidation of phenols easily forms unsaturated dicarboxylic acids with 4 carbon atoms, which do not produce a large amount of acetic acid. However, saturated dicarboxylic acids and unsaturated dicarboxylic acid of glutaconic acid with 5 carbon atoms can produce a higher yield of acetic acid. Therefore, it is possible to increase the yield of acetic acid from lignin by controlling reaction pathways to enhance the formation of saturated dicarboxylic acids and unsaturated dicarboxylic acid of glutaconic acid with 5 carbon atoms.

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