

Reactivity of lignin in supercritical methanol studied with some lignin model compounds

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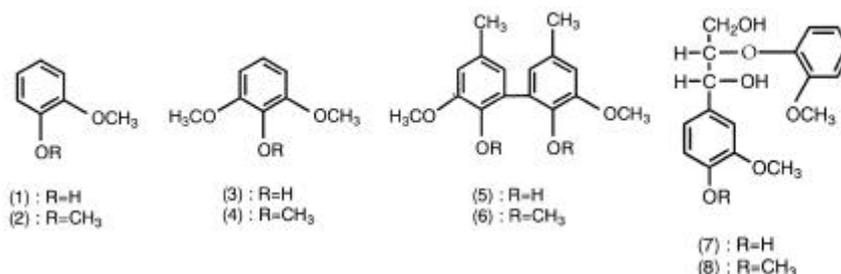
Behaviors of lignin in supercritical methanol ($>239^{\circ}\text{C}$; $> 8.09\text{MPa}$) were studied by using lignin model compounds. As a result, β -ether linkage of β -O-4 type of lignin model compound was cleaved off rapidly, while that of the biphenyl linkage of 5-5 type was stable during the supercritical treatment of methanol. This result can suggest that the supercritical methanol treatment is very effective to depolymerize lignin into the lower molecular products as the methanol-solubles mainly by the cleavage of the dominant β -ether structure in lignin.

Introduction

Behaviors of lignin in woody biomass, which is a complex material with polymerized structure of phenylpropane units such as guaiacyl and syringyl moieties, remain unclear in supercritical fluid. In this paper, therefore, reaction of lignin in softwood and hardwood was studied in supercritical methanol by using a series of simple aromatic model compounds and dimeric biphenyl and β -O-4 lignin model compounds.

Materials and methods

Materials Guaiacol (1), veratrole (2), 2,6-dimethoxyphenol (3), 1,2,3-trimethoxybenzene (4), 2,2'-dihydroxy-3,3'-dimethoxy-5,5'-dimethylbiphenyl (5), 2,2',3,3'-tetramethoxy-5,5'-dimethylbiphenyl (6), guaiacylglycerol- β -guaiacyl ether (7) and veratrylglycerol- β -guaiacyl ether (8) were provided for supercritical methanol treatment.



Supercritical methanol treatment of lignin model compounds

To start a treatment of model compounds in supercritical methanol, the reaction vessel with 10.0mg lignin model compound dissolved in 5.0ml of methanol was quickly heated by immersing it into the tin bath preheated at 270°C and maintained under supercritical conditions for 1 to 20min. The obtained supercritical conditions of methanol were $250\text{--}270^{\circ}\text{C}$ in temperature and $15\text{--}18\text{MPa}$ in pressure. After an adequate reaction time, the reaction vessel was moved into the water bath to quench the reaction. The resulting reaction mixture was directly analyzed by HPLC and separated by using TLC. The isolated compounds were acetylated and analyzed by $^1\text{H-NMR}$ spectra.

Results and Discussion

Reactivity of the aromatic rings in lignin Reactivity of the aromatic rings in lignin in supercritical methanol was evaluated by using guaiacol (1) and veratrole (2) as model compounds for guaiacyl nuclei, and 2,6-dimethoxyphenol (3) and 1,2,3-trimethoxybenzene (4) as those for syringyl nuclei. As a result, 98% of compound (1), 99% of compound (2), 91% of compound (3) and 97% of compound (4) were respectively recovered after 10min treatment. Therefore, aromatic rings of softwood and hardwood lignins consisting, respectively, of guaiacyl type of nucleus and guaiacyl and syringyl types of nuclei can be stable under supercritical conditions of methanol at 270°C .

Reactivity of condensed and β -O-4 structures in lignin Reactivity of lignin was then investigated, focusing on the linkages between phenylpropane ($\text{C}_6\text{-C}_3$) units in lignin by using biphenyl and β -O-4

types of dimeric lignin model compounds (5)~(8). β -ether structure which is represented by β -O-4 model compounds (7) and (8), is the most abundant linkage of the natural lignin. On the other hand, condensed structure, which is represented by biphenyl model compounds (5) and (6), is an important linkage of lignin, especially in softwood. As condensed structures in lignin, phenolic and non-phenolic biphenyl model compounds (5) and (6) were recovered 78% and 91%, respectively, after 10min treatment. Therefore, condensed structure in lignin is comparatively stable under the supercritical treatment of methanol at 270°C. As to β -O-4 model compounds, they were found to be very reactive in supercritical conditions especially in phenolic form. Fig. 1 shows degradation pathway of β -O-4 model compound (7) and (8). Phenolic model compound (7) was first converted into guaiacol and coniferyl alcohol (9), and the latter product was further methylated at 2-position (10). On the other hand, non-phenolic model compound (8) was converted into its α -methyl ether (11), and then, into *cis* and *trans* isomers of enol ethers (12), followed by the successive cleavage of β -ether linkage.

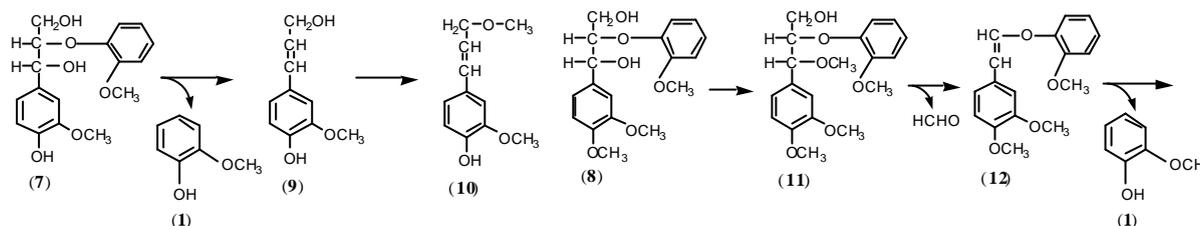


Fig. 1. Degradation pathway of β -O-4 model compounds (7) and (8).

Time-course change in the amount of guaiacol, which directly indicates the β -ether cleavage during supercritical methanol treatment is shown in Fig. 2. Guaiacol is produced very quickly from phenolic β -O-4 model compound (7), whereas the formation rate of guaiacol is comparatively small for non-phenolic model compound (8), especially in the early stage of the reaction. This shows that phenolic β -ether bonding is more easily cleaved than non-phenolic one under supercritical condition of methanol at 270°C. Then, we examined the same experiment as written above, from 180°C to 350°C. Fig. 3 shows arrhenius plot for cleavage velocity of β -ether linkage. The cleavage velocity of phenolic β -O-4 model compound (7) is faster than that of non-phenolic model compound (8) in every treatment temperature. Activated energy for cleavage of non-phenolic model compound (8) was larger than that of phenolic model compound (7). Therefore, cleavage velocity of non-phenolic model compound (8) will be close to that of phenolic model compound (7) in much higher temperature.

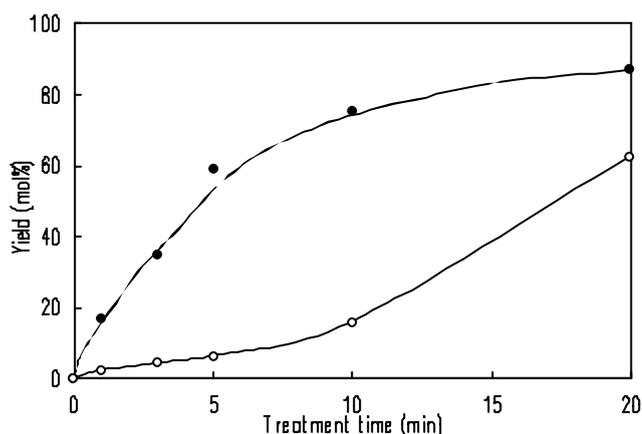


Fig. 2. Yields of guaiacol from phenolic and non-phenolic β -O-4 types of lignin model compounds (7) and (8) in supercritical methanol.

● : Phenolic model compound (7) ○ : Non-phenolic model compound (8)

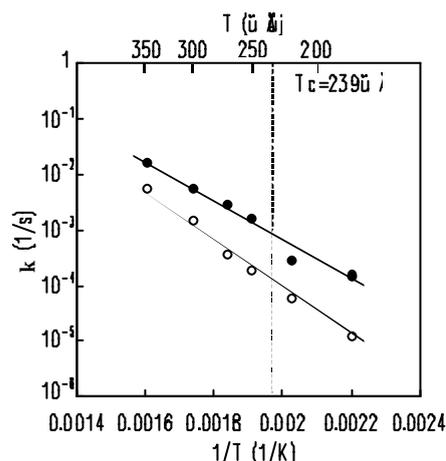


Fig. 3. Arrhenius plot for cleavage velocity of β -ether linkage

● : Phenolic model compound (7)
○ : Non-phenolic model compound (8)

