Thermogravimetric and Mass-Spectrometric Analyses of Japanese Cedar Wood (Cryptomeria japonica) for Basic Study of Gasification

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Thermal weight change of Japanese cedar wood (Cryptomeria japonica) in helium with steam or steam-oxygen was measured and temperature dependences of produced compounds were analyzed by means of a thermogravimetric-mass spectrometric analyzer. Weight loss increased when adding oxygen. It suggested that oxygen accelerated gasification reactions. Decomposition of holocellulose started at around 200°C, and ended at around 390°C or 380°C, at which corresponding curve of the thermal weight change bent. Decomposition of lignin started around 250°C. Simultaneous decompositions of holocellulose and lignin caused rapid weight loss in temperature range of 250-380°C or 250-390°C.

Key Words

Biomass, Gasification, Thermogravimetric-mass spectrometric analysis, Skimmer interface

1. Introduction

Biomass gasification is expected to reduce CO2 emissions and to prevent global warming. Various types of gasification have been developed. Advanced ones, such as entrained-flow or fluidized-bed, use steam or a mixture of steam-oxygen as a gasification agent and traditional ones, such as fixed-bed, use insufficient air.

We modified a commercially available thermogravimetric analyzer (TG, Rigaku, model TG8120+HUM1), so that its inside atmosphere was controllable to be helium alone, or with steam, oxygen or both. We connected a gas chromatograph-mass spectrometer (GCMS, Agilent, model hp5890+hp5791A, or Shimadzu, model GCMS-QP5050A) to the TG for identifying produced compounds 1) 2). The TG/GCMS analyses of Japanese cedar wood showed that holocellulose decomposed to oxygenated cyclic compounds and lignin decomposed to phenol derivatives 3).

Although the TG/GCMS analyses were useful for studying gasification reactions, it was very difficult to measure temperature dependences of the produced compounds because they were collected in a liquid nitrogen trap at predetermined temperature. We modified the TG again so that a quadrupole-type mass spectrometer (MS, Canon-Anelva, model M-400QA) was operable together. A unique skimmer interface was used for connecting them and for real-time monitoring of thermal behavior 3) ~ 5). Thermal and atmospheric effects on gasification reactions of Japanese cedar wood by means of the TG/MS were reported in this manuscript.
2. Experiments

Elemental and chemical analyses of Japanese cedar wood (*Cryptomeria japonica*) were reported previously. For effective exposure to the atmospheric gas, pulverized Japanese cedar wood of about 2 mg was loosely packed in a shallow cylindrical pan made of alumina, diameter and height of which were 5 mm and 2.5 mm, respectively. In this series of measurements, total flow rate of the dry and wet helium was almost kept constant of 500 sccm (standard cubic centimeter per minute), 500 cm³/min at 0 °C and 0.1013 MPa. Relative humidity of the mixed gas was controlled to be 70% at 40 °C. Dry oxygen of 10 sccm was introduced from an extra-port to the mixing chamber when needed. Heating rate was set to be 0.33 °C/s (=20 °C/min).

Fig. 1 shows schematics of a system setup of the TG/MS. The skimmer interface was consisted of outer and inner ones. Each of them had a small hole at its top. Middle space between them was sucked by means of a rotary pump to keep pressure difference between the TG and the MS stably: the TG main chamber was kept at atmospheric pressure and the MS was lower than 10 mPa. The skimmer interface enabled quick MS analyses before the produced compounds reacted or changed: the compounds easily reacted or changed, for example during passing through a long capillary, because of their high reactivities.

A needle-valve of variable conductance (Swagelok, model SS-1RS4-A) was installed between the skimmer interface and the rotary pump to control flow of the evolved gas from the TG to the MS: flow of the evolved gas from the TG to the rotary pump decreased as conductance of the needle-valve decreased, consequently, its flow to the MS increased. Pressure in the MS was controlled to be about 10 mPa, upper limit of the MS, to maximize its sensitivity. A UV lamp was used for fragment-less ionization, that was a kind of soft ionization and caused neither fragmentations nor double-charged ion peaks. Its advantage was that one peak in a mass spectrum indicated one species, which lead needlessness chromatographic separation. The MS could not distinguish compounds having the same molecular weight or isomers, however, this problem was avoided when selecting compounds based on the previous TG/GCMS analyses or on other information, as discussed later.

3. Results and Discussion

Fig. 2 shows thermal weight changes of the Japanese cedar wood in He+H₂O (blue) and He+H₂O+O₂ (red). Its weight loss increased when adding oxygen. It meant that oxygen accelerated decompositions of the cedar wood.

We selected furfuryl formate (126 amu), 5-methylfurfural (110 amu), furfural (96 amu) and 2-methylfuran (82 amu) from the oxygenated cyclic compounds.

![Fig. 1 System setup of TG/MS](image1)

![Fig. 2 Thermal weight changes of Japanese cedar wood in He+H₂O (blue) and He+H₂O+O₂ (red). Vertical axis was normalized by its weight at 120 °C](image2)
Fig. 3 shows temperature dependences of 5-methylfurfural. It gradually increased above 200 °C, around which the weight started decreasing. It rapidly decreased above 390 °C (He+H2O) or 380 °C (He+H2O+O2), at which corresponding TG curve bent. It meant that the TG curve bent when decomposition of holocellulose ended. Other 3 compounds had similar dependences.

We selected dihydroeugenol (166 amu), eugenol (164 amu), creosol (138 amu), guaiacol (124 amu) and phenol (94 amu) from the phenol derivatives.

Fig. 4 shows temperature dependences of dihydroeugenol. When atmosphere was He+H2O, it gradually increased above 250 °C, became maximum at around 380 °C, then gradually decreased till about 700 °C. When atmosphere was He+H2O+O2, it also increased above 250 °C, rapidly decreased above 380 °C, and was hardly detected above 410 °C. Dihydroeugenol and eugenol had similar dependences probably because their molecular weights were near.

Fig. 5 shows temperature dependences of creosol. When atmosphere was He+H2O, it gradually increased above 250 °C and gradually decreased till 500 °C. When atmosphere was He+H2O+O2, it also increased above 250 °C, rapidly decreased above 380 °C, and was hardly detected above 410 °C. Creosol and guaiacol had similar dependences.

Fig. 6 shows temperature dependences of phenol. When atmosphere was He+H2O, it had 2 peaks, which suggested that phenol was produced through 2 different processes. The peak at around 390 °C gradually increased above 250 °C and rapidly decreased above 390 °C. It was attributable to decomposition of lignin. The peak around 470 °C was attributable to decomposition of other phenol derivatives of higher molecular weights. When atmosphere was He+H2O+O2, little phenol was detected and its
temperature dependence was not clear.

Phenol derivatives of higher molecular weights were detected till higher temperatures than those of lower weights: dihydroeugenol and eugenol were detected till about 700 °C (He+H2O) or 500 °C (He+H2O+O2). Phenol was hardly detected above 420 °C. Temperature dependences of creosol and guaiacol were between them. Those dependences suggested that lignin of complicated structure was more hardly gasified than simple one, because phenol derivatives of high molecular weights were probably produced from lignin of complicated structures.

Decomposition of holocellulose started at around 200 °C and ended at around 390 °C or 380 °C when atmosphere was He+H2O or He+H2O+O2, respectively. Decomposition of lignin started at around 250 °C. Simultaneous decompositions of holocellulose and lignin caused rapid weight loss in temperature range of 250-380 °C or 250-390 °C. Selection of compounds were based on our previous TG/GCMS analyses of Japanese cedar wood 1). We selected compounds, whose isomers were not detected, at first. As an example, we selected 5-methylfurfural because no other compounds having molecular weight of 110 amu, such as catechol, were detected. We used other information when the TG/GCMS analyses were not clear. As an example, the TG/GCMS analyses identified a compound of 124 amu as guaiacol or mequinol, however, we determined it as guaiacol because Japanese cedar was a kind of conifer, its lignin was composed of coniferyl alcohol, and guaiacol was produced from coniferyl alcohol 7).

When adding oxygen, weight loss of the Japanese cedar wood increased, but amounts of both oxygenated cyclic compounds and phenol derivatives decreased. The previous TG/GCMS analyses showed that kinds of produced compounds and their amounts decreased when adding oxygen 5). These atmospheric effects suggested that both oxygenated cyclic compounds and phenol derivatives were intermediates and that oxygen accelerated their decompositions to gases.

4. Conclusion

The TG/MS analyses combined with the TG/GCMS analyses were useful for studying thermal and atmospheric effects on biomass gasification. We estimated that oxygen accelerated gasification reactions of the Japanese cedar wood because its weight loss increased and amounts of produced compounds decreased. However, other estimations were possible, such that oxygen changed reaction processes or pathways, therefore, amounts of the oxygenated cyclic compounds and the phenol derivatives decreased. Clarifying details of gasification reactions and processes needs advanced studies.

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