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Lignin Pyrolysis to Value-Added Chemicals: A Mechanistic Approach

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Abstract : The thermochemical conversion of lignin has received an increasing interest in the frame of different biorefinery concepts for the production of chemicals or energy. It is needed to better understand the physical and chemical conversion of lignin for feeder and reactor designs. In-situ rheology reveals the viscoelastic behaviour of lignin upon thermal conversion. The softening, re-solidification (char formation), swelling and shrinking behaviours are quantified during pyrolysis in real-time [1]. The in-situ rheology of an alkali lignin (Protobind 1000) was conducted in high torque controlled strain rheometer from 35°C to 400°C with a heating rate of 5°C.min-1. The swelling, through glass phase transition overlapped with depolymerization, and solidification (crosslinking and “char” formation) are two main phenomena observed during lignin pyrolysis. The onset of temperatures for softening and solidification for this lignin has been found to be 141°C and 248°C respectively. An ex-situ characterization of lignin/char residues obtained at different temperatures after quenching in the rheometer gives a clear understanding of the pathway of lignin degradation. The lignin residues were sampled from the mid-point temperatures of the softening range and solidification range to study the chemical transformations undergoing. Elemental analysis, FTIR and solid state NMR were conducted after quenching the solid residues (lignin/char). The quenched solid was also extracted by suitable solvent and followed by acetylation and GPC-UV analysis. The combination of 13C NMR and GPC-UV reveals the depolymerization followed by crosslinking of lignin/char. NMR and FTIR provide the evolution of functional moieties upon temperature. Physical and chemical mechanisms occurring during lignin pyrolysis are accounted in this study. Thanks to all these complementary methods.

Keywords : pyrolysis, bio-chemicals, valorization, mechanism, softening, solidification, cross linking, rheology, spectroscopic methods

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