Temperature dependence of aspen torrefaction kinetics

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ABSTRACT

Torrefied biomass provides opportunities for an alternative, renewable fuel in the energy market. Much work on torrefaction is based on weight loss transients without much insight into the evolution of volatile species. A previous model from our group has been developed that predicts the degradation of raw biomass into specific chemical species during torrefaction (water, acetic acid, carbon monoxide, carbon dioxide, formic acid and furfural) in three consecutive reaction steps. The goal of this work is to understand how the kinetics of torrefaction change with temperature. Kinetic parameters for aspen wood were obtained for the first 90 min of 260–300 °C (1000 °C/s) torrefaction. The pre-exponential factors were 3.32E9, 1.43E11, and 2.08E14 min^{-1}, and the activation energies 1.05E2, 1.27E2, and 1.72E2 kJ/mol for the three reactions. Kinetic parameters found correspond well to similar values from global weight loss studies, and suggest that increased torrefaction severity leads to progressively more recalcitrant forms of torrefied biomass. These continuous production traces for the volatile organic species yield insight into torrefaction, and require careful consideration of torrefaction time and temperature to design the desired solid fuel product.

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1. Introduction

Currently 42% of the electricity generated in the United States comes from coal combustion [1,2]. Coal is known to produce one-third of the CO_2 emissions in the United States and releases other harmful pollutants such as CO, SO_x, NO_x, particulates, and mercury. Because of the growing concern of global warming, the need to find renewable CO_2 neutral feedstock is immediate. Biocoal (or torrefied biomass) [3–6] can be an immediate solution in coal utility boilers. This renewable fuel can be used as a drop-in replacement for coal firing due to its high energy density, similar properties to coal, low emissions and potential for CO_2 neutrality [3,6,7].

Biocoal is produced from the torrefaction of biomass, at temperatures from 200 to 300 °C in an oxygen free environment. During torrefaction, mostly the hemicellulose portion of the biomass degrades through a complex coupled chemical-kinetic-heat-and-mass-transfer process [7–9]. There are small contributions from cellulose and lignin during this process; with the contribution of cellulose increasing significantly at temperatures above 300 °C [8,10]. When the biomass is heated up quickly in an inert atmosphere, biomass is dehydrated, the viscoelastic properties are

changed, and the calorific value increases [6,11]. In addition, the energy requirements to reduce the size biocoal is substantially smaller, up to an order of magnitude, when compared to raw biomass [4,5,7,12,13]. Biocoal is then able to be a drop-in replacement for pulverized coal.

In order to have a better control of the torrefaction process and develop more efficient reactors for biocoal production, the torrefaction of biomass and the kinetics of species evolution, and changes in the residual biomass need to be better understood. Much gravimetric work has been done to model changes during torrefaction such as parallel reaction [7,14–16] and consecutive reactions models [10,17–20]. These models are useful for targeting throughput in equipment design, but provide little insights into the value-added benefits of torrefaction such as the improved fuel and physical properties over raw biomass mentioned above. A detailed understanding of the feedstock degradation during the torrefaction process, or the gas species evolution, is necessary for prediction of product quality changes with reaction conditions.
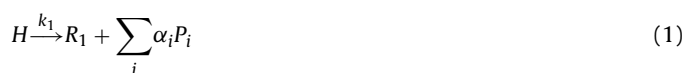
One specific approach to modeling torrefaction kinetics is to develop equations around weight loss data. One such model that is well accepted in literature is the two stage degradation of hemicellulose (xylans) developed by Di Blasi and Lanzetta [17]. This two stage model first degrades to a solid intermediate through rate constant k_1, and volatiles through kv_1, followed by a sequential step to torrefied biomass through k_2 and more volatile products through

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kv_2. This model predicts one stage of degradation at early times, and one stage for degradation over long processing times. The rate constants for each stage are also combined to give a global rate constant for that step ($k_1 = k_B + kv_1$, $k_2 = k_C + kv_2$). This was further developed by Di Blasi and Branca in subsequent years to include a similar third degradation stage (constants now k_B and kv_1, k_D and kv_2, and k_C and kv_3, respectively) when whole wood species (beech) were studied instead of xylans [21,22]. Further, these rate constants were combined to predict the pseudo-reactions where k_1 is the sum of the constants for volatile production and the production of the solid intermediate ($k_1 = kv_1 + k_B$) in reaction one. The six rate coefficients were therefore combined and analyzed as three global constants ($k_1 = kv_1 + k_B$, $k_2 = kv_2 + k_D$, $k_3 = kv_3 + k_C$) from 528 K to 584 K (6000 s), and 573 K to 708 K (up to 2000 s). The first reaction (k_1) was reported to dominate from 528 K to 593 K, the second (k_2) from 528 K to 708 K, and the third (k_3) from 603 K to 708 K. While these models may be convenient for estimating material throughput in equipment design, they do not provide any process insight into product quality, or any information on a chemical level.

Several studies have investigated modeling of torrefaction and coupling information about volatile species evolution [10,18–20,23,24]. Prins et al. studied the torrefaction of willow over 225–300 °C using the Di Blasi and Lanzetta model discussed above [10]. This was quickly followed by a subsequent study investigating the product distribution that is observed [23]. These were later combined to accurately predict the volatile product evolution over a range of temperatures and times [19]. More recently, Nocquet et al., took a similar approach using beechwood, cellulose, lignin, and xylan standards [20,24]. In the kinetic study, the two-stage Di Blasi and Lanzetta model was used to model the decomposition of the cellulose, hemicellulose, and lignin fractions of the biomass, with a stoichiometry parameter for the production of the respective volitile species [20]. With a correction facor to account for the interaction of the related consituents of virgin wood, they were able to accurately predict the volitile evolution at descite points, and also match a continuious mass loss signal. In order to move beyond a discrete point understanding of volitile torrefaction species, however, our group previously investigated a model based strictly around gas-phase species kinetics [18].

The previous study predicts the first 90 min of torrefaction at 300 °C, and the yield of products in a three-step torrefaction model [18]. This model was able to accurately predict the amount of various chemical species evolved during torrefaction and was based on the degradation of the hemicellulose material at 300 °C. The reaction model is shown below.

$$H \xrightarrow{k_1} R_1 + \sum_i \alpha_i P_i \qquad (1)$$

$$R_1 \xrightarrow{k_2} R_2 + \sum_i \beta_i P_i \qquad (2)$$

$$R_2 \xrightarrow{k_3} C + \sum_i \gamma_i P_i \qquad (3)$$

In this model the initial hemicellulose (H) is degraded with reaction rate constant k_1 into a reaction intermediate R_1 and forms a suite of products $\{P_{i,1}\}$. The first reaction intermediate R_1 is then degraded with rate constant k_2 into a second reaction intermediate R_2 and produces more of these products $\{P_{i,2}\}$. The second reaction intermediate is then degraded with rate constant k_3 into the biocoal product (C) along with an additional release of reaction products $\{P_{i,3}\}$. This model accounts for the production of major torrefaction products through characteristic mass spectrometer (MS) ion fragments of: water (18 m/z), carbon monoxide (28 m/z), formic acid

(29 m/z), carbon dioxide (44 m/z), acetic acid (60 m/z) and furfural (95 m/z).

This paper aims to deepen this model by applying this model over a range of torrefaction temperatures, and investigate the kinetics of torrefaction purely on the gas-phase reactions. In this work we take a lumped parameter assumption, where that the reaction rate coefficients are the same for each compound evolved, but the intensities of the specific species change with a stoichiometric coefficient (α, β, γ). These coefficients represent a relative amount of volatile product generated from each consecutive reaction stage, and are unique for each species—each of the six compounds investigated have a stoicheometeric parameter for each reaction. If this model is valid over the temperature range, then the stoichiometric coefficients should be independent of temperature for each of Eqs. (1)–(3). This assumption was validated in this research. This approach to predicting torrefaction is novel, but was previously investigated at only at 300 °C [18]. By obtaining gas-phase kinetics, accurate predictions of the volatile yields can be obtained for both isothermal and non-isothermal conditions. The dynamic evolution of these species was investigated, and unique implications of interpreting torrefaction through weight loss data in the absence of these novel results is discussed.

2. Materials and methods

As in our previous study [18] we used aspen biomass for this current research. Aspen samples were debarked then dried in an oven at 105 °C until no difference in mass was observed. A Thomas Wiley® knife mill (NR. 3557524 359264) was used to reduce the size of the wood particles. To obtain particle sizes of 0.5–0.6 mm a W.S. Tyler Rotap (model RX-29, serial 9774) was used. The aspen samples were roughly cylindrical with diameters of approximately 0.5 mm and length ranging from 1 to 3 mm.

2.1. Torrefaction experiments

To obtain kinetic data, the dried aspen wood samples were torrefied using a CDS Analytical micro-pyrolysis unit (model 5200HP Pyroprobe). The aspen was torrefied at temperatures of 260 °C to 300 °C at 10 °C intervals for 90 min. The volatile species evolved were continuously analyzed using a Trace GC Ultra (Model K8880181) gas chromatograph by ThermoFisher and a quadrupole mass spectrometer (Trace DSQII, ThermoFisher). The GC was fit with an inert, non-retentive, 10 m fused silica column (Restek, Rxi Guard Column). This eliminated any interaction with the compounds in the GC, and acted as a transfer line from the torrefaction reactor to the MS.

Aspen samples of 0.1–0.2 mg were weighed to within an accuracy of 1 μg using a microbalance (Citizen Scales Inc., Model CM5). The samples were then placed in a quartz reaction tube (25 mm × 2 mm OD) and held in place by two small pieces of glass wool on either end of the reaction tube. The samples were loaded into the micro-pyrolysis unit such that the wood chips were within the center of the heating zone and rapidly heated to the desired temperature. Rapid heating (1000 °C/s) was accomplished using a platinum heating filament that surrounded the quartz reaction tube. Ultra high purity helium (99.999%) was used as the carrier gas in order to create an inert atmosphere within the reaction zone and to transport the gaseous and vapor products into the inlet port of the GC through a heated stainless steel transfer line (300 °C). The GC column was kept at 300 °C for all experiments and the flow of helium gas kept at 1.5 ml/min (superficial velocity of 50.9 cm/s). After the samples passed through the GC, they then entered the quadrupole mass spectrometer where the ion fragments' intensities with respect to time were recorded. The mass spectrometer