THE CHEMISTRY AND STRUCTURE OF TORREFIED BIOMASS

by

GERALD CHARLES ATKINSON LINDO

(Under the Direction of James Kastner and Sudhagar Mani)

ABSTRACT

Torrefaction has been identified as a potential means of enhancing energy production from biomass by improving feedstock handling logistics. Using thermogravimetric analysis, torrefaction of pine wood (*Pinus radiata*) was shown to follow a two step kinetic model. Based on the HPLC analysis of torrefaction products, it was proposed that this two-step model represents rapid hemicellulose loss followed by slower degradation of cellulose. Thermogravimetric analysis showed that torrefaction raised the activation energy of wood with respect to gasification by up to 100%, but longer treatment was shown to lower the activation energy to within 20% of the original. Based on NMR analysis, it is proposed that the apparent reactivity changes were due to disruption of cellulose crystallinity.

INDEX WORDS: bio-energy, torrefaction, *Pinus radiata*, thermogravimetric analysis, mass loss kinetics, wood chemistry
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DEDICATION

To my grandfather.
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Many thanks to my family. You helped me keep it all together through trial after trial and refused to let me lose.

Many thanks to Drs. Kastner and Mani for their extraordinary patience.

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CHAPTER 1

INTRODUCTION

“Even if char formation during wood pyrolysis... is well documented, their formation during heat treatment by mild pyrolysis has not been yet clearly demonstrated... Such carbonaceous materials could be at the origin of some of the new properties of the material.” – G.N. Inari.

The US Energy Information Administration projects that world energy consumption will increase from 472 quadrillion Btu in 2006 to 552 quadrillion Btu in 2015 and 678 quadrillion BTU in 2030 — a total increase of 44 percent over the projection period. The prospect of the resultant unstable, increasing crude oil prices and the need to curtail the environmental impact of fossil fuel usage has led to increased interest in alternatives to fossil fuels as a means of diversifying energy sources and lowering emissions. (DOE/EIA, 2009)

Energy from biomass – carbonaceous substances derived from living matter – is one of many potential sources of fuel to meet current and future energy demands. Biomass is abundant and renewable, especially in countries with a strong agricultural base (DOE/GO, 2007). Plant-derived biomass energy feedstocks have the prospect of having zero or negative net carbon dioxide emissions due to the uptake of carbon dioxide during photosynthesis. Biomass energy can also open new markets for agriculture and forestry products, potentially boosting the economies of rural areas (Demirbas, 2009). Biomass can be used to produce thermal and electrical energy, but is also unique among alternatives to fossil fuels in the potential to supply carbon-based liquid transportation fuels (NSF 2008; Sadaka and Negi, 2009).
Biomass energy feedstocks are relatively low in thermal energy content and bulk density than fossil fuels such as coal or petroleum, as outlined in Table 1. The transportation cost of a given unit of raw biomass energy is more expensive than fossil energy, since that given unit of energy has greater mass and volume. (Bridgeman 2008, NSF 2008). Technologies that densify biomass feedstocks and improve heating values would reduce these transportation costs. Such methods are necessary if biomass-derived energy is to be cost-competitive. The development of such technologies and methods is a growing challenge to industrial, chemical and agricultural engineers (NSF 2008).

Torrefaction is a process of thermally treating biomass at low temperatures (200-300 C) under a non-reactive gaseous environment. The process results in a large fraction of roasted solid biomass, called torrefied biomass/bio-coal. The evolving volatile fractions contain both condensable and non-condensable gases (Prins et al. 2006a, b; Bridgeman, 2008; Sadaka and Negi, 2009). It has been demonstrated that torrefaction generates a biomass that is more energy dense, has a 10-20 % higher heating value, has a higher bulk density, and lowers the moisture content of the biomass (Bridgeman, 2008). Torrefaction also improves the grindability, stability and hydrophobicity of woody material, which makes other densification options such as pelletization easier (Prins et al. 2006A; Bridgeman, 2008; Sadaka and Negi, 2009). Torrefaction may thus be a worthwhile process to integrate into a biomass energy supply chain.

In addition to the impact on the energy density of biomass, there is emerging evidence that torrefaction also affects the downstream processes by which biomass feedstocks are converted to energy. It has been demonstrated in the literature and preliminary investigations that torrefied wood is less reactive to gasification than untreated wood (Couhert, 2009). In addition, data suggest that torrefaction does not impair the reactivity of biomass during combustion. A
study of the torrefaction of willow wood has demonstrated that torrefaction results in a combustion process that is more exothermic, with shorter ignition times and longer combustion times (Bridgeman, 2008). The impact of torrefaction on biological conversion of biomass via fermentation processes is not well studied, though it is an area of research interest for the production of fuel alcohol from depolymerized sugars (NSF 2008).

For torrefaction to become a viable technology to improve biomass energy supply chains, further studies on the effects of torrefaction on the chemical and structural characteristics of biomass are necessary, with the aim of identifying and explaining impacts on biomass conversion into usable energy. Investigations on the chemical effects of thermal energy transfer on lignocellulosic material are not new, but most studies have provided inadequate information about the events that occur during torrefaction. Previous studies have only generated mass-loss models of torrefaction with crude treatments of reaction mechanisms (Branca et al, 2005; Di Blasi, 2008). A mechanistic understanding of torrefaction chemistry is necessary if downstream conversion effects are to be understood.

Optimization of torrefaction must involve a balancing of various logistical and conversion-related factors. To understand, employ and optimize torrefaction technology in a method that makes it valuable for industrial-scale production of energy from biomass, a better understanding of the chemical and structural changes that occur in lignocellulosic material during the process, and how these qualities are affected by process conditions are required. These process variables are primarily the temperature of torrefaction and the residence time of the material during the process. The overall motivation of this study was to elucidate in detail the structural and chemical events that occur during torrefaction and to investigate the impact of torrefaction pretreatment on biomass downstream conversion. The results of this study will allow
for a fuller understanding of the ways torrefaction affects the key qualities of biomass feedstock and the conversion of these feedstocks. This will enable a better assessment and optimization of the technology. The ultimate aim is to reduce the cost of bioenergy to the consumer. Using pine wood as a feedstock (an especially abundant bio-energy feedstock in areas of the American Southeast) concentrations of hemicellulose and cellulose monomers after torrefaction were assayed as a function of torrefaction conditions (time and temperature). Extractable solid, gaseous and condensable products were monitored for major identifiable compounds. Additionally, structural investigations of and crystallinity changes within the solid product were conducted. From these findings a mechanism of reaction was proposed, and used to explain and model physical and chemical properties of torrefied wood as functions of process conditions. To further examine the effect of torrefaction on a downstream conversion process, torrefied biomass was gasified using a bench scale apparatus.
CHAPTER 2
LITERATURE REVIEW

2.1 Characteristics of lignocellulosic biomass

There are several types of biomass, including agricultural residues, herbaceous crops, and woody tree species. Agricultural residues and herbaceous crops include grasses, straws, legumes, corn, sorghum, and many other species. Woody biomass includes both deciduous (hardwood) and coniferous (softwood) trees. Wentzl (1970) provides a comprehensive discussion of woody biomass structure and composition. Among deciduous wood species are ash, aspen, beech, birch, elm, poplar and many other trees. Coniferous species include cypress, fir, hemlock, larch, pine, redwood, spruce, tamarack, eucalyptus, evergreen, and others. Woody and herbaceous types of biomass are composed primarily of carbohydrates and lignin. Though wood is generally considered to be only lignocellulosic material, it also contains other so-called extraneous materials (NREL, 1992).

Extraneous materials are classified as extractives or non-extractives based on their solubility in water and organic solvents (Fan et al. 1982). Extractive components in woody biomass include mainly terpenes, (isoprene alcohols and ketones), resins (fats, fatty acids, alcohols, resin acids, and phytosterols), and phenols (primarily tannins), and are generally more volatile than the carbohydrate and lignin fractions. Non-extractives are mainly inorganic components such as alkali earth carbonates and oxalates, silica crystals, as well as small amounts of non-cell-wall materials like starches, pectin, and proteins. Inorganic non-extractives, often referred to ash, have melting points higher than the temperature range over which wood
combusts. The type and amount of extraneous components vary widely among biomass species (NREL, 1992).

The carbohydrate portion of biomass is made up of holocellulose, composed of the high molecular weight polysaccharides cellulose and hemicellulose. Cellulose is the main component of wood, representing about 50% of the dry weight of wood. Cellulose is a linear polymer of anhydro-D-glucose units connected by 4,3-glucosidic bonds. Native cellulose exists as a fibrous crystal with the so-called cellulose-I structure, though other crystalline forms may be formed by physical and chemical processing (Chang et al. 1981, NREL, 1992).

Cellulose crystals (cellulose-I) are organized into compacted crystalline microfibers measuring 35-40 Angstroms in width and about 500 Å in length, with a typical crystal consisting of 1000 polymer units. Cellulose crystallinity is believed to be one of the primary reasons for the relative recalcitrance of the molecule and the resistance of materials such as wood and paper to reaction.

Hemicelluloses are shorter chain, amorphous polysaccharides of cellulans and polyuronides. Cellulans are polymers made up of six carbon sugars (mannose, galactose, and glucose) and five carbon sugars (xylose and arabinose). Polyuronides are similar to cellulans, but contain significant quantities of hexuronic acids as well as some methoxyl, acetyl, and free carboxylic groups. Hardwoods are 23%-35% hemicellulose, composed of 20%-30% xylan and 3%-5% glucomannan; xylan represents 80%-91% of total hardwood hemicellulose. Softwoods are 24%-36% hemicellulose, composed of 8%-14% xylan and 16%-22% glucomannan; xylan represents only 27%-47% of total softwood hemicellulose. The xylan in softwoods is not acetylated and contains arabinose side groups. Softwood glucomannan is acetylated and contains galactose side groups (Chum et al. 1985).
Lignin is composed of polymerized phenylpropanoic acids in a complex three-dimensional structure that generally lacks discernible order. Polymerization occurs by a free radical mechanism resulting in a random structure. Monomers are held together by ether and carbon-carbon bonds (Fan et al. 1982). The amount of lignin in coniferous softwoods (25%-35%) is greater than in deciduous hardwoods (18%-25%), straws (10%-20%), and agricultural residues (10%-15%) (Fan et al. 1982; Hindan et al. 1990 NREL, 1992).

Hemicellulose is considered to act as the glue between lignin and cellulose components. Hence, hemicellulose and lignin are envisioned to form an effective sheath around cellulose fibers, which adds structural strength to the wood matrix. It is not clear, however, if covalent bonds exist between hemicellulose and lignin (NREL, 1992).
Figure 2.1: Cell wall diagram. a | Cell wall containing cellulose microfibrils, hemicellulose, pectin, lignin and soluble proteins. b | Cellulose synthase enzymes are in the form of rosette complexes, which float in the plasma membrane. c | Lignification occurs in the S1, S2 and S3. Taken from Sticklen (2009).
2.2 The torrefaction process

Torrefaction is a thermal pre-treatment of biomass performed at atmospheric pressure in an inert, oxidant-free environment over relatively long residence times. Temperatures between 200 and 300°C are used, which produces a solid uniform product with very low moisture content and a calorific value that is relatively high compared to untreated material (Prins 2006A). Several studies have shown that torrefaction increases the energy density, the hydrophobic nature, and grindability properties of biomass (Uslu et al., 2008; Bridgeman 2008; Prins 2006A). Torrefied biomass typically retains 70% of its pre-treatment weight and 90% of the original energy content (Bridgeman (2008) refers to values first reported by Ranu Pentananunt, A.N.M. Mizanur Rahman and S.C. Bhattacharya in 1990, and Prins (2006A) obtains similar values when torrefying beech wood at 250°C for 30 minutes).

The torrefaction process generally involves the initial heating and drying of the biomass, followed by a holding period at a target torrefaction temperature. It is during the holding period, at temperatures above 200°C, that the torrefaction reaction occurs and where mass loss takes place. The process may be considered terminated after the product is cooled below 200°C. (Uslu et al., 2008). Studies by Prins, (2006A, B), Uslu (2008), Bridgeman (2008) and Couhert (2009) all used holding time and temperature as the primary variables in defining different torrefaction treatments, though there is wide variation in the holding times used from study to study (ranging from minutes to tens of hours).

2.3 The effect of torrefaction on wood material properties

It was reported separately by Uslu et al (2008) and Prins (2006A) that during torrefaction the calorific value of the material increased. The net calorific value of torrefied biomass was in
the range of 18–23 MJ/kg LHV or 20–24 MJ/kg HHV. They propose that this is because biomass loses relatively more oxygen and hydrogen compared to carbon. Subsequently, the moisture uptake of torrefied biomass was limited due to the dehydration reactions during the torrefaction reaction. They suggested that the destruction of OH groups in the biomass by dehydration reactions caused the loss of capacity to form hydrogen bonds with water. In addition, non-polar unsaturated structures were formed which makes the torrefied biomass hydrophobic. Uslu states: “The torrefied biomass also became more porous with a volumetric density of 180–300 kg/m³, depending on the initial biomass density and torrefaction conditions.” It is more fragile as it loses its mechanical strength, making it easier to grind or pulverize. These latter mechanical property results are confirmed by Bridgeman (2008).

By reducing recalcitrance to mechanical treatment and increasing energy content of biomass, torrefaction improves densification. Uslu (2008) reports that the heating value of torrefied biomass pellets has been measured at 20-22 MJ/kg, whereas the energy density of conventional pellets reaches up to 17 MJ/kg. Additionally, the bulk density of torrefied pellets was found to be 15% higher than conventional pellets. (Uslu et al 2008). The pressure required for densification could be reduced by a factor of 2 at 225°C, and the overall energy consumption of densification could be reduced by a factor of 2 compared to biomass pelletization. Torrefaction reduced power consumption required for size reduction by up to 70–90% compared to conventional biomass pelletization. Torrefaction treatments also allows different types of type of size reduction machinery to be deployed in pelleting processes, such as cutting mills and jaw crushers instead of hammer mills. These findings strongly suggest that integration torrefaction into a biomass supply chain would have a positive impact on the logistics of biomass transportation.
2.4 Studies on the effect of torrefaction on thermal conversion of biomass into energy

The effect of torrefaction on thermochemical conversion is less studied than the effect on factors affecting logistics. Bridgeman (2008) in his study of the combustion characteristics of torrefied willow, reed canary grass and wheat straw found that the volatile component of biomass that evolved during combustion both were reduced and altered for torrefied biomass. Bridgeman found that torrefaction produced a more thermally stable product with greater heats of reaction during combustion. At higher temperatures of torrefaction mass yields were lower, but the energy yield of the torrefied product under combustion was higher by up to 20%. The torrefied fuel can contain up to 96% of the original energy content on a mass basis (depending on the intensity of the torrefaction process). The combustion of both the char and volatile portions of torrefied biomass were more exothermic compared to the raw fuels. For willow wood, Bridgeman found torrefaction led to a product that was quicker to ignite and longer burning.

Some progress has also been made on clarifying the effect of torrefaction on gasification. Couhert (2009) submitted beech wood to “light” torrefaction and “severe” torrefaction, as defined by temperature (240°C and 260°C). Both untreated wood and torrefied wood were steam gasified in an entrained flow reactor at 1400°C over very short residence times. Analysis of the syngas showed that in both cases significant increases in hydrogen and carbon monoxide concentrations (7% and 20% respectively), were observed with the torrefied wood versus untreated wood, though no significant differences were seen between the light and severe treatments.
2.5 The chemistry and kinetics of the thermal treatment of wood under inert atmospheres

An understanding of the kinetics of torrefaction allows for the development of computational tools for the design and optimization of reactors and processes. Inasmuch as torrefaction is a heat treatment of wood under non-oxidizing conditions, it is useful to approach the modeling of torrefaction as one would approach the modeling of pyrolysis of wood.

By necessity, the models heretofore developed for the kinetics of wood undergoing thermal treatments in non-oxidizing environments are highly generalized. As has been previously discussed, lignocellulosic material is highly complex on a molecular and microscopic scale, with many species of varying or undetermined structure with complex interactions. Models developed describing the processes are often highly simplified.

For pyrolysis reactions with high heating rates and relatively short residence times, one-step models have been developed. Shafizadeh and Chin (1977) proposed a model that may be generalized as:

\[
\text{WOOD} \xrightarrow{k_c} \text{CHAR} \quad \text{TARS} \quad \text{GAS} \quad k = k_c + k_L + k_G
\]

*Figure 2.2: Sahfizadeh’s pyrolysis model*

In this model, the decomposition of wood is assumed to occur as a one-step irreversible process with each product stream (solids, condensible liquids or tars, and non-condensible gases) has an associated kinetic parameter. While such a gross lumping of reactions and wood subcomponents is dubious in terms of strict analytical chemistry, the rapid reaction rates that occur with sufficiently high temperatures limits the overall variability in mechanism or
interactions that can occur within a given material. The result is a kinetic model that, while crude, is effective at predicting the overall yield of the three major pyrolysis product streams (Di Blasi, 2008).

Models such as that proposed by Shafizadeh and Chin do not give information regarding the chemical nature of the product streams. The stipulations of high heating rate and temperature limits the kinetic parameters derived from such models to the particular reactor type and configuration from which the model was derived. Furthermore, variations in the starting material greatly influence the product yields. The result is that there exist a wide variety of kinetic models with limited applications (Di Blasi 2008).

It is of particular note that these one step-models are designed for high temperatures, high heating rates and low residence times, conditions which are not encountered during torrefaction. Data further suggests that the mechanism of reactions in the torrefaction range cannot be satisfactorily explained by simple one-step models.

Multi-step consecutive mechanisms have been proposed have as improvements upon the one step models described previously. Prins (2006b) proposed a highly-cited model of this kind that serves for the basis of much work, including the work proposed herein.

The core component of any multistep mechanism is the concept that more than one reaction occurs to the material undergoing pyrolysis. Such mechanisms may be generalized as sequential irreversible reactions, usually first order:

\[
A \xrightarrow{k_{vo}} V_1 \quad B \xrightarrow{k_{vo}} V_2 \quad D \xrightarrow{k_{vo}} V_3
\]

\[
k_1 = k_{vo} + k_a \quad k_3 = k_{vo} + k_c \quad k_5 = k_{vo} + k_c
\]

*Figure 2.3: A generalized multistep mechanism. A represents the original fuel material and C the product, while B and D are intermediates. Di Blasi, 2008*
The nature of the intermediates formed in such a reaction is of some dispute. Prins (2006b) proposes a depolymerized, “activated” form of the material with enhanced reactivity which was based upon a model proposed by Shafizadeh and others as an improvement upon his previous work (Antal and Varhegyi, 1995). Still more complicated models exist: for example, the Broido-Shafizadeh model may be generalized as:

![Figure 2.4: The Broido-Shafizadeh model for wood pyrolysis (Antal and Varhegyi, 1995)](image)

The models proposed by Prins, Shafizadeh and Broido describe the mass loss of wood under pyrolysis condition very well, even under low temperature and low heating rate conditions (Prins, 2006B; Antal and Varhegyi, 1995). However, these models all have the major drawback of being purely conceptual. The experiments upon which these measurements are based were done by means of classical thermogravimetry. The majority of multi-component mechanisms consist of devolatization reactions, which can be applied to predict only the rate of weight loss, and only then provided that the total amount of matter to be released in the gas/vapor phase is already known (whether assigned or measured). Thus, these methods postulate the existence of intermediates that are never directly measured (Di Blasi, 2006. Antal and Varhegyi (1995) noted that they were “pleasantly surprised” that a form of the Broido-Shafizadeh model worked well for the pyrolysis of cellulose, despite a lack of any corroboration of the mechanism. The mechanism is often inferred from the shape of thermogravimetric mass loss curves; for instance,
Bridgeman (2008), Prins (2006b) and Branca (2005) all noted distinct changes in the mode of the graphs of the isothermal decomposition of reed canary grass, willow and beech wood respectively. Prins (2006b) goes on to postulate that this is due to the concurrence of two reactions; a fast initial reaction that produces an active intermediate that then proceeds to slowly decompose. This is offered, again, without chemical corroboration.

Given the lack of model validation in the literature referenced models, a vital component of this research proposal is the chemical analysis of torrefied material at various torrefaction holding times, allowing for the validation of torrefaction models.

A third subset of models of cellulose pyrolysis may further be defined: those models that assume multiple concurrent reactions. The strength of these models is that they attempt to make the chemistry behind heat treatment processes more explicit by considering the three major wood components each as reactive species decomposing concurrently. Branca et al (2005) and Di Blasi (2008), in one of her more widely-cited review articles (referenced by many authors cited here), details the current knowledge of wood chemistry as it is relevant to thermal conversion. There are many chemicals and many reactions that are involved in the thermal reactions of wood in inert environments, but the reactions may be categorized as belonging to three regimes: reactions of hemicellulose, cellulose and lignin. These occur primarily within the approximate ranges of 200-300°C, 300-350°C and 250-500°C, respectively, though it should be added that on a long enough time scale all the major wood components react at low temperatures, as has been demonstrated by some of our own work, as well as by Prins (2006B), Bridgeman (2008), Branca (2005), Antal and Varhegyi (1995), and others. The overall mass loss as determined by thermogravimetry is thus considered to be the sum of the mass loss due to these three reactions.
Several studies of lignocellulosic behavior under heat have been conducted at temperatures that would impact all three of these substances (above 500°C; reviewed by Babu, 2008). Torrefaction, by contrast, is generally conducted at lower temperatures (200-300°C) that would impact hemicellulose and to a lesser extent lignin content, but not cellulose. This again underlines the limitations of some of the previous models that lump wood components into a single reactive species. Furthermore, investigations of individual model compounds have been shown not to be relevant to real-world biomass conversion kinetics, possibly due to interaction effects between compounds (Fushimi, 2009), the presence of small amounts of catalytically-active inorganic salts in biomass, and alterations of these model compounds from their natural state during extraction processes that enhance reactivity (Nowakowski, 2007). The absence of these structural and interaction effects confounds the use of model compounds in the development of reaction models for whole wood. (For a deeper understanding of the chemistry involved and the subsequent validation of any models, whole-wood chemical studies are necessary.

Inari et al (2007) investigated the chemical changes involved in a “mild pyrolysis” – a thermal treatment at 240°C for several hours – of beech heartwood sawdust using x-ray photoelectron spectroscopy and carbon-13 NMR with magic-angle spinning. Their study showed that the qualitative chemical changes in wood, thus treated, were due to the formation of char, and to a lesser extent lignin cross-linking. Though the temperature of treatment (240°C) was not considered to be within the range of temperatures under which cellulose depolymerization is thought to occur(300-350°C), the observed changes in NMR spectra could not be explained solely as degradation of hemicelluloses to volatile by-products. They note that “Even if char formation during wood pyrolysis at higher temperatures from 300 to 450°C is well
documented, their formation during heat treatment by mild pyrolysis has not been yet clearly demonstrated... Such carbonaceous materials could be at the origin of some of the new properties of the material.”

2.6 Review Summary

Wood is a highly complex material. Torrefaction of wood has been shown to improve its handling characteristics, energy density and combustion characteristics, making torrefaction a useful technology from a logistical standpoint. However, the chemistry of the torrefaction process is not well studied. The kinetics of the process as well as the nature of the chemical changes is not clearly defined, due to a number of confounding factors: the inability to track individual chemical species separately via thermogravimetry; the altered behavior of model compounds when isolated; and the possibility of changes in reaction mechanism over different temperature ranges. There are furthermore some conflicting and findings with regard to the effect of torrefaction on thermochemical conversion, since studies find the process improves the reactivity of wood (Bridgeman, 2008), and decreases reactivity in other cases (Couhert 2009).

A more detailed study of the chemistry of torrefaction would be useful in the improvement of kinetic models, thereby enabling the eventual optimization of the technology. Such a study will also allow us to validate existing torrefaction models that, while useful in describing mass loss, are “black boxes.”
Chapter 3

Aims and Objectives

It is known that torrefaction has a positive impact on biomass logistics, but the impact on conversion of biomass to energy is not fully understood.

It is proposed that the chemical and structural changes that occur during the torrefaction of pine chips be characterized, and the kinetics of the gasification of torrefied pine chips be also quantified and characterized. This was to be done for the purposes of understanding observed effects of torrefaction on gasification and other thermochemical conversion processes. This knowledge will allow for the optimization of torrefaction, specifically the identification of a set of optimal conditions and parameters that would positively affect gasification.

The aims of this study were:

1. To propose a mechanism for torrefaction based on experimental data
   a. To propose a model for torrefaction mass loss.
   b. To propose models for chemical and physical changes observed during torrefaction, based on temperature and torrefaction time.

2. To identify and quantify the chemical and structural changes in wood as a result of torrefaction.
   a. To quantify the changes in carbohydrate and lignin concentrations within pine wood resulting from torrefaction as functions of temperature and holding time.
   b. To identify and quantify condensable emissions and non-condensable emissions produced during torrefaction as functions of time and torrefaction temperature.
   c. To identify and quantify changes in crystallinity and other microstructural
qualities of pine wood that result from torrefaction.

3. To quantify the effect of torrefaction on gasification in oxygen.
   a. To model mass loss of torrefied pine wood during gasification and to compare with the gasification of untreated wood.
CHAPTER 4
MATERIALS AND METHODS

4.1 Materials

Clean white pine chips (*Pinus radiata*) were used for all studies. The material was found to have the following composition: 15.19% hemicellulose, 48.57% cellulose, 26.16% lignin and 10.08% extractives, on an ash-free dry basis. Ash was found to be 0.27% of the mass on a dry basis. Analysis was conducted externally at the Feed and Environment Water Lab (Athens GA), using the acid detergent fiber method.

4.2 Torrefaction Mass Loss Kinetics

Mass loss kinetics experiment of ground pine chip sample (approximately 15 mg, 0.20 mesh) was analyzed in a thermogravimetric analyzer (SDTA851e, Mettler Toledo, Columbus OH) under torrefaction condition. The temperature was raised from room temperature to 105 °C at 10°C/minute, and then held at that temperature to dry the sample for 10 min. The temperature was then increased to a target torrefaction temperature (200, 215, 230 245 260 275, or 300°C) at the same heating rate and kept for 3 hr. The real time mass loss data for each condition was recorded. Experiments were done in triplicate.

Mass loss data over time was used to describe the torrefaction kinetics using various models. Empirical reaction kinetics models found in the literature (See Appendix B) were fitted to the experimental data using a simplex search algorithm written in MATLAB code (see Appendix A). The goodness of fit was evaluated by minimization of Sum of Square of Errors (SSE) and high Co-efficient of determination (R^2) as criteria for selecting the best fit model.
\[ SSE = \sum (m - \hat{m})^2 \]  
\[ R^2 = 1 - \frac{SSE}{\sum (m - \bar{m})^2} \]  

In the equations above, \( m \), \( \hat{m} \) and \( \bar{m} \) represent the measured mass, modeled mass and mean mass respectively. \( SSE \) and \( R^2 \) for each model and experiment were minimized using a search algorithm. The requirement of simplicity while also requiring low \( SSE \) and a high \( R^2 \) lead to the fitting of increasingly complex model function to the data lead to an increase in the complexity of the model function as different models were tested. The final model selected was the least complex model that described the data. Appendix B contains the results of unsuccessfully fitted models.

A four factor mechanistic reaction kinetics model was developed as no single tested model described the torrefaction reaction kinetics. The model used for torrefaction kinetics is similar to that originally proposed by Di Blasi (2006) after a literature search and her own experiments on xylan. Prins (2008b) adopted the model and fit it to the torrefaction of willow wood. The model proposes that wood breaks down in the following manner,

\[
\text{Wood} \rightarrow \text{intermediate \ (k_1)} \\
\text{Wood} \rightarrow \text{volatiles (I) \ (k_{v1})} \\
\text{Intermediate} \rightarrow \text{char \ (k_2)} \\
\text{Intermediate} \rightarrow \text{volatiles (II) \ (k_{v2})}
\]  

Each of the reactions is assumed first order and irreversible. The kinetic parameters for equations 5.1-4 will be referred to as \( k_1, k_{v1}, k_2 \) and \( k_{v2} \) respectively.

This is a lumped model that does not take into account the individual fractions (lignin, cellulose and hemicellulose). However, this gives the model the advantage of not being overly parameterized. Given that our experiments only allow us to measure mass, rather than individual
species, a simple model such as this one is desirable. Simpler models (e.g., single step and two step models; see appendix B) did not satisfactorily describe the mass loss behavior, using the minimization of the model sum of squared error as the criterion.

The following is included by way of illustration. Perhaps the simplest model one can suggest for any reaction is a single step irreversible reaction:

$$A \rightarrow B \quad (4.7)$$

Presuming that A is the reactive solid wood and B is a volatile material, and that the reaction has a rate constant k, then the measured mass at any given time ($M_t$), define $M_0$ may be written as:

$$M_t = M_0 e^{-kt} \quad (4.8)$$

In the case where mass is normalized to a starting value of 1, the equation simplifies to:

Normalized mass = $e^{-kt} \quad (4.9)$

It is deducible a priori that this model is likely to fail. As time approaches infinity in this model, the value for $M_t$ approaches zero, which is not valid, since with experimental data indicates residual mass at the end of each run. Using the code `extractnfit.m` and calling the fitting function `onefacfunc.m`, it was found that the model performs poorly. Coefficients of determination ranged from -0.2 to 0.6.

Similarly poor results were seen with adjusted models with one or two factors. It is apparent that the model proposed below is the simplest model that performs adequately.

The key assumptions in model development are that there are initially zero concentrations of char and intermediate, and a normalized unit concentration of wood. Using the TGA, one cannot measure the masses of volatiles evolved, nor differentiate between wood and intermediates, but one can monitor the overall mass, which would be a summation of the masses
of wood (colored red below), intermediate (green) and char (blue). Since mass and not molar quantities are measured, a relationship between the molar masses of each of the solid components must be estimated. These are F1 (intermediate/wood) and F2 (char/intermediate), which were estimated graphically using a procedure similar to that of Repellin et al (2010, in press). F1 and F2 were estimated to be 0.7 and 0.35 respectively. This estimation was based on the estimated final mass and the estimated intermediate mass.

\[
F_2 = \frac{\text{final mass}}{\text{initial mass}} \bigg|_{\text{maximum } T} 
\]

(4.10)

\[
F_1 = \frac{F_2}{2}
\]

(4.11)

F2 is defined for long torrefactions at the maximum temperature, under the assumption that these are the most complete torrefaction conditions.

Using these assumptions, the following expression for mass M as a function of time was developed – again the derivation of this equation must be shown:

\[
\int_0^t M'(t) = e^{-t(k_1-kv_1)} - F_1 \frac{k_1}{k_2 - k_1 + kv_1 + kv_2} (e^{-t(k_2+kv_2)} + e^{-t(k_1+kv_1)}) \\
- \frac{k_1 \times k_2}{(k_2 + kv_2)(k_1 - kv_1)(k_2 - k_1 + kv_1 + kv_2)} (k_2 - k_1 - kv_1 - kv_2) \\
- k_1 \times e^{-t(k_2-kv_2)} + kv_1 \times e^{-t(k_2-kv_2)} + k_2 \times e^{-t(k_1-kv_1)} + kv_2 \\
\times e^{-t(k_1-kv_1)}
\]

(4.12)

4.3 Batch torrefaction experiments

Batch torrefaction experiments were conducted using a batch reactor (Figure 4.1) to quantify the yield and composition of solid, liquid and gas fractions. A steel reactor vessel
(approximately a 1 ft³ with thermocouple ports for temperature monitoring) was partially filled with whole pine chips that had been previously dried in an oven for 24 hours at 105°C. This reactor was placed in a muffle furnace and nitrogen gas was flowed through it onto the condenser apparatus. The reactor was connected using a flexible 7/8” metal hose to a double-reflux primary condenser apparatus, which consisted of two Allihn reflux condensers (borosilicate glass, 24/40 joints, 240mm, Fisher Scientific, PA) and a Graham-type condenser (Pyrex, 24/40, 500mm, Fisher Scientific, PA) in series with two three-port 250mL round-bottomed flasks (Pyrex, 24/40 joints, Fisher Scientific, PA). The gas line passed from the condensers through a 150mm ball flow meter and on to a set of secondary metal condensers consisting of four 350x100mm steel tubes connected by ½” Swagelok pipes in an ice bath, then to an exhaust port. All condensers were cooled in ice baths. Each torrefaction experiment was conducted at target holding temperatures of 225, 250, and 275 °C. Holding times for each temperature were 1, 2 and 3 hours, yielding a total of 9 treatments.

Solid samples were collected at the end of each torrefaction experiment. Liquid and gas samples were taken for the 3 hour treatments only, since it is assumed that the results for the 1 and 2 hour treatments would be truncated versions of the results for the 3 hour treatments. Liquid samples were taken by emptying the primary condenser apparatus at intervals over the course of the torrefaction treatments. Gas samples were taken simultaneously from the exhaust port and also retained for analysis. Both liquid and gas samples were taken and once the reactor temperature passed 150°C and every 10-15 minutes thereafter, and then in longer 20-45 minute intervals once the target temperature had been reached. The liquid samples were placed in weighed vials and sample mass at each sample point was recorded. Gas flow measurements were taken concurrently with the gas sampling.
The solids samples were stored in airtight bags at 4°C, and were used for further analysis using NMR and HPLC (Sections 4.4, 4.5). The liquids were stored at 4°C in sealed vials and analyzed using GC-MS and GC-FID (4.6) within a week of acquisition. Gases were collected in Tedlar sample bag and analyzed immediately after collection using GC-TCD (4.7).

Figure 4.1: Schematic of batch reactor used for bench-scale torrefaction

4.4 Assays of composition of torrefied samples using High Pressure Liquid Chromatography (HPLC)

HPLC analysis was conducted on the solid torrefied material samples torrefied under 9 different treatments (each of 225, 250 and 275°C treated for 1, 2 or 3 hours) to determine the composition of the treated material. The National Renewable Energy Laboratory’s standard sugar/lignin assay procedure was used to analyze the composition of the torrefied biomass (NREL/TP-510-42618). Weighed samples of ground untreated and torrefied wood (~60 mg, dried for 12 hours at 105°C) were digested with 0.45 mL of 72% sulfuric acid for 1 hour at 30
˚C. Samples were then diluted to 4% acid with 16.8 mL of deionized water. A secondary hydrolysis was carried out for 1 hour at 121°C in an autoclave. The hydrolysate was filtered and the undigested residue was weighed.

Final concentrations of sugars in each sample were measured using an HPLC (LC-20AT using a Coregel 64H column, Shimazdu, Colombia MD) with a liquid flow rate of 0.600 mL/min at 60°C and a refractive index detector. The chromatograms were quantified using standard curves for glucose, xylose, arabinose, lactate, formate, acetate and furfural. A sugar recovery sample containing known quantities of acid-treated sugars were also analyzed, as per the published method.

The concentration of each analyzed substance was calculated as a percentage of the initial sample mass. Each sample was analyzed in triplicate. Treatment groups were tested via pair-wise comparison based on a 1-way ANOVA and Tukey’s Honestly Significant Difference method, using a 0.05 significance level. This method was chosen to minimize the type-I error rate.

4.5 NMR assays of torrefied wood samples

Nuclear magnetic resonance experiments were conducted to observe qualitative chemical and structural changes in the torrefied solids. Carbon 13 (13C – CP/MAS) NMR of samples for the three treatment temperatures and the 1 and 3 hour treatment times was conducted in consultation with Dr. Johannes Liesen at the Georgia Institute of Technology in Atlanta, GA. A Bruker Avance 300 spectrometer, operating at a carbon resonance frequency of 75.5 MHz at a temperature of 20°C was used. The dried samples were ground for 2 minutes at 10000 rpm in a knife mill, and approximately 100mg were packed into 6x10mm ZrO₂ rotors. The samples were spun at 6.5 kHz. The cross-polarization contact time was 1 ms; the delay time was 4s; and the
90° pulse for proton was 5 μs. For each run, 2400 readings were taken. The method was adapted from Sievers et al (2009) and Park et al (2009).

The resultant NMR spectra were analyzed using peak assignments described by Sievers et al (2009), who summarizes previously obtained literature values. Crystallinity estimates were made by comparing the ratio of integrals of peaks assigned to crystalline and amorphous cellulose.

4.6 GC-FID assays of condensable products

The liquid samples were analyzed to identify and quantify major components. Condensate samples were analyzed using a flame ionization detector after separation via gas chromatography. The GC-FID was an Agilent 5890 with an HP-5 column with argon as a carrier gas. The temperature on the column was 50°C and was ramped to 200°C at 6 C min⁻¹. The injection port temperature was 200°C. 1µL samples were used. The injection was splitless. Peaks for analysis were previously identified on an Agilent GC-MS with an identical method and column. Acetic acid and furfural were selected as compound of interest. Standard curves were developed using acetic acid and furfural in acetone (see Appendix D).

4.7 GC-TCD assays of non-condensable products

Gaseous samples of the torrefaction exhaust gas were analyzed to determine composition. A GC-TCD was used (3000A Micro GC Agilent, Santa Clara CA), with four columns (molecular sieve, Plot U, OV-1 and alumina) with argon and helium as carrier gas. Standardization was conducted using a standard gas mixture designed for the device purchased from Agilent and
built-in standard curves. Carbon monoxide and carbon dioxide concentrations in the gas samples were analyzed.

4.8 Thermogravimetric analysis of the gasification of torrefied wood samples

Gasification of torrefied samples was conducted at the bench scale to determine the effect of torrefaction on solid conversion. Samples of dried ground untreated pine weighing approximately 15 mg were placed in alumina crucibles and torrefied in the TGA (described previously) under nitrogen flowing at 20 mL min\(^{-1}\). During torrefaction, the samples were heated at 30 \(^{\circ}\)C min\(^{-1}\) from 25 \(^{\circ}\)C to the target temperature, held at that target temperature for a variable time, and then allowed to cool to ambient temperature. The sample weight and temperature were continuously recorded. This torrefaction procedure was conducted in triplicate in a factorial experimental design using three target temperatures (225, 250 and 275 \(^{\circ}\)C), and three holding times (1, 2 and 3 hours).

Following torrefaction, the samples were gasified by being heated in the TGA from 25 \(^{\circ}\)C to 700 \(^{\circ}\)C at 30 \(^{\circ}\)C min\(^{-1}\). The samples were heated under 5% oxygen in argon mixture (purchased from AirGas, Toccoa, GA). The gas flow rates were varied using mass flow controllers to deliver 25% of the stoichiometric oxygen requirement for complete carbon oxidation to carbon dioxide over the 22.5 minute reaction, based on the post-torrefaction mass of the sample. The carbon content assumed for these calculations was based on the sample weight and ultimate analysis of previously torrefied samples (using a CHNS-932, Leco. St. Joseph MI). During gasification the sample weight and temperature were continuously recorded.

Generally, the mass loss during unsteady-state heating may be defined as the function:

\[
\frac{d\alpha}{dt} = Ae^{-\frac{E}{RT}(f(\alpha))}
\]  

(4.13)
where $\alpha$, the extent of reaction, may be written as:

$$\alpha = \frac{x_{t=0} - x_{t}}{x_{t=0} - x_{final}}$$  \hspace{1cm} (4.14)

$X$ is the measured mass, $A$ is the frequency factor, $R$ is the universal gas constant, $E$ is the activation energy, $T$ is temperature, and $t$ is time. The function $f(\alpha)$ varies considerably with the nature of the reaction. Guo and Lua (2000) provide a variety of possible functions (see table 5.4 below).

*Table 4.1: Various functions describing temperature-driven mass loss. Adapted from Guo and Lua (2000).*

<table>
<thead>
<tr>
<th>No.</th>
<th>Model</th>
<th>$f(\alpha)$</th>
<th>$g(\alpha) = \int_0^\alpha d\alpha/f(\alpha)$</th>
<th>Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sigmoid rate equations</td>
<td>$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$</td>
<td>$[-\ln(1-\alpha)]^{1/2}$</td>
<td>A2</td>
</tr>
<tr>
<td>2</td>
<td>Avrami-Erofe’ev</td>
<td>$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$</td>
<td>$[-\ln(1-\alpha)]^{2/3}$</td>
<td>A3</td>
</tr>
<tr>
<td>3</td>
<td>Avrami-Erofe’ev</td>
<td>$4(1-\alpha)[-\ln(1-\alpha)]^{4/3}$</td>
<td>$[-\ln(1-\alpha)]^{4/3}$</td>
<td>A4</td>
</tr>
<tr>
<td>4</td>
<td>First order</td>
<td>$1-\alpha$</td>
<td>$-\ln(1-\alpha)$</td>
<td>F1</td>
</tr>
<tr>
<td>5</td>
<td>Contracting area</td>
<td>$2(1-\alpha)^{1/2}$</td>
<td>$1-(1-\alpha)^{1/2}$</td>
<td>R2</td>
</tr>
<tr>
<td>6</td>
<td>Contracting volume</td>
<td>$3(1-\alpha)^{2/3}$</td>
<td>$1-(1-\alpha)^{2/3}$</td>
<td>R3</td>
</tr>
<tr>
<td>7</td>
<td>One-dimensional</td>
<td>$1/(2\alpha)$</td>
<td>$\alpha^2$</td>
<td>D1</td>
</tr>
<tr>
<td>8</td>
<td>Two-dimensional</td>
<td>$[-\ln(1-\alpha)]^{-1}$</td>
<td>$(1-\alpha)-\ln(1-\alpha)+\alpha$</td>
<td>D2</td>
</tr>
<tr>
<td>9</td>
<td>Three-dimensional</td>
<td>$3/2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$</td>
<td>$[-\ln(1-\alpha)]^{1/3}$</td>
<td>D3</td>
</tr>
<tr>
<td>10</td>
<td>Ginstling-Brounshtein</td>
<td>$3/2[(1-\alpha)^{-1/2}-1]^{-1}$</td>
<td>$1-2\alpha/3(1-\alpha)^{2/3}$</td>
<td>D4</td>
</tr>
</tbody>
</table>

For non isothermal reactions, via the Coats-Redfern method, if $dT/dt$ a constant $\beta$ (30 °C min$^{-1}$ in these experiments), a modified Arrhenius plot may be generated based on the equation:

$$\ln \left(\frac{g(\alpha)}{T^2}\right) = \ln \left(\frac{AR}{\beta E}\right) - \frac{E}{RT}$$  \hspace{1cm} (4.15)

The function $g(\alpha)$ is the integral of $(1/f(\alpha))$. The slope of the plot of gives $-E/R$ and the intercept is $\ln(A*R/(\beta *E))$. 

29
The approach used in selecting the model was similar to the approach used for the torrefaction curve fitting (minimization of SSE and maximization of $R^2$). Initial fitting of all the functions in table 4.1 above resulted in the selection of a first order model to describe the mass loss.

The model was further improved by the recognition of a triple modality in all of the gasification mass loss curves. For every gasification experiment including the untreated control, each curve features a small initial mass loss below 200°C, attributed to water desorption; a rapid secondary mode loss phase during which most of the overall mass loss occurred; and a tertiary mode of slower mass loss during the final portion of the reaction.

Figure 4.2: A typical gasification mass loss curve, showing the three mass loss modes.
Accordingly, the data was trimmed such that the initial desorption phase was not considered, and the secondary and tertiary reaction modes were separated using an algorithm that divided the data at the point of maximization of the second derivative (See `eyeball.m` in Appendix A), Figure 4.3 below shows the results of a typical trimming operation.

![Figure 4.3: A typical gasification mass loss curve, after trimming. Blue represents data from reaction mode 2, while red represents reaction mode 3.](image)

A first order reaction mechanism was subsequently applied to the two main reaction modes, corresponding to the equation:

\[
\frac{d\alpha}{dt} = Ae^{-\frac{E}{R\theta}}(\ln(1 - \alpha))
\]  

(4.16)
Literature suggests that the two main reaction modes are due to the decomposition of different fractions of the biomass (Guo and Lua, (2000), Branca et al (2005) Di Blasi (2008)).
CHAPTER 5
RESULTS AND DISCUSSION

5.1 Torrefaction Mass Loss Kinetics

The 4-factor equation was fit to data for long torrefactions. In general, fit results were excellent, with coefficients of determination higher than 0.9. The fact that simpler one step models failed while the multistep model fit well leads to the conclusion that torrefaction is best modeled as a two stage devolatilization process.

The shape of the mass loss curves corroborate the conclusion which was reached via the curve-fitting procedure. The shapes of the mass loss curves, especially at higher temperatures, indicate a dual-mode reaction consisting of an initial exponential phase followed by a phase of mass loss with near-constant slope. This observation of two reaction stages is consistent with our model selection. Figures 5.2-5.4 give a closer view of some of the mass loss curves, illustrating their shape.
Figure 5.1: Curve fitting results for a torrefaction mass loss experiment conducted at 230°C
Figure 5.2: Curve fitting results for a torrefaction mass loss experiment conducted at 275°C
Figure 5.3: Fitting results for the proposed model on average mass loss results for torrefaction mass loss experiments. The red lines represent the fitted model for each temperature.

This suggests an initial quick reaction followed by a second, slower reaction. This in turn suggests that the transition of the wood to the intermediate form is relatively rapid, and that subsequent conversion from intermediate to char is slow. It is suggested by literature that this intermediate form may be described as partially depolymerized wood.

The kinetic constants determined by our fitting procedure were graphed on Arrhenius plots. The intercept and slope of the plots was used to estimate the activation energy and pre-exponential factors for each kinetic factor, assuming:

\[ k_x = A \cdot e^{-E/RT} \]  \hspace{1cm} (5.1)
Where $k_x$ is an arbitrary kinetic constant (min$^{-1}$), $A$ is the pre-exponential frequency factor (min$^{-1}$), $E$ is the activation energy (J/mol), $R$ is the universal gas constant (8.314 J mol$^{-1}$K$^{-1}$), and $T$ is the absolute temperature (K).

Figure 5.4: Arrhenius plot for the $k_1$ kinetic constant for the torrefaction of pine wood, determined from the model fitting procedure.

Figure 5.5: Arrhenius plot for the $k_{v1}$ kinetic constant for the torrefaction of pine wood, determined from the model fitting procedure.
Figure 5.6: Arrhenius plot for the $k_2$ kinetic constant for the torrefaction of pine wood, determined from the model fitting procedure.

Figure 5.7: Arrhenius plot for $k_{v2}$ kinetic constant for the torrefaction of pine wood, determined from the model fitting procedure.
Table 5.1: Activation energies and frequency factors for kinetic coefficients for torrefaction mass loss, determined from Arrhenius analysis

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Pre-Exponential Factor (A), min⁻¹</th>
<th>Activation Energy, J/mol</th>
<th>% Estimated Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>k₁</td>
<td>2858</td>
<td>675.4</td>
<td>8.4</td>
</tr>
<tr>
<td>kv₁</td>
<td>19.12</td>
<td>519.1</td>
<td>2.6</td>
</tr>
<tr>
<td>k₂</td>
<td>0.2268</td>
<td>334.2</td>
<td>3.1</td>
</tr>
<tr>
<td>kv₂</td>
<td>36.24</td>
<td>697.5</td>
<td>1.9</td>
</tr>
</tbody>
</table>

The relatively low value of the frequency factor for k₂ vs. k₁ supported the suggestion of a slow initial reaction followed by a fast second reaction. This was again consistent with our observations. The derived model function may thus be said to adequately describe the mass loss that occurs during torrefaction, both from a goodness-of-fit perspective and the basis of Arrhenius analysis.

The values of the reaction rate constants calculated using the frequency factors and activation energies above compare favorably to values published by Prins (2006b) for willow wood torrefaction. Prins pre-exponential factors are on the order of $10^4 - 10^7$ s⁻¹, and his activation energies are on the order of $10^5$ J/mol. These numbers are larger than those reported here, but due to the structure of the Arrhenius equation, cancel each other out. When further adjusted for the difference in time (his report was on a per second basis rather than a per minute basis) and weight (his reports weight loss as kilograms rather than milligrams) then the comparison is close. Sample calculations are given below. Proposed values and Prins’ reported values agree closely for k₁ and k₂, while the proposed values for k₁ are about 4 times higher. The one severe discrepancy was the kv₂ values.
Table 5.2: Comparison of reaction rate constants calculated from the proposed parameters to reaction rate constants calculated Prins’ reported kinetic parameters (2006b).

<table>
<thead>
<tr>
<th></th>
<th>Proposed values at 250 C, min(^{-1})</th>
<th>Prins’ reported activation energy, J/mol</th>
<th>Prins reported pre-exponential factor, kg kg(^{-1}) s(^{-1})</th>
<th>Prins' values at 250 C, converted to min(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>k1</td>
<td>2.37E+03</td>
<td>7.60E+04</td>
<td>2.48E+04</td>
<td>617</td>
</tr>
<tr>
<td>kv1</td>
<td>16.6</td>
<td>1.14E+05</td>
<td>3.23E+07</td>
<td>15.2</td>
</tr>
<tr>
<td>k2</td>
<td>0.206</td>
<td>1.52E+05</td>
<td>1.10E+10</td>
<td>0.122</td>
</tr>
<tr>
<td>kv2</td>
<td>29.9</td>
<td>-</td>
<td>-</td>
<td>0.176</td>
</tr>
</tbody>
</table>

The comparison is of use inasmuch as knowing that the proposed values are within an order of magnitude of reported values is confirmatory. However, the reactions are for different species under different conditions. A main inference may be drawn: the reactions of torrefaction occur in two steps, with the first step much faster than the second.

5.2 Batch torrefaction yields

The yields of the solid, liquid and gas fractions of the torrefied materials are reported below for the 3 hour treatments times. This data was used in subsequent calculations relevant to liquid and gas analysis. Only the yields for the 3 hour treatment times are used, since it assumed that emission data for 2 hour runs are a subset of the data for the 3 hour treatment times.
Table 5.3: Average mass yield data for torrefaction of wood for 3 hour residence times

<table>
<thead>
<tr>
<th>Treatment temperature</th>
<th>Solid yield, % ±3.2</th>
<th>Liquid yield, % ±2.5</th>
<th>Gas yield, % ±2.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>225</td>
<td>86.1</td>
<td>0</td>
<td>13.9</td>
</tr>
<tr>
<td>225</td>
<td>77.1</td>
<td>2.91</td>
<td>20.0</td>
</tr>
<tr>
<td>250</td>
<td>64.0</td>
<td>7.01</td>
<td>29.0</td>
</tr>
</tbody>
</table>

Note that yields reported here are from duplicate trials rather than triplicate, due to the cancellation of one replicate of yield data due to a mechanical failure in the condenser apparatus. Accurate condensate measurement was not possible for these experiments. The recorded yield was zero for both samples prepared at 225°C because insufficient condensate was collected for any further analysis.

5.3 Analysis of non-condensable products

The exhaust gases from the batch torrefaction where collected and analyzed using a GC-TCD. The resulting data was a mole fraction of carbon dioxide and carbon monoxide in the off-gas, based on a nitrogen flow rate of 2 L/min. There was no significant difference in the concentration of carbon monoxide in the torrefaction exhaust gas over different temperatures, but significant differences in carbon dioxide emissions (Figures 5.8-13).
Figure 5.8: Carbon monoxide concentrations in torrefaction exhaust gas at during treatments at 225°C.

Figure 5.9: Carbon monoxide concentrations in torrefaction exhaust gas at during treatments at 250°C.
Figure 5.10: Carbon Monoxide concentrations in torrefaction exhaust gas at during treatments at 275°C.

![Graph showing Carbon Monoxide concentrations over time for replication 2 and 3.]

Figure 5.11: Carbon dioxide concentrations in torrefaction exhaust gas at during treatments at 225°C.

![Graph showing Carbon dioxide concentrations over time for replication 2 and 3.]

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Figure 5.12: Carbon dioxide concentrations in torrefaction exhaust gas at during treatments at 250°C.

Figure 5.13: Carbon dioxide concentrations in torrefaction exhaust gas at during treatments at 275°C.
Using the off-gas compositional data along with the time taken between reading and the overall flow rate (assumed to be sum of the nitrogen flow rate and the generated gas flow rate); the overall volumes of carbon monoxide and carbon dioxide emitted were calculated. The quantity of carbon monoxide and dioxide emitted per mass of biomass used was calculated by normalizing against the mass of pine chip used in each case.

Table 5.4: Carbon monoxide and dioxide emissions per kilogram of wood during torrefaction

<table>
<thead>
<tr>
<th>Gas</th>
<th>Emissions at 225°C, L/kg</th>
<th>Emissions at 250°C, L/kg</th>
<th>Emissions at 275°C, L/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>4.58 ±10%</td>
<td>5.01 ±22%</td>
<td>3.19 ±9.4%</td>
</tr>
<tr>
<td>CO2</td>
<td>3.14 ±30%</td>
<td>22.7 ±22%</td>
<td>47.5 ±65%</td>
</tr>
</tbody>
</table>

Error values were high overall. This was likely due to the relatively low concentrations detected for both gasses, which would amplify the effect of small variations in detected concentration on the final result. While there was a clear indication of increasing CO₂ emissions with increasing torrefaction temperature, carbon monoxide emissions seemed unaffected.

5.4 Analysis of condensable products

Figure 5.14 and 5.15 below detail the concentrations of furfural and acetic acid in the torrefaction condensate collected during batch torrefaction. On the HP-5 column acetic acid elutes approximately 2 minutes after injection, and furfural elutes 6 minutes after that. There was no significant pattern observed in furfural evolution, though emission at 275°C appears lower than at 250°C. It was inferred for this that furfural concentrations in the torrefaction condensate
are roughly constant, though the actual quantity evolved may vary with liquid yields. Acetic acid
evolution clearly increases with higher temperature treatments.

Figure 5.14: Acetic acid concentration in torrefaction condensate for second (-2) and third (-3)
replications at 250 and 275°C. All experiments had 3hr residence times.

*Figure 5.14: Acetic acid concentration in torrefaction condensate for second (-2) and third (-3)
replications at 250 and 275°C. All experiments had 3hr residence times.*
Figure 5.15: Furfural concentrations in torrefaction condensate for second (-2) and third (-3) replications at 250 and 275°C. All experiments had 3hr residence times.

Note that the average heating rate of the batch torrefaction reactor was 5°C/minute. Therefore, torrefaction target temperatures are considered to be attained after the 50th minute.

5.5 Composition of torrefied samples using HPLC

The concentrations of glucose, arabinose, xylose, lactate and acetate in the hydrolysate samples and the resultant conversion of hemicellulose and cellulose were determined. The masses of the undigested fraction for each of hydrolysis were also recorded. When corrected for sugar loss due during the acid hydrolysis, averaged over replications and normalized for sample weight, the following overall mass data may be reported:
Table 5.5: Compositional summary of torrefied biomass samples via HPLC. % values given are mass percentages based on the starting dry mass of the treated wood. Error values are based on the maximum standard error among measured values for each analyte.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Glucose ±3%</th>
<th>Xylose ±1.8%</th>
<th>Arabinose ±3%</th>
<th>Lactate ±3%</th>
<th>Acetate ±3%</th>
<th>∑ sugars ±5.8%</th>
<th>∑ all ±7%</th>
<th>% undigested ±2.2%</th>
<th>% mass accounted for, ±9.2%</th>
</tr>
</thead>
<tbody>
<tr>
<td>control</td>
<td>44.1</td>
<td>18.9</td>
<td>0.85</td>
<td>0.16</td>
<td>5.74</td>
<td>63.8</td>
<td>69.73</td>
<td>20.8</td>
<td>90.6</td>
</tr>
<tr>
<td>225°C, 1hr</td>
<td>48.5</td>
<td>18.9</td>
<td>0.22</td>
<td>0.33</td>
<td>1.39</td>
<td>67.5</td>
<td>69.26</td>
<td>25.0</td>
<td>94.3</td>
</tr>
<tr>
<td>225°C, 2hr</td>
<td>49.5</td>
<td>18.1</td>
<td>0.24</td>
<td>0.00</td>
<td>0.85</td>
<td>67.9</td>
<td>68.74</td>
<td>25.2</td>
<td>93.9</td>
</tr>
<tr>
<td>225°C, 3hr</td>
<td>45.9</td>
<td>17.5</td>
<td>0.09</td>
<td>0.00</td>
<td>0.50</td>
<td>63.5</td>
<td>63.99</td>
<td>26.7</td>
<td>90.7</td>
</tr>
<tr>
<td>250°C, 1hr</td>
<td>41.2</td>
<td>10.0</td>
<td>0.00</td>
<td>0.31</td>
<td>0.62</td>
<td>51.2</td>
<td>52.15</td>
<td>37.4</td>
<td>89.7</td>
</tr>
<tr>
<td>250°C, 2hr</td>
<td>39.0</td>
<td>6.17</td>
<td>0.00</td>
<td>0.17</td>
<td>0.86</td>
<td>45.1</td>
<td>46.16</td>
<td>41.0</td>
<td>87.1</td>
</tr>
<tr>
<td>250°C, 3hr</td>
<td>39.8</td>
<td>7.34</td>
<td>0.00</td>
<td>0.16</td>
<td>0.78</td>
<td>47.1</td>
<td>48.03</td>
<td>45.5</td>
<td>93.6</td>
</tr>
<tr>
<td>275°C, 1hr</td>
<td>46.2</td>
<td>1.29</td>
<td>0.00</td>
<td>0.65</td>
<td>0.60</td>
<td>47.5</td>
<td>48.77</td>
<td>39.8</td>
<td>88.6</td>
</tr>
<tr>
<td>275°C, 2hr</td>
<td>41.4</td>
<td>1.13</td>
<td>0.00</td>
<td>0.55</td>
<td>0.54</td>
<td>42.5</td>
<td>43.60</td>
<td>45.6</td>
<td>89.2</td>
</tr>
<tr>
<td>275°C, 3hr</td>
<td>40.0</td>
<td>1.07</td>
<td>0.00</td>
<td>0.54</td>
<td>0.52</td>
<td>41.1</td>
<td>42.11</td>
<td>41.7</td>
<td>83.8</td>
</tr>
</tbody>
</table>

Average concentrations of 5 analytes – glucose, xylose, arabinose, lactate and acetate – are given for the three treatment temperatures over the holding time range (1, 2 and 3 hours, with the zero hours for the control values).
Figure 5.16: Glucose concentrations in wood over torrefaction residence times for 3 different torrefaction temperatures. The value at 0 hrs was the concentration in the untreated control.

Figure 5.17: Xylose concentrations in wood over torrefaction residence times for 3 different torrefaction temperatures. The value at 0 hrs was the concentration in the untreated control.
Figure 5.18: Arabinose concentrations in wood over torrefaction residence times for 3 different torrefaction temperatures. The value at 0 hrs was the concentration in the untreated control.

Figure 5.19: Lactate concentrations in wood over torrefaction residence times for 3 different torrefaction temperatures. The value at 0 hrs was the concentration in the untreated control.
Figure 5.20: Acetate concentrations in wood over torrefaction residence times for 3 different torrefaction temperatures. The value at hrs was the concentration in the untreated control.

The average concentration values were tested for statistically significant differences using Tukey’s Honestly Significant Difference test. The results, summarized in the figures below, show that while there are not significant changes in the glucose concentrations analyzed, and the lactate / acetate increases over treatment time were too small to be considered significant, there were significant changes in the arabinose and xylose concentrations.

Glucose concentrations are statistically undistinguishable over all samples.
Figure 5.21: Pair-wise comparison of measured glucose concentrations in hydrolyzed treated wood samples.

Xylose concentrations are not significantly different between the control and the treatments at 225°C, but the treatments at 250 and 275°C are significantly different from the control. Note that for the latter two treatment temperatures show no significant differences from each other, nor with respect to time of treatment, except for the 1 hour treatment at 250°C, which has significantly higher xylose concentrations than the treatments at 275°C.
Arabinose concentrations for all treated samples were significantly lower than for the control samples. The treated samples were not significantly different from each other.
Both lactate and acetate concentrations were not significantly different from each other, over all treatments and controls; however, acetate concentrations were only significantly different from zero in the control samples, while lactate concentrations were only significantly higher than zero in the treatments at 275°C.

Figure 5.23: Pair-wise comparison of measured arabinose concentrations in hydrolyzed treated wood samples.
Figure 5.24: Pair-wise comparison of measured lactate concentrations in hydrolyzed treated wood samples.
Figure 5.25: Pair-wise comparison of measured acetate concentrations in hydrolyzed treated wood samples.

It was apparent from the xylose and arabinose results in particular that the greatest changes in the levels of these substances relative to the control occur before 1 hour of treatment time. It was also apparent that glucose concentrations were not affected by torrefaction.

The method called for observation of unknown peaks eluting before glucose, which indicate incomplete hydrolysis and the presence of cellobiose. No such peaks were observed. Additionally, the sugar recovery standard analysis showed that 98% of glucose, 94% of xylose and 96% of arabinose were recovered after acid treatment, so over-hydrolysis was not an issue.

Figure 5.23 below shows the composition of the analyzed samples with respect to their pre-digestion masses. Fractional sums of less than 100% are indicative of mass that was unaccounted for, whether by digestion into an unidentified fraction or by experimental error.
It was apparent therefore that torrefaction resulted in rapid release of arabinose, acetate and the somewhat slower release of xylose, all theoretically from the hydrolysis of hemicellulose. Glucose remained the same fraction of the mass as an overall value. Since it was known that there is overall mass loss during torrefaction from batch and TGA experiments, the lack of a concentration increase in glucose must mean that glucose, too, was being lost during torrefaction. If hemicelluloses alone were being lost, there would be an increase in the fraction of the wood that was glucose, and the overall mass loss would have a hard cap equal to the fraction of hemicellulose in untreated wood.

**Figure 5.26:** Compositional summary of wood samples via acid digestion. Percentages are given as mass percentages based on the pre-hydrolysis oven-dry mass.
The rapid 5-carbon sugar loss compared well with the overall observation of a fast reaction followed by a slow one. At lower temperatures, the rapid initial mass loss was due to arabinose loss, while at higher temperatures mass loss was due to release of xylose and arabinose. There must also have been slow glucose loss over time.

The increase in the undigested portion may be explained in two ways. The original NREL method calls for identification of this fraction as lignin, so the increase in the relative quantity of this fraction may have been an indication of increased lignin concentrations as wood was treated for longer times and at higher temperatures. Alternatively, the undigested fraction may also have included breakdown products of the sugars and lignin. More thorough analysis of the undigested solid would answer this question.

It must also be noted that xylose and arabinose were reported, but the particular HPLC method used in this work resulted in the co-elution of mannose and galactose peaks with xylose. Softwood hemicellulose is typically less than 50% xylose and the rest is glucomannan with some arabinose. The glucomannan is acetylated in hardwoods, so the loss in the acetate fraction again corresponds to hemicellulose loss.

The trace peak that was assigned to lactate based on retention time may have been a result of the acid digestion of glucose. None of the samples were significantly different from each other, but the highest temperature samples did yield a peak assigned to lactate that was significantly different from zero. If this was peak was indeed due to lactate formation, it may have been that the 275 °C samples were somewhat more susceptible to over-hydrolysis.
5.6 Thermogravimetric analysis of the gasification of torrefied wood samples

It was proposed that the two main mass loss phases (i.e. the second and third mass loss modes) were due to sugar and lignin decomposition respectively.

The results using equation 4.16 yielded good fits; the average coefficient of determination was 0.94 for the secondary mode and 0.91 for the tertiary mode. The activation energy for each mode is reported in Table 5.6 below. The values are in the range of activation energy reported for pyrolysis of biomass by Guo and Lua (2000), who report 100-170 kJ/mol for palm fibers.
Table 5.6: Gasification activation energies obtained via regression.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activation Energy for secondary mode, J/mol</th>
<th>Coefficient of determination for secondary mode</th>
<th>Activation Energy for tertiary mode, J/mol</th>
<th>Coefficient of determination for tertiary mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0.956E+05</td>
<td>0.98</td>
<td>5.06E+04</td>
<td>0.96</td>
</tr>
<tr>
<td>Control</td>
<td>0.940E+05</td>
<td>0.98</td>
<td>4.98E+04</td>
<td>0.96</td>
</tr>
<tr>
<td>Control</td>
<td>9.62E+04</td>
<td>0.98</td>
<td>4.44E+04</td>
<td>0.96</td>
</tr>
<tr>
<td>225-1h</td>
<td>1.59E+05</td>
<td>0.96</td>
<td>3.91E+04</td>
<td>0.86</td>
</tr>
<tr>
<td>225-1h</td>
<td>1.65E+05</td>
<td>0.97</td>
<td>4.06E+04</td>
<td>0.86</td>
</tr>
<tr>
<td>225-1h</td>
<td>1.63E+05</td>
<td>0.97</td>
<td>3.61E+04</td>
<td>0.86</td>
</tr>
<tr>
<td>225-1h</td>
<td>1.41E+05</td>
<td>0.93</td>
<td>4.19E+04</td>
<td>0.94</td>
</tr>
<tr>
<td>225-2h</td>
<td>1.55E+05</td>
<td>0.94</td>
<td>4.61E+04</td>
<td>0.95</td>
</tr>
<tr>
<td>225-2h</td>
<td>1.48E+05</td>
<td>0.94</td>
<td>4.65E+04</td>
<td>0.95</td>
</tr>
<tr>
<td>225-3h</td>
<td>9.97E+04</td>
<td>0.83</td>
<td>4.57E+04</td>
<td>0.96</td>
</tr>
<tr>
<td>225-3h</td>
<td>1.28E+05</td>
<td>0.99</td>
<td>4.83E+04</td>
<td>0.96</td>
</tr>
<tr>
<td>225-3h</td>
<td>1.19E+05</td>
<td>0.98</td>
<td>5.05E+04</td>
<td>0.96</td>
</tr>
<tr>
<td>250-1h</td>
<td>2.05E+05</td>
<td>0.99</td>
<td>2.64E+04</td>
<td>0.80</td>
</tr>
<tr>
<td>250-1h</td>
<td>1.91E+05</td>
<td>0.98</td>
<td>2.90E+04</td>
<td>0.82</td>
</tr>
<tr>
<td>250-1h</td>
<td>1.95E+05</td>
<td>0.99</td>
<td>3.12E+04</td>
<td>0.83</td>
</tr>
<tr>
<td>250-2h</td>
<td>1.34E+05</td>
<td>0.88</td>
<td>4.58E+04</td>
<td>0.95</td>
</tr>
<tr>
<td>250-2h</td>
<td>1.40E+05</td>
<td>0.88</td>
<td>4.85E+04</td>
<td>0.96</td>
</tr>
<tr>
<td>250-2h</td>
<td>1.39E+05</td>
<td>0.90</td>
<td>5.15E+04</td>
<td>0.96</td>
</tr>
<tr>
<td>250-3h</td>
<td>1.09E+05</td>
<td>0.96</td>
<td>5.75E+04</td>
<td>0.96</td>
</tr>
<tr>
<td>250-3h</td>
<td>1.12E+05</td>
<td>0.96</td>
<td>6.21E+04</td>
<td>0.96</td>
</tr>
<tr>
<td>250-3h</td>
<td>1.32E+05</td>
<td>0.98</td>
<td>4.55E+04</td>
<td>0.96</td>
</tr>
<tr>
<td>275-1h</td>
<td>1.54E+05</td>
<td>0.95</td>
<td>3.96E+04</td>
<td>0.86</td>
</tr>
<tr>
<td>275-1h</td>
<td>1.58E+05</td>
<td>0.93</td>
<td>3.81E+04</td>
<td>0.86</td>
</tr>
<tr>
<td>275-1h</td>
<td>1.52E+05</td>
<td>0.98</td>
<td>8.58E+04</td>
<td>0.87</td>
</tr>
<tr>
<td>275-2h</td>
<td>1.52E+05</td>
<td>0.92</td>
<td>3.97E+04</td>
<td>0.87</td>
</tr>
<tr>
<td>275-2h</td>
<td>1.55E+05</td>
<td>0.92</td>
<td>4.09E+04</td>
<td>0.87</td>
</tr>
<tr>
<td>275-2h</td>
<td>1.51E+05</td>
<td>0.87</td>
<td>4.10E+04</td>
<td>0.86</td>
</tr>
<tr>
<td>275-3h</td>
<td>1.26E+05</td>
<td>0.82</td>
<td>3.50E+04</td>
<td>0.85</td>
</tr>
<tr>
<td>275-3h</td>
<td>1.37E+05</td>
<td>0.86</td>
<td>3.63E+04</td>
<td>0.89</td>
</tr>
<tr>
<td>275-3h</td>
<td>1.51E+05</td>
<td>0.89</td>
<td>3.99E+04</td>
<td>0.91</td>
</tr>
</tbody>
</table>
The activation energies for each of the ten treatments were compared using Tukey’s honestly significant difference test to minimize type I errors. The results of the pair-wise comparisons are presented in Figures 5.27-28 below.

For the second phase, the activation energies of the torrefied material with respect to gasification for all the three hour treatments are not significantly different from each other or the untreated control over all holding temperatures. For all holding temperatures, the activation energies peaked after 1 hour of treatment then fell as torrefaction holding times were lengthened. Thus, the effect of torrefaction is to initially lessen the reactivity of the wood with respect to gasification; this refractory effect is lessened as torrefaction time is extended.
Figure 5.27: Pair-wise comparison of calculated activation energies for the second reaction mode during non-isothermal gasification of torrefied pine wood. The mean values and the corresponding 95% confidence intervals are shown.

For the tertiary reaction mode, none of the activation energies are significantly different from each other for any of the treatments.
Figure 5.28: Pair-wise comparison of calculated activation energies for the third reaction mode during non-isothermal gasification of torrefied pine wood.

The HPLC data was reviewed to interpret this result. The sugar concentration data showed no significant differences in glucose concentrations between samples. The changes in xylose and arabinose concentration did not coincide with the observed trends in activation energy. Xylose concentrations were clearly influenced by treatment temperature, but no significant differences are seen between the three retention times for each of the three treatment temperatures. Arabinose concentrations fell to statistically indistinguishable levels after any treatment whatsoever. Therefore, no relationship was seen between concentration and torrefaction holding time for any of the sugars. Sugar concentration differences were therefore not a valid explanation for the observed behavior, which was clearly related to torrefaction holding time.
Figure 5.29 below shows the activation energy for the second reaction mode for all temperatures against torrefaction holding time. The x axis is set at 95.2 kJ/mol, the average value for the untreated control.

![Figure 5.29: Activation energy for the second mass loss mode during gasification of wood torrefied at various temperatures and holding times.](image)

5.7 NMR assays of torrefied wood samples

Peaks in the NMR spectra of the wood samples have been identified by Park et al (2009) and Sievers et al (2009). These peaks assignments are listed in the table 5.6 below.
Table 5.7: Peak assignments for the carbon 13 NMR of pine wood samples.

<table>
<thead>
<tr>
<th>Peak chemical shift, ppm</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>Acetyl in hemicellulose</td>
</tr>
<tr>
<td>56</td>
<td>Amorphous cellulose</td>
</tr>
<tr>
<td>63</td>
<td>Crystalline cellulose C\textsubscript{6} - correct others</td>
</tr>
<tr>
<td>73</td>
<td>Cellulose C2, C3 and C5</td>
</tr>
<tr>
<td>82</td>
<td>Hemicellulose sugars, amorphous cellulose</td>
</tr>
<tr>
<td>89</td>
<td>Cellulose C4</td>
</tr>
<tr>
<td>105</td>
<td>Cellulose C1</td>
</tr>
<tr>
<td>110-127</td>
<td>Unsubstituted olefinic and aromatic carbons (lignin)</td>
</tr>
<tr>
<td>127-147</td>
<td>Quaternary olefinic or aromatic carbons</td>
</tr>
<tr>
<td>143+</td>
<td>Oxygen substituted aromatic carbons, carboxylic acids,</td>
</tr>
<tr>
<td></td>
<td>lignin carbonyl groups</td>
</tr>
</tbody>
</table>

Park et al (2009) identify 2 peaks in the carbon-13 NMR spectrum of cellulose that correspond to crystalline cellulose (63 and 89 ppm) and two more corresponding to amorphous cellulose (56 and 82 ppm). Due to interference from the broad lignin peak at 82 in some samples, the peaks at 63ppm and 56ppm were selected for integral comparison as a qualitative measure of relative amorphous nature of the samples. The integral in each case was taken from 40 to 58 ppm for the amorphous fraction, and from 40 to 69ppm to capture the amorphous and crystalline peaks in that range. The range used was consistent for all NMR spectra. An amorphous fraction value was calculated by the ratio of the two integrals, representing an approximation of the ratio of amorphous to total cellulose in the samples.

While more rigorous studies are possible, these NMR results indicate that for each treatment temperature there is a relative increase in the ratio of amorphous to total cellulose as holding time is increased. Additionally, for 225°C and 250°C torrefaction for 1 hour decreased the ratio of amorphous to total cellulose integrals relative to the control. It may be inferred that torrefaction under milder conditions made wood relatively more crystalline, while extended holding time and elevated temperatures caused wood to be more amorphous.
It must be added that the quality of this result is hampered because of the inability to compare all the peaks corresponding to amorphous and crystalline cellulose, due to interference from other overlapping peaks (specifically at the region around 82 ppm). The result is difficult to compare to Park (2009) because her investigations were of pure cellulose crystallinity, without the interfering peaks encountered in whole wood. Nevertheless, the result is indicative of structural changes in torrefied wood relative to untreated wood.

*Table 5.8: Normalized peak integrals of amorphous and crystalline regions of the NMR spectra of Avicel, untreated wood and torrefied samples.*

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amorphous cellulose integral from 40-58 ppm (arbitrary units)</th>
<th>Amorphous + crystalline integral from 40-69 ppm</th>
<th>Ratio of amorphous to total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avicel</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Untreated wood</td>
<td>1.00</td>
<td>2.79</td>
<td>0.36</td>
</tr>
<tr>
<td>Torrefied at 225, 1h</td>
<td>0.63</td>
<td>2.27</td>
<td>0.28</td>
</tr>
<tr>
<td>Torrefied at 225, 3h</td>
<td>1.12</td>
<td>2.62</td>
<td>0.43</td>
</tr>
<tr>
<td>Torrefied at 250, 1h</td>
<td>0.68</td>
<td>1.75</td>
<td>0.39</td>
</tr>
<tr>
<td>Torrefied at 250, 3h</td>
<td>1.00</td>
<td>2.26</td>
<td>0.44</td>
</tr>
<tr>
<td>Torrefied at 275, 1h</td>
<td>0.61</td>
<td>1.32</td>
<td>0.47</td>
</tr>
<tr>
<td>Torrefied at 275, 3h</td>
<td>0.30</td>
<td>0.63</td>
<td>0.48</td>
</tr>
</tbody>
</table>

Qualitative observations were made upon further inspection of the NMR spectra (see Appendix C). Qualitatively, confirmation of the loss of hemicellulose could be seen in the deepening of the groove at 82 ppm in all the treated wood samples relative to the untreated wood, an observation supported by the very deep groove in the Avicel sample (Fig. 30-32). The appearance of this feature was due to the loss of interference, which sharpened the cellulose peak at the same point.
**Figure 5.30:** Annotated carbon 13 NMR spectrum of untreated pine wood.

**Figure 5.31:** Annotated carbon 13 NMR spectrum of crystalline cellulose (Avicel).
A change in the region upfield from 150 ppm was also observed. This change can was seen especially in the samples treated at 250 and 275°C. Low, broad peaks that clearly deviated from the baseline of untreated wood or Avicel was seen (Fig. 32). A similar deviation was seen in the region around 40 ppm. The upfield changes may have been due to the observed increase in concentration of lignin in the treated samples, or due to changes in the lignin structure. The downfield changes were not attributable to any particular fraction; the region generally corresponds to tertiary aliphatic carbons.

Figure 5.32: Annotated carbon-13 NMR spectra of wood torrefied for 3 hours at 250°C
CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

The mass loss kinetics during torrefaction suggests a two step reaction: a relatively quick first stage devolatilization, followed by a second, slower reaction. Data from solid analysis suggests that this first reaction is the loss of hemicelluloses, while the secondary reaction may be depolymerization of cellulose. Lumped kinetic parameters for the reaction are reported. In future work, it may be useful to plot initial and ending rate data for each holding temperature to over long holding times, to determine rates for each of these two processes separately.

HPLC analysis shows that most of the xylose and arabinose in *Pinus radiata* was lost during the first hour of torrefaction, suggesting that the quicker first stage reaction was the depolymerization of hemicellulose and release of xylose and arabinose (i.e., hemicelluloses hydrolysis). This corresponded to an emission of acetic acid, which it is proposed was due to the disintegration of the polyuronide side groups in the hemicellulose fraction. For a more detailed study of this initial reaction, it is necessary to conduct studies on biomass torrefied for less than one hour, since it was over this residence time that most of the arabinose was lost.

As torrefaction time is lengthened, an increase in the fraction of torrefied wood that did not dissolve under acid hydrolysis was observed. This fraction contained acid-insoluble lignin, but may have also contained breakdown products of xylose and arabinose. Further studies of the hydrolysis residue are recommended to reveal the fate of xylose, arabinose and lignin.

It was observed that short torrefaction times increase the lumped activation energy of wood with respect to gasification in our bench-top TGA apparatus. This corresponded to the
destruction of the more reactive portion of the biomass; i.e., the hemicellulose fraction. Longer torrefaction times subsequently lowered the activation energy to untreated control levels. The NMR studies also support these findings. The NMR studies indicated that cellulose crystallinity was reduced in the wood during prolonged torrefaction treatment, which would reduce the activation energy of the gasification reactions. Further exploration of the crystallinity or the degree of polymerization of torrefied biomass may provide insight into the observed gasification behavior. Coupled with studies of the hydrolysis residue, this may also be relevant to the question of whether torrefaction is a suitable pretreatment for biological conversion of biomass by sugar fermentation. The results show that glucose concentrations (i.e., cellulose) were not significantly affected by torrefaction, so fermentation of torrefied biomass may be viable.

Since torrefaction is to be used as an economical pretreatment for wood intended for thermal conversion, optimization of the process is of great interest. Relatively long torrefaction at low temperatures is recommended. TGA experiments show that 3 hour torrefactions result in more reactive feedstock than 1 hour torrefactions. The reactivity of material torrefied for 3 hours is not statistically different whether the material is torrefied at 225°C or 275°C, and higher temperatures result in lower overall solid yields. It is therefore recommended that torrefaction be conducted at low temperatures for a maximum amount of reactive product and a minimization of energy input. While our experiments showed that 3 hours was the best of the tested treatments, actual torrefaction times would vary with reactor configuration and heat transfer rates.
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torrefaction, fast pyrolysis and pelletisation. Energy v 33, n 8, p 1206-1223.


30. Yu, F, R. Ruan and P Steele. *Consecutive reaction model for the pyrolysis of corn cob.*

Transactions of the ASABE, 51(3) 1023-1028)
APPENDIX A

MATLAB™ CODE USED IN ANALYSIS

Index:

Torrefaction data processing
  extractnfit.m
  fitadjfunc.m
  inert.m
  onefacfunc.m
  twofacfunc.m

Gasification data processing
  eyeball.m
  gasifproc.m
extractnfit.m

%%% Data Extractor
% Gerald C. Lindo
%%% this script reads excel sheets, takes out the data of interest - in this
%%% case, time and normalised mass - and puts the data into a MatLab array
%%% for later use.

%%% in this code, we are reading the file 'longtorr.xls' and fitting it to
%%% the torrefaction model using 'fitfunc.m'

%%% Starting up...
%%% defining temperatures, filenames, etc.
clear all
close all
temps = [200, 215, 230, 245, 260, 275, 300];

for n=1:3
    files= {'longtorr1.xls', 'longtorr2.xls', 'longtorr3.xls'};

for i = 1:length(temps)

%%% reading in and processing data
%%% this section reads the data in the excel files and assigns it to
%%% vecors "time" and "normmass." a short operation is performed to
%%% normalise the mass and reset time to zero.

%%%First, the raw data...
    rawtime = xlsread(files{n}, i, 'd10:d1000');
    rawtemp = xlsread(files{n}, i, 'f10:f1000');
    rawmass = xlsread(files{n}, i, 'g10:g1000');

% then, we find the isothermal region...

    range = find(rawtemp==temps(i));
    time = (rawtime(range)-rawtime(range(1)))/60;
    abstemp = rawtemp(range)+273;
    normmass = rawmass(range)/rawmass(range(1));

%%% Calling the fitting function
    [estimates, model] = fitfunc(time, normmass);

%%% this gives the estimates for factors; see called funtion for in order
coefficients(1,1:length(estimates))= estimates;

%%% Plotting
%%% figure
%%% plot(time, normmass, '*')
%%% hold on
    [sse, FittedCurve] = model(estimates);
$\text{sst} = \sum ((\text{normmass} - \text{mean}(\text{normmass}))^2)$;
Rsq = 1-(sse/sst);
plot(time, FittedCurve, 'r', 'linewidth', 2)

xlabel('Time (minutes)', 'fontsize',16)
ylabel('Mass (normalized to dry weight)', 'fontsize',16)

title([Fitting model function to data for temp = ', num2str(temps(i)), '; R^2 = ', num2str(Rsq)],'fontsize', 15);

legend('data', 'model function ')
hold off
coefficients(i,(length(estimates)+1)) = Rsq;
coefficients(i,(length(estimates)+2)) = sse;
end

% displays each coefficient in column order, along with a R^2 for the fit.
% Each row represents a different temperature.
coefficients
filename=strcat('prins_fit_', num2str(n));
save (filename, 'coefficients', '-ascii', '-tabs');

end
% Gerald C Lindo
% Implementation of a 4 factor model for torrefaction

% this script takes the data generated from dataextractor and does a least squares fit of the model to given data
% Model:
%   A---->B---->C
%      \   |
%       \  |
%       Volatile
% The measured mass is the sum of A, B and C, and the volatiles are lost. Each reaction is modeled as a first order irreversible reaction. The constant are K1 for A to B, K2 for B to C, kv1 from A to volatiles and KV@ for B to volatiles. A represents the starting material, B represents an activated intermediate, and C represents the solid product of torrefaction.
% This model is similar to one used by Prins.

function [estimates, model] = workedfunc(t, normmass)
% Call fminsearch. starting point updated after each run
start_point = [ 0.1 0.001 0.0001 0.0001 ];
model = @fitmodel;
options = optimset('MaxFunEvals',1000000000000);
estimates = fminsearch(model, start_point);
% expfun accepts curve parameters as inputs, and outputs sse, the sum of squares error for the model function, and the FittedCurve.
function [sse, FittedCurve] = fitmodel(params)
k1 = params(1);
kv1 = params(2);
k2 = params(3);
kv2 = params(4);

s1 = 1/exp(t.*(k1-kv1));
s2 = 1/exp(t.*(k2-kv2));

FittedCurve = s1 - 0.7*k1*(s2-s1)/(k2-k1+kv1+kv2) - 0.3*k1*k2*(k1-k2-kv1-kv2 -k1*s2+kv1*s2 +k2*s1+kv2*s1)/( (k2+kv2)*(k1-kv1)*(k2-k1+kv1+kv2)) ;
size(FittedCurve);
size(normmass);
Residuals = FittedCurve' - normmass;
sse = sum(Residuals .^ 2);
end
end

78
% Gerald C Lindo
% Implementation of a simple one-factor function for torrefaction with an
% inert portion
% this script takes the data generated from dataextractor and does a least
% squares fit of the model to given data
% Model:
% A------> volatile + inert
% The volatiles are lost. We that the measured mass is the sum of the
% reactant A, plus an inert substance I that does not participate. This is
% an improvement on the one-factor model in that as time approaches infinity
% the mass approaches a constant, which comports with experimental results.

function [estimates, model] = inertfunc(time, normmass)
% Call fminsearch. starting point updated after each run
start_point = [1 1];
model = @fitmodel;
estimates = fminsearch(model, start_point);

function [sse, FittedCurve] = fitmodel(params)

k1 = params(1);
I = params(2);

FittedCurve = exp(-k1*time) + I;

Residuals = FittedCurve - normmass;
sse = sum(Residuals .^ 2);
end
end
% Gerald C Lindo
% Implementation of a simple one-factor function for torrefaction
% this script takes the data generated from dataextractor and does a least
% squares fit of the model to given data
% Model:
%     A-----> volatile
% the measured mass is simply A, and the volatiles are lost.
% it is anticipated that this model will fail. for it to be reasonable,
% then the mass as time approaches infinity would be zero, which is not
% observed.

function [estimates, model] = onefacfunc(time, normmass)
% Call fminsearch. starting point updated after each run
start_point = [0.00614141601562509];
model = @fitmodel;
estimates = fminsearch(model, start_point);
% expfun accepts curve parameters as inputs, and outputs sse,
% the sum of squares error for the model function,
% and the FittedCurve. 
function [sse, FittedCurve] = fitmodel(params)

k1 = params(1);

FittedCurve = exp(-k1*time);

Residuals = FittedCurve - normmass;
sse = sum(Residuals .^ 2);
end
end
% Gerald C Lindo
% Implementation of Prins model for torrefaction

% this script takes the data generated from dataextractor and does a least
% squares fit of the model to given data
% Model:
%   A----->B
%     \
%     \
%     Volatile
% A and B and the starting materials and the solid product respectively.
% The measured mass is the sum of A and B, and the volatiles are lost.

function [estimates, model] = twofacfunc(time, normmass)
% Call fminsearch. starting point updated after each run
start_point = [.1 1] ;
model = @fitmodel;
estimates = fminsearch(model, start_point);
% expfun accepts curve parameters as inputs, and outputs sse,
% the sum of squares error for the model function,
% and the FittedCurve.
    function [sse, FittedCurve] = fitmodel(params)

        k1 = params(1);
k2= params(2);

        FittedCurve = (1 - .35*k1/(k1+k2))*exp(-(k1+k2)*time) + 0.35*k1/(k1+k2);

        Residuals = FittedCurve - normmass;
sse = sum(Residuals .^ 2);
    end
end
When processing the data from the gasification of torrefied wood on the Mettler TGA, it was clear that there was a dual modality in the data. Such a modality was encountered before in our torrefaction results as well. The overall shape of the graphs can be characterised as two convoluted exponential curves, a rapid early reaction followed by a slow, almost zero-order reaction.

This dual-mode data lends itself to piecewise analysis, i.e. attempting to divide the data and to determine kinetics for each portion separately, rather than attempting a fit of the whole data.

The question then arises: can we systematically decide where to divide the data, i.e. where one mode / reaction ends and the other starts? One needs a more robust method than simply "eyeballing" the data. This code attempts this.

Herein is defined a function that takes a data vector, estimates the point where the mode changes, splits the data in two and returns two vectors.

```matlab
function [a,b] = eyeball(m)
% diff(diff(m)) estimates the second derivative of matrix m via Eulers method.
% the code searches for the maximum value of this 2^{nd} derivative
[val,index] = sort(diff(diff(m)), 'descend');
a = m(1:(index(1)+2));
b = m((index(1)+3):end);
```
gasifproc.m

%% Analysis of the gasification kinetics of torrefied pine chips

% This code models mass loss of pine chips during unsteady-state heating as
% the function:
% \[ \frac{d(\alpha)}{dt} = A \exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \]
% where:
% \[ \alpha = \frac{(X(0) - X)}{(X(0) - X(\text{final}))} \]
% X is the measured mass, A is the frequency factor, R is the gas
% constant, E is the activation energy, T is temperature, t is time and
% n is the order of the reaction.
% Via the Coats-Redfern method (ref: Yu et al, Transactions of the ASABE,
% 51(3) 1023-1028), if \(dT/dt\) a constant beta, we can generate a modified
% Arrhenius plot wherein the slope gives \(-E/R\) and the intercept is
% \[ \ln\left(\frac{A*R}{\beta*E}\right) \]
% This code calculates the CR function assuming first and second order
% behavior. This is done for 3 replications of each of 9 treatments.

%% Initiating...

clear all
close all

%global variables
beta=30;

% generating the list of files to be processed.
filedir = dir ('*.txt');

% here begins the processing loop:

for i= 1:length(filedir)
    % Initial processing: data extraction
    idata=importdata(filedir(i).name,' ', 10);
    time = idata.data((180:end),1);
    Ts = idata.data((180:end),3) + 273;
    Mnorm = idata.data((180:end),5);
    name = filedir(i).name;
    alpha = (Mnorm(1) - Mnorm)/( Mnorm(1)-Mnorm(end));

    % figure
    % plot(time, Mnorm)
    % title(sprintf('Plot of mass over time for sample %s', filedir(i).name))
    % xlabel('time (s)')
    % ylabel('mass, normalised')
    %
    %
    % figure
%% plot (time, alpha)
%% title('Plot of fractional reaction over time')
%% xlabel('time (s)')
%% ylabel('extent of reaction')

%% splitting the data into sections

[Mnormf, Mnorms] = eyeball(Mnorm);

alphaf = (Mnormf(1) - Mnormf)/( Mnormf(1)-Mnormf(end));
alphas = (Mnorms(1) - Mnorms)/( Mnorms(1)-Mnorms(end));

Tsf = Ts(1:length(alphaf));
Tss = Ts((length(alphaf)+1):end);
timef = time(1:length(Mnormf));

%% Using Coats-Redfern method

%% for first section
Tinvf = 1./Tsf;
CRonef = real( log( -log(1-alphaf) ./ (Tsf.^2) ) );
rangef = find(isinf(CRonef)==0);

[cfonef, Sonef] = polyfit(Tinvf(rangef),CRonef(rangef),1);
[yhatf,deltaf] = polyval(cfonef, Tinvf(rangef), Sonef);

sseonef = sum((yhatf-CRonef(rangef)).^2);
sstonef = sum((CRonef(rangef) - mean(CRonef(rangef))).^2);
Rsqonef = 1-(sseonef/sstonef);

Eonef = -cfonef(1)*8.3144;
Aonef = (beta*Eonef*exp(cfonef(2)))/8.3144;

%% for second section
CRones = real( log( -log(1-alphas) ./ (Tss.^2) ) );
Tinvs = 1./Tss;
ranges = find(isinf(CRones)==0);

[cfones, Sones] = polyfit(Tinvs(ranges),CRones(ranges),1);
[yhats,deltas] = polyval(cfones, Tinvs(ranges), Sones);

sseones = sum((yhats-CRones(ranges)).^2);
sstones = sum((CRones(ranges) - mean(CRones(ranges))).^2);
Rsqones = 1-(sseones/sstones);
Eones = -cfones(1)*8.3144;
Aones = (beta*Eones*exp(cfones(2)))/8.3144;

figure

plot (CRone(range), CRone(range))
title('Coates-Redfern plot assuming first order')
xlabel('1/T, (K^-1)')
ylabel('Coats-Redfern Function')

Exporting the data

end

xlswrite('torr-gas-an-trim.xls', data)

First section

perform a 1-way Anova of the integrals
Efirst = cell2mat(reshape(data(:,2), 3,10));
treatments = {'control', '225-1h', '225-2h', '225-3h', '250-1h', '250-2h', '250-3h', '275-1h', '275-2h', '275-3h'};
[p, table, stats] = anova1(Efirst, treatments);

Perform a multiple pairwise comparison of the treatment groups. Alpha is
0.05. The LSD method is used.
c = figure;
[Ecompf] = multcompare(stats, 'alpha', 0.05, 'ctype', 'hsd');
title('Comparison results for activation energies of second reaction segment')
saveas(c, 'ecompf.tif')

second section

Escnd = cell2mat(reshape(data(:,5), 3,10));
[p, table, stats] = anova1(Escnd, treatments);

Perform a multiple pairwise comparison of the treatment groups. Alpha is
0.05. The LSD method is used.
d = figure;
[Ecomps] = multcompare(stats, 'alpha', 0.05, 'ctype', 'hsd');
title('Comparison results for activation energies of third reaction segment')
saveas(d, 'ecomps.tif')
APPENDIX B

APPROACHES USED IN THE MODELING OF MASS LOSS DURING TORREFACTION

B.1 The modeling code

A model detailed understanding of the code can be had by reading the comments in the file extracnfit.m, or the corresponding HTML report. Briefly, the file reads the time, mass and temperature data from the text files output by the Mettler TGA and identifies the isothermal region of the overall torrefaction process (since it is anticipated that kinetic constants and perhaps reaction mechanisms will vary with temperature, it is prudent to use isothermal conditions to estimate kinetic constants). A fitting function is called, that imposes a chosen model onto the data and estimates the kinetic parameters by minimizing the error sum of squares (SSE), i.e. by choosing those values for the relevant model parameters that minimize the sum of the squared residuals over the entire data set. Additionally, the functions are graphed alongside the data for comparison and an $R^2$ value for the fit is generated. The code is modular in the sense that one may write or choose any fitting function to call.

For any iterative search function, the starting point is important to the final estimated values. As such, start points for every parameter estimate were varied in the 0 to 1 range for all the operations described hereafter (this range was chosen because all data was normalized within that range). It found that varying the start point had no appreciable effect on the final parameter estimates, or on overall fit (judged graphically and by comparison of SSE and and $R^2$ values).
B.2 Modeling Results

B.2.1 A simple first-order irreversible model

Perhaps the simplest model one can suggest for any reaction is a single step irreversible reaction:

\[ A \rightarrow B \]

If we presume that A is the reactive solid wood and B is a volatile material, and that the reaction has a rate constant \( k \), then the measured mass at any given time \( (M_t) \) may be written as:

\[ M_t = M_0 e^{-kt} \]

In the case where mass is normalized to a starting value of 1, the equation simplifies to:

Normalized mass = \( e^{-kt} \)

Before even doing a single simulation, we know that this model is likely to fail. As time approaches infinity in this model, the value for \( M_t \) approaches zero, which does not comport with experimental experience. Using the code and calling the fitting function onefacfunc.m, we obtain the following results:

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Replication 1</th>
<th>Replication 2</th>
<th>Replication 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Estimate</td>
<td>( R^2 )</td>
<td>SSE</td>
</tr>
<tr>
<td>200°C</td>
<td>2.45E-04</td>
<td>-0.47</td>
<td>0.05</td>
</tr>
<tr>
<td>215°C</td>
<td>3.55E-04</td>
<td>0.42</td>
<td>0.06</td>
</tr>
<tr>
<td>230°C</td>
<td>5.57E-04</td>
<td>0.49</td>
<td>0.14</td>
</tr>
<tr>
<td>245°C</td>
<td>9.31E-04</td>
<td>0.68</td>
<td>0.26</td>
</tr>
<tr>
<td>260°C</td>
<td>1.64E-03</td>
<td>0.68</td>
<td>0.69</td>
</tr>
<tr>
<td>275°C</td>
<td>2.49E-03</td>
<td>0.60</td>
<td>1.61</td>
</tr>
<tr>
<td>300°C</td>
<td>6.14E-03</td>
<td>0.82</td>
<td>2.91</td>
</tr>
</tbody>
</table>

Note the poor \( R^2 \) values.
B.2.2 A simple model with an inert term

Since we know that as time approaches infinity the overall mass does not approach zero, one might suggest an improvement of the previous model:

\[ A + I \rightarrow B + I \]

\[ M_t = M_0 e^{-kt} + I \]

In this case, \( I \) is a constant representing an inert term. It is that portion of the overall mass that does not react and remains as a residue, providing for the non-zero final mass that is consistently observed. Fitting this model to the data using the inertfunc.m code, we obtain the following:

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Replication 1</th>
<th></th>
<th>Replication 2</th>
<th></th>
<th>Replication 3</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Replication</td>
<td>k</td>
<td>I</td>
<td>R²</td>
<td>SSE</td>
<td>k</td>
<td>I</td>
</tr>
<tr>
<td>200C</td>
<td>1.43E-04</td>
<td>-0.01</td>
<td>0.94</td>
<td>0.0040</td>
<td>1.21E-04</td>
<td>-0.01</td>
</tr>
<tr>
<td>215C</td>
<td>1.85E-04</td>
<td>-0.02</td>
<td>0.92</td>
<td>0.0066</td>
<td>1.11E-03</td>
<td>-0.09</td>
</tr>
<tr>
<td>230C</td>
<td>3.19E-04</td>
<td>-0.02</td>
<td>0.94</td>
<td>0.0133</td>
<td>3.66E-04</td>
<td>-0.02</td>
</tr>
<tr>
<td>245C</td>
<td>5.55E-04</td>
<td>-0.03</td>
<td>0.96</td>
<td>0.0286</td>
<td>6.24E-04</td>
<td>-0.03</td>
</tr>
<tr>
<td>260C</td>
<td>9.52E-04</td>
<td>-0.05</td>
<td>0.96</td>
<td>0.0783</td>
<td>1.06E-03</td>
<td>-0.06</td>
</tr>
<tr>
<td>275C</td>
<td>1.70E-03</td>
<td>-0.08</td>
<td>0.96</td>
<td>0.2019</td>
<td>1.53E-03</td>
<td>-0.09</td>
</tr>
<tr>
<td>300C</td>
<td>3.67E-03</td>
<td>-0.14</td>
<td>0.98</td>
<td>0.3998</td>
<td>3.65E-03</td>
<td>-0.14</td>
</tr>
</tbody>
</table>

We have much improved \( R^2 \) and SSE values; this function fit the overall data better. However, we have a physically meaningless negative value for our inert term in all cases; furthermore, the inert term varies considerably for a starting material that was consistent. One might argue that in the ramp up time to the target torrefaction temperature that some non inert species were lost, thus concentrating the inter values at higher temperatures; this explanation is unconvincing given the relative brevity fo the ramp up time compared to the rest of the experiment, and still does not explain the negative values obtained.
B.2.3 A two-factor function

A more complicated model that accounts for residual mass may be appropriate.

\[
A \xrightarrow{k_1} B \\
\downarrow k_2 \\
\text{volatiles}
\]

In this model, A and B represent solids; therefore the measured mass is a sum of the masses of A and B. Starting with the equation:

\[
\frac{dA}{dt} = -(k_1+k_2)A_t
\]

we derive

\[
A_t = A_0e^{-(k_1+k_2)t}
\]

Starting with :

\[
\frac{dB}{dt} = k_1A
\]

and substituting our derived value for A, we obtain:

\[
B_t = -k_1A_0/k_1k_2*(e^{-(k_1+k_2)t} - 1)
\]

Mass = \( A_t + B_t = A_0 e^{-(k_1+k_2)t}(1 - k_1/k_1k_2) + k_1/k_1k_2 \)

This model is implemented using twofacfunc.m, and the results are displayed in table 3 below.
Table B.2: Parameter estimates and fitting results for twofacfunc.m

| Temperature | Replication 1 | | | Replication 2 | | | Replication 3 | | |
|-------------|---------------|-------------|-----------------|---------------|-------------|-----------------|---------------|-------------|
|             | k1            | k2          | R^2             | SSE            | k1           | k2          | R^2             | SSE            | k1               | k2          | R^2             | SSE            |
| 200°C       | -0.0159       | 0.0324      | 0.94            | 0.0039         | -0.0285      | 0.0579      | 0.94            | 0.0023         | -0.0312          | 0.0635      | 0.91            | 0.0032         |
| 215°C       | -0.0228       | 0.0466      | 0.92            | 0.0065         | -0.0198      | 0.0457      | 1.00            | 0.0135         | -0.0183          | 0.0375      | 0.95            | 0.0049         |
| 230°C       | -0.0174       | 0.0362      | 0.95            | 0.0112         | -0.0146      | 0.0304      | 0.96            | 0.0104         | -0.0169          | 0.0352      | 0.96            | 0.0103         |
| 245°C       | -0.0135       | 0.0288      | 0.97            | 0.0186         | -0.0130      | 0.0279      | 0.98            | 0.0198         | -0.0132          | 0.0284      | 0.97            | 0.0200         |
| 260°C       | -0.0120       | 0.0270      | 0.98            | 0.0379         | -0.0126      | 0.0287      | 0.98            | 0.0433         | -0.0127          | 0.0288      | 0.98            | 0.0443         |
| 275°C       | -0.0104       | 0.0259      | 0.98            | 0.1218         | -0.0135      | 0.0327      | 0.98            | 0.0998         | -0.0135          | 0.0326      | 0.98            | 0.0946         |
| 300°C       | -0.0067       | 0.0232      | 0.95            | 0.7249         | -0.0067      | 0.0232      | 0.95            | 0.7261         | -0.0067          | 0.0234      | 0.95            | 0.7428         |

Note again the good $R^2$ and lowered SSE values compared to our first model. However, we again encounter a physically meaningless negative value for the first kinetic constant.
Figure C.1: Carbon-13 1D spectrum of untreated wood
Figure C.1: Carbon-13 1D spectrum of Avicel (crystalline cellulose)

Figure C3: Carbon-13 1D spectrum of wood torrefied for 1 hour at 225 C
Figure C4: Carbon-13 1D spectrum of wood torrefied for 3 hours at 225°C

Figure C5: Carbon-13 1D spectrum of wood torrefied for 1 hour at 250°C
Figure C6: Carbon-13 1D spectrum of wood torrefied for 3 hours at 250 C

Figure C7: Carbon-13 1D spectrum of wood torrefied for 1 hour at 275 C
Figure C8: Carbon-13 1D spectrum of wood torrefied for 3 hours at 275 C