

Biomass pyrolysis chemistry and global kinetics at high heating rates

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The initial step of biomass thermal conversion involves the primary decomposition of the lignocellulosic matrix that is composed of three interconnected polymeric materials: cellulose, hemicellulose, and lignin. Pyrolysis mechanisms typically include a superposition of the kinetic mechanisms for the individual components of the biomass material. The validity and development of these mechanisms is currently being investigated [1,2]. A reliable description of the global kinetics of biomass pyrolysis is the building block for accurately describing the high temperature chemistry that occurs in developing biomass thermochemical conversion systems. These accurate chemical models of biomass gasification and combustion can be used as input in systems analysis models to adjust engineering parameters such as gas velocities, particle residence times, and heat transfer rates to optimize the design and performance of developing gasification technologies.

A new continuous feed, laminar entrained flow reactor (LEFR) has been recently built and characterized for determining biomass pyrolysis kinetics, gasifier tar production rates, and alkali metal release rates. This reactor is capable of heating rates on the order of 10^3 - 10^4 K/s, typical of heating rates found in developing gasifiers and in industrial boilers. This reactor has been coupled to a molecular beam sampling mass spectrometer (MBMS) system to follow the chemistry of the gas phase products as they evolve during biomass thermochemical conversion processes.

The time-temperature history of a particle in the LEFR was the primary focus of a detailed characterization study [3], as this relationship in theory could exclusively determine the extent to which the solid material reacts. The local gas temperature is a function of the furnace settings, heat transfer in the reactor, and fluid mixing processes. Particle temperatures are influenced by radiative and convective transport, internal conduction, chemical reactions, and perhaps by wall impact. Particle residence times are a function of the local gas flow rate and on the path the particle takes inside the reactor, which depends on particle density, gravity, size, heat capacity, and to some degree on particle starting location. Clearly, a simple model is not sufficient to capture the complexity of this problem. Computational Fluid Dynamics (CFD) simulations were employed to model many of these complex processes, as the geometry and input conditions can be accurately measured. CFD can then be used to generate a time-temperature profile for a particle, which is credible because the model boundary conditions are based measured quantities.

The results of the LEFR characterization study indicated it is possible to control particle pyrolysis. A combination of measurements and theoretical modeling contribute to the detailed understanding of the operating qualities of the reactor. Excellent agreement exists between the model and the measurements when overlapping data exist between the two analytical techniques. Maintaining kinetic, rather than heat transport control is important to experimental value. Maintaining small (<50 μ m) particle sizes is critical to both the control regime and to particle velocity lag in the reactor.

This experimental apparatus has been previously applied to the investigation of global cellulose pyrolysis kinetics [4]. In this paper we build on these initial pyrolysis studies and investigate the pyrolysis kinetics of several biomass samples. The samples come from a NIST collection of standard biomass samples [5] that are well characterized, and uniform. Detailed chemical analyses of the bagasse, *populus deltoides*, *pinus radiata*, and wheat straw samples can be found in reference 5. These samples were chosen for

investigation because they may be readily obtained by other researchers, and may be used with confidence to repeat or expand upon the existing body of research on these uniform materials. Also, the samples represent a range of practical biomass materials and include a soft wood, a hard wood, a grass, and an agricultural residue. The biomass samples as received had been ground to about 2 mm chips. These particles are much too large for the feeding system and were further size reduced using a Spex 6700 cryomill for about ½ hour at roughly 77°K. Grinding in the cryomill is necessary, as room temperature grinding typically results in a more fibrous sample that is difficult to feed into the LEFR using our existing feeder design. Cryomilling is also capable of creating sufficiently small particles for kinetically controlled experiments.

The high temperature pyrolysis gases from the biomass samples have been sampled using established procedures [3,4]. Solid feedrates are typically between 0.1 and 0.5 g/hr. Changing the temperature inside the reactor varies pyrolysis severity. Particle residence times are typically around 0.5 s. Thermal reactions for each biomass sample are found to occur at reactor temperatures as low as 320°C. This is roughly 80°C cooler than the initiation of reactions for the Avicel microcrystalline cellulose particles previously studied [4].

Mass spectra from this study were analyzed by factor analysis to determine relationships between mass spectral peaks. Similar to the results from the cellulose pyrolysis experiments [4], the high molecular weight biomass pyrolysis vapors were found to undergo thermal reactions at fairly moderate temperatures. These primary-to-secondary gas phase reactions are thought to compete directly with the pyrolysis reaction for the samples. Factor analysis could not de-convolute the cellulose, hemicellulose, and lignin components based on thermal history. This suggests that either the reaction kinetics of these constituents are similar at the temperatures of this experiment, or that assuming that biomass reacts as the superposition of its three principal components is a poor assumption for high heating rate modeling of biomass pyrolysis. Results from this study were compared to the biomass pyrolysis models of Miller and Bellan [1] and Di Blasi and Russo [2], which are based on the superposition assumption. Based on these models at the conditions of this reactor, the lignin was expected to react much slower than the other two constituents react. The presence of spectral peaks typically associated with lignin at low temperatures suggested that the lignin from the biomass samples reacted much faster at high heating rates than was expected based on the rates of the models.

References

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