Visualization of physicochemical phenomena during biomass pyrolysis in an optically accessible reactor

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Abstract

The thermochemical conversion of biomass via fast pyrolysis requires detailed descriptions of both the kinetic and heat and mass transport rates, which are often in direct competition. To investigate the evolution of products, whole biomass and biomass constituents (e.g. cellulose and lignin) are pyrolyzed in a novel optically accessible reactor. This enables real-time, in situ observation of the temporal evolution of light-oxygenates, volatile sugars, and phenolic compounds above the biomass pile during melting, agglomeration, ejection, and volatilization under realistic heating rates (\sim 100 K/s). Both cellulose and lignin underwent liquefaction, but liquid coalescence in lignin limits vapor transport. This is overcome by dispersing extracted lignin in an inert matrix, and confirms the predominant mass transport of pyrolysis products from whole biomass, cellulose, and lignin occurs via devolatilization. These results differ from prior work on single-particle pyrolysis and reveal thermochemical mechanisms that are relevant for typical large-scale pyrolysis processes with transport limitations.

Keywords: biomass fast pyrolysis, lignocellulosic biomass, optical characterization

1. Introduction

Biomass fast pyrolysis is a leading technology for the production of renewable fuels and chemicals and is positioned to fill an important role in the global energy portfolio if several key challenges can be overcome [1, 2]. Thermal processing of biomass is an attractive candidate for generating high-value products from raw biomass feedstocks [3, 4]. Optimized thermochemical conversion of biomass must address the variability in feedstock composition, the wide range of commodities used as possible feedstocks, and geographic localization of biomass resources. This article examines the influence of these factors on the physicochemical processes which drive product formation during biomass pyrolysis. Feedstock sample sizes and operating conditions inside of an optically accessible reactor correspond to a regime where thermal and mass transport effects are present, as is common in industrial-scale reactors.

Fast pyrolysis of lignocellulosic biomass is a thermochemical conversion pathway in which biomass is heated rapidly $(100-1000 \ ^{\circ}C \ ^{s-1})$ to temperatures ranging from 400–600 $\ ^{\circ}C$ in the absence of oxygen, followed by rapid thermal quenching to produce solid (char), liquid (bio-oil), and gaseous (noncondensable vapor) products. The bio-oil fraction contains hundreds of different compounds of varying molecular weight and degrees of polymerization, which complicates subsequent upgrading to commodity chemicals and fuels [5]. Furthermore, lignocellulosic biomass is composed of varying amounts of cellulose, hemicellulose, lignin, extractives, and ash depending on the type of biomass and growing conditions [6]. The variability in biomass feedstock composition, the multiphase and multiscale nature of the fast pyrolysis process, and the diverse product species pose significant challenges in describing the complex physicochemical processes that drive product formation [1]. Improved understanding of these phenomena will allow for the development of predictive pyrolysis models and present opportunities for optimization of pyrolysis conditions and reactor designs for the production of high-value commodity chemicals and fuels.

Several recent reviews have highlighted the major hurdles in developing biomass pyrolysis into a more targeted and robust technology for high-yield production of commodity chemicals [1, 7]. Among these challenges is a lack of fundamental understanding of the physicochemical mechanisms of biomass pyrolysis including intraparticle transport processes, as recently highlighted by Pecha et al. [8]. In particular, the following questions are raised: How do aerosols form and transport away from pyrolyzing biomass? How does feedstock morphological retention or phase change affect the mechanisms of product formation? Finally, what is the role of the intermediate liquid compounds [7, 1]? Thus far, two main approaches have been used to address these questions: first, high-speed imaging of pyrolyzing samples to monitor physical changes to the feedstock during pyrolysis; and second, rapid collection of pyrolysis products for ex-situ analysis to infer primary mechanisms of product formation. Unfortunately, neither of these approaches is able to fully capture the multiscale and multiphase nature of this problem.

The ability to visualize changes in feedstock phase and mor-

phology while observing the transport of ejected particles provides new opportunities to understand the physical processes which drive product formation in biomass fast pyrolysis. For example, the evolution of microstructure during the the pyrolysis of poplar wood samples was examined by Haas and colleagues using hot stage microscopy [9]. They were able to visualize the effects of non-uniform heat transfer across a sample of biomass and observed entrapment of pyrolysis products within the complex plant structure. On the macro- or mesoscale, several studies have utilized high-speed photography to image cellulose pyrolysis on a heated surface and have shown the formation of a liquid intermediate from which vapors escape via bubbling [10, 11, 12]. These observations led to the proposed mechanism of 'reactive boiling ejections' driving primary aerosol generation and the transport of moderate- and high-molecular weight, non-volatile pyrolysis species and inorganic particles downstream. Montoya et al. utilized a modified pyrolysis probe and high-speed camera to study the dynamics of the liquid intermediate during biomass pyrolysis [13, 14]. In the first study, a population balance model was developed using data from high speed photography of bubble formation and collapse within liquid formed from organosolv lignin and sucrose. Defining the mass yield as the ratio of the mass of aerosols normalized by the mass of the initial sample, the authors predict primary aerosol yields of 21.2% by mass (w/w) from Organosolv lignin and 17.4% w/w from sucrose. In the second study, the authors pyrolyzed several biomass components to better understand which fraction of biomass might be responsible for char produced from lignocellulosic feedstocks. The authors concluded that the presence of ash in hemicellulose, the variability in feedstock composition, and the corresponding variation in microstructure play key roles in the retention of the original morphology.

Such visual observations of biomass undergoing pyrolysis have provided critical insights into relevant mass transport phenomena which control downstream product yields. However, to fully map the physicochemical pathways taken by constituent reactants, experiments capturing relevant mass and thermal transport are necessary. In pyrolysis systems, the competition between mass transport and kinetic rates determines the dominant mechanisms and final product yields [15]. Several studies characterized the primary products generated during fast pyrolysis through analysis of pyrolysis vapors exiting the reactor. For example, the use of micropyrolysis reactors using closely coupled gas chromatography and mass spectrometry as well as rapid quenching of primary products for offline characterization have revealed a large range of small phenolic molecules (monomers and dimers) produced during primary pyrolysis [5, 16, 17, 18, 19]. These observations support the theory that some major fraction of the biomass depolymerizes to volatile components in the form of monomers and dimers, as opposed to ejective boiling mechanisms inferred from visual analysis. Oligomers are then formed downstream of the pyrolyzing biomass through chemical condensation reactions of monomers and dimers, which physically condense to liquid or particulate aerosols in the pyrolysis stream.

The role of phase change, the relative importance of aerosol

ejection and vaporization in mass transport of pyrolysis products, and competition between secondary cracking and repolymerization reactions in both the liquid intermediate and vapor phase are, therefore, not well understood despite these previous studies. Although visual observations of pyrolyzing biomass have yielded significant insights, additional characterization with direct observations of mesoscale (as opposed to single micro-particle) phenomena are required. The direct observation of melting, agglomeration, ejection, volatilization and condensation processes is necessary as the composition and physical structure of biomass can have significant effects on these physicochemical pathways during pyrolysis. The majority of existing studies have examined biomass constituents, but the variability and unique morphology present in whole biomass requires additional scrutiny to determine the dominant pathways for production of monomers and oligomers from whole biomass.

In this article we examine the coupled physical and chemical changes during biomass fast pyrolysis (>130 $^{\circ}C s^{-1}$) with observations of product formation through high-speed visualization of planar laser Mie scattering in a well-characterized thermal environment for whole red oak and several biomass components. A fast pyrolysis reactor and cold carrier gas system are used to generate a thermal boundary layer between the hot pyrolysis product stream and the cold gas through which monomer and oligomer products and intermediates condense, distinguishing them from other ejected condensed-phase products. Observation of laser Mie scattering in the pyrolysis reactor allows direct correlation of feedstock degradation and the transport mechanisms near the primary reaction zone by tracking near-surface aerosols and vapor condensation across the developing thermal boundary layer. The goal of this work is to examine the dominant transport mechanisms relevant to biomass pyrolysis and understand how product formation progresses through the various steps of heating, melting and agglomeration, and devolatilization/ejection to form downstream products.

2. Methods

2.1. Optically-accessible filament pyrolysis reactor

The optically accessible pyrolysis reactor and imaging system utilized in this paper are illustrated in Figure 1(a) and (b). The Joule-heated filament consisted of a 0.375-in wide by 0.005-in thick nickel ribbon wire that was formed into a 'U'-shaped cup and suspended between two copper electrodes which supplied current to the filament. The shell of the reactor was constructed from a square $3\text{-in} \times 3\text{-in}$ stainless steel tube with $1\text{-in} \times 4\text{-in}$ quartz windows mounted on all four sides. The shell was mounted on top of a ceramic base that had 64-1/16-in holes spaced 0.25-in apart that allowed for a uniform velocity nitrogen purge through the test section. An analog-controlled programmable power supply (Sorensen XFR 7.5-300) was used to supply specified current ramps to the filament strip and was interfaced with a custom data acquisition system to synchronize the power supply, cameras, and data acquisition.

For pyrolysis tests, 1 mg of biomass was evenly distributed in a narrow pile 5-7 mm in length along the 'U'-shaped filament heater and rapidly heated through a current-controlled ramp. To achieve a heating rate of 135 °C s⁻¹ and peak temperature of ~500 °C, a current set point of 83 A for 4 s was followed by a set point of 53 A for the remainder of the test. In order to ensure a consistent strip surface chemistry, the nickel strip was heated in air to allow for oxidation of the surface before any pyrolysis experiments. Although nickel-oxide has been used in chemical looping reactors as a catalyst to eliminate tar [20], the current experiments have limited contact area and duration which minimize any catalytic effects. In other pyrolysis experiments with wire meshes, Hoekstra et al. evaluated nickel, chromium, and molybdenum and reported negligible catalytic effects [21]. To establish a thermal boundary layer and control operation, a cold sweep gas of nitrogen runs past the filament and biomass sample continuously with an average velocity of 4.1 mm/s.

The reactor thermal environment was characterized by complementary multi-point thermocouple measurements and acetone planar laser-induced fluorescence (PLIF) thermometry; resulting temperature maps are included in Figure 1(d). First, PLIF was utilized as a non-intrusive temperature measurement technique relying on the temperature-dependent response of acetone fluorescence [22]. Acetone PLIF excitation was achieved using the fourth harmonic of a Nd:YAG laser (266 nm) collimated to a laser sheet approximately 25 mm tall and 0.5 mm wide with a fluence of \sim 350 mJ/cm². Fluorescence was imaged with a time-gated intensified CCD camera (Princeton Instruments PI-MAX2) with with a Nikkor 55 mm, f/1.2 lens. Acetone was seeded into a nitrogen flow at constant concentration by bubbling the nitrogen through liquid acetone at a constant temperature. The thermal response of acetone was characterized for this setup by passing the acetone-seeded nitrogen flow through two tubes, one heated and one maintained at ambient temperature. Once the acetone PLIF response was known, the pyrolysis reactor was characterized by passing the same concentration of acetone in nitrogen through the reactor as the sweep gas and capturing the thermal response for the heating profile used in the pyrolysis experiment. Results were captured at a rate of 5 Hz and phase-locked to the temperature ramp controller. For the acetone-PLIF thermal characterization, the filament heater was not loaded with biomass samples, but an identical temperature ramp was maintained.

To characterize the thermal environment with higher temporal resolution, a 0.003-in., k-type thermocouple was traversed throughout the reaction zone at 34 locations, resulting in the phase-averaged temperature maps in the right panels of Fig. 1(d). The thermocouple locations are overlaid on the 0.0 s temperature map, and all were located at the center plane along the length of the filament. At each location, the temperature was recorded at a rate of 250 Hz for an unloaded filament strip. The time evolution at several locations, highlighted by the white stars in the left-most panel of Fig. 1(d), are shown in Fig. 1(c). Data from three experimental runs and three heights above the filament heater are shown to illustrate the highlyrepeatable temperature ramps achievable in the reactor. The phase-averaged isocontour maps represent data for at least three tial interpolation. Finally, temperature profiles taken using a fine wire thermocouple at three different locations during the pyrolysis of 1 mg cellulose were found to be consistent with bare filament temperature profiles within the stated deviation.

runs at each location and cubic triangulation was used for spa-

2.2. Materials

Northern Red Oak (Quercus rubra) was obtained from Wood Residuals Solutions (Montello, WI). Bark-free chips were ground and sieved using the appropriate ASTM sieves in series resulting in a distribution of red oak diameters from 75-212 µm (sieves #18, #30, #40, #70, #200). Typical L/D ratios for the resulting red oak particles were 1-10. Corn stover lignin, isolated using the organosolv process, was provided by Archer Daniels Midland (ADM) and was then ground and sieved to (75-212 μm). Sigmacell Cellulose (Type 50) was obtained from Sigma-Aldrich and used as received. Levoglucosan was obtained from Carbosynth Limited and used as received. In order to match the characteristics observed during the pyrolysis of whole biomass, lignin was dispersed in a silica matrix in a 2:1 ratio by first mechanically mixing the appropriate mass of fumed silica (Aerosil COK 84, Evonik Industries) with ADM lignin followed by addition of 30 mL of isopropyl alcohol and subsequent sonication for 15 minutes to ensure a homogeneously dispersed mixture. The suspension was placed in a vacuum oven at approximately 10 inHg of vacuum and 40 °C for 15 h. Finally, the precipitate was ground and sieved to obtain fine particles less than 212 µm in size.

2.3. Imaging System and Analysis

Imaging experiments were performed simultaneously using two cameras to capture both physical changes to the sample and Mie scattering from the condensed products (Figure 1(b)). The Mie scattering images represent qualitative changes in the volume fraction of condensing product species, but particle sizes are not explicitly determined. However, future studies could utilize the angular dependence of Mie scattering for a quantitative measurement of particle size and quantity [23]. Color microscopic imaging experiments were performed using a DSLR camera (Nikon D7200) at a framerate of 60 Hz with a long working-distance microscope objective (MX-5, Infinity Photo-Optical) held at a 27-degree angle to the surface plane and was focused on the sample. This resulted in a magnification of 80 pixels/mm with a depth of field of ~1 mm. Mie scattering images were captured at 250 Hz through a reactor window adjacent to the DSLR using a high-speed CMOS camera (Fastcam Model SA5, Photron) and an objective lens (Nikon Micro-NIKKOR f/2.8, 105mm) mounted with a 632 nm bandpass filter (Edmund Optics, 65-227). The exposure was held at 4.0 ms to optimize light collection. The resulting field of view was 30 mm high by 15 mm wide, with an in-plane resolution of approximately 50 µm. Illumination for Mie scattering was provided by a 632.8 nm, 10 mW HeNe laser (Model 1135P by JDSU) which was formed into a 40-mm tall by 1.25-mm thick laser sheet that was passed through the center of the optically-accessible pyrolysis reactor at an angle of 27 degrees above the surface plane.



Figure 1: The optically accessible pyrolysis reactor is depicted in (a) a schematic of the cross-sectional view showing the laminar flow and heating filament and (b) a top view showing the laser sheet and camera locations. A high-speed CMOS camera is used to image laser scattering from aerosols and a DSLR camera is used to image the evolving biomass sample inside of the U-shaped filament. Panel (c) shows three typical temperature histories measured at the strip surface and 1.25 and 7.5 mm above the filament using a fast-response thermocouple. Temperature maps above the heated filament are shown in (d) for a typical acetone-PLIF thermometry (5.0 s, left) with the corresponding interpolated thermocouple temperature maps (right). White stars indicate the thermocouple positions shown in panel (c), and red dots indicate the thermocouple couple positions used for the interpolated maps in (d).

This sheet was centered over the heated strip to give a twodimensional slice of the product condensation and particle field over the biomass sample during pyrolysis. A fiber-optic lamp (Fiber-lite Model-190, Dolan Jenner) illuminated the sample and relevant features of the reactor from the same observation window used with the CMOS camera.

Image contrast and brightness were uniformly adjusted for each feedstock and an logarithmic false-color map was applied to highlight features across a wide dynamic range. The timedependent scattering intensity was evaluated using integrated bin regions above the filament to track the condensed product evolution.

3. Results and Discussion

The optically accessible pyrolysis reactor allows for simultaneous observation of biomass degradation (phase change and mass loss from the sample), as well as direct observation of product formation and condensation pathways. A series of tests are shown in Figure 2 and discussed in the subsequent sections for the fast pyrolysis of biomass constituents and whole biomass. Pyrolysis of each feedstock was observed repeatedly, and typical results are presented. In addition, video sequences are available electronically in the supplementary material. For each time instant, the top image shows a color micrograph of the biomass feedstock on the heating filament, and the false color images below correspond to the laser scattering of condensed-phase products above the heating filament. Temperature maps corresponding to each time instant in Figure 2 are shown in Figure 1(d). First, we examine the pyrolysis of cellulose and levoglucosan—a major product of cellulose pyrolysis. Next, technical lignin extracted by the organosolv process is pyrolyzed with and without the addition of an inert silica matrix in order to investigate and overcome the mass transfer limitations unique to technical lignin pyrolysis. These results are compared with the detailed observations of whole biomass (red oak) pyrolysis.

As evident in Figure 2, during pyrolysis tests the evolved products condense in the thermal boundary layer above the dynamically heated biomass sample. Interpreting these results relies on knowledge about the local temperature gradients inside of the pyrolysis reactor along with typical product yields and reaction mechanisms of biomass pyrolysis found in literature. The thermal boundary layer between the cool nitrogen sweep gas and warm, bouyantly-driven product flow provides a thermal gradient which drives product condensation. In the test section, the bulk flow is vertical, such that the first observable condensed products are present at locations closest to the strip for a particular condensation band. In the subsequent sections, the location of condensation is correlated to the local temperature to identify broad classes of condensing products. The visual observation of these layers requires significant particle or aerosol size and number density, which can take some time to form through either collisional growth of nano-scale conden-



Figure 2: Shown are Mie scattering intensity images of the fast pyrolysis of biomass constituents—(a) cellulose, (b) technical lignin, and (c) technical lignin dispersed in an inert matrix—and whole biomass—(d) red oak. Each row corresponds to a unique feedstock, with frames from left to right indicating a different time instant. For each time instant, the color micrographs of the heated filament and the laser-scattering from products above the filament are shown with the instantaneous temperature of the heated filament indicated. Scattering intensity for each sequence is shown on a different logarithmic colormap to enhance contrast. Temperature maps corresponding to each instant are included in Fig. 1(d). Video sequences for each feedstock are included in the Electronic Supplementary Material.

sates or growth of condensates from initial nucleation sites. In the subsequent discussion, the thermal boundary layer characterization is compared to observed condensate formation using the product boiling point as a surrogate for the condensation process.

3.1. Fast Pyrolysis of Cellulose and Levoglucosan

We first consider the pyrolysis of cellulose and levoglucosan. For pyrolysis of sigmacell cellulose, the simultaneous images of the biomass feedstock on the reactor heating filament and the laser scattering region above the filament are shown in Figure 2(a). For the sequences presented in Figure 2, video sequences are available in the electronic supplementary material. As observed in the color micrographs, browning of the bulk pile is observed throughout the reaction. The first indication of product condensation is evident at 3.46 s in the region above the strip, when the strip temperature has reached 315 °C. Prior to this time, there is minimal evidence of expansion/shrinkage of the feedstock or release of volatile products. At 3.51 s (strip temperature of 324 °C), the first visual indication of melting is present for small cellulose particles away from the pile, which corresponds to a rapid increase in the laser scattering signal from products condensing downstream. Of particular interest are the presence of two distinct condensation bands which form along the thermal gradient between the buoyantly-driven hot products and cold sweep gas starting at 3.54 s. As the cold nitrogen carrier gas is introduced below the filament (see Figure 1(a)), the condensation bands correspond to distinct temperature regions within the boundary layer where the carrier gas and vapor products meet. A distinct lack of signal inside of the condensation bands suggests that products are not forming via ejective boiling but rather through evaporation of products from the pyrolysis zone and subsequent condensation or polymerization reactions forming aerosols/droplets downstream along the interface with the cold sweep gas.

As the filament temperature continues to rise (3.70–3.97 s, strip temperature ranging from 365-429 °C), liquid appears at the interface between the solid biomass and strip heater. Surface tension causes the liquid to form small droplets that lift the remaining solid feedstock away from the filament. Reduced heat transfer through the liquid intermediate and solid pile result in large thermal gradients across the sample, thereby slowing the rate of liquid formation and resulting in both liquid and solid phases persisting throughout much of the remaining reaction. Montoya et al. previously attributed the simultaneous presence of liquid and solid phases to poor heat transfer to the particles caused by Leidenfrost effects, where vapor formation reduces contact area between the heated surface and the biomass [14]. The color micrographs of the cellulose pile show two distinct phenomena: during initial melt, there is some evidence of solid particles or mixed phase particles being pushed away from the heated surface due to devolatilization and vapor production (3.54–3.86 s). In the final pyrolysis stages, only liquid is observed which makes direct contact with the filament. This Leidenfrost behavior is observed in early stages of pyrolysis and devolatilization of the solid biomass particles, which may limit the effective heating rate of the remaining solid

biomass pile. The synchronized image sequences are included in the electronic supplementary material (Fig. A.7a), showing additional detail.

The final liquid intermediate is seen at 4.07 s (strip temperature of 430 °C) with minimal char present on the strip at the conclusion of the reaction. The integrated scattering signal, shown in Figure 6 and discussed in Section 3.4, reveals some unsteadiness associated with a nucleation/boiling process, but there is little evidence of condensed-phase particles or aerosols transporting directly away from the sample through the laser sheet. The absence of larger condensed products is consistent with the transmission electron microscopy measurements of cellulose aerosols collected in a liquid solvent quench reported by Teixeira et al., but the current measurements provide direct insitu evidence that thermal ejection of aerosols and droplets (in the Mie scattering regime) are not responsible for significant mass transport from pyrolyzing cellulose as previously suggested [12, 14].

Patwardhan et al. [16] utilized a micropyrolysis reactor to characterize the fast pyrolysis products of glucose-based carbohydrates and identified over 20 low-molecular-weight products. Of these products, levoglucosan, formic acid, glycoaldehyde, 5-hydroxymethyl furfural (HMF), and 2-furaldehyde (furfural) account for 82 wt% of the total identifiable yield during micropyrolysis experiments. By comparing the time-resolved scattering images with related gas-phase temperature maps for the unloaded strip, the local temperature of the outer condensation band is estimated as 125 °C and the inner condensation band is near 190 °C. Due to the transient reactor configuration, the condensation temperature of an individual component depends on the local partial pressure of products and the density of nucleation sites which can be difficult to identify in a complex system. However, the individual product boiling point can serve as a proxy for condensation point and allows for the identification of products condensing in each band shown in Figure 2(a). Examining the condensation band alongside the strip and gas phase temperatures, the inner condensation band is consistent with levoglucosan or a similar light sugar due to its vapor pressure and boiling point of 385 °C [24, 25, 26, 27]. The remaining major products (formic acid, glycoaldehyde, HMF, and furfural) have boiling points ranging from 100-165 °C and likely make up the products found in the outer condensation band.

To examine the structure of the condensation bands using a simpler feedstock, levoglucosan was pyrolyzed under identical conditions. Briefly, the levoglucosan begins to melt on the strip surface at 1.80 s as a thin condensation layer is seen in the outer boundary layer downstream. A rapid boiling event occurs at 3.14 s and, subsequently, scattering signal from condensed products is observed at the inner edge of the thermal boundary layer. No visible residue was present on the strip following levoglucosan heating. To compare the spatial location of the condensate bands for these feedstocks, a representative image of cellulose pyrolysis is shown in Figure 3, and different color maps are used to overlay images of levoglucosan before and after the rapid boiling phenomena. The spatial location of products formed during levoglucosan pyrolysis prior to



Figure 3: Overlaid images from cellulose and levoglucosan before and after the levoglucosan boiling/devolatization show good correspondence between the product band locations.

the boiling event corresponds closely with the outer condensation band of cellulose, while condensation taking place after levoglucosan boiling corresponds to the cellulose inner condensation band. Unlike the dual-condensate band structure observed for cellulose, however, persistent and separate condensate bands are not observed for the heating of levoglucosan. Although degradation of levoglucosan has been observed in catalytic and ash-containing environments and may be observed in the early timescales herein, the dominant scattering signal corresponds to the rapid boiling and subsequent re-condensation event. Although this analysis neglects gas expansion effects and the timescales differ between cellulose and levoglucosan due to differences in the temperatures of devolatilization and boiling, the correspondence of the product location indicates the presence of levoglucosan and lighter volatiles in the condensation bands of cellulose pyrolysis. In addition, by comparing the relative scattering signal between the inner and outer bands of cellulose pyrolysis, a shift in the rate of production away from light condensates towards levoglucosan is evident as the strip temperature rises.

Vinu and Broadbelt developed a detailed mechanistic model to describe the competing reactions in fast pyrolysis of cellulose and other glucose-based carbohydrates utilizing both experimental and computational approaches [28, 29, 30]. This model incorporates a sequential reaction mechanism for cellulose pyrolysis consisting of an initiation reaction of random glycosidic bond cleavages at any position in the cellulose chain followed by end-chain initiation and de-propagation (unzipping) reactions to break down cellulose and form levoglucosan. The authors show the maximum reaction rate for kinetic-limited decomposition to levoglucosan occurs close to mid-conversion. Utilizing these detailed mechanistic models, the formation of levoglucosan is completed within 1.75 s during pyrolysis of cellulose in a pure-kinetic regime at 500 °C, with the entire reaction concluding in 4-5 s. In contrast, the results presented here are not in a pure kinetically-controlled regime, but have

both heat and mass transfer limitations which influence product formation. Reduced heat flux into the solid cellulose due to presence of multiple phases throughout the reaction results in the persistence of both initiation and unzipping reactions and leads to the production of levoglucosan and other products for most of the reaction. As a result, we see continuous production of both heavy and light compounds throughout the reaction and observe a total reaction duration of approximately 4.3 s, comparing favorably with the global timescale expected for a pure kinetic process [31].

3.2. Fast Pyrolysis of Organosolv Lignin from Corn Stover

Pyrolysis of a second major constituent in lignocellulosic biomass, lignin, was explored using technical lignin extracted from corn stover via the organosolv process. This feedstock was pyrolyzed under the same conditions described previously and selected results are shown in Figure 2(b). Here, the first evidence of phase transition is visible at 2.15 s (strip temperature of 130 °C) near the edges of the biomass pile. The entire pile transitions to liquid by 2.70 s (strip temperature of 194 °C). Lignin has been shown to melt between 150-154 °C and experience a glass transition resulting in increased fluidity between 150-200 °C [32, 33]. From 2.70-3.30 s (strip temperature 194-289 °C), individual particles of lignin melt into droplets that coalesce into a single liquid mass at the same time that condensed products are first observed in the thermal boundary layer above the sample. Between 3.30-4.27 s (surface temperature 289-475 °C) the viscous liquid swells, providing evidence of volatiles releasing within the melt to form bubbles that eventually erupt and collapse at the surface of the melt. Two such events are highlighted in Figure 4(a). Similar observations have been made previously on the melting, swelling, and bubbling of pyrolyzed lignin [11, 13, 14]. Our work is the first to couple this liquid phase phenomena to observed mass transport away from the molten feedstock. As evident in the scattering images taken from 3.31–4.26 s in Figures 2(b) and 4(a), large droplets are rapidly ejected directly from the molten lignin due to the collapse of bubbles at the surface, accompanied by vapor jets which subsequently condense.

After 3.86 s the frequency of bubble growth and collapse decreases and the surface of the melt solidifies. Since the melt does not appreciably cool, this solidification is attributed to oligomerization and dehydration to form char. During this time, aerosols originate near the surface of the char and become entrained in the boundary layer above the filament. Several condensation bands in the thermal boundary layer are evident downstream, suggesting the production of multiple products of varying molecular weight. Contrary to the two discrete condensation bands present for cellulose, the multiple bands observed during the pyrolysis of technical lignin are confined within the thermal boundary layer and suggest products with similar condensation temperatures. Zhou et al. examined the influence of extraction techniques and lignin origin on the yields of pyrolysis products [34]. Differential thermogravimetric analysis for corn stover lignin extracted via the organosolv process revealed two peaks in mass loss between 150-400 °C, with a prominent shoulder in the second peak. The first strong peak



Figure 4: Comparison of near-surface behavior during pyrolysis of (a) technical lignin and (b) lignin dispersed in an inert matrix. Lignin shows the presence of condensed species and high-velocity ejections from the sample, but the addition of an inert matrix eliminates vapor explosion ejecta.

was attributed to ferulate and coumaric groups while the shoulder of the second peak is attributed to the devolution of small phenolic compounds (at ~275 °C) from β -ether cleavage. The second strong peak is related to the release of large molecular weight phenols near 360 °C. Correlating these transition points to the current study, the initial products observed in the boundary layer as a single condensation band at 3.31 s correspond to the production of small phenolic compounds while the dual condensation band evident in later frames is evidence of additional production of larger molecular weight compounds at elevated strip temperatures.

Agglomeration of technical lignin is a well-known phenomenon and has been identified as a major hurdle towards processing lignin in continuous pyrolysis reactors [35]. This behavior is a result of the extraction technique used to obtain the technical lignin and likely fails to replicate the behavior of native lignin in whole biomass [36]. Several techniques have been employed to limit agglomeration of technical lignin through chemical or physical modification. Mukkamala mixed calcium formate with lignin prior to pyrolysis and found reduced agglomeration and improved liquid and carbon yields [37]. Zhou et al. utilized a calcium hydroxide pretreatment on technical lignin and were able to overcome the problem of agglomeration in a continuous fluidized bed pyrolyzer [38]. Their analysis suggested that phenolic hydroxyl, aldehydes, and carboxylic acid groups are responsible for the melting and agglomeration of lignin and chemical pretreatment is capable of reducing or eliminating these functionalities. De Wild et al. utilized a 10% mixture of natural clay mineral combined with technical lignin to create 2-mm extruded pellets which greatly reduced the agglomeration tendency of pure lignin when used in a fluidized bed pyrolyzer [39].

To alleviate the agglomeration of technical lignin in the current study, organosolv lignin was dispersed with an inert silica matrix. The tendency of technical (extracted) lignin to agglomerate into a single liquid mass exacerbates the formation of bubbles within the melt and leads to ejection of large condensates, as observed in Figure 2(b). This is particularly evident when the lignin is heated from below, as all volatile products must flow through the melt. To investigate the ability of physical modification to prevent agglomeration, organosolv lignin was mixed in a 2:1 ratio of lignin to an inert silica matrix, Aerosil COK 84, with the goal of limiting coalescence by dispersing a non-reactive solid throughout the sample. The sequence in Figure 2(c) shows the formation of a thin liquid melt layer over the whole sample area without evidence of the boiling ejections seen for pure organosolv lignin (Figure 2(b)). The first evidence of melt occurs around 2.29 s and corresponds to a strip temperature of 147 °C. The sample swells modestly at 2.29-3.30 s (strip temperature 287 °C) with little agglomeration compared to pyrolysis in the absence of silica. Also at this instant the first condensed products are visible, with the condensation band initiating downstream from the filament where the gas temperature is ~175 °C. The scattering signal increases until around 4.1 s and then quickly decreases. Multiple condensation bands are evident from 3.86-4.30 s (strip temperature 399-475 °C), but are more tightly grouped when compared to the bands observed in cellulose pyrolysis.

An additional distinct mechanism of product formation consists of products forming inside of the filament cup (in the high temperature region) and emanating from the surface of the sample from 4.00-4.40 s, when the local gas temperatures approach 300 °C. Though products are continually convected upwards via buoyancy, these products are persistent and appear to originate from a quasi-steady production of aerosols in the high temperature region just above the biomass sample. Two frames highlighting this product formation mechanism are included in Figure 4(b), in contrast to the near-surface product formation observed for pure organosolv lignin. The presence of these visible products inside of the high temperature filament cup region indicates a mechanism which can rapidly form or allow coalescence of condensed particles or aerosols in the high temperature region along the strip centerline. However, these aerosols represent a small fraction of the total mass formed in these experiments, as reflected by the relative percent scattering signal observed in these high temperature condensation regions. Finally, the observed condensed-phase products along the centerline are significantly higher in the case of lignin in an inert matrix as compared to cellulose.

3.3. Fast Pyrolysis of Red Oak

Red oak samples were pyrolyzed at the same reactor conditions to examine the relative importance of the physicochemical phenomena identified for cellulose and technical lignin in the pyrolysis of whole biomass. Simultaneous images of the reactor heating filament with red oak feedstock (75–212 μ m) and the laser scattering region above the filament are shown in Figure 2(d). Initial browning and swelling of the bulk pile is evident from the micrographs taken at 0.00 s and 3.50 s. The first condensable products appear downstream from the filament at 3.50 s (strip temperature 329 °C) and correspond closely to the first visible sign of feedstock melting. From 3.70-4.20 s (strip temperature 370-458 °C) the sample rapidly depolymerizes as the solid transitions to liquid and quickly evaporates or undergoes charring reactions. The reaction concludes around 4.30 s (strip temperature of 471 °C), as indicated by the minimal scattering signal from condensed products downstream and no visible change in the residual char on the strip surface.



Figure 5: (a) Distinct Mie scattering bands reveal the condensation of different compound classes within the thermal boundary layer during the pyrolysis of red oak (75–212 μ m). (b) Aerosol formation from pyrolyzing red oak is observed in the high temperature region directly above the filament, magnified and rescaled from Figure 2(d). The scattering intensity from this near-filament region is significantly less than scattering from the downstream condensed products.

Although direct association of the condensation bands with specific product classes is complicated by the number of products from the pyrolysis of whole biomass, the multiple condensation features can be interpreted using the cellulose and lignin pyrolysis studies and product yields found throughout literature. Dalluge et al. pyrolyzed red oak in a screw-type auger pyrolysis reactor and identified approximately 69% by mass (w/w) of the product yields of the original dry feedstock, including a range of products from both the carbohydrate and lignin fractions of the whole biomass [40]. Of these products, 12.6% were identified as lignin-originating products, 6.08% were sugars, 3.93% were carbohydrate dehydration products, and 7.76% were light oxygenates with a wide range of boiling points. In the present work, as the red oak first begins to depolymerize and melt from 3.50–3.70 s, the scattering signal indicates the production of a single condensation band with an obvious 'dark zone' above the filament where no products are visible. The initial condensation occurs at a location where the temperature is approximately 125-150 °C. From 3.80-4.20 s, a discrete secondary condensation band is evident in the outer boundary layer (visible in Figure 5(a) outside of the triple condensation band). This secondary band forms in a similar location to the light oxygenates produced during cellulose pyrolysis. Furthermore, the magnified inner region in Figure 5(a) at 4.20 s shows multiple closely grouped condensation bands similar to those observed during the pyrolysis of lignin in a silica matrix, indicating the presence of multiple products of varying molecular weight.

In addition to the evaporation and condensation transport modes, aerosols are formed directly above the surface of the solid feedstock from 3.70–4.10 s. These products are apparent in Figure 5(b) which highlights the near filament region magnified from Figure 2(d). These products appear in the same location as those observed in the high temperature centerline region in the lignin-silica pyrolysis shown in Figure 2(c), and the timescales of formation in both red oak and lignin/silica are similar. Maximum signal from this near surface condensation appears at 4.0–4.10 s in both samples. Again, the overall scattering signal in this near surface formation or condensation process is three orders of magnitude lower than the downstream condensation, and represents a minor contribution to overall product formation.

Comparing the near-surface observations of product formation and mass transport to literature helps identify the relative importance of the proposed mechanisms in whole biomass pyrolysis. Bai et al. utilized a micropyrolyzer with fast solvent quenching to analyze the products formed during lignin pyrolysis and for several monomer and dimer model compounds [5]. They concluded that reoligomerization of small compounds dominated thermal cracking reactions for temperatures up to 500 °C and suggest primary production of monomers and dimers could quickly be subject to secondary reactions which form larger compounds. An alternative explanation for pyrolysis of lignin consists of ejective boiling phenomena similar to those proposed by Dauenhauer et al. and Montoya et al., where boiling of the molten intermediate is capable of generating aerosols directly via bubble breakup and can generate particles both within the optical detection limits of this experiment as well as smaller aerosols [10, 11, 12, 14]. Here, the dominating presence of a dark-zone with condensation across the thermal boundary layer suggests a majority of the products produced are through evaporation and condensation to form larger compounds downstream. Conversely, condensed-phase products directly emerging from the biomass surface via gas expansion effects or ejective boiling play a minor role in overall transport.

3.4. Comparing the timescales of product evolution

Some idea of the relative role of kinetics and thermal transport can be examined by studying the integrated signal as a function of time for various feedstocks, as illustrated in Figure 6. As expected, the level of molecular complexity or the degree of polymerization plays a role in determining the timescales for product formation. Levoglucosan (green curve) begins boiling at 3.20 s, yet the peak scattering signal is delayed until 3.50 s. This delay can be interpreted as the transport time of volatiles from the strip to regions in the boundary layer driving significant condensation of products. The initial rise in levoglucosan scattering signal prior to reaching the boiling point is attributed to feedstock degradation during melting. For cellulose (red curve), a temporal delay in product formation is observed relative to levoglucosan, and, in contrast, consists of an extended period of steady scattering signal. The variation in scattering signal is attributed to unsteadiness associated with minor gas ejections during liquid intermediate boiling. The delay of product formation and the extended reaction duration in cellulose is attributed to transport limitations and the kinetic timescales associated with the unzipping and depolymerization processes.



Figure 6: The integrated scattering signal above the pyrolyzing biomass is shown for the each feedstock under consideration. All signals are normalized by the maximum signal observed for organosolv lignin and are offset vertically for clarity. The integrated signal gives a qualitative description of the rate of evolution of products, which are dominated by condensation above the pyrolyzing samples.

For technical lignin, the integrated scattering signal (yellow curve of Figure 6) exhibits significant unsteadiness. This variation corresponds to intense ejection events where strong scattering signals are observed for droplets and condensing volatiles ejected from a collapsing bubble. These ejections occur infrequently (approximately 10 large ejections per second) and coupled with the scattering results (Figure 2(b) and supplement video sequence of Figure A.7b), this behavior suggests the majority of the evolved products-both vapor and aerosolsare transported away from the particle bed by natural convection, not by direct ejection. As seen in Figure 6 (black line), the steady evolution of the integrated scattering signal from organosolv lignin within the silica matrix indicates inhibition of bulk product ejection, providing a better method to study the contribution of lignin physicochemistry during whole biomass pyrolysis. Comparing the two integrated scattering traces for OS lignin and OS lignin in the matrix shows the same initiation temperature, but an extended duration for the OS ligninindicating transport and kinetic limitations. Finally, a steep decrease in product formation for OS lignin in the matrix at the end of the reaction (4.5 s) suggests a reduction in the charring reactions which continue out to 6 s for technical lignin.

The integrated scattering signal evolution is also shown in Figure 6 for red oak (blue curve). Here, the timescales of product formation can be compared to the biomass constituents. As with cellulose and lignin dispersed in the inert matrix, the evolution of products is steady, without the rapid ejecta observed for lignin and the boiling during cellulose degradation. Red oak exhibits a delay in product formation compared to all other feedstocks. The total duration of product formation is dependent on the heat and mass transfer limitations of the feedstock, in addition to the chemical kinetics. With this in mind, the total reaction durations for levogluosan is shorter than red oak and cellulose due to a lower degree of molecular complexity, while lignin and lignin-silica have longer product formation timescales due to (1) reduced heat and mass transfer from the unique agglomeration of technical lignin and (2) the reduced thermal conductivity of lignin-silica. Further, the plant cell structure and the separation of lignin fragments by cellulose and hemicellulose in whole biomass likely work to inhibit the agglomeration and boiling ejection features seen in technical lignin-only pyrolysis.

4. Conclusions

Fast pyrolysis of biomass in a novel, optically-accessible reactor enabled in situ tracking of product evolution from cellulose, extracted lignin, and whole red oak. Simultaneous imaging of morphological feedstock changes and laser scattering of condensable products revealed devolatilization as the predominant transport mechanism from whole biomass and cellulose. Vapor products subsequently condensed in the thermal boundary layer above the pyrolyzing biomass—forming bands corresponding to distinct classes of products. Lignin, however, underwent coalescence after liquefaction, resulting in thermal ejection of droplets. Dispersing the lignin within an inert matrix eliminated ejection, yielding product formation similar to cellulose and whole biomass pyrolysis.

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Appendix A. Mie scattering videos

Video sequences corresponding to the simultaneous images presented in Figure 2 are available in the electronic supplementary material.





(a) Video sequence of the fast pyrolysis of cellulose, corresponding to Figure 2(a).



(c) Video sequence of the fast pyrolysis of lignin dispersed in an inert matrix, corresponding to Figure 2(c).

(b) Video sequence of the fast pyrolysis of technical lignin, corresponding to Figure 2(b).



(d) Video sequence of the fast pyrolysis of whole red oak biomass, corresponding to Figure 2(d).

Figure A.7: Video sequences found in the electronic supplementary material.