

A comparative study of decomposition behaviors between hardwood and softwood in supercritical methanol

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The supercritical methanol biomass conversion system with batch-type reaction vessel was applied to study the chemical conversion of cedar and beech woods to liquid fuels and useful chemicals. As a result, over 90% of cedar and beech woods was decomposed and liquefied in methanol after 30 min supercritical treatment at 350°C-43MPa. In addition, beech wood was easily decomposed and liquefied to a greater extent than cedar wood at 270°C-27MPa. It was further indicated that observed differences are mainly originated from intrinsic properties in lignin structure between softwood and hardwood.

Introduction

Biomass resources will become more important in the future as alternatives of fossil resources. However, the fossil resources are scarce in Japan, whereas woody biomass resources are plentiful. In addition, according to our recent investigation, 110 million tons of wastes including the lignocellulosics are annually generated in which 33 million tons are not utilized effectively. Therefore, the technology, which converts them into the valuable liquid fuels and chemicals, will become important to solve energy and environmental problems. In our laboratory, the supercritical fluid biomass conversion system with a batch-type reaction vessel has been applied to study the chemical conversion of woody biomass to such useful substances. If methanol is selected as the solvent for supercritical treatment, advantages can be as follows: 1)The critical temperature ($T_c=239^\circ\text{C}$) and pressure ($P_c=8.09\text{MPa}$) of methanol which are lower than those of water can offer the milder conditions of the reaction. 2)The methanol with reaction products can be utilized as liquid fuel because methanol itself is the liquid fuel. 3)The liquid fuel from only biomass resources can be created by using bio-methanol synthesized by pyrolysis of biomass. In this study, therefore, the chemical conversion of biomass resources with supercritical methanol was made so as to achieve the 100% biomass-based liquid fuel and useful chemicals.

Materials and methods

As woody biomass sample, the Japanese cedar, sugi (*Cryptomeria japonica*) and the Japanese beech, buna (*Fagus crenata*) woods were selected. Supercritical methanol treatment was conducted by using a biomass conversion system with a batch-type reaction vessel described in a previous work[1]. The reaction vessel with a 5ml volume is made of Inconel-625. This system can cover a range in pressure and temperature up to 200MPa and 500°C, respectively. To start a treatment, 5ml of methanol was fully fed with 150mg of the wood powder (80mm mesh). Then the reaction vessel was quickly heated by immersing it into the tin bath preheated at an adequate temperature and maintained under supercritical conditions ($>T_c=239^\circ\text{C}$, $>P_c=8.09\text{MPa}$) for 1 to 30 min. After an adequate reaction time, the reaction vessel was moved into the water bath to quench the reaction. The obtained reaction mixture was filtrated with 0.2 μm membrane filter to separate methanol-soluble portion and methanol-insoluble residue. The methanol-insoluble residue was analyzed by acid hydrolysis and nitrobenzene oxidation to determine the Klason lignin content and the yield of nitrobenzene oxidation products, respectively. In addition, the clear filtrate from acid hydrolyzates in the Klason lignin determination was analyzed by the UV-VIS spectrophotometry and the high performance liquid chromatography (HPLC) to determine the acid-soluble lignin content and the yield of glucose, respectively. Then, the decomposition rate constant k of lignin and cellulose in wood was computed by the following equation:

$$X=X_0\exp(-kt) \quad (1)$$

where X is the lignin content in the methanol-insoluble residue or the yield of glucose in the filtrate from acid hydrolyzate on the original wood basis. The lignin content refers to the sum of the Klason lignin and acid-soluble lignin contents.

Results and discussion

Fig.1 shows the changes in the methanol-insoluble residues and the lignin content in the residue of the cedar and beech woods as treated in supercritical methanol at various conditions. In the condition of 270°C -27MPa, the beech wood was easier to be liquefied in methanol than cedar wood, and lignin in the beech was liquefied to a greater extent than that of the cedar. In the condition of 350°C -43MPa, however, over 90% of the cedar and beech woods was decomposed and liquefied in methanol after 30min supercritical treatment. In addition, the lignins in the cedar and beech were proceeded to be liquefied at an early stage of the treatment and after 3 min treatment, the lignin remained constant to be about 1-3% on the original wood basis.

Fig.2 shows the arrhenius plot for the decomposition rate constants of cellulose and lignin in the cedar and beech in subcritical and supercritical methanol. The decomposition rate constants of the cellulose in the cedar and beech woods were almost equal in the values and they rapidly increased over 300°C treatment temperatures. The result was similar even in the case of avicel which is microcrystalline cellulose[2]. Besides, the decomposition rate constant of the lignin in the beech was larger than that of the cedar at the low temperatures. It was further indicated that observed differences are mainly originated from intrinsic properties in lignin structure between softwood and hardwood. For example, the yield of the nitrobenzene oxidation products from methanol-insoluble residue on the lignin basis decreased with an increase in the supercritical treatment time, indicating that the methanol-insoluble residue becomes lesser in the non-condensed linkages of the lignin. In fact, by the experiments using lignin model compounds at 270°C and 350°C, it has been proven that the biphenyl type of lignin model compound was stable, though the β -ether linkage of phenolic β -O-4 model compound was rapidly cleaved off in the supercritical methanol[3][4]. These results indicated that the non-condensed lignin is easily depolymerized further than the condensed lignin in supercritical methanol. Therefore, hardwood lignin which has more non-condensed structures is readily depolymerized and liquefied in the supercritical methanol, compared with softwood lignin.

References

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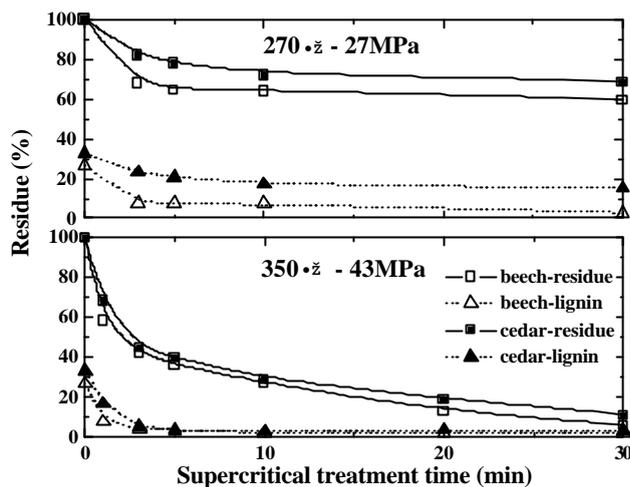


Fig.1 Changes in the methanol-insoluble residues and the residual lignin of the cedar and beech woods as treated in supercritical methanol at various conditions. (upper : 270°C -27MPa, bottom : 350°C -43MPa) The lignin content is a part of the methanol-insoluble residue on the original wood basis.

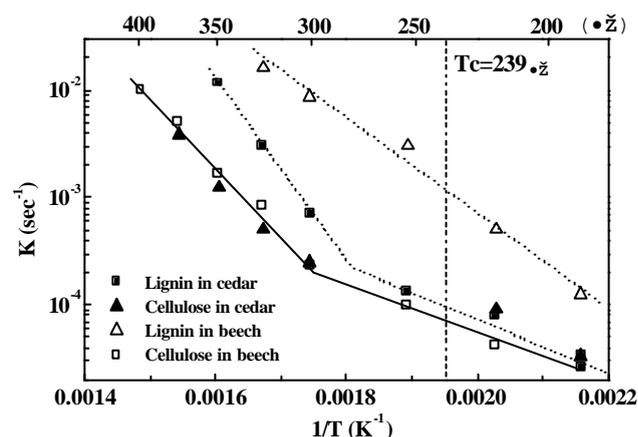


Fig.2 Arrhenius plot for the decomposition rate constants of lignin and cellulose in the cedar and beech woods in sub- and supercritical methanol.