Improving Biomass Processes via Structure Characterization and Valorization of Humins and Process Intensification

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Tuesday, Dec 10th, 2019-10:00 AM- CLB 366

Due to increasing concerns of global warming, research on the conversion of biomass to renewable chemicals and fuels has received considerable attention. The concept of "biorefinery" has been proposed but constructing an economically feasible biorefinery remains challenging due to technical difficulties associated with the formation of side products impacting the process economics. Humins are carbonaceous, polymeric byproducts that are formed during acid-catalyzed, hydrothermal processing of sugars to bio-based platform molecules, such as 5-hydroxymethyl furfural (HMF). Currently, humins are a low-value byproduct used mainly for combustion. The deposition of these solid particles on reactors and processing equipment increases the maintenance costs. Minimization of humins formation and/or their valorization are essential for improving process economics. The lack of thorough understanding of humins' structure hinders efforts towards their valorization. To bridge this gap, this dissertation develops methods to understand the microstructure of humins through solubility experiments. First, we have conducted dissolution experiments in various solvents and correlated the solubility data to molecular properties of solvents to develop suitable descriptors. By doing this, we have identified solvents for high solubility of humins at room temperature and provided insights into the mechanism of humins dissolution. Next, Liquid Chromatography- Mass Spectrometry (LC-MS) was used to determine and compare the masses of components in the humins solubilized in different solvents. Finally, a six-stage dissolution experiment was done to investigate the structural inhomogeneity of humins. Both Fourier Transform Infrared Spectroscopy (FT-IR) and LC-MS were used to characterize the solubilized and insoluble humins obtained at each stage. Based on our results, an inhomogeneous structure where macromolecular and molecular components are connected through weak forces, was proposed.

To understand the formation and growth of humins, we use ultra-Small Angle X-ray Scattering (USAXS) to investigate the evolution of size, morphology, volume fraction and number concentration of humins formed during dehydration of fructose and rehydration of 5-

hydroxymethylfurfural (HMF)in acidic solutions. The radius of gyration (Rg) of suspended humins particles grows linearly with time and is accompanied by an increase in polydispersity (PD), before possible precipitation occurs. The scattering patterns indicate fractal-like structures. The apparent activation energy of humins growth is 102±0.4 kJ/mol. The trends in the number of particles over time reveal competing processes entailing the continuous formation of new particles (nucleation) leading to increasing polydispersity with time and the aggregation of existing particles and possible precipitation. The direct observation of growth of humins indicates that humins form primarily from HMF rather than fructose.

Having understood and valorized the humins byproduct, we shift the focus to applying process intensification to glucose chemistry for improving the HMF yield. We have built a flow microchannel reactor with good heat and mass transfer for the conversion of glucose to HMF. Comparison with batch reactor data demonstrated the highest ever HMF productivity (% yield per time) compared to literature works conducted using glucose in aqueous flow reactors. The effect of preheating the $CrCl_3$ catalyst and its speciation on the catalytic activity was also systematically studied by combining reactivity tests and UV-Visible Spectroscopy (UV-Vis) experiments. When preheating times of $CrCl_3$ are short, the glucose consumption rate increases due to Cr^{3+} hydrolysis forming the catalytically active $[Cr(H_2O)_5(OH)]^{2+}$ species. As the preheating time of $CrCl_3$ increases further, the glucose consumption rate drops as a result of Cr(III) oligomers and solids formation which reduce the active species concentration.