3-5-1 リグニン芳香核モデルとしてのグアヤコール及び シリンゴールの熱分解経路

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Thermal decomposition pathways of guaiacol and syringol as model lignin aromatic nuclei

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Wood lignins include guaiacyl (2-methoxyphenoxy)- and syringyl (2, 6-dimethoxyphenoxy)-types of aromatic nuclei, and their compositions are quite different in wood species, especially hardwood and softwood. In this work, thermal decomposition pathways of guaiacol (2-methoxyphenol) and syringol (2,6-dimethoxyphenol) were studied, which are models of guaiacyl- and syringyl-nuclei, respectively. Heat-treatment was conducted in a closed ampoule reactor under the conditions of N_2/ 600°C/ 40-600 s. From the present results, pyrolysis pathways of guaiacol and syringol were clarified, and additional OCH_3 group in syringol was found to result in higher coke formation reactivity. Roles of pyrolysis intermediates in coke and gas formation are also discussed.

1. Introduction

Softwood and hardwood lignins have different compositions of aromatic nuclei, i.e. guaiacyl-type in softwood and guaiacyl-syringyl-types in hardwood. Such difference may affect the pyrolysis and secondary reaction behaviors of lignins. In our previous study [1], we compared the pyrolysis behaviors of Japanese cedar (Cryptomeria japonica, a softwood) and Japanese beech (Fagus crenata, a hardwood) milled wood lignins (MWLs). As a result, the following features were identified as the different points between their MWLs; coke formation was more extensive in beech; GC/MS-detectable tar yield was much lower in beech; the GC/MS-detectable tar compositions became similar at longer heating time, although the compositions at short heating time were quite different. To clarify the pyrolysis characteristics of aromatic nuclei in lignin, pyrolysis pathways of guaiacol and syringol were studied in this paper, focusing on the role of additional methoxyl (OCH_3) group in syringol.

2. Experimental

10 mg of sample was heated in a closed ampoule reactor under the conditions of N_2/ 600°C/ 40-600 s. After heat treatment, the ampoule was cooled by flowing air for 1 min, and non-condensable gases were analyzed by Micro GC. Then, inside of the ampoule was extracted with methanol (2 ml). The soluble portion was analyzed by GC/MS to determine the low molecular weight (MW) products. The amounts of gaseous, tar and char factions were determined by weight difference after gas collection or extraction.

3. Results and discussion

3.1 Guaiacol and syringol pyrolysis

As shown in Fig. 1, the coke yields were generally higher in syringol than guaiacol. The gas yields were also higher in syringol (1.3 times at 600 s). Thus, additional OCH_3 group in syringol was found to enhance the coke formation reactivity with higher gas yield. This was also suggested from the temperature-dependency experiments (400-600°C/ 120 s). Syringol and guaiacol started to form coke at 450°C, and the yields from syringol were almost double (23.5-35.0 wt%) of those (10.9-15.0 wt%) from guaiacol.

Figure 2 illustrates the formation and decomposition behaviors of the GC/MS-detectable low MW products. These were found to be grouped into three-types, i.e. the O-CH_3 homolysis and the OCH_3 rearrangement products as well as PAH. The O-CH_3 homolysis products disappeared shortly (~120 s), while the OCH_3 rearrangement products were comparatively stable and observed even at 600 s. Their yields, especially the OCH_3 rearranged products, were lower in syringol than guaiacol. This is explainable with the higher coke yield from syringol as discussed later. The pyrolysis intermediates from syringol may be converted into coke preferentially.

A proposed formation mechanism of these low MW tar components from syringol is illustrated in Fig. 3. The O-CH_3 homolysis (H) and OCH_3 rearrangement (R) starting from phenoxy radical form are the key reaction types. The homolysis forms phenoxy radical and methyl radical, which are further converted into
phenols (i.e. catechols, pyrogallols) and CH₄, respectively.

On the other hand, the OCH₃ rearrangement forms o-quinonemethides as reactive intermediates, which are further converted into the aromatics with methyl substituents (i.e. cresols, xyleneols). Hosoya et al. reported that this pathway is also related to the coke formation [2]. Additional OCH₃ group in syringol makes the chance of this rearrangement reaction twice as compared with guaiacol. This may increase the coke yield, while decrease the low MW tar yield from syringol. This was also supported by the pyrolysis experiments of 3-methoxycatechol and 2-methoxy-6-methylphenol as pyrolysis intermediates of syringol. Both compounds produced substantial amount of coke in 80 s, when other intermediates without OCH₃ group did not form any coke.

3.2 Intermediates pyrolysis

Pyrolysis of each low MW product was also conducted under the similar pyrolysis conditions to understand the role (fate) of these intermediates. The homolysis products (catechols and pyrogallols) produced mainly CO even at comparatively short pyrolysis times of 80 and 120. Contrary to this, the rearrangement products (cresols and xyleneols) formed mainly CH₄ and H₂ and their reactivity were much lower than the homolysis products. These results were consistent with the gas formation and tar decomposition behaviors in guaiacol and syringol pyrolysis. Higher disappearing rate of the homolysis products from syringol (Fig. 2) was explainable with their higher decomposition reactivities.

4. Conclusions

Pyrolysis pathways of guaiacol and syringol were clarified at the molecular level, and additional OCH₃ group in syringol was found to lead to more effective coke formation. These lines of information will be useful for effective process proposal in fast pyrolysis and gasification.

5. References