ABSTRACT

JONES, ANDREW. Torrefaction as a Pretreatment for the Thermochemical Conversion of Treated Lumber.--. (Under the direction of Dr. Stephen S. Kelley)

Torrefaction of biomass as a pretreatment useful for subsequent thermochemical production of bioenergy and has been extensively studied for the past few decades. Many of the chemical processes are relatively well-known, but the capital and operating costs have hindered its commercial adoption. One way to lower the overall costs of the product is to lower the costs of the feedstocks, which is a major contributor to the overall costs, is to use treated waste lumber. Treated lumber waste is difficult to dispose of, making it a lower-cost feedstock for bioenergy production. In this work, the common wood treatments including creosote, copper salts, and flame-retarding treatments were used as examples of lower cost feedstocks. Treated lumber samples and controls were torrefied and analyzed. Specifically, thermogravimetric analysis (TGA) was used to evaluate thermal decomposition, decomposition kinetics, mass loss, and proximate analysis. In addition, the organic and inorganic elemental content, grinding energy, energy density, and particle size were measured. Torrefaction at 300˚C for 40 min was found to minimize differences between the chemical treatments in terms of thermal decomposition and grinding energy. Increasing the severity of the torrefaction increased the carbon content and energy density in all samples except for lumber treated with a commercial phosphorus flame retardant. Increasing the torrefaction temperature and time (to 300˚C for 40 min), increased the carbon content and energy density for all samples. For the flame-retardant sample, the effects of torrefaction temperature and time were significant for treatment of 200˚C for 20 min but limited with additional treatment. Grinding energy is greatly reduced for all torrefaction treatments, and the particle size of ground products decreases as torrefaction intensity increases. Torrefaction can

be an effective pretreatment that dramatically improves the potential for the use of biomass for bioenergy and homogenizes the properties of treated wood wastes which could allow the co-processing of these materials into bioenergy.

Torrefaction as a Pretreatment for the Thermochemical Conversion of Treated Lumber.

by
Andrew Jones

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APPROVED BY:

Dr. Stephen S Kelley
Committee Chair

Dr. Sunkyu Park
Committee member

Dr. Fanxing Li
Committee member

BIOGRAPHY

Andrew Jones is a master's student and research assistant in the department of Forest Biomaterials. Raised in Roxboro, North Carolina and attended North Carolina State University from 2017-2021 to receive his bachelor's degree in Sustainable Materials and Technology with a minor in Business Administration. Andrew's father worked for a coal fired power plant which inspired his interest in energy production, contributing to the reason he researched renewable energy production. He maintained a research position throughout his academic career starting in the Department of Crop and Soil Sciences as a research assistant for the Peanut Genetics program. After graduation, Andrew will continue renewable energy research as a chemical engineer at Research Triangle Institute.

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CHAPTER 1: Introduction and Review of Literature

1.1 Renewable Energy

Energy production from burning fossil fuels is still one of the most prominent forms of energy production used today despite the known effects of its carbon emissions. Despite recent interest in renewables, CO2 emissions are rising, and atmospheric concentrations of CO_2 are above the safe global limit of 410 ppm. [1] Fossil fuels are used despite their known harms due to their efficiency in both power generation and economic efficiency. It is understood that our planet is warming due to carbon emissions and greenhouse gases in our atmosphere. Nevertheless, we continue to burn them because better alternatives are not yet capable of supplying the current demand that nonrenewable energy production does. Renewable energy is not yet capable of this demand primarily due to the cost of energy conversion. [1, 2] Historically, this subject has more interest in academia than commercially. One type of renewable energy of interest recently is biofuels, converting carbonaceous materials from plant matter into fuels. Biomass conversion is a net zero carbon emission process because the carbon emitted back to the atmosphere after burning is carbon that the biomass sequestered from the atmosphere during its lifetime. [1, 4] Biofuels are of interest to lessen carbon emissions from transportation and nonrenewable energy production; the feedstocks are abundant, renewable, and carbon neutral. [*1, 3, 4]* Fuel research and development could lessen the impact of global warming from GHGs, add options to nations' energy portfolios, and improve rural economic development. [1, 15]

1.2 Bioenergy and Biofuel

Biofuel research has been studied in academia for decades, which has led to a steady continuum of technical and commercial developments for the last half-century. The first major development was converting food crops like wheat and corn into bioethanol. The second major advancement began using inedible lignocellulosic material instead of competing with food crops. More advancements came with using algal and microbial systems instead of traditional biomass and even growing these algal sources in labs to lessen the impact of removing them from ecosystems. [1, 7] This review will focus on inedible lignocellulosic material, specifically woody biomass as a precursor for gasification. The classification of generations of development in biofuel research is defined in a few different ways in literature. However, it is the consensus that there are four generations; the first is the edible crops to fuel, the second is inedible crops to fuel, the third focuses on converting algal and microbial growth to fuel, and the fourth using lab-grown algal and microbial components to convert creating a carbon sink. [1, 17]

1.3 Biochemical and Thermochemical Conversion Processes

1.3.1 Biochemical routes

Biochemical biomass conversion involves hydrolysis to extract lignin and sugars from biomass to create liquid fuels. [15] Hydrolysis and fermentation make the alcohols needed to create a bioethanol product, so selecting feedstock with a relatively high sugar content, such as corn or sugar cane gives higher yields of alcohol. [15, 17] this bioethanol can be blended with gasoline to reduce the carbon emissions resulting from transportation. [17] Another route would be extraction, followed by transesterification, creating biodiesel. Biochemical conversion has advantages but is more complicated and expensive than most thermochemical conversions. [15]

1.3.2 Thermochemical routes

Thermochemical routes have the options of combustion, gasification, torrefaction, and pyrolysis. Combustion often refers to the co-combustion of biomass with coal to produce heat, creating steam that turns a turbine to create electricity. Combustion happens at 800-1200 ˚C with sufficient oxygen to fully oxidize the biomass.[16] Gasification is a process that is roughly a century old; this process heats biomass in low oxygen or steam atmospheres to partially oxidize the biomass and create products of syngas which can be refined further to gas products such as methane and hydrogen; this occurs at 800-1200˚C. [15, 16] Pyrolysis occurs at 350-600 ˚C and has no oxygen present to prevent oxidation. Pyrolysis creates bio-oils which are refined to make fuels. [15, 16] Torrefaction is a thermochemical process similar to pyrolysis but carried out at lower temperatures to enhance biomass qualities and is used most commonly as a pretreatment before other thermochemical processes. Figure 1.1 shows the different routes of conversion of biomass into biofuels or bioenergy. [15]

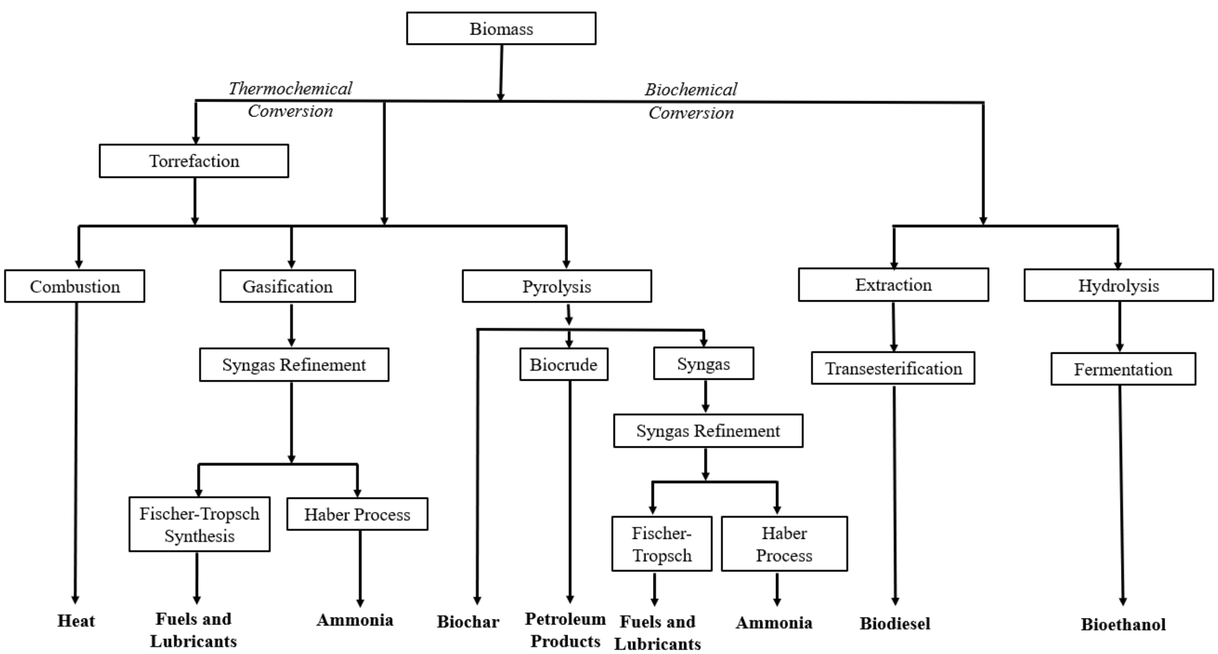


Figure 1.1 Biomass conversion routes to biofuels [15]

1.3.3 Problems Raw Biomass Cause in Conversion

Using raw biomass for biofuel and bioenergy conversion has many negative qualities, such as high moisture, low energy density, low bulk density, hygroscopic nature, heterogeneity, and poor grindability. [1, 3, 6, 10] These factors lead to low conversion efficiency in all thermochemical conversion processes and make front-end processes like transport more difficult and costly. With all its disadvantages, biomass is still an ideal candidate for its abundance, quick regeneration, carbon neutrality, and when compared to coal, it has lower sulfur and nitrogen levels. [1]

1.4 Torrefaction

Pretreatments to combat these negative qualities have proven successful, and one such pretreatment is torrefaction. There is dry torrefaction, where biomass is heated and charred under an inert atmosphere. Wet torrefaction uses hot compressed water, and some dilute acids. Steam torrefaction uses high-pressure and temperature steam to achieve torrefaction. [1] This study will focus on dry torrefaction, carried out at temperatures ranging from 200-300˚C using an inert gas, usually nitrogen or argon, to prevent oxidation and combustion. There is some debate over the range of temperatures at which torrefaction can be carried out, 200-300˚C [1, 2], 225-300˚C [3], 250-300˚C [8], and 300˚C [10], but most agree that 200-225˚C is a mild torrefaction and 275-300˚C is a severe torrefaction. [1, 2] Heating rate and resonance time is debated as well, but it is the consensus that temperature is the most important parameter. [1,30] During torrefaction, volatile components are removed, and the product is a dark char that is more homogenous with improved energy density, bulk density, moisture content, biodegradation risk, grindability, H/C and O/C ratios, and changes from hygroscopic to hydrophobic. [1, 2, 3, 5] This makes it easier to react or combust, cheaper to transport, and better suited for long-term storage. [8] Resonance times for torrefaction differ in literature, from half an hour to 3 hours. The difference in resonance times found in literature is not troublesome because when compared to temperature, time is not as significant to the intensity of torrefaction. [30]

1.5 Biomass Components

Biomass has three main components hemicellulose, cellulose, and lignin. The proportion of each of these varies depending on the species and type of biomass. Hemicelluloses, represented by xylan's chemical formula [$C_5H_8O_4$], generally comprise 10-40% of the weight of biomass and degrade anywhere from 225-315˚C. Cellulose [$C_6H_{10}O_5$] makes up 25-60% of the weight in biomass and degrades at 260-400˚C. Lignin [$C_9H_{10}O_3$] makes up 10-30% of the weight in biomass and degrades anywhere from 160-900 ˚C. [1] For this reason, hemicellulose burns off first, and a portion of lignin is denatured. Leaving behind a majority of cellulose and lignin which have a higher carbon ratio than hemicellulose. [1] Burning off hemicelluloses increases the relative carbon content and biomass's energy density.

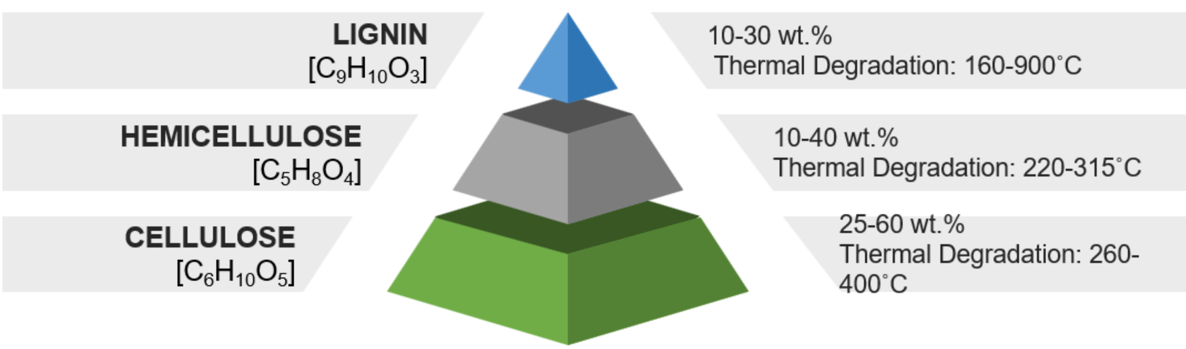


Figure 1.2 Biomass components and temperatures of thermal degradation [1]

1.6 Torrefaction effects

1.6.1 Moisture and Hydro Behavior

Moisture in biomass is a vital parameter concerning transportation, storage, biological degradation, and thermal degradation. [1, 2] The application will determine how much moisture is acceptable in the feedstock. In syngas production, 15-30 wt. % is acceptable, for pyrolysis ten wt. % or less is required. In transportation, the limiting factor for load size will be weight or volume, so reducing freight weight by removing unneeded water can substantially lower costs. [2] Assuming mass is the limiting factor in transport, a 20 wt. % reduction from drying could result in a roughly 20% reduction in transportation costs. Torrefaction improves the biological degradation of biomass for a few reasons: mainly lowered moisture, hemicellulose degradation, and lignin modification. [1] Microbial growth requires moisture, so lowering it decreases microbial degradation. Hemicellulose supports fungal growth that rots biomass, so reducing hemicellulose reduces the available nutrients for fungal growth. [1, 11, 12] Lignin also supports fungal growth but degrades thermally anywhere from 160-900˚C. So, torrefaction partially degrades or denatures lignin, leaving an unrecognizable polymer for enzymes involved in fungal degradation. [1, 11, 12] The transformation of the biomass from hygroscopic to hydrophilic is due to the partial destruction of hydroxyl groups of the cell wall that readily accept hydrogen bonding with water. [1, 13] It has been reported that torrefaction reduces the equilibrium moisture content temperatures of up to 260˚C because there is also an increase of hydrophobic micropores. However, at a temperature of 290˚C, Chen [13] reported a slight increase in equilibrium moisture content, possibly due to increased macropores in the torrefied material. [13]

One study reports that even partial hemicellulose degradation can significantly improve the hydrophilicity of biomass; any reduction in the amount of hydroxyl groups will improve hydrophobicity. [10]

1.6.2 Carbon Ratio

During torrefaction, deoxygenation is a dominant reaction, decreasing H/C and O/C ratios as the increase torrefaction intensity increases. [1,10] The first reaction in torrefaction is dehydration, followed by devolatilization. Dominate reactions include the loss of H_2O and -OH and –COOH groups attached to biopolymers in cell walls. [1] After devolatilization, carbon is lost as CO_2 and other oxygenates. The amorphous hemicelluloses make up the majority of the biomass weight loss, followed by cellulose, and some of the branched lignin structures. This decomposition sequence results in a relative increase in the carbon content. [1, 10] Van Krevlin diagrams as seen in Figure 1.3 are commonly used to reflect the relative differences in the composition of different fuel products, based on their O/C and H/C ratios.

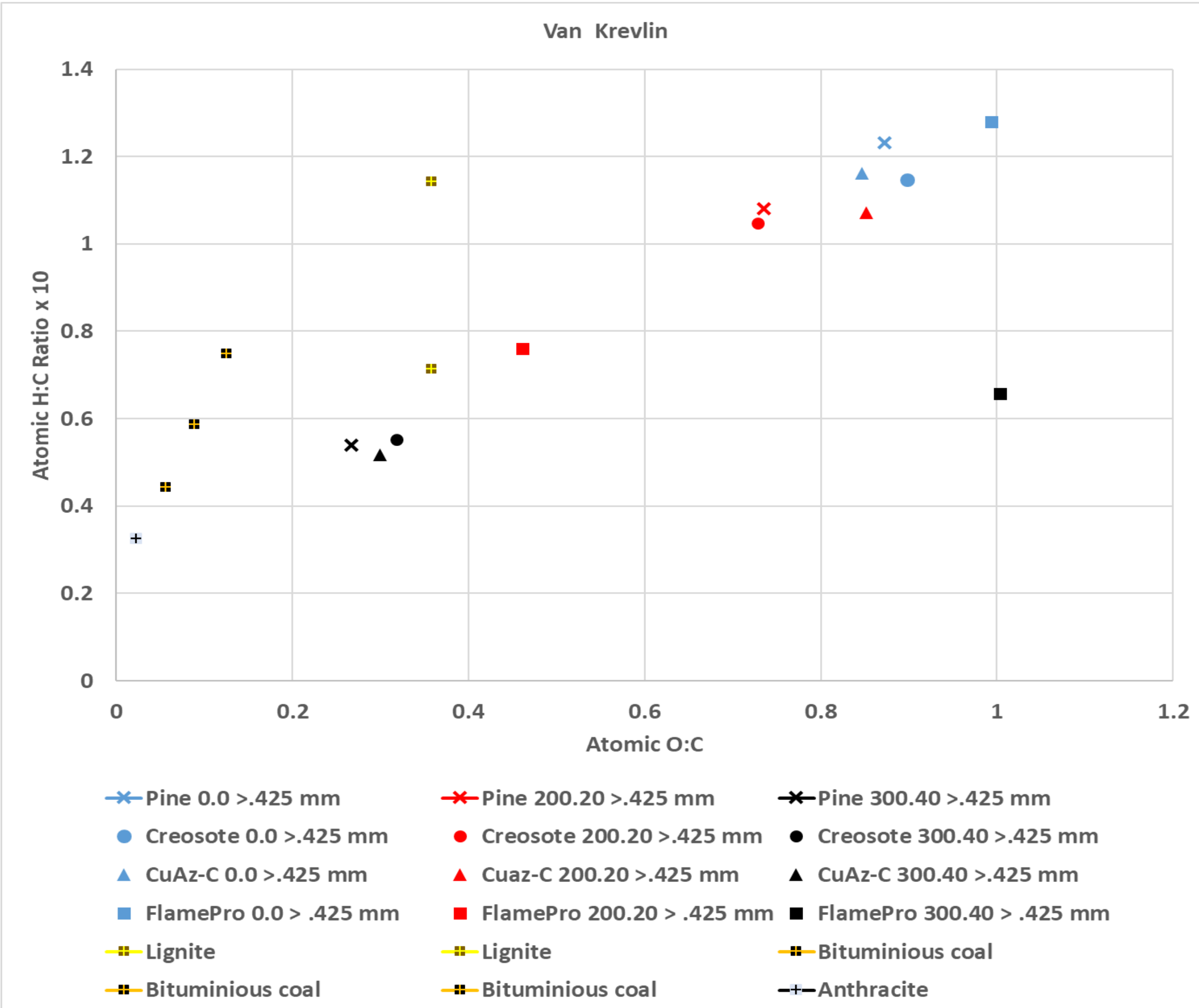


Figure 1.3 Van Krevlin Diagram

1.6.3 Energy Density

Energy density increases with the intensity of torrefaction, which is correlated to the relative increase in the carbon content of the torrefied biomass. [3, 10] At the same time, there are a number of secondary factors that impact the calorific value of biomass: including moisture, ash, and specific elements. [1] One study found that the torrefaction of pine chips increased the HHV of raw chips from 18.5 MJ kg^{-1} to 25.4 MJ kg^{-1} for chips torrefied at 300˚C. [3] Another study using beech wood chips found the HHV of raw chips to be 19.5 MJ kg^{-1} and 21.6 MJ kg^{-1}

for chips torrefied at 300 ˚C. [10] A study using eucalyptus chips measured 19.4 MJ kg^{-1} for raw chips and a 34% increase in HHV to its most intensely torrefied sample, measuring 25.9 MJ kg^{-1} for chips torrefied at 280˚C for 3 hours; this same study used a matrix of times and temperatures, e.g., 1, 2, and 3 hours at 240, 260, and 280˚C respectively.[14] To highlight the importance of temperature relative to time, the HHV of three samples torrefied at 260 ˚C for 3 hours had an HHV of 23.3 MJ kg^{-1}, samples torrefied at 280˚C for 3 hours had an HVV of 25.9 MJ kg-1, and samples torrefied at 280 ˚C for 2 hours had an HHV of 25.2 MJ kg^{-1}. [14]

Table 1.1

Torrefied Biomass High Heating Values (HHV) as found in literature.

Biomass	Torrefaction		HHV	Reference
	Time (h)	**Temperature (˚C)**	**(MJ kg^{-1})**	
Pine	0	0	18.46	[3]
	0.5	225	19.48	
	0.5	250	20.08	
	0.5	275	21.82	
	0.5	300	25.38	
Logging Residue	0	0	18.79	[3]
	0.5	225	19.79	
	0.5	250	21.21	
	0.5	275	22.03	
	0.5	300	26.41	
Bituminous Coal	0	0	27.72	[3]
Beech	0	0	19.46	[10]
	1.1	250	19.82	
	1.1	280	20.42	
	1.1	300	21.61	
Eucalyptus	0	0	19.4	[14]
	0	240	19.6	
	0.25	240	20.1	

Table 1.1 (continued).

	0.5	240	22.2	
	1	240	21.8	
	2	240	22.5	
	3	240	21.9	
	0	260	19.7	
	0.25	260	20.6	
	0.5	260	22.7	
	1	260	22.8	
	2	260	22.9	
	3	260	23.3	
	0	280	20.8	
	0.25	280	22.8	
	0.5	280	23.4	
	1	280	25.0	
	2	280	25.2	
	3	280	25.9	

1.6.4 Mass / Density

There are three common ways to characterize the density of biomass: bulk density, apparent density, and true density. Bulk density is commonly used in storage and transport. It is calculated by dividing the mass by the volume of solids, without consideration for the pores within particles, and the void space in-between particles. [18] Apparent density is commonly used in industry and calculated from the volume that the solid particle and the pores are considered but the spaces between particles are not considered. This method is most common in industrial designs. It can be calculated by submerging the sample in water and noting the difference in volume but is limited to imperfect estimation of water retention in pores. [18] True density is calculated from the volume of solids, excluding pores and void space between particles. [18] These differences are noted because each technique is unique and comparisons across techniques may not be correlated. We can expect mass density and volume to decrease as the intensity of torrefaction increases. One study found the apparent density of raw biomass chips to be 500 kg/m^2 for raw biomass, 489 kg/m^2 for biomass torrefied at 200 ˚C for 180 minutes, and 297 kg/m^2 for torrefactions of 300 ˚C for 180 minutes. Which suggests a more significant impact on volatile components from temperature increases relative to increases in time. [18] In the same study, the decrease in size of the biomass as a result of torrefaction was even more pronounced, with the relative size of biomass torrefied at 300 ˚C for 180 minutes being 18% of raw biomass. [18] Mass decreases significantly due to torrefaction time and temperature, but less so with regards biomass type. For Pine, roughly a 10% reduction in weight for torrefaction at 225 ˚C for 30 minutes and roughly 50% reduction for torrefaction at 300 ˚C for 30 minutes. [12]

Table 1.2

Mass yield and density with respect to torrefaction conditions as found in literature.

Biomass (Chip)	Torrefaction		**Mass yield (wt.%)**	**Density (kg/m^3)**	**Ref.**
	Time (h)	**Temperature (˚C)**			
				Apparent density	
Poplar	0	0	100	500	[18]
	3	200	91	489	
	3	220	81	445	
	3	240	72	444	
	3	260	60	395	
	3	280	45	340	
	3	300	34	297	

Table 1.2 (continued).

				<u>Bulk Density</u>	
Beech	0	0	100	280	[10]
	1.1	250	98		
	1.1	270	88		
	1.1	280	84		
	1.1	300	75		
Pine	0	0	100	381	[3]
	0.5	225	89	342.4	
	0.5	250	82	331.8	
	0.5	275	73	376.1	
	0.5	300	52	400.2	
Logging residue	0	0	100	351.3	
	0.5	225	88	351.7	
	0.5	250	81	336.6	
	0.5	275	70	331.5	
	0.5	300	52	330.5	

1.6.5 Grindability

Grinding energy is an important parameter for biomass conversion to fuel thermochemical processes because small homogenous particles are required for the high throughput feeding of biomass solids. At the same time, grinding raw biomass is an energy-demanding process, and thus a high-cost process. Thus, lowering the required grinding energy lowers the cost of the feedstock, and indirectly the costs of the final product. Biomass becomes brittle, and the required grinding energy reduces as torrefaction intensifies. [1, 2, 3, 5, 6]

Increased brittleness is caused by the decomposition of hemicellulose, cellulose depolymerization, and changes in the lignin structure; these factors greatly reduce the strength of the cell wall. [2] Prior work has suggested a two-stage mechanism for this reduction in grinding energy; the first stage involves dehydration of carbohydrates and a reduction of the glass transition temperature of the lignin. [20] The second stage has more pronounced effects and corresponds to the degradation of wood, as measured by anhydrous weight loss. [20] The same study also found that for the first eight wt. % of anhydrous weight loss, the grinding energy decreases rapidly; after eight wt.% anhydrous weight loss, the grinding energy continued to decrease but at a slower rate. [20]

In terms of biomass utilization in a commercial power plant the grindability of biomass, or torrefied biomass, differs from that of coal because different size reduction processes are used. A ball mill is commonly used for coal, but a knife mill is a better option for untreated biomass due to the fibrous structure of biomass. [19] Using a process modeled after the Hardgrove Grindability Index, which is commonly used to measure coal grindability, the grindability of biomass can be quantified by recording the grinding energy, particle size distribution, and averages after grinding. [2, 14] An intense torrefaction can reduce grinding energy to roughly 10% of the specific grinding energy for raw biomass. [14]

Table 1.3

Torrefied Biomass specific grinding energy as found in literature.

Biomass (Chip)	Torrefaction		Screen Size (mm)	Specific Grinding Energy	Ref.
	Time (h)	**Temperature (˚C)**			
				(kW h/t)	
Pine	N/A	N/A	N/A	237.7	[3]
	0.5	225	N/A	102.6	
	0.5	250	N/A	71.4	

Table 1.3 (continued).

	0.5	275	N/A	52.0	
	0.5	300	N/A	23.9	
Logging Residue	N/A	N/A	N/A	236.7	
	0.5	225	N/A	113.8	
	0.5	250	N/A	110.4	
	0.5	275	N/A	78.0	
	0.5	300	N/A	37.6	
				(kWh $Mg^{-})^{1}$	
Southern Yellow Pine	N/A	N/A	2	353.53	[5]
	N/A	N/A	1	405.78	
	N/A	N/A	0.5	1073.75	
	0.5	250	2	32.08	
	0.5	250	1	45.17	
	0.5	250	0.5	116.39	
	0.5	270	2	16.32	
	0.5	270	1	28.79	
	0.5	270	0.5	60.94	
	0.5	290	2	12.85	
	0.5	290	1	20.39	
	0.5	290	0.5	43.02	
SY Pine (pellets)	N/A	N/A	2	72.53	[5]
	N/A	N/A	1	67.04	
	N/A	N/A	0.5	327.22	
	0.5	230	2	20.47	
	0.5	230	1	30.82	
	0.5	230	0.5	146.10	
	0.5	250	2	9.06	
	0.5	250	1	14.84	
	0.5	250	0.5	62.20	
	0.5	270	2	7.71	
	0.5	270	1	15.5	
	0.5	270	0.5	50.74	
	0.5	290	2	4.24	
	0.5	290	1	10.84	
	0.5	290	0.5	34.00	

1.6.6 Particle Size

Particle size is important in the initial biomass torrefaction and subsequent thermochemical conversion processes because biomass has relatively poor heat transfer, and particle size affects heat transfer. [1] Prior to torrefaction particle size is influential because biomass's poor heat transfer affects the uniform composition across a particle. Biomass is commonly chipped due to the dominate interest of the pulp and paper industry, but for thermochemical processes smaller, more uniform particles are desired. After torrefaction, particle size is important for designing reactors and as a measure of grinding quality. For fluidized bed, combustion, and gasification the particle size is particularly important, as the size and density of the particle will affect its behavior and resonance time in a fluidized bed. [21] Not only does it affect resonance time, but particle size and heat transfer, and even the molecular scale gas-solid interactions affect these gasification products. For example, in raw biomass larger particles form more char and tar than smaller particles. Some of the differences in reaction products are due to the longer residence time for the gases within the particle and the transport of the gases from the center to the exterior. [21] To add complexity transport of gases in the wood's original radial direction relative to its original axial direction also differ, fibers aligned in the axial direction tend to have more escaping gas causing the shrinkage in diameter but not length. [18, 21] One study attributes this reduction in diameter but not length to the hemicellulose burning off first. The thermally stable semi-crystalline cellulose dominates the fibrous structure of the biomass and helps maintain the original fibrous structure of the wood in the axial direction relative to the radial direction. [18]

The particle size of torrefied products is measured after fine grinding as a secondary measure of grinding efficiency. Since coal is often used as a baseline for comparison to torrefied wood products, similar methods for measuring efficiency are used. When measuring coal grindability, the Hardgrove Grindability index is used, in which the mass fractions of sieved material after milling quantify the efficiency of grinding or milling. [19, 22] Since biomass is more fibrous than coal, modifications are made to the specifics of the Hardgrove grindability index. Measuring mass fractions of particle sizes after sieving is common when measuring biomass grindability. [2, 19] As torrefaction intensity increases, the mean particle size of torrefied and ground material decreases significantly. [1, 2, 3, 10, 14, 18, 21] Figure 1.4 below shows the particle size yield with respect to torrefaction, compared alongside coal samples of varying HGI ratings presented from Bridgeman et al.[22] Samples labeled A were torrefied at 290˚C for 10 minutes, B torrefied at 240˚C for 60 minutes, C torrefied at 240˚C for 10 minutes, and D torrefied at 290˚C for 60 minutes. [22]

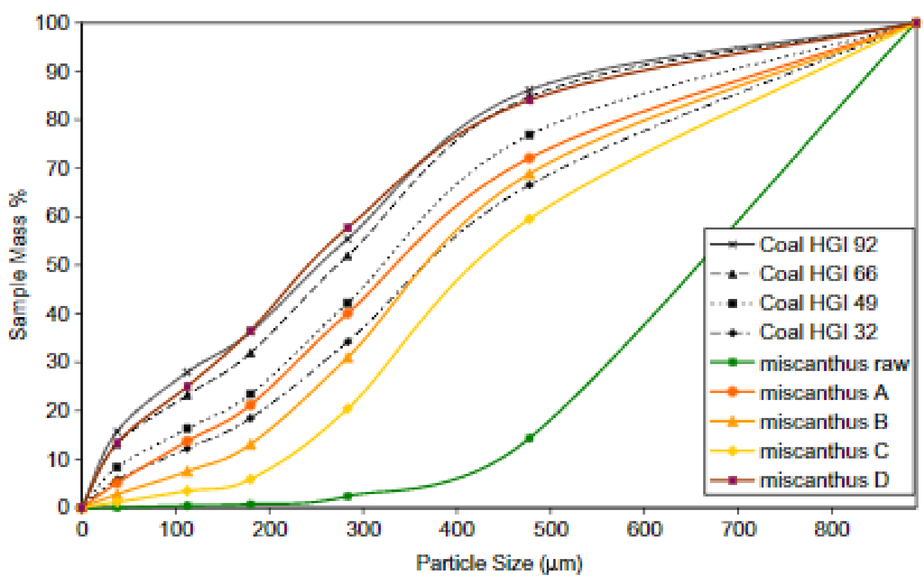


Figure 1.4 Accumulative sieve sizes yields for ground biomass.[22]

1.7 Torrefaction Reaction Systems

Torrefaction is carried out at 200-300 ˚C in an inert atmosphere, so many different laboratory furnaces and instruments can accommodate these conditions. There are classifications of the different types of reactors, usually named for how they move the biomass and selected based on the qualities of the feedstock. [1] The most common reactors are fixed bed, moving bed, screw, rotary drum, and microwave reactors. [1] Fixed bed reactors, such as tube furnaces, are standard in laboratory scale tests because they are easy to use and cheap; however, they are not common in commercial settings because biomass's poor heat transfer limits sample size, and continuous processes are preferred over batch processes. [1] A rotary drum reactor is a continuous process in which the biomass enters a rotating drum that is angled and can adjust resonance time in the heating zone by changing the angle and speed of the rotations. [1] The screw-type reactor is similar to the rotary drum in that it moves the biomass through the heating zone continuously, except the material is pushed along by an auger or screw instead of an angled rotating drum. [1] Microwave reactors can apply heat directly to the material instead of transferring it from heated walls or gas. This factor makes heating more efficient due to biomass's poor heat transfer qualities. [1] Moving bed reactors are different from the others because they are heated from a counter-current flow of hot gases rather than heating via contact with sidewalls or microwaves. In a moving bed reactor, the material is fed from a hopper into a vertical column where the heated inert gases flow upward; short resonance times are possible because the heat transfer is very efficient, but this setup is usually more costly than others reactors. [1]

1.8 Treated Lumber

1.8.1 Decay-resistant treatments

Lumber is often treated with chemicals to improve its decay resistance; preservatives are applied like paint to the boards' exterior or pressure-treated into the board's core. Laws on the chemicals allowed in wood preservation are updated as we learn about the harmful effects of the chemicals used on humans and other organisms. In the past, creosote, pentachlorophenol (penta), and chromated copper arsenic (CCA) were used as biocides to treat lumber for decay resistance. [23] Creosote is a coal and tar byproduct used primarily in railroad ties, utility poles, and pilings and makes up roughly 15% of the treated lumber in North America. [23] Pentachlorophenol is oil-based and used in many noncommercial applications, such as utility poles and cross arms; it makes up about 5% of the treated lumber in North America. [23] CCA is a water-based metallic preservative preferred over creosote and pentachlorophenol in residential applications because it does not leave surface residues. [23] Until its ban in 2003, it accounted for 70-80% of the treated lumber in North America. [23] Since CCA's ban, similar inorganic treatments have replaced its use in residential applications, but none are as effective at long-term decay resistance. These replacements are water-born and rich in copper or borates. Copper Azole (CA), alkaline copper quaternary (ACQ), and copper xyligen (CX) are inorganic copper-containing examples and have low leaching risk but are of concern in marine applications and are corrosive to metal fasteners. [23] Preservatives containing borates are non-metallic, water-based, non-toxic, and not corrosive to metal fasteners. However, they are easily leached out of the wood, so their uses are limited to applications where they will have little to no contact with water. [23]

1.8.2 Fire-resistant treatments

Fire-resistant lumber treatments can be pressure treated into the wood, or intumescent treatments can be applied to the outer surface. [24] Intumescent materials expand 50-200 times their initial volume when heated, creating an insulating layer between the heat source and the flammable wood underneath. [24] Traditionally preservatives used in fire retarding lumber include halogens, phosphorus, nitrogen, boron, or inorganic metals as their active ingredient. [24] Halogen-based compounds use chlorine or bromine coatings to inhibit combustion by releasing oxygen and hydroxyl volatiles that suppress the fire before the wood reaches ignition temperature. [24] Phosphorus-based treatments work by promoting charring which creates a layer of insulation that prevents a rise in temperature sufficient to ignite the inner portion and by blocking the escape of flammable gases. [24] Nitrogen-based treatments dilute the flammable gases and oxygen exiting the wood with nonflammable gases, choking the combustion reaction. [24] When boron salts are used in flame retardants, they release water and act as a catalyst in cellulose dehydration. The water released and the glassy layer formed keeps volatile gases from escaping and act as insulation.[24] Silica-containing compounds act similarly, creating glassy layers of silica that are thermally stable and protect the wood underneath. [24] Inorganic metals and salts are often applied with other compounds that combine the effects of other treatments, such as blocking flammable gases and promoting char layers. The most common additives, magnesium and aluminum, work by cooling the source and diluting flammable gases. [24]

1.8.3 Treated Lumber in Thermochemical Conversions

Treated lumber makes large portions of wood waste streams, an estimated 30 million cubic meters of wood each year. Even though the application of these materials is limited due to the toxic and harmful nature of the chemicals they contain. [25] Thermochemical conversion to fuel or energy could be of great interest, but its effects on these conversion processes have yet to be studied thoroughly. Safely capturing potentially toxic chemicals is a big concern when converting treated lumber with thermochemical processes. A safe manner would include extracting arsenic as a dry solid instead of allowing it to volatilize, as attempted in this gasification study with CCA-treated lumber. [26] It is crucial to find ways to safely remove arsenic from CCA-treated wood because the alternative is to separate CCA-treated lumber before conversion, leaving a large portion of wood waste with no apparent use. Arsenic is more challenging to extract from CCA-treated lumber than copper or chromium because, unlike copper or chromium, it volatilizes below operating temperatures in gasification, combustion, or pyrolysis. [26] Copper and chromium remain in the ash content of the products, but arsenic can produce toxic arsenic oxide gas. [26] The arsenic oxides that are volatile in thermal degradation depend on which gases are present to interact with; in air, the arsenic oxides volatilized at higher temperatures than in the presence of hydrogen, which was used to mimic gas products released in wood combustion. [27] However, arsenic is not the only concern of treated wood in thermochemical conversion. One study found that the combustion of treated lumber is unsafe even when arsenic is absent due to dioxin and furan products. [28] Thermya is a company that claims to have a solution to arsenic extraction. They do low-temperature pyrolysis to create a charcoal product and centrifuge to separate the carbon from the other minerals in the charcoal. [29]

1.9 Applications

Torrefaction is an excellent pretreatment for two thermochemical conversions: combustion and gasification. As mentioned, torrefaction increases: surface area, energy density, carbon content, and hydrophobicity. These make it comparable to coal for applications of co-combustion. Currently, the cost of coal is less than torrefied biomass, preventing its commercialization. [30] Torrefaction improves biomass for gasification; with smaller and dryer particles than raw biomass, the resonance time in a gasifier is much lower for torrefied products than that for raw biomass. [30] Gasification usually occurs as a two-stage mechanism, pyrolysis followed by gasification. However, torrefaction followed by gasification is more cost-efficient due to the energy savings of lower temperatures used in torrefaction than pyrolysis. [30]

1.10 Challenges

Torrefaction, while it improves most qualities of biomass as a fuel candidate, does exaggerate some issues as well. Syngas quality rises with increased torrefaction during biomass gasification, but the overall gasification efficiency decreases with increased torrefaction intensity. This drop-off is due to the energy lost burning volatile matter. [30] The ash content of torrefied products causes another issue, elements in ash such as potassium, chlorine, and sodium increase relative concentrations as the wood around it degrades as volatile matter. Silica and alkali metals cause slagging in boilers when combusted, and this buildup will eventually cause stoppages for maintenance. Chlorine is also an issue in the ash content of torrefied products because of its corrosive nature in boiler systems. [30] The most significant problem facing the commercialization of torrefied biomass is cost; coal will continue to be used until their prices are comparable. [30]

1.11 Biomass Improvements

Torrefaction is an excellent pretreatment to improve many of biomass's qualities as a candidate for biofuel conversion. It improves the cost and efficiency of raw biomass’s thermochemical conversion by reducing the moisture content, affinity towards water, grinding energy, and particle size. It increases carbon content, energy density, surface area, resistance to decay, and density. These relieve transportation and storing costs as well as increase the efficiency of conversion. However, with all of these improvements, commercialization is still held back by the cost of production.

1.12 Gaps/ Future Work

To further decrease the cost of thermochemical conversion for torrefied biomass, taking a step away from incremental increases in efficiency is required. Utilizing biomass sources with zero or negative costs could lower the cost of conversion to match or surpass that of coal. This biomass with negative costs could be lumber wastes treated with wood preservatives that currently have no uses, but this will come with additional challenges. To utilize treated lumber, care must be taken to deal with potentially toxic byproducts and emissions properly. The problems that ash causes in the thermochemical conversion of biomass will likely worsen from using treated lumber, so dealing with these may also prove challenging. Still, the potential benefits of utilizing treated lumber for thermochemical conversion are too great to ignore.

CHAPTER 2: Materials and Methods

2.1 Biomass materials

Various samples were selected for treatment and analyses, including untreated lumber controls and lumber subjected to common commercial treatments. These treatments included samples with organic and inorganic reagents intended to limit biological decay or fire spread. Out-of-service creosote-treated railroad ties of unknown age were also examined.

This wide variety of samples was chosen to represent materials commonly found in construction and demolition piles and wood materials that cannot be recycled and where disposal is difficult or expensive. In addition, Southern Yellow Pine was chosen as a control sample since most treated lumber is treated pine.

The composition of wood wastes were evaluated at three different recycling facilities in Raleigh, North Carolina. Due to safety concerns, landfills are strict concerning scavenging, so collection from landfills was limited. Based on these observations, materials were obtained from North Carolina State University's internal recycling facility, scrap material with unknown commercial treatments from Capitol City Lumber in Raleigh, North Carolina, and out-of-service railroad ties piled beside the Amtrak service rail line in Raleigh, NC. The types of treated lumber, organic and inorganic, were chosen based on their high volumes of use and well problems with disposal at the end of their service life. The inorganic treated samples include lumber treated for biological decay resistance: Copper Chromated Arsenic, Micronized Copper Azole, Alkaline Copper Quaternary, and Copper Azole type-C. The trade names of included samples were: Ecolife, Yellawood, DuraPine, and a second inorganic treatment intended for fire resistance with the trade name of FlamePro was evaluated. Organically treated lumber included creosote-treated railroad ties, both new and used. Table 2.1 provides a brief overview of samples and conditions.

It is worth noting that CCA was banned for residential use due to its toxicity, but it still makes up a large portion of wood in service and waste streams. MCA is also a pressure treatment impregnated into the wood, and it is rated for residential applications, including above-ground, ground contact, and freshwater contact. ACQ is another water-based pressure treatment that can be used above ground, ground contact, freshwater contact, and saltwater contact. CuAz-C is a water-based treatment used in the same applications as ACQ. FlamePro is the only sample that is a treatment for fire resistance instead of as a biocide to prevent decay, it does not disclose the chemicals used in the treatment, but from testing, it was found that phosphorus is a major component in its treatment. FlamePro is rated for interior, above-ground applications such as roof systems. Ecolife, KDAT Yellawood, and Durapine are all biological treatments for residential use in above-ground applications.

2.2 Sample Preparation and Storage

Two different thermal treatment reactors were used, each requiring different particle sizes. First, a muffle furnace treated 0.5 mm powders packed into a ceramic crucible. Second, a muffler furnace with a 1 Liter steel Parr reactor produced larger volumes of material, allowing for larger particles.

Production of 0.5 mm Particles: To partially homogenize starting material and reduce the moisture content to below 5%, the samples of lumber were ground into a chip using a Weima model WL-4, a single rotor shredder. Then oven-dried at 105 ˚C. The shredder has an internal screen that is useful in producing homogenous particle sizes and can also be changed to adjust the size of particles that can pass through. This internal screen was removed and cleaned after each sample run to prevent cross-contamination. The moisture content was measured by weighing the sample before drying and reweighing the sample every 12 hours until the weight was constant, signaling that all moisture had been removed. The incoming moisture content varied by sample, ranging from 8-54% dry basis. The dry samples were stored in sealed 5-gallon buckets. Next, the chipped samples were ground to 0.5 mm powders using a Wiley mill to homogenize further. Small, homogenized particles allow uniform packing into the crucibles used in the different torrefaction treatments.

Due to the geometry of the samples and limited sample sizes, the MCA, ACQ, CCA, and Ecolife could not be ground effectively using the Weima shredder. For these samples, a woodworking planer was used to create shavings of the samples. The shavings were collected with a vacuum attached to the planer. These shavings are thin and 3-4mm long, but easily Wiley milled to a 0.5 mm powder to match the shredded samples.

Figure 2.1: A) Non-torrefied 7mm chip, B) Shaving product from planer, C) Finely ground 0.5mm powder from Wiley Mill

Samples for Production of Large Volumes in Muffle Furnace: samples torrefied using the muffle furnace and Parr reactor were also ground using the industrial shredder, dried, and stored in sealed five-gallon buckets alongside the other samples. Samples were fed into a chip classifier and size separated to homogenize. The chip classification machine was a “Chip Class” from Testing Machines Incorporated and had round sieve openings of >3/8”, >7mm, >3mm, and <3mm. Uniform chip size was essential when measuring grinding energy. Therefore, this study utilized chips with a diameter of >7mm for further experiments.

This study focuses on wood material from processed and recycled cut lumber; it excludes timber, forest residues, pellets, or raw woody biomass. Cut lumber products have no leaves, branches, bark, or sapwood; they only contain heartwood. The lumber's dimensions varied, including railroad ties, 2x4s, 4x4s, 2x6s, 1x8s, and sheets of plywood. Loading the lumber into the industrial shredder required pieces no longer or wider than 3 feet, so the lumber was cut to size before grinding. The railroad tie required a chainsaw, the plywood a table saw, and all other samples required a miter saw. After shredding, the particle size of each starting material was partially homogenized.

Figure 2.2: 1.) Product from Industrial grinder, 2.) Non-torrefied 7mm chip, 3.) 200C 20 min 7mm chip, 4. 300C 40 min 7mm chip

2.3 Alternative Torrefaction Processes

2.3.1 Torrefaction Process 1- Screening

Torrefaction process 1 was preliminary experiments with a broad range of samples and torrefaction conditions. The preliminary stage included five unknown samples and seven known samples. The known samples came from FlamePro, creosote, KDAT Yellawood, Durapine, plywood, and southern yellow pine as a control. The conditions tested for this preliminary stage was 200˚C for 20 min, 200˚C for 40min, 240˚C for 20min, 240˚C for 40min, 300˚C for 20min, and 300˚C for 40min which can be seen in Table 2.1. This initial process aimed to identify samples of interest and test the impact of torrefaction time and temperature. Based on prior work it appeared that temperature had a larger impact on the chemical and physical changes of the biomass than time. [1,30] Anhydrous weight loss was recorded as an indicator of torrefaction intensity. The samples in this stage were also subject to Thermogravimetric Analysis (TGA) testing for further characterization.

Table 2.1 Condition of torrefaction used in Stage 1

	20 min	**40 min**
200˚C	200˚C for 20 min	200˚C for 40 min
240˚C	240˚C for 20 min	240˚C for 40 min
300˚C	300˚C for 20 min	300˚C for 40 min

2.3.2 Torrefaction Process 2 – Sample Preparation for More Extensive Evaluation

The second testing stage focused on two conditions: a 'light' torrefaction of 200˚C for 20 minutes and a 'heavy' torrefaction of 300˚C for 40 minutes which can be seen in Table 2.2. These samples were characterized by anhydrous weight loss, TGA analysis, and more detailed analysis, including X-ray fluorescence spectrometry for inorganic chemical composition and bomb calorimetry. The tests in this stage aimed to gather a proximate analysis using the TGA, investigate changes in calorific content resulting from torrefaction using bomb calorimetry, and use XRF analysis to see how torrefaction affects the chemical composition of the biomass.

Table 2.2: Condition of torrefaction used in Stage 2

	20 min	**40 min**
200 ˚C	200 ˚C for 20 min	N/A
300 ˚C	N/A	300 ˚C for 40 min

2.3.3 Stage 3 Adding samples

In this stage, two concentrations of CCA (.25 and .60 pounds of chemical per cubic foot or pcf), two concentrations of MCA (.06 and .15 pcf), a sample of ACQ (.25pcf), and a newer nonmetallic wood treatment called Ecolife Stabilized Weather-Resistant Wood. Due to the small amount of samples provided, and the large capacity shredder used for the pretreatment of the other samples, these were prepared with a wood planer. Specifically, a DeWalt DW735 planer was used to create small shavings of the samples collected in a mesh bag, then ground to a 0.5 mm powder using the Wiley mill. The particle size was the same as in Processes 1 and 2. These samples were torrefied under the same conditions from Process 2, a light torrefaction (200˚C for 20 minutes) and heavy torrefaction (300˚C for 40 minutes). After torrefaction, the samples from Processes 2 and 3 were subjected to the same tests.

2.3.4 Torrefaction Process 4 – Larger Volume of Sample

In the previous stages, three grams of starting material were put into the tube furnace for each torrefaction run. Depending on the sample and torrefaction condition, this amount provided 1-2 grams of the final torrefied product. Another consideration with these powdered samples is that they limited the option for measuring grinding energy, a key benefit of torrefaction. [1,2,3,5,6] A larger particle size and sample size are needed to measure grinding energy. Thus, a new system for torrefaction was developed. This new method utilized a 1-liter Parr reactor within a muffle furnace to torrefy much larger sample volume and particle sizes.

Due to their common usage, samples of southern yellow pine, creosote-treated railroad ties, FlamePro fire retardant wood, and CuAz-C were used in this fourth process.

Samples used for this stage of work included: southern yellow pine as a control, two common decay control treatments, e.g., creosote railroad ties representing an industrial application, and CuAz-C as a treatment commonly sold direct to consumers, and one flame retardant treatment, e.g., for their abundance, FlamePro.

Before torrefaction, all the samples were sieved using a chip classifier. The chip classifier had sizes >3/8", >7mm, >3mm, and <3mm with round openings in the grate. Samples collected from the >7mm screen were chosen to measure grinding energy due to their relative abundance and size relative to the grinder. Details of the grinding work can be found below.

2.4 Torrefaction Experiments

2.4.1 Small-Scale Tube Furnace

A bench-scale tube furnace was used for the torrefaction of wood powders in Processes 1-3. This procedure consisted of loading 3 g of finely ground biomass into the ceramic crucible, which was then heated at a rate of 15C/min to 200˚C and 300˚C and held for 20 and 40 minutes, respectively. Nitrogen was delivered to the tube at 1 liter per minute to prevent combustion. Nitrogen flowed for five minutes prior to heating to purge out any oxygen and continued to flow until the furnace had cooled to room temperature. The tube furnace used was an MTI Corporation GSL-1500x, utilized with quarts tubes and ceramic crucibles. Two biomass-filled crucibles were placed in the tube for simultaneous torrefaction to increase the efficiency of runs.

Precautions were taken to allow for complete cooling of the samples under nitrogen for 30 min after the thermocouple was at room temperature (25˚C).

2.4.2 Larger Volume Muffle Furnace/Parr Reactor

Torrefaction using the muffle furnace was conducted for samples intended for grinding energy experiments. The muffle furnace was needed to scale up torrefaction, which allowed larger particles to be torrefied. This system allowed 200 grams of starting material >7mm in diameter to be torrefied. A one-liter Parr reactor vessel was used to contain the chip inside the muffle furnace; this vessel was fitted with a secondary thermocouple and a dip tube to deliver nitrogen evenly throughout the vessel. The vessel was large with thick steel walls, and biomass had poor heat transfer qualities. These factors meant that heating rates of 15˚C/min as used in the tube furnace would lead to poor and uneven torrefaction. If heated too quickly, the outer portion of biomass would be torrefied more intensely than the inner portion, so a slow heating rate was used. Using a thermocouple located within the vessel amongst the biomass was necessary instead of the temperature recorded by the furnace's thermocouple. The vessel and biomass took much longer to heat than the inside of the furnace itself; differences of 100˚C or more could be expected during the ramp-up to the final temperature. Heating rates averaged 1-2˚C per minute during the ramp-up to the final temperature. Once the vessel's internal thermocouple measured 200˚C, the hold period of 20 minutes began, and for the heavy torrefaction, once 300˚C was reached, the 40-minute hold period began. The temperature fluctuated +/- 3˚C during this hold time. Nitrogen continued to flow at 2LPM during heating and cooling and continued to flow for 1 hour after the thermocouple within the vessel measured room temperature. Exhaust from the muffle furnace vented directly into a chemical fume hood exhaust system.

Similar to some reactions that occurred in the tube furnace, if the sample was taken out of the reaction too soon, some of it would exotherm resulting in an increase in temperature. Reactions in which this occurred were discarded. Between runs, the Parr reactor was rinsed with acetone and washed with soap and warm water to remove residual pyrolysis vapor condensate.

Figure 2.3 Muffle Furnace Set up: 1. Exhaust, 2. Internal Thermocouple, 3. Gas Tank regulator, 4. Thermocouple control box (display), 5. Gas Flow meter.

Figure 2.4 Parr Reactor Vessel: A.) Inside the Muffle Furnace B.) Lid unattached to show dip-tube.

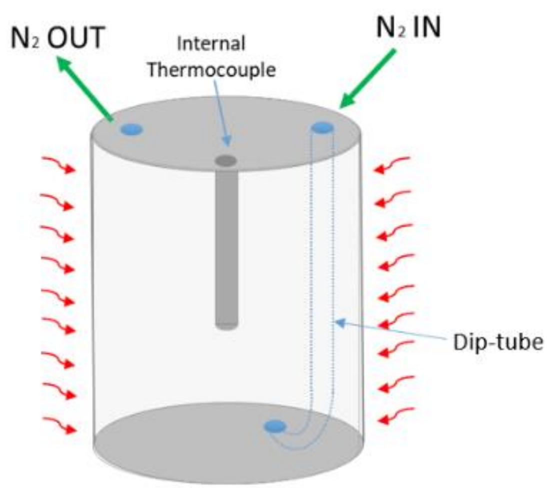


Figure 2.5: Parr reactor torrefaction vessel

Table 2.3

Samples, conditions, method of torrefaction, moisture content, and stages involved.

Sample Type	Torrefaction				Pretreatment	
	Temperature (℃)	**Time (minutes)**	**Tube Furnace**	**Muffle Furnace**	**Moisture Content (% dry basis)**	**Processes Involved**
Pine	0	0			8.8	1,2,4
	200	20	X	X		1,2,4
	200	40	X			1
	240	20	X			1
	240	40	X			1
	300	20	X			1
	300	40	X	X		1,2,4
CuAz-C	0	0			53.8	1,2,4
	200	20	X	X		1,2,4
	200	40	X			1
	240	20	X			1
	240	40	X			1
	300	20	X			1
	300	40	X	X		1,2,4
FlamePro	0	0			15.2	1,2,4
	200	20	X	X		1,2,4

Table 2.3 (continued)

	200	40	X			1
	240	20	X			1
	240	40	X			1
	300	20	X			1
	300	40	X	X		1,2,4
Creosote	0	0			11	1,2,4
	200	20	X	X		1,2,4
	200	40	X			1
	240	20	X			1
	240	40	X			1
	300	20	X			1
	300	40	X	X		1,2
Plywood	0	0			14.7	1,2,4
	200	20	X	X		1,2,4
	200	40	X			1
	240	20	X			1
	240	40	X			1
	300	20	X			1
	300	40	X	X		1,2,4
KDAT	0	0			17.6	1,2
	200	20	X			1,2

Table 2.3 (continued)

	200	40	X			1
	240	20	X			1
	240	40	X			1
	300	20	X			1
	300	40	X			1,2
DuraPine	0	0			19.5	1,2
	200	20	X			1,2
	200	40	X			1
	240	20	X			1
	240	40	X			1
	300	20	X			1
	300	40	X			1,2
.60 CCA	0	0			8.6	1,2
	200	20	X			1,2
	300	40	X			1,2
.25 CCA	0	0			8.3	3
	200	20	X			3
	300	40	X			3
.25 ACQ	0	0			8.9	3
	200	20	X			3
	300	40	X			3

Table 2.3 (continued)

Ecolife	0	0			10	3
	200	20	X			3
	300	40	X			3
.15 MCA	0	0			8.1	3
	200	20	X			3
	300	40	X			3
.06 MCA	0	0			9.0	3
	200	20	X			3
	300	40	X			3

2.5 TGA Experiments

2.5.1 Proximate Analysis

TGA Analysis was carried out using a TA instruments TGA-550 in platinum pans with nitrogen as the inert gas flowing at 50ml per min. Samples were characterized by heating at 15 ˚C / min to 105˚C, where it was held for 10 minutes to evaporate any moisture. Then the sample was heated from 105-900˚C at 15˚C / min and held for another 10 minutes. After this hold, nitrogen gas flow ceased, and 50ml/min of air was introduced into the furnace at 900˚C and held for another 10 minutes to allow for the combustion of residual char. The volatile matter was characterized by weight loss from 105-900 ˚C. At 900˚C, only fixed carbon and ash content remained. After air was introduced, the carbon content burned off, and only ash remained. The data was analyzed using TRIOS software by Waters/TA instruments.

2.5.2 Heating Rate Experiments

Heating rate experiments were carried out using TA Instruments TGA-550 to investigate the effect of heating rate on the reaction kinetics of biomass's thermal degradation. Three heating rates were employed 1˚C /min, 20˚C/min, and 40˚C/min. Samples examined: Pine, CuAz-C, creosote, and FlamePro, all of which torrefied at 300˚C for 40 min. Samples were heated in a nitrogen environment to 105˚C and held for 10 minutes to evaporate any moisture, then increased to 500˚C at their respective heating rate and held for 1 minute. The model from which the method heating rates and temperatures were chosen came from a 2020 round-robin study conducted by Anca-Couce etc., in which they heated biomass to 110˚C and held it for 10 minutes before data was collected to exclude moisture from the calculation and then began heating rates as low as 1K/min and as high as 40K/min up to 500˚C. [34] They used derivative curves to analyze activation energies measuring temperatures at which specific decomposition conversion values were reached.

The Flynn-Wall-Ozawa method for calculating activation energy was used from the collected TGA data with three different heating rates. ASTM E1641-18 was used as a guide for the calculations. For weight loss calculations, the mass percent at 105˚C, after initial moisture evaporated, was treated as the starting point or 100% mass. Weight loss labels of 2%, 4%, 5%, and 6%, as seen in section 4.2.4, are weight reductions from this starting point at 105˚C. These act as checkpoints to reference the temperature at which these fractions of decompositions occur across the different heating rates. With these data points, a scatterplot of the logarithm of the heating rate in K/min on the Y-Axis and an inverse in temperature (1/T (K)) on the X-axis will give us a straight line whose slope is a function of activation energy.

$$\frac{d\alpha}{dT} = A(1-\alpha)\exp\left[-\frac{E}{RT}\right]/\beta \qquad (1)$$

Where:

α	=	fraction reacted (dimensionless)
A	=	pre-exponential factor (min^{-1})
β	=	heating rate (K/min)
E	=	activation energy (J/mol)
R	=	gas constant (8.314 J/ (mol K))
T	=	absolute temperature (K)
exp	=	Euler's number exponential
Dα/dT	=	rate of change of α with *T*

The FWO method rearranges Eq.1 to solve for activation energy using Doyle's approximation, as seen in Eq.2. Where E is the estimation of activation energy from Doyle's approximation in the first iteration. b is a value found using Numerical Integration Constants as found in ASTM E1641-18.

$$E = -\left(\frac{R}{b}\right) \Delta \log[\beta] \,/\, \Delta\left(\frac{1}{T}\right) \qquad (2)$$

The first iteration is calculated using the value of b= 0.457 to give a first approximation of activation energy. With this first approximation value, calculate E/RT and choose a different b value accordingly. This process was repeated until the difference in activation energy between iterations was less than 1%. The value for β used is the heating rate, which is the midpoint in the range of heating rates. The second half of the equation, $\Delta \log[\beta] \,/\, \Delta(\frac{1}{T})$, is the slope of the trend lines in Figure 3.5.

2.6 Bomb Calorimetry

ASTM D4809-18 Bomb Calorimetry was conducted with a Parr model 1108 oxygen bomb calorimeter. One gram of powdered sample was used to obtain calorific content. The bomb was charged with high-pressure oxygen, surrounded by a layer of water, and ignited using a fuse wire so that the heat was transferred to the water surrounding the reaction vessel. This water jacket was stirred and had a submerged thermocouple to measure the temperature rise. With a known amount of water, the temperature increase of the water can be used to calculate the heat of the reaction or its caloric value. The calorimeter was purged with 3MPa of oxygen and refilled with 3 MPa before firing. The temperature rise was recorded in 30-second intervals for a total of 15 min. Tests had a cooling period before the next test, and 2 kg of deionized water was used to fill the vessel after every run so that the starting point was maintained at room temperature. Following each run, 25 ml of an alkali solution was used to clean crucibles and the bomb so that sulfur could not build up and affect calculations. The sulfur content of the samples was needed in calculations for calorific content; this was obtained from chemical composition experiments carried out at the University of Virginia Department of Material Science and Engineering.

2.7 Chemical Composition

2.7.1 XRF Analysis

X-ray fluorescence spectrometry was carried out at the University of Virginia Department of Material Science and Engineering. The instrument used was a benchtop Panalytical Epsilon 3x Energy Dispersive XRF spectrometer fitted with an Ag anode x-ray tube and 50-micron Be window. It uses Omnian standard-less analysis software to detect individual elements at < 1 ppm. Elemental composition is normalized to the total biomass content.

2.7.2 C/H/N/O Analysis

Carbon, hydrogen, nitrogen, and oxygen content was measured at Midwest Microlabs using ASTM standard D53737-14, which involves combusting the sample at 990˚C in ultra-pure oxygen with a closed system. Gas products from combustion were filtered through copper to remove oxygen, then through silver salts to remove halogens, phosphorus, and sulfur. Gas analysis was completed after every removal step. H_2O and CO_2 were removed, which left only nitrogen behind. With gas analysis done after each step, all three elements were taken in one run. With known carbon, hydrogen, nitrogen, and ash content, the oxygen content was estimated from back calculation.

2.8 Grinding Energy

Grinding energy experiments were modeled after the work of Manouchehrinejad and others. (3, 5, 6, 10, 14, 19) Energy consumption was measured using a mill and power logger, and qualitative measurement of grinding quality was done by sieving the ground product. The sieving of this ground product inspired the following research question. Does the particle size of torrefied products affect their thermal or chemical properties? To investigate, the largest, smallest, and medium particle sizes were chosen for additional analysis. The analyses performed on the different particle sizes included TGA for proximate analysis and heating rate experiments, XRF for chemical composition, C/H/N analysis for Van Krevlin diagrams, and microscopy to investigate particle shape. Bomb calorimetry would also be of interest, but the sample size was insufficient.

Grinding Energy Experiments were carried out on an IKA MF 10 basic micro fine grinder drive and an IKA 10.1 cutting-grinding head. The mill's lowest speed setting (3000 rpm) was used. The bottom grate had a 2mm pass-through sieve, and power consumption was recorded using an Onset UX 120-018 power logger. The logger recorded watt-hour (Wh) measurements in one-second intervals. Twenty-eight grams of material was ground until all material had passed through the bottom grate. The grinding time and energy were greatest for raw samples, so these conditions were used for the subsequent torrefied samples.

The specific method involved loading the biomass sample into the hopper, starting the grinder and power logger for 10 seconds to establish a baseline before the sample was dropped into the grinding chamber. After each run, the mill was cleaned using compressed air to remove any fine powder accumulation on the screen. A loss of up to a quarter of a gram of material could be expected to remain behind in the grinder after each run. A nitrile glove was used to create a seal between the grinder's material outlet and the collection beaker placed underneath to prevent further material loss or exposure to breathing airborne particles.

The baseline energy could be subtracted from the total grinding energy. Then, the required grinding energy watt-hours (Wh) could be compared between samples and torrefaction conditions.

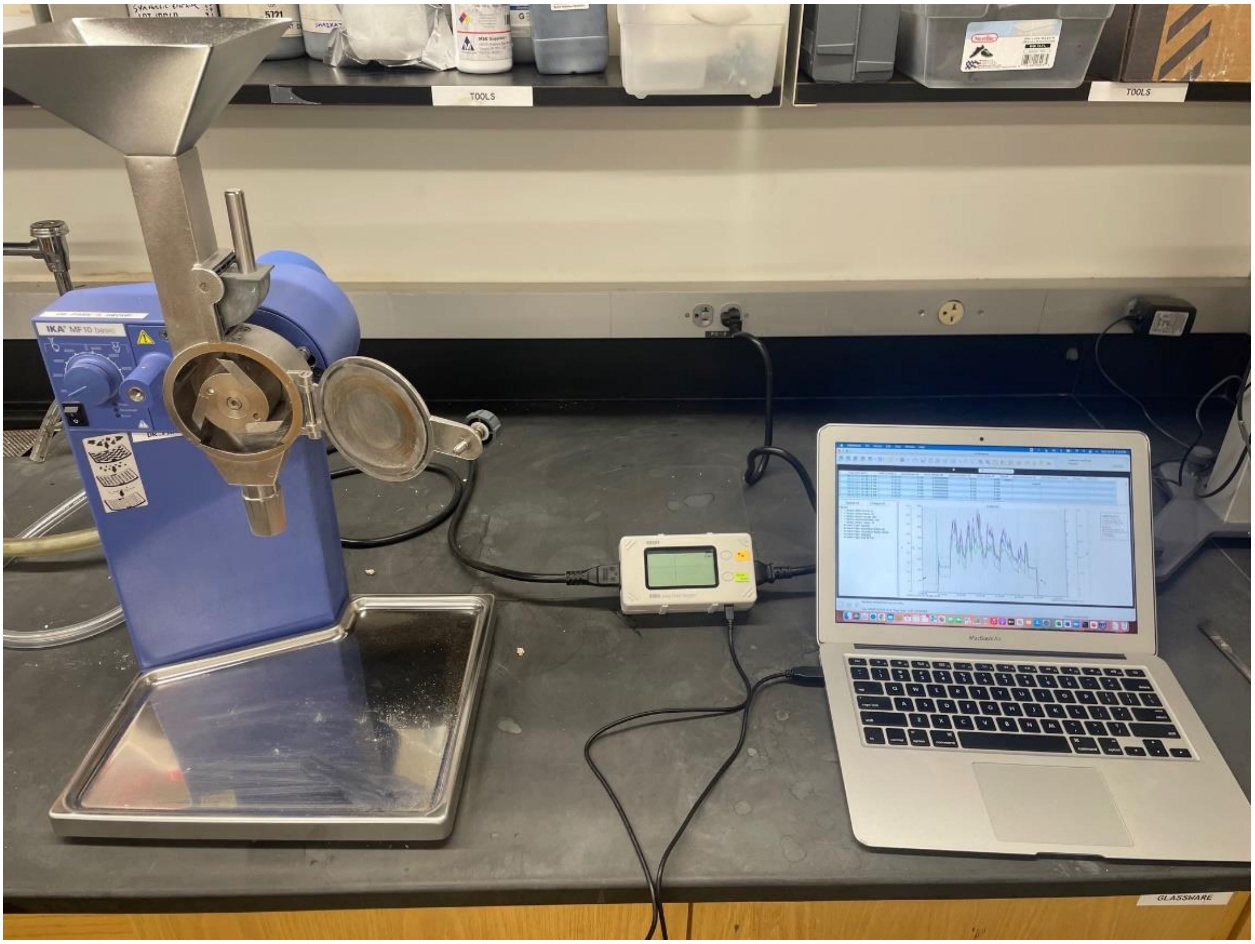


Figure 2.6 Grinding Energy Experiment Setup

Following grinding, the collected powders were sieved for 3 minutes using a Gilson model SS-3 vibratory shaker on its maximum intensity setting. This shaker used vibratory and vertical tapping actions that fired every second to disrupt particles further and prevent any blinding in the sieves. Screen blinding is of particular concern when relatively fibrous samples are analyzed. Sieve sizes used were >1mm, >.710 mm, >.425mm, >.250 mm, >.106 mm, and <.106mm. Mass percentages of material in each sieve class were measured to give an additional measure of grinding quality. The scale used for this measurement was accurate to the milligram. The transfer process lost one to two percent of the total sample.

Chapter 3: Results and Discussion

3.1 Effect of torrefaction intensity on mass yield

As torrefaction occurs, moisture and volatiles are released from the biomass, decreasing the overall mass. After moisture removal, any further weight loss during torrefaction is known as anhydrous weight loss. Anhydrous weight loss from torrefaction serves as an indicator of the overall intensity of torrefaction and changes in biomass composition. [20]

Table 3.1 shows the association between torrefaction conditions and the anhydrous weight loss of woody biomass. The torrefaction condition of 200˚C for 20 min results in an initial weight loss of 7-19%. Torrefaction conditions of 300˚C for 40 min resulted in a loss of 59-72% of the initial weight. One exception to this trend is the FlamePro sample, which lost significantly more mass than that of the other samples after a torrefaction of 200˚C for 20 min and 48.7% after its torrefaction at 300˚C for 40 min. These differences reflect its specific chemical treatment.

Anhydrous weight loss is commonly an essential parameter when calculating conversion economics of biomass-based processes. The cost of transportation is determined by either the volume or the mass of the freight; if the mass is the limiting factor, then reducing the mass will directly reduce transportation costs. In addition, since the biomass is commonly purchased on a weight basis the mass loss associated with torrefaction will impact the cost of the final fuel product.

Table 3.1

Overview of samples, torrefaction conditions, anhydrous weight loss, and dry basis moisture content.

Sample	Torrefaction	Pretreatment		
	Temperature (℃)	**Time (minutes)**	**Anhydrous Weight Loss (%)**	**Moisture Content (% dry basis)**
Pine	0	0		8.8
	200	20	15	
	300	40	67.6	
CuAz-C	0	0		53.8
	200	20	13	
	300	40	64.3	
FlamePro	0	0		15.2
	200	20	36	
	300	40	48.7	
Creosote	0	0		11
	200	20	14	
	300	40	66.7	
Plywood	0	0		14.7
	200	20	12.3	
	300	40	59	

Table 3.1 (continued)

KDAT	0	0		17.6
	200	20	13	
	300	40	66.3	
DuraPine	0	0		19.5
	200	20	7	
	300	40	65	
.60 CCA	0	0		8.6
	200	20	20.3	
	300	40	60.7	
.25 CCA	0	0		8.3
	200	20	14	
	300	40	66.3	
.25 ACQ	0	0		8.9
	200	20	15.3	
	300	40	68.7	
Ecolife	0	0		10
	200	20	17.7	
	300	40	72.3	

Table 3.1 (continued).

.15 MCA	0	0		8.1
	200	20	18.7	
	300	40	70	
.06 MCA	0	0		9.0
	200	20	19	
	300	40	69.7	

3.2 Thermal Decomposition properties

3.2.1 Thermal decomposition of samples with respect to torrefaction intensity

The torrefaction process partially decomposes biomass, leading to improved thermal stability for the residue. This effect is shown when torrefied material shifts thermal decomposition curves towards higher temperatures in TGA curves. Thermal analysis of biomass shows the temperatures at which treated samples are most thermally stable before decomposition occurs. As seen in Figure 3.1, the greatest weight loss occurs between 300˚C and 400˚C. This is why the samples torrefied at 300˚C for 40 minutes lost a significant portion of the thermally liable components relative to the samples that were not torrefied or at 200˚C for 20 minutes. Decomposition rates and temperatures reflect the intensity of torrefaction that the samples were subjected to.

Common TGA thermograms are shown in Figure 3.1 below. Three of four samples showed a sharp decline in weight around 300˚C. This sharp decline denotes its decomposition peak or the temperature at which there is the greatest rate of decomposition. This significant decline can only be observed in samples that have not been torrefied or were torrefied at 200˚C for 20 min; while samples torrefied at 300˚C for 40 min do not show this drop-off because they already experienced this weight loss during torrefaction. Uniquely, the FlamePro peak decomposition occurs at lower temperatures when compared to the others due to the presence of phosphorus in its treatment. This difference can be seen in Figure 3.1c; the curves for decomposition are spread out more evenly than the other samples. Phosphorus promotes charring in the lumber treated with it, which works as a flame retardant by creating an insulating barrier for the layers of wood within it. [25] Since phosphorus is present in FlamePro, the sample torrefied at 200˚C for 20min experienced a more intense char formation than the Pine, Creosote, or CuAz-C samples. This more intense char formation is evident by the higher percentage of retained weight prior to combustion at 900˚C. This FlamePro sample retained almost 50 wt.% of its fixed carbon compared to approximately 20 wt.% for the Pine, CuAz-C, or Creosote. Alternatively, this evidence could mean that phosphorus was consumed completely before 200˚C, which is the reason for improved thermal stability at 300˚C.

These results help to distinguish the relationship between torrefaction conditions and the source of the biomass. For example, as shown in Figure 3.1, non-torrefied samples and samples torrefied at 200˚C for 20 min are very similar, shown by the proximity of their curves. Samples torrefied at 300˚C for 40 min are very different from either, with its curve much higher than the other conditions. This separation from the other two conditions displays that 300˚C for 40min has a significantly higher impact on weight loss than 200˚C for 20 min.

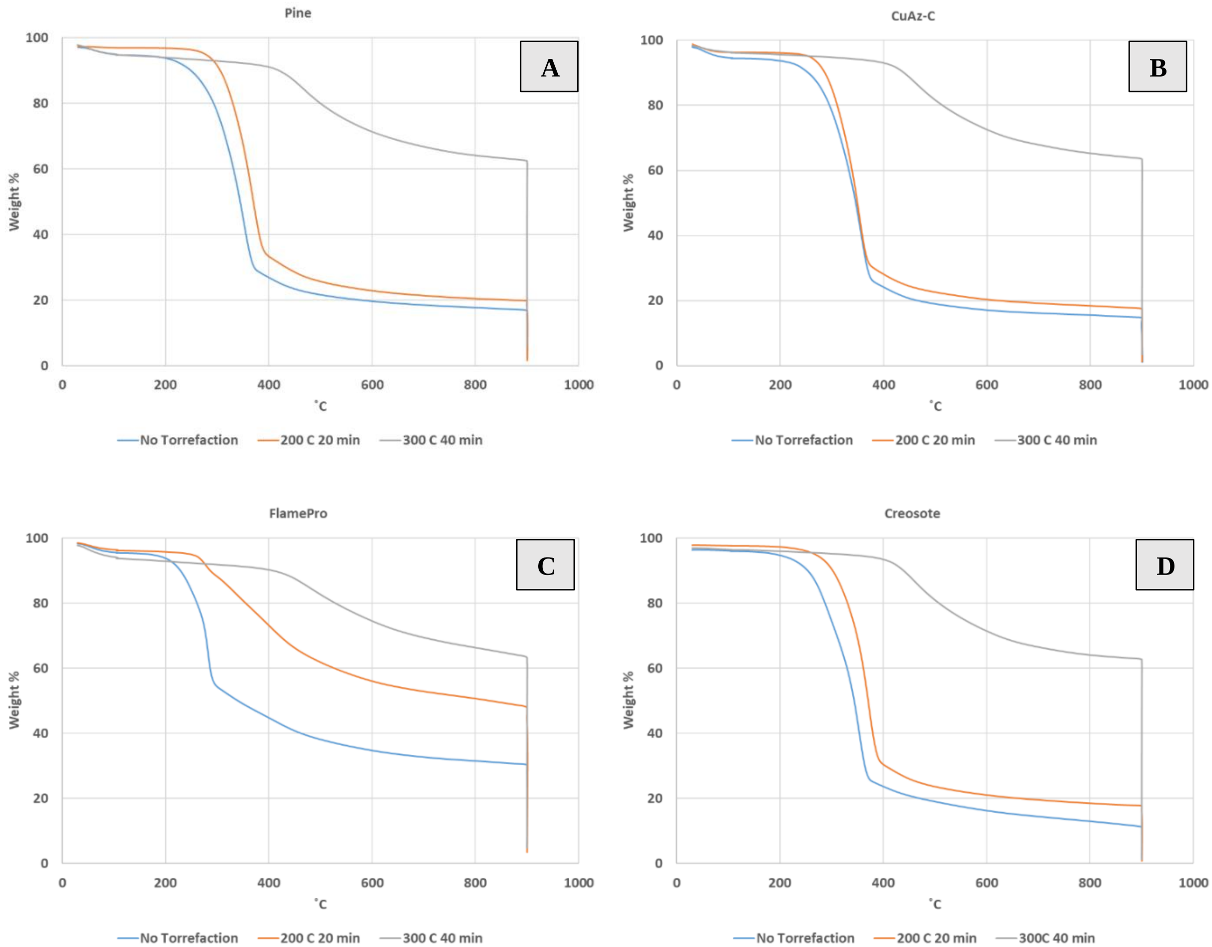


Figure 3.1: TGA curves for different types of lumber, comparing the differences in thermal decomposition for samples not torrefied, torrefied at 200˚C for 20 min, and torrefied at 300˚C for 40 min.

3.2.2 Thermal decomposition with respect to individual sample material

This study considers the impacts of using different types of treated lumber as well as untreated lumber, as a representative of wood waste found in construction and demolition wastes. In addition, thermal degradation of different wood types determines the impacts of torrefaction conditions. Furthermore, biomass feedstocks show different responses to torrefaction, suggesting different types of lumber may need to be torrefied separately.

From the results, Figure 3.2a showed that the starting material for Creosote, Pine, and CuAz-C have similar thermal decomposition profiles, while FlamePro was conspicuously different. The thermal treatment at 200˚C for 20 min improved the thermal stabilities of all the starting materials. Furthermore, thermal treatment at 300˚C for 40 min of the samples showed even better improvements in thermal stability. In Figure 3.2c, similar thermal decompositions can be observed for all three starting materials, while FlamePro is significantly different. With no torrefaction, it was more thermally stable than Pine, CuAz-C, or Creosote. Following, torrefaction of 200˚C for 20min, showed greater weight loss. While at 300˚C for 40min, it decomposes much like the other samples. Figure 3.2a shows that FlamePro begins decomposition before Pine, CuAz-C, or Creosote but ultimately loses less weight than the other just before combustion. In Figure 3.2b, FlamePro separates itself from the other samples seen by almost 50% weight retention before combustion compared to the 20% weight retention at 900˚C from Pine CuAz-C or Creosote. 900˚C is a point from which many comparisons are made because at this temperature with an inert atmosphere, only the thermally stable components of fixed carbon and ash content remain.

The differences shown from FlamePro suggest that it could be separated from other lumber before torrefaction. For example, suppose torrefaction is effective at lower temperatures than Pine, CuAz-C, and Creosote. In that case, separating and performing batch torrefaction for this material at lower temperatures may be worthwhile to save energy costs. On the other hand, by 300˚C for 40 min, all torrefied material is uniformly decomposing. Thus, if all samples are torrefied together, torrefaction conditions should be at least 300˚C for 40 min.

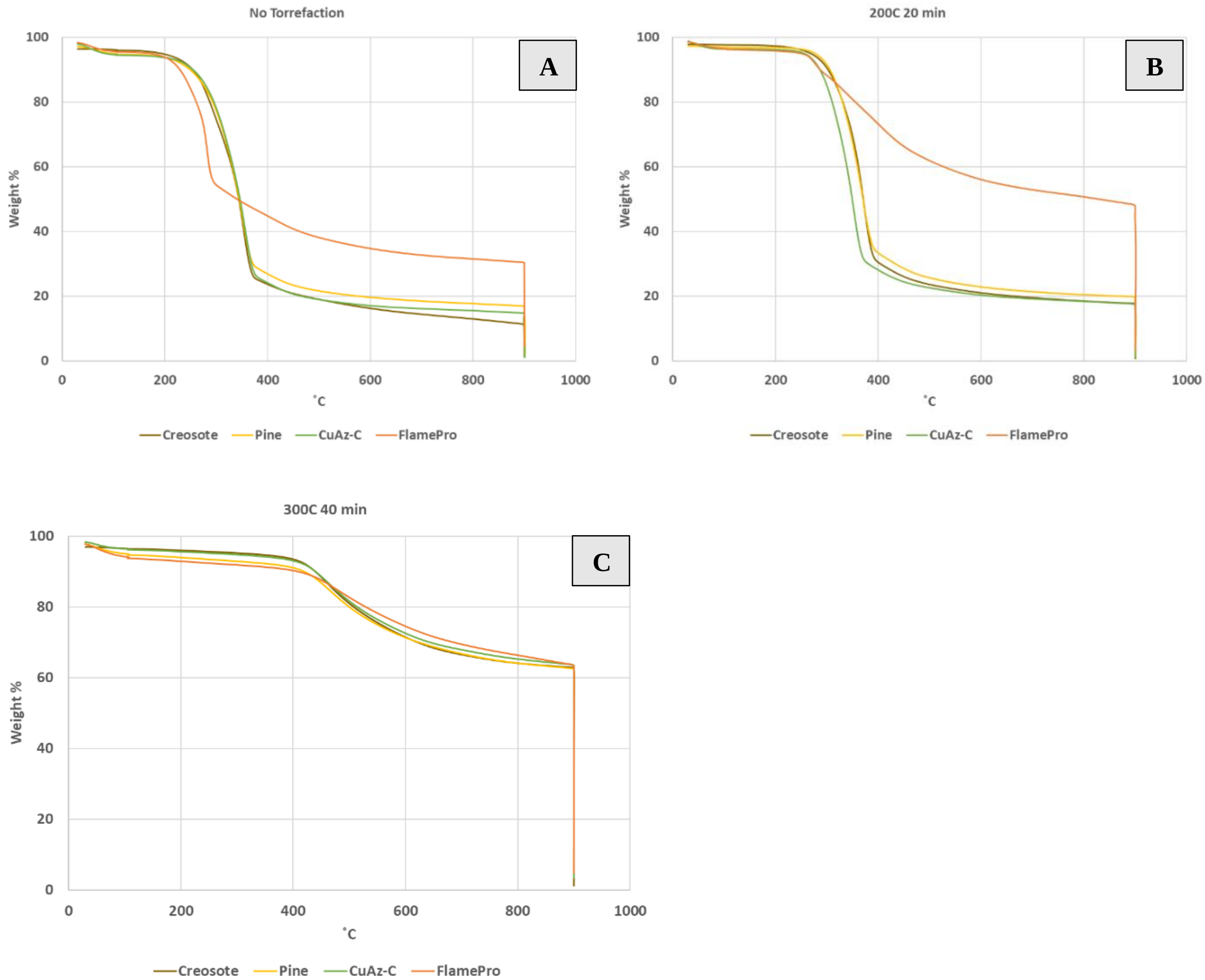


Figure 3.2 TGA curves for different torrefaction conditions, comparing differences in thermal degradation observed in samples from Pine lumber, Creosote, CuAz-C, and FlamePro treated lumber.

3.2.3 Thermal decomposition with respect to particle size

Grinding biomass is commercially useful for biomass intended to be gasified or co-combusted with coal. In a fluidized bed gasifier, particle size, density, and energy density can influence residence time and the behavior of a particle in the fluidized bed. For these reasons, the effects of particle sizes are of interest.

This section presents a comparative analysis of the treated samples based on their grinding properties and particle sizes. Initially, the effect of particle size on thermal stability was evaluated. Based on the results in Figure 3.3, only minor differences in thermal decomposition kinetics can be seen from the different particle sizes, e.g., from <.106mm to >1mm. Three sizes were compared, <.106mm, >.425mm, and >1mm. Sample sizes of <.106mm and >.425mm from all four samples decomposed almost identically, with only slight differences found in samples of particle size >1mm.

Differences observed in thermal decomposition with respect to particle size were minimal and majorly within acceptable experimental error. For this reason, no conclusions can be made from the results observed without further investigation of particle sizes.

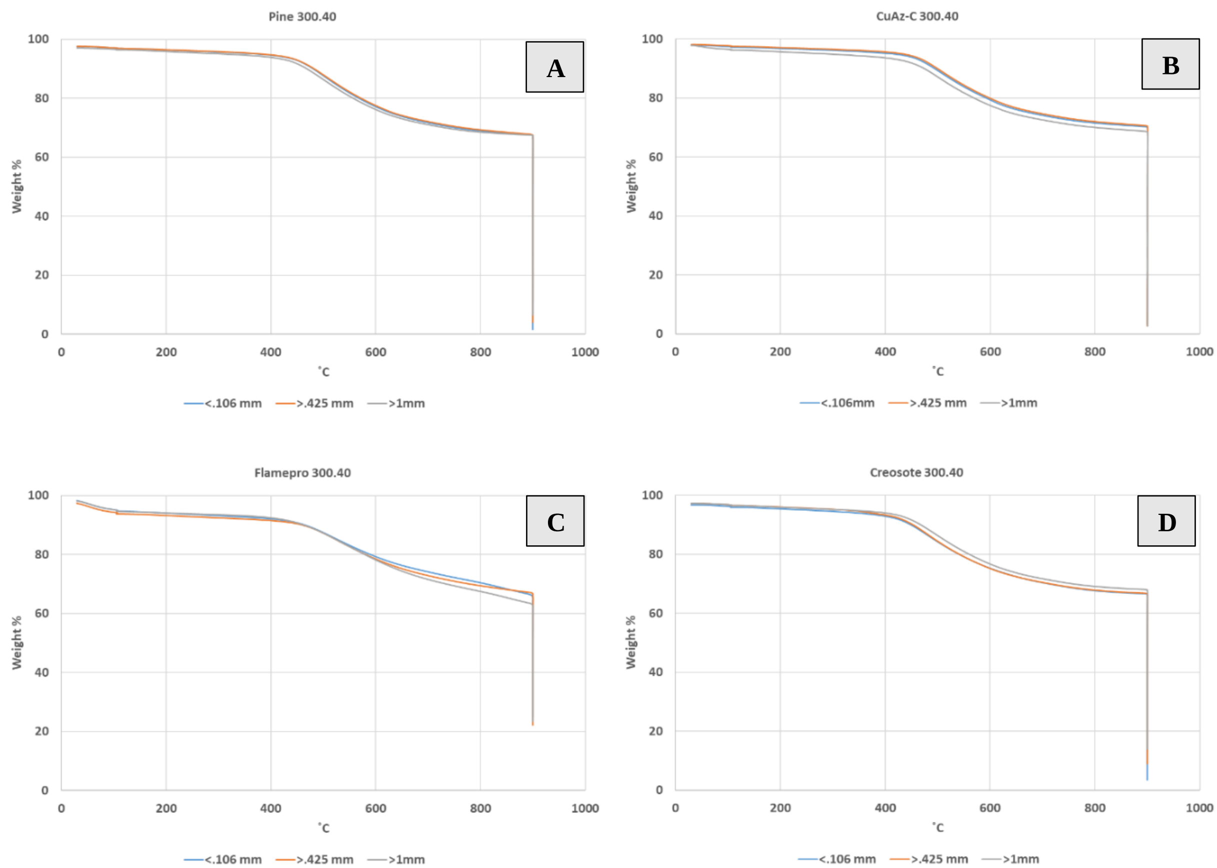


Figure 3.3 TGA curves for different types of lumber that were subject to torrefaction at 300˚C for 40 min, comparing differences in thermal degradation caused by differences in particle size.

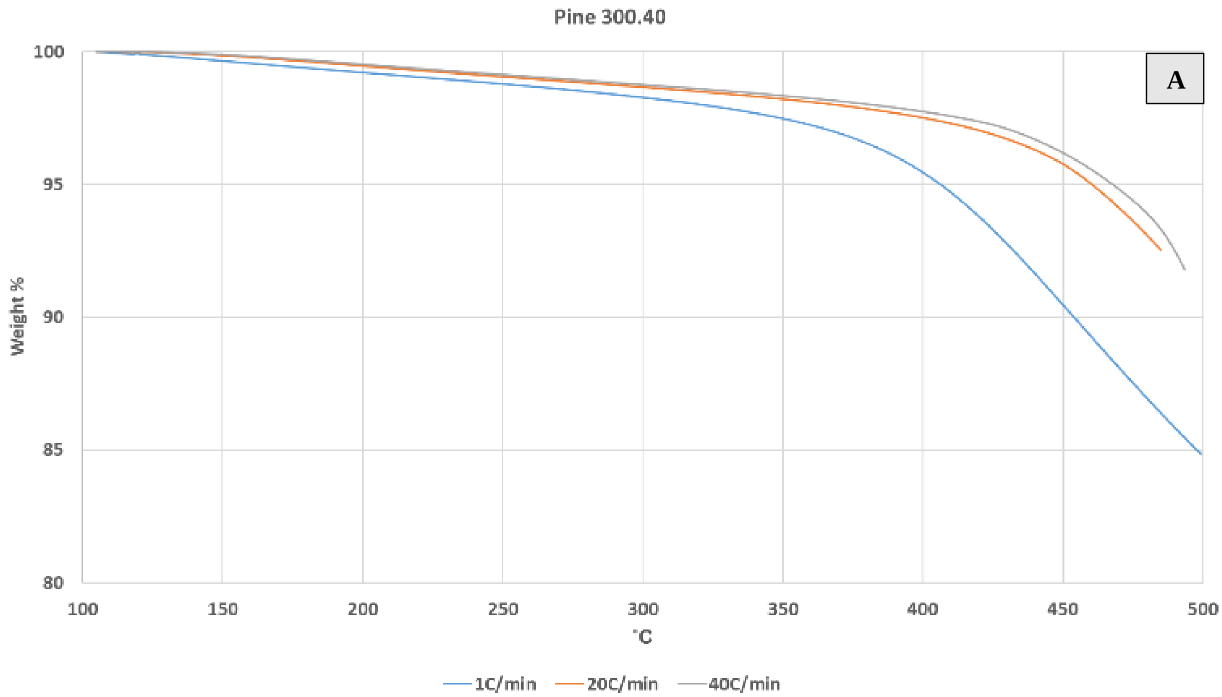
3.2.4 Thermal Decomposition Kinetics

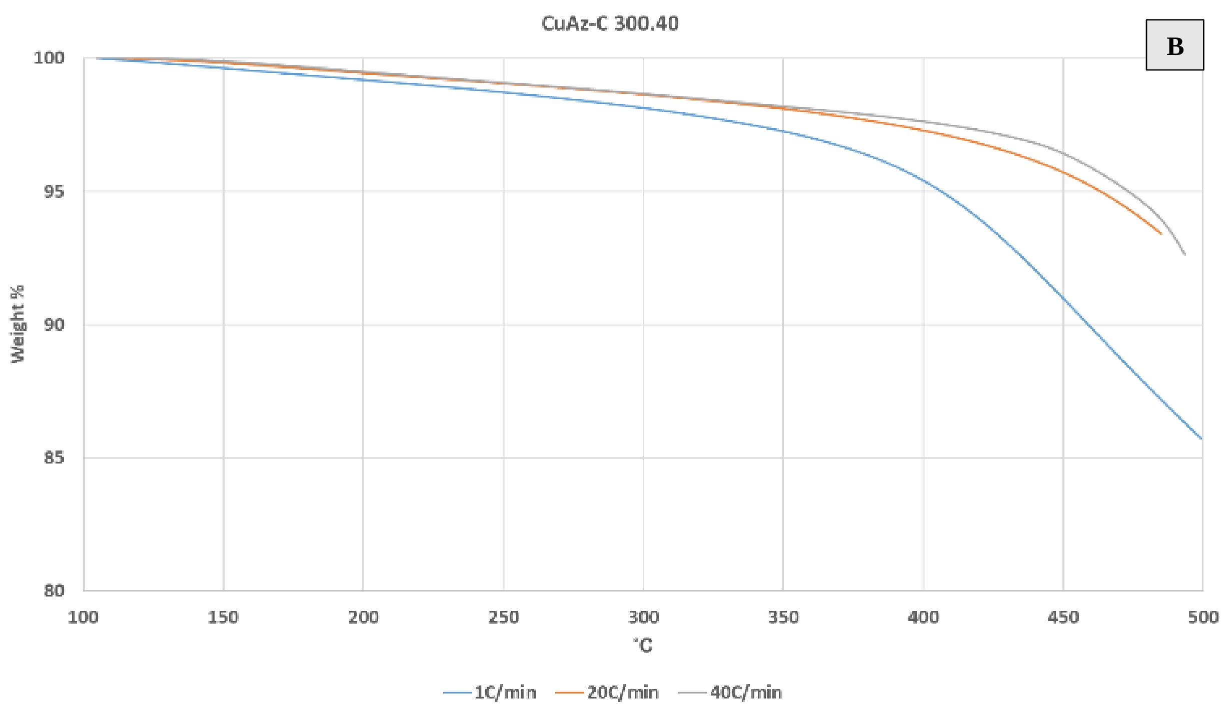
For kinetic analysis, ASTM E1641-18 was used to perform the Flynn-Wall-Ozawa method for calculating activation energy and reaction parameters. Modifications to this process were made; instead of calculating activation energy at one conversion point, usually α= 0.05, weight loss points were analyzed at 2wt.%, 4wt.%, 5wt.%, and 6wt.% weight loss. In all calculations the moisture was excluded from the weight loss points. This was done by setting the mass percentages at 105˚C as 100% of the mass and measuring the temperature where 2, 4, 5, and 6 percent mass loss occurred. These temperature points collected from the data displayed in Figure 3.4 are plotted as points in Figure 3.5, which are used to calculate the activation energies shown in Table 3.2. kinetics analysis investigates reaction rates and energy required to initiate the decomposition reactions associated with the mass loss points. This data is useful when considering industrial reactor conditions, such as gasification reactions.

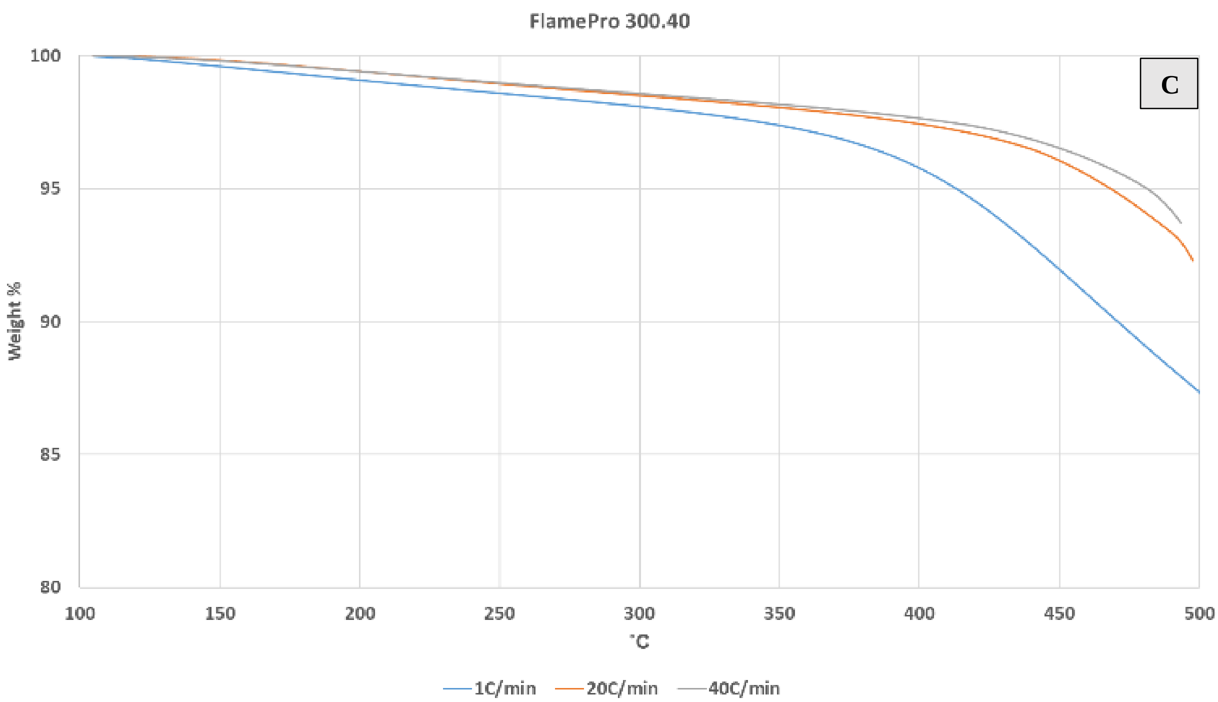
In Figure 3.4, as expected, the slowest heating rate, 1˚C/min, begins decomposition at the lowest temperatures. For heating rates of 20ºC/min and 40ºC/min the initial decompositions occur at higher temperatures.

From the slopes of trend lines plotted in Figure 3.5, activation energy is calculated using Eq. 2. As the rate of change, or slope, of these trendlines increases, the associated activation energy increases. R-squared values displayed for the trend lines show that the lines fit the data points and have a minimum of 0.99.

Figure 3.4: TGA curves for different biomass samples, comparing differences in heating rates of 1˚C/min, 20˚C/min, and 40˚C/min. This figure is made up of four graphs (A through D).


Pine 300.40
A
Weight %
100
95
90
85
80
100
150
200
250
300
350
400
450
500
˚C
1C/min
20C/min
40C/min


CuAz-C 300.40
B
Weight %
100
95
90
85
80
100
150
200
250
300
350
400
450
500
˚C
1C/min
20C/min
40C/min


FlamePro 300.40
C
Weight %
°C
1C/min
20C/min
40C/min

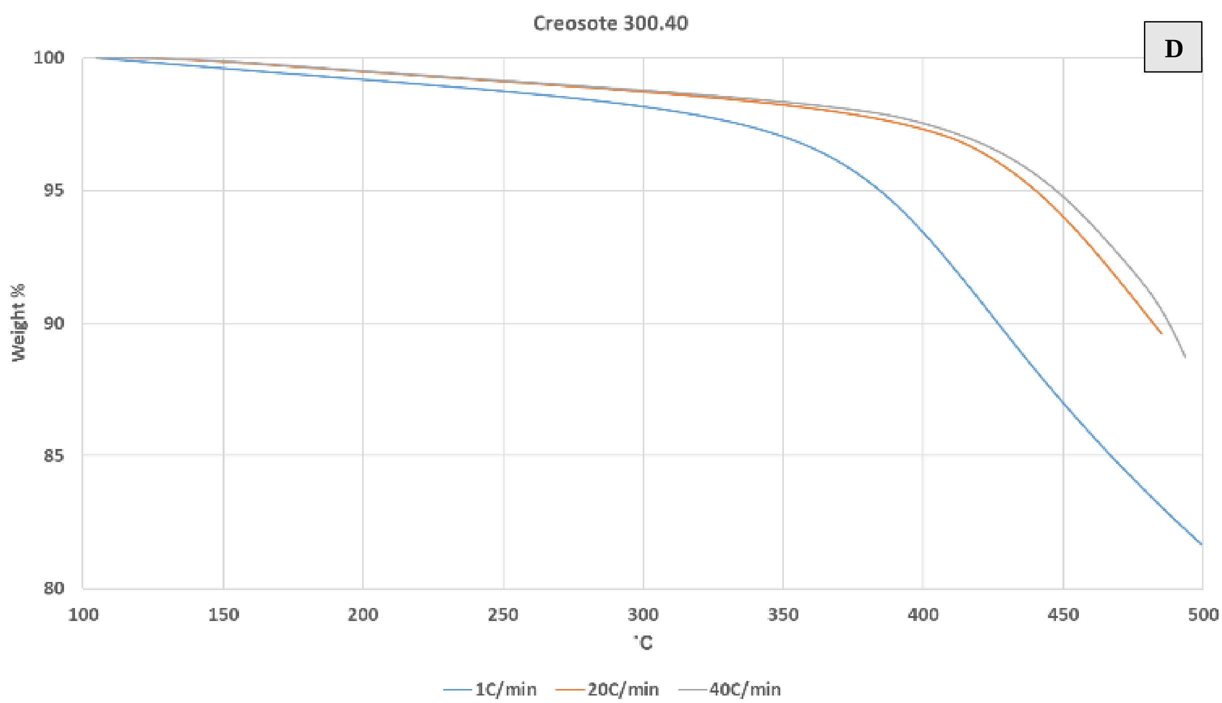
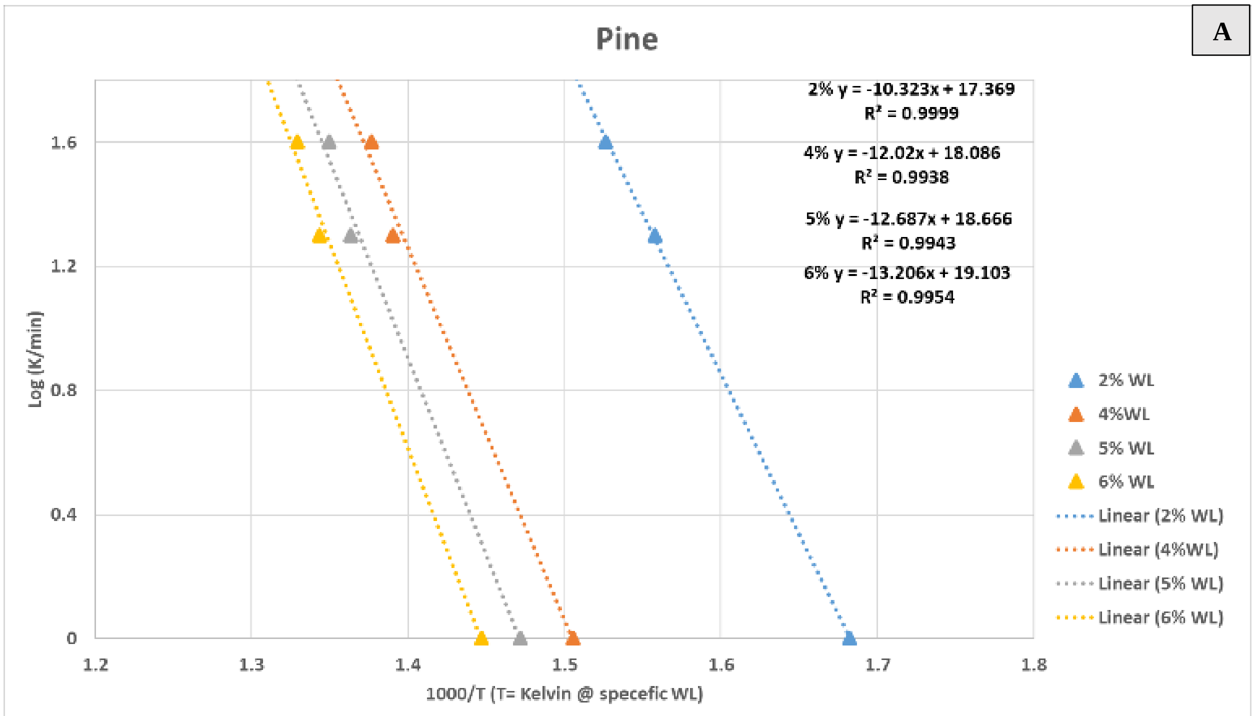
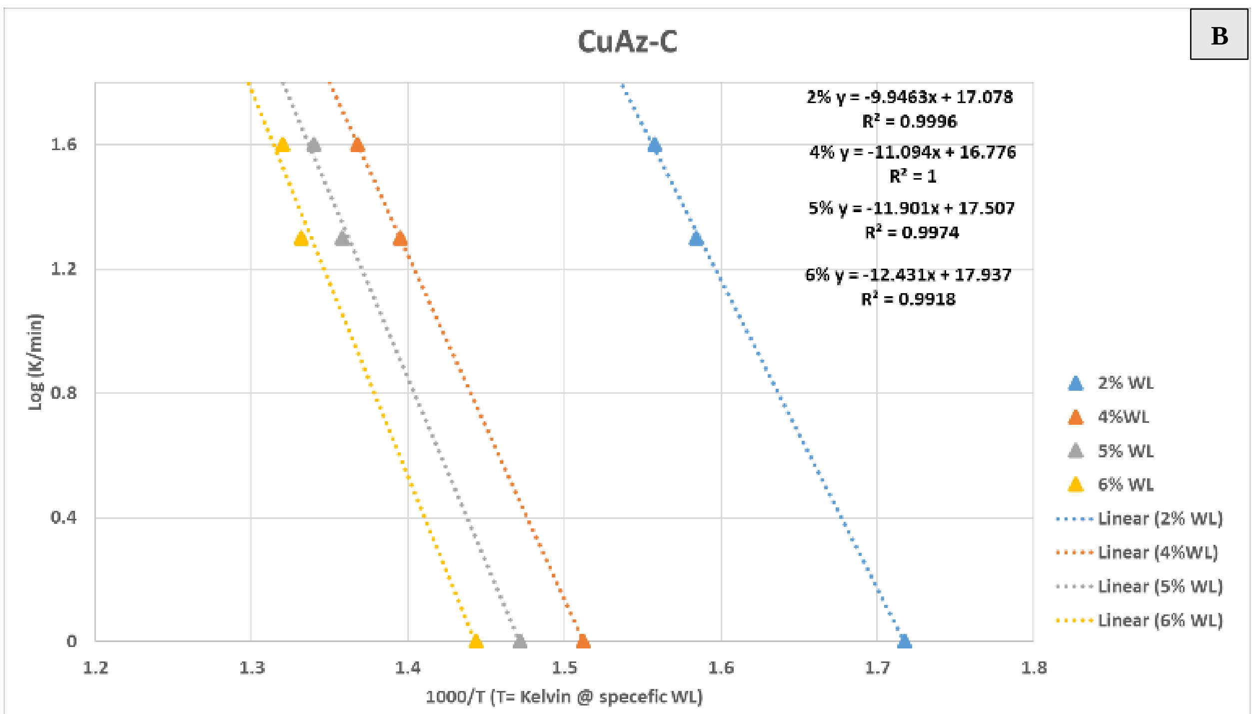
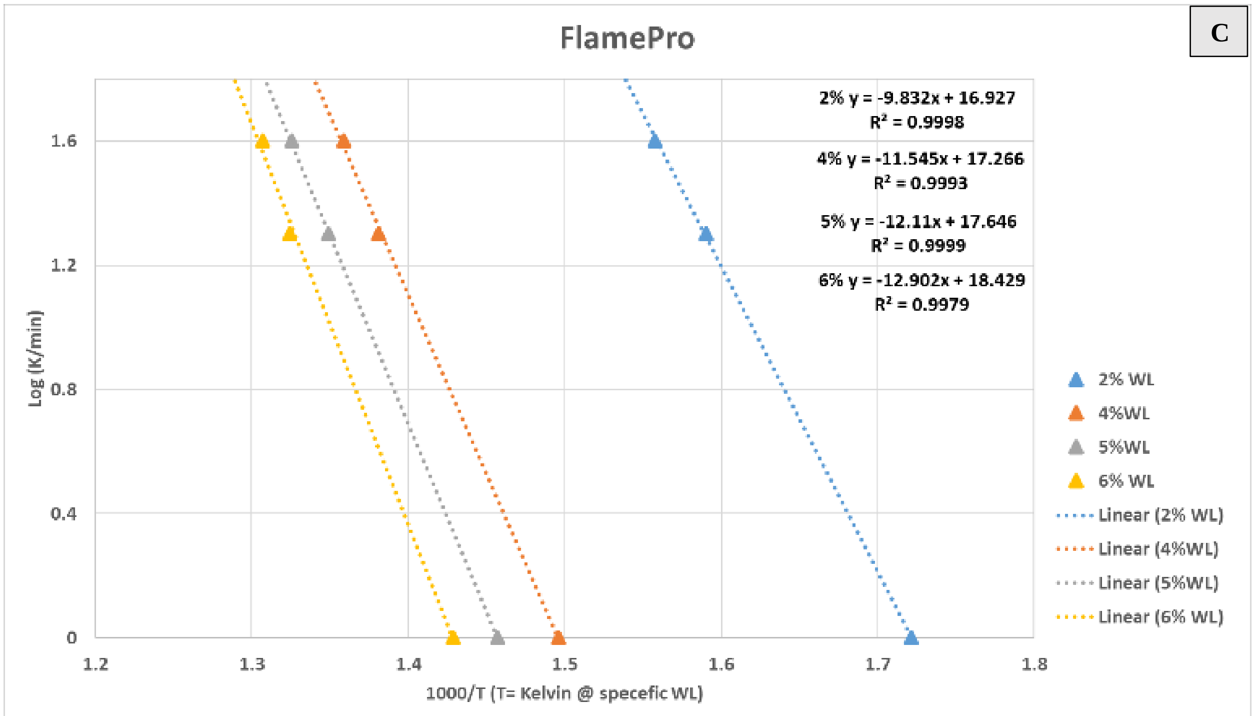

Creosote 300.40
D
Weight %
°C
1C/min
20C/min
40C/min

Figure 3.5 Log of heating rate (K/min) and inverse of T, temperature (K) at which specific mass loss has occurred. This figure is made of four graphs (A through D).


A
Pine
2% y = -10.323x + 17.369
R² = 0.9999
4% y = -12.02x + 18.086
R² = 0.9938
5% y = -12.687x + 18.666
R² = 0.9943
6% y = -13.206x + 19.103
R² = 0.9954
Log (K/min)
1000/T (T= Kelvin @ specefic WL)
2% WL
4%WL
5% WL
6% WL
Linear (2% WL)
Linear (4%WL)
Linear (5% WL)
Linear (6% WL)


B
CuAz-C
2% y = -9.9463x + 17.078
R² = 0.9996
4% y = -11.094x + 16.776
R² = 1
5% y = -11.901x + 17.507
R² = 0.9974
6% y = -12.431x + 17.937
R² = 0.9918
Log (K/min)
1000/T (T= Kelvin @ specefic WL)
2% WL
4%WL
5% WL
6% WL
Linear (2% WL)
Linear (4%WL)
Linear (5% WL)
Linear (6% WL)


C
FlamePro
2% y = -9.832x + 16.927
R² = 0.9998
4% y = -11.545x + 17.266
R² = 0.9993
5% y = -12.11x + 17.646
R² = 0.9999
6% y = -12.902x + 18.429
R² = 0.9979
Log (K/min)
1000/T (T= Kelvin @ specefic WL)
2% WL
4%WL
5%WL
6% WL
Linear (2% WL)
Linear (4%WL)
Linear (5%WL)
Linear (6% WL)

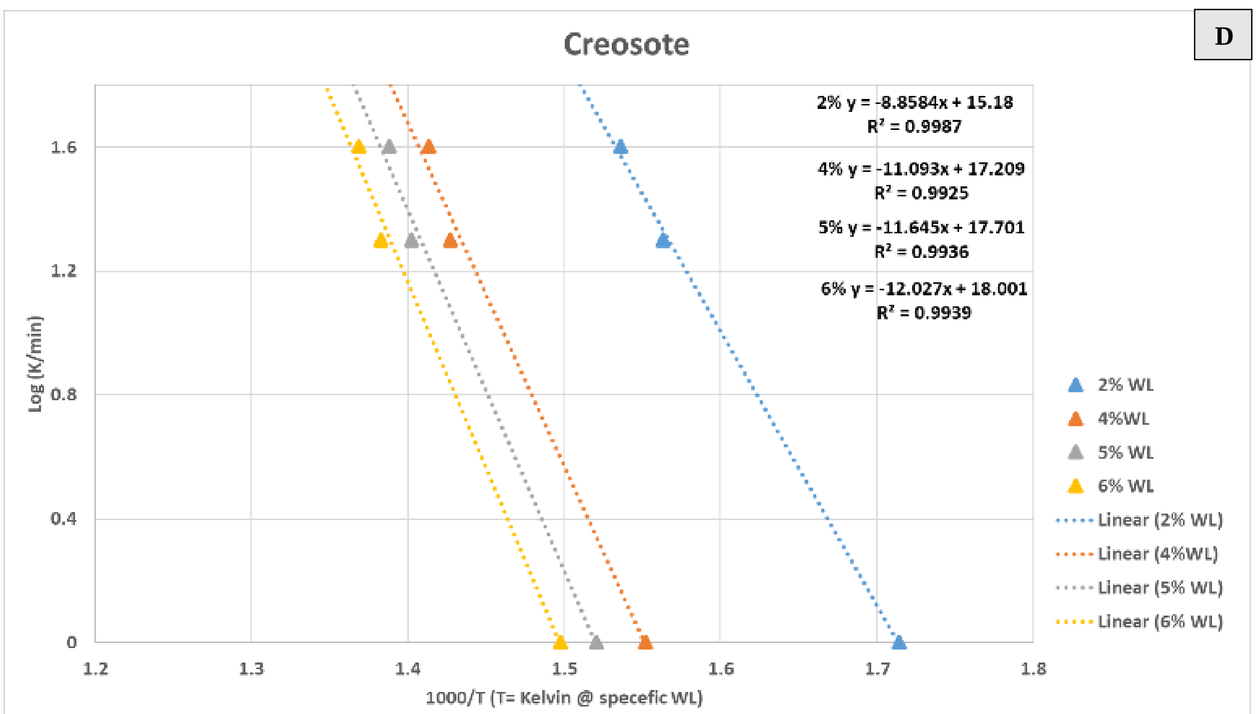

D
Creosote
2% y = -8.8584x + 15.18
R² = 0.9987
4% y = -11.093x + 17.209
R² = 0.9925
5% y = -11.645x + 17.701
R² = 0.9936
6% y = -12.027x + 18.001
R² = 0.9939
Log (K/min)
1000/T (T= Kelvin @ specefic WL)
2% WL
4%WL
5% WL
6% WL
Linear (2% WL)
Linear (4%WL)
Linear (5% WL)
Linear (6% WL)

Table 3.2

Overview of Temperatures at which selected weight percent were lost, as well as activation energy required to lose this selected weight percent.

Sample	Torrefaction Condition		**Heating Rate (˚C/min)**	**Temperature @ WL% (˚C)**			
	Temperature (˚C)	**Time (minutes)**		2%	4%	5%	6%
Pine	300	40	1	321.28	391.2	406.26	417.89
Pine	300	40	20	368.89	446.01	460.32	471.22
Pine	300	40	40	381.96	453.31	467.73	479.13
Activation Energy (kJ/mol)	N/A	N/A	N/A	**186.98**	**218.20**	**231.82**	**240.78**
Creosote	300	40	1	310.23	371.17	384.45	394.69
Creosote	300	40	20	366.62	427.58	440.04	450.05
Creosote	300	40	40	377.96	434.48	447.34	457.47
Activation Energy (kJ/mol)	N/A	N/A	N/A	**159.10**	**200.93**	**211.39**	**218.32**

Table 3.2 (continued).

CuAz-C	300	40	1	309.16	388.16	406.39	419.61
CuAz-C	300	40	20	358.02	443.56	463.29	477.75
CuAz-C	300	40	40	368.93	458.09	473.25	484.5
Activation Energy (kJ/mol)	N/A	N/A	N/A	**180.55**	**202.72**	**217.94**	**228.15**
FlamePro	300	40	1	307.8	395.36	413.07	426.69
FlamePro	300	40	20	355.55	451.1	468.22	481.93
FlamePro	300	40	40	368.87	462.95	481.28	491.94
Activation Energy (kJ/mol)	N/A	N/A	N/A	**178.48**	**210.96**	**222.26**	**236.79**

In Table 3.2 and Figure 3.4 both, it is observed that the activation energy of the Pine control sample was the highest across all four weight loss points. FlamePro has the second highest activation energy behind Pine in 4%, 5%, and 6% weight loss points, and was very similar to the CuAz-C treated sample at 2% weight loss. Creosote has the lowest activation energy of all samples across every weight loss point. Based on the unique TGA thermograms for FlamePro it was anticipated that it might have the lowest activation energy. Based on initial TGA results showing thermal decomposition, one would expect Pine and Creosote's activation energies to be more similar than what is observed.

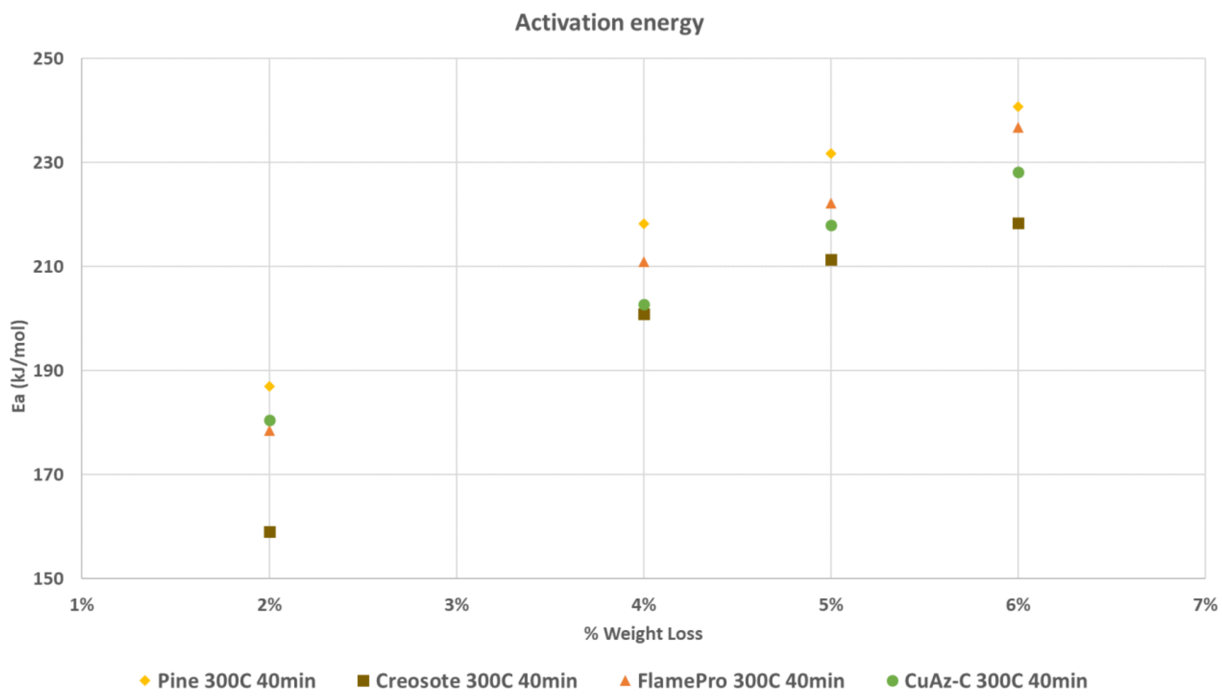


Figure 3.6 Activation energy

3.3 Effect of torrefaction on elemental composition

3.3.1 Inorganic Elements

Changes in torrefaction intensity can also cause differences in the inorganic composition, with some elements exiting with the volatiles during torrefaction, but most inorganic elements remain in the residue. In this second instance, the absolute value of the thermally stable elements does not change, but their relative mass percentage of the residues will increase due to the loss of the organic fractions. Examples of thermally stable elements increasing can be seen in copper in CuAz-C and phosphorus in FlamePro. In both cases, the element roughly doubles its mass percentage from torrefaction at 300˚C for 40min. The sulfur present in the creosote sample is an example of an element that may be volatilizing during torrefaction; it is present in no torrefaction and 200˚C for 20 min but not present in samples torrefied at 300˚C for 40 min.

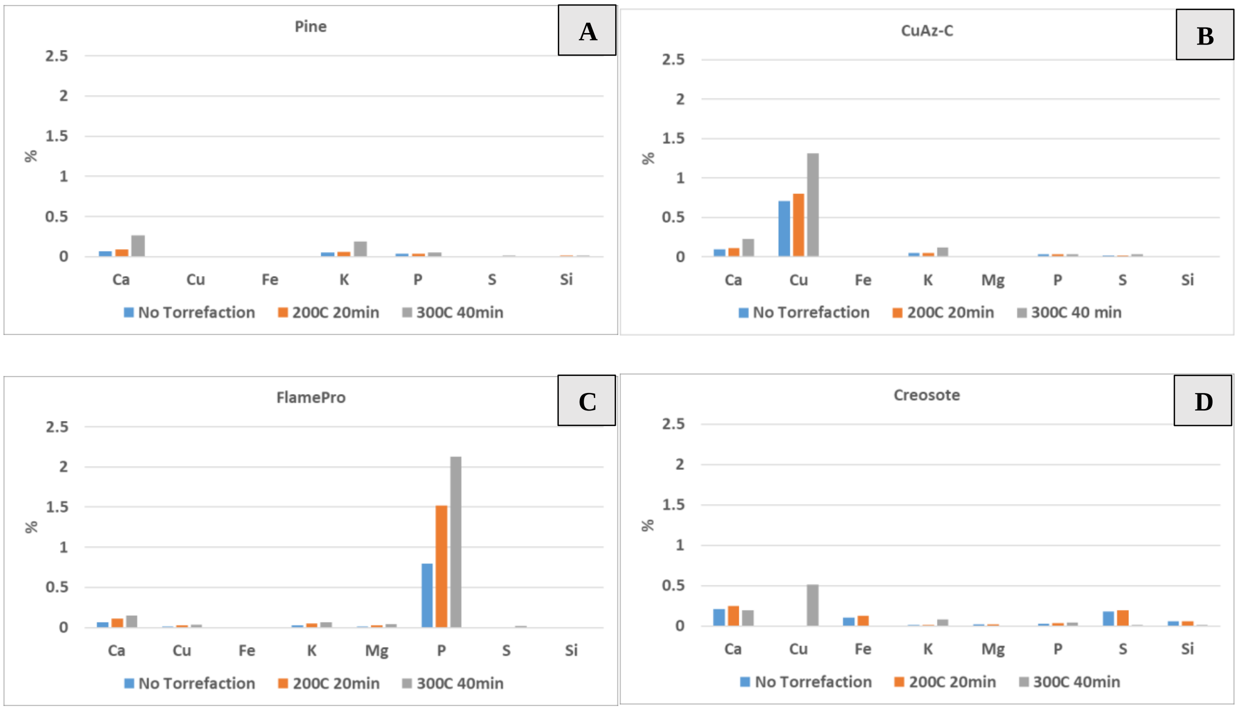


Figure 3.7 Comparison of comment inorganic elements in different types of treated lumber before and after torrefaction as determined by XRF analysis.

The inorganic content of a variety of wood and herbaceous biomass has been found to vary with particle size. Table 3.5 shows that in these samples it can be observed that there is an increase in ash's mass percentage as particle size decreases. This prior work raises the question of how the ash might be distributed for the torrefied materials with different particles sizes. This was also observed for the torrefied samples where the smaller particles retain more inorganic elements than larger particles. Examples are seen in Figure 3.8, with the copper in CuAz-C, phosphorus in FlamePro, and calcium, iron, and sulfur in Creosote.

Alternatively, the impact decreased particle size has on density could help to explain results in Figure 3.8. Another possibility is that the amount of void space in the materials decreases with reducing particle size, leading to a denser particle. Hence, more ash is likely to be obtained in materials of smaller particles instead of larger particles. This decreasing void space could be interpreted by the results obtained and presented in Figure 3.8. The amount of these elements also varied in these samples depending on the type of lumber treatment given to the material.

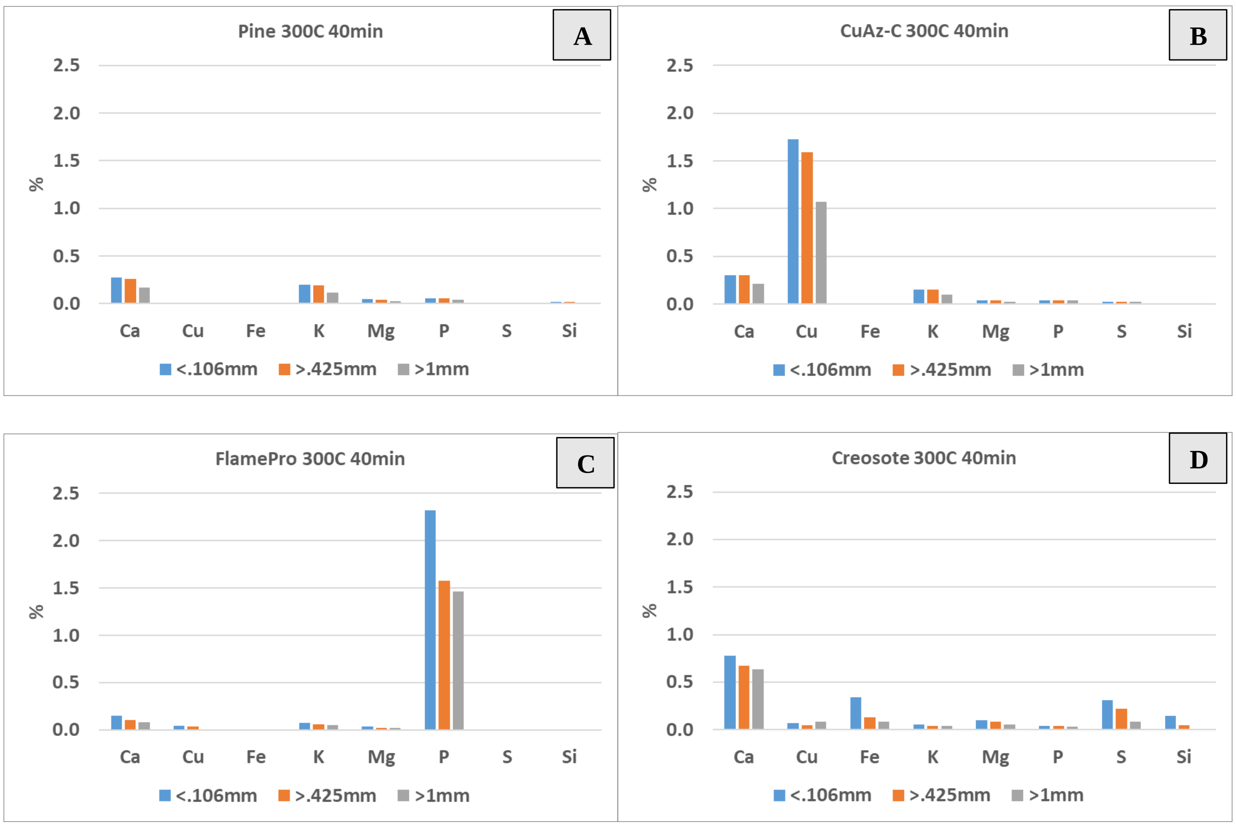


Figure 3.8 Effects of particle size on the composition of selected elements from different types of lumber torrefied at 300˚C for 40 min.

3.3.2 Organic Elements

Solid fuels are often compared to one another based on their organic content. Carbon is known as an energy-dense element in solid biofuels, so measuring the carbon ratio to the other organic components present in the sample will indicate its performance as a fuel. Therefore, Van Krevlin diagrams like the one shown in Figure 3.9 are commonly used to compare solid fuels such as coal. By measuring biomass's organic content, we can compare its expected performance as a fuel to well-known alternative fuels such as lignite, coal, and anthracite.

Torrefaction is known to dehydrate and decompose hemicellulose first, followed by lignin and cellulose decomposition, leaving behind carbon rich residues. For most torrefaction conditions the highest majority of the three components that remain after torrefaction is cellulose. [1] Therefore, torrefaction products have increased C/H and C/O ratios. [1] Table 3.3 shows the relationship between torrefaction conditions and the carbon, hydrogen, nitrogen, and oxygen mass percentages of the residues. Figure 3.9 is a Van Krevlin diagram displaying the impact of varying torrefaction conditions on the O/C and H/C ratios. The Pine and Creosote samples showed a modest increase of approximately 50 wt.% to 55 wt.% in carbon with torrefaction at 200˚C for 20 min, and then a significant increase in the carbon content to almost 75 wt.% with the more severe torrefaction conditions. For CuAz-C, there was essentially no change in the carbon content with torrefaction at 200C for 20 min, but torrefaction at 300˚C for 40 min produced a residue with 74 wt.% carbon. FlamePro, showed unusual behavior with the less severe conditions producing a significant increase (64 wt.%) and then the more severe conditions produced a residue with about 50 wt.%.

The phosphorus in FlamePro's chemical treatment is designed to promote char which is consistent with the results for the less severe conditions (200˚C for 20 min).

Table 3.3

Overview of samples, torrefaction conditions, Carbon, Hydrogen, Nitrogen, and Oxygen as found in C/H/N/O analysis. Comparing differences in these concentrations as a result of differing torrefaction conditions.

Sample	Torrefaction Condition		Carbon (wt.%)	Hydrogen (wt.%)	Nitrogen (wt.%)	Oxygen (wt.%)
	Temperature (˚C)	**Time (minutes)**				
Pine	0	0	50.0	6.2	0.1	43.7
Pine	200	20	54.3	5.9	0.0	39.9
Pine	300	40	75.6	4.1	0.2	20.2
Creosote	0	0	49.6	5.7	0.1	44.6
Creosote	200	20	54.5	5.7	0.1	39.7
Creosote	300	40	72.6	4.0	0.3	23.1
CuAz-C	0	0	50.9	5.9	0.06	43.1
CuAz-C	200	20	51.0	5.5	0.02	43.5
CuAz-C	300	40	73.9	3.8	0.1	22.1
FlamePro	0	0	46.9	6.0	0.6	46.6
FlamePro	200	20	64.4	4.9	0.9	29.7
FlamePro	300	40	48.1	3.2	0.5	48.3

Figure 3.9 is a Van Krevlin diagram comparing torrefaction's impacts on O/C and H/C ratios of biomass samples as well as those of lignite, coal, and anthracite. Lowering O/C and H/C ratios improve biomass's qualities as a fuel, so sample fuel qualities improve as they progress

from the top right to bottom left portions of this graph. The values for Pine, Creosote, CuAz-C, and FlamePro were collected in this work. While the values for peat, lignite, coal, and anthracite were found in literature.[32] As seen in Figure 3.9, samples' O/C and H/C ratios improved as torrefaction intensity increased, with the exception of FlamePro torrefied at 300˚C for 40 min.

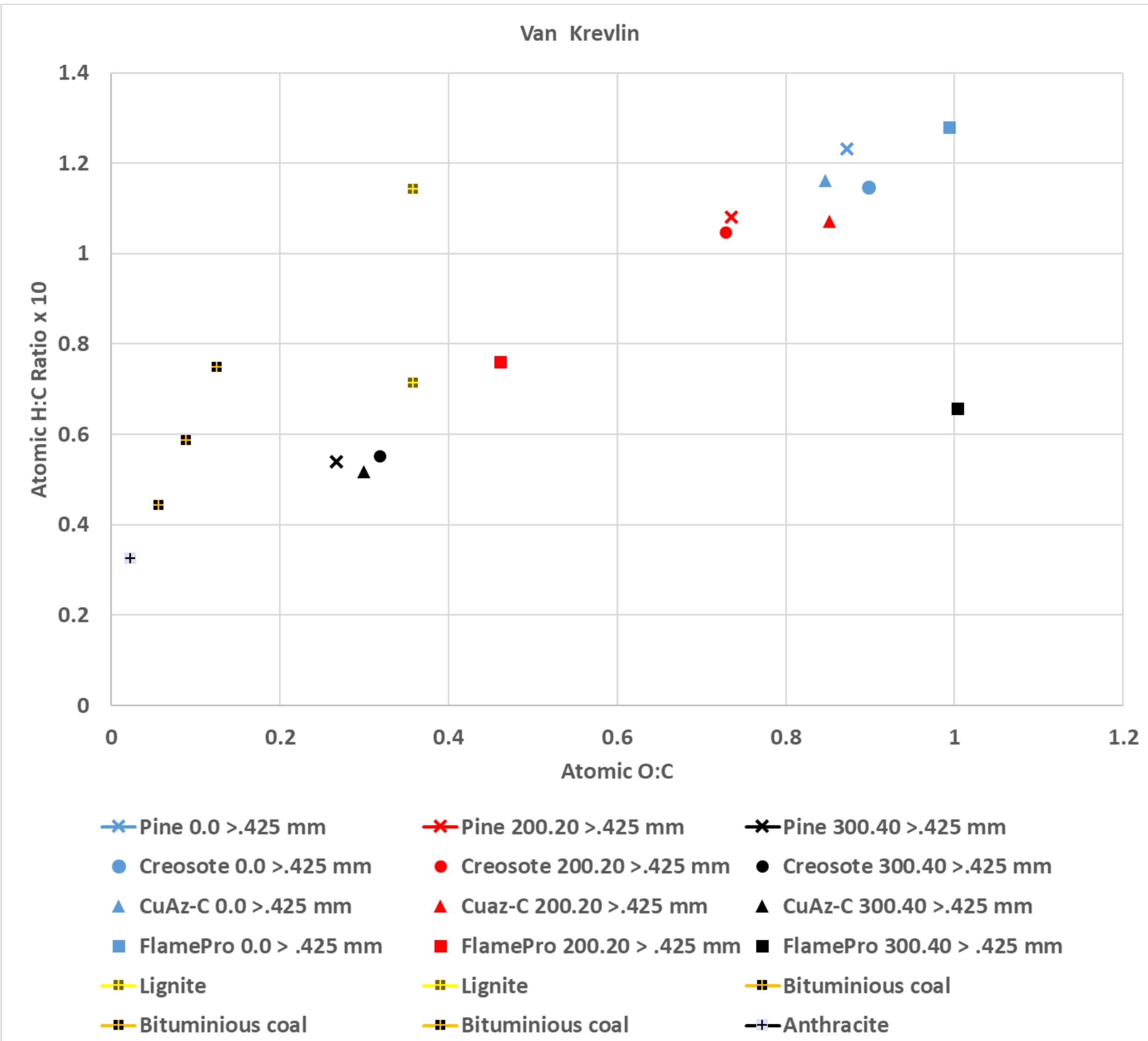


Figure 3.9 Van Krevlin diagram comparing samples from different types of lumber and torrefaction conditions. The Y-axis is the atomic hydrogen-to-carbon ratio multiplied by 10, and X-axis is the atomic Oxygen to Carbon ratio.

Particle size is a key operational parameter for fluidized bed reactors. The chemical composition as a function of particle sizes was also studied.

Using the Pine samples torrefied at 300˚C for 40min, fractions between <.106mm and >.425mm, and greater than >1mm were isolated. The <.106mm and >.425mm contained roughly 6wt.% more carbon than the other sizes. Based on this, of torrefied samples the effects of particle size were modest.

Table 3.4

Overview of samples, particle size, torrefaction conditions, and organic contents of Carbon, Hydrogen, Nitrogen, and Oxygen as found in C/H/N/O analysis. Comparing differences in these concentrations as a result of differing particle sizes.

		Torrefaction Condition					
Sample	**Size (mm)**	**Temperature (˚C)**	**Time (minutes)**	**Carbon (%)**	**Hydrogen (%)**	**Nitrogen (%)**	**Oxygen (%)**
Pine	<.106	300	40	73.6	4.2	0.7	21.5
Pine	>.425	300	40	73.4	3.9	0.6	22.1
Pine	>1	300	40	79.5	4.2	0.7	15.6

3.4 Effect of torrefaction on fuel characteristics of biomass

3.4.1 Proximate Analysis

Proximate analysis of biomass is used as an indication of a material's potential as a fuel. Moisture is evaporated during gasification and combustion so proximate is a good indicator. Volatile matter produced from a biomass fuel are commonly water from dehydration reactions, CO_2, and oxygen rich fragments which have relatively low energy content. Due to carbon's high energy density, maximizing fixed carbon is economically attractive. Ash content is analyzed because it contains many of the metals and inorganics in untreated biomass and affects reactor efficiency. Alkaline earth metals, such as sodium and potassium, are known to affect the decomposition of the carbohydrates in biomass.[33] Ash also can accrue in gasification reactor systems, causing the need for occasional cleaning and maintenance.

Thermogravimetric analysis was used to calculate the proximate analysis data. Torrefaction is a known process for lowering moisture, decreasing volatile matter, and increasing fixed carbon. These effects are seen with the chemically treated wood samples used in this work. As seen in Table 3.5, the torrefied samples' moisture content was lower than those of the original starting materials. The moisture content of FlamePro was observed to be the highest, possibly due to the phosphorus in its chemical lumber treatment. As the intensity of torrefaction increases, the percentage of volatile matter decreases, as was expected, due to increased torrefaction temperature. For Pine, CuAz-C, and Creosote, a slight decrease in volatile matter occurred after torrefaction at 200˚C for 20 min, with a much more significant decrease in volatile matter after torrefaction at 300˚C for 40 min. FlamePro volatile matter decreased by roughly 17% after a torrefaction of 200˚C for 20 min and decreased roughly 18% more from torrefaction at 200˚C for 20 min to 300˚C for 40 min. Fixed carbon also behaved as expected, with increased fixed carbon content percentage as torrefaction intensity increased. Fixed carbon increased only slightly from no torrefaction to 200˚C for 20 min but increased significantly after torrefaction of 300˚C for 40 min; FlamePro is an exception to this with significant increases in fixed carbon after both 200˚C for 20 min and 300˚C for 40 min. Ash percentages increased with increased torrefaction intensities for Pine and CuAz-C; for FlamePro and creosote ash, percentages were highest when samples were not torrefied.

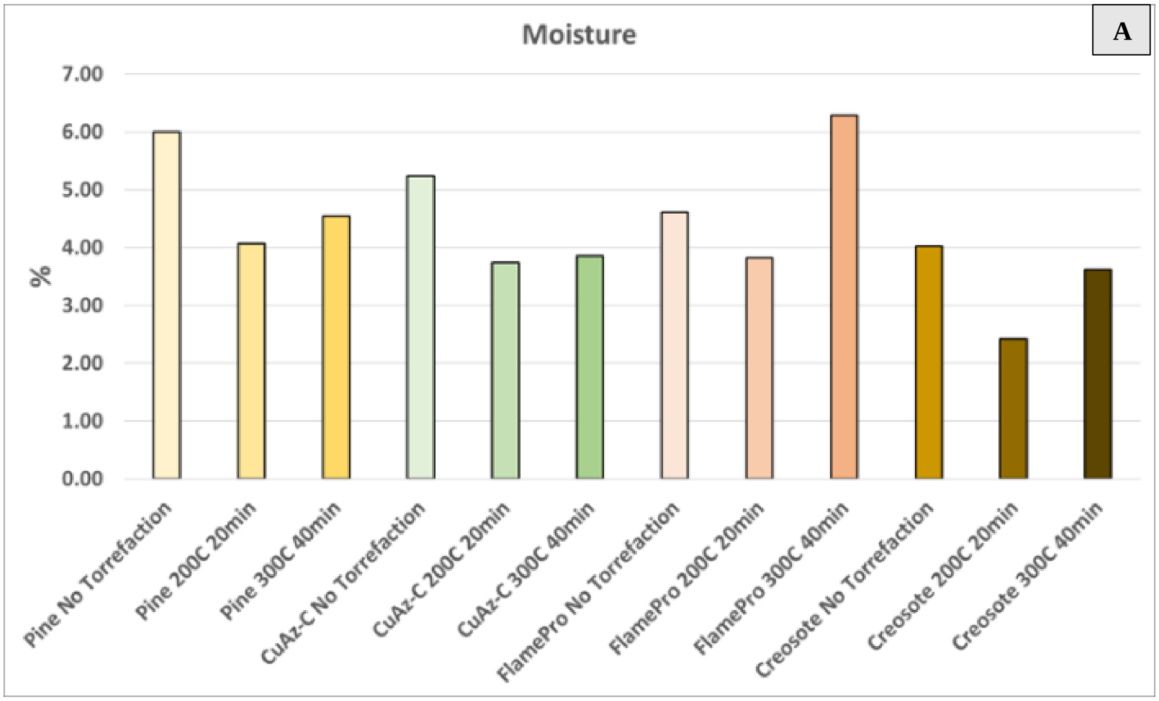
Moisture and ash percentages varied between samples and conditions, so results are inconclusive. However, fixed carbon and volatiles behaved as expected; fixed carbon rose with torrefaction intensity, and volatiles decreased with increased torrefaction. Therefore, torrefaction proved to be beneficial in these regards.

Table 3.5

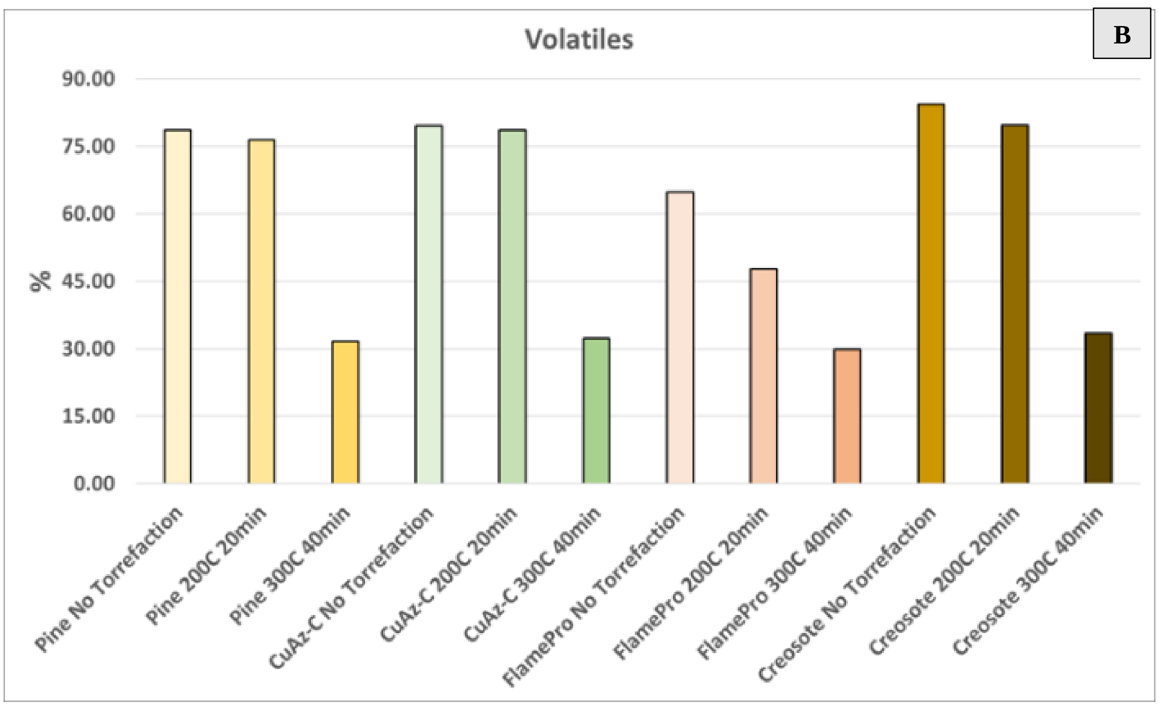
Summary of the effects of torrefaction conditions on proximate analysis as determined by TGA experiments.

Sample	Torrefaction		**Moisture (%)**	**Volatiles (%)**	**Fixed Carbon (%)**	**Ash (%)**
	Temperature (˚C)	**Time (minutes)**				
Pine	0	0	6.00	78.63	14.56	0.81
Pine	200	20	4.07	76.45	17.93	1.55
Pine	300	40	4.55	31.63	61.07	2.75
Creosote	0	0	4.02	84.41	9.66	1.86
Creosote	200	20	2.42	79.75	16.86	0.96
Creosote	300	40	3.62	33.42	61.72	1.24
CuAz-C	0	0	5.24	79.54	13.20	1.69
CuAz-C	200	20	3.74	78.61	16.10	1.56
CuAz-C	300	40	3.85	32.35	60.30	3.49
FlamePro	0	0	4.61	64.86	24.84	5.70
FlamePro	200	20	3.82	47.70	44.69	3.79
FlamePro	300	40	6.28	29.86	58.97	4.89

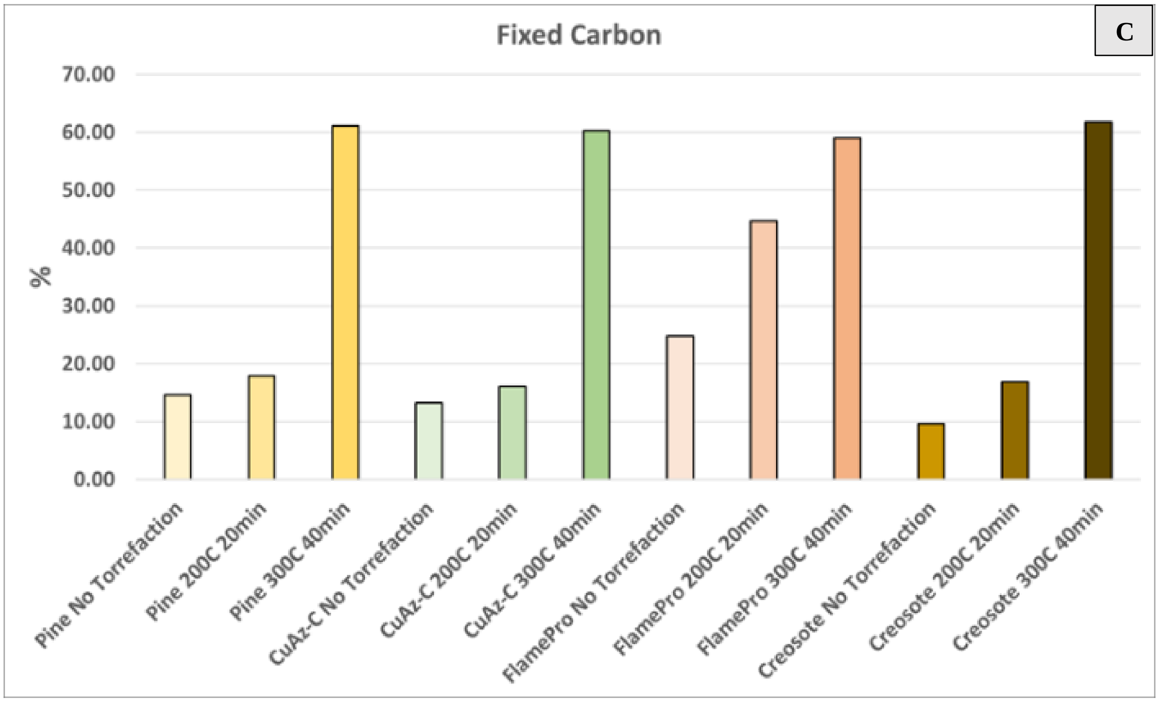
Figure 3.10 Comparisons of (A) moisture, (B) volatile, (C) fixed carbon, and (D) ash content for non-torrefied and torrefied samples

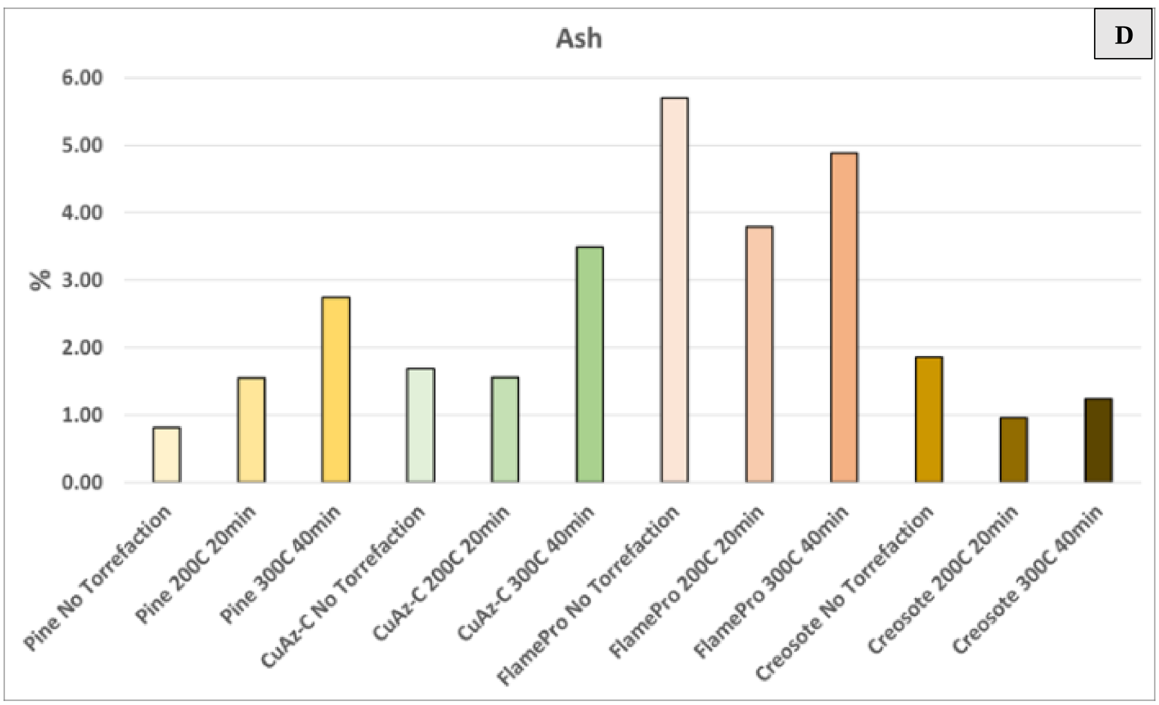


A
Moisture
%
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
Pine No Torrefaction
Pine 200C 20min
Pine 300C 40min
CuAz-C No Torrefaction
CuAz-C 200C 20min
CuAz-C 300C 40min
FlamePro No Torrefaction
FlamePro 200C 20min
FlamePro 300C 40min
Creosote No Torrefaction
Creosote 200C 20min
Creosote 300C 40min



B
Volatiles
%
90.00
75.00
60.00
45.00
30.00
15.00
0.00
Pine No Torrefaction
Pine 200C 20min
Pine 300C 40min
CuAz-C No Torrefaction
CuAz-C 200C 20min
CuAz-C 300C 40min
FlamePro No Torrefaction
FlamePro 200C 20min
FlamePro 300C 40min
Creosote No Torrefaction
Creosote 200C 20min
Creosote 300C 40min


C
Fixed Carbon
%
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
Pine No Torrefaction
Pine 200C 20min
Pine 300C 40min
CuAz-C No Torrefaction
CuAz-C 200C 20min
CuAz-C 300C 40min
FlamePro No Torrefaction
FlamePro 200C 20min
FlamePro 300C 40min
Creosote No Torrefaction
Creosote 200C 20min
Creosote 300C 40min


D
Ash
%
6.00
5.00
4.00
3.00
2.00
1.00
0.00
Pine No Torrefaction
Pine 200C 20min
Pine 300C 40min
CuAz-C No Torrefaction
CuAz-C 200C 20min
CuAz-C 300C 40min
FlamePro No Torrefaction
FlamePro 200C 20min
FlamePro 300C 40min
Creosote No Torrefaction
Creosote 200C 20min
Creosote 300C 40min

3.4.2 Caloric Content

Caloric content was measured using a Parr model 1108 bomb calorimeter using one gram of dried sample. Torrefaction is utilized to increase biomass's energy density of biomass, so an increase in energy density was expected with increased torrefaction. Decreasing the mass and increasing the energy density of biomass is critical to reducing transportation costs for delivered energy.

Table 3.6 and Figure 3.11 confirmed this increase in energy density with increased torrefaction intensity. Torrefaction at 200˚C for 20 min resulted in smaller increase in the energy density than torrefaction at 300˚C for 40 min, with FlamePro samples as the only exception. Pine increased energy density by 20 wt. % after 200˚C for 20 min and 62 wt.% after 300˚C for 40 min. CuAz-C increased energy density by 9 wt. % after 200˚C for 20 min and 54 wt. % after 300˚C for 40min. Creosote increased energy density by 9 wt. % after 200˚C for 20min and 55 wt. % after 300˚C for 40min. FlamePro increased energy density by 32 wt. % after 200˚C for 20min and 37 wt. % after 300˚C for 40 min.

Torrefaction successfully and significantly raised the caloric content of the biomass analyzed. FlamePro is the only sample that benefitted from a torrefaction at 200˚C for 20min to a greater degree than at 300˚C for 40 min, suggesting a sufficient torrefaction of this sample could be carried out at conditions less severe than 300˚C for 40min.

Table 3.6

Overview of samples, torrefaction conditions, caloric content, percent increase in embodied energy, remaining mass fraction, and energy yield.

Sample	Torrefaction		**Caloric content (cal/g)**	**Remaining Mass (1-AWL%) (%)**	**Energy Yield (cal/g * mass fraction)**
	Temperature (˚C)	**Time (minutes)**			
Pine	0	0	4048	1	4048
Pine	200	20	4845	.85	4118.3
Pine	300	40	6539	.324	2118.6
Creosote	0	0	4399	1	4399
Creosote	200	20	4797	.86	4125.4
Creosote	300	40	6803	.333	2265.4
CuAz-C	0	0	4101	1	4101
CuAz-C	200	20	4463	.87	3882.81
CuAz-C	300	40	6328	.357	2259.1
FlamePro	0	0	4078	1	4078
FlamePro	200	20	5374	.64	3439.4
FlamePro	300	40	5572	.513	2858.4

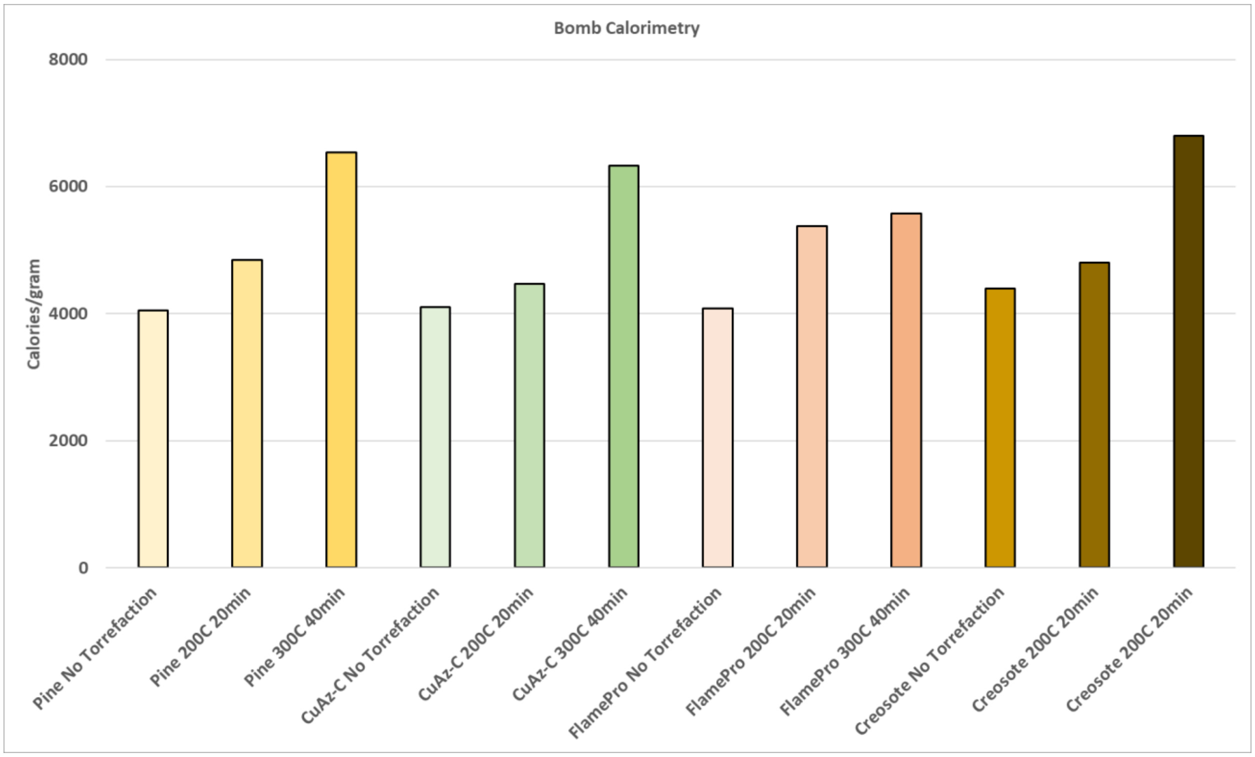


Figure 3.11 Column chart created from data collected from bomb calorimetry experiments compares the calorific content of different lumber types and torrefaction conditions.

3.5 Effect of particle size on fuel characteristics on torrefied biomass

3.5.1 Proximate Analysis

Proximate analysis comparing compositions of different particle sizes, as presented in Table 3.7, was carried out using TGA. From these results, it can be observed that there are slight variations in the moisture content, volatiles, and fixed carbon but with no clear trend. Ash percentages also had relatively minor differences.

Table 3.7

Overview of samples, torrefaction condition, particle size, and proximate analysis as found in TGA experiments. Comparing differences in moisture, volatile, fixed carbon, and ash content with respect to different particle sizes.

Sample	Torrefaction		**Size (mm)**	**Moisture (%)**	**Volatiles (%)**	**Fixed Carbon (%)**	**Ash (%)**
	Temperature (˚C)	**Time (minutes)**					
Pine	300	40	<.106	3.2	29.1	66.7	1.0
Pine	300	40	>.425	3.1	29.0	67.2	0.7
Pine	300	40	> 1	3.6	28.8	67.0	0.5
Creosote	300	40	<.106	4.1	29.3	63.0	3.7
Creosote	300	40	>.425	3.5	29.7	65.2	1.7
Creosote	300	40	> 1	3.5	28.4	66.5	1.6
CuAz-C	300	40	<.106	2.8	26.9	66.8	3.5
CuAz-C	300	40	>.425	2.5	26.8	68.1	2.6
CuAz-C	300	40	> 1	3.8	27.5	66.5	2.3
FlamePro	300	40	<.106	5.3	28.1	60.6	6.0
FlamePro	300	40	>.425	6.3	26.5	62.2	5.0
FlamePro	300	40	> 1	5.4	30.9	59.2	4.5

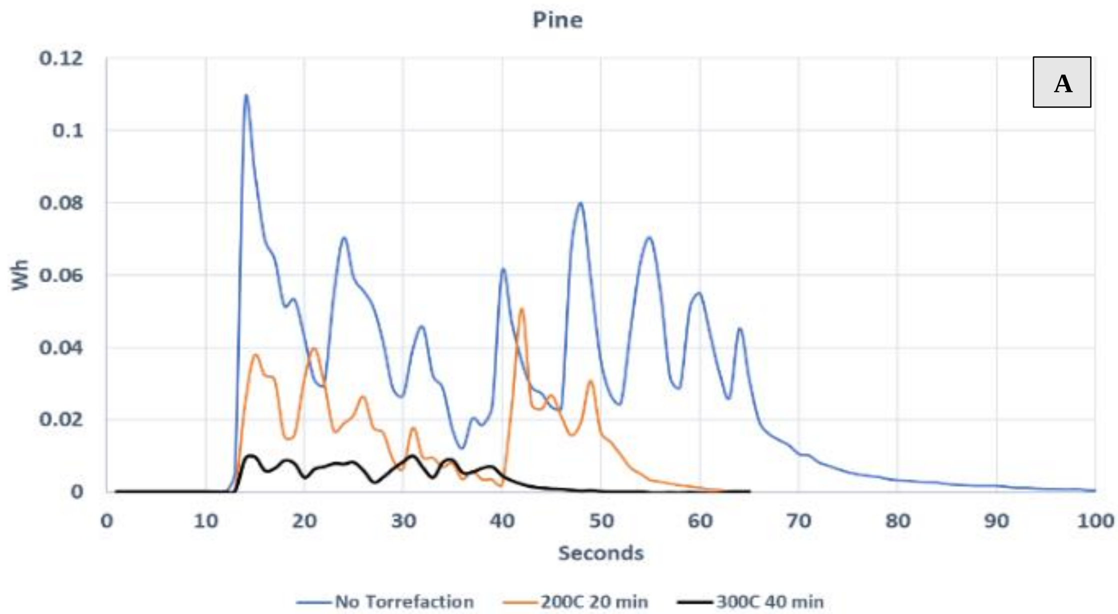
3.6 Effect of torrefaction on grindability

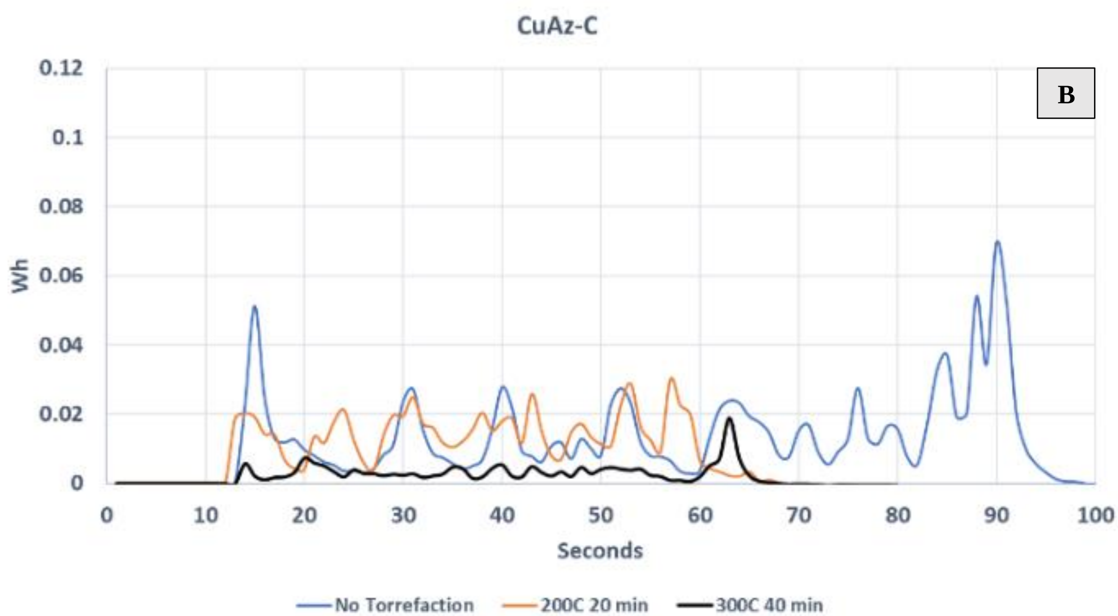
There are several studies showing that torrefaction will significantly decrease grinding energy [5,6,19,25]. To the best of our knowledge this question has not been studied for treated lumber, thus one goal of this work was to confirm that torrefaction reduced the grinding energy of treated lumber samples comparably to non-treated lumber.

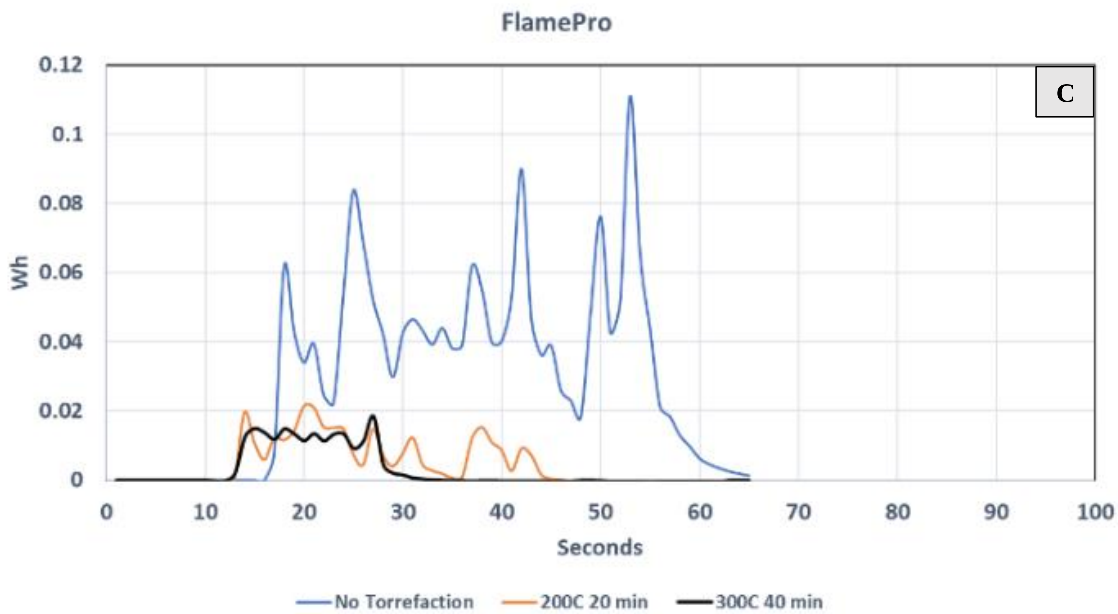
3.6.1 Required grinding energy

As seen in Table 3.8 below, grinding energy was significantly reduced from increased torrefaction intensities. Figure 3.12 is data collected from the IKA MF 10.1 mill with an inline energy logger. Twenty-eight grams or one ounce of sample were ground for each torrefaction intensity, and the total energy consumed was subtracted from the baseline energy of the empty mill. This IKA MF 10.1 mill utilized rotating shearing blades similar to a Wiley mill. Different methods of grinding will provide different results [19]. After torrefaction at 200˚C for 20 min, the average required energy dropped to 34% of the non-torrefied samples. After torrefaction at 300˚C for 40 min, the average required energy for grinding dropped to 10% of the required grinding energy of non-torrefied samples.

Figure 3.12 Raw data peaks collected from energy consumption measured grinding experiments. Units displayed on Y-axis are baseline corrected watt-hours, units on X-axis are seconds passed in the mill. Compares differences in required grinding energy with respect to different torrefaction conditions. This figure is made of four graphs (A through D).


Pine
A
0.12
0.1
0.08
0.06
0.04
0.02
0
Wh
0
10
20
30
40
50
60
70
80
90
100
Seconds
No Torrefaction
200C 20 min
300C 40 min


CuAz-C
B
0.12
0.1
0.08
0.06
0.04
0.02
0
Wh
0
10
20
30
40
50
60
70
80
90
100
Seconds
No Torrefaction
200C 20 min
300C 40 min


FlamePro
C
0.12
0.1
0.08
0.06
0.04
0.02
0
Wh
0
10
20
30
40
50
60
70
80
90
100
Seconds
No Torrefaction
200C 20 min
300C 40 min

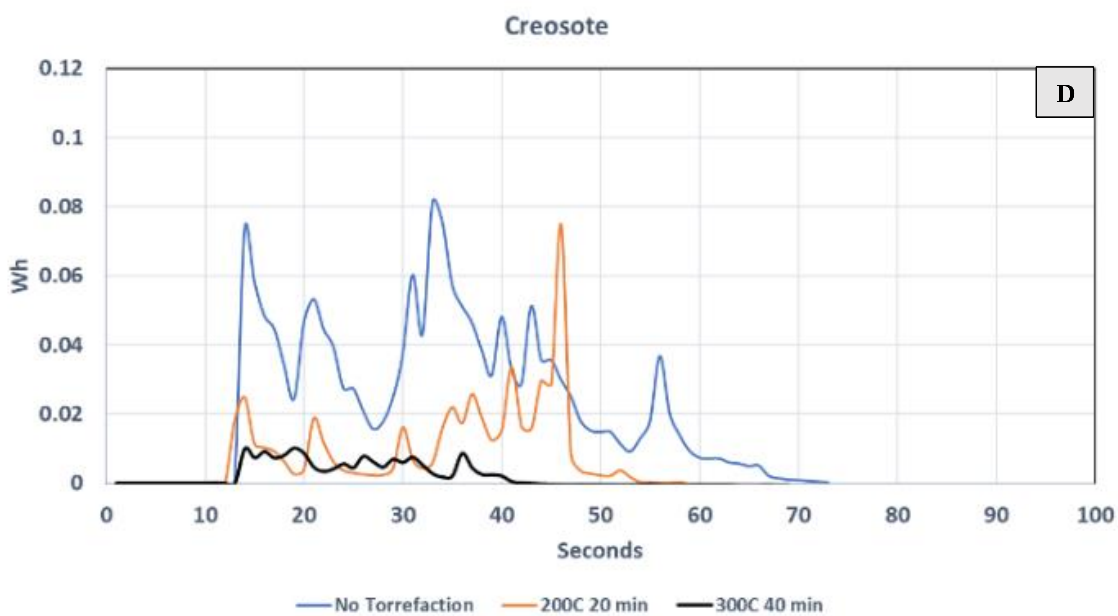

Creosote
D
0.12
0.1
0.08
0.06
0.04
0.02
0
Wh
0
10
20
30
40
50
60
70
80
90
100
Seconds
No Torrefaction
200C 20 min
300C 40 min

Table 3.8

Table showing samples, torrefaction conditions, energy consumption in watt-hours, and an energy ratio. This energy ratio is a comparison of the non-torrefied sample compared to its torrefied counterparts.

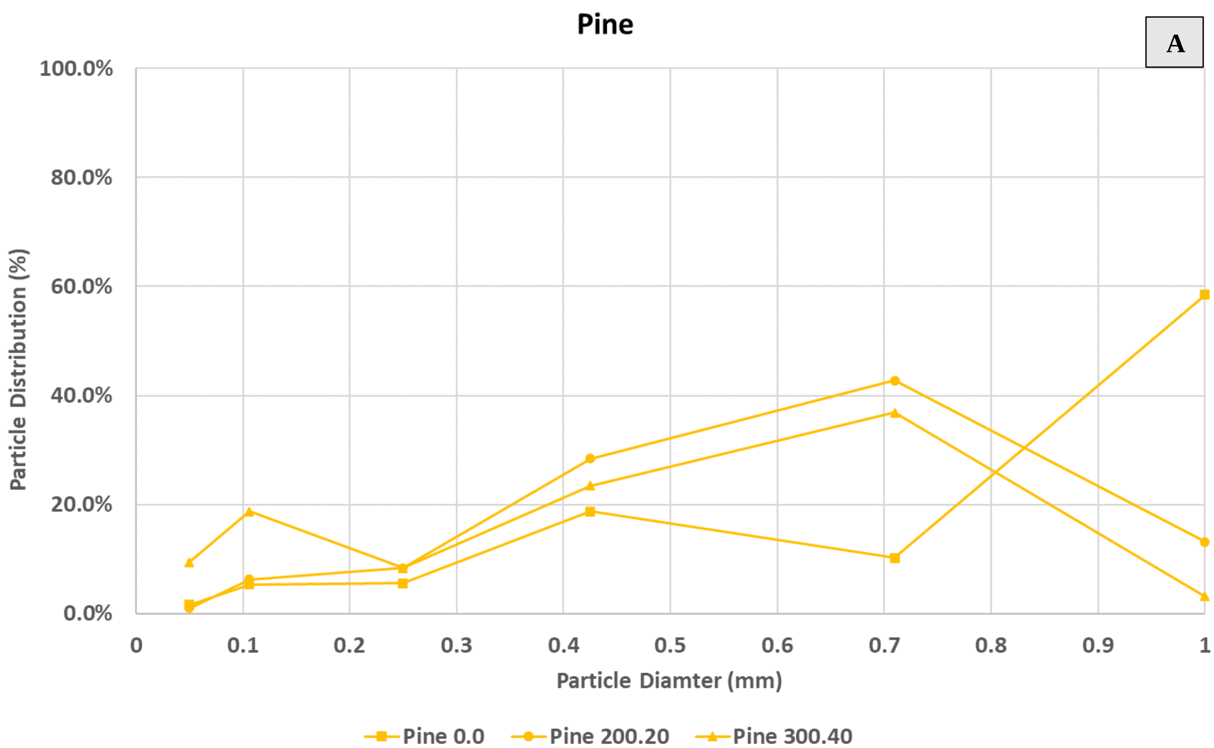
Sample	Torrefaction		**Energy Consumption (Wh)**	**Energy Ratio (%)** $\left(\frac{\textbf{Energy Consumed (Wh)}_{\textbf{torrefied}}}{\textbf{Energy Consumed (Wh)}_{\textbf{(non-torrefied)}}}\right)$
	Temperature (˚C)	**Time (minutes)**		
Pine	0	0	2.5	100
Pine	200	20	0.75	30
Pine	300	40	0.18	7
Creosote	0	0	1.65	100
Creosote	200	20	0.54	32
Creosote	300	40	0.15	10
CuAz-C	0	0	1.27	100
CuAz-C	200	20	0.75	59
CuAz-C	300	40	0.18	14
FlamePro	0	0	1.9	100
FlamePro	200	20	0.3	16
FlamePro	300	40	0.19	10

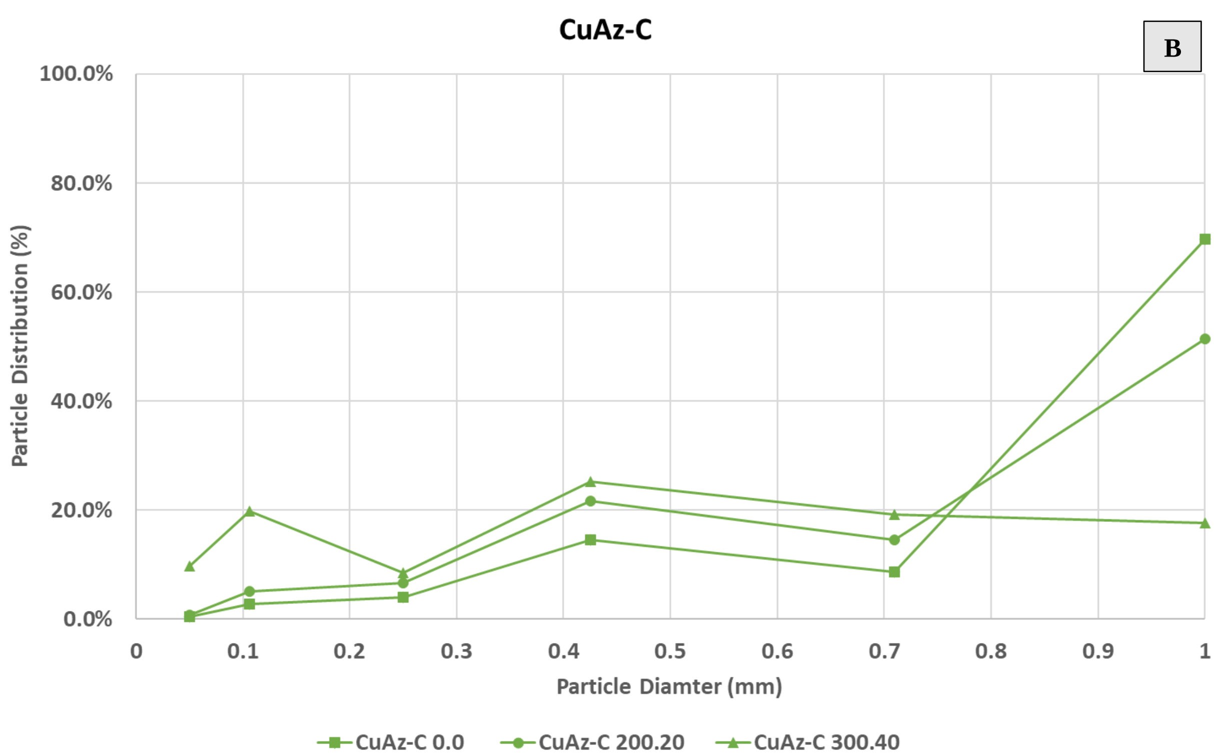
3.6.2 Particle size distribution

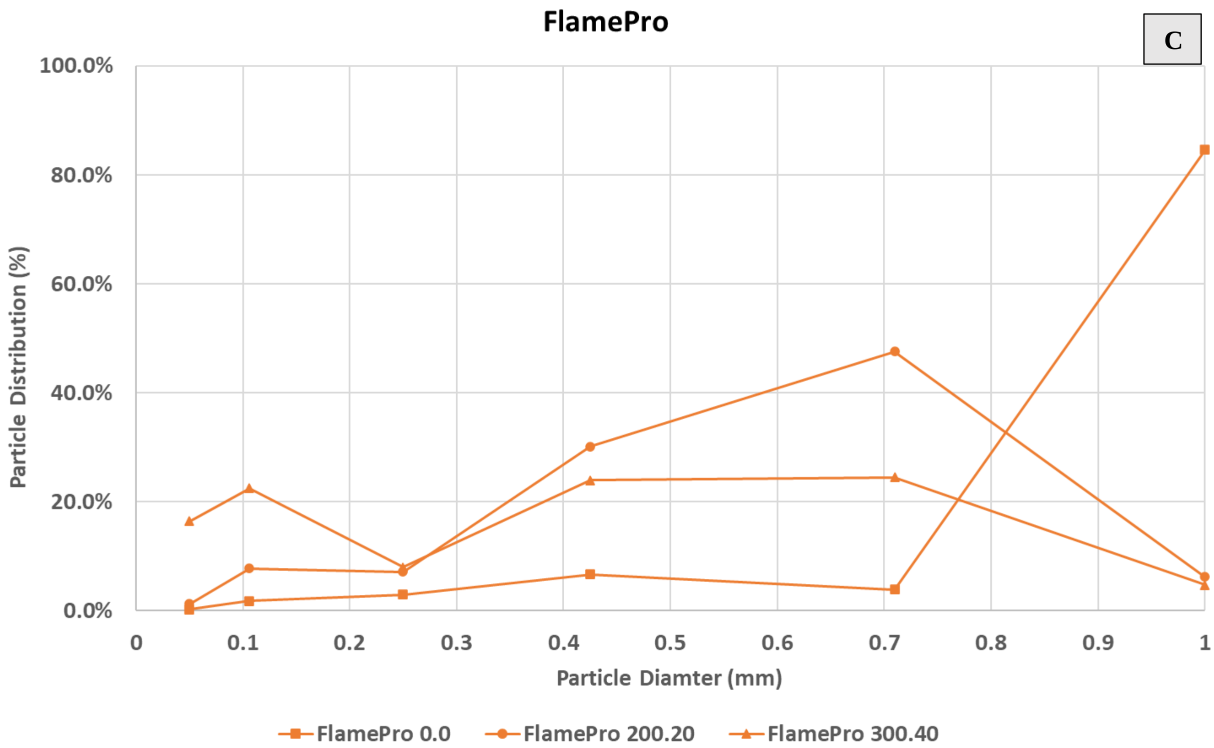
After grinding experiments, the torrefied and ground products are sieved and weighed. Particle size affects residence time and efficiency in the reactor during the gasification process; thus, knowing and controlling the particle size and distribution are important for commercial operations.

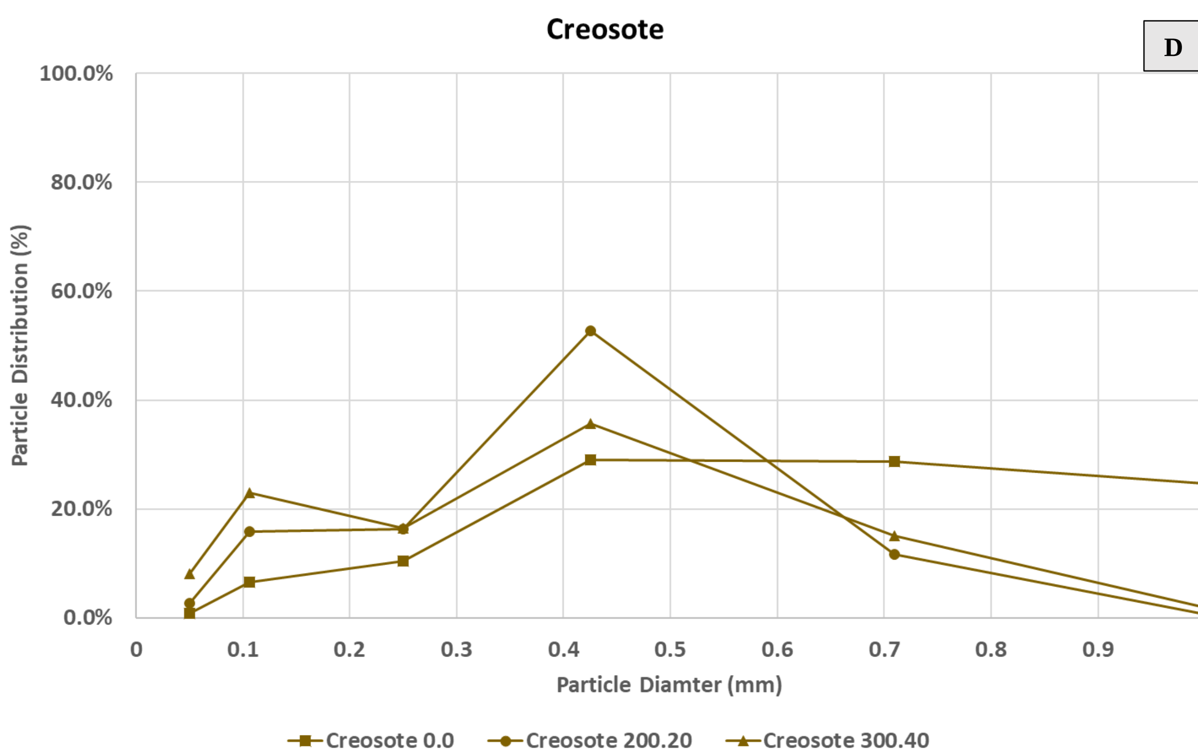
Figure 3.13 shows the particle sizes for the Pine control and chemically treated woods , e.g., CuAz-C, FlamePro, and Creosote for the non-torrefied and torrefied wood. One trend observed from this data is that the higher severity of torrefaction promotes higher yields of smaller sample sizes. For example, non-torrefied Pine's the size range >1mm was the dominate fraction, while for Pine torrefied at 200˚C for 20 min and at 300˚C for 40 min, the greatest percent yield moved to >.710mm. For CuAz-C not torrefied and torrefied at 200˚C for 20 min, the greatest yield is the size >1mm, but at 300˚C for 40 min, the greatest yield is >.425mm. Another way of looking at this data is by using the figures on the right-hand side of Figure 3.13, the cumulative particle distribution. If we look at the particle diameter values on the X-axis at which 50% or more of the particles have passed, this particle size gets smaller with increased torrefaction. For example, 50% of the particles are 0.75mm or less for Pine that is non-torrefied, for Pine torrefied at 200˚C for 20 min, 50% are .450mm or less, and for Pine torrefied at 300˚C for 40 min 50% are .350mm or less.

Figure 3.13 Line graphs created from mass percentages of sieved material after grinding experiments. Particle sizes are: <.106mm, >.106mm, >.250mm, >.425mm, >.710mm, and >1mm. A-D are particle size distribution in mass % for each of the six particle sizes. This figure is made of four graphs (A-D).


Pine
A
100.0%
80.0%
60.0%
40.0%
20.0%
0.0%
Particle Distribution (%)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Particle Diamter (mm)
Pine 0.0
Pine 200.20
Pine 300.40


CuAz-C
B
100.0%
80.0%
60.0%
40.0%
20.0%
0.0%
Particle Distribution (%)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Particle Diamter (mm)
CuAz-C 0.0
CuAz-C 200.20
CuAz-C 300.40


FlamePro
C
100.0%
80.0%
60.0%
40.0%
20.0%
0.0%
Particle Distribution (%)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Particle Diamter (mm)
FlamePro 0.0
FlamePro 200.20
FlamePro 300.40


Creosote
D
100.0%
80.0%
60.0%
40.0%
20.0%
0.0%
Particle Distribution (%)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Particle Diamter (mm)
Creosote 0.0
Creosote 200.20
Creosote 300.40

Chapter 4. Conclusion

4.1 Answers to Research Questions

The overarching goal of this project was to determine whether waste wood from commonly chemical treatments could be used as a biofuel in gasification. Torrefaction was used as a pretreatment to lower the oxygen content and reduce the grinding energy. The effects of torrefaction on both the organic and inorganic components were measured.

If torrefaction produced a treated lumber product with significant difference this could limit the use of some chemically treated materials as a feedstock for gasification. Alternatively, if the differences in the final torrefied product are minimal, this would be ideal, meaning that a mixed pile of C&D wastes can be converted to biofuel with other biomass feedstock without modifications.

This study shows evidence that supports the use of treated lumber as a potential candidate for biofuel conversion through gasification. Furthermore, evidence supports the treated lumber being sufficiently similar to untreated lumber after torrefaction to allow pretreating and gasifying together. Contrarily, FlamePro showed evidence that it would produce a different fuel quality than other treatments if pretreated and gasified under the same conditions.

During the research, a secondary goal or research question arose: Does particle size after torrefaction and grinding affect fuel properties such as caloric value or the amount or composition of the ash? If so, are these differences significant enough for the majority of ash or inorganic contents to be removed just from sieving them? Results showed that >1mm particles had 6% more carbon and 6% less oxygen than>.425mm or <.106mm particles. In addition, the ash was higher in proportion in <.106 mm particles than >.425mm or >1mm particles. However, these differences were relatively small, suggesting that torrefaction at 300^{o}C for 40 min was effective at creating ‘homogenous’ feedstocks from these very different starting materials.

After torrefaction at 200C for 20 min of the samples studied, anhydrous weight losses are expected to be around 10-20%, as seen in Table 3.1. However, the fire-treated sample FlamePro had an anhydrous weight loss of 36% under these conditions. After a more intense torrefaction at 300C for 40 min, anhydrous weight losses of around 60-70% are expected, yet FlamePro again differed with an anhydrous weight loss of 49%.

TGA experiments revealed thermal degradation differences caused by chemical treatment types, as seen in Figure 3.2. FlamePro behaved much differently than the rest of the samples under the conditions of no torrefaction and a torrefaction of 200C for 20 min. However, after a torrefaction of 300C for 40 min, the TG curves of all studied samples were very similar.

Treated lumber samples have lower activation energies than untreated pine samples when torrefied at 300C for 40 min. The main takeaway from kinetics analysis is that there are noticeable differences in activation energy caused by different treatment types, and these differences are accurately ranked.

From C/H/N/O analysis, it is observed that torrefaction increases carbon content and reduces volatile matter as advertised, but chemical treatment can significantly affect this. The energy efficiency for gasifying torrefied FlamePro will differ from other samples. Figure 3.7 also shows us that Pine, Creosote, and CuAz-C torrefied at 300C for 40 min have similar atomic values as coal. These three samples have a lower (better) O: C ratio than lignite and a lower (better) H: C ratio than lignite and some bituminous coal.

As expected, the inorganic elemental composition is affected by chemical treatment, and if lumber is treated with certain chemicals, they remain present in the wood. Torrefaction intensity does impact this; however, if the chemicals the lumber is treated with volatilizes at temperatures lower than torrefaction temperatures, then this chemical's concentration will decrease with torrefaction. Contrarily, if the compound is thermally stable beyond temperatures used in torrefaction, then the relative concentration of this chemical will increase as volatile matter escapes around it.

Proximate analysis results show that volatile matter decreases with torrefaction intensity, fixed carbon and ash increase with torrefaction intensity, as expected. That said, the results of fixed carbon increasing throughout all three torrefaction conditions conflict with the results obtained from C/H/N/O analysis.

From the results seen in Figure 3.11, the calories per gram of energy rise linearly for all samples except for FlamePro. Increasing energy density from torrefaction is expected and directly correlates to increasing fixed carbon. For FlamePro, embodied energy rises significantly from No torrefaction to 200C for 20 min and increases only slightly from 200C for 20 min to 300C for 40 min.

Torrefaction dramatically decreases the required grinding energy for biomass. The severity can be observed in Table 3.8 and Figure 3.12. Another observation from this data is that torrefaction makes grinding energy more uniform. The range for energy consumed for non-torrefied biomass samples is 0.85 Wh; for torrefaction at 200C for 20 min, the range is 0.45Wh, and torrefaction at 300C for 40 min has a range of 0.04 Wh.

As stated, relatively small particles are needed for gasification and combustion. This requirement makes particle size examinations, like the ones characterized by Figure 3.13, necessary. These results will be beneficial for a techno-economic analysis or mass balances. If specific particle sizes are required in a reactor, they must be sieved and separated. Maximizing the yield of acceptable particle sizes is vital because the material has undergone value-adding stages such as torrefaction and milling. This sieving step is a critical point from the perspective of process efficiency. The cost reduction from grinding torrefied biomass should cover the added costs of a low yield from sieving. If not, grinding and sieving should occur before torrefaction so that a less unusable material goes through value-adding steps. Mass is lost throughout many steps of biomass conversion to biofuel, as seen in Figure 4.1, depending on the size of acceptable material in the gasification or combustion reactor will determine the available yield of ground material. In Figure 4.1, the variables for Pine are displayed but the values for other measured samples can be found in Table 4.1. Sieving yield in Figure 4.1 is calculated as if the acceptable particle size range is between 0.250-0.710mm cross diameter and torrefaction conditions are 300˚C for 40 min.

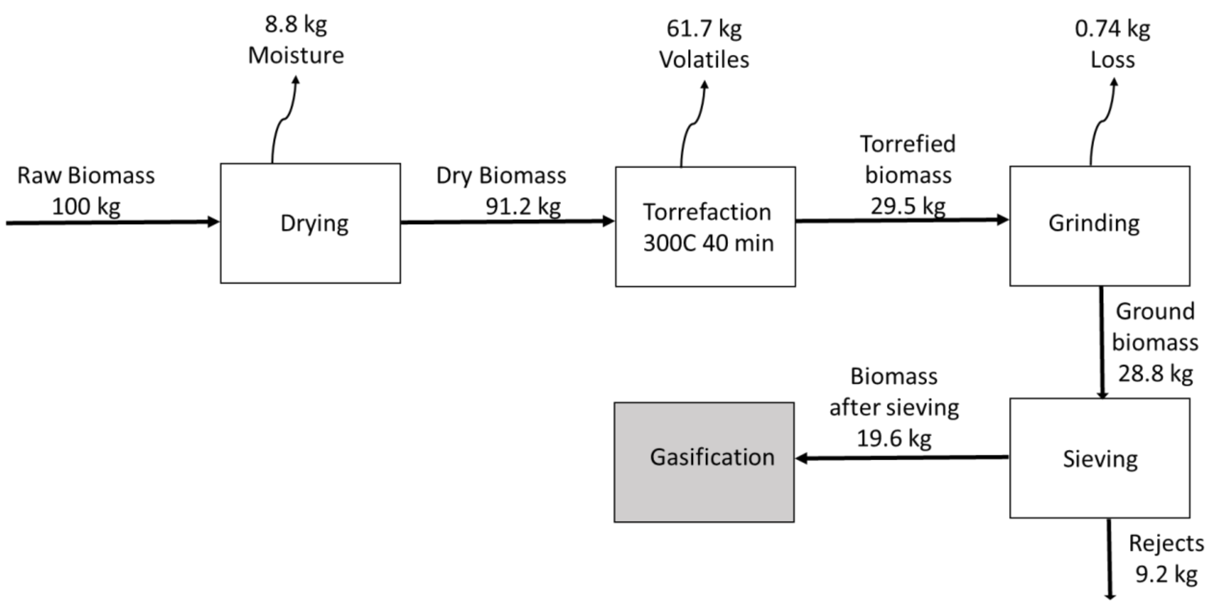


Figure 4.1 Simplified Mass Balance of Conversion Process for Pine.

Table 4.1
Alternate inputs for Figure 4.1 with measured values for Pine, Creosote, CuAz-C, and FlamePro materials all torrefied at 300ºC for 40 min.

	Pine	Creosote	CuAz-C	FlamePro
Moisture (%)	8.8	11	53.8	15.2
Anhydrous Weight Loss (%)	67.6	66.7	64.3	48.7
Grinding Losses (%)	2.5	0.2	3.4	2.9
Sieving Yield (%)	68	67	53	56

4.2 Contributions to the Field

This work is essential for the following generations if we want to reduce carbon consumption in the energy sector. Utilizing biomass as a fuel is both renewable and carbon neutral. Treated lumber was chosen as a starting material to reduce feedstock costs for the torrefaction and gasification process. Torrefaction and gasification are well-documented processes and undoubtedly work, but gasification is currently too expensive to implement commercially and take the place of other cheaper processes that produce electricity. By utilizing a feedstock that is free of cost or has negative costs such as treated lumber from waste the economic return will increase. Furthermore, if carbon credits are available revenue could be increased by switching to carbon-neutral biomass.

From evidence collected in this study, one can conclude that torrefaction has adds value to treated lumber in many of the same ways that it does biomass. Furthermore, torrefaction decreases the differences observed between treated lumber and raw biomass. To the effect that raw biomass and treated lumber could be torrefied together and have a product that is more homogenous than its feedstock. A pretreatment process like torrefaction that can homogenize the feedstock materials allows for a wider range of materials that can be gasified.

Particle size distribution has been studied for raw and torrefied biomass but never for treated lumber samples. The same is true for differences in fuel characteristics of treated lumber caused from different particle sizes. Conversion efficiency is heavily dependent on the yield of useable material, the data gathered on particle size distribution for treated lumber will help in determining its conversion efficiency. Furthermore, from analyzing fuel characteristics like ash content and inorganics present in different particle sizes predictions on the fuel performance for certain particle sizes can be made.

4.3 Future Works

A limitation for this study is that, health and environmental concerns for chemicals used in lumber treatment being emitted to the atmosphere were not taken into consideration for a materials feasibility as a biofuel, this should be considered in future works. Also, this study focused on the pretreatment process of biomass for gasification via torrefaction. To better understand treated lumber in gasification reactions, tests of torrefied treated lumber in actual gasification reactors are needed. Partners in this project have already begun gasification reactor testing of torrefied treated lumber, but at the time of this publication results are not yet available.

A suggestion for future work on this subject would be a process simulation and technoeconomic analysis. The purpose for this project is to lower the costs of gasification to make feasible at an industrial scale, a technoeconomic analysis would track the progress of the achievements made at the lab scale. The mass balance diagram shown is Figure 4.1 is a simplified version of the process simulations required for accurate technoeconomic analyses to be performed, these could be modeled in Aspen or WinGems to give accurate results for a range of conditions.

4.4 Recommendations

Global reliance on fossil fuels is potentially catastrophic if we cannot reduce climate change in the near future. There is currently not a single renewable energy source that could completely replace the demand for fossil fuels for energy, and this paper does not claim that gasifying treated lumber will. However, a diverse portfolio of renewable energy options are capable of significantly mitigating the need for fossil fuels and this is a new potential option.

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