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RESEARCH PAPER

Effects of hydroxyl and hydrogen free radicals on the liquefaction of cellulose in sub/supercritical ethanol

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Abstract: With salicylic acid as hydroxyl radical (HO·) trap and carbon tetrachloride as hydrogen radical (H·) trap, the effects of HO· and H· radicals on the liquefaction of cornstalk cellulose in sub/supercritical ethanol was investigated in an autoclave. The results indicated that the concentration of HO· radical increases with the increase of salicylic acid amount added in the feed from 0 to 4 mL; meanwhile, the bio-oil yield is increased from 29.3% to 47.9%, whereas the residue yield is decreased from 26.7% to 24.3%. The activity of HO· increases with the increase of reaction temperature from 250 to 320°C; meanwhile, the bio-oil yield is increased from 35.9% to 58.2%, whereas the residue yield is reduced from 51.8% to 20.4%. On the other hand, the concentration of H· radical decreases with the increase of carbon tetrachloride from 0 to 2 mL; meanwhile, the bio-oil yield is decreased from 24.7% to 20.7%, whereas the residue yield is increased from 54.1% to 59.1%. The liquefaction of cellulose is enhanced within 30 min due to the increase of H· activity; after that, the bio-oil yield begins to decline due to the inhibition of H· activity by CCl_4. Current results proved that ethanol can produce HO· and H· radicals under sub/supercritical state; the concentration and activity of HO· and H· radicals are dependent on the reaction conditions, which may determine the product yield and distribution for the liquefaction of cellulose in sub/supercritical ethanol.

Keywords: cellulose; liquefaction; sub/supercritical ethanol; free radical; radical trap

Cellulose from biomass is the most abundant renewable energy reserves with carbon and hydrogen elements on the earth. The liquefaction of cellulose in supercritical fluid has been considered as an excellent way for the production of bio-oil and platform chemicals. In comparison with pyrolysis, the supercritical liquefaction often gives higher yield and selectivity to bio-oil and has received considerable attention. However, the mechanism for the liquefaction of cellulose in supercritical fluid has not been well clarified up to now. For the liquefaction of rice straw in supercritical ethanol, Chen[1] reported that ethyl and hydroxyl radicals produced from ethanol could attack C–O and C–H bonds in lignin, respectively, which enhanced the liquefaction reactions. It was also found that the concentration and activity of ethanol free radicals increased with the increase of reaction temperature[2,3]. Edita et al[4], Hessein et al[5] further proved that ethanol could produce free radicals such as H·, HO· and CH_3· under sub/supercritical conditions and the concentration of free radicals had an obvious influence on the liquefaction of cellulose[4,5]. Meanwhile, the cleavage of C–C, C–O and –OH groups in cellulose was enhanced by the free radicals[6].

Unstable and active transition state fragments, i.e. free radicals, are produced during chemical reactions, which are important for clarifying the reaction mechanism in spite of their short lifetime. Because free radical traps can selectively increase or decrease the concentration and activity of certain free radicals, they have been widely used to investigate the effect of free radicals on a chemical reaction. OH· can react with many organic compounds, especially with aromatic compounds; with salicylic acid as an OH· trap[7–9], the yield of OH· could be indirectly derived by measuring the yield of hydroxylation products (dihydroxy-benzoic acid) with HPLC or GC. On the other hand, carbon tetrachloride (CCl_4) could trap H· inside the cavitation bubble, which had a significant effect on the ultrasonic emulsion polymerization of styrene[10].

In this work, the effects of various free radicals released from sub/supercritical ethanol on the liquefaction of cornstalk cellulose were investigated, with salicylic acid as the OH· radical trap and CCl_4 as the H· radical trap. The results obtained here should be helpful for the development of better

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reactor and process for the liquefaction of biomass in sub/supercritical ethanol.

1 Experimental

1.1 Materials and reagents

Cornstalk was collected from a farm in Guangzhou, China. The feedstock was milled to fine powder by passing through a 40-mesh sieve. The powder material was dried at 60°C for 12 h before use. Anhydrous ethanol, acetone, salicylic acid carbon tetrachloride and sodium hydroxide in analytical grade and sodium chlorite in industrial grade were used in this work.

1.2 Cellulose preparation

Water-soluble products in cornstalk cellulose were removed according to the standards of GB/T2677.1—93 to GB/T2677.10—95. Lignin was treated with sodium chlorite solution to obtain holocellulose. The insoluble residue was prepared by treating holocellulose with sodium hydroxide solution, which was then dried at 60°C for 12 h and kept in a desiccator at room temperature.

1.3 Experimental procedure

The liquefaction tests were conducted in an autoclave (PARR 4521M, USA, 1.0 L), following the procedures illustrated in Figure 1. The autoclave could stand for a pressure of 13 MPa and a temperature of 350°C, well above the critical temperature of 243°C and critical pressure of 6.34 MPa of ethanol. After the liquefaction test, the mass-based yields of bio-oil (BO), gaseous products (GAS), and solid residues (RE) were determined.

The functional groups in the solid residues, which were pressed into a self-supported wafer by using the KBr pelleting method, were characterized by FT-IR (VERTEX 70).

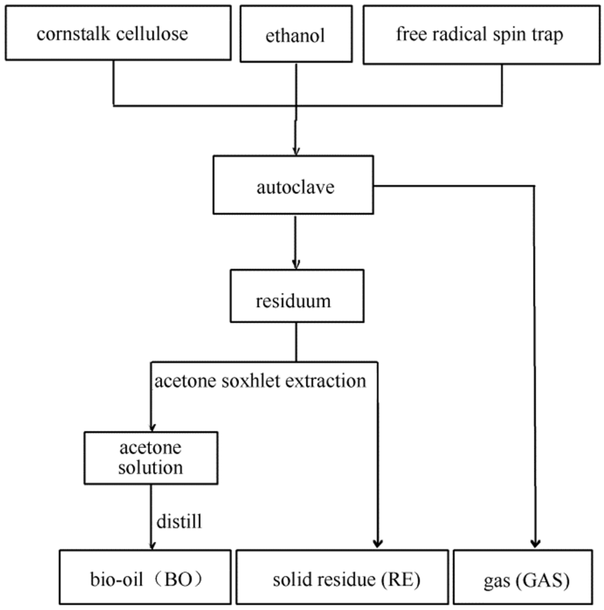

Fig. 1 Procedures for the liquefaction of cellulose in sub/supercritical ethanol

(Gas products, GAS; Bio-oil, BO; Residue, RE)

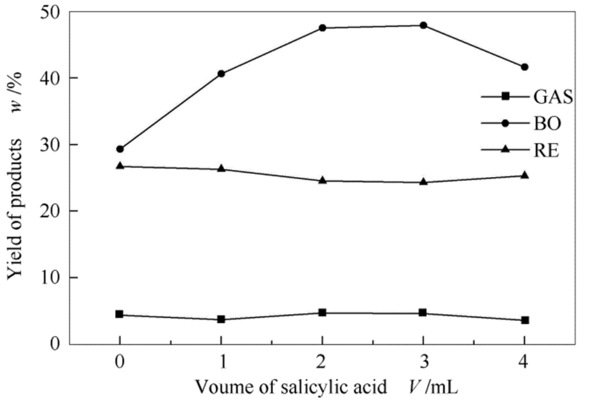

Fig. 2 Effect of the HO· concentration (amount of salicylic acid added in the feed) on the yields of various products for cellulose liquefaction in 100 mL ethanol under 11.0–12.0 MPa and 320°C for 60 min

2 Results and discussion

2.1 Effects of hydroxyl radicals on cellulose liquefaction

2.1.1 About the HO· concentration and the amount of salicylic acid

The liquefaction of cellulose was conducted in 100 mL ethanol at 320°C for 60 min, during which the pressure rose up to 11.0–12.0 MPa. The concentration of HO· was changed by adjusting the amount of salicylic acid from 0 to 4 mL. Figure 2 displays the effects of HO· concentration on the yields of GAS, BO and RE for cellulose liquefaction in sub/supercritical ethanol.

As the liquefaction of cellulose was conducted at 11.0–12.0 MPa and 320°C, abundant active free radicals were produced from supercritical ethanol, which could enhance the formation of gaseous products[11]. The concentration of HO· increases with the increase of the amount of salicylic acid added in the feed. As shown in Figure 2, however, the yield of gaseous products declines slightly when more fragments and free radicals are transformed to non-gaseous products due to the stronger redox activity of HO·; that is, the formation of gaseous products may be inhibited by higher concentration of HO·.