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Hydrothermal production of formic and acetic acids from syringol^{*}

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Abstract: The production of formic and acetic acids (or salts) by hydrothermal oxidation of syringol, a model compound for lignin, was investigated using a batch reactor. Results show that the highest yields of formic and acetic acids were, respectively, 59.6% and 11.3% at the reaction condition of 0.5 mol/L NaOH, 120% H₂O₂ supply and 280 °C. These results will inform studies aiming to develop more environmental friendly lignin conversion processes by obtaining products beyond a CO₂ end product.

Key words: Lignin, Syringol, Formic acid, Acetic acid, Hydrothermal process

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1 Introduction

In view of the decreased availability of fossil fuels and the climate changes caused by the anthropogenic rise of atmospheric CO₂ concentration, the search for alternative renewable energy has become increasingly important (Effendi *et al.*, 2008). Biomass is thought to be a primary candidate for the future because it is by far the most abundant renewable source of fixed carbon, and has received an enormous amount of attention as a consequence of its availability and its potential to produce higher value (compared to CO₂) products. Biomass is made up of three main components: cellulose, hemicellulose, and lignin. Among them, lignin is the second most abundant natural raw material (Gosselink *et al.*, 2004), and can generally be obtained from black liquor. This black

liquor waste is discharged from paper mills in large quantities, the disposal of which can pose a major problem (Mohan and Karthikeyan, 1997; Zhang and Chuang, 2001).

In addition to pyrolysis and enzymatic/alkaline/acid hydrolysis (Pu *et al.*, 2008; Yu *et al.*, 2008), hydrothermal processes are receiving increased attention for the utilization of biomass as a natural wood biomass with a water content does not require dehydration before hydrothermal reactions. As well, water at high temperature and pressure behaves as a reaction medium with outstanding properties (Akiya and Savage, 2002; Watanabe *et al.*, 2004). The hydrothermal process may be used as both a solvent and reactant simultaneously in various biomass applications, including bio-oil production (Feng *et al.*, 2004a; 2004b), gasification (Matsumura *et al.*, 2005; 2006; Osada *et al.*, 2006), and liquefaction (Klein *et al.*, 1990; Sasaki *et al.*, 1998; Krammer and Vogel, 2000). Hydrothermal studies for biomass recycling have also conducted (Jin *et al.*, 2004; 2005; Kishida *et al.*, 2005; Suzuki *et al.*, 2006; Zhou *et al.*, 2006; Jin *et al.*, 2008). Previous studies have shown that acetic acid was easily obtained from cellulose biomass (Jin *et al.*, 2005; Suzuki *et al.*, 2006). However, in recent research, glucose, a model compound of a carbohy-

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drate biomass, was easily converted into formic acid under hydrothermal conditions (Jin *et al.*, 2008). In this paper, we investigated the hydrothermal production of formic acid and acetic acid from syringol, a model compound for lignin. Operating conditions were also investigated in terms of which conditions yield high amounts of formic acid and acetic acid.

2 Experiment

Together with guaiacol, syringol (and its derivatives) are characteristic products of lignin pyrolysis. Syringol (analytical reagent grade), as a representative corresponding to lignin, was chosen as the test material. A 30% solution of hydrogen peroxide was used as the oxidant. The oxygen supply was defined as the ratio of the amount of H₂O₂ supplied to the stoichiometric demand for complete oxidation of carbohydrates to carbon dioxide and water (molar ratio 18:1 for C₈H₁₀O₃), assuming 1 mol of H₂O₂ yields 1/2 mol of O₂.

The present experiments were performed using a batch reactor consisting of SUS 316 tubing. Experimental procedures and techniques have been described in (Jin *et al.*, 2005). Briefly, 0.07 g of syringol and 1.7 cm³ of H₂O₂-water mixture were introduced into the reactor to occupy 60% of the total reactor volume. Then, the reactor was immersed in a salt bath, preheated to the desired temperature for reaction. The reactor was shaken during the reaction to mix the contents. After the desired reaction time, the reactor was removed from the salt bath and immersed into a cold water bath. The reaction time was defined as the time that the reactor was kept in the salt bath. The actual reaction time is shorter than the apparent reaction time, because the time required to raise the temperature of the reaction medium from 20 to 300 °C was about 15 s. Reaction pressures with and without H₂O₂ supply were about 17 and 9 MPa, respectively. All experiments were performed with degassed water and a purging of the reactor with nitrogen.

After the reaction, liquid samples were collected for gas chromatography-mass spectrometry (GC/MS) and high-performance liquid chromatography (HPLC) analyses. In cases where NaOH was added, after filtration, the pH of the solution was adjusted to 3 with HCl for analysis. GC/MS analyses were performed

using a GC (HP 5890 Series II, USA) equipped with an HP-INNOWAX capillary column (30 m×0.25 mm ID, 0.25-μm film thickness) and an MS (HP 5898B, USA). HPLC (Waters, USA) analyses were performed on two RSpak KC-811 (Shodex, Japan) columns in series with a UV (Waters 486, USA) detector (210 nm). Quantitative estimation of formic acid and acetic acid was based on the average value obtained from the HPLC analysis of at least three samples with the relative errors always less than 10%. Details on the conditions for GC/MS and HPLC analyses can refer to (Jin *et al.*, 2005).

3 Results and discussion

First, the effect of the reaction temperature on the yields of formic acid and acetic acid from the oxidation of syringol was investigated using 100% H₂O₂ supply for 60 s. Fig. 1 shows the variation in the yield of formic acid, the yield of acetic acid, and gross yield of formic and acetic acids from 250 to 300 °C. The organic acid yield is defined as the percentage of organic acid to initial syringol on the carbon base. The yields of both formic acid and acetic acid initially increased till 280 °C, and then decreased with further increases in reaction temperature (Fig. 1). The yields of formic acid and acetic acid were 8.1% and 16.2%, respectively. These results indicate that considerable yields of formic acid and acetic acid, especially for formic acid, can be obtained by hydrothermal oxidation of syringol.

To better explain the effect of reaction temperature, Fig. 2 shows the HPLC chromatogram of the liquid samples after reaction of syringol with 70% H₂O₂ supply for 60 s at 250, 280 and 300 °C. Selection of a H₂O₂ supply at 70% was helpful to detect further reaction products. As shown in Fig. 2, the peaks labeled 1–12 represent a variety of low molecular weight carboxylic acids with the carbon numbers of 1–6 and substituted phenols of 1,2-benzenediol, 1,4-benzenediol and 1,2,4-benzenetriol, which have also been reported by other researchers (Thornton and Savage, 1990; Joglekar *et al.*, 1991; Martino and Savage, 1997; Portela *et al.*, 2001). These organic acids mainly included unsaturated dicarboxylic acids (muconic acid, glutaconic acid, maleic acid, and fumaric acid), saturated dicarboxylic

acids (succinic acid, malonic acid, and oxalic acid), and saturated monocarboxylic acids (acetic acid and formic acid). The peaks of both formic acid and acetic acid at 280 °C become larger than at 250 and 300 °C, but other peaks become smaller at 280 °C (Fig. 2). It also further illustrates that the optimal reaction temperature of 280 °C facilitated the production of formic acid and acetic acid from syringol and decreased the formation of other products.

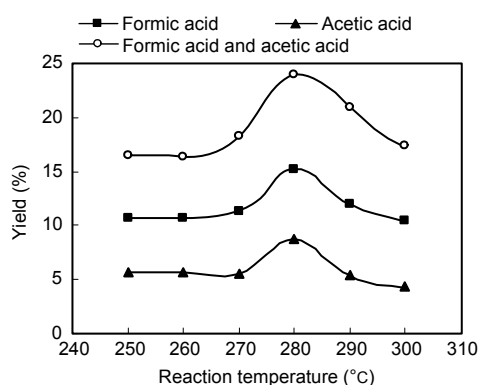


Fig. 1 Effect of the reaction temperature on the yields of formic acid and acetic acid from hydrothermal oxidation of syringol (100 % H₂O₂ supply; 60 s; 250, 280 and 300 °C)

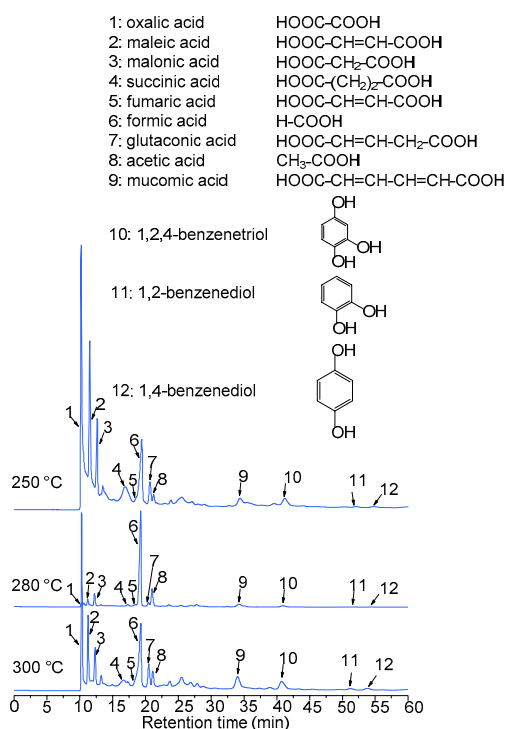


Fig. 2 HPLC chromatogram of the liquid samples after reaction of syringol (70% H₂O₂ supply; 60 s; 250, 280 and 300 °C)

Subsequently, the effect of H₂O₂ supply on formic acid and acetic acid production was examined at 280 °C. There was no significant effect on the yields of formic acid and acetic acid for the H₂O₂ supply in the range from 100% to 140% (Fig. 3). However, the yields at 120% H₂O₂ supply were slightly higher than those at either 100% or 140% H₂O₂ supply. Moreover, 140% H₂O₂ supply increased the cost of production and accelerated the corrosion of reactors. Therefore, selection of 120% H₂O₂ supply should be more suitable from the viewpoint of economic production of formic acid and acetic acid.

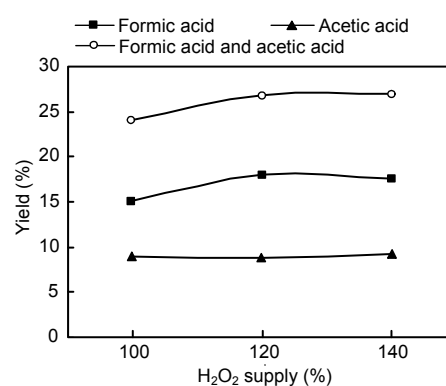


Fig. 3 Effect of the H₂O₂ supply on the yields of formic acid and acetic acid from hydrothermal oxidation of syringol (100%–140% H₂O₂ supply; 60 s; 280 °C)

Because it has been reported that the addition of base can prevent the decomposition of organic compounds (Jin *et al.*, 2008) and accelerate the breakdown of syringol, the effects of NaOH concentration and reaction time on the production of formic acid and acetic acid were investigated with 120% H₂O₂ supply at 280 °C. Fig. 4 shows the influence of NaOH concentration on the yields of formic acid and acetic acid in the oxidation of syringol. It should be noted that, in the above cases, the products were formate or acetate salts, rather than formic or acetic acids, owing to the alkaline conditions. But, for simplicity, we have used consistent terminology. From Fig. 4, it can be seen that the yields of formic acid and acetic acid increased drastically while the NaOH concentration increased to 0.5 mol/L, and then the rate of increase was reduced. This shows that the optimal NaOH concentration is 0.5 mol/L for the condition of 120% H₂O₂ supply and 280 °C. Fig. 5 shows the effect of reactions time on formic acid and acetic acid at the optimal reaction conditions. The yields of acetic acid

were almost the same. Yields of formic acid, however, were increased significantly until a reaction time of 60 s, and then decreased thereafter. This was likely owing to the fact that formic acid was much easier to decompose than acetic acid. At optimal conditions, the yield of formic acid, the yield of acetic acid and gross yield of both acids are 59.6%, 11.3%, and 78.9%, respectively.

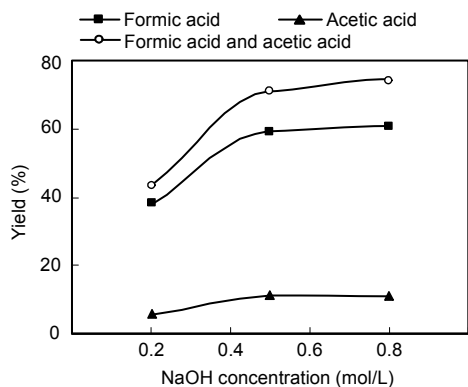


Fig. 4 Effect of the base on the yields of formic acid and acetic acid from hydrothermal oxidation of syringol (120% H_2O_2 supply; 60 s; 280 °C; 0.2–0.8 mol/L NaOH)

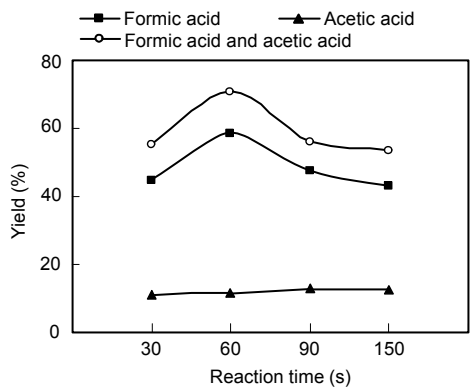


Fig. 5 Effect of the reaction time on the yields of formic acid and acetic acid from hydrothermal oxidation of syringol (120% H_2O_2 supply; 280 °C; 0.5 mol/L NaOH)

Finally, to investigate the reaction mechanism, intermediate products after reaction using syringol were identified in detail by GC/MS, in addition to the HPLC results presented in Fig. 2. Fig. 6 shows the GC/MS chromatogram of the liquid samples obtained at 280 °C for a reaction time of 60 s with an oxygen supply of 70%. As shown in Fig. 6, the identified major intermediate products were 3-methoxy-1,2-benzenediol and 2,6-dimethoxy-1,4-benzenediol, in addition to formic acid and acetic acid. On the basis of

intermediate products in Fig. 2 and Fig. 6, and the reaction paths of ring-opening for substituted phenols (Devlin and Harris, 1984; Gopalan and Savage, 1994; Scheck and Frimmel, 1995; Martino and Savage, 1997), a potential reaction pathway for hydrothermal oxidation of syringol was proposed in Fig. 7, although the detailed mechanism is extremely complex and is not yet fully understood.

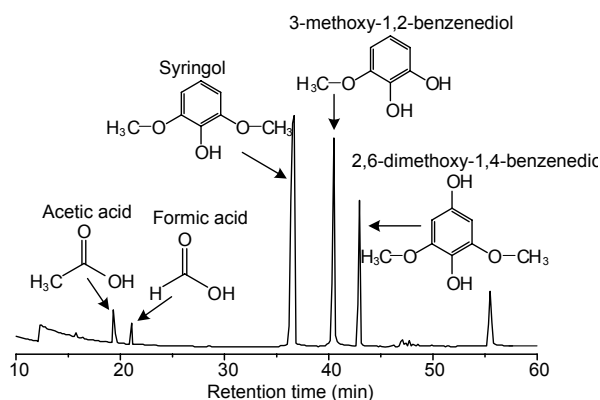


Fig. 6 GC/MS chromatogram of the liquid samples after reaction of syringol (70% H_2O_2 supply; 60 s; 280 °C)

In Fig. 7, first of all, syringol was oxidized into 3-methoxy-1,2-benzenediol and 2,6-dimethoxy-1,4-benzenediol, which were further oxidized into *o*-benzoquinone and *p*-benzoquinone via 1,2-benzenediol and 1,4-benzenediol. Secondly, produced benzoquinones were subsequently oxidized into muconic acid and 2,5-dioxo-3-hexenedioic acid by ring-opening reactions. Thirdly, unsaturated dicarboxylic acids with 6 carbon atoms, muconic acid and 2,5-dioxo-3-hexenedioic acid, were oxidized step by step into a series of carboxylic acids of 2–4 carbon atoms, which was oxidized at the position of the double bond or the end carbons into the end products including formic acid, acetic acid, CO_2 , and H_2O . In our experiments, *o*-benzoquinone, *p*-benzoquinone and 2,5-dioxo-3-hexenedioic acid were not identified. This is possibly because the carbonyl groups of benzoquinones and 2,5-dioxo-3-hexenedioic acid are highly unstable under hydrothermal oxidation conditions, and easily cleaved into carboxylic acids.

In the proposed reaction pathway, muconic acid is an important intermediate product (Fig. 7). Hence, we conducted additional experiments for detection of reaction products of muconic acid under the experiment conditions of 0.5 mol/L NaOH, 120% H_2O_2

supply and 280 °C for 60 s. The results showed that unsaturated dicarboxylic acids (glutaconic acid, maleic acid, and fumaric acid), saturated dicarboxylic acids (succinic acid, malonic acid, and oxalic acid), and saturated monocarboxylic acids (acetic acid and formic acid) were detected, and the yields of formic acid and acetic acid were 62.1% and 10.5%, respectively. These observations further support the proposed reaction pathway for hydrothermal oxidation of syringol as shown in Fig. 7.

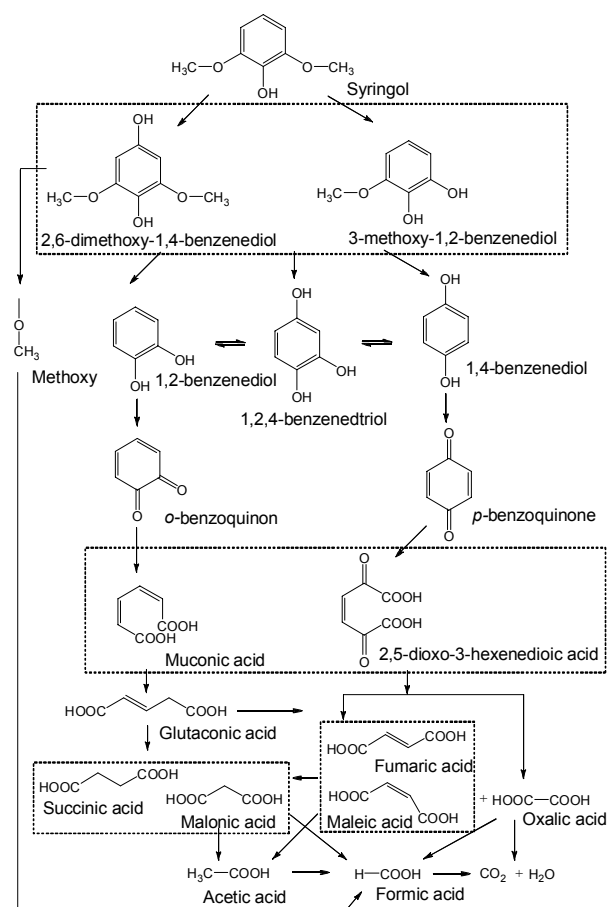


Fig. 7 Proposed reaction pathway for hydrothermal oxidation of syringol

4 Conclusions

This work showed that the highest yields of formic acid and acetic acid through hydrothermal oxidation of syringol were, respectively, 59.6% and 11.3% under operating conditions of 0.5 mol/L NaOH, 120% H₂O₂ supply, and 280 °C. The results of this study will be beneficial to the development of more

environmental friendly processes for the conversion of lignin biomass into higher value products rather than the carbon end product CO₂. A potential reaction pathway for hydrothermal oxidation of syringol into formic acid and acetic acid is proposed.

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