

Effects of pyrolysis oil recycling and reaction gas atmosphere on the physical properties and reactivity of charcoal from wood

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Biomass char, so called “charcoal”, has become an alternative fuel to replace fossil coal. This work reports on optimization of biomass pyrolysis to maximize charcoal and fixed carbon yields, which directly affects the productivity of the process. Our previous study [1] showed a promising method to increase the charcoal yield by pyrolysis oil collection and cold recycling/embedding. Meanwhile, the method did not alter bulk chemical qualities of the charcoal such as the carbon content. In addition, using CO₂ as pyrolysis atmosphere significantly increased the charcoal yield under practical conditions (slow heating of 20 mm size particles at temperature below 700 °C). In this follow-up study, more detailed characterizations of physical properties and CO₂ gasification reactivity are carried out to assess the suitability of the charcoals produced for thermochemical conversion processes. Another objective of this study is to investigate the effect of reaction conditions on charcoal properties. This is particularly important because local pyrolysis conditions inside large particles differ significantly from that of pulverized particles.

Charcoal samples were prepared from 20 mm woodchips (spruce and birch) under different pyrolysis conditions, i.e. temperature (300, 500, and 700 °C), heating rate (isothermal reactor and 3 °C min⁻¹), pyrolysis oil embedding on woodchip, and reaction gas atmosphere (N₂ and CO₂). Thermogravimetric analysis was carried out on pulverized charcoal to determine the gasification reactivity of charcoal under 20% CO₂ in N₂ at 850 °C with rapid heating (ca. 500 °C min⁻¹). In addition, several analytical techniques were employed to examine charcoal properties, i.e. scanning electron microscopy, nitrogen adsorption, and Raman spectroscopy.

The results from determination of specific surface area using nitrogen adsorption isotherm and BET-algorithm showed that pyrolysis temperature and heating rate have significant effects on the specific surface area of the charcoal. Charcoal produced at a high pyrolysis temperature had a higher specific surface area due to a higher devolatilization degree. Likewise, the charcoal had a higher specific surface area when it was produced at a low heating rate, i.e. less charcoal matrix destructive pyrolysis conditions. Meanwhile, other parameters such as original biomass, pyrolysis oil embedding, and reaction gas atmosphere (N₂ or CO₂) showed no clear effects on the specific surface area. Estimation of the size of fused aromatic clusters in the charcoal was done by comparing the intensity ratio (I_D/I_G) of Raman spectra. This ratio represents proportion between aromatic fused ring (>6 rings) and amorphous structure of small aromatic ring (3-5 rings). At elevated pyrolysis temperature, number of aromatic fused rings increased indicating gradual ordering of the carbon structure. On the other hand, the other pyrolysis parameters showed no significant effects on the aromatic structure. SEM images did not reveal significant difference on >µm scale in the morphology and microstructure of charcoal produced from studied reaction parameters.

By combining the results from characterization of physical properties and gasification reactivity of charcoal, this work is expected to contribute with knowledge on reaction behavior of charcoals produced a wide range of relevant different methods and operating conditions involving pyrolysis oil recycling. Increased charcoal yields are reported from the impregnations, and a detailed description of associated charcoal properties is provided.

References:

- [1] A. Phounglamcheik, T. Wretborn, K. Umeki, Biomass pyrolysis with bio-oil recycle to increase energy recovery in biochar, in: 25th Eur. Biomass Conf. Exhibition, Stockholm, 2017: pp. 1388–1392. doi:10.5071/25thEUBCE2017-3CV.2.6.