MECHANISM OF HYDROCHAR FORMATION FROM BLACK LIQUOR

Elsa Weiss-Hortala, Mines Albi, RAPSODEE UMR CNRS 5302, France elsa.weiss@mines-albi.fr Hélène Boucard, Mines Albi, RAPSODEE UMR CNRS 5302, France Fabienne Espitalier, Mines Albi, RAPSODEE UMR CNRS 5302, France Radu Barna, Mines Albi, RAPSODEE UMR CNRS 5302, France Ange Nzihou, Mines Albi, RAPSODEE UMR CNRS 5302, France

Key Words: hydrochar, black liquor, carbon microparticles.

Hydrothermal carbonization is gaining increasing attention, since hydrochar demonstrates benefits for a large range of applications (biofuel, energy storage, electrodes...) [1]. The generation of solid is basically performed from solid materials (biomass or waste) making difficult the understanding of the phenomena involved. The aim of this study is to better understand the generation of hydrochar in subcritical conditions using black liquor. Black liquor (BL) is an alkaline liquid residue of paper industry containing high concentration of dissolved organics (lignin, partially hydrolyzed cellulose), and a high inorganics content (K, Na, Ca, S...). that makes it a high-value biomass. BL was chosen for its high water, organic and inorganic contents of respectively 80, 14 and 6 wt%. The study has been performed in batch reactor at 350°C, under autogenous pressure for various reaction times (0.5 to 24h).

Analysis of the reaction residue shows that for short reaction times (< 2h), carbonaceous microparticles are formed. At longer reaction time the size of the particles increased and then decreased (Figure 1). Their size is influenced by reaction time, and the heating and cooling rates as well. Available theories of carbonization were suitable to explain the particle generation up to 1.5h and above 6h. For instance, up to 90 min, the particles are formed due to the sursaturation of phenols and aldehydes in the droplets of oily phase dispersed in the aqueous phase [1]; above 6h, nucleation occurs in the transition media forming new microparticles due to phase equilibria [2]. In the mean time, the composition in the liquid does not vary significantly while the particle size increased. To account for the particle size and composition evolving, an hypothesis has been formulated involving the physical reorganization of the solid phase (coalescence of the transition layer) resulting in a coalescence of carbon particles.



Figure 1 – particle size distribution (in volume) versus reaction time at 350°C

[1] S. Román, J. Libra, N. Berge, E. Sabio, K. Ro, L. Li, B. Ledesma, A. Álvarez, S. Bae, "Hydrothermal Carbonization: Modeling, Final Properties Design and Applications: A Review", Energies, 11, 216, 2018
[2] V. K. La Mer, "Nucleation in Phase Transitions," Ind. Eng. Chem., 44, 1952
[3] M. Inagaki, K. C. Park, and M. Endo, "Carbonization under pressure," New Carbon Mater., 25, 409–420, 2010.