Materials and Chemicals from Renewable and Waste Carbon Sources: Reaction Engineering and Spectroscopy

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Carbon from renewable and waste resources is abundant and sustainable; already carbon is a chief component in many existing technologies (fuels, plastics, activated carbon) and many emerging ones (graphene, carbon nanotubes). Using renewable and waste carbon resources for materials and chemicals is likely to play a key role in a sustainable future that mitigates the negative impacts of global climate change. In my group's work, we are developing spectroscopy techniques to study reaction engineering of processes: 1) to convert bio-polymers and waste plastics into simple chemical building blocks and 2) to re-polymerize bio-renewable resources into valuable materials using hydrothermal carbonization.

In terms of polymer degradation, my group is developing in situ spectroscopic and reaction engineering methods to study the complex liquid-phase reactions of de-crystallization, hydrolysis, and de-polymerization required for energy efficient chemical reactors that achieve high yields at mild conditions. We will present the design of a view-cell reactor designed for Raman monitoring of polymer degradation in subcritical water and acid-catalyzed hydrolysis. Using this cell, we have found that cellulose degradation occurs via end-chain de-polymerization without loss of crystallinity over a wide range of temperatures and acid concentrations. These findings contribute to our understanding of the important bottle-neck in cellulose utilization. Upgrading of biorenewable molecules has promise to convert abundant resources into valuable chemicals. Here, we have studied the use of ZSM-5 zeolite under liquid-phase conditions to achieve a 100-fold improvement in process intensity compared to the vapor phase, while modifying the product distribution to favor butanol – a valuable product with uses as a chemical and fuel molecule. This work provides the basis for low cost production of bio-renewable plastics such as polyethylene and poly(ethylene terephthalate).

In re-polymerization, my group is actively studying hydrothermal carbonization as an energy efficient method to produce valuable carbon materials to be used as catalysts, water purification adsorbents, and energy storage materials. A major challenge in this area is characterization of the hydrothermal char product, a supramolecular and defect-rich material consisting of aromatic, aliphatic, and heterocyclic components. We will present simulation and experimental results that establish a new method for interpreting Raman spectra to obtain information on their aromatic structure and configuration. The new interpretation method improves the use of Raman as a lost-cost and convenient way to characterize complex hydrothermal chars. A second challenge is utilization of low-cost waste materials for hydrothermal carbonization. We have used off-line vibrational spectroscopy and thermal analysis to study the extraction and hydrolysis of valuable compounds from coffee factory waste. Here, we find that valuable semi-volatile compounds can be extracted by hot water at relatively mild conditions (≤ 150 °C), whereas hydrolysis and carbonization occur at higher temperature. For polymer waste, we have studied polystyrene de-polymerization in a molten salt reactor. A third challenge is tailoring hydrothermal chars for specific applications. To address this challenge, we have used a mechano-chemical reactor

engineering approach to introduce specific defects into hydrothermal char. Using a combination of spectroscopic techniques, including Raman spectroscopy, we find that the mechano-chemical reactor promotes formation of surface-bound carboxylate groups and aggregation of aromatic domains. Mechano-chemical reactors have promise for targeted functionalization of hydrothermal chars for specific application.