



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 to 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.

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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 [9]. 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 [9]. As a result of these activities in 2012, 6526 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 [7]. These emissions can be linked to electricity generation (38%), transportation (32%), industry (14%), and residential and commercial applications (9%) [7]. 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 [4,31]. 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 [19]. As temperature increases further (>700 °C) biomass in an oxidative environment can produce a mainly gaseous fuel (syngas) [19]. 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 [20,21,31].

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 [5,10,11,13,22–24,29]. 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 [29]. 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

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radical at the broken $\beta(1 \rightarrow 4)$ glycosidic linkage sites and reforming [29]. 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 [5,13,18,24,26,30]. 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 [27]. 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 [15,17]. 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 [17]. 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 [16,17].

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 occurs 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 [2,3,6,8,32,33]. 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 1 mm screen. The whole samples were then sieved (W.S. Tyler Rotap, RX-29) and particles between 500 and 600 μm (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, ~50 μm particle microcrystalline cellulose powder; *hemicellulose*: Poly(β -D-xylopyranose[1 \rightarrow 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 inline 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, 10 m). 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 [15,17].

Biomass samples were loaded in quartz reaction tubes (25 mm \times 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 1 μg (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 [15,17]. 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 [22–24]. 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 the 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 [24]. 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. [22]. The pyrolysis of lignin results primarily in formation isomers of methylated or ethylated phenolic compounds, along with non-condensable gases and smaller organic compounds [23].

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 (0–3 min) 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.

2.3. 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 [15,17]. 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

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