Unified Kinetic Model for Torrefaction-Pyrolysis

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Abstract

Thermochemical conversion is a promising pathway to renewable fuels. Torrefaction is the low temperature conversion to a primarily solid fuel, and pyrolysis is a higher temperature process that produces mainly a liquid bio-oil product. Though these processes are both thermal degradation routes in an inert atmosphere, they are often presented as different processes. A novel six stage consecutive model is proposed to describe a unified view of torrefaction and pyrolysis. The reactions lump chemical species formation in the six reaction stages and represent decomposition of cellulose, hemicellulose, and lignin. Activation energies of 104, 129, 154, 217, 256, and 285 kJ/mol were found through modeling of 32 unique gas-phase species fragments and weight loss dynamics for degradation from 260-425°C. It is demonstrated that there is a unified process that occurs, and can describe the degradation of the structural components in biomass. These dynamics yield important insight into the thermal degradation mechanism such as the chemical product detachment dynamics, and the influence of process severity.

Keywords

Thermal degradation, Biomass pyrolysis, Kinetic model, Molecular detachment

1. Introduction

In 2013, the United States consumed approximately 97.4 quadrillion BTUs of primary energy, of which approximately 83% was derived from fossil energy sources (35.1 quads as petroleum, 26.6 quads as natural gas, 18.1 quads as coal) primarily to satisfy demand for heat, power, and transportation fuels (Fichman, 2015). These three fossil fuel categories make up approximately 95%, 89%, 91%, and 66% of the energy consumption of the transportation, industrial, residential and commercial, and electric power sectors respectively (Fichman, 2015). As a result of these activities in 2012, 6,526 million metric tons of CO₂-equivalence (82% as direct CO₂, 9% methane, 6% nitrous oxide, 3% fluorinated gases) were released by these U.S. activities alone (EPA, 2014). These emissions can be linked to electricity generation (38%), transportation (32%), industry (14%), and residential and commercial applications (9%) (EPA, 2014). From this simple high-level look at the energy patterns of the U.S. it is clear that more emphasis needs to be placed on the meeting the objectives set forth by renewable energy initiatives such as the renewable fuel standard (and subsequent updates in the RFS II) to address fossil consumption in the transportation sector and the state mandated renewable energy portfolios to address fossil fuel use for heat and power in the electric utility and industrial sectors. Though there are many possible ways to address these energy requirements in a more sustainable way, the most compelling near-term solution may be to develop a renewable drop-in fuel replacement. Such a fuel will permit the retention of existing infrastructure and distribution/consumption practices. The thermochemical conversion of biomass can offer drop-in solutions to these three most prevalent fossil fuels.

Thermal conversion in an oxygen free environment at mild temperatures (200-300°C) results primarily in a more carbonaceous solid fuel and is referred to as torrefaction (Chew & Doshi, 2011; van der Stelt et al., 2011). At slightly higher temperatures (350-500°C) the thermal depolymerization of material is referred to as pyrolysis and mainly produces a liquid biocrude oil comprised of many different organic compounds (Mohan et al., 2006). As temperature increases further (>700°C) biomass in an oxidative environment can produce a mainly gaseous fuel (syngas) (Mohan et al., 2006). Though these conversion processes can produce promising alternative fuels and much work is being done to model the decomposition and provide mechanistic insight, there is still no clear understanding of the fundamental mechanisms that occur during torrefaction and pyrolysis (Nocquet et al., 2014a; Nocquet et al., 2014b; van der Stelt et al., 2011).

Proposed mechanisms for torrefaction and pyrolysis are generally represented as the structural polymers (cellulose, hemicellulose, and lignin) in lignocellulosic biomass degrading through a series of smaller macro-molecule polymer units intermediates, to smaller trimer, dimer, and monomer units, and ultimately a suite of distinct organic products formed through decomposition of polymer end units, or monomer/dimer scission/fragmentations (Collard & Blin, 2014; Huang et al., 2010; Isahak et al., 2012; Kelkar et al., 2014; Patwardhan et al., 2011a; Patwardhan et al., 2011b; Patwardhan et al., 2009; Shen & Gu, 2009). Of these components cellulose is studied most often perhaps due to its' uniform nature. Shen and Gu looked at further developing mechanistic understanding of cellulose pyrolysis through 3-D TG-FTIR and GC-MS (Shen & Gu, 2009). They found that in the absence of secondary reactions levoglucosan, the main

product from cellulose pyrolysis, is consistently formed through first the depolymerization of cellulose chains to monomer units, and then to levoglucosan through hydrogen abstraction and formation of a hydroxyl radical at the broken $\beta(1\rightarrow4)$ glycosidic linkage sites and reforming (Shen & Gu, 2009). This type of formation pathway for levoglucosan and other cellulose based organics is also supported by other works, and has been studied in the presence of alkali-based minerals that act as catalysts (Collard & Blin, 2014; Kelkar et al., 2014; Li et al., 2001; Patwardhan et al., 2009; Ponder et al., 1992; Trendewicz et al., 2015). More recently in support of this Sánchez-Jiménez et al. found that cellulose pyrolysis most closely obeys kinetic laws governed by a random chain scission mechanism (Sánchez-Jiménez et al., 2013). These results suggest that there is a progressive degradation of biomass polymers during pyrolysis to smaller chains and ultimately gas-phase chemical species, indicative of consecutive-type chemical reactions.

Previously, our group proposed such a lumped consecutive kinetic model to describe the gas-phase evolution of species during torrefaction (Klinger et al., 2013; Klinger et al., 2014b). It was found that a minimum of three first order reactions were required to describe the transient characteristics of the formed volatile species: water, carbon monoxide, carbon dioxide, acetic acid, formic acid, and furfural (Klinger et al., 2014b). Though the degradation process was found to be consistent over the temperature ranges studied (up to 300°C), it was found that mechanistic interpretations through mass loss alone are not sufficient to gain chemical mechanistic insights (Klinger et al., 2014a; Klinger et al., 2014b).

To gain further insight into the mechanisms of biomass degradation, this type of lumped chemical species analysis is extended in this work to include pyrolysis-ranged processing conditions. Though pyrolysis and torrefaction are often studied independently or presented as separate processes, it is asserted here that they are a single unified process that occur at kinetically different rates. This idea that torrefaction and pyrolysis are similar processes can be observed in other modeling studies, combined torrefaction-pyrolysis processing experiments, and works that investigate chemical species distribution (Branca et al., 2014; Branca et al., 2003; Di Blasi et al., 2013; Eseltine et al., 2013; Westerhof et al., 2012; Westover et al., 2013). In this work, thermal degradation of biomass is investigated through a proposed unified model to describe both torrefaction and pyrolysis. This work is novel in that it moves beyond weight-loss measurements and discrete product distributions, and uses a series of dynamic chemical species to establish kinetic parameters. In addition to an approximate weight-loss measurement, 32 individual molecular ions were traced as transient species to obtain chemical dynamics during the degradation process. This type of approach can effectively be used to describe and model the process on a chemical level, but also be used to provide insights to other mechanistic works.

2. Materials and Methods

Micro-torrefaction and pyrolysis experiments carried out in this work used debarked aspen wood. A knife mill (Thomas Wiley®, NR. 3557524 359264) was used to reduce particles with a 1mm screen. The whole samples were then sieved (W.S. Tyler Rotap, RX-29) and particles between 500-600µm (32-28 Tyler mesh) were isolated to maintain uniform, repeatable thermochemical conversion. Proxies used for pure

carbohydrate/fiber components were similar to commercially available products through a supplier such as Sigma-Aldrich (*cellulose*: Avicel® PH-101, ~50µm particle microcrystalline cellulose powder; *hemicellulose*: Poly(beta-D-xylopyranose[1→4], xylan from beechwood; *lignin*: Sigma-Aldrich 471003, low sulfonate kraft lignin, ~10,000 average molecular weight). Before experiments were carried out, all samples were dried at 105°C until no difference in mass was observed.

2.1 Pyrolysis Experiments

A resistive filament pyrolyzer (CDS 5200HP Pyroprobe) was used to process the aspen samples. The pyrolysis unit was connected to an in-line gas chromatograph (Trace GC Ultra, ThermoFisher) and mass spectrometer (Trace DSQII, ThermoFisher) for gas-phase product detection and characterization. The GC was fit with a non-retentive fused silica guard column (Restek, Rxi Guard Column, 10m). The GC oven was maintained at the same temperature as the system transfer lines (300°C), and transferred the materials from the GC inlet to the MS with minimal interaction as described in previous work (Klinger et al., 2013; Klinger et al., 2014b).

Biomass samples were loaded in quartz reaction tubes (25 mm x 2 mm OD) and were surrounded by the resistive heating coil for radiative heat transfer (1000°C/s). The biomass was held in the center of the coil's heating zone by minimal amounts of quartz wool. A sample size of 0.10-0.20 mg was used, and measured by a microbalance accurate to 1µg (Citizen Scales Inc., Model CM5). High purity helium (99.999%) acted as the carry gas throughout the system, and a flow rate of 1.5 mL/min was maintained through the GC column (50.9 cm/s superficial velocity). Molecular fragments in the range 15-350 m/z

were recorded at a rate of ~5 Hz over the course of 90 minute experiments. The Total Ion Current (TIC) chromatogram is a summation of all molecular fragment intensities at each time point, and was recorded as a proxy for total sample mass loss.

Previously, our group investigated the kinetics of thermal degradation in the range of traditional low-temperature pyrolysis (torrefaction) temperatures up to 300°C (Klinger et al., 2013; Klinger et al., 2014b). In transition into pyrolysis-ranged processing, six temperatures were studied here: 315, 330, 350, 375, 400, and 425°C. To model pyrolysis in this range molecular fragments relating to cellulose, hemicellulose, and lignin (described below) were used along with the overall weight loss proxy, the TIC signal.

2.2 Product Distribution and Molecular Fragmentation

Pyrolysis is well-known to produce a complex mixture of organic compounds that is dependent on feedstock properties, sample sizes, and processing severity (heating rates, temperature, and duration) among other factors. To understand the chemical speciation from the carbohydrate/fiber fractions of biomass, studies have been performed on pure samples of cellulose, hemicellulose, and lignin (Patwardhan et al., 2011a; Patwardhan et al., 2011b; Patwardhan et al., 2009). Major products from each of the three components are shown in Table 1 along with their major molecular ions produced in a mass spectrometer according to the National Institute of Standards and Technology (NIST). The major ion fragments presented are from highest abundance to lowest, and the compounds are listed in order of typical retention times. The most prominent species produced from pyrolysis of cellulose are non-condensable gases (CO and CO₂), water, levoglucosan, and smaller amounts of other anhydrosugars and furans (Patwardhan et al., 2009). The major

species from the pyrolysis of hemicellulose are non-condensable gases, water, organic acids (formic and acetic), and smaller amounts of other anhydrosugars, aldehydes, etc. (Patwardhan et al., 2011a). The pyrolysis of lignin results primarily in formation isomers of methylated or ethylated phenolic compounds, along with non-condensable gases and smaller organic compounds (Patwardhan et al., 2011b).

[TABLE 1.]

To determine the sensitivity of the experimental system, pure components (cellulose, hemicellulose, lignin) were run in the Py-GC-MS system described above at 350°C. Average mass spectral fingerprints across the major production time (0-3min) were extracted for comparison with major ion fragments observed by others (Table 1), and for interpretation of chemical species evolution. When major ions observed in this empirical work were combined with major product ions observed by others, 32 unique mass-to-charge fragments were identified to describe the degradation of cellulose, hemicellulose, and lignin within the biomass structure during pyrolysis. A summary of these ions are discussed later in section 3.2.

2.2 Modeling Approach

Previously, a model for low-temperature pyrolysis was proposed to describe the process based on removal of gas-phase species in a three consecutive reaction mechanism (Klinger et al., 2013; Klinger et al., 2014b). The model assumes that the same basic lumped parameter reactions occur at all temperatures, but at different rates as governed by temperature. The chemistry of the process, then, is independent of temperature and a desired processing severity can be obtained through either time or temperature. As the

temperature of pyrolysis was increased, the structure of the biomass is degraded more quickly, and more completely as the more recalcitrant portions of the biomass are broken down at an observable rate. To address this production in the extended temperature range, more consecutive reactions were added to describe this progressive structural deformation. As the temperature was increased to the highest temperature studied (425°C), it was determined that a minimum of three additional reactions were needed to predict the evolution of gas-phase species observed. This model can be summarized as:

for reaction j from (2,3,...,6), where $k_{j,i}$ is the reaction specific rate coefficient for species i , R is a solid reaction intermediate that represents a partially degraded biomass with fragmented carbohydrate/fiber fractions, $\alpha_{j,i}$ is a stoichiometry factor for reaction j and species i , and $P_{j,i}$ is a gas-phase product, species i for reaction j . For each reaction stage, there is a single rate coefficient, and a unique stoichiometry factor for each chemical species. As discussed above, however, the stoichiometry parameters are proposed to be independent of temperature – meaning that a single stoichiometric parameter applies across all six reaction stages for each chemical product. For each species there are six stoichiometric parameters, one for each reaction. The six rate coefficients were fit independently for each species. The reaction rate constants are responsible for describing the dynamics of each gas-phase species in the lumped chemical reactions, and the quantity of species produced by each of the consecutive reactions is dictated by the stoichiometry parameters. These stoichiometry variables relate to the mechanistic chemistry that occurs

in a lumped set of reactions. Each of the six proposed stages likely represent many near-parallel reactions that occur at, or near, the same observable rate to produce the many organic products of pyrolysis. These lumped reactions may, for example, represent the suite of probable reactions at a carbohydrate polymer chain end or the result of a random scission along the backbone. The reactions with similar dynamics, then, give an aggregated result for the respective degradation stage.

It is important to note that the proposed novel unified torrefaction-pyrolysis applies over the entire temperature range (260-425°C), however the sensitivity of the process to system temperature masks several reaction stages and makes them unmeasurable due to very slow or fast kinetics. A reaction was classified as having very slow kinetics when the characteristic time was greater than two hours, and very fast kinetics when the characteristic time was less than fifteen seconds. When a reaction fell in either of these regimes, an extrapolated value obtained over a range of the valid temperatures was used during the fitting procedure. A matrix showing the temperature-reaction linkages during the model fitting procedure is shown in Table 2. As the reaction temperature increases, the initial reactions (Rxn 1-3) become kinetically very fast, and the later reactions (Rxn 4-6) are kinetically very slow over the initial temperature range. As discussed in our previous work (Klinger et al., 2013; Klinger et al., 2014b), the first three reaction steps apply up to 300°C. Rxn 1 becomes very fast above 330°C. Rxn 2 becomes very fast above 350°C. Rxn 3 becomes very fast above 375°C. Rxn 4 is observable from 330-400°C. Rxn 5 is observable above 330°C. Rxn 6 is observable above 350°C.

[TABLE 2.]

The model fitting procedure was performed by minimizing the squared difference between the experimental data, and product profiles predicted by the model over the 90 minute experiments. During the model fitting procedure a complete mass balance was maintained. As the solid mass product degrades, an equal total mass of volatile species was released. Because the dynamic traces are production rates, mass balance is ensured at any reaction time from a sum of profile integrals of biomass, intermediate solids, char, and volatile components in equality to the original mass. Product profiles were obtained using a forward finite difference numerical method with a similar time step of the experimental data (5 Hz). The model parameters were allowed to vary for the appropriate reactions according to the temperature-reaction dependence shown in Table 2.

3. Results and Discussion

Over the time-course of the pyrolysis experiments, the values for the TIC chromatogram were extracted as a proxy for the overall mass loss observed by the biomass sample. Sample traces over the range of torrefaction and pyrolysis temperatures for the TIC chromatogram are shown in Figure 1, and represent the total rate of volatile species production with time. The TIC signal represents a summation of all molecular fragments, and the overall trace is a convolution of the production rates from the proposed six reaction stages. The stoichiometric parameters discussed represent the contribution from each reaction stage for a given molecular fragment, and can be used to display the contribution from each stage without convolution. For this TIC signal, the stoichiometric parameters do not have interpretable meaning, and instead the discussion is focused on the results of the rate constants. For comparison of the dynamics, the data in Figure 1 were normalized

to unity production. When normalized to the same production quantity, the data present a clear temperature dependence of the process where relatively high temperatures (425°C, 400°C) result in production occurring almost entirely within the first two minutes with high initial production rate. Conversely, the lower temperatures (<330°C) result in much smaller initial production rates, however, the production is sustained over a much longer duration to reach the same production intensity. Overall, the rates appear monotonic in nature as noted previously, but there are shifting contributions from late-time reactions to early-time reactions that need to be carefully traced with increasing temperature. The six consecutive reaction model was applied to these TIC traces to determine the rate constants associated with the overall mass loss observed by the biomass.

[FIGURE 1.]

3.1 Kinetic Model

As discussed above, the TIC chromatograms were fit with the six consecutive reaction model. A summary of typical results for four temperatures are shown in Figure 2. The fit rate constants shown in the figures have units of min^{-1} . The model is able to predict the observed behavior of the signal well, with an average coefficient of determination of 0.98 at all temperatures and between duplicates. Although the model consists of six reactions, it is important to note that only a portion of them occur at an observable rate at the reported temperature as displayed in Table 2. At 280°C, the experimental trace is explained almost entirely with Rxn 1 ($k^{-1} \sim 2.4\text{min}$) and Rxn 2 ($k^{-1} \sim 10\text{min}$), with small contributions from Rxn 3. At 330°C, the first four reactions define the observed behavior with characteristic times of 0.34, 0.91, 3.7, and 50 minutes respectively. Four reactions

(Rxn 3-6) were also fit from the 375°C traces with characteristic times of 0.52, 2.3, and 14 minutes for Rxn 3-5 and small contributions from Rxn 6. As the temperature is increased to the 425°C, only Rxn 5 and 6 were fit with characteristic times of 0.44 and 2.4 minutes respectively.

[FIGURE 2.]

Average fitting results for the TIC chromatograms are displayed in an Arrhenius plot as Figure 3. Error bars showing deviation for the fit kinetic rate constants between replicate experiments fall within the data symbols, and were omitted. Linear regression of the parameters from the six reactions yields activation energies of 104, 129, 154, 217, 256, and 285 kJ/mol respectively, with coefficient of determination values (from data in Figure 3) of 0.99, 0.99, 0.99, 1.00, 1.00, and 0.99 respectively. This suggests that as the degradation continues through the consecutive stages, the remaining solids become more recalcitrant and require more energy to continue degrading. Though these values do not give any direct insight into the structure of the intermediates, they can be used in process modeling and may provide insight to probing the structural changes observed during biomass degradation. Such solid state work has also concluded that scission reactions occur early in pyrolysis processing on weaker oxygen and hydrogen bonds, leading to a more rigid and carbonaceous structure (Azargohar et al., 2014; Kim et al., 2011; Westover et al., 2013). This mechanistic insight can be combined for greater understanding of thermal degradation, or use in quantum simulations.

[FIGURE 3.]

3.2 Component-based Model Fitting

As discussed earlier, pure wood components of cellulose, hemicellulose, and lignin were processed to interpret the major chemical species formed during pyrolysis at 350°C. Sample sizes were maintained around the same sizes of aspen of 0.10-0.20 mg. Through many of the same molecular ions listed in Table 1 above were consistently observed, the ten molecular fragments with the highest relative abundance were targeted for qualitative comparison. The data were normalized to the intensity of the maximum fragment. These fragments are related to their respective carbohydrate parent-fraction, and the modeling of their gas-phase evolutions is then directly related to their parent fraction's degradation. The most abundant molecular fragments are shown in Table 3. Major fragments identified from cellulose primarily includes 59.9 m/z ($\text{C}_2\text{H}_4\text{O}_2^-$), 72.9 m/z ($\text{C}_3\text{H}_5\text{O}_2^-$), and 56.9 m/z ($\text{C}_3\text{H}_5\text{O}^-$). These three fragments can all be related to levoglucosan, and agrees with major product formation identified in literature (Patwardhan et al., 2009). Other fragments identified (42.9 m/z, $\text{C}_2\text{H}_3\text{O}^-$; 68.9m/z, C_3HO_2^- ; 28.9m/z, CHO^- ; etc.) are primarily related to other anhydrosugars, glycolaldehyde, and carbon dioxide. The hemicellulose results show the most abundant fragments include 43.9 m/z (CO_2^-), 17.9 m/z (H_2O^-), 27.9 m/z (CO^-), 42.9 m/z ($\text{C}_2\text{H}_3\text{O}^-$), and 30.9 m/z (CH_3O^-) relating to water, carbon dioxide, organic acids, and furan/xylopyranose species. These identified fragments also agree with major chemical species observed by others (Patwardhan et al., 2011a). Molecular fragments with the highest intensity from lignin include fragments similar to others mentioned above as well as 46.9 m/z (CH_3S^-), 63.8 m/z (C_5H_4^-), and 54.9 m/z (C_4H_7^-) relating to aliphatic linkages containing sulfur, and benzene-ring and hydrocarbon containing species. These observations can also be related to major phenolic compounds observed in literature

(Jackson et al., 2009; Patwardhan et al., 2011b; Zhang et al., 2014). To investigate the degradation of structural components of biomass during pyrolysis, the molecular fragments present in the highest intensity were combined with those observed by others (presented in Table 1) in a set of 32 representative fragments related primarily to cellulose (*C*), hemicellulose (*H*), and/or lignin (*L*): 18 m/z (*C, H, L*), 19 m/z (*C, H*), 28 m/z (*C, H, L*), 29 m/z (*C, H, L*), 31 m/z (*H*), 39 m/z (*C*), 43 m/z (*C, H*), 44 m/z (*C, H, L*), 45 m/z (*L*), 47 m/z (*L*), 48 m/z (*L*), 53 m/z (*C, H*), 55 m/z (*C, L*), 56 m/z (*C*), 57 m/z (*C, H, L*), 60 m/z (*C, H, L*), 64 m/z (*L*), 69 m/z (*C*), 70 m/z (*C*), 73 m/z (*C, H, L*), 94 m/z (*L*), 95 m/z (*H*), 96 m/z (*C*), 98 m/z (*C*), 107 m/z (*L*), 109 m/z (*H, L*), 124 m/z (*H*), 137 m/z (*H*), 153 m/z (*L*), 154 m/z (*L*), 165 m/z (*L*), and 168 m/z (*L*).

[TABLE 3.]

The six consecutive reactions were also applied to the dynamic traces of the 32 unique ion fragment independently from the weight loss proxy. A summary of these data traces along with the model fits at a processing temperature of 350°C are shown in Figure 4. Because of the nature of tracing molecular fragments instead of a unique chemical compound, the magnitude of fragments in Figure 4 were not mass calibrated and are therefore on an arbitrary scale as detected by the instrument. The production rate traces for the molecular fragments appear to have similar behaviors with slightly varying weights given to reactions occurring at early, middling, and late times. If individuals ions that are both primarily related to a single structural component of biomass and produced in a large quantity from that fraction, then some general observations about the degradation of cellulose, hemicellulose, and lignin can be extracted: (1) unique hemicellulose fragments

observed within the pure component studies such as 124 m/z and 137 m/z are produced at very early times, and that indicates a relatively lower reaction energy requirement for degradation, (2) fragments uniquely related to phenolic compounds such as 168 m/z have a production rate that occur over a longer duration indicating a higher energy required for product formation, and (3) cellulose-based fragments such as 39 m/z, 56 m/z have production rates between the other components, and likely a middling decomposition energy. These observations are also noted in other literature works (Collard & Blin, 2014; Sarvaramini et al., 2013; Yang et al., 2007). To interpret the distribution of production between the six reaction steps, Figure 5 shows the average stoichiometry parameters for the molecular fragments that were identified uniquely to either cellulose, hemicellulose, or lignin in ratio to the first reaction parameter. This demonstrates the relative production attributed to the parent fraction as pyrolysis severity increases. There is significant product from all portions in all reactions, however, hemicellulose qualitatively demonstrated relatively lower production in Rxn 4-6 (high production in Rxn 1-3), cellulose exhibits the highest relative production from late-time reactions (4-6), and the distribution of lignin is middling. This again supports the observations that hemicellulose has a relatively smaller required decomposition energy compared to the high energy required for cellulose noted above, and by others. Table 4 lists the average stoichiometry factor ratios obtained for all molecular fragments across all temperatures. These values show the relative distribution of production between the six reaction stages. From the values In Table 4 obtained from the fitting procedure, it is demonstrated that some of the various organic fragments are produced even at lower processing temperatures, as the earlier reaction have lower

activation energies (as shown above for TIC, and following). In general, these early reactions would dominate at lower temperatures (torrefaction) as the rates for the later reactions would be very slow in comparison. This predicts that although more product is formed at higher temperatures, there will be formation of a liquid oil product during torrefaction or slow (conventional) pyrolysis.

Although the production of the various chemical species are distributed between reactions with different characteristic times within the consecutive model, the dynamic behaviors of all species are captured with a 0.99 average coefficient of determination. The time-dependent traces of the chemical species removal provide direct insight to changes in the parent biomass and can yield mechanistic insight. The molecular fragment traces were fit independently from the TIC chromatogram results presented previously. Molecular fragment traces were fit at all pyrolysis temperatures.

[FIGURE 4.], [FIGURE 5.], [TABLE 4.]

A summary of the reaction rate constants fit for the 32 molecular fragments with the six stage consecutive model is shown in Figure 6. Values fit for the molecular fragments are shown as data points, and the dashed lines represent the average value obtained from the TIC chromatogram fitting discussed previously. The values for rate constants here were obtained independently, and are independent of fragment type/origin. Further, they are in agreement with the values that were obtained from the previous fitting routine with the mass loss proxy. This agreement validates that: (1) the six stage consecutive model predicts the formation of chemical species from the lumped reactions, and (2) there is a close linkage between the total degradation of the biomass and the

evolution of any specific chemical species. It is supported that there is an underlying mechanism responsible for the degradation of all species, such as chain scission kinetics. This type of model is also hypothesized for the pyrolysis of cellulose and other polymers in recent literature (Pérez-Maqueda et al., 2014; Sánchez-Jiménez et al., 2013).

These kinetic rate constant fitting values are also summarized in Arrhenius plots in Figure 6. Data points are the average rate constant value from all molecular fragments, and the dashed lines are produced with the TIC chromatogram fitting in a previous section. Data for pyrolysis-range temperatures are shown in the bottom left plot, and torrefaction-range temperatures are shown in the bottom right plot. This demonstrated that the proposed lumped six consecutive reaction model is able to describe torrefaction, and pyrolysis on both a weight loss basis and for chemical speciation. This kinetic model unifies the ideas of torrefaction and pyrolysis in a single lumped parameter model. Further, this validates that the processes have similar mechanisms that occur at different kinetic rates due to the system temperature.

[FIGURE 6.]

The rate constants for product formation can also be aggregated back to their parent component fraction (as discussed above). The fragments related to cellulose in ratio to the respective TIC value yield (rate constant from fragment trace fitting/rate constant from TIC fitting) an average value of 0.99 ± 0.04 , while hemicellulose and lignin have average values of 1.02 ± 0.04 and 1.00 ± 0.05 respectively. This again validates that there is an underlying mechanism, or set of mechanisms, that are responsible for the removal of each chemical species and the overall changes observed by the biomass. Further, it is asserted that these

data are representation that a single process is occurring over the investigated temperature range, any observed differences are from changes in temperature induced reaction rate changes.

The close agreement between the proposed kinetic model and empirical data suggests validity for predicting the chemical dynamics of torrefaction and pyrolysis. Though the instrument was not mass calibrated for the experimental work, normalized data were used to extract qualitative and quantitative data. The kinetic data were collected under conditions where the chemical reactions were rate limiting, using small biomass particles and very fast heating/product quenching rates. These ideal experimental conditions allow for collection of intrinsic reaction data. These intrinsic parameters are a basis for obtaining predictions at any desired processing condition. The model, though, does not attempt to include any effects that heat and mass transport (from large particles), or secondary cracking reactions (from mineral content or long gas residence times) have on the product distribution. In addition, the lumped solid reaction intermediates compositions are unknown and act as quasi-species in the reactions. Further model developments such as the effect of conductive heat transport and effects of alkali mineral content are needed in future work to apply the presented chemical dynamics in process-scale reactors.

4. Conclusions

A novel six consecutive reaction model is presented that can describe a unified view of torrefaction and pyrolysis from 260-425°C. Fitting torrefaction and pyrolysis data for weight loss and chemical species gas-phase removal to a six stage consecutive model yields kinetic parameters of 104, 129, 154, 217, 256, and 285 kJ/mol respectively. It was

429 also demonstrated that there is an underlying mechanism responsible for the degradation of
430 the structural components of biomass. The dynamic chemical species traces presented here
431 can be used to describe torrefaction and pyrolysis in a set of lumped reactions, and also
432 yield mechanistic insight.
433

434 **Acknowledgements**

435 We would like to acknowledge National Science Foundation grant MPS/CHE -
436 ENG/ECCS – 1230803 for support of this work through a Sustainable Energy
437 Pathways grant and the Richard and Bonnie Robbins Endowment.

Works Cited

- Azargohar, R., Nanda, S., Kozinski, J.A., Dalai, A.K., Sutarto, R. 2014. Effects of temperature on the physicochemical characteristics of fast pyrolysis bio-chars derived from Canadian waste biomass. *Fuel*, **125**(0), 90-100.
- Branca, C., Di Blasi, C., Galgano, A., Broström, M. 2014. Effects of the Torrefaction Conditions on the Fixed-Bed Pyrolysis of Norway Spruce. *Energy & Fuels*, **28**(9), 5882-5891.
- Branca, C., Giudicianni, P., Di Blasi, C. 2003. GC/MS Characterization of Liquids Generated from Low-Temperature Pyrolysis of Wood. *Industrial & Engineering Chemistry Research*, **42**(14), 3190-3202.
- Chew, J.J., Doshi, V. 2011. Recent advances in biomass pretreatment – Torrefaction fundamentals and technology. *Renewable and Sustainable Energy Reviews*, **15**(8), 4212-4222.
- Collard, F.-X., Blin, J. 2014. A review on pyrolysis of biomass constituents: Mechanisms and composition of the products obtained from the conversion of cellulose, hemicelluloses and lignin. *Renewable and Sustainable Energy Reviews*, **38**(0), 594-608.
- Di Blasi, C., Branca, C., Masotta, F., De Biase, E. 2013. Experimental Analysis of Reaction Heat Effects during Beech Wood Pyrolysis. *Energy & Fuels*, **27**(5), 2665-2674.
- EPA. 2014. Inventory of U.S. Greenhouse Gas Emissions and Sinks 1990-2012. *U.S. Environmental Protection Agency*, **EPA 430-R-14-003**.
- Eseltine, D., Thanapal, S.S., Annamalai, K., Ranjan, D. 2013. Torrefaction of woody biomass (Juniper and Mesquite) using inert and non-inert gases. *Fuel*, **113**(0), 379-388.
- Fichman, B.T. 2015. Monthly Energy Review DOE/EIA-0035(2015/01). 1 ed, (Ed.) U.S.EIA, Vol. 2015, Office of Energy Statistics. Washington, DC, pp. DOE/EIA-0035(2015/01).
- Huang, J., Liu, C., Wei, S., Huang, X., Li, H. 2010. Density functional theory studies on pyrolysis mechanism of β -d-glucopyranose. *Journal of Molecular Structure: THEOCHEM*, **958**(1-3), 64-70.
- Isahak, W.N.R.W., Hisham, M.W.M., Yarmo, M.A., Yun Hin, T.-y. 2012. A review on bio-oil production from biomass by using pyrolysis method. *Renewable and Sustainable Energy Reviews*, **16**(8), 5910-5923.
- Jackson, M.A., Compton, D.L., Boateng, A.A. 2009. Screening heterogeneous catalysts for the pyrolysis of lignin. *Journal of Analytical and Applied Pyrolysis*, **85**(1-2), 226-230.
- Kelkar, S., Li, Z., Bovee, J., Thelen, K.D., Kriegel, R.M., Saffron, C.M. 2014. Pyrolysis of North-American grass species: Effect of feedstock composition and taxonomy on pyrolysis products. *Biomass and Bioenergy*, **64**(0), 152-161.
- Kim, K.H., Eom, I.Y., Lee, S.M., Choi, D., Yeo, H., Choi, I.-G., Choi, J.W. 2011. Investigation of physicochemical properties of biooils produced from yellow poplar

- wood (*Liriodendron tulipifera*) at various temperatures and residence times. *Journal of Analytical and Applied Pyrolysis*, **92**(1), 2-9.
- Klinger, J., Bar-Ziv, E., Shonnard, D. 2013. Kinetic study of aspen during torrefaction. *Journal of Analytical and Applied Pyrolysis*, **104**(0), 146-152.
- Klinger, J., Bar-Ziv, E., Shonnard, D. 2014a. Predicting Properties of Torrefied Biomass by Intrinsic Kinetics. *Energy & Fuels*, **29**(1), 171-176.
- Klinger, J., Klemetsrud, B., Bar-Ziv, E., Shonnard, D. 2014b. Temperature dependence of aspen torrefaction kinetics. *Journal of Analytical and Applied Pyrolysis*, **110**(0), 424-429.
- Li, S., Lyons-Hart, J., Banyasz, J., Shafer, K. 2001. Real-time evolved gas analysis by FTIR method: an experimental study of cellulose pyrolysis. *Fuel*, **80**(12), 1809-1817.
- Mohan, D., Pittman, C.U., Steele, P.H. 2006. Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review. *Energy & Fuels*, **20**(3), 848-889.
- Nocquet, T., Dupont, C., Commandre, J.-M., Grateau, M., Thiery, S., Salvador, S. 2014a. Volatile species release during torrefaction of biomass and its macromolecular constituents: Part 2 – Modeling study. *Energy*, **72**(0), 188-194.
- Nocquet, T., Dupont, C., Commandre, J.-M., Grateau, M., Thiery, S., Salvador, S. 2014b. Volatile species release during torrefaction of wood and its macromolecular constituents: Part 1 – Experimental study. *Energy*, **72**(0), 180-187.
- Patwardhan, P.R., Brown, R.C., Shanks, B.H. 2011a. Product Distribution from the Fast Pyrolysis of Hemicellulose. *ChemSusChem*, **4**(5), 636-643.
- Patwardhan, P.R., Brown, R.C., Shanks, B.H. 2011b. Understanding the Fast Pyrolysis of Lignin. *ChemSusChem*, **4**(11), 1629-1636.
- Patwardhan, P.R., Satrio, J.A., Brown, R.C., Shanks, B.H. 2009. Product distribution from fast pyrolysis of glucose-based carbohydrates. *Journal of Analytical and Applied Pyrolysis*, **86**(2), 323-330.
- Pérez-Maqueda, L.A., Sánchez-Jiménez, P.E., Perejón, A., García-Garrido, C., Criado, J.M., Benítez-Guerrero, M. 2014. Scission kinetic model for the prediction of polymer pyrolysis curves from chain structure. *Polymer Testing*, **37**, 1-5.
- Ponder, G.R., Richards, G.N., Stevenson, T.T. 1992. Influence of linkage position and orientation in pyrolysis of polysaccharides: A study of several glucans. *Journal of Analytical and Applied Pyrolysis*, **22**(3), 217-229.
- Sánchez-Jiménez, P.E., Pérez-Maqueda, L.A., Perejón, A., Criado, J.M. 2013. Generalized master plots as a straightforward approach for determining the kinetic model: the case of cellulose pyrolysis. *Thermochimica Acta*, **552**, 54-59.
- Sarvaramini, A., Assima, G.P., Larachi, F. 2013. Dry torrefaction of biomass – Torrefied products and torrefaction kinetics using the distributed activation energy model. *Chemical Engineering Journal*, **229**(0), 498-507.
- Shen, D.K., Gu, S. 2009. The mechanism for thermal decomposition of cellulose and its main products. *Bioresource Technology*, **100**(24), 6496-6504.
- Trendewicz, A., Evans, R., Dutta, A., Sykes, R., Carpenter, D., Braun, R. 2015. Evaluating the effect of potassium on cellulose pyrolysis reaction kinetics. *Biomass and Bioenergy*, **74**(0), 15-25.

525 van der Stelt, M.J.C., Gerhauser, H., Kiel, J.H.A., Ptasiński, K.J. 2011. Biomass upgrading
 526 by torrefaction for the production of biofuels: A review. *Biomass and Bioenergy*,
 527 **35**(9), 3748-3762.
 528 Westerhof, R.J., Brilman, D.W.F., Garcia-Perez, M., Wang, Z., Oudenhoven, S.R.,
 529 Kersten, S.R. 2012. Stepwise fast pyrolysis of pine wood. *Energy & fuels*, **26**(12),
 530 7263-7273.
 531 Westover, T.L., Phanphanich, M., Clark, M.L., Rowe, S.R., Egan, S.E., Zacher, A.H.,
 532 Santosa, D. 2013. Impact of thermal pretreatment on the fast pyrolysis conversion
 533 of southern pine. *Biofuels*, **4**(1), 45-61.
 534 Yang, H., Yan, R., Chen, H., Lee, D.H., Zheng, C. 2007. Characteristics of hemicellulose,
 535 cellulose and lignin pyrolysis. *Fuel*, **86**(12-13), 1781-1788.
 536 Zhang, M., Resende, F.L.P., Moutsoglou, A. 2014. Catalytic fast pyrolysis of aspen lignin
 537 via Py-GC/MS. *Fuel*, **116**(0), 358-369.

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Table 1: Major products formed from pyrolysis of pure component species.

Table 2: Experimental matrix showing the temperature range for each reaction during model fitting.

Table 3: Top ten most abundant ions formed during pyrolysis at 350°C.

Table 4: Stoichiometry parameters for the 32 modeled molecular fragments.

Figure 1: Experimental traces of the total chromatogram for a range of temperatures.

Figure 2: Typical model fits for TIC traces.

Figure 3: Arrhenius plot for kinetic modeling of TIC signal. Solid symbols represent modeling results. Empty symbols represent values used in modeling as predicted by straight line trends (dashed lines).

Figure 4: Typical experimental traces for 32 mass fragment traces and model fits. Data shown were taken at 350°C.

Figure 5: Average stoichiometry factor ratios for unique structural component fragments

Figure 6: Summary of fit rate constants (data points) for molecular fragments at 315°C (Top, Left), 330°C (Top, Right), 350°C (Middle Top, Left), 375°C (Middle Top, Right), 400°C (Middle Bottom, Left), 425°C (Middle Bottom, Right), Arrhenius Plot for the 32 fragments for pyrolysis (Bottom, Left), and Torrefaction (Bottom, Right). Dashed lines show the respective average value obtained from the TIC chromatogram

Cellulose (Patwardhan et al., 2009)		Hemicellulose (Patwardhan et al., 2011a)		Lignin (Patwardhan et al., 2011b)	
Product	Major Ions	Product	Major Ions	Product	Major Ions
CO	28	CO	28	CO	28
CO ₂	44	CO ₂	44	CO ₂	44
H ₂ O	18,17	H ₂ O	18,17	H ₂ O	18,17
Formic acid	29,46,45	Formic acid	29,46,45	Acetaldehyde	29,44,43
Furan/acetone	68,39,40	2-methylfuran	82,53,81	Acetic acid	43,45,60
Glycolaldehyde	31,32,29	Acetic acid	43,45,60	Phenol	94,66,65
2-Methyl furan	82,53,81	Acetol	43,31	2-methoxyphenol (o-guaiacol)	109,124,81
2-Furaldehyde	96,95,39	2-furaldehyde	96,95,39	4-vinyl phenol	63,91,107,120
2-Furan methanol	98,41,53	Dianhydro-xylopyranose 1	27,43,55,86,114	2-methoxy-4-vinyl phenol	135,150,107,77
5-(Hydroxymethyl)-2-furancarboxaldehyde	69,29,57	Dianhydro-xylopyranose 2	29,58,85,114	2,6-dimethoxy phenol	154,139
Anhydroxylopyranose	39,69,98,144	Anhydro-xylopyranose	29,43,73,86,114	4-methyl-2,6-dimethoxyphenol	107,125,153,168
1,6-Anhydro-b-D-glucopyranose(Levogluconan)	60,57,73	Other Anhydro-xylopyranose	29,57,73,86,114	3', 4'-dimethoxy acetophenone	165,180
1,6-Anhydro-b-D-glucofuranose	73,44,69	Xylose	73,60,31,43	Sinapyl alcohol	168,210

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Rxn	315°C	330°C	350°C	375°C	400°C	425°C
1	X	X	<i>Fast</i>	<i>Fast</i>	<i>Fast</i>	<i>Fast</i>
2	X	X	X	<i>Fast</i>	<i>Fast</i>	<i>Fast</i>
3	X	X	X	X	<i>Fast</i>	<i>Fast</i>
4	<i>Slow</i>	X	X	X	X	<i>Fast</i>
5	<i>Slow</i>	<i>Slow</i>	X	X	X	X
6	<i>Slow</i>	<i>Slow</i>	<i>Slow</i>	X	X	X

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Rank	Cellulose (m/z)	Hemicellulose (m/z)	Lignin (m/z)
1	59.9	43.9	43.8
2	72.9	17.9	17.9
3	56.9	27.9	46.9
4	42.9	42.9	47.9
5	68.9	30.9	44.9
6	28.9	136.9	63.8
7	69.9	108.9	56.9
8	55.9	28.9	59.9
9	43.9	123.9	72.9
10	54.9	56.9	54.9

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Fragment (m/z)	$\alpha 1 / \alpha 1$	$\alpha 2 / \alpha 1$	$\alpha 3 / \alpha 1$	$\alpha 4 / \alpha 1$	$\alpha 5 / \alpha 1$	$\alpha 6 / \alpha 1$
18	1.0	1.2	3.6	7.5	2.4	0.8
19	1.0	1.5	1.7	4.9	5.8	2.7
28	1.0	1.5	3.7	12.2	8.4	1.7
29	1.0	1.4	1.5	4.0	3.1	0.3
31	1.0	1.5	1.8	6.7	4.9	0.3
39	1.0	1.6	1.6	5.6	4.6	1.6
43	1.0	1.3	1.3	3.6	1.8	0.2
44	1.0	0.9	1.1	3.2	2.4	0.4
45	1.0	1.3	1.3	1.7	1.4	0.3
47	1.0	1.4	1.7	6.2	7.3	2.0
48	1.0	1.3	1.4	5.0	4.0	1.4
53	1.0	1.5	2.5	6.3	5.8	2.2
55	1.0	1.6	1.4	3.3	3.5	1.3
56	1.0	1.4	1.6	5.9	4.4	1.8
57	1.0	1.7	1.7	4.8	4.1	2.7
60	1.0	1.4	1.1	1.7	2.0	0.8
64	1.0	1.5	3.4	10.3	7.9	5.3
69	1.0	1.5	1.5	5.5	6.0	2.3
70	1.0	1.3	1.5	5.1	7.1	3.8
73	1.0	1.3	1.7	2.1	2.9	3.4
94	1.0	1.0	1.9	2.3	1.5	2.3
95	1.0	1.6	1.1	3.2	1.9	1.1
96	1.0	1.5	1.0	2.4	1.7	0.7
98	1.0	1.5	1.2	9.5	4.7	1.2
107	1.0	1.6	2.2	4.9	3.0	2.5
109	1.0	1.4	1.8	3.7	2.4	2.2
124	1.0	1.6	1.3	2.1	1.8	1.9
137	1.0	1.8	2.0	2.2	1.1	1.1
153	1.0	0.5	1.5	2.8	1.7	1.3
154	1.0	2.1	3.7	6.7	4.2	1.8
165	1.0	1.6	2.8	3.1	1.7	0.7
168	1.0	1.5	3.5	8.0	3.5	1.7

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