Production of aromatic compounds and functional carbon materials by pulse current pyrolysis of woody biomass

Pyrolysis is an important technology involving the efficient conversion of biomass materials to fuel and chemicals in a short time. Pyrolysis employing the pulse current heating method can be applied to satisfy these requirements in the selective conversion of wood biomass to useful chemical substances. The optimization of pyrolysis conditions is necessary for improving the applicability of this heating method in the production of pyrolysis oil and char with the required characteristics.

This research was carried out for the purpose of utilizing both pyrolysis oil and char that were obtained from woody biomass, and for selectively producing functional carbon composite materials and pyrolysis oil containing useful compounds. The pyrolysis products were characterized, and the effects of the pyrolysis conditions on product distribution, pyrolysis oil composition, and carbon composite material composition were investigated.

In Chapter 1, we have applied rapid pyrolysis by pulse current heating for this purpose. Japanese cedar wood was pyrolyzed at various temperatures by pulse current heating, and the compositional and structural changes in the degraded products were characterized using GC-MS, FT-IR, Raman spectroscopy, and elemental analysis. We found that ammonia was adsorbed on the char obtained by the pyrolysis at 500 °C and observed a sharp dependence of the adsorptivity on the pyrolysis temperature. Under this condition, phenolic compounds such as guaiacol, catechol, 4-vinyl guaiacol, and vanillin were produced as the major components of the pyrolysis oil. Deoxygeneation proceeded linearly as a function of the pyrolysis temperature and that pyrolysis at 800 °C produced aromatic hydrocarbons such as naphthalene, acenaphthylene, anthracene, and pyrene along with the current platform chemicals such as benzene, toluene, and styrene. The functionality of residual char as an ammonia adsorbent and the co-production of aromatic chemicals can be highlighted as a new process designed for efficient usage of woody biomass.

In Chapter 2, the relationship between adsorption ability and pyrolysis conditions for Todo-fir char was investigated. Pyrolysis under an air atmosphere was effective in generating acidic functional groups such as carboxylic acid groups, and it improved the properties of the Todo-fir char. A pyrolysis temperature of 300 °C was found to be most effective, and the change in the chemical structure of cellulose was reflected in the formation of acidic functional groups by the pyrolysis of Todo-fir in air. From these results, it was concluded that pyrolysis under an air atmosphere was effective in generating acidic functional groups such as the carboxyl group, which improved the ability of the product to adsorb basic substances like ammonia.

In Chapter 3, the influence of catalysts on the compositions of char and pyrolysis oil obtained by pyrolysis of wood biomass with pulse current heating was studied. The effects of catalysts on product compositions were analyzed using GC-MS and TEM. The compositions of some aromatic compounds changed noticeably when using a metal oxide species as the catalyst. The coexistence or dissolution of amorphous carbon and iron oxide was observed in char pyrolyzed at 800 °C with Fe_3O_4. Pyrolysis oil compositions changed remarkably when formed in the presence of a catalyst compared to that obtained from the uncatalyzed pyrolysis of wood meal. We observed a tendency toward an increase in the ratio of polyaromatic hydrocarbons in the pyrolysis oil composition after catalytic pyrolysis at 800 °C. When iron oxides and TiO_2 were used as catalysts, the composition ratio of aromatic hydrocarbon compounds such as naphthalene was shown to increase, even at a processing temperature of 500 °C. Pyrolysis of biomass using pulse current heating and an adequate amount of catalyst is expected to yield a higher content of specific polyaromatic compounds.

In Chapter 4, the pyrolysis of rice husks, Todo-fir, and cellulose by pulse current heating was examined to elucidate the influences of reaction temperature on their product distributions and chemical properties of the resulting oil and char fractions for utilization of pyrolysis products obtained from biomass. Some common characteristics were found for each product distribution: The maximum yield of pyrolysis oil obtained from each material was observed at 500–600 °C. In contrast, the following characteristic properties of pyrolysis products obtained from each material were observed: High ash content and char yields at each processing temperature were found in the rice husk pyrolysis products. Aromatic hydrocarbons were detected in the pyrolysis oil obtained from rice husks at lower temperature pyrolysis. The yield of pyrolysis oil obtained from rice husks was lower than that from Todo-fir, and the yield of pyrolysis oil obtained from Todo-fir tended to be higher than those from rice husks and cellulose at all temperatures. Plenty of levoglucosan was detected in the pyrolysis oil obtained from cellulose at 500–800 °C, although the yield of the pyrolysis oil was not so high. In the pyrolysis oil obtained from rice husks, such aromatic hydrocarbons as benzene and styrene, as well as polycyclic aromatic hydrocarbons like naphthalene, phenanthrene, anthracene, and pyrene, were detected at 600–800 °C.

The chemical structure and microscopic structure of the carbon composite materials obtained at each pyrolysis temperature were shown by investigating the relationship between the pyrolysis conditions and the catalytic effect of the metal oxide. Since suitable pyrolysis conditions for producing ammonia adsorbent and the characteristics of the metal oxide carbon composite material were shown, char obtained as a pyrolysis residue was considered to contribute to the production of a useful material in addition to pyrolysis oil. Moreover, this method was applied for the production of silica carbon composite material along with the pyrolysis oil, by using rice husk, a previously unutilized biomass, as the raw material. Accordingly, the results of this research are expected to contribute to the effective use of unused resources for producing pyrolysis oil containing useful compounds and functional carbon composite materials.