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Hydrolysis kinetics of benzyl phenyl ether in high temperature liquid water

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Abstract

The application of high temperature liquid water (HTLW) to decomposition of lignin as efficient and green solution for phenolic compounds recovery was studied. Benzyl phenyl ether (BPE), the lignin model compound, was treated at temperatures ranging from 220 to 250 °C. BPE undergo hydrolysis in HTLW, and main products were phenol and benzyl alcohol with the minimum selectivities of 75.7% and 82.8%, respectively. Lower temperature led to higher selectivity in 220–250 °C temperature range. The kinetics on BPE hydrolysis was studied and the activation energy was determined as 150.3 ± 12.5 kJ/mol with the first-order kinetic equations. Based on products distribution, the reaction mechanism for decomposition of benzyl phenyl ether was proposed. The investigated process provides insights into the design of a commercial method for utilization of lignin.

Keywords: Hydrolysis; Kinetics; Benzyl phenyl ether; High temperature liquid water; Lignin model compound

In response to depletion of fossil resources, the potential for using the biomass as a source of both commodity and specialty chemicals attracts more attentions nowadays. Ether, especially aromatic ether, prevails in lignin, which is a good source of phenolic monomers [1]. Various approaches have been attempted to cleave the ether in lignin, such as pyrolysis [2], acid hydrolysis [3], supercritical fluid treatment [4], and hydrogenation [1]. However, these methods have the disadvantages such as low selectivity, serious pollution, difficult recovery, and undesired by-products in abundance. An efficient and green technology was needed.

High temperature liquid water (HTLW), defined as hot water between 100 and 374 °C, is a useful medium for chemical reactions. Properties of HTLW are temperature-dependent and can be manipulated to optimize the reaction environment, for example, the ion product increases by 3–4 orders of magnitude from its value at ambient conditions its maximum value at around 250 °C, which enhances acidity/basicity in favor of acid- or base-catalyzed hydrolysis [5]. These properties make HTLW a very promising technology for biomass refinery [6,7].

Few studies have been performed on the decomposition of lignin in HTLW. Wahyudiono et al. [8] carried out the decomposition of lignin to phenolic compounds in near- and supercritical water. The results showed that higher temperatures promoted the conversion of lignin into its derivate compounds. Pourali et al. [9] carried out the hydrolysis of rice bran to produce valuable materials in HTLW. Phenolic compounds were mainly produced from

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decomposition of lignin, carbohydrate, and phenolic compounds. For the purpose of further understanding the mechanism and kinetics of the lignin hydrolysis in HTLW, benzyl phenyl ether (BPE) was selected as model compound for lignin. The behavior of lignin model in HTLW was the first to be investigated.

1. Experimental

A carefully measured amount of BPE was added into the batch reactors consisted of 316 L stainless steel tubes with volume of around 14.5 mL, and 10 mL deionized water was loaded. Thus, these experiments took place essentially under water the saturation vapor pressure at each reaction temperature. After a desired time, not including the heat up time of *ca.* 20 min, the reactor was removed from the furnace and placed into water to quench the reaction. Samples in the reactor were discharged into a 50 mL volumetric flask. The reactor was then washed with methanol five times, with each washing being added to the flask. Then the volumetric flask was filled with methanol. The standard deviations were determined from replicate experiments.

The liquid products was identified by fragmentation patterns from GC–MS (Agilent 6890GC/5973 MSD) and by matching HPLC retention times with known standards and quantitatively analyzed by HPLC (Agilent 1100).

2. Results and discussion

Fig. 1 shows the effect of initial concentration on BPE hydrolysis at 240 °C. It shows conversion rates of BPE were similar at 0.01 and 0.02 g/mL. The conversions being invariant under nearly concentration signal first-order kinetics for the hydrolysis reaction. Fig. 2 shows the effect of temperature on the BPE hydrolysis. Reactions were conducted at 220, 230, 240 and 250 °C with an initial BPE concentration of 0.02 g/mL. The BPE conversion was affected by both temperature and time. BPE conversions were essentially 100% for 3 h at 250 °C, and 26.6% for 3 h at 220 °C.

The selectivities of phenol and benzyl alcohol from BPE at 220, 230, 240 and 250 °C are shown in Figs. 3 and 4. The reaction temperature had a significant effect on reaction selectivities. Compared to phenol selectivity of about 102% at 220 °C for 4 h, the selectivity at 250 °C was 76.1% for 4 h. At the same condition, the selectivity of benzyl alcohol was from 99.2% (220 °C) to 83.9%(250 °C). In addition, decrease of benzyl alcohol selectivity as a function of time was much slighter than the phenol. Selectivities of benzyl alcohol were 93.4% at 240 °C for 0.5 h and 90.1% at 240 °C for 4 h, with only 3.4% decrease. However, the phenol decreased by 12.2%. The decline of selectivities on phenol and benzyl alcohol indicated that higher temperature promoted the conversion of BPE into its derivative compounds. BPE sample at 240 °C for 4 h was analyzed by GC–MS. Besides the phenol and benzyl alcohol, other derived products such as benzylphenol (2- or 4-), dibenzylphenol and dibenzyl ether were found in MS fraction. Benzyl cation (**5**) from benzyl alcohol caused alkylation of phenol to yield benzylphenol (**6**, **7**) and dibenzylphenol (**8**), and interacted with benzyl alcohol to yield dibenzyl ether (**9**) [10], and the increase in temperature enhanced the alkylation reaction.

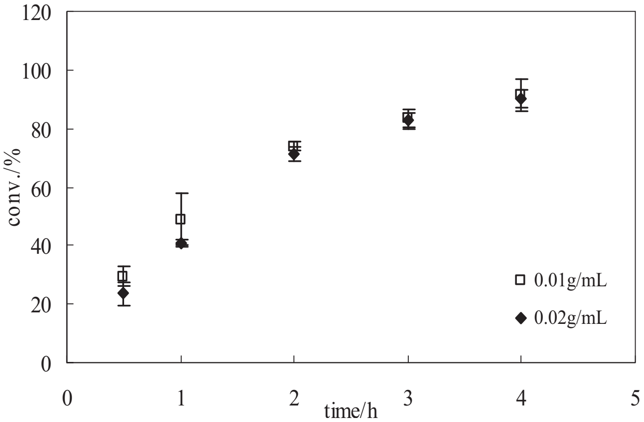

Fig. 1. Effect of initial BPE concentration on BPE conversion.

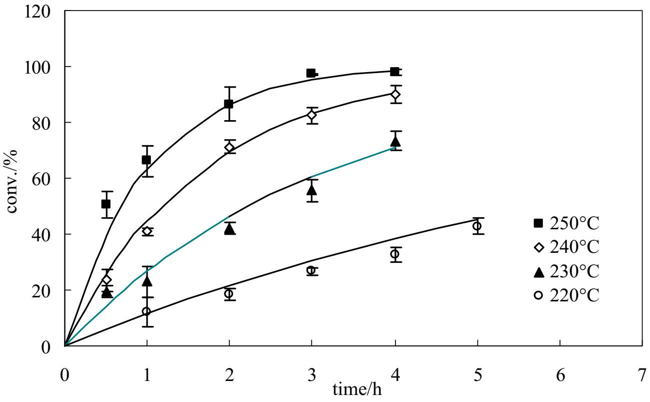

Fig. 2. Effect of different temperatures on BPE conversion.

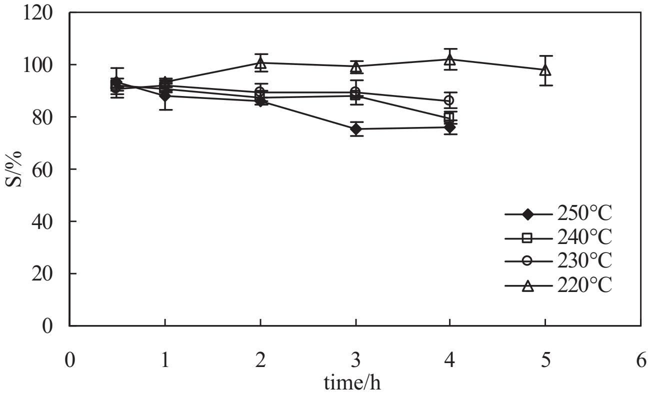

Fig. 3. Effect of different temperatures on the selectivity of phenol from BPE conversion.

Fig. 5 shows the hydrothermal stability of benzyl alcohol and phenol at reaction temperature of 240 °C with the initial concentration of 0.02 g/mL. Benzyl alcohol was quite stable at these reaction conditions, and its conversion was only 5.2% for 4 h. However, phenol was not stable at 240 °C. The conversions were around 25% within 4 h reaction time.

It is well-established that the formation of phenoxyl radical (**10**) is thermodynamically favored [11], which could cause condensation polymerization. The by-products of 4-phenoxyphenol (**11**), diphenoxyphenol (**12**) from these

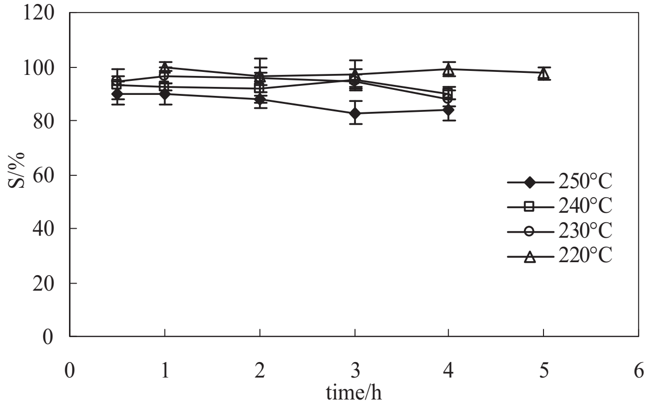

Fig. 4. Effect of different temperatures on the selectivity of benzyl alcohol from BPE conversion.

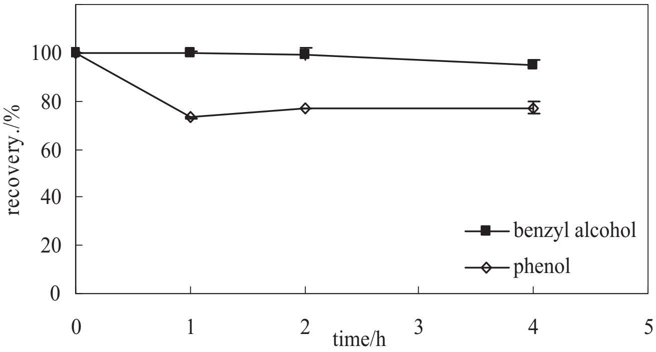

Fig. 5. Hydrothermal stability of phenol and benzyl alcohol.

reactions by GC–MS analysis contributed to the instability of phenol. Moreover, part of phenol would be quickly oxidized with a small amount of air in the tube at high temperature [12], which also led to the instability of phenol. The main oxidation intermediate products were identified by the GC–MS as maleic acid (**13**), acrylic acid (**14**) and so on. Through GC–MS analysis of benzyl alcohol sample, we identified low concentrations of components which were benzaldehyde (**15**) and dibenzyl ether (**9**). The reaction of benzyl alcohol under hydrothermal conditions without the presence of air was discussed by Hirashita [13], where small amount of benzaldehyde was also yielded. Therefore, benzaldehyde in our experiments was probably not generated from the reaction with oxygen. One is forced to provide for a pathway similar to that proposed by Martino et al. [14]: benzaldehyde may be formed by *β*-scission of the oxy radical (**16**) from the decomposition of benzyl alcohol. It was short-lived and rare (see Fig. 6).

With BPE conversion in Fig. 2, we calculated *pseudo*-first-order of BPE hydrolysis. The values were $0.1209 \pm 0.0084\ \mathrm{h}^{-1}$, $0.3106 \pm 0.0342\ \mathrm{h}^{-1}$, $0.5913 \pm 0.0203\ \mathrm{h}^{-1}$, and $1.0028 \pm 0.1025\ \mathrm{h}^{-1}$ at 220 °C, 230 °C, 240 °C, and 250 °C, respectively. The Arrhenius parameters was determined by linear regression of $-\ln k$ vs $1000/RT$, which were $\log_{10}A(\mathrm{h}^{-1}) = 34.6 \pm 2.9$ and $E_a = 150.3 \pm 12.5$ kJ/mol. These kinetics results are the first to be reported

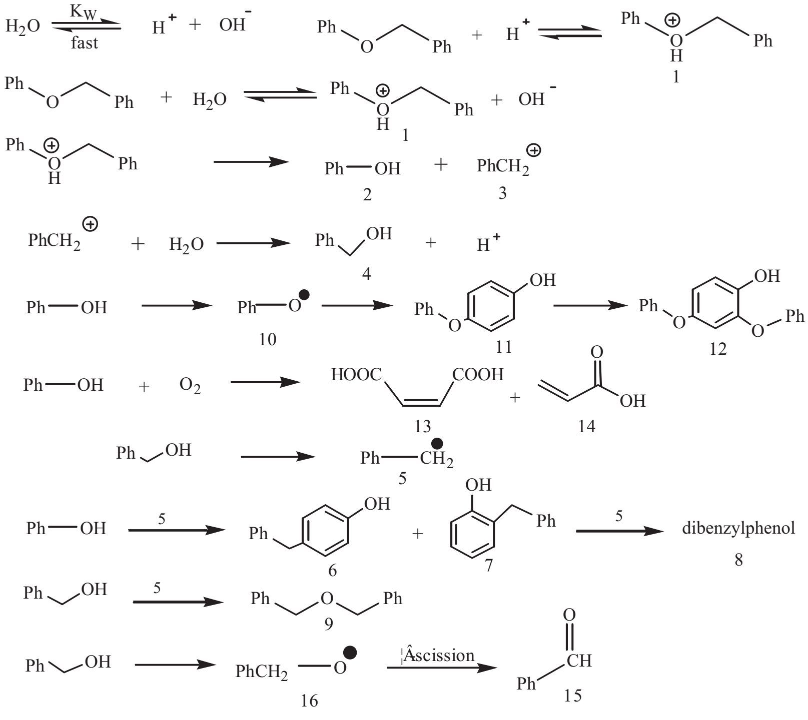

Fig. 6. Postulated reaction mechanism for hydrolysis of BPE in HTLW.

for the hydrolysis of BPE. The curves in Fig. 2 show that the conversion profiles calculated by the model do a very good job of representing the experimental data at all temperatures. This data fitted provided estimation for the rate constants at each temperature.

The hydrolysis of ethers in HTLW is postulated to be cleaved by an ionic S_N1 mechanism due to the stable and charged carbocation intermediates (**1**) [5], formed from protonation of ether by water and by H^+ generated from self-dissociation of water. The intermediate then decomposed unimolecularly in the rate-determining step to form an alcohol (**2**) and a carbon cation (**3**). After that, the carbon cation reacted with water to generate another alcohol (**4**) and H^+, recycled to ether. The thermodynamic stability of radicals, providing a quantitative basis for rational design of radical reactions in organic synthesis, can be predicted by radical stabilization energy (RSE). More negative was the RSE of radical, more stable was the radical [15]. The RSE of the benzyl radical (−50.4 kJ/mol) was lower than benzene radical (+10.3 kJ/mol), indicating the benzyl radical was more stable than benzene group. Combined with previous sections, ionic mechanism of hydrolysis of BPE in HTLW was shown in Fig. 6.

3. Conclusions

Benzyl phenyl ether undergoes hydrolysis on the time scale of hours in liquid water at temperatures around 240 °C. Phenol and benzyl alcohol are main products. Oxygen presence and high temperature affected the reaction selectivities of phenol and benzyl alcohol and the distribution of products. BPE exhibited first-order kinetics and the activation energy was determined as 150.3 ± 12.5 kJ/mol. Based on these results, HTLW could be a promising medium in the decomposition of lignin ethers and phenolic compounds recovery.

Acknowledgments

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