Char reactivities in pyrolysis of Japanese cedar and Japanese beech woods at a gasification temperature

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Primary pyrolysis and secondary reactions behaviors were compared between Japanese cedar wood (a softwood) and Japanese beech wood (a hardwood) under the conditions of oven-dried/ N₂/ 600°C/ 40-600 s by using a closed ampoule reactor. Their demineralized samples were also used. As a result, a major difference was observed for the char gasification reactivities in the secondary reaction stage (120-600 s). Only the yield of beech wood char decreased significantly from ~20% to 3% in this period and gave CO, CO₂, CH₄ and H₂. Although demineralization substantially reduced the beech wood char reactivity, the beech wood char had still higher reactivity than the cedar wood char. In contrast, thermogravimetric (TG) analysis under N₂ flow gave similar DTG curves for both chars. In co-pyrolysis of the chars (obtained by pyrolysis for 40s) with wood samples, char reactivity difference became observable. This also indicates that such a high gasification reactivity of the beech wood char is related to the pyrolysis environment including water, low molecular weight products etc.

1. Introduction
Gasification is known to proceed in a two-stage process, which includes a primary pyrolysis to form primary volatile (tar) and char and their decomposition to gaseous products, tar and char in the secondary reaction stage. Hosoya et al. have reported the primary pyrolysis behaviors [1], influences of the inorganic substances on primary pyrolysis [2], gasification reactivities of primary products [3] and tar conversion and reactivities [4], focusing on softwood and the constituent polymers.

There are two major types of wood species, i.e. softwood and hardwood. Hemicellulose and lignin structures are known to be different between these two types of species. Thus, such different chemical structures are expected to affect the gasification characteristics. However, few papers have focused on these differences especially at the molecular level. Under these circumstances, primary pyrolysis and secondary reactions behaviors were compared between Japanese cedar (Cryptomeria japonica) wood (a softwood) and Japanese beech (Fagus crenata) wood (a hardwood). This paper especially focuses on char reactivity. Formation behaviors of the components in tar and gas fractions were already reported [5].

2. Experimental
Extractive-free wood flours prepared from Japanese beech and Japanese cedar woods and their demineralized (by acid-washing) samples (oven-dried, 105°C for 24 h) were used. Sample (10 mg) was heated in a closed ampoule reactor in N₂ by inserting the ampoule in a muffle furnace (600°C) for 40-600 s. After heat treatment, the ampoule was cooled by flowing air for 1 min, and non-condensable gases were analyzed by gas chromatography (GC) with thermal conductivity detector (TCD). Two types of the chars were observed; one is primary char (at the bottom of reactor) and the other is secondary char (at the upper side of the glass wall). The amounts of gaseous, tar and char factions were determined by weight difference after gas collection or extraction. The primary chars obtained after pyrolysis for 40 s were also analyzed with thermogravimetry (TG) under the N₂ flow. These
chars were also co-pyrolyzed with wood or demineralized wood (N₂/600°C/120 s) to get information of the reactivities under the pyrolysis environments.

3. Results and discussion

3.1 Gas, tar, char and water formation behavior

As shown in Fig. 1, the char yields from cedar wood were almost constant (about 30 wt%) between 120 and 600 s, the yield from beech wood decreased greatly (22 to 3 wt%) along with the increasing formation of CO, CO₂, CH₄ and H₂. Accordingly, gasification reactivity of char was found: beech >> cedar. Although, this high reactivity was decreased substantially by demineralization, the beech wood char still had higher reactivity. Demineralization rather increased the char reactivity for cedar. Interestingly, such high char reactivity was not observed with air-dried wood. These results suggest that water, even in a small content, may change the primary char formation pathways and this may result in lowering the char gasification reactivity.

3.2 TG analysis of char

As shown in Fig. 2, the DTG peaks shifted slightly higher temperature region. However, no remarkable differences were observed enough to explain high gasification reactivity of the beech wood char.

3.3 Co-pyrolysis of char with wood

Figure 3 shows the char recoveries of char (40 s, 2 mg) + wood sample (8 mg) mixtures in N₂ at 600 °C for 600 s. The char recovery was estimated by subtracting the char yield in pyrolysis of wood sample (8 mg) from the obtained residue. Under these conditions, the beech wood char clearly had higher reactivity than the cedar wood char. Interestingly, the inorganic substances in woods increase the reactivity of beech wood char, while decrease cedar wood char.

These different char reactivities would arise from the different chemical structures of cedar and beech woods.

4. References