

BIOMASS PYROLYSIS CHEMISTRY AND GLOBAL KINETICS AT HIGH HEATING RATES

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Introduction

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 of interest [1-3]. A graphical summary of two global biomass pyrolysis models [1,3] at the experimental conditions of this study is presented in Figure 1.

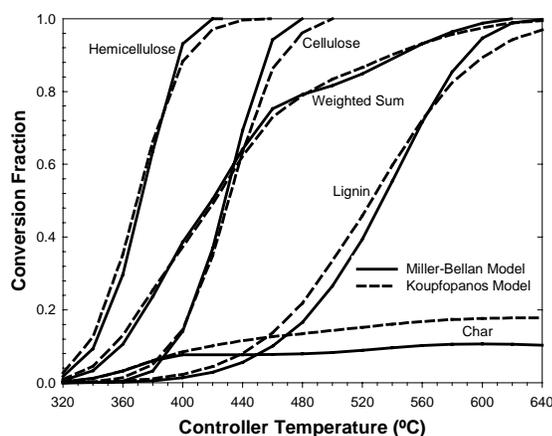


Figure 1. Predictions of the Miller-Bellan (solid) [1] and Koufopoulos et al. (dashed) [3] global biomass pyrolysis models at the LEFR reaction conditions.

Experimental Methods

A new continuous feed, laminar entrained flow reactor (LEFR) was recently built and characterized [4] 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 - 10^5 K/s, typical of those found in developing gasifiers and in industrial boilers. This reactor is 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.

To quantitatively determine biomass pyrolysis kinetics, it is important to understand in detail the many complex physical and chemical processes that a reacting particle undergoes from beginning to end in the reactor. This was the goal of a previous characterization study of the LEFR [4] in which a combination of measurements and theoretical modeling contributed to the detailed understanding of the operating qualities of the reactor. Computational Fluid Dynamics (CFD) simulations were employed to model particle trajectories and residence times and calculate gas temperature profiles. The CFD models included boundary conditions based on measured quantities (e.g. wall temperatures and gas flow rates) so credible time-temperature profiles for particles could be calculated and used in kinetic models to determine global pyrolysis rates. Temperatures are

referred to herein by the furnace temperature controller setting at which data were collected, however, it is important to realize that under set reactor conditions the particles actually undergo a specific time-temperature history [4,5].

The results of the LEFR characterization study [4] indicate it is possible to maintain kinetic, rather than heat transport control and to minimize particle velocity lag in the reactor with small (<50 μm) particles. These guidelines were followed during an investigation of global cellulose pyrolysis kinetics [5]. In this paper we build on these initial pyrolysis studies and investigate pine (*pinus radiata*) pyrolysis kinetics, a NIST standard biomass material [6]. The LEFR pyrolysis kinetic measurements for three other NIST standards; sugarcane bagasse, poplar (*populus deltoids*), and wheat straw can be found in the references [7].

Experimental results

The pine pyrolysis mass spectra contained mass peaks commonly associated with cellulose pyrolysis products [5]. Low temperature lignin products were also identified in the pine pyrolysis mass spectra by large peaks that correspond to the lignin precursors (p-coumaryl alcohol, $m/z = 150$; coniferyl alcohol, $m/z = 180$; synapyl alcohol, $m/z = 210$). Higher molecular weight species with $m/z = 272$, and several species above $m/z = 300$, were also observed and are associated with lignin decomposition [8].

The pine pyrolysis mass spectra, recorded over a range of temperatures, were analyzed by multivariate analysis to group spectral elements that behave in a similar fashion and to provide a concise and reproducible method for representing a complex and extensive set of mass spectral data. This type of analysis performed on previous batch experimental results suggest that there are three distinct pyrolysis product groups (e.g. Evans and Milne, [8]). Based on the superposition theory for global biomass pyrolysis, distinct pyrolytic product groups should be evident in the primary pyrolysis products as suggested by Figure 1.

Multivariate analysis revealed four principal components that described most of the variance ($\sim 95\%$) in the pine pyrolysis mass spectra. Often, a challenge with multivariate analysis techniques is assigning physical and chemical significance to the statistical relationships that are resolved. Associating the peaks identified in the reconstructed Factor Spectra, shown in Figure 1, from the pine pyrolysis mass spectral data can help to interpret the chemical nature of the four principal components.

The Primary Lignin component spectra includes all the mass peaks above $m/z = 150$. Most of these masses correspond to the products associated with primary lignin pyrolysis products. However, lower molecular weight species are also included in this component suggesting that pyrolysis products from other lignocellulosic constituents may be grouped in the Primary Lignin factor as well. Peaks at $m/z = 73$, 85, and 114 are prominent in the Primary Lignin factor spectra and the bulk of the variance of $m/z = 144$ is attributed to this factor. These lower molecular weight peaks are generally assigned to polysaccharide pyrolysis products. Therefore, while this factor is named "Primary Lignin," the contribution from pyrolysis products of other lignocellulosic components is not completely separated.

The most dominant peak in the Tertiary factor at $m/z = 28$ is assigned to CO^+ but may have minor contributions from N_2^+ and C_2H_4^+ . The peak at $m/z = 26$ is assigned to acetylene (C_2H_2^+). Methane is a commonly recognized biomass pyrolysis product and is assigned to the peak at $m/z = 16$. Benzene and naphthalene are assigned to the peaks at $m/z = 78$ and $m/z = 128$, respectively. These aromatic hydrocarbons are thermally stable and tend to evolve from hydrocarbons under high severity pyrolysis. The peak at $m/z = 44$ is assigned to CO_2^+ but could involve contributions from C_3H_8^+ , and

$C_2H_3O^+$ as acetaldehyde or ethenol. Minor peaks at $m/z = 92$ and 94 in all Tertiary factor spectra are assigned to toluene ($C_7H_8^+$) and phenol, $C_6H_6O^+$. The identified products in the Tertiary factor are all considered tertiary biomass pyrolysis products [8]. The factor score plots (see Figure 3) show that scores of the Tertiary factor are low at low reaction temperatures, but increase with increasing pyrolysis severity, as is expected with the tertiary products.

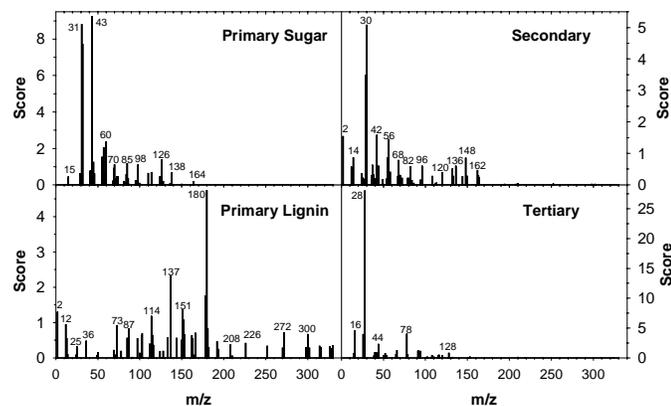


Figure 2. Factor spectra from the pine pyrolysis experiments based on the four-component analysis of the LEFR mass spectral data.

The Primary Sugar factor contains intense peaks at $m/z = 32$ and 31 assigned to methanol (CH_4O^+ and CH_3O^+). Electron impact or thermal fragments of levoglucosan ($C_6H_{10}O_5$) are assigned to peaks at $m/z = 57$, 60 , 73 , and 98 . The peak at $m/z = 126$ is assigned to 5-(hydroxymethyl)-2-furfural, a common polysaccharide pyrolysis product. Other products may also contribute to the signal at $m/z = 126$. As discussed above, some of the lower molecular weight peaks associated with the Primary Lignin factor are also common to the Primary Sugar factor.

The Secondary factor contains prominent peaks at $m/z = 30$ (formaldehyde), $m/z = 42$ (ketene), $m/z = 56$ (butene or 2-propenal), $m/z = 68$ (furan), $m/z = 82$ (2-methylfuran), and $m/z = 96$ (furfural). A variety of phenolic compounds can be associated with peaks at $m/z = 94$, 108 , 120 , 122 , and 148 . Levoglucosan has a molecular weight of 162 and it is tempting to assign the observed peak to the parent ion, however, it may likely result from a higher molecular weight phenolic compound. These compounds are generally identified as secondary products that form by the gas phase decomposition of larger primary pyrolysis products [8].

Discussion and Conclusions

Factor scores determined from the pyrolysis mass spectra recorded for each of the four NIST biomass samples can be found elsewhere [7]. The variation of the average factor scores as a function of furnace controller temperature for pine pyrolysis is plotted in Figure 3. The Primary Lignin scores are highest at the lowest temperatures ($\sim 340^\circ\text{C}$), which suggests that the measured relative contribution of lignin is highest at the earliest stages of pyrolysis. The model predictions for lignin pyrolysis indicate that lignin does not start reacting until the controller temperatures are set to 400°C . At furnace controller temperatures of 500°C - 520°C , the models predict 50% lignin conversion. Clearly, the models predict that lignin reacts much slower than is suggested by the LEFR data. These discrepancies are not completely surprising, as testing of these models with data at high heating rates has been minimal.

It is more difficult to comment on the model predictions of polysaccharide pyrolysis because the multivariate analysis of the pine mass spectral data does not clearly resolve separate contributions

from hemicellulose and cellulose pyrolysis. The pyrolysis models are a good representation of the pyrolysis regime studied in the LEFR experiments if the hemicellulose and cellulose fractions are combined into a single component in the models that gives rise to "primary sugars" as measured in the experiments.

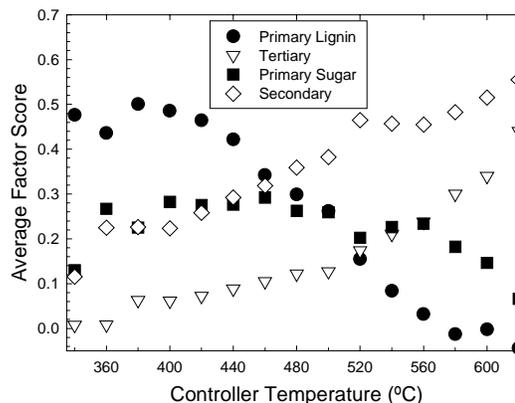


Figure 3. Factor scores from the pine pyrolysis experiments based on the four-component analysis of the LEFR mass spectral data.

If in fact hemicellulose and cellulose react as predicted by the two global biomass pyrolysis models, there should be distinctive pyrolysis regimes where hemicellulose contributes to the polysaccharide signals at the lowest temperatures and the cellulose pyrolysis products begin to form at higher temperatures. The models predict that 50% of the hemicellulose should have reacted as the cellulose begins to react (360°C - 380°C in the models). The multivariate analysis of the pyrolysis mass spectral data did not clearly suggest a statistically important distinction between these two components. It is not clear from the experiments whether this is because hemicellulose and cellulose do not react in separate regimes, or because the pyrolysis products are so similar there is no mass spectral difference between early and late polysaccharide pyrolysis products. The peaks associated with polysaccharide pyrolysis products that were resolved in the Primary Lignin factor could be indicative of a cellulose/hemicellulose distinction. More detailed information is necessary before this can be confidently determined.

References

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