Physicochemical Properties and Thermal Decomposition of Torrefied Woody Biomass and Energy Crop

by

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Abstract

Torrefaction was performed on pine, sweetgum, and switchgrass to determine its effect on the properties and degradation profiles of the biomass, and the influence of feedstock moisture content on the enthalpy of torrefaction was also studied. Torrefaction did improve fuel characteristics of the biomass made it similar to that of coal. The biomass was made less hygroscopic by decreasing the amount of moisture absorbed by up to 50%. The volatile matter concentration of the biomass decreased, while the fixed carbon content increased to levels similar to lignite coal. The elemental composition also improved with lower oxygen levels and higher carbon content, which were increased by nearly 50%. The energy content of the biomass also increased with torrefaction pretreatment. Energy content was found to increase by up to 25%, depending on the intensity of the treatment. Untreated and treated biomass, and treated biomass and coals blends were analyzed using thermogravimetric analysis. Torrefaction had an effect on the degradation profiles of the biomass. Biomass was found to be slightly less reactive at lower temperatures due to the loss of hemicellulose in during torrefaction. Activation energies were found using the isoconversional method. The activation energies were different for untreated and treated biomass samples, but the trends were inconsistent. Torrefaction did not have an effect on the isoconversional reaction kinetics of the biomass. For the biomass and coal blends, activation energies were found to increase with the concentration of biomass in the mixture. Differential scanning calorimetry showed moisture content had a linear effect on the enthalpy of torrefaction.

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Chapter 1. Introduction

It is evident in today's energy use that renewable energy must be utilized to reduce the dependence on fossil fuels. The use of fossil fuels causes many concerns in areas of national security, the environment, and the availability of the fuel. National security is of major concern because more than 70% of petroleum used originates from foreign lands (EIA 2012). Nearly all transportation vehicles operate on petroleum products. The military also relies heavily on petroleum for vehicle operation and power generation, and a global conflict could greatly jeopardize its ability to operate if they could not receive fuel for operations.

Environmental problems arise from the nature of fossil fuels and the methods by which the fossil fuels are extracted from the ground. Coal sometimes contains abnormally high concentrations of harmful metals, such as arsenic and mercury, which are harmful to living organisms. Coal mining also creates great concern because of the methods which are used to obtain coal. Large strip mining operations can greatly alter the conditions of the environment by removing large acreages of natural habitat. Underground mining is an especially dangerous occupation for humans. Underground mining exposes coal seams which can combust and cause underground fires (e.g. Centralia, Pennsylvania) which may last decades or even centuries. These fires create heat and release harmful gases which can be very harmful and potentially deadly to any living thing. Underground mining can be very dangerous because of toxic gas explosions which result in the mine shafts to collapse (e.g. Sago Mine 2006 and Upper Big Branch Mine 2010).

Availability is possibly the most important and central concern for fossil fuels. The modern human relies so heavily on electricity in every aspect of his/her life, and virtually all businesses and companies require electricity to operate. Fossil fuel availability of national security concern, because the United States does not produce enough fossil fuels domestically, particularly petroleum fuels, to sustain its energy usage (EIA, 2012). Much of the petroleum that is used by the United States is imported from foreign countries which can be politically corrupt and quite hostile to the United States. In addition to the origin of these fuels, humans have to go to great lengths and use dangerous methods to obtain these precious fossil fuel resources, and these methods cause great concern.

Bioenergy can be generated in different ways. It can be converted to a value added liquids and gaseous products such as ethanol, synthesis gas, or bio-oil, or it can generate electricity via direct combustion or gasification. Bioenergy is produced from organic materials, which are any form of biomass such as food crops, organic wastes, and forestry products. The Southeast particularly has an abundance of forest resources, and these resources can provide a considerable amount bio-based energy; however, utilizing these sources presents problems. Existing infrastructure for generating energy uses low moisture and oxygen content fuels, such as coal. The major challenge is either adapting this infrastructure to accommodate lower quality biomass fuel, which can be very costly, or creating a biomass product that can be utilized in a current steam generation or gasification plant. It is for this reason that methods to upgrade the biomass are being explored.

The method being researched in this study is torrefaction. Torrefaction is a treatment process for biomass meant to reduce oxygen content and moisture absorption, which increases the energy content. In this study, selected biomass feedstocks were torrefied. The effects of torrefaction pretreatment on the fuel properties of the biomass were examined. The topics and objectives were as follows:

1) Physicochemical Properties
    a) Determine the effect of torrefaction on the physicochemical properties of the biomass samples
2) Thermal Analysis
    a) Determine the effect of torrefaction on the degradation profiles and reaction kinetics of the biomass samples
    b) Determine the degradation profiles and reaction kinetics of a treated pine and coal mixture
    c) Determine the effect of moisture content on the energy required for torrefaction

Chapter 2. Literature Review

2.1. Energy overview

In 2010, the United States consumed 98 quads (103 EJ) of energy, and of this, 83% was generated from fossil fuels (coal, natural gas, petroleum) (EIA, 2012). Figure 2.1 shows the sources of energy for the United States and how those sources were consumed. Petroleum was 37% of total energy consumption, natural gas was 25%, and coal was 21%. Each of these three sources is non-renewable. Also of concern is that 70% of petroleum consumed was imported from foreign countries. These two characteristics present serious challenges for meeting the growing energy demand for the United States.

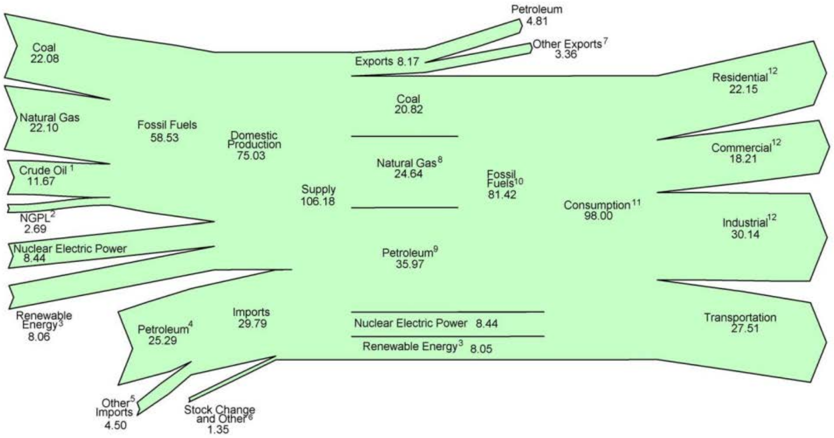


Figure 2.1: 2010 Energy Flow Diagram, Quadrillion BTUs (EIA, 2012)

On the other hand, renewable energy represents 8% of the total energy consumed. The sources of renewable energy were hydroelectric power, biomass, geothermal, solar and photovoltaic, and wind. Coal and petroleum can easily be stored for future use, such as in the Strategic Petroleum Reserve that began in 1975. With the exception of biomass, none of the renewable sources can be stored for future use or transported to a separated location. This is one reason bioenergy is such an attractive form of renewable energy.

The fossil fuel of particular interest in this work is coal since both coal and biomass are both initially solid compounds, and coal provides a stable base load of energy for combined heat and power generation. Coal is partially decomposed matter of biological origin, formed as a result of anaerobic conditions, moisture effects, and high pressure. It has a high carbon and low oxygen content which make it an ideal fuel source. In 2010, the United States operated 1,285 coal mines that produced 1,085 million short tons (984 million tonnes) of coal (EIA, 2012). Coal is shipped from the mines to coal plants, and shipment methods include trucks, rail cars, and ships. Once it reaches the plant, it is pulverized and sent to boilers for combustion. In some cases the coal is pulverized, mixed with water, and shipped as fuel slurry via pipeline to the plant for combustion. The heat from combustion of coal is used to produce steam which is used to turn an electrical generator to produce electricity. Electricity is needed 24 hours a day and 7 days a week so burning coal is a continuous process. Turbines are stopped only when maintenance is needed or demand is low, but plants have multiple turbine units that can operate when one or more turbines are offline or if overall demand is high.

With the consumption of large quantities of nonrenewable resource annually, coal reserves are depleting. As of November 2011, the United States was estimated to have over 259 billion short tons (235 billion tonnes) of recoverable coal reserves (EIA, 2012). At the current rate of consumption, reserves of coal could be completely exhausted within 250 years. If annual consumption continues to increase as expected, that time period could even decrease.

2.2. Bioenergy

Biomass is formed as a result of plant photosynthesis. During photosynthesis, solar energy is captured and used to convert carbon dioxide (CO_2) and water (H_2O) into glucose ($C_6H_{12}O_6$) which is then used as food for the plant to grow. Since energy that is stored in the plant is from solar radiation, biomass is classified as a renewable resource.

The “Billion-Ton” report of 2005 was performed to determine if the United States could produce enough dry biomass to displace 30% of domestic petroleum consumption. The report showed that 368 million dry tons (334 million tonnes) of biomass could be produced sustainably on forestlands and 998 million dry tons (905 million tonnes) of biomass could be produced sustainably on agricultural lands in the United States. The findings concluded that a sufficient biomass supply could indeed be produced on an annual basis. In addition to this, it also suggested that additional biomass could be produced if more agricultural land were devoted to perennial grasses and woody crops (Perlack et al., 2005).

Two-thirds of the state of Alabama is covered in forestland, which is over 22.7 million acres, ranking Alabama third nationally in commercial forestland (Hendricks and Christie, 2008). Of that 22.7 million, 9.4 million was classified as softwood, 3.4 million as oak-pine, and 9.9 million as hardwood(Hendricks and Christie, 2008). In the same year, the forestry industry in the state received $680 million in stumpage revenue from the sale of forest products (Hendricks and Christie, 2008). This amount of revenue makes the forestry a large industry for the state of Alabama. With such a large inventory and an already evolved industry, forest products represent great potential as a bioenergy feedstock.

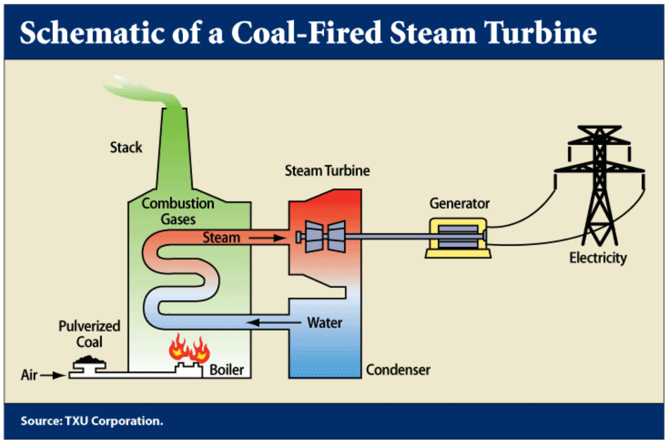
In 2005, loblolly pine (*Pinus taeda*) and sweetgum (*Liquidambar styraciflua*), were listed as the two most populous tree species in Alabama as both species can be found on a variety of sites (Hartsell and Johnson, 2009). Loblolly pine can reach up to 30 m tall and 1 m in diameter, while sweetgum can reach up to 36 tall and 1.2 m in diameter (Samuelson and Hogan, 2006). International Paper Company studied the production of the two trees under intensive management, and it was found that pine and sweetgum could produce 15.2 Mg/ha/yr and 10.9 Mg/ha/yr of total biomass, respectively (Williams and Gresham, 2006).

Switchgrass (*Panicum virgatum*) is a perennial grass native to North America. It is a tall grass that can grow up to 3.7 meters in height. Because of its high yield and resistance to the Southeastern pests and diseases, it is being studied as a bioenergy feedstock (McLaughlin et al., 1999; McLaughlin and Adams Kszos, 2005). Auburn University tested switchgrass on a site in Alabama and was able to produce a yield of over 25 Mg/ha/yr (McLaughlin et al., 1999). Switchgrass naturally occurs as two major types, a thick stem lowland type better suited for warmer climates and a thin stemmed upland type better suited for mid to northern climates, so it is able to grow in a variety of conditions (McLaughlin et al., 1999).

Bioenergy can be produced directly from biomass feedstock, such as electricity production from direct combustion of biomass in a boiler or combustion of producer gas from biomass gasification. Other methods for deriving energy from biomass include the use of conversion technologies to produce value added energy products that are used to generate energy. In addition to electricity production, gasification can be used as a conversion technology to produce liquid fuels from producer gas. Other common methods to produce liquid fuels are bio-oil production from pyrolysis, and ethanol production from fermentation.

Both woody and herbaceous biomass can be used for electricity and liquid biofuels. Approximately 60% of the bioenergy produced in 2010 was generated via direct combustion or gasification for electricity (EIA, 2012). Wood and waste products were the main feedstock, and the energy was used primarily by industry (EIA, 2012). The remaining 40% of bioenergy was produced via biochemical conversion processes for liquid fuel (EIA, 2012). The products were ethanol and biodiesel, although liquid biofuels can also be produced by gasification and fuel synthesis or pyrolysis. Lignocellulosic biomass can be used for each of these processes with the exception of biodiesel, which uses vegetable or animal oils as feedstock.

Direct combustion is the simplest method for producing energy from biomass. Biomass may be burned in its solid form to produce heat in a residential setting such as in a fireplace or stove. Large scale direct combustion requires burning biomass to produce steam for a turbine (Figure 2.2). Typically coal is burned to produce steam, but co-combustion of biomass and coal has been studied (Heinzel et al., 1998; Spliethoff and Hein, 1998; Wils et al.). Co-combustion has a number of advantages and disadvantages. It can increase boiler efficiency (if moisture content is low) and decrease NO_x emissions (Demirbaş, 2003; Wang et al., 2011b), but it can also create slagging and fouling problems, especially with herbaceous crops (Al-Mansour and Zuwala, 2010; Basu et al., 2011; Demirbaş, 2003).


Schematic of a Coal-Fired Steam Turbine

Source: TXU Corporation.

Figure 2.2: Coal power plant schematic (Combs et al., 2008)

A common method for producing energy from biomass is through gasification, which can be used for direct energy production or as a conversion technology. During gasification, biomass is broken down at high temperatures (800-1000°C) and partially oxidized primarily producing carbon monoxide, CO, and hydrogen gas, H_2 (Figure 2.3). This gas can then be directly supplied for electricity production using technologies such as internal combustion engines or gas turbines or reformed to produce value-added products such as in the Fischer-Tropsch process. Gasification of biomass has been used for over 100 years, but due to its high capital costs and competition with other fuel sources and technologies, it has made very little impact commercially (Basu et al., 2011; Bridgwater, 1995).

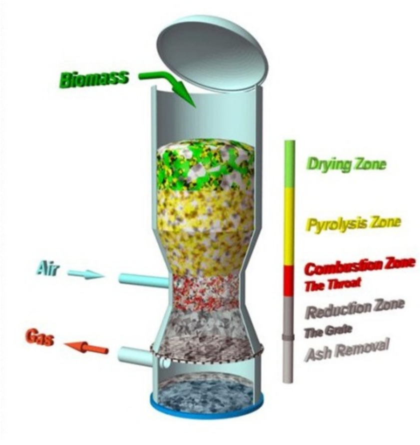


Figure 2.3: Schematic of a gasifier (Zafar, 2008)

Pyrolysis is a conversion technology attracting much research for energy production (Bridgwater, 2012; Thangalazhy-Gopakumar et al., 2011; Thangalazhy-Gopakumar et al., 2010; Wang et al., 2011a). Pyrolysis is a thermal treatment of biomass under inert conditions over a wide temperature range (200-600°) depending on the desired product. After undergoing pyrolysis, the initial biomass is converted into three phases: a solid (bio-char), a liquid (bio-oil), and waste gases (Figure 2.4). Higher temperature will create a higher bio-oil quantity, but if bio-char is the desired product, lower temperatures are preferred. The bio-char can then be used in the previous methods of direct combustion or gasification for energy production. The bio-oil is a liquid product that could be refined to produce transportation fuels or other value-added chemicals.

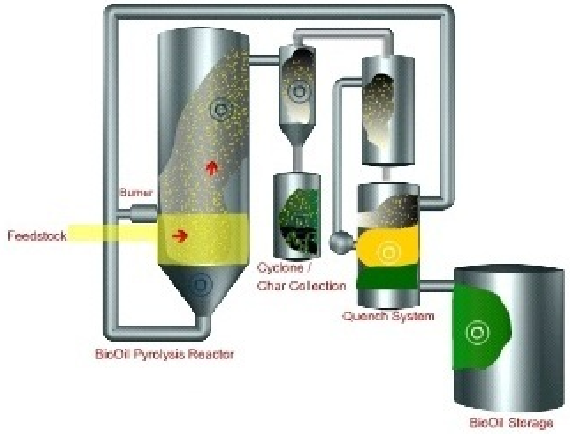


Figure 2.4: Schematic of a pyrolysis reactor (Jacquot, 2007)

Another conversion technology is production of ethanol, where starch or cellulose and hemicellulose in biomass is broken down into simple sugars which are fermented to make ethanol (Figure 2.5). Ethanol is currently the most produced biofuel product in the United States, and the majority of the feedstock used for ethanol production is starch obtained from corn (EIA, 2012). Ethanol can also be produced from lignocellulosic materials such as woody or herbaceous biomass (Felix and Tilley, 2009; von Sivers and Zacchi, 1996). These materials could potentially be a more attractive feedstock than corn due their abundance and minimal conflict with other industries. Cellulosic ethanol is a well-known bioenergy product, because the Renewable Fuel Standards (RFS) set forth in the United States House Bill H.R.6 (Energy Independence and Security Act of 2007) states that 21 billion gallons of cellulosic ethanol and advanced biofuels must be produced by the year 2022.

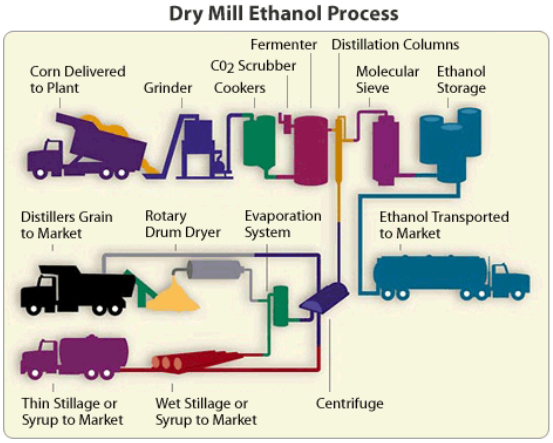


Figure 2.5: Schematic of ethanol production from corn

The abundance of biomass and its renewable nature make it a very promising alternative to conventional fossil fuels, but the inherent characteristics of biomass compared to fossil fuels create problems for energy production. One of the problems associated with biomass is its hygroscopic nature, and moisture content has a considerable effect on the biomass. Bulk density of biomass is greatly affected by moisture content, and density will effect transportation costs of the feedstock (Fasina, 2008; Mani et al., 2006; Mozammel et al., 2006; Tumuluru et al., 2011; Wu et al., 2011). This is especially important since the largest fraction of cost in bioenergy processes originates from the logistics, representing up to 50% of the total cost (Allen et al., 1998; Rentizelas et al., 2009). Moisture content can also affect the combustion efficiency. High moisture content in biomass results in lower overall efficiency of the combustion process, since a considerable amount of energy is needed to remove the moisture (Porteiro et al., 2010; Tumuluru et al., 2011).

Another major problem with biomass compared to fossil fuels is its high oxygen content. Typical oxygen content values of biomass materials are 30-45% by weight (Yin, 2011). This value is much higher than that of a conventional fossil fuel such as coal. The oxygen content of coal can range from 24% for lignite coal (Vamvuka et al., 2003) down to 8% for anthracite coal (Li et al., 2011). This high oxygen content of biomass causes biomass to have a lower calorific value compared to that of coal. Heating values of biomass materials are near 18 MJ/kg which are much less than of coal which can range from 25-35 MJ/kg depending on the type of coal. These lower heating values combined with the lower bulk density of biomass result in a significantly higher volume of biomass being needed to produce the same energy output as coal (Wu et al., 2011; Zulfiqar et al., 2006).

2.3. Torrefaction

Torrefaction is a thermal treatment of biomass typically in the temperature range of 200-300°C with reactor residence times from 15 minutes to 3 hours. The reaction is performed under atmospheric conditions in the absence of oxygen with the inclusion of an inert carrier gas. The treatment allows the moisture and most reactive volatiles to vacate the final product, typically referred to as bio-char. The process typically retains 70% of the original mass and 90% of the original energy in the bio-char. This remaining 70% mass is primarily composed of the lignin and cellulose portions of the biomass, while the hemicellulose is mostly volatilized and removed (Chew and Doshi, 2011). The mass lost during torrefaction are high oxygen content and low energy content compounds, which improves the fuel quality of the biomass. Table 2.1 shows the properties of some torrefied products.

Table 2.1: Properties of untreated and torrefied biomass (Bridgeman et al., 2008)

Sample	Elemental Analysis (wt%, dry)				HHV (MJ/kg)
	C	H	N	O	
Reed canary grass (RCG)	48.6	6.8	0.3	37.3	19.5
RCG - 290°C, 30 min.	54.3	6.1	0.1	36.3	21.8
Wheat straw (WS)	47.3	6.8	0.8	37.7	18.9
WS - 290°C, 30 min.	56.4	5.6	1	27.6	22.6
Willow (W)	49.9	6.5	0.2	39.9	20
W - 290°C, 30 min.	54.7	6	0.1	36.4	21.9

The other products of torrefaction are waste volatiles, some of which are condensable and others non-condensable (Prins et al., 2006b). Non-condensable gases are commonly carbon dioxide, carbon monoxide, methane, and hydrogen; and the condensable gases are water, acetic acid, and a number of other oxygenates (Bridgeman et al., 2008; Prins et al., 2006b). Some oxygenates that have been observed are formaldehyde, acetyladehyde, methanol, acetone, formic acid, lactic acid, furfural, and phenol (Bergman et al., 2004; Bridgeman et al., 2008; Prins et al., 2006a; Prins et al., 2006b).

Pretreating biomass via torrefaction is currently being performed only in research settings, but economic models of the process would include feedstock price, investment cost, production cost, and fuel price (Uslu et al., 2008). Maximum capacity of a commercial torrefaction plant process is estimated to be 30-40 MW, while the cost of production (excluding feedstock costs) is estimated to be ~\$50-75/ton (\$55-83/tonne) (Uslu et al., 2008). Production cost includes biomass preparation and treatment. Size reduction is a major part of biomass preparation, which is an area where torrefaction can be advantageous. Treating biomass has been shown to significantly reduce the specific grinding energy of biomass up to 85-90%, which would greatly increase preparation efficiency (Bergman et al., 2004; Phanphanich and Mani, 2011). The total production cost can be estimated by the process efficiency which is the ratio of the energy in the product to the total energy input of the feedstock plus the process energy (Ciolkosz and Wallace, 2011; van der Stelt et al., 2011). Studies show that the total process efficiency could be near 80% (van der Stelt et al., 2011).

Torrefaction was carried out on bagasse, birch, and pine (Pach et al., 2002). The treatment setup used for torrefaction was a cylindrical reactor with a device equipped to remove the liquid products and measure the gaseous products. Biomass was torrefied at temperatures of 230°C, 250°C, and 280°C and reactor residence times of 1, 2, and 3 hours. Solids yield ranged 67.1-92.4% for pine, 63.8-87.5% for bagasse, and 68.9-86.9 for birch. While solids decreased for all samples, ash content increased (Pach et al., 2002). This can be expected as volatiles are partially removed during the torrefaction process leaving a higher percentage of inorganic matter. Similar effects of temperature and time have been reported elsewhere (Felfli et al., 2005; Pentananunt et al., 1990). With this mass loss, many OH group receptor sites in the biomass are removed, and the biomass less readily absorbs moisture from the atmosphere (Uslu et al., 2008). Torrefaction has been proven to reduce moisture absorption of wood sawdust and briquettes by up to 73% (Acharjee et al., 2011; Li et al., 2012).

Phanphanich and Mani (2011) studied the torrefaction of pine chips and logging residues at temperatures ranging from 225°C to 300°C with 30 min of residence time (Phanphanich and Mani, 2011). The study found that the heating value of the biomass increased with temperature due to the drop in oxygen content of the biomass. At 300°C heating value was 25.38 MJ/kg for torrefied pine chips which was a 37% increase. Also at 300°C, heating value of torrefied logging residues was 26.41 MJ/kg, which was a 41% increase. These values are quite comparable to the energy content of lignite coal, 28 MJ/kg. Prins et al. (2006) also observed increases in energy content, but not to the same magnitude. Increases in energy content of 17% and 20% were observed for willow at 270°C and beech at 280°C, respectively (Prins et al., 2006a). The lower increases in energy content could be due to the nature of the different types of biomass or the decrease in temperature which would not remove as much oxygen from the raw biomass. Similar results show increasing energy content with torrefaction treatment (Medic et al., 2012; Patel et al., 2011).

The effects of using torrefaction prior to gasification were modeled to determine if pretreatment improved the gasification process (Prins et al., 2006b). Untreated biomass can sometimes become over-oxidized during gasification. The lower oxygen content of torrefied feedstock may possibly improve this problem which would provide a higher quality fuel. It was also proposed that if heat from the gasifier is used to pretreat the sample, the chemical exergy of the entire process could increase. Prins et al. (2006b) suggested that this integrated process could be tested to perform an economic study for its feasibility (Prins et al., 2006b).

The effect of torrefaction pretreatment on the quality of pyrolysis bio-oil was also examined (Meng et al., 2012). Loblolly pine was torrefied at 270, 300, and 330°C for 2.5 minutes and then fast pyrolysis was performed on the torrefied product in a fluidized bed reactor at 500°C. Torrefied biomass did show increased thermal resistance to pyrolysis, but it did produce bio-oils with lower oxygen to carbon ratios and lower moisture contents compared that of untreated biomass. It also showed a higher quantity of lignin compounds, making it better for phenolic-based chemical production (Meng et al., 2012).

2.4. Physicochemical Properties

2.4.1. Bulk Density

Bulk density is an important parameter that must be considered when transporting and storing large quantities of biomass. Bulk density is the ratio of the mass of a material to its volume, and it plays a crucial role in the economic analysis of a bioenergy supply chain. Biomass has to be transported from where it is harvested to where it is processed. When transportation vehicles are a given volume, the bulk density can be used to determine the amount of mass that can be moved during transit. Examples of some biomass bulk densities are given in Table 2.2. The values are be used to calculate feedstock cost and estimated transportation costs. If the material is to be stored inside a silo or tank, the bulk density is used to design those storage containers. The logistics for the transportation and storage of biomass for energy purposes are the largest fractions of the overall cost (Rentizelas et al., 2009).

Table 2.2: Average bulk density of agricultural crops (Chevanan et al., 2010)

Material	Mean length (mm)	Density (kg/m³)
Switchgrass	3.3	105.2
	12.3	45.3
Wheat straw	3.4	50.5
	12.3	25.1
Corn stover	3.3	66.6
	12.8	34.4

2.4.2. Moisture Absorption

Biomass is hygroscopic, which means it readily absorbs water molecules from the atmosphere. As mentioned previously, this can be a serious problem since moisture content has a significant effect on logistics and conversion processes. Higher moisture contents cause cohesion and arching in bulk biomass materials, which can inhibit flow, and create greater combustion problems , and moisture has a considerable effect on bulk density, which can create big challenges when designing for a transportation and storage system (Fasina, 2008; Tagawa et al., 2002; Wu et al., 2011).

2.4.3. Proximate Analysis

The proximate analysis of a material quantifies the percentages of moisture, ash, volatiles, and fixed carbon in the sample (Table 2.3). The ash percentage of a sample is the inorganic residue that remains after a sample has undergone complete oxidation. Coal contains high ash, but the constituents of biomass ash and coal ash are much different. Since combustion systems are typically designed for coal, biomass ash content can create major problems. Biomass ash is very high in alkali metals and, as a result, is highly reactive. During combustion, it can react with gases such as sulfur and chlorine to cause slagging, fouling, and corrosion problems (Jenkins et al., 1998; Vamvuka et al., 2003). Some systems may even limit the maximum ash content of a fuel due these possible problems (Steenari and Lindqvist, 1999).

Table 2.3 shows the proximate analysis of some biomass types. Biomass contains a high percentage of volatile matter when compared to coal, which is generally less than 40% by weight. This might be seen as a disadvantage for biomass since the high volatile content is typically accompanied by high oxygen content, which decreases heating value (Jenkins et al., 1998; McKendry, 2002). The high volatile content of biomass may, however, be beneficial when co-firing with coal. Combustion efficiency of the mixture can be increased since the ignition temperature is decreased with the addition of biomass. The volatiles in biomass promote better burnout of the fuel and lower NO_x emissions (Hein and Bemtgen, 1998).

Table 2.3: Proximate analysis and heating value of biomass samples

Biomass type	Moisture (wt%)	Fixed Carbon (wt%)	Ash (wt %)	Volatile (wt%)	Heating value (MJ/kg)
Peanut shell	8.12	13.6	5.99	80.41	18.46
Hybrid poplar	9	6.87	3.44	86.69	17.14
Ash tree	8.75	14.12	5.75	80.13	18.06
Pine cone	9.25	15.15	6.89	77.96	18.55

Proximate analysis has been shown to give reliable results for the estimation of the heating value of biomass using mathematical models (Table 2.4) (Erol et al., 2010; Sheng and Azevedo, 2005; Yin, 2011). Most of these models are limited by the sample type or region from where the sample was taken, but attempts have been made to improve these models to predict heating value across a wide variety of solid fuels (Parikh et al., 2005). This could prove useful as proximate analysis data can be collected with common laboratory instruments and with minimal laboratory training.

Table 2.4: Heating value from proximate analysis (Erol et al., 2010)

Equation	Average absolute error (%)
$HHV = 15.2 + 0.192[FC]$	2.2843
$HHV = 14.2 + 0.38[FC] - 0.00721[FC]^2$	1.8518
$HHV = 356 - 3.2[FC] - 3.41[VM + Ash]$	1.9291
$HHV = 34.4 - 0.226[VM + Ash] + 0.0356[VM] + 0.00019[VM * Ash]$	2.2054

Some studies have also been performed to determine if correlation exists between proximate analysis and elemental composition (Parikh et al., 2007; Shen et al., 2010). Currently, these models are constrained by the sample type, but if expanded to predict across a range of biomass types, they could also be useful.

2.4.4. Elemental Analysis

Elemental analysis is an important characteristic of biomass as it displays exactly which atomic elements a sample contains. Elemental composition can vary across biomass types depending on the type of biomass and the region from which the biomass was acquired, but the typical elemental composition of biomass has four elements: carbon, hydrogen, oxygen, and nitrogen. It is important to know the composition in order to balance chemical equations to predict resulting products from a chemical reaction. This data can also be used to accurately estimate heating value of biomass (Table 2.5) (Friedl et al., 2005; Sheng and Azevedo, 2005; Yin, 2011).

Table 2.5: Heating value from elemental analysis (Yin, 2011)

Equation	Unit	Author(s)
HHV = 0.3259[C%] + 3.4597	MJ/kg	(Sheng and Azevedo, 2005)
HHV = 0.301[C%] + 0.525[H%] + 0.064[O%] - 0.763	MJ/kg	(Friedl et al., 2005)
HHV = 0.4373[C%] - 1.6701	MJ/kg	(Tillman, 1979)
HHV = 0.2949[C%] + 0.8250[H%]	MJ/kg	(Yin, 2011)

2.4.5. Energy Content

The energy content (or heating value) of a material is the ratio of the enthalpy of complete combustion to the mass of the sample. It is one of the most important parameters for a biomass sample and is used to design bioenergy systems. Heating value can be defined in two ways, lower and higher heating value. The difference between the two values is the state of the water after combustion: water in vapor phase = lower heating value (LHV), water in liquid phase = higher heating value (HHV). Lower heating value can sometimes be misleading because it does not include the latent heat of vaporization of the water products, which can produce thermodynamic heating efficiencies >100%. Using higher heating value is practical for energy systems that allow the water in the reaction products to condense, such as in a boiler. The higher heating value is stated in this work and is most commonly used in literature, which typically reports dry HHV values of 16-22 MJ/kg for biomass (Parikh et al., 2005). As mentioned previously, energy content is strongly related to chemical and physical composition of the biomass and can be estimated by either proximate or elemental analyses data for a range of biomass types (Erol et al., 2010; Friedl et al., 2005; Parikh et al., 2005; Parikh et al., 2007; Shen et al., 2010; Sheng and Azevedo, 2005; Yin, 2011).

2.5. Thermal Analysis

2.5.1. Thermogravimetric Analysis

Thermogravimetric analysis is a technique used to determine the weight loss of a material at a specific temperature or when it is subjected to a specific heating pattern. The technique is performed with a thermogravimetric analyzer (TGA). The degradation process that occurs could be a pyrolysis or combustion process, depending on the atmosphere in which it occurs. Multiple studies have been performed to determine weight loss of many types of biomass under inert conditions (Chen and Kuo, 2011; Damartzis et al., 2011; Lapuerta et al., 2004; Mangut et al., 2006; Reina et al., 1998). They have even been performed in the presence of a catalyst to determine its effect on the resulting products (Chattopadhyay et al., 2009; Zhaosheng et al., 2008). This pyrolysis process can be used to examine, or even predict the different components of the biomass such as moisture, hemicellulose, cellulose, and lignin content (Carrier et al., 2011; Chen et al., 2011; Stenseng et al., 2001).

Figure 2.6 shows the typical weight loss profile of a biomass sample. Initial weight loss in biomass around ~100°C is regarded as the release of moisture (Chen et al., 2011; Mothé and de Miranda, 2009). The moisture loss is very important as it can be used to design a biomass dryer. The next stage of weight loss varies between biomass types but is generally considered to active pyrolysis (Kumar et al., 2008). It encompasses the volatilization of the hemicellulose,

cellulose, and part of the lignin portions of the biomass (Jeguirim and Trouvé, 2009; Jiang et al., 2010; van der Stelt et al., 2011). In-depth analysis of this stage of pyrolysis can reveal how the different components of the biomass behave at different heating patterns. This information can be used to design a pyrolysis reactor that targets specifics percentages of the biomass such as the hemicellulose portion or the hemicellulose and cellulose portions. These data can also be used to calculate torrefaction or pyrolysis reaction kinetics of the biomass, which will be discussed later in more detail (Arias et al., 2008; Lapuerta et al., 2004; Zhou et al., 2006).

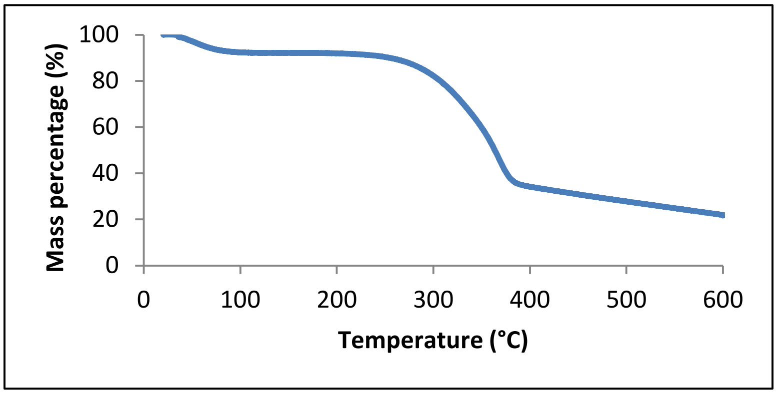


Figure 2.6: Pyrolysis profile of untreated loblolly pine

Combustion processes have also been studied in-depth by thermogravimetric analysis (Chen and Kuo, 2011; Lapuerta et al., 2004). Co-firing of biomass is performed in many installations worldwide, but, as mentioned previously, the inherent characteristics of biomass can cause problems in combustion furnaces (Al-Mansour and Zuwala, 2010; Basu et al., 2011; Demirbaş, 2003). Since co-firing of biomass with coal is a promising option for bioenergy, often times these studies focus on combustion characteristics of biomass and coal blends (Chen and Wu, 2009; Sahu et al., 2010; Varol et al., 2010). Thermogravimetric analysis allows for these processes to be studies in the lab, rather than at a plant. This allows researchers and engineers to make more appropriate design modifications to combat these problems.

The parameters activation energy, E, and pre-exponential factor, A, are used to define the characteristics of a chemical reaction. The reaction kinetic parameters have traditionally been used to analyze homogeneous reactions, but recent studies suggest that these parameters can be applied to the heterogeneous pyrolysis and combustion reactions of biomass (Gil et al., 2010; Huang et al., 2011). The validity of using non-isothermal analysis to find kinetics parameters of heterogeneous materials has been the subject of much debate, since it was originally derived for homogeneous substances; however, it has been suggested the accuracy of these kinetic parameters could be improved by testing the heterogeneous substance at multiple heating rates (White et al., 2011). Still, there is a range of calculated activation energies, as shown in Table 2.6, depending on the researcher, the model, and the complexity of lignocellulosic biomass.

Thermogravimetric analysis is used to investigate degradation behavior of the biomass, which is then used to develop kinetic models. There are many mathematical methods used to determine the reaction kinetics, but nearly all of them are based on the Arrhenius equation, $k = Ae^{\left(-E/_{RT}\right)}$. Reported variables for the reaction are activation energy, E, and pre-exponential factor, A. Table 2.6 shows different calculated activation energies of almond shell. Accurate modeling of the degradation reactions of biomass is essential to understanding the behavior of a sample when heated inside a reactor or boiler. This knowledge is can be used to design the conversion system and to maximum the efficiency of the conversion process (Cai et al., 2008; Gil et al., 2010).

Table 2.6: Kinetics parameters of almond shell (White et al., 2011)

Heating rate (°C/min)	Temp. range (°C)	Reaction scheme and order	E_a (kJ/mol)	Author(s)
5-100	25-850	Single step, 1st order	42.4	(Balci et al., 1993)
5-100	25-850	Single step, 1st order	92.9	(Balci et al., 1993)
10	100-700	2 parallel reactions, nth order	112.3-239.2	(Caballero et al., 1997)
5-45	100-800	2 parallel reactions, 1st order	106.2-225.3	(Font et al., 1991)

2.5.2. Differential Scanning Calorimetry

Differential scanning calorimetry is a method to determine the heat required to increase or decrease the temperature of a sample. It is performed with a differential scanning calorimeter (DSC) which heats a sample cell and an empty reference cell at a controlled rate and measures the differential endothermic or exothermic heat flow of the sample cell compared to the reference cell as a function of time. In bioenergy research, it can be used to model a torrefaction or pyrolysis process. Several studies have been conducted to determine the enthalpy of pyrolysis for a biomass sample (Daugaard and Brown, 2003; He et al., 2006; Van de Velden et al., 2010). He et al. (2006) found that 360 kJ/kg of energy was required to heat pine wood to ~250°C while 582 kJ/kg was required to heat it to a pyrolysis temperature of 550°C. Van de Velden et al. (2010) reported slightly less energy input to heat similar woody biomass to the same pyrolysis temperature of 550°C (Van de Velden et al., 2010). Energy requirement for the process was 342, 207, and 434 kJ/kg for spruce, poplar, and sawdust, respectively.

The enthalpy of the torrefaction or pyrolysis of a sample is very important for the implementation of bioenergy, and biomass type, size, and moisture content are all variables which can affect this property (He et al., 2006; Park et al., 2007; Stenseng et al., 2001). Enthalpy of torrefaction or pyrolysis is an important thermal characteristic of biomass that is used to design the thermal reactor and predict the efficiency of the process. The process efficiency is a major characteristic that can determine the actual potential of a bioenergy source or process when compared to conventional energy sources and processes.

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Chapter 3. Physicochemical Properties

3.1. Introduction

Biomass is a significant energy source in the Southeastern United States, but the fuel characteristics of biomass are different from conventional fossil fuels such as coal and oil. Biomass has low carbon and high oxygen contents, which cause the calorific value to be much less than that of coal, and it also requires a significant amount of energy to reduce its size, which is necessary in most of the biomass to energy processes. In order to make biomass better suited for use in current energy production facilities, certain pretreatments are performed on the biomass to upgrade its fuel qualities. The pretreatment used in this study is torrefaction. Torrefaction is a thermal pretreatment of biomass to improve the fuel qualities of biomass. In this chapter, the effect of torrefaction on those fuel properties was examined, and the objective was to determine the effect of torrefaction on the physicochemical properties of the biomass samples.

3.2. Materials & Methods

3.2.1. Biomass Preparation

Loblolly pine (*Pinus taeda*) and sweetgum (*Liquidambar styraciflua*) trees were felled at the Mary Olive Thomas Research Forest of Auburn University. After felling, the trees were whole-tree chipped with a Morbark brush chipper (Figure 3.1) (Model Beever M12R, Winn, MI). The chips were then spread under a roof with open sides to air dry the chips down to a moisture content of 10-15% (w.b.). The chips were then fractionated to remove the large (>19 mm) and small chips (<3.36 mm) with the use of a Kason vibrating screen separator (Appendix C) (Kason Corporation, Millburn, NJ). After screening, the pine and sweetgum chips were analyzed for bulk density and particle size distribution, but for other analysis finer particles were required. The chips were first ground using a hammer mill (Appendix C) (C.S. Bell Company, Tiffin, OH) fitted with a 3.18 mm (1/8") screen followed by grinding with a Wiley Mill (Appendix C) (Thomas Scientific Model 3383-L10, Swedesboro, NJ) fitted with a 40 sieve screen (0.42 mm).

Figure 3.1: Morbark M12R brush chipper

Switchgrass (*Panicum virgatum*) was acquired from the E.V. Smith Research Center of Auburn University in Shorter, Alabama. The switchgrass was also allowed to air dry. It was then chopped with a Retsch heavy-duty cutting mill (Figure 3.2) (Model SM2000, Haan, Germany) fitted with a 6 mm screen. The particles were fractionated to remove the small particles (<0.707 mm) with the Kason separator. As in the case of wood chips, chopped switchgrass was analyzed for bulk density and particle size distribution, but the switchgrass was further chopped with the Retsch cutting mill fitted with a 1 mm screen and a Wiley Mill fitted with the 40 sieve screen (0.42 mm) for other analysis.

Figure 3.2: Retsch heavy-duty cutting mill SM2000

3.2.2. Treatments

Each of the three biomass types were treated at three temperature set points (225, 250, and 275°C) and three times (15, 30, and 45 minutes) for a total of 9 treatments for each biomass type. There were 27 treatments total with 3 samples per treatment, and treatments were randomized. Preliminary tests were performed using a closed, batch reactor, but the torrefied product showed uneven treatment among the particles. It is for this reason that the treatments were conducted in open top aluminum pans using a batch style process in a furnace (Figure 3.3) (Thermo Scientific Model BF51842PFMC-1, Asheville, NC) so to achieve better heat transfer through the particle bed. A thermocouple wire connected to an Omega datalogger (Appendix C) (Model HH147U, Stamford, CT) was inserted in through the vent of the furnace and into the bed of one of the samples to be treated. The temperature of the biomass was recorded every five seconds for the length of the treatment. Volatiles from the furnace were swept away by a centrifugal fan. Before and after each treatment, the biomass samples were weighed using a balance (A & D Company model GX-4000, San Jose, CA), and the moisture content was also found using an Ohaus moisture analyzer (Figure 3.4) (model MB45, Parsippany, NJ). The mass of sample to be treated was based on the bulk density and volume of the sample. A thin layer of sample of approximately 2.5 cm (~1 in.) was placed in each pan. The reason for the small layer of sample was to prevent uneven heating of the sample bed during treatments. The volume of sample in each pan was ~0.3 L, and since bulk densities of the treated samples were different, the mass of a sample was dependent on biomass type. Mass was measured using a balance (Appendix C) (A&D Company model GX-4000, San Jose, CA). Initial mass of a woody biomass sample was ~65 grams, and initial mass of a switchgrass sample was ~45 grams. It is for this reason that biomass type was not treated as an independent variable.

Figure 3.3: Thermo Scientific furnace and treatment pans

After the samples were placed inside the furnace chamber, it was completely purged with nitrogen gas at the maximum flow rate of the furnace flowmeter of 4.7 L/min (10 ft^3/hr) to remove all oxygen. Since the volume of the furnace chamber was 56.6 liters (2 ft^3), this process took 12 minutes. The flow rate was then decreased to the minimum flow rate of the flow meter of 0.47 L/min (1 ft^3/hr), and the furnace was preheated to the desired temperature set point at a heating rate of ~22°C/min. Treatment time was said to begin when the furnace reached the desired set point. At the end of the treatment time, the biomass samples were pulled from the furnace and immediately placed in desiccators to prevent further treatment and combustion. Once the pans cooled to room temperature, the samples were weighed and moisture analysis was performed to determine solids retained in each sample. After bulk density of the treated samples was determined, each sample was size reduced with a conventional coffee grinder (Appendix C) (Hamilton Beach Model 80335, Southern Pines, NC).

Figure 3.4: Ohaus moisture analyzer MB45

3.2.3. Particle Size

Particle size of the raw samples was determined using a Retsch Dynamic Image Analyzer (Figure 3.5) (model Camsizer, Haan, Germany). Approximately 200 g of each biomass sample was placed in the hopper for analysis. The sample was dropped in front of the measuring cameras to record particle size. The Camsizer recorded the size of each particle, and particle distribution was reported on a volumetric basis.

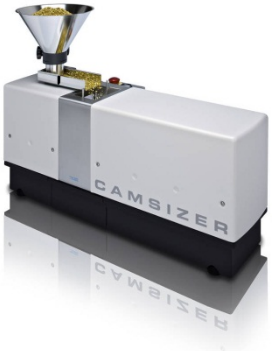

Figure 3.5: Retsch Camsizer Dynamic Image Analyzer

3.2.4. Bulk Density

Bulk density (ρ_{dry}) of the samples was dtermined using a bulk density apparatus (Figure 3.6) (Ohaus) and a 100 mL beaker. The apparatus consisted of a hopper and a container of known volume 1.1 L (1 quart dry). The volume of the samples was <1.1 L so the 100 mL beaker was used to find bulk density instead of the 1.1 L container. Mass of the samples was found using an A&D balance and the actual dry volume to the top lip of the beaker was found to be 130 mL. Dry density, ρ_{dry}, of each sample was calculated using the equation:

$$\rho_{dry} = \frac{m_s}{V_{beaker}}(1 - MC) \qquad \text{Eqn. 2.1}$$

where m_s is the mass of the sample, V_{beaker} is the actual volume of the beaker (130 mL), and MC is the moisture content of the sample.

Figure 3.6: Ohaus bulk density apparatus

3.2.5. Moisture Absorption

Maximum moisture absorption was found by placing the biomass inside an insulated environmental chamber with specific temperature and humidity conditions controlled by a conditioner (Figure 3.7) (Parameter Generation and Control, Inc. Model 9221-2110, Black Mountain, NC). The chamber was kept constant at 25°C and 90% relative humidity. Initial moisture content of each sample was measured with an Ohaus moisture analyzer. The samples were put in aluminum pans, and initial mass of each sample was measured with a balance. The samples were placed in the chamber, and the weight of the sample was measured every hour for the first 5 hours, then at 24 and 48 hours. The change in weight was used to calculate moisture contents for each time. Moisture absorption was found for each sample, and an average of the three samples was reported for each set of treatment conditions.

Figure 3.7: Parameter Generation and Control conditioning chamber

3.2.6. Proximate Analysis

Proximate analysis of the products included moisture, ash, volatile, and fixed carbon content. Moisture content of each sample was found using an Ohaus moisture analyzer. Ash content was found according to NREL/TP-510-42622 (2005) (NREL, 2005). For volatile matter determination, samples were shipped to Hazen Research Laboratory, Golden, CO, for analysis using ASTM 3175 (2011) (ASTM, 2011). Fixed carbon (FC) of the samples was found according to the equation:

$$FC\% = 100\% - ash_{dry}\% - volatile\% \qquad \text{Eqn. 2.2}$$

Each test was performed in triplicate, and the average was reported. Results were given on a dry basis.

3.2.7. Elemental Analysis

Elemental analysis of the biomass samples was performed using an elemental analyzer (Figure 3.8) (Perkin Elmer Model 2400 CHNS/O, Waltham, MA). A small sample was placed in the analyzer, and results for carbon, hydrogen, and nitrogen content were returned by the analyzer. Helium was used as a carrier gas. Samples were analyzed, and an average of three samples was reported on a dry basis for each set of treatment conditions. Results were corrected for moisture content and reported on a dry basis. Oxygen was calculated using the equation:

$$Oxygen\,\% = 100\% - carbon\,\% - hydrogen\,\% - nitrogen\,\% - ash\,\% \qquad \text{Eqn. 2.3}$$

Figure 3.8: Perkin Elmer elemental analyzer

3.2.8. Energy Content

The energy content of the biomass was measured with a bomb calorimeter (Figure 3.9) (IKA Works Inc. Model C200, Wilmington, NC). Approximately 0.5 grams of sample were weighed with a balance (Radwag Model WAX 110, Radom, Poland) and pressed into a pellet using a pelleting press (IKA Works Inc. Model C21, Wilmington, NC). The final weight of the pellet was found with the balance, and it was placed in the bomb calorimeter. Mass of the sample was input in the calorimeter and the heating value was returned in units of J/g. Each sample was analyzed, and an average of the three samples was reported for each set of treatment conditions. Results were given on a dry basis.

Figure 3.9: IKA C200 bomb calorimeter

3.2.9. Data Analysis

Microsoft Excel (Microsoft Office 2010, Redmond, WA) was used for data analysis and visuals. Statistical analysis was performed with SAS software (Version 9.2, Cary, NC). When applicable, the data were analyzed with 95% confidence. Statistical analysis was performed on the biomass types (pine, sweetgum, and switchgrass) separately because of their different natures. The switchgrass bulk density was much lower than that of the woody biomass, and, as a result, the initial masses of the samples being treated were different. Since the mass to be treated was different, the results were expected to be different.

3.3. Results & Discussion

Biomass is composed of three components: hemicellulose, cellulose, and lignin. During torrefaction, the biomass undergoes a change in mass which is a result of volatilization of part of the biomass. Hemicellulose is the most volatile portion of biomass, followed by cellulose, and finally lignin. Torrefaction was performed at low temperatures to target the part of the biomass that was previously the hemicellulose portion. It should be noted that ANOVA tests show that temperature and time had significant effects on all the properties discussed in this chapter. Also, an interaction effect between temperature and time occurred for each property.

3.3.1. Particle Size

Figure 3.10 shows the size range of the raw particles that were treated. As specified, the size range for the untreated woody biomass was 3 to 19 mm, and the untreated switchgrass size range was 1 to 6 mm. The dips in the particle sizes for pine and sweetgum could be caused by the presence of limbs and leaves or needles since the trees were chipped whole. The drop could represent the boundary between the size range of the chips and the size range of the debris.

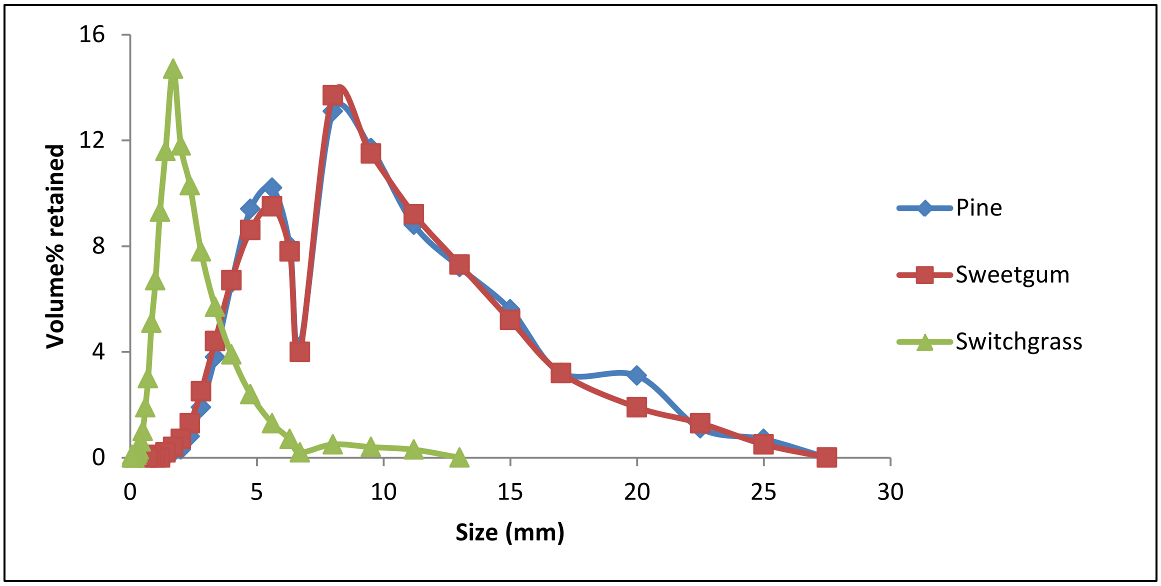

Figure 3.10: Size distribution of biomass samples prior to treatment

3.3.2. Treatments

Figure 3.11 shows the temperature profile of each biomass type during the 45 minute treatment at 250°C. The woody biomass never reached the set-point temperature of the furnace during any treatment, and the same could be said about switchgrass for treatments of 30 minutes or less with the exception of the treatment at 275°C (Appendix A). To confirm that a temperature differential between the walls of the furnace and the middle of the furnace wasn't the cause of this occurence, one run was performed to measure the temperature in the middle of the furnace without a sample. The temperature in the middle of the furnace was actually equal to or greater than the set-point temperature throughout the test (Appendix A). This test was performed without the presence of the nitrogen gas, which could possibly have been the reason for the temperature differential. Another reason for the temperature differential between the biomass and the furnace set-point could be that the biomass was still absorbing heat, which caused the thermocouple to record temperatures below the set-point.

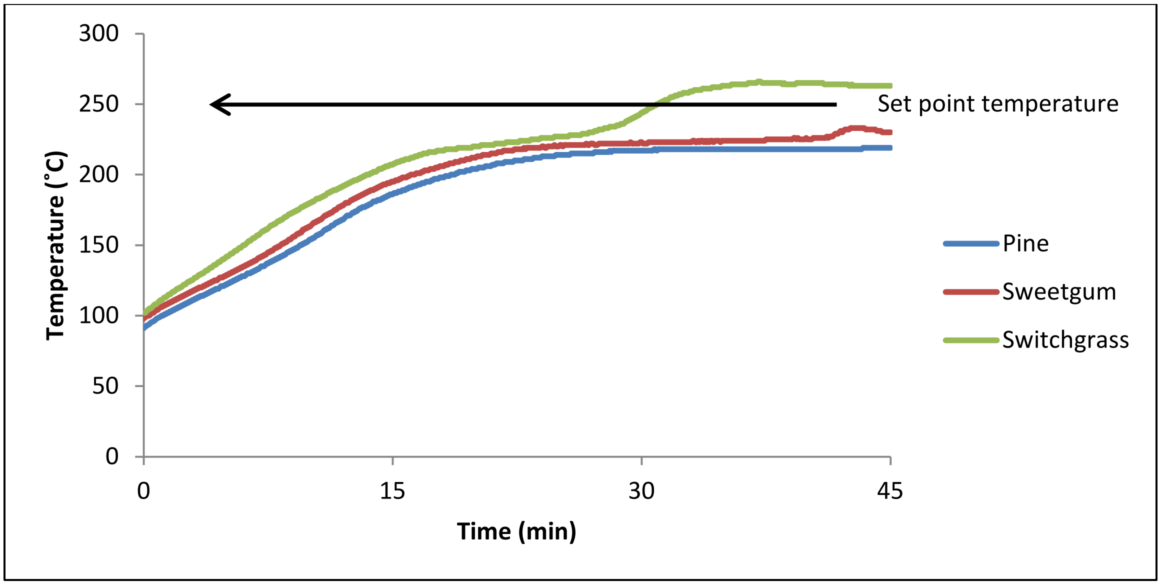

Figure 3.11: Sample temperatures during 250°C treatment

For the all the 45 minutes treatments and the 275°C treatment for 30 minutes, the temperature of the switchgrass actually rose above the set-point temperature of the furnace in the final stages of treatment, which would indicate an exothermic reaction. Switchgrass samples had less mass than did the woody biomass samples, which could explain the greater temperature. A pyrolysis process for a lignocellulosic material is a combination of endothermic and exothermic reactions, and the exothermic reactions typically happen during the final 40% weight loss which represents lignin decomposition (Park, 2008). This could explain the temperature increase in switchgrass since weight loss was approaching nearly 60% in each case.

To confirm that exothermic reactions could have occurred, a differential scanning calorimeter (DSC) (TA Instruments Model Q200, New Castle, DE) was used to heat each biomass type to 275°C and then hold at that temperature (Figure 3.12). The biomass samples (<50 sieve) reach 275°C in ~12 minutes (20°C/min), and an exothermic reaction clearly followed for each biomass. To ramp the biomass to the torrefaction temperature, the biomass absorbed heat, but once it reached the desired temperature and was held at that temperature, it released heat. This might suggest that using a process similar to fast pyrolysis would be more advantageous since batch reactors could lose some of the potential energy in the biomass.

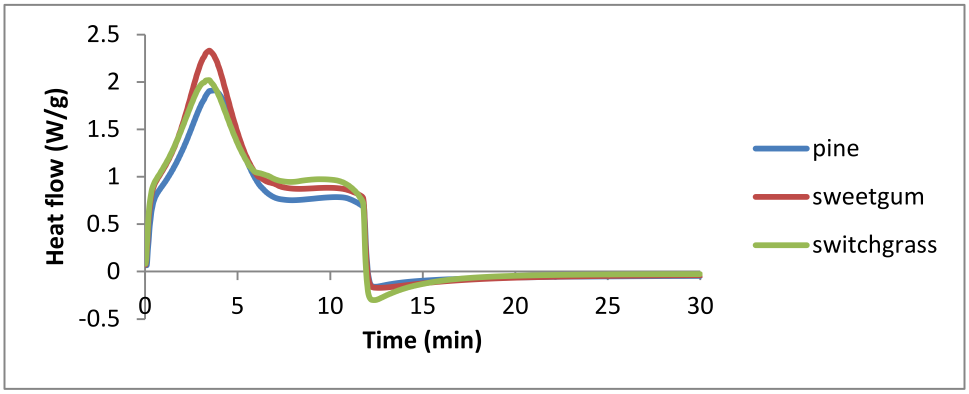

Figure 3.12: Heat flow of biomass ramped at 20°C/min to 275°C and held for 30 minutes

Table 3.1 shows the percent solids retained for each set of treatment parameters. The untreated biomass had no solids loss so it was reported as N/A. The range of values was 97.96-46.67%, 98.86-46.43%, and 94.56-34.34% for treated pine, treated sweetgum, and treated switchgrass, respectively. The open top pans promoted more volatilization which resulted in less solid yield in the torrefied product when compared to studies that used a closed reactor design (Pimchuai et al., 2010; Prins et al., 2006a). This was the case because the pans allowed heat to be transferred more uniformly through the biomass instead of radiating from the walls of a reactor.

The visual difference of the biomass subjected to torrefaction is the color of the samples. Carbonization of the biomass increased with the intensity of torrefaction. In Figure 3.13, samples on the far left are untreated, and the intensity of torrefaction increases from left to right, with the samples treated at 275°C and 45 minutes on the far right.

Figure 3.13: Ground torrefied pine samples

Table 3.1: Solids yield and dry bulk densities for biomass samples[†]

	Pine		Sweetgum		Switchgrass	
Sample[†]	Solids yield (wt%)	Bulk Density (g/L)	Solids yield (wt%)	Bulk Density (g/L)	Solids yield (wt%)	Bulk Density (g/L)
Untreated	N/A[†]	159.2	N/A	182.1	N/A	117.1
225-15	98.0_{a}	146.4_{aa}	98.9_{h}	170.5_{ee}	94.6_{n}	111.9_{kk}
225-30	90.1_{b}	140.8_{aa}	87.4_{i}	166.1_{ee}	73.9_{o}	91.0_{ll}
225-45	74.1_{c}	126.4_{bb}	79.9_{j}	154.0_{ff}	51.9_{p}	82.6_{mm}
250-15	90.7_{b}	145.6_{aa}	90.8_{i}	266.4_{ee}	75.5_{o}	104.2_{nn}
250-30	78.2_{d}	128.4_{bb}	72.4_{k}	$149.6_{ff,gg}$	53.0_{p}	73.6_{oo}
250-45	66.3_{e}	114.3_{cc}	62.6_{l}	141.1_{hh}	40.7_{q}	74.6_{oo}
275-15	80.7_{d}	129.1_{bb}	74.0_{k}	$146.9_{gg,hh}$	60.3_{r}	90.0_{ll}
275-30	61.5_{f}	113.8_{cc}	60.5_{l}	133.9_{ii}	41.3_{q}	75.4_{oo}
275-45	46.7_{g}	102.6_{dd}	46.4_{m}	126.2_{jj}	34.3_{s}	77.0_{oo}

[†]Sample ID = the first number represents temperature of torrefaction and the second number represents time of torrefaction

[†]N/A = not applicable

[†]Values with same subscripts are statistically similar

3.3.3. Bulk Density

The bulk densities of the raw and treated samples are shown in Table 3.1. The results for dry densities of the raw chips were similar to previous numbers (Harris and Phillips, 1986). The densities for treated biomass consistently decrease, with only two exceptions for switchgrass, as solids retained decrease. Mass clearly decreased as indicated by the solid yield percentage, but it is also possible that the volume of the sample changed. If the volumes were unchanging, the density of an untreated biomass sample could be multiplied by the solids yield to get an expected density for a treated sample. The expected densities ($\rho_{expected}$) were plotted as a linear function of the measured densities ($\rho_{measured}$) for each biomass type as in the equation:

$$\rho_{expected} = \rho_{measured} * \beta_1 + \beta_0 \qquad \text{Eqn. 2.4}$$

If the expected and measured densities were equal, the slope (β_1) and intercept (β_0) values of Equation 2.4 would be one and zero, respectively. A t-test was perform with the null hypothesis and alternate hypothesis being

$$H_0 = \beta_1 = 1, \beta_0 = 0, densities\ are\ equal$$

$$H_1 = \beta_1 \neq 1\ or\ \beta_0 \neq 0, densities\ are\ not\ equal$$

SAS regression analysis shows with 95% confidence the slopes to be greater than one and the intercepts to be non-zero (Table 3.2). H_0 was rejected, and H_1 was assumed to be true. Torrefaction does change the volume of the sample, as well as the dry bulk density.

Table 3.2: Model parameters and confidence intervals for bulk densities

	β_1	β_0
Pine	1.56 (1.36, 1.76)	-77.85 (-103.71, -51.99)
Sweetgum	1.85 (1.63, 2.07)	-142.34 (-175.72, -108.97)
Switchgrass	1.51 (1.23, 1.78)	-62.15 (-86.54, -37.77)

3.3.4. Moisture Absorption

Initial moisture contents were 3 to 7% for all biomass samples, and absorption rates were the highest within the initial two hours in the chamber for every sample At 24-48 hours, the moisture contents appeared to be unchanging for each biomass type. During this time period, the moisture content of the untreated pine samples changed only 0.05% per hour, while the treated samples changed less than 0.04% per hour. All sweetgum and switchgrass samples changed less than 0.02% per hour during the final 24 hours. Each of the samples behaved similarly to the curves of pine moisture absorption in Figure 3.14 (see Appendix A). Due to these minimal changes, the moisture content at 48 hours is considered to be the maximum. Table 3.3 shows the maximum moisture contents of each biomass sample. Statistical analysis shows that torrefaction does significantly decrease moisture absorbed.

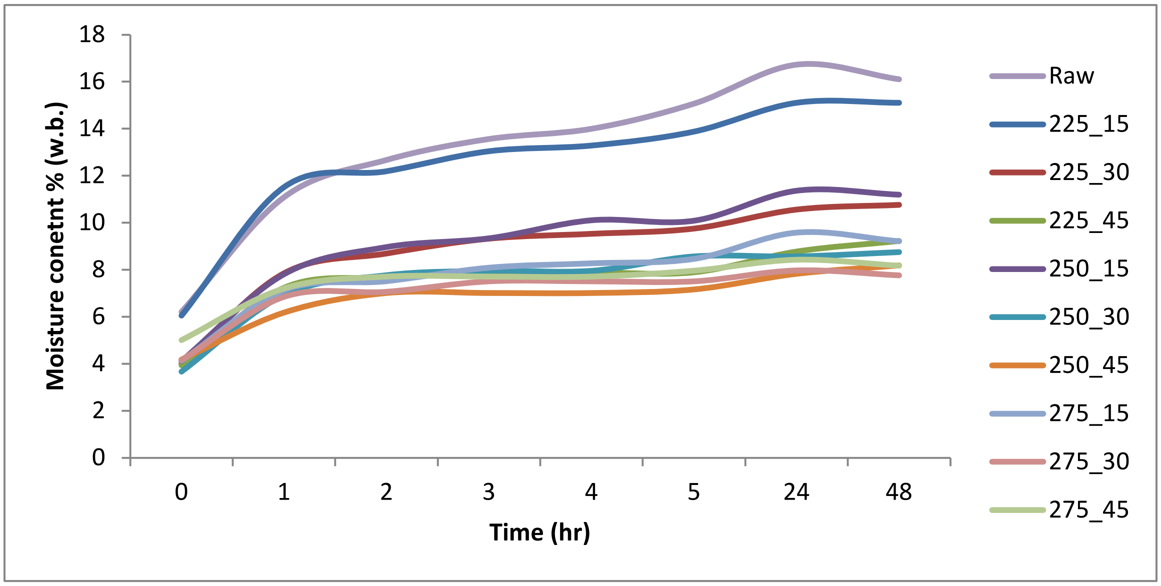

Figure 3.14: Moisture absorption of pine at 25°C and 90% RH

Table 3.3: Maximum moisture contents (w.b.) of samples at 25°C and 90% RH[†]

	Pine		Sweetgum		Switchgrass	
Sample[†]	Initial MC%	48 hr MC%	Initial MC%	48 hr MC%	Initial MC%	48 hr MC%
Pine	6.22	16.12_{a}	5.37	15.87_{f}	5.84	15.92_{o}
225-15	6.07	15.12_{b}	3.80	14.22_{g}	4.73	12.52_{p}
225-30	4.03	10.78_{c}	2.82	9.20_{h}	4.14	9.54_{q}
225-45	3.95	9.24_{d}	3.68	$9.08_{h,j}$	5.30	9.54_{q}
250-15	4.13	11.21_{c}	4.30	9.93_{i}	4.66	$9.44_{q,r}$
250-30	6.68	8.77_{d}	5.04	$8.69_{j,l}$	4.53	$8.94_{r,s}$
250-45	4.20	8.20_{e}	5.55	$9.04_{h,j}$	5.92	10.59_{t}
275-15	4.15	9.23_{d}	3.45	$8.35_{l,m}$	2.58	8.80_{s}
275-30	4.18	7.78_{e}	4.45	8.16_{m}	6.34	$9.26_{q,r,s}$
275-45	5.02	8.19_{e}	5.46	$8.44_{l,m}$	7.09	11.05_{t}

[†]Values Sample ID = the first number represents temperature of torrefaction and second number represents time of the torrefaction

[†]Values with the sample subscripts are statistically similar

The maximum moisture absorbed for the untreated samples was around 15-16% for each biomass type. The most minor treatment conditions of 225°C and 15 minutes only decreased the maximum moisture absorbed by 6% for pine, 10% for sweetgum, and 21% for switchgrass. When either the temperature or time was increased above 225°C or 15 minutes, a more significant drop in moisture absorbed was observed for each biomass type. Figure 3.15 shows maximum moisture contents of the sweetgum samples. At the eight treatments more intense than 225°C and 15 minutes, moisture absorbed was decreased by 37-49%. Similar results were found for the other biomass types (see Appendix A), as maximum moisture absorption for pine was decreased by 30-52% and switchgrass by 31-45%.

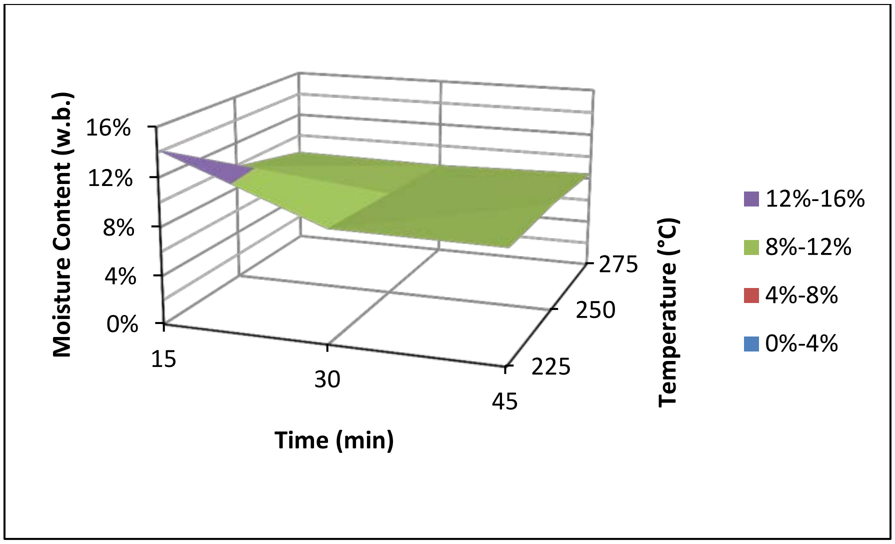

Figure 3.15: Surface plot of 48 hour moisture contents of sweetgum samples

3.3.5. Proximate Analysis

Table 3.4 shows the results for proximate analysis of the samples. Ash and fixed carbon contents of the treated samples increased while volatiles decreased as the temperature and time of treatment increased. At the most intense treatment conditions, each biomass type showed a decrease in volatile content of up to ~50%, while ash percentages approximately doubled, and fixed carbon percentages more than doubled. Only volatile matters are driven off the biomass during torrefaction, leaving the ash and fixed carbon portions. These trends agree with other studies of torrefied biomass (Couhert et al., 2009; Pach et al., 2002; Prins et al., 2006a).

Table 3.4: Physicochemical properties

	Elemental Analysis (wt%, dry)				Proximate Analysis (wt%, dry)			
Sample	C	H	N	O	Ash	Volatiles	Fixed Carbon	HHV (MJ/kg, dry)
Pine	50.90	6.11	0.48	41.84	0.72	80.79	18.49	20.178
225-15	51.15	5.99	0.61	41.65	0.63	80.53	18.84	20.503
225-30	53.67	5.70	0.78	39.02	0.87	76.37	22.75	21.112
225-45	58.63	4.88	0.88	34.70	0.94	65.45	33.61	22.501
250-15	53.02	5.95	0.78	39.28	1.00	76.57	22.43	21.279
250-30	57.14	5.27	0.84	35.83	0.96	70.03	29.02	22.396
250-45	62.26	4.68	0.87	31.16	1.08	59.75	39.17	24.010
275-15	56.59	5.49	0.74	36.28	0.94	70.90	28.16	21.909
275-30	64.17	4.81	0.81	29.27	0.98	56.53	42.49	24.719
275-45	71.48	3.47	0.92	22.81	1.40	43.17	55.43	26.678
Sweetgum	49.76	5.96	0.36	42.61	1.39	81.41	17.20	19.649
225-15	49.20	5.96	0.34	43.45	1.09	82.24	16.66	20.426
225-30	52.16	5.57	0.41	40.56	1.35	78.43	20.22	20.910
225-45	54.27	5.19	0.49	38.47	1.65	73.27	25.08	22.461
250-15	51.70	5.76	0.47	40.67	1.46	78.40	20.15	19.918
250-30	55.77	5.17	0.55	36.72	1.87	71.54	26.59	21.609
250-45	59.68	4.71	0.63	32.88	2.18	60.02	37.80	22.672
275-15	55.70	5.37	0.55	36.66	1.79	70.87	27.34	21.574
275-30	60.61	4.92	0.66	31.39	2.53	59.64	37.84	23.369
275-45	68.39	3.89	0.76	24.04	3.08	44.27	52.65	25.860
Switchgrass	48.26	5.98	0.62	42.59	2.71	79.18	18.12	19.498
225-15	49.11	5.78	0.56	41.90	2.77	79.38	17.85	19.389
225-30	54.27	5.36	0.76	36.01	3.75	67.45	28.80	21.409
225-45	62.29	4.32	0.83	27.45	5.39	48.25	46.36	23.988
250-15	54.40	5.33	0.40	36.36	3.67	69.85	26.48	21.018
250-30	61.04	4.65	0.63	28.56	5.37	49.37	45.25	24.344
250-45	69.73	3.34	0.65	20.09	6.62	39.00	54.38	25.451
275-15	58.05	4.94	0.50	32.49	4.21	60.03	35.76	22.625
275-30	70.73	3.55	0.61	19.11	6.40	38.68	54.92	26.246
275-45	74.04	2.93	0.63	15.74	7.24	34.82	57.94	25.952
Coal	66.74	3.76	1.89	11.61	16.00	29.29	54.70	26.946

3.3.6. Elemental Analysis

Table 3.4 shows the results for elemental analysis of each sample. Of particular importance are the values for carbon and oxygen percentage. Carbon increased while oxygen decreased with increases in temperature and time. Similar trends have been observed with the torrefaction of eucalyptus (Arias et al., 2008). Carbon percentages for each biomass type increased from 48-51% for the raw biomass to 68-74% (depending on the biomass types) for the maximum treatment temperature of 275°C and time of 45 minutes, and oxygen contents for each biomass decreased from 42-45% for raw biomass to 22-27% for the maximum treatment conditions. Hydrogen content slightly decreased as treatment increased while nitrogen very slightly increased.

Elemental analysis was also performed on a sample of coal from Alabama Power's electrical generating plant in Gorgas, AL, to compare values of the torrefied biomass to the coal. Carbon and oxygen values for the coal were 67% and 28%, respectively. When subjected to torrefaction, biomass elemental composition can become similar to that of coal.

3.3.7. Energy Content

Energy content for the biomass also increased with treatment. Table 3.4 shows the energy content of each sample at each set of treatment conditions. Initial energy content for each biomass type was 19.5-20 MJ/kg on a dry basis. The energy content for each biomass type was found to consistently increase with increases in treatment temperature and time. It increased by up to ~35% for the most intense treatments. Lignin is the least reactive portion of biomass and also the most energy dense which means it would constitute a large portion of the sample after treatment which would increase the energy content (ASME, 1987). The higher carbon percentage and lower oxygen percentage in each sample also contributes to an increase in energy content.

SAS was used to determine the relationship of proximate and elemental analysis on the energy content of the untreated and treated biomass samples. Stepwise regression was used with an 85% significance level. The results for linear stepwise regression yielded the equation

$$HHV = 24.529 + 11.102(Carbon) - 31.853(Moisture) - 25.767(Ash) - 11.543(Volatile)$$

Results show that this model accounts for 96% of the variation (R^2 = 96%) in the data set. Torrefied biomass displays a strong dependence on the proximate and elemental analysis of this biomass.

3.3.8. Energy Density

Bulk density and energy content were used to calculate an energy density for the biomass samples. Calculated dry energy densities of the untreated biomass samples are shown in Table 3.5. Torrefaction decreased the energy density for each biomass sample, and the maximum energy densities were the untreated samples. These results initially indicate that torrefaction should be performed after transport to ensure the maximum amount of energy is moved per load. It should be noted that bulk density was measured when moisture content was <10%. Biomass volume can change and be modeled as a function of moisture content (Tagawa et al., 2002). This theory is also limited by the small sample size used to measure bulk density. More detailed research should be performed to determine a more applicable conclusion.

Table 3.5: Calculated energy densities for the biomass samples

	Energy density (MJ/m³)		
Sample	Pine	Sweetgum	Switchgrass
Untreated	3211	3577	2283
225-15	3003	3483	2169
225-30	2972	3475	1948
225-45	2845	3458	1982
250-15	3098	3315	2191
250-30	2876	3232	1791
250-45	2744	3198	1900
275-15	2829	3168	2036
275-30	2815	3128	1979
275-45	2737	3264	1999

3.4. Conclusions

Three biomass types were torrefied across a range of treatment conditions, and the properties of the samples were analyzed. Considerable changes to the physical properties occurred with treatment. ANOVA tests shows that temperature and time of treatment had significant statistical influence on the all the physicochemical properties that were found. This open-topped, batch style process allowed for treatment through the particle bed with even charring occurring throughout the sample. A temperature differential between the biomass bed and the furnace set-point was observed. The actual temperature of the biomass was less than the set-point temperature for all the samples except for four switchgrass samples, but significant mass loss still occurred along with increased carbon and energy content and decreased moisture absorption. The temperature differential could have been because the top portion of sample was absorbing the heat from the furnace, which insolated the inner particles. Another reason for the temperature differential could be that the flow of nitrogen into the furnace caused the biomass samples to be lower than the set-point temperature of the furnace These findings combined with the treatment being shorter than in other studies suggests that lower set-point temperatures could be explored using a treatment process that promotes better heat transfer through the biomass.

3.5. References

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Chapter 4. Thermal Analysis

4.1. Introduction

Thermal analysis can be used to research the pyrolysis and combustion characteristics of a biomass sample. Thermogravimetric analysis is a type of thermal analysis used to model pyrolysis and combustion profiles of biomass by measuring the weight of a sample as a function of time when the sample undergoes a specific heating pattern. Pyrolysis and combustion behavior is an important characteristic of biomass, which can be used to efficiently design a reactor or boiler for bioenergy production. These profiles can also be used to obtain the lignocellulosic composition of biomass (hemicellulose, cellulose, and lignin) and how those constituents behave at different temperatures (Carrier et al., 2011). It can even be used to determine the proximate analysis of a biomass sample (Elder, 1983; Mayoral et al., 2001; Ottaway, 1982). Kinetic parameters are commonly calculated from thermogravimetric profiles of biomass samples (Gil et al., 2010; Huang et al., 2011; Van de Velden et al., 2010; White et al., 2011). These parameters are used to model the dependence of the decomposition of biomass on temperature changes (Agrawal, 1992; White et al., 2011).

Differential scanning calorimetry is another type of thermal analysis that measures the endothermic or exothermic behavior of biomass as a fuction of temperature or time when the biomass is subjected to a specific heating pattern. It is most commonly used to model pyrolysis processes (Stenseng et al., 2001). Modeling the heat transfer of the biomass can be used to efficiently design a pyrolysis reactor.

In this chapter thermogravimetric analysis and differential scanning calorimetry were performed on the biomass samples and the objectives were to

a) determine the effect of torrefaction on the degradation profiles and reaction kinetics of the biomass samples;
b) determine the effect of treated biomass concentration on the combustion profiles and reaction kinetics of treated pine and coal mixtures; and
c) determine the effect of moisture content on the energy required for torrefaction.

4.2. Materials & Methods

4.2.1. Biomass Preparation

The desired particle size for thermal analysis was 40-50 sieve size (0.42-0.297 mm). As stated in Chapter 3, untreated biomass was size reduced using a number of methods, and treated biomass was size reduced using a coffee grinder. To attain the desired particle size, each biomass sample was sieve by hand using size 40 and 50 USA standard test sieves (VWR, Radnor, PA).

4.2.2. Data Analysis

All data were plotted using Microsoft Excel (Microsoft Office 2010, Redmond, WA). Statistical analysis was performed for the calorimetry data on each biomass type separately using SAS (Version 9.2, Cary, NC).

4.2.3. Thermogravimetric Analysis

One treated and untreated sample of each biomass type was heated to examine the effects of torrefaction on the thermal degradation and reaction kinetics. The treated sample was chosen based on findings for moisture absorbed from the previous chapter. A significant drop in moisture absorbed occurred for the samples torrefied at higher temperatures and/or times of 225°C and 15 minutes. Treatment temperature was desired to be minimized, and, as a result, the samples treated at 225°C and 30 minutes were chosen. Tests were carried out by a thermogravimetric analyzer (TGA) (Figure 4.1) (Shimadzu Model TGA-50H, Columbia, MD). A known amount of samples (~7-8 mg) were heated in aluminum crucibles from 25 to 600°C using heating rates of 5, 10, 20, 30, and 40°C/min. Runs were performed with nitrogen and air as carrier gases to simulate pyrolysis and combustion processes, respectively. The TGA measured the weight and temperature of the sample each second.

Figure 4.1: Shimadzu TGA-50H thermogravimetric analyzer

Thermal analysis was also performed on coal samples and blends of coal and treated pine. The treated pine was blended with the coal at biomass concentrations of 10, 20, and 30% by mass. The effect of biomass concentration on the thermal degradation and reaction kinetics was examined. Tests were performed using the Shimadzu TGA, and aluminum crucibles were used in the same temperature range of 25 to 600°C with heating rates of 10, 20, 30, and 40°C/min. Air was used as a carrier gas to simulate a combustion process, and temperature and weight were recorded each second.

The isoconversional method was used to determine the reaction kinetics, specifically the activation energy (E), of the samples for both the inert and oxidative atmospheres. The equation for conversion rate ($\frac{d\alpha}{dt}$) for the degradation of biomass was defined as

$$\frac{d\alpha}{dt} = kf(x) \qquad \text{Eqn. 4.1}$$

Kinetic reaction models obey a rate law that follows the Arrehnius equation which defines *k*:

$$k = Aexp^{\frac{-E}{RT}} \qquad \text{Eqn. 4.2}$$

where *R* is the universal gas constant, 8.314 J/mol K, *T* is the temperature in Kelvin, and *A* and *E* are kinetics parameters pre-exponential factor (1/s) and activation energy (J/mol), respectively. The degree of conversion expression *f(x)* and can be defined as

$$f(x) = (1 - \alpha)^n \qquad \text{Eqn. 4.3}$$

where *n* is the reaction order. The dimension parameter α represents the degree of conversion which is further explained as

$$\alpha = \frac{m_0 - m_i}{m_0 - m_f} \qquad \text{Eqn. 4.4}$$

where m_0 was the mass at 150°C, m_f was the final mass, and m_i was the instantaneous mass. The mass at 150°C was used as the initial mass of the sample so that *α* would only represent solid mass loss. If equations 4.2 and 4.3 are substituted into Equation 4.1, the result is

$$\frac{d\alpha}{dt} = Aexp^{\frac{-E}{RT}}(1 - \alpha)^n \qquad \text{Eqn. 4.5}$$

Taking the natural log for Equation 4.5 results in

$$ln\left(\frac{d\alpha}{dt}\right) = ln(A) + n * ln(1 - \alpha) - \frac{E}{RT} \qquad \text{Eqn. 4.6}$$

Using Microsoft Excel (Microsoft Office 2010, Redmond, WA), data points for the degrees of conversion 0.1, 0.2, 0.3 ….. 1.0 were found. The values of $ln(^{d\alpha}/_{dt})$ were plotted as a function of *1/T*. Linear models were fitted to the data points of each heating rate for equal degrees of conversion, α. The slope of a curve was calculated and defined as $^{E}/_{R}$, which was used to find activation energy. The intercept of a curve was $ln(A) + n * ln(1 - a)$, which was used to calculate the pre-exponential factors at different reaction orders.

4.2.4. Differential Scanning Calorimetry

The energy required to heat the biomass samples from ambient temperature to torrefaction temperature, 25-225°C, at different moisture contents was found using a differential scanning calorimeter (DSC) (Figure 4.2) (TA Instruments Model Q200, New Castle, DE). A known amount of samples (~6-7) mg were analyzed in aluminum "Tzero" pans and lids in order to allow gases to escape from the sample during heating, and nitrogen was used as a carrier gas. Mass of each sample was found using a balance (Radwag Model WAX 110, Radom, Poland). The mass was input into the calorimeter, and samples were heated from 25 to 550°C at a heating rate of 20°C/min. Each test was performed in triplicate. The DSC measured heat flow and temperature of the sample each second. The provided compatible software (TA Instruments Universal Analysis 2000, Version 4.7A, New Castle, DE) was used to analyze the data from the DSC. To calculate the effect of temperature on the energy input using the software, a straight baseline was drawn on the heat flow curve from 25-225°C. The software then calculated the area between the curve the linear baseline and reported the results as J/g, the energy input divided by the initial mass. A general method for calculating enthalpy for biomass pyrolysis can be seen in Equation 4.1 (He et al., 2006):

$$\frac{Q}{m_0} = \int_0^t \frac{\left(m_i c_p \frac{dT}{dt} + m_i \dot{H}_p\right)}{m_0} dt \qquad \textbf{Eqn. 4.1}$$

where Q is the energy requirement for biomass pyrolysis, m_0 is the initial sample mass, t is the run time, m_i is the instantaneous mass, c_p is the specific heat of the sample, dT/dt is the heating rate, and $\dot{H}_p$ is the reaction heat flow of the biomass. Calorimetry was performed on each biomass type at four moisture contents, and each test was performed in triplicate.

Figure 4.2: TA Instruments Q200 differential scanning calorimeter

Specific moisture contents for the biomass types were achieved by sealing the untreated biomass samples inside desiccators containing saturated salt solutions. Salts used were lithium choloride (LiCl), magnesium choride ($MgCl_2$), sodium chloride (NaCl), and potassium nitrate

(KNO_3). A small volume (50 mL) of demineralized water was put in the bottom of each desiccator. Salts were mixed with the water until the mixture became saturated and salt crystals were no longer able to dissolve and remained present below the surface of the solution. Aluminum pans containing raw biomass samples (5 g) were placed above the solutions on an aluminum grate inside each desiccator. The desiccators were placed inside an ESPEC environmental chamber (Figure 4.3) (Model ESL-2CA, Hudsonville, MI) in order to maintain a constant temperature of 25°C which stabilized the relative humidity and moisture content. The saturated salt solutions provided different relative humidities (LiCl – 11%, $MgCl_2$ – 33%, NaCl – 75%, KNO_3 – 94%) to achieve different moisture contents (Labuza, 1984). The moisture content of each biomass sample was measured using an Ohaus moisture analyzer (Model MB45, Parsippany, NJ).

Figure 4.3: Desiccators in Espec environmental chamber

4.3. Results & Discussion

4.3.1. Thermogravimetric Biomass Pyrolysis

Figure 4.4 and 4.5 show the mass loss curve (TG) and mass loss rate curve (DTG) of untreated pine, sweetgum, and switchgrass in nitrogen atmospheres. Degradation of lignocellulosic biomass under inert conditions can be broken down into three distinct stages. The first stage is dehydration (<150°C), followed by active pyrolysis (150-400°C), and, lastly, passive pyrolysis (>400°C) (Figure 4.4) (Kumar et al., 2008). The initial stage of weight loss in the curve can be attributed to the removal of the moisture in the biomass. The DTG curves for each untreated and treated biomass sample at every heating showed the differential weight loss to be 0 at 150°C; therefore, the moisture has completely evaporated by 150°C for each heating rate. Similar studies acknowledged this same occurrence for lignocellulosic materials (Kumar et al., 2008; Sanchez-Silva et al., 2012; Vuthaluru, 2004)

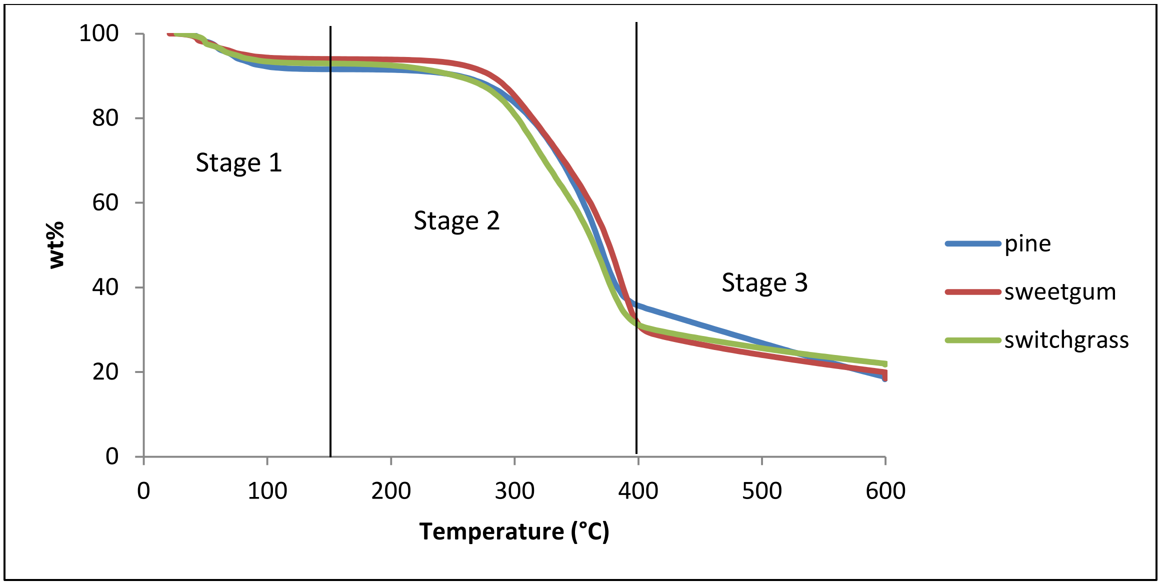

Figure 4.4: TG pyrolysis profile of untreated biomass at 10°C/min

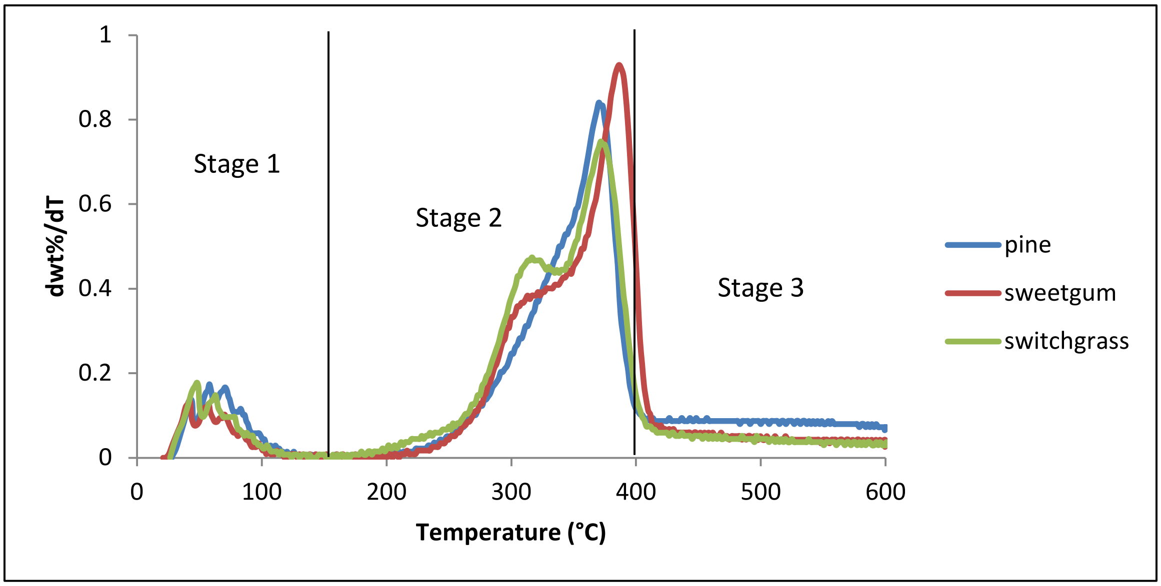

Figure 4.5: DTG pyrolysis profile of untreated biomass at 10°C/min

More significant weight loss took place during the second stage of the process. This active pyrolysis process occurred between the temperatures of 150-400°C. Figure 4.5 shows existence of a slight shoulder that occurs at 340-350°C for untreated pine. This represents degradation of the hemicellulose portion of the biomass (van der Stelt et al., 2011). Cellulose degradation also began at this temperature but is more prominent at higher temperatures because of its long chain structure. Lignin degradation also occurred during the second stage, but due to its complex structure, degradation occurred over a wide temperature range (Jiang et al., 2010; van der Stelt et al., 2011). Sweetgum and switchgrass have this same shoulder characteristic, but the appearances are much more apparent than on the pine curve. The reason for this is that grass and hardwood typically have a higher percentages of cellulose and hemicellulose and lower percentages of lignin than softwood (McKendry, 2002). Less lignin decomposition during the pyrolysis of the sweetgum and switchgrass could explain the more prominent peaks for hemicellulose and cellulose. The maximum rate of degradation took place at temperatures of 370-400°C, depending on heating rate. This primarily represents the maximum degradation of cellulose and hemicellulose in the biomass. In Figure 4.7, the peaks on the graph shift right with increasing heating rate, which proves that there is a thermal lag occurring for the higher heating rates (Damartzis et al., 2011). Similarly, Figure 4.6 shows that higher heating rates cause the solids degradation to begin at higher temperatures. This thermal lag is consistent with all of the biomass samples. The final stage of pyrolysis (400-600°C), or passive pyrolysis (Kumar et al., 2008), is the degradation of the most complex portion of the biomass, which is the reason for minor weight loss. The residual mass percentage at 600°C was near the combined ash and fixed carbon percentages mentioned in the previous chapter.

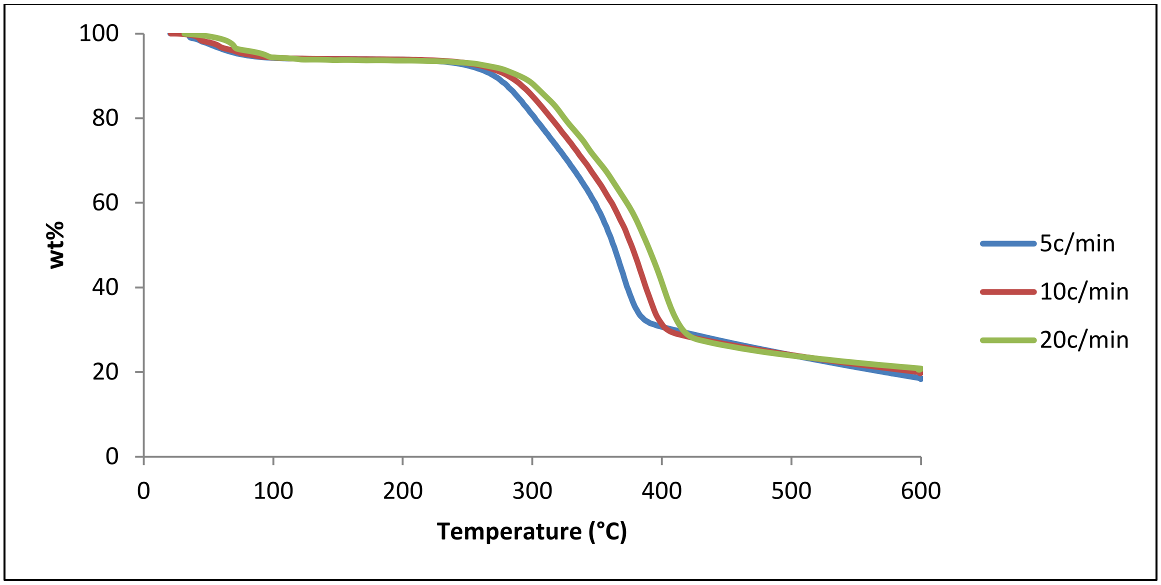

Figure 4.6: TG pyrolysis profile of untreated sweetgum

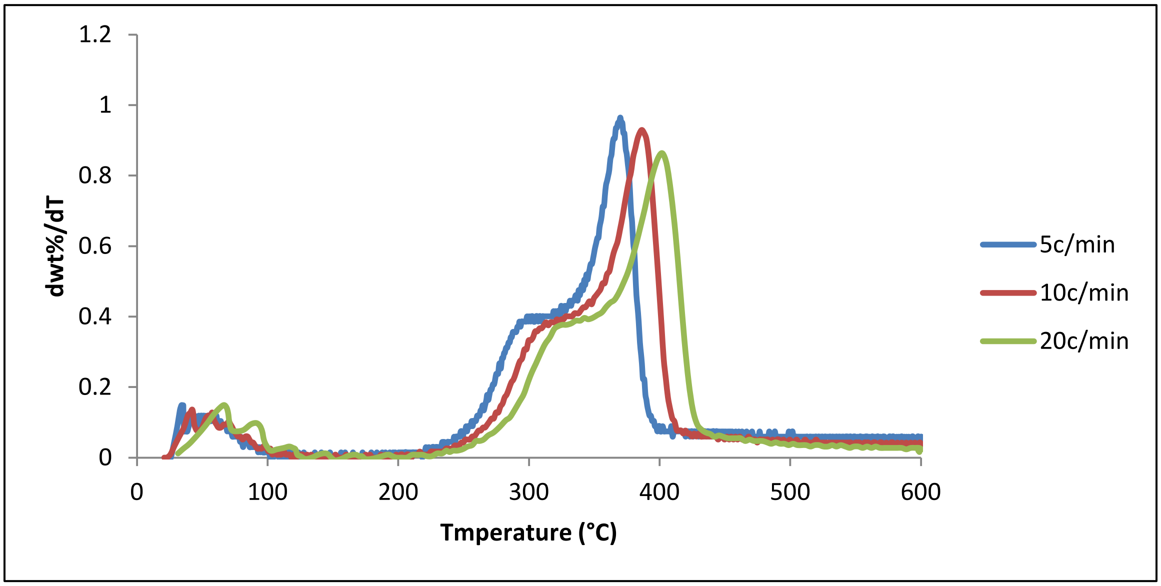

Figure 4.7: DTG pyrolysis profile of untreated sweetgum

Figures 4.8, 4.9, and 4.10 show the TG curves of untreated and treated biomass samples at a heating rate of 10°C/min, and Figures 4.11, 4.12, 4.13 show the DTG curves Hemicellulose is the constituent in biomass that is primarily removed during the torrefaction process (van der

Stelt et al., 2011). The TGA data shows that the hemicellulose shoulders exists at temperatures higher than the torrefaction temperature in Chapter 3, which would seem to indicate that hemicellulose mass loss could not have occurred at the treatment temperatures. That assumption is, however, not true, because treatment time has a significant impact on mass loss as mentioned in previous chapter. This is apparent as the DTG graphs show that the hemicellulose shoulder present on the untreated biomass curve is smaller for the torrefied biomass than the untreated biomass. In the case of switchgrass, the shoulder is completely gone (Figure 4.13). Similarly, the TG graphs show that the initial solids losses occur at higher temperatures (Figure 4.8, 4.9, and 4.10). This indicates that the volatilization could have removed the entire hemicellulose portion. Another difference is the height of the peaks for the TGA curves. Torrefied biomass peaks are all higher than the peaks for the untreated biomass. Since part of the hemicellulose has been removed from the biomass during torrefaction, the concentrations of cellulose could be greater for the treated biomass than for the untreated. This could explain why the primary peak representing cellulose decomposition is higher. Another reason could be that the torrefied biomass was more porous than the untreated biomass. Increasing the surface area of the material would increase the degradation rate.

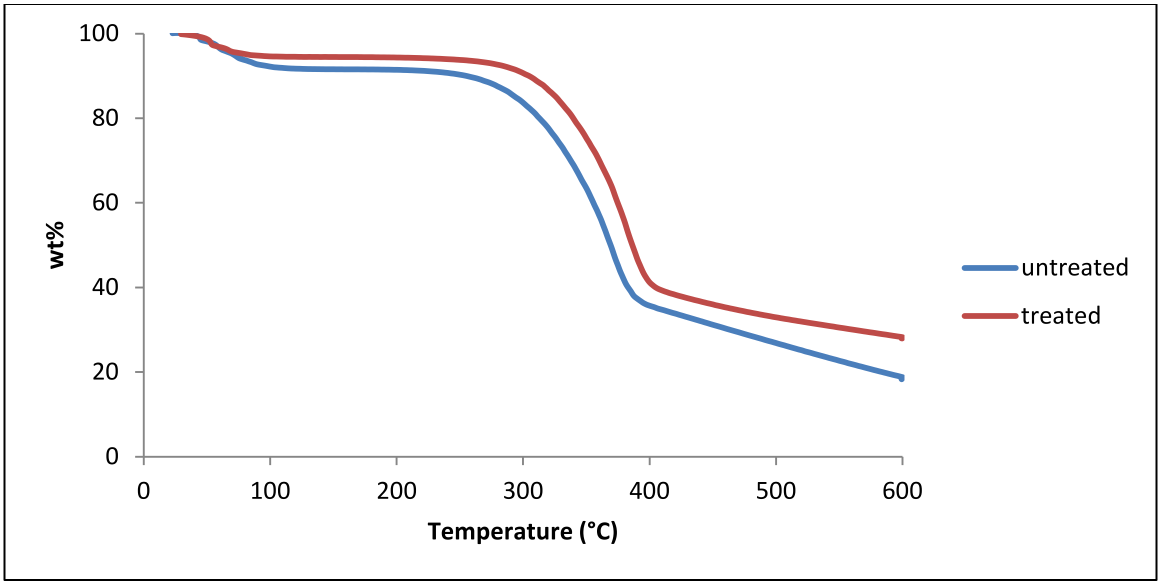

Figure 4.8: TG pyrolysis profile of pine at 10°C/min

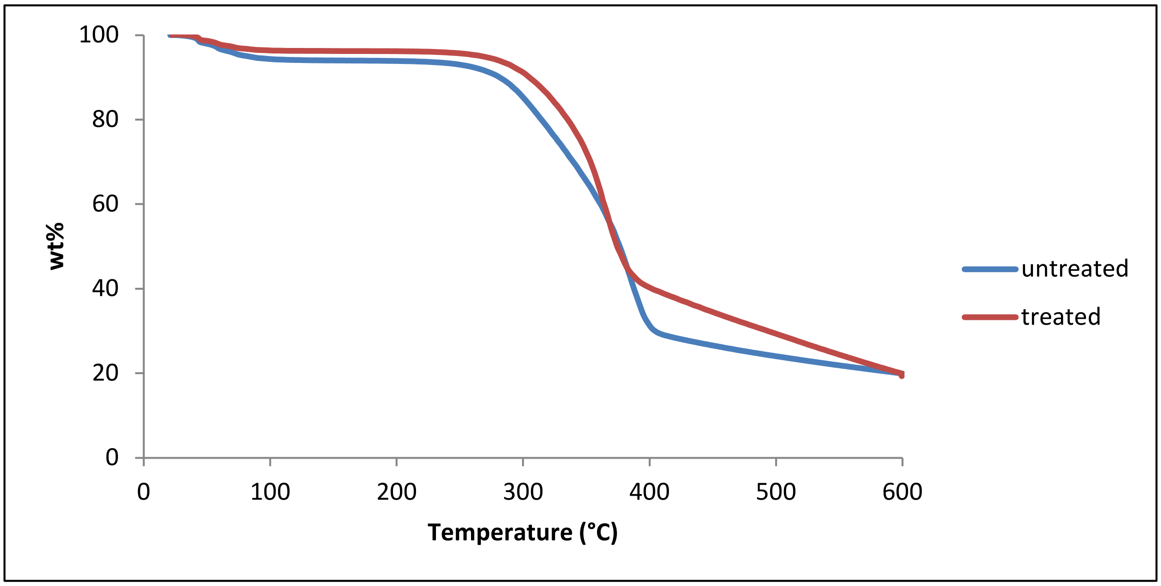

Figure 4.9: TG pyrolysis profile of sweetgum at 10°C/min

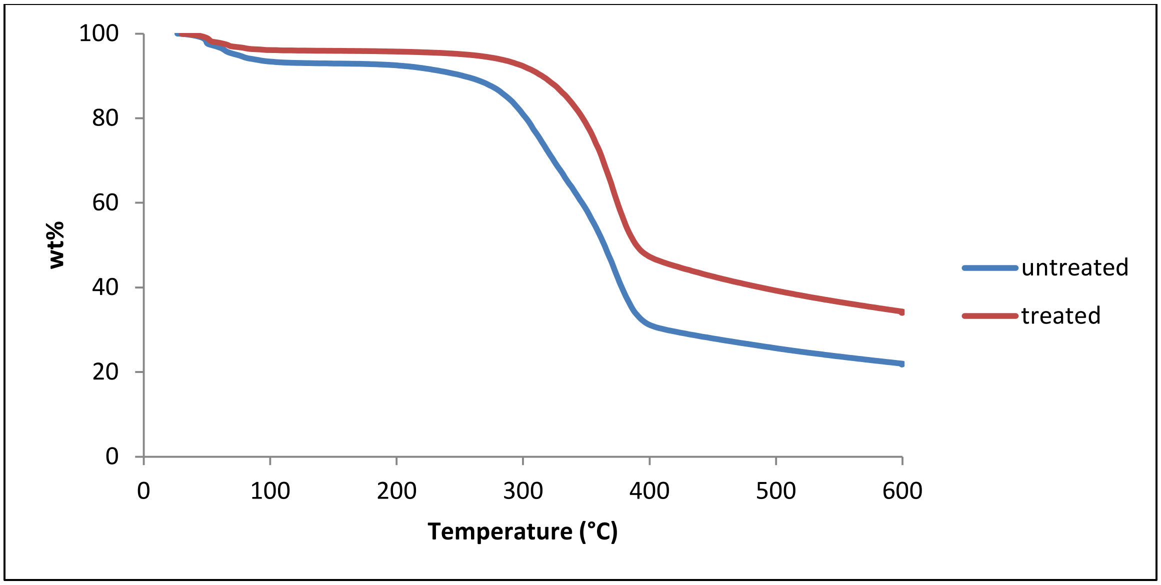

Figure 4.10: TG pyrolysis profile of switchgrass at 10°C/min

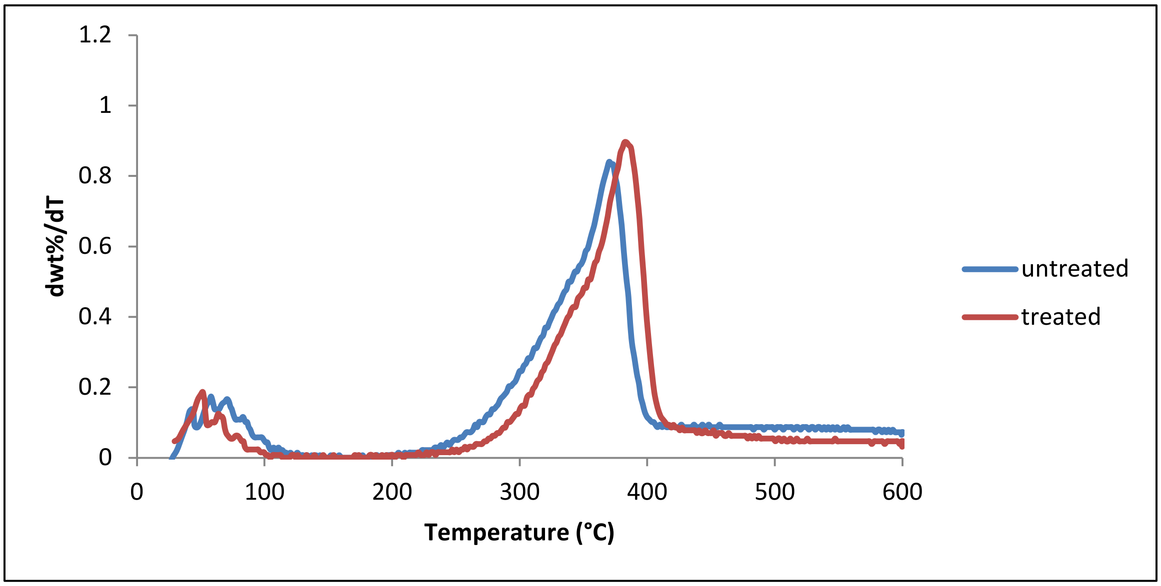

Figure 4.11: DTG pyrolysis profile of pine at 10°C/min

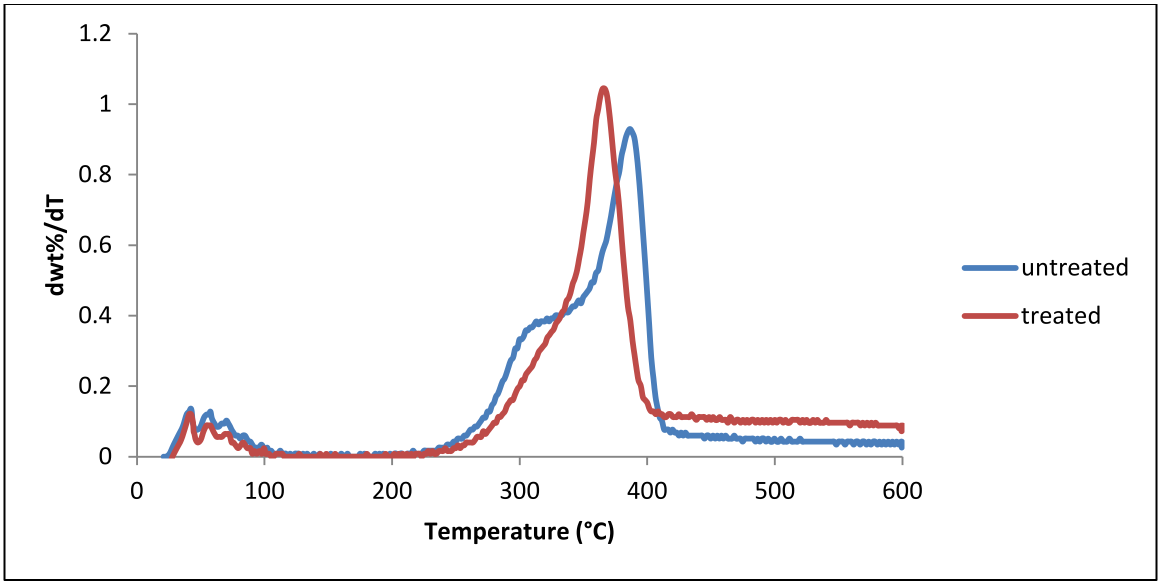

Figure 4.12: DTG pyrolysis profile of sweetgum at 10°C/min

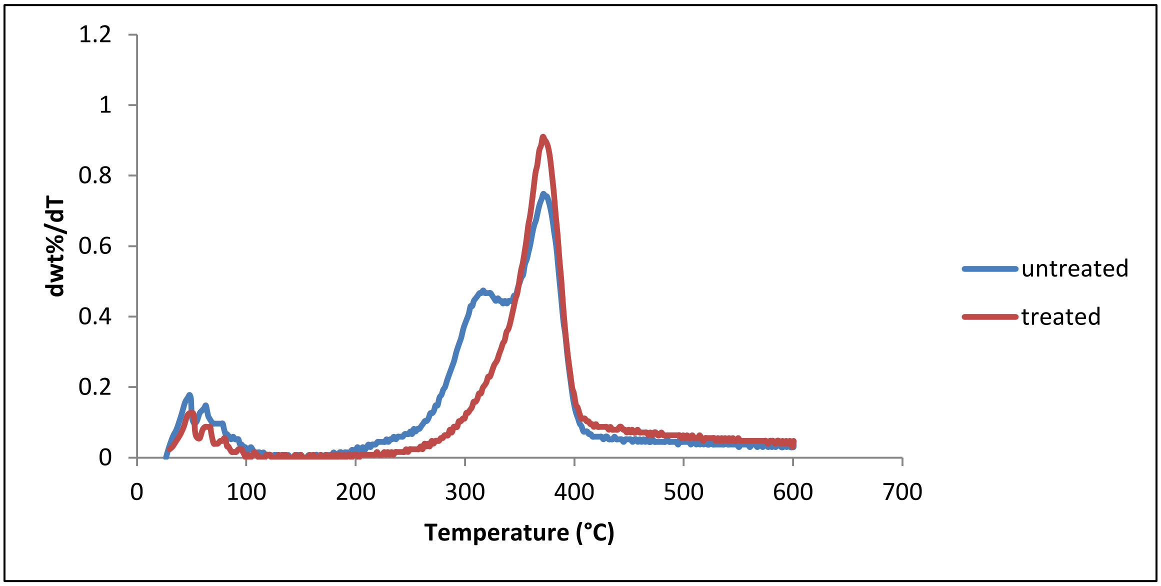

Figure 4.13: DTG pyrolysis profile of switchgrass at 10°C/min

An example of an isoconversional graph used to fit the kinetic model can be seen in Figure 4.14. All linear models had R^2 fitted values equal to or greater than 0.85, with the exception of the treated switchgrass at $\alpha = 0.5$. Table 4.1 shows the calculated activation energies of the biomass samples for pyrolysis processes. Activation energy is generally considered to be the sensitivity of the material to temperature changes. The maximum rates of mass loss of the treated biomass are greater than the maximum rates of mass loss for the untreated samples, which would seem to indicate that the treated biomass would be more sensitive to temperature changes. This would seem true for the pine and switchgrass since the activation energies appear to slightly increase with treatment. The activation energies of sweetgum, however, do not show a definite trend as they increase and decrease for the values of α in Table 4.1. Pre-exponential factors were also calculated and can be found in Appendix B.

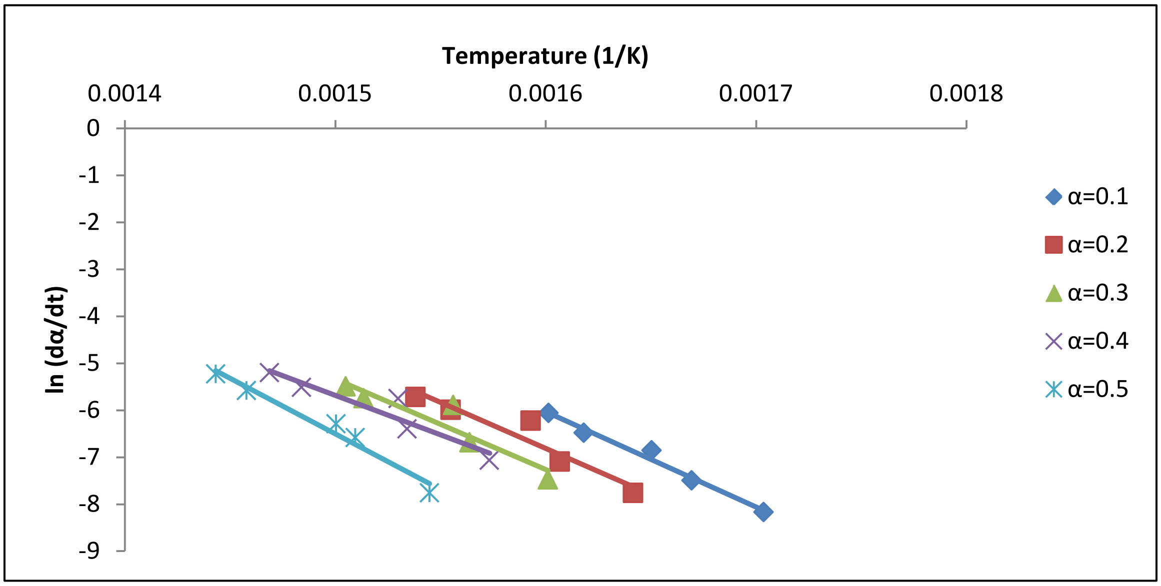

Figure 4.14: Isoconversional plot for pyrolysis of treated pine

Table 4.1: Activation energies (kJ/mol) for pyrolysis of biomass samples

	Pine		Sweetgum		Switchgrass	
α	Untreated	Treated	Untreated	Treated	Untreated	Treated
0.1	149.7	165.2	158.4	169.5	140.9	166.3
0.2	150.8	159.4	173.7	162.1	145.1	182.0
0.3	137.6	156.6	176.0	147.1	165.3	177.1
0.4	135.2	136.6	171.1	136.6	157.9	178.4
0.5	131.4	192.2	160.9	168.9	168.9	298.5

4.3.2. Thermogravimetric Biomass Combustion

The combustion of lignocellulosic biomass can also be divided into three stages: moisture release (<150°C), volatile combustion (150-400°C), and residual char combustion (>400°) (Kumar et al., 2008). Those three stages can be seen very distinctly in Figure 4.15 and Figure 4.16. The first stage, moisture release, is a common occurrence in biomass materials due to their hygroscopic nature (Tumuluru et al., 2011; Wu et al., 2011). The second stage is very similar to the previous graphs for inert atmospheres. It represents the combustion of the volatile matter in the biomass which occurs at ~150-400°C, and has been observed by others (Varol et al., 2010; Wongsiriamnuay and Tippayawong, 2010). These graphs also show the presence of a secondary peak in this area representing the least volatile fraction of the biomass, mainly hemicellulose. This secondary peak is also present in the previous figures showing an inert atmosphere. Similarly, the shoulder is more prominent for the sweetgum and switchgrass than for the pine. The primary peaks during this phase of combustion occur at temperatures of 325-360°C, depending on the heating rate. This primary peaks in each figure are representative of the highest rate of devolatilization of the volatile matter, mostly cellulose with some lignin. The final stage of combustion, beginning at ~400°C, is the char combustion, which is considered to be mostly lignin and fixed carbon. By 600°C complete oxidation had taken place for each biomass sample, and the remaining weight was considered to the inorganic constituents. The curves in Figure 4.17 and Figure 4.18 show multiple heating rates which again confirm the presence of a thermal lag in the sample at higher heating rates (Damartzis et al., 2011).

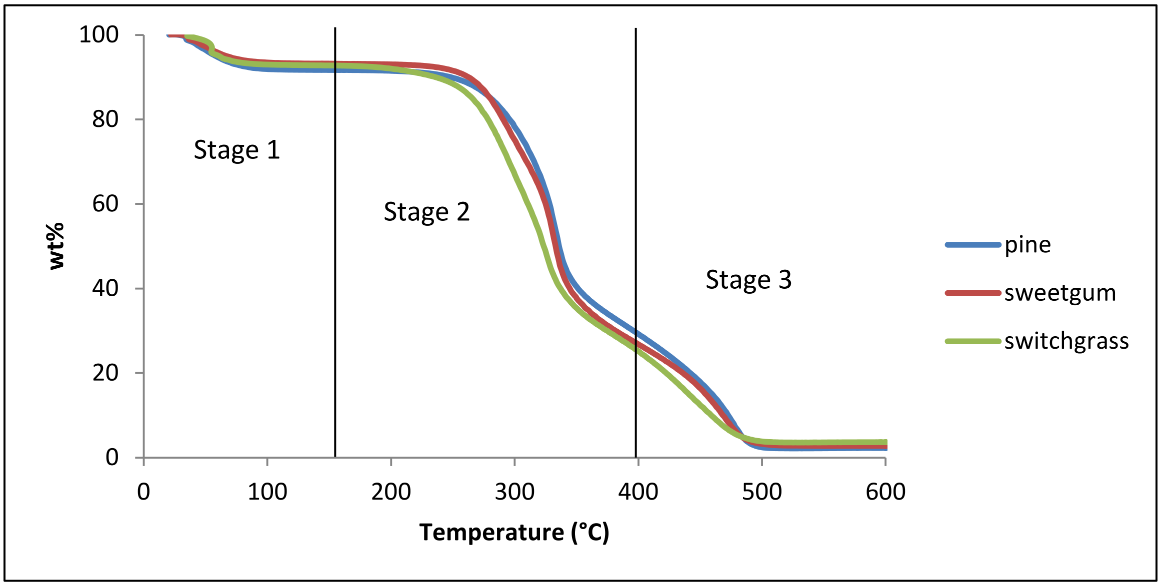

Figure 4.15: TG combustion profile of untreated biomass at 5°C/min

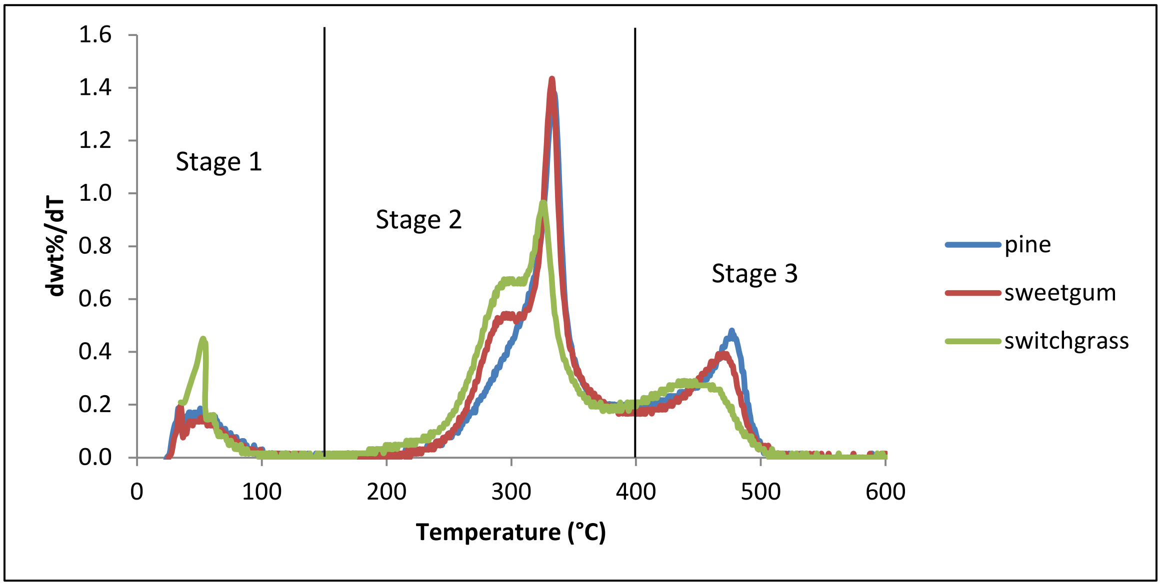

Figure 4.16: DTG combustion profile of untreated biomass at 5°C/min

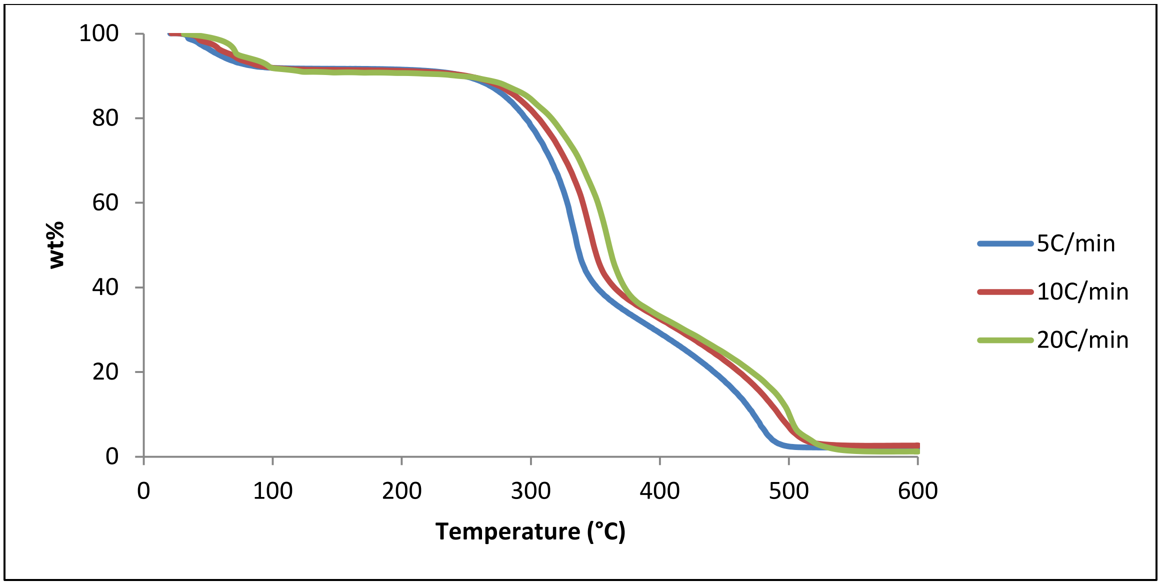

Figure 4.17: TG combustion profile of treated pine

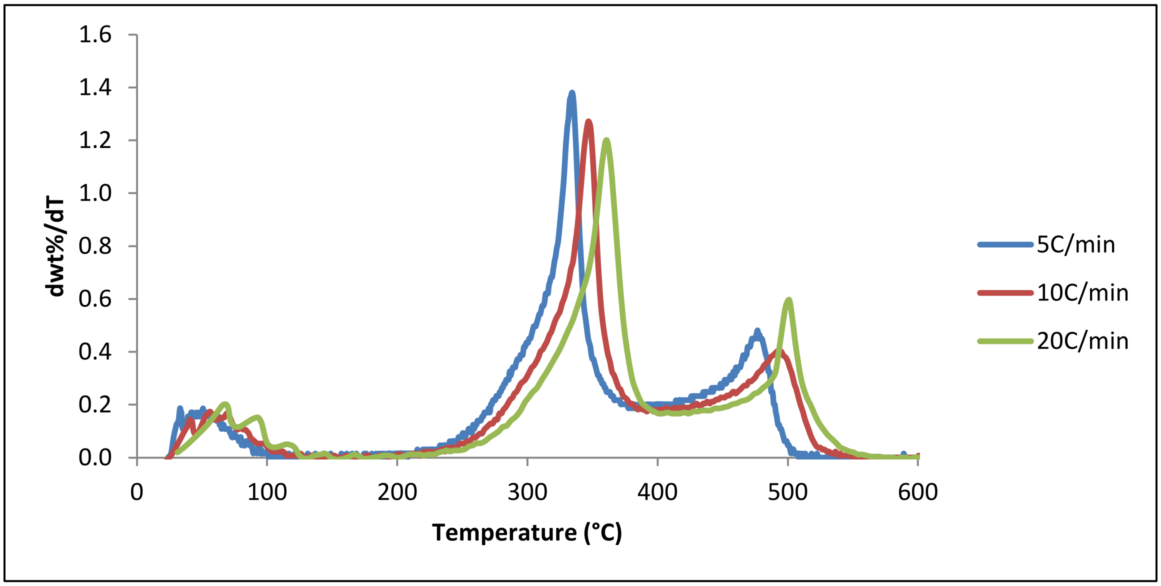

Figure 4.18: DTG combustion profile of untreated pine

Figures 4.19, 4.20, and 4.21 show that torrefaction pretreatment increases the temperature at which the degradation of the solid portion starts. The effect of torrefaction was further examined on the mass loss rate of pine, sweetgum, and switchgrass were examined in Figure

4.22, 4.23 and 4.24. The torrefied biomass, like the untreated biomass, has three distinct peaks, or segments. These peak temperatures remained largely unchanged by the pretreatment even though the rate of mass loss does change. It should also be noticed that for each biomass type, the beginning of combustion occurs at nearly the same temperature for both treated and untreated samples, ~200°C. The major differences are the secondary shoulder peaks on the untreated biomass and the rates of mass loss. The untreated biomass shows a secondary peak during the second stage of mass loss, ~200-400°C, and this secondary peak is removed from the degradation curve of the torrefied biomass. This can be attributed to the previous removal of the hemicellulose fraction during torrefaction (Arias et al., 2008).

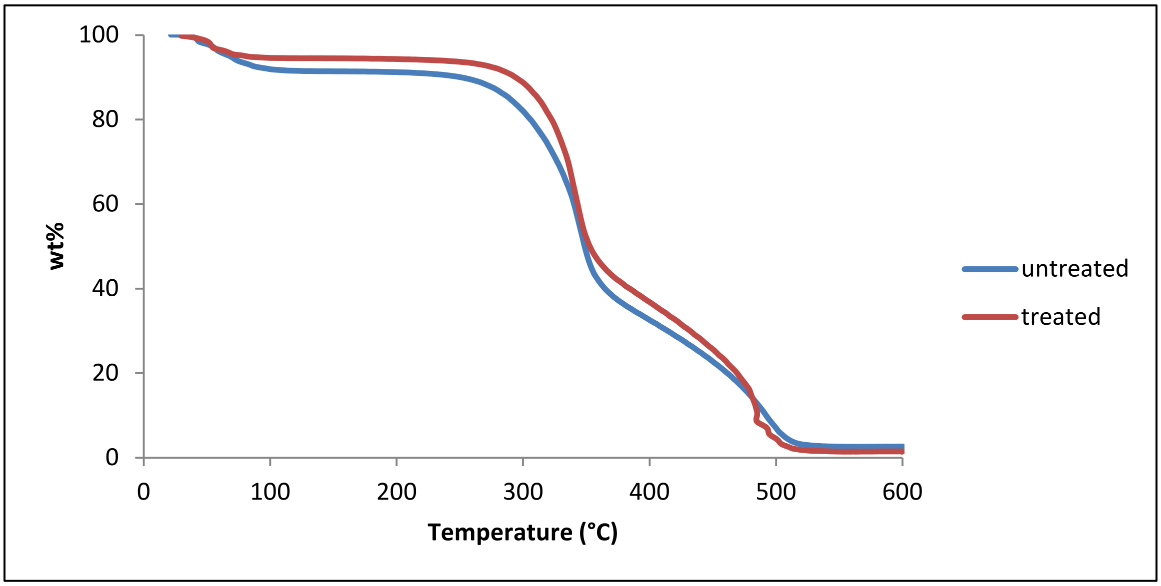

Figure 4.19: TG combustion profile of pine at 10°C/min

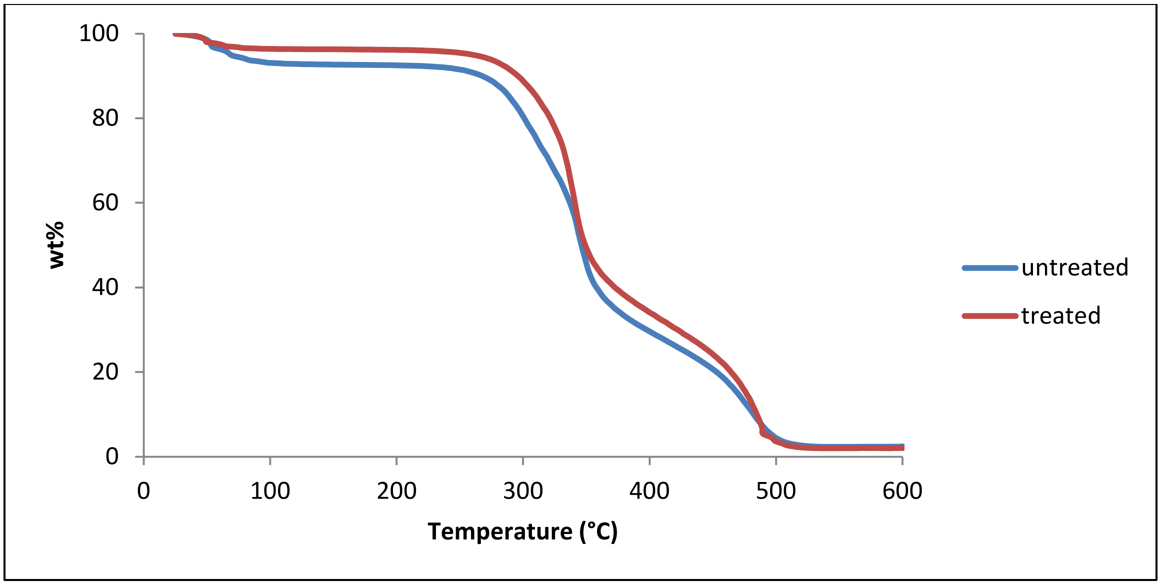

Figure 4.20: TG combustion profile of sweetgum at 10°C/min

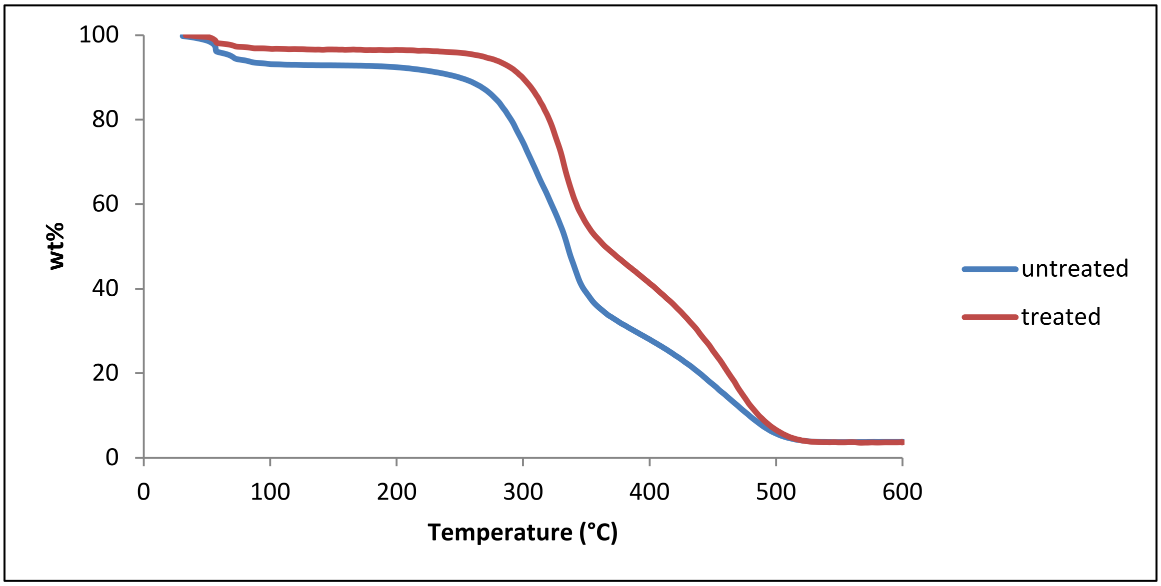

Figure 4.21: TG combustion profile of switchgrass at 10°Cmin

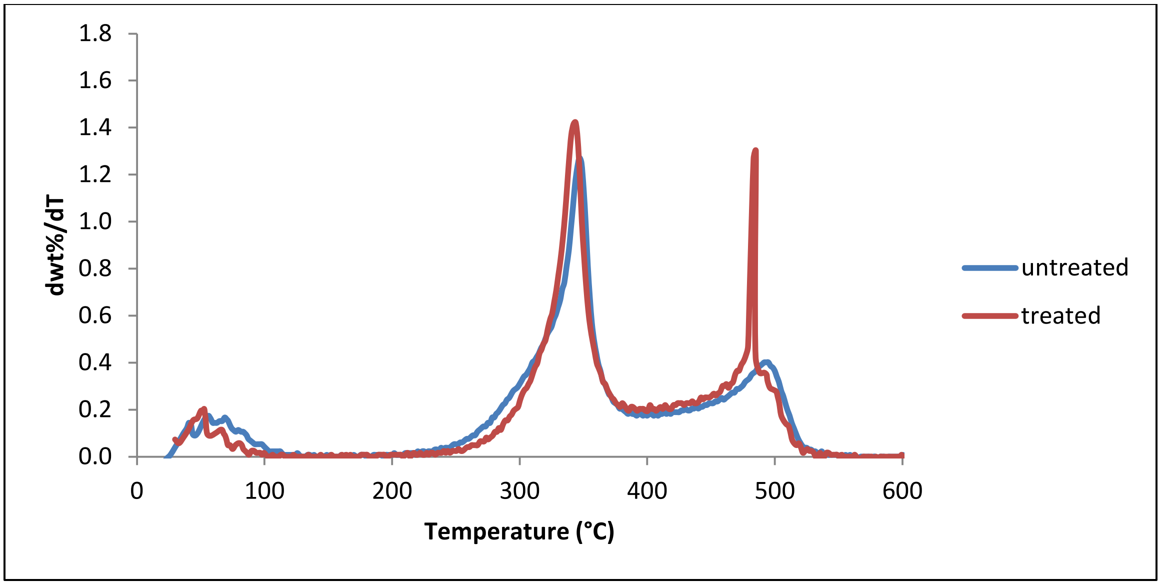

Figure 4.22: DTG combustion profile of pine at 10°C/min

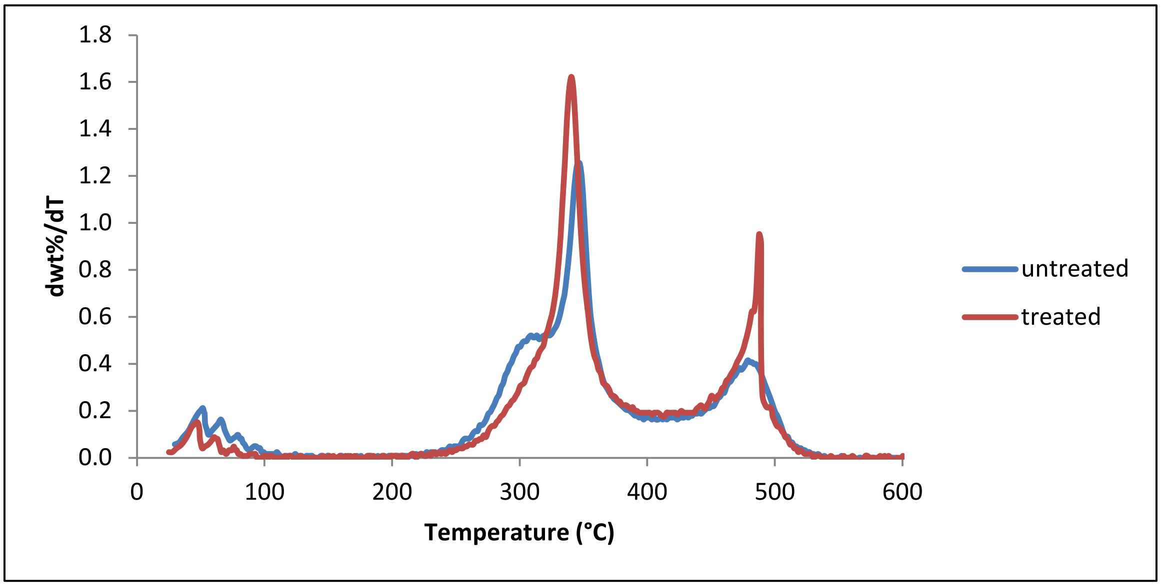

Figure 4.23: DTG combustion profile of sweetgum at 10°C/min

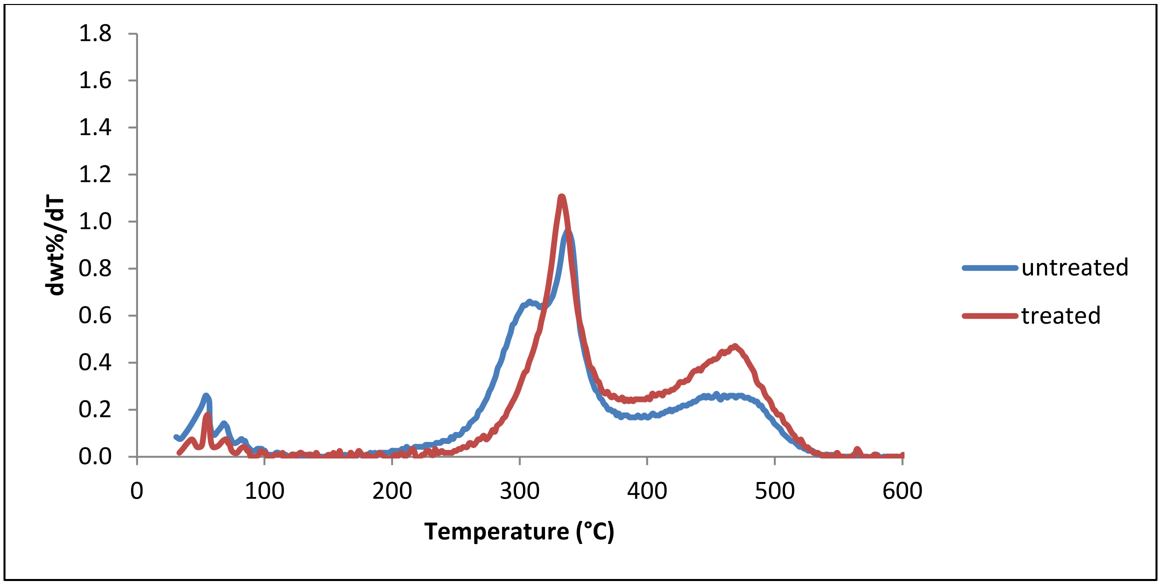

Figure 4.24: DTG combustion profile of switchgrass at 10°C/min

Figures 4.22, 4.23, and 4.24 show that the peaks for treated biomass are higher than for untreated biomass; therefore, maximum mass loss rate increased for each biomass type after being pretreated with torrefaction. This same observation was made in other studies for torrefied biomass (Arias et al., 2008; Bridgeman et al., 2008). The hemicellulose components are largely volatilized during the torrefaction process, and the resulting bio-char has yields of higher percentages of cellulose and lignin content. Since the two primary solids loss peaks represent the degradation of cellulose and lignin, it would be true that the maximum percent of mass loss during these regions would increase with a decrease in hemicellulose content.

Table 4.2 shows the activation energies of a combustion process for the samples. Each of the calculated activation energies has an R^2 equal to or greater than 0.85. Pre-exponential factors were also calculated and can be found in Appendix B. There seems to be a contradiction between the combustion DTG curves and the combustion activation energies for the woody biomass. Similar to the pyrolysis DTG curves samples, the mass loss rate curves of the treated biomass samples have higher mass loss values, or higher peaks, than do the curves for the untreated samples. This would seem to indicate that the treated samples are more sensitive to changes in temperature, hence the increased mass loss rates; however, the activation energies of the samples do no definitively show that. When comparing the activation energies for treated and untreated biomass samples, they do not show a specific trend for the pine and sweetgum samples. The activation energies increase, decrease, or remain the same for the different values of α. Even though the DTG curves suggest that the treated samples are more sensitive to temperature change, the activation energies do not suggest this. The treated switchgrass samples, however, do show increases, with one exception at $\alpha = 0.6$, in activation energies, which is consistent with the DTG curves.

Table 4.2: Activation energies (kJ/mol) for combustion of biomass samples

	Pine		Sweetgum		Switchgrass	
α	Untreated	Treated	Untreated	Treated	Untreated	Treated
0.1	159.2	129.4	139.2	145.5	129.2	178.9
0.2	156.7	155.0	175.9	166.1	147.5	173.4
0.3	162.2	163.1	190.5	165.8	152.4	187.2
0.4	145.6	155.8	151.6	145.7	172.7	209.3
0.5	171.7	246.5	147.5	206.1	156.0	211.2
0.6	236.8	172.1	261.1	273.3	236.3	171.5

4.3.3. Thermogravimetric Biomass and Coal Combustion

The thermal degradation DTG curves of biomass, coal, and biomass/coal blends in an oxygenated atmosphere can be seen in Figure 4.26. The DTG curve for 100% coal shows weight loss similar to other studies (Gil et al., 2010; Wang et al., 2009). Degradation begins at ~350°C and appears to reach a maximum rate at ~550°C. The TG curves in Figure 4.25 show that the samples containing coal do not complete combust and that at 600°C, weigh loss appears to continue. When comparing DTG curve for the coal to the DTG curve for the torrefied pine, it can be seen that the peaks for pine are taller and thinner than the coal. As mentioned previously the two decomposition peaks of biomass are attributed to the volatile matter and char. The coal has a much lower and less reactive volatile content than the torrefied pine. This can be seen by the single peak in the coal curve. The char portion of the biomass and coal do appear to degrade at the same temperature, but degradation occurs slower for the coal. Coal has a higher carbon content than biomass, which causes more carbon-carbon bonding (Munir et al., 2009). C-C bonds are stronger than carbon-oxygen and carbon-hydrogen bonds, which cause the degradation process of coal to be slower and require higher temperatures.

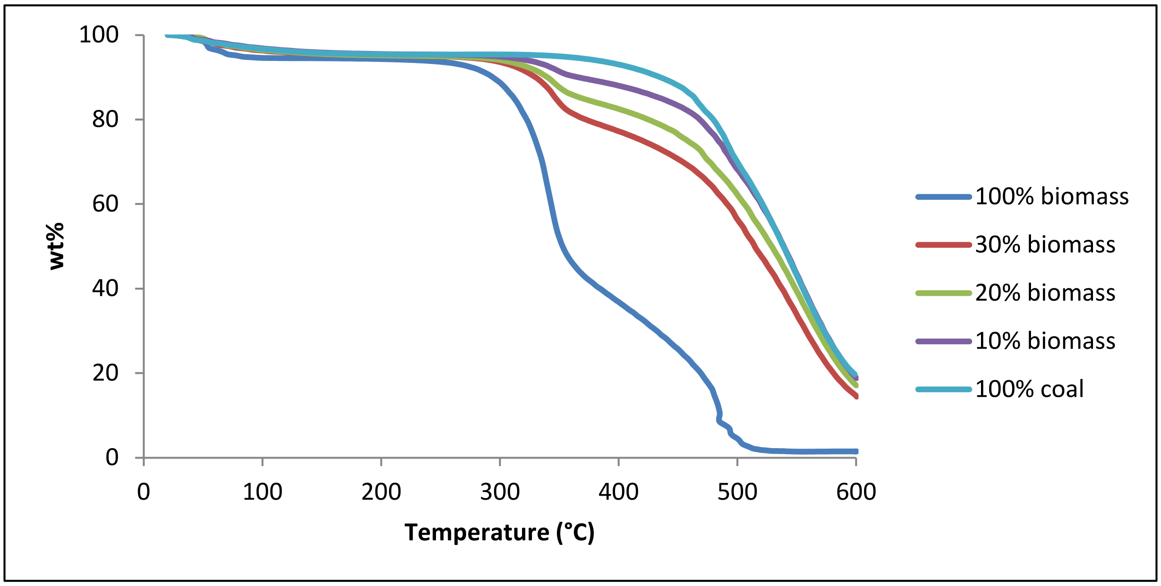

Figure 4.25: TG combustion profile of torrefied biomass/coal mixtures at 10°C/min

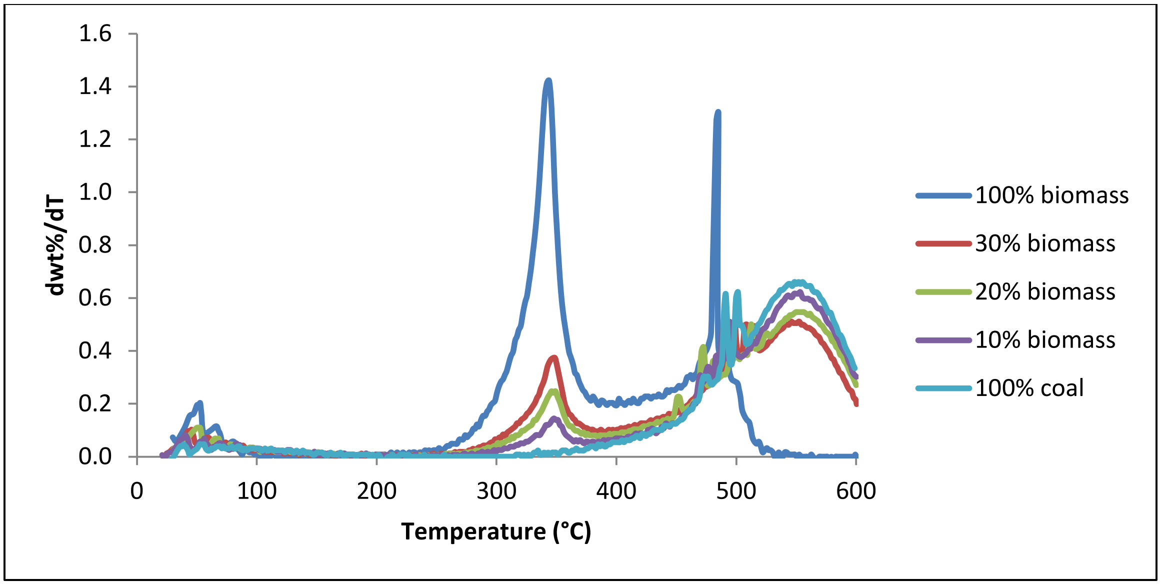

Figure 4.26: DTG combustion profile of torrefied biomass/coal mixtures at 10°C/min

Figure 4.26 also shows biomass mixed with coal at 10, 20, and 30% biomass. These curves show the previously mentioned characteristics of pure 100% biomass and 100% coal combined. Combustion of the volatile matter of the biomass at lower temperatures can be seen in the mix. The combustion of coal remains unchanged, with the exception of the lower peak which is because of the lower concentration of coal. The primary difference is the behavior of the char portion of the biomass. A single pronounced peak is not visible, which would indicate that combining biomass and coal together has an effect on the degradation of the char. The curves for heating rates of 20°C/minute show the same behavior.

Table 4.3: Activation energies (kJ/mol) for combustion of biomass/coal blends

	Biomass percentage				
α	0%	10%	20%	30%	100%
0.1	213.4	157.1	180.4	138.8	129.4
0.2	107.8	148.7	175.8	129.1	155.0
0.3	84.0	104.4	145.3	97.5	163.1
0.4	40.2	58.6	68.8	120.2	155.8

The calculate activation energies for the biomass/coal blends are shown in Table 4.3. The activation energy of coal for intial volatilization is quite high at 213.4 kJ/mol compared to other studies (Gil et al., 2010; Sahu et al., 2010). The only explanation of this could be that the coal in this study is of lower quality with a portion of volatiles more reactive that in the other studies, however, this theory is not supported by the DTG curve of coal (Figure 4.26).

Gil et al. (2010) observed that the activation energies decreased with an increase in pine concentration of a pine/coal blend. Table 4.3 clearly shows that, with the exception of $\alpha = 0.1$, the activation energies clearly increase with biomass concentration. Although this work does not agree with Gil et al. (2010), this would be consistent with these numbers that show 100% treated pine has much higher activation energies than 100% coal. The activation energies of the blend decreased with increasing values of α which is indicative that the biomass portion has been removed, leaving only coal.

4.3.4. Differential Scanning Calorimetry

Differential Scanning Calorimetry was used to determine the enthalpy of torrefaction for the biomass. The torrefaction temperatures studied in this work were 225, 250, and 275°C. Since moisture evaporation was complete by 200°C, energy input for torrefaction was calculated with a straight baseline from 25°C to the minimum torrefaction temperature of 225°C. The energy required to heat the biomass from 225°C to the maximum DSC temperature of 550°C was ignored. This reason for this was due to the fact that the heat flow to the sample at 225-550°C remained near zero. This can clearly be seen for the heat flow of a pine sample at 18.52%

moisture content in Figure 4.27. Each biomass type and moisture content showed this same occurrence in the temperature range of 225-550°C.

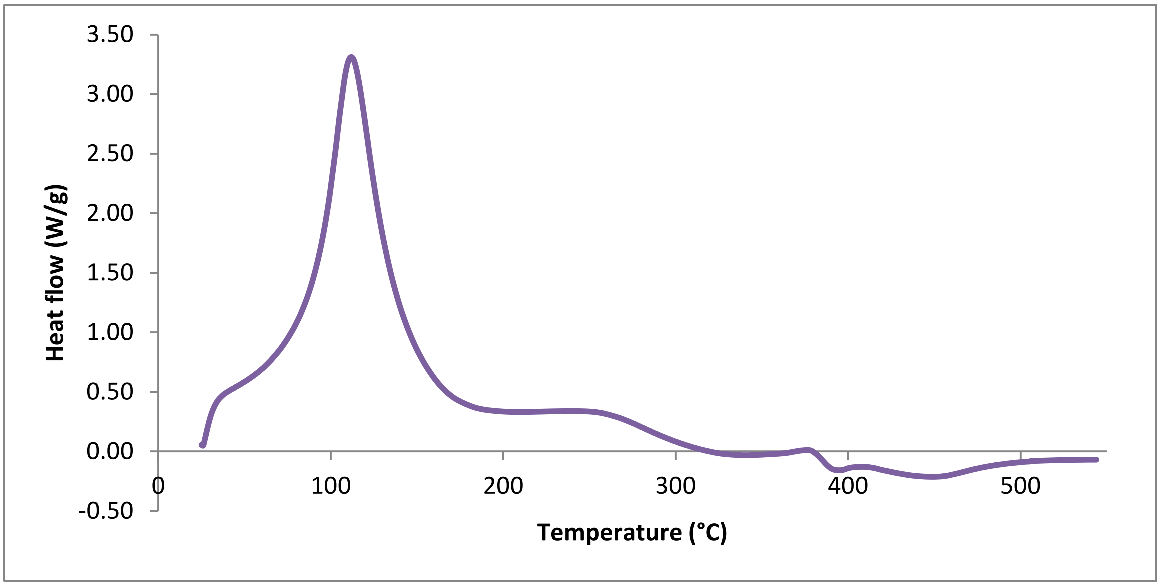

Figure 4.27: Energy flow to heat pine to 550°C at 18.52% moisture content

DSC curves for biomass can be divided into four sections: 1) heating and drying of biomass <170°C, 2) heating of biomass (170-250°C), 3) degradation of biomass (250-400°C), and 4) heating and aggregation of char (>400°C) (He et al., 2006). Since the temperature range of interest is 25-225°C, only the drying of biomass and heating of biomass occurred during this period.

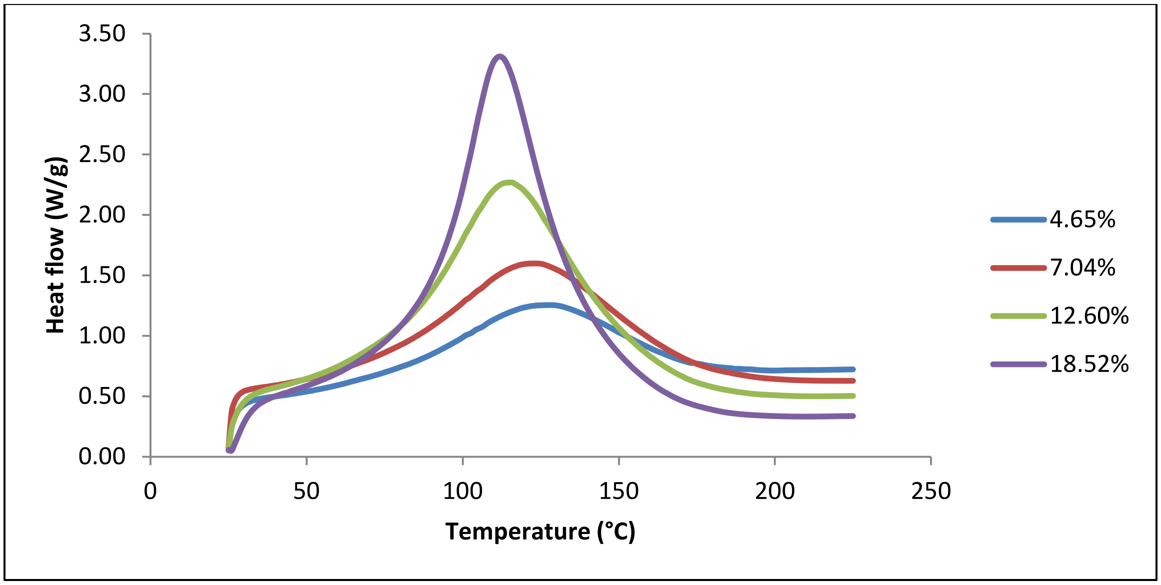

Figure 4.28: Energy flow to heat pine to 225°C at different moisture contents

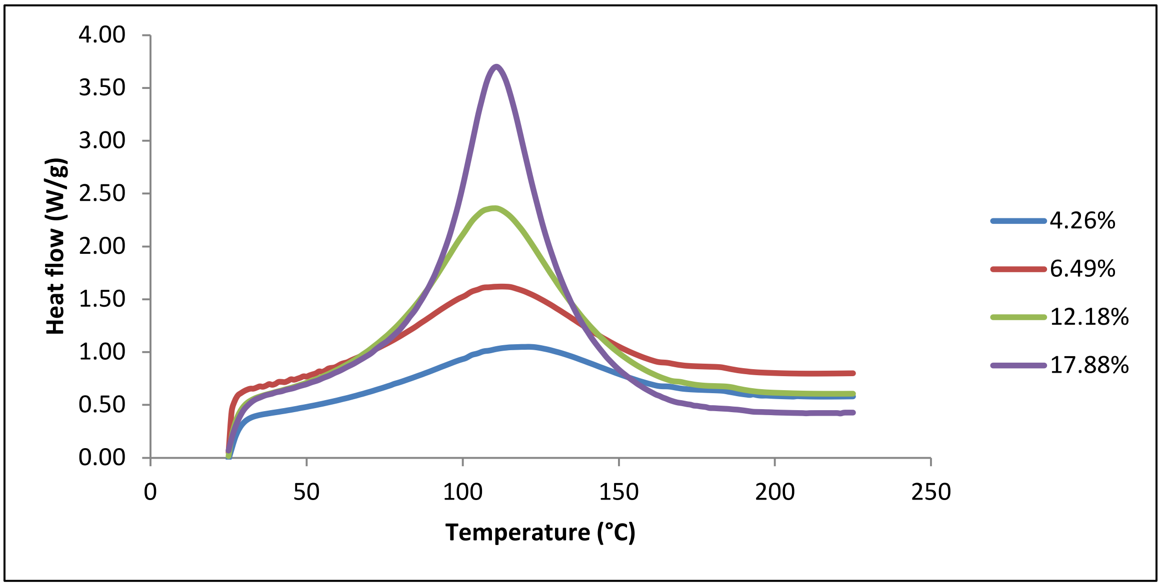

Figure 4.29: Energy flow to heat pine to 225°C at different moisture contents

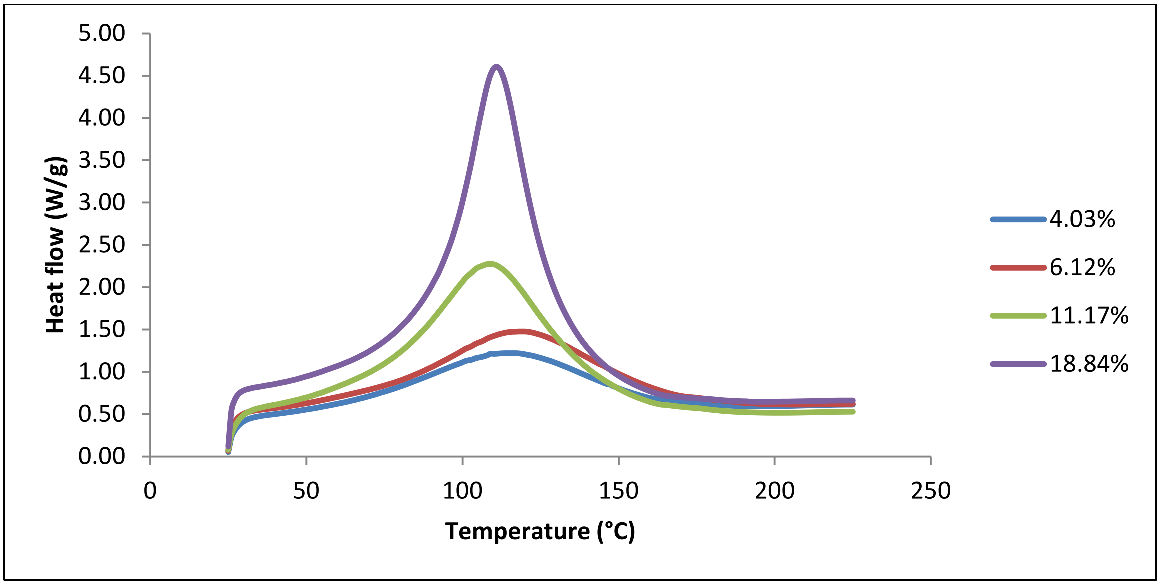

Figure 4.30: Energy flow to heat switchgrass to 225°C at different moisture contents

Figures 4.28, 4.29, and 4.30, show the graphs of heat flow, $\dot{Q}$, vs. temperature, T, for each biomass type at each moisture content. A prominent peak is visible for every curve in the temperature range of 100-150°C, which is attributed to the moisture release. Higher moisture contents clearly increase the height of this peak and appear to have an effect on the energy input. After the moisture is released, heating of the biomass occurred (He et al., 2006). This appears to remain stable up to the torrefaction temperature of 225°C, which would indicate that little to no degradation reactions in the biomass had taken place. This is somewhat similar to Figure 4.4, which shows that initial solids loss begins at 200-250°C for each biomass type. The average enthalpy of torrefaction, *h*, and average moisture content of three tests for each biomass type is shown in Table 4.4.

Table 4.4: Enthalpy of torrefaction

Pine		Sweetgum		Switchgrass	
MC% (w.b.)	h (J/g)	MC% (w.b.)	h (J/g)	MC% (w.b.)	h (J/g)
4.65	310.0_a	4.26	277.3_d	4.03	259.1_g
7.04	362.3_a	6.49	328.4_d	6.12	300.6_h
12.60	434.4_b	12.18	446.8_e	11.17	410.3_i
18.52	509.8_c	17.88	574.7_f	18.84	609.9_j

Values with the same subscripts are statistically similar

Moisture content significantly increased the energy required to increase the temperature the biomass to the torrefaction temperature of 225°C. The effect was modeled using simple linear regression, and the results are shown in Figure 4.31 and in Table 4.5. The enthalpy of pyrolysis was strongly correlated with the moisture content of the samples.

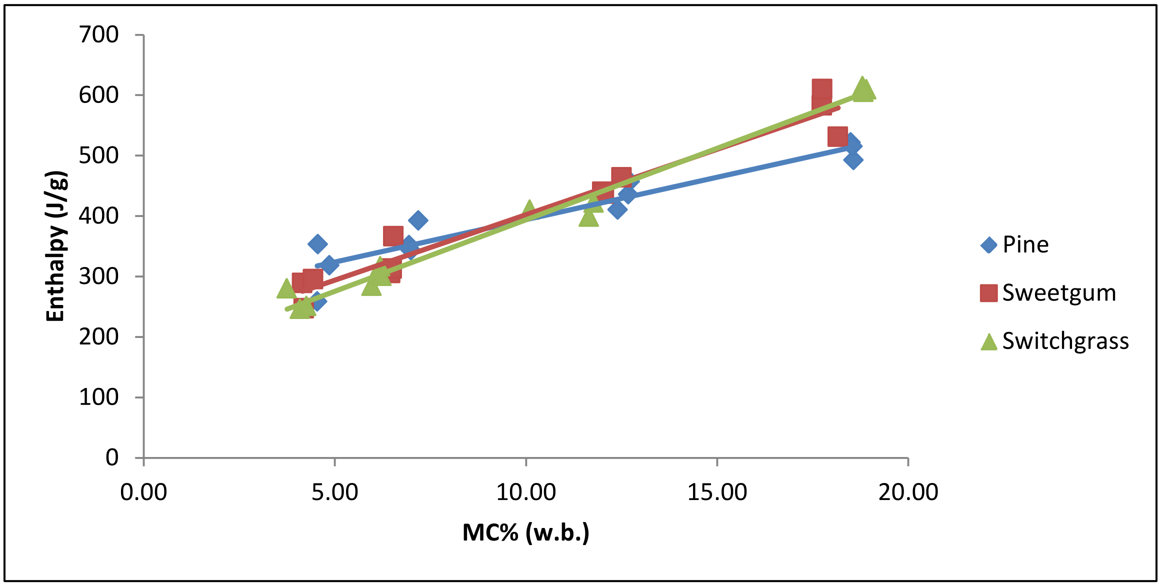

Figure 4.31: Enthalpy of torrefaction vs. moisture content

Table 4.5: Regression equations for enthalpy as a function of moisture content (w.b.)

Biomass	Equation	R²
Pine	$h = 253.85 + 14.04(MC\%)$	0.8972
Sweetgum	$h = 185.85 + 21.65(MC\%)$	0.9543
Switchgrass	$h = 157.49 + 23.65(MC\%)$	0.9847

Using the equations in Table 4.5, the total energy required to heat the solid portion can be assumed to be the values of the intercept in each equation, while the intercept represents the influence of moisture on the enthalpy of torrefaction. The values of slope and intercept for pine are significantly different from those of sweetgum and switchgrass. The values for slope for the sweetgum and switchgrass are near the enthalpy of vaporization for water, but the slope for pine is much lower. This slope for pine is also associated with a higher intercept value than that of sweetgum and switchgrass. Looking back at the TGA data in Figure 4.5, pine solids degradation actually began at a slightly lower temperature than sweetgum or switchgrass, which could mean that solid degradation could have been greater for the pine. If more solid degradation occurred for pine than for sweetgum or switchgrass, this could explain why the intercept would be higher for pine, and this increase would inversely create a lower slope value.

This higher intercept value and lower slope value could also be due to the nature of the biomass. The temperature range for the removal of moisture was assumed to be 25-150°C, and solid volatile removal was assumed to occur at 150-225°C. The temperature range of 25-150°C was examined to determine the requirement for removing the moisture from the biomass samples, and the results are shown in Table 4.6.

Table 4.6: Caloric requirement for moisture removal (25-150°C)

Pine		Sweetgum		Switchgrass	
MC% (w.b.)	h (J/g)	MC% (w.b.)	h (J/g)	MC% (w.b.)	h (J/g)
4.65	2970	4.26	3694	4.03	3490
7.04	2768	6.49	2928	6.12	2966
12.60	2120	12.18	2476	11.17	2672
18.52	1947	17.88	2460	18.84	2746

The enthalpy values for pine are less than the values for the sweetgum and switchgrass. This could be due to the nature of the biomass. These lower values would agree with the lower value of slope for pine compared to sweetgum and switchgrass in Table 4.5. It should also be noted that the enthalpy for moisture removal decreases with increasing the moisture content. Moisture is stored in different parts of the biomass (lumen, cell wall, etc.). Increasing the moisture content could cause the moisture to be stored in a part of the biomass which allows it to be more easily removed, which would result in lower overall caloric requirement for moisture removal.

The area of 150-225°C was examined to determine the difference between heating the solid portions of the biomass. It was found that the average value to heat the solid portion of each biomass type during this temperature range was 184, 151, and 123 Joules per gram of solid mass for pine, sweetgum, and switchgrass, respectively. Pine solid heating and removal required more energy during this period, followed by sweetgum and switchgrass. This would confirm that biomass type causes differences in the linear parameters.

The energy content of untreated biomass was 20.178, 19.649, and 19.498 MJ/kg for pine, sweetgum, and switchgrass, respectively. Given these energy values and the values of the intercepts in Table 4.5, the energy required to heat the solid portions for the biomass to torrefaction temperature was 1.26%, 0.94%, and 0.81% of the total biomass calorific value for the pine, sweetgum, and switchgrass, respectively.

4.4. Conclusions

Untreated and treated biomass samples were analyzed for their pyrolysis and combustion characteristics. Blends of torrefied pine and coal analyzed for combustion characteristics. Reaction kinetics were also found for each process using the isoconversional method. Thermogravimetric analysis showed that the treated biomass samples did not show the typical shoulder characteristic on the degradation curves for biomass that represents hemicellulose degradation. This is because the hemicellulose was volatilized during the torrefaction process. The loss of hemicellulose resulted in another change for the biomass. The degradation peaks were higher for the treated biomass, which could be attributed to the increase in cellulose and lignin concentration because of the hemicellulose volatilization. Since cellulose and lignin make up higher portions of the treated biomass, more mass loss would occur in the same temperature range, resulting in higher mass loss rates. Another reason could be that torrefied biomass would be more porous than the untreated biomass due to the removal of hemicellulose. This increased surface area could promote higher mass loss rates. Reaction kinetics for both the pyrolysis and combustion processes of the biomass samples did not show any real trends. The activation energies seem to mostly increase and decrease at random. Activation energy is typically regarded as the sensitivity of the biomass to temperature changes, but this theory did not necessarily agree with the DTG curves of the samples.

The treated pine and coal mixture combustion characteristics showed changes with the concentration of biomass. Ignition of the samples began at lower temperatures because biomass is more reactive at lower temperatures. The peaks which represent the combustion of the char portion of the biomass seem to disappear when it is mixed with coal which could suggest that the addition of coal had an impact on the combustion of the char. The combustion of the coal portion remained unchanged when it was mixed with biomass. The degradation of the coal percentage began at the same temperature regardless of biomass concentration, but the height of the DTG curve for coal degradation was lower. This was expected since the mass percentage of coal decreased. Reaction kinetics showed a slight trend with the addition of biomass. The presence of biomass mostly increased the activation energy of the sample due to the fact that biomass is more sensitive to temperature changes that coal.

The biomass was also analyzed to determine the effect of moisture content on the enthalpy of torrefaction. Results show that moisture content did have a significant effect on the amount of energy required to heat the biomass samples from 25-225°C. Increasing the moisture content of the sample increased the enthalpy of torrefaction. In fact, this effect was quite linear and could be accurately modeled with simple linear regression. The actual energy required to heat the solid mass of the biomass was less than 1.3% of the original calorific value of each biomass type.

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Chapter 5. Conclusions and Recommendations

Torrefaction pretreatment had a significant effect on the physicochemical properties of the biomass. The untreated biomass samples had low carbon content (48-51%) and high oxygen content (41-43%), which caused low energy content (19-20 MJ/kg). Torrefaction increased the energy content of the biomass by increasing carbon content and decreasing oxygen content. Energy content for each biomass type was increased by 32-35% while carbon content was increased 35-50%, depending on biomass type. The fixed carbon content of the biomass more than tripled with torrefaction treatment, and this was accompanied by a decreasing volatile matter content, approximately 50% decrease. These elemental and proximate analyses results yielded values roughly equal to lignite coal. Fuel properties of the biomass improved with torrefaction.

The moisture absorbed by each biomass was decreased by ~50%, which could have a significant effect on logistics and combustion. Another property that affects logistics is bulk density, which slightly decreased. The bulk densities multiplied by energy contents yield a decrease in energy density (MJ/m^3). This would initially indicate that biomass should be transported prior to treatment; however, there are limiting factors for this conclusion. It should be noted that a small volume of sample was used to find bulk density, and it was found at low moisture contents (<10%). Biomass does swell with increasing moisture content, and it weighs considerably more, which can affect fuel costs. A larger, more comprehensive study should be performed to more accurately determine the effect of torrefaction on the logistics costs of biomass.

The most significant effect of torrefaction on the thermogravimetric analysis of biomass (inert and oxidative) was the observed loss of hemicellulose. The caused the biomass to lose the peak or shoulder on the DTG curves that is representative of hemicellulose degradation. The loss of hemicellulose was assumed to cause increases in cellulose and lignin content due to the higher DTG peaks that represent cellulose and lignin degradation. Activation energies for the nitrogen and air atmospheres seem to mostly increase and decrease at random with torrefaction. This could indicate that torrefaction has no effect on activation energy. A more likely conclusion would address the practicality of kinetic analysis. Either isoconversional kinetics analysis is not an effective way to determine thermal degradation or kinetic analysis is not appropriate for heterogeneous solids.

Increasing the concentration of biomass in the treated pine and coal mixture had an effect on the degradation characteristics of the blend. The ignition temperature was lowered with the inclusion of biomass, and the DTG peaks for coal and biomass char degradation were decreased. The presence of coal seemed to have an effect on the degradation of the char portion of the biomass.

Moisture content, as expected, was found to have a significant effect on the enthalpy of pyrolysis. The energy needed to heat the biomass to 225°C was significantly increased with increasing moisture contents. This energy was plotted as a function of moisture content using simple linear regression, and the results showed that the trend was quite linear. The indicates that knowing the moisture content of a sample could potentially be used to predict the amount of energy need to treat any sample and the efficiency of the torrefaction process.

A batch reaction was used to perform torrefaction on the biomass. Considerable changes to the physicochemical properties were observed even though the temperature of the biomass was less than the set-point temperature of the furnace, with the exception of the torrefaction of switchgrass for longer times. This is because the top portion of sample was absorbing the heat from the furnace and insolating the sample particles in the middle of the bed. A better reactor design for torrefaction would be a reactor that promotes more uniform heat transfer at a faster rate, such as with a fluidized bed or an auger reactor. The particle agitation and convection could promote a faster and more uniform treatment. These methods could possibly achieve the same desirable fuel qualities with lower temperatures and shorter times

Appendix A. Physicochemical properties

Table A.1: Torrefaction treatments of pine

			Mass of solids (g)				
Temp (˚C)	Time (min)	Pan #	Initial	Final	Solids ret.	Mean	Std. dev.
225	15	1	56.22	55.05	97.91%	97.96%	0.16
		2	56.16	55.12	98.14%		
		3	56.28	55.05	97.82%		
225	30	1	56.71	50.34	88.77%	90.15%	1.28
		2	58.63	53.53	91.30%		
		3	57.87	52.30	90.38%		
225	45	1	57.54	41.36	71.89%	74.15%	2.05
		2	58.33	44.26	75.89%		
		3	57.19	42.70	74.67%		
250	15	1	58.87	53.02	90.05%	90.71%	1.53
		2	57.17	52.86	92.46%		
		3	58.11	52.07	89.61%		
250	30	1	58.40	45.57	78.03%	78.21%	0.85
		2	56.55	44.76	79.14%		
		3	57.46	44.52	77.47%		
250	45	1	56.37	35.79	63.49%	66.32%	3.77
		2	55.37	39.09	70.60%		
		3	56.83	36.87	64.88%		
275	15	1	55.47	44.59	80.40%	80.66%	1.58
		2	56.90	46.85	82.35%		
		3	58.34	46.22	79.23%		
275	30	1	57.96	35.67	61.55%	61.47%	1.64
		2	58.29	36.76	63.07%		
		3	59.17	35.38	59.79%		
275	45	1	55.40	27.20	49.10%	46.67%	2.31
		2	55.79	25.88	46.39%		
		3	55.85	24.86	44.51%		

Table A.2: Torrefaction treatments of sweetgum

			Mass of solids (g)				
Temp (˚C)	Time (min)	Pan #	Initial	Final	Solids ret.	Mean	Std. dev.
		1	57.41	56.78	98.90%		
225	15	2	57.73	57.31	99.26%	98.86%	0.42
		3	57.55	56.64	98.42%		
		1	56.30	49.60	88.10%		
225	30	2	57.08	51.07	89.47%	87.45%	2.42
		3	55.70	47.22	84.77%		
		1	57.46	44.84	78.04%		
225	45	2	57.18	47.16	82.48%	79.92%	2.30
		3	57.86	45.84	79.23%		
		1	55.79	50.17	89.93%		
250	15	2	55.70	51.84	93.06%	90.84%	1.93
		3	56.58	50.66	89.53%		
		1	55.47	40.43	72.89%		
250	30	2	51.75	36.40	70.35%	72.41%	1.87
		3	57.03	42.20	73.99%		
		1	57.58	33.82	58.73%		
250	45	2	58.02	38.08	65.64%	62.56%	3.52
		3	57.15	36.18	63.31%		
		1	56.80	41.33	72.76%		
275	15	2	56.68	43.35	76.48%	73.99%	2.16
		3	57.23	41.62	72.73%		
		1	55.43	33.04	59.60%		
275	30	2	55.68	34.44	61.85%	60.47%	1.21
		3	57.40	34.42	59.96%		
		1	57.91	25.00	43.16%		
275	45	2	57.17	28.31	49.53%	46.43%	3.19
		3	56.51	26.34	46.61%		

Table A.3: Torrefaction treatments of switchgrass

			Mass of solids (g)				
Temp (˚C)	Time (min)	Pan #	Initial	Final	Solids ret.	Mean	Std. dev.
		1	41.92	39.86	95.08%		
225	15	2	40.24	38.29	95.16%	94.56%	0.97
		3	39.84	37.23	93.44%		
		1	40.44	29.17	72.13%		
225	30	2	41.45	31.02	74.84%	73.90%	1.54
		3	42.62	31.85	74.74%		
		1	43.79	22.41	51.18%		
225	45	2	44.70	22.59	50.53%	51.86%	1.77
		3	42.72	23.01	53.86%		
		1	39.56	28.77	72.71%		
250	15	2	40.15	30.58	76.18%	75.53%	2.56
		3	41.96	32.60	77.70%		
		1	40.70	19.94	49.00%		
250	30	2	41.90	24.33	58.07%	52.99%	4.63
		3	42.89	22.26	51.91%		
		1	40.94	17.44	42.60%		
250	45	2	39.33	15.52	39.47%	40.73%	1.65
		3	41.45	16.63	40.11%		
		1	41.43	25.53	61.63%		
275	15	2	42.33	25.55	60.35%	60.28%	1.39
		3	41.26	24.28	58.85%		
		1	40.25	17.79	44.19%		
275	30	2	42.47	17.37	40.90%	41.26%	2.77
		3	41.14	15.92	38.69%		
		1	41.40	13.90	33.58%		
275	45	2	41.49	14.81	35.69%	34.34%	1.18
		3	40.91	13.80	33.73%		

Table A.4: Bulk densities (dry basis) of pine

Temp (˚C)	Time (min)	Pan	Density	Mean	Std. dev.
Untreated			158.6	159.2	4.82
			154.6		
			164.2		
225	15	1	154.1	146.4	6.64
		2	142.5		
		3	142.7		
225	30	1	141.8	140.8	5.13
		2	145.3		
		3	135.2		
225	45	1	129.1	126.4	2.49
		2	125.9		
		3	124.2		
250	15	1	141.4	145.6	5.28
		2	151.5		
		3	143.8		
250	30	1	129.0	128.4	7.02
		2	135.1		
		3	121.1		
250	45	1	110.5	114.3	3.61
		2	117.7		
		3	114.6		
275	15	1	125.8	123.1	3.69
		2	133.1		
		3	125.8		
275	30	1	117.0	113.8	6.83
		2	118.5		
		3	106.0		
275	45	1	101.9	102.6	0.66
		2	102.7		
		3	103.2		

Table A.5: Bulk densities (dry basis) of sweetgum

Temp (˚C)	Time (min)	Pan	Density	Mean	Std. dev.
Untreated			182.3	182.1	1.81
			183.7		
			180.2		
225	15	1	171.1	170.5	0.60
		2	169.9		
		3	170.6		
225	30	1	164.5	166.2	5.24
		2	172.0		
		3	161.9		
225	45	1	151.4	154.0	5.79
		2	160.6		
		3	149.9		
250	15	1	166.5	166.4	2.60
		2	169.0		
		3	163.8		
250	30	1	147.3	149.6	5.06
		2	155.4		
		3	146.1		
250	45	1	138.0	141.1	4.47
		2	139.0		
		3	146.2		
275	15	1	149.3	146.8	4.13
		2	149.2		
		3	142.1		
275	30	1	135.8	133.9	2.06
		2	131.7		
		3	134.1		
275	45	1	129.4	126.2	4.33
		2	128.0		
		3	121.3		

Table A.6: Bulk densities (dry basis) of switchgrass

Temp (˚C)	Time (min)	Pan	Density	Mean	Std. dev.
Untreated			116.3	117.1	4.14
			121.6		
			113.4		
225	15	1	113.6	111.9	2.42
		2	109.1		
		3	112.9		
225	30	1	92.3	91.0	5.37
		2	85.1		
		3	95.6		
225	45	1	81.8	82.6	0.85
		2	83.5		
		3	82.5		
250	15	1	104.2	104.3	1.15
		2	103.1		
		3	105.4		
250	30	1	72.9	73.6	2.27
		2	76.1		
		3	71.7		
250	45	1	75.8	74.6	1.02
		2	74.2		
		3	73.9		
275	15	1	85.3	90.0	4.14
		2	93.2		
		3	91.4		
275	30	1	80.0	75.4	3.96
		2	73.2		
		3	73.1		
275	45	1	77.5	77.0	1.32
		2	75.5		
		3	78.0		

Table A.7: Moisture absorption of pine at 25°C and 90% RH

		MC% (w.b.)									
Temp	Time	Initial	1 hr	2 hr	3 hr	4 hr	5 hr	24 hr	48 hr	Mean	Std. dev.
Untreated		7.00	11.54	12.95	14.32	14.99	15.65	17.57	16.30	16.12	0.26
		6.11	11.12	13.11	13.76	14.39	15.02	16.84	16.24		
		5.57	10.65	12.00	12.67	12.67	14.59	15.83	15.83		
225	15	6.76	11.54	12.29	13.03	13.76	13.76	15.17	15.17	15.12	0.33
		6.53	12.66	13.37	14.07	14.07	14.75	15.43	15.43		
		4.91	10.40	10.97	12.09	12.09	13.18	14.77	14.77		
225	30	4.34	7.48	8.69	9.27	9.27	9.27	10.43	10.43	10.78	0.34
		4.01	8.01	8.65	9.27	9.89	9.89	10.50	11.10		
		3.73	8.11	8.80	9.48	9.48	10.15	10.81	10.81		
225	45	2.78	6.28	7.61	7.61	7.61	7.61	8.26	8.90	9.24	0.31
		4.18	7.57	7.57	8.23	8.23	8.23	9.50	9.50		
		4.91	7.90	7.90	7.90	7.90	7.90	8.62	9.33		
250	15	4.49	8.21	8.81	9.39	9.97	9.39	11.10	11.10	11.21	0.48
		4.03	7.50	9.14	9.67	10.20	10.72	12.25	11.75		
		3.88	7.78	9.01	9.01	10.20	10.20	10.79	10.79		
250	30	3.58	6.56	7.13	7.70	7.70	8.26	8.26	8.81	8.77	0.16
		4.26	6.97	8.27	8.27	8.27	8.91	8.91	8.91		
		3.21	7.30	7.95	7.95	7.95	8.59	8.59	8.59		
250	45	4.89	6.89	7.53	7.53	7.53	8.17	8.17	8.17	8.20	0.30
		3.50	5.23	6.35	6.35	6.35	6.91	7.45	8.52		
		4.21	6.47	7.20	7.20	7.20	6.47	7.92	7.92		
275	15	3.80	6.22	6.81	7.39	7.39	7.96	9.08	9.08	9.23	0.24
		4.32	7.84	7.84	8.41	8.96	8.96	10.05	9.51		
		4.32	7.36	7.95	8.53	8.53	8.53	9.66	9.10		
275	30	4.01	7.18	7.18	7.18	7.18	7.18	7.94	7.94	7.78	0.31
		4.69	6.69	7.34	7.98	7.98	7.98	8.61	7.98		
		3.83	6.72	6.72	7.42	7.42	7.42	7.42	7.42		
275	45	5.48	7.05	7.82	7.82	7.82	8.58	9.32	7.82	8.19	0.32
		4.60	6.91	7.66	7.66	7.66	7.66	7.66	8.39		
		4.99	7.71	7.71	7.71	7.71	7.71	8.36	8.36		

Table A.8: Moisture absorption of sweetgum at 25°C and 90% RH

		MC% (w.b.)									
Temp	Time	Initial	1 hr	2 hr	3 hr	4 hr	5 hr	24 hr	48 hr	Mean	Std. dev.
Untreated		6.13	10.27	11.57	13.45	14.06	15.26	16.42	15.84	15.87	0.04
		5.15	9.04	11.12	12.12	12.61	13.58	15.92	15.92		
		4.82	9.21	10.96	12.10	12.65	13.75	15.85	15.85		
225	15	4.23	8.27	9.69	10.16	11.07	11.97	14.14	14.14	14.22	0.09
		3.68	8.99	10.23	10.84	11.43	12.61	14.31	14.31		
		3.49	8.91	8.91	10.91	11.40	11.88	14.21	14.21		
225	30	2.50	5.93	7.24	7.24	7.88	7.88	9.13	9.13	9.20	0.35
		3.21	6.50	7.14	7.14	7.76	8.37	9.58	9.58		
		2.76	4.89	4.89	6.26	6.26	6.93	8.24	8.88		
225	45	3.62	6.06	7.23	7.23	7.81	7.81	8.94	8.94	9.08	0.20
		3.75	6.05	7.16	7.16	7.71	7.71	9.31	9.31		
		3.64	6.09	6.69	7.27	7.27	7.85	9.55	8.99		
250	15	3.77	5.34	6.10	7.59	7.59	7.59	9.74	9.74	9.93	0.69
		4.87	6.22	7.55	7.55	8.19	8.83	10.69	10.69		
		4.27	5.03	6.52	7.24	7.24	8.66	9.35	9.35		
250	30	5.05	5.05	6.85	7.44	7.44	8.02	8.59	8.59	8.69	0.13
		4.77	4.77	6.74	6.74	7.38	8.01	8.01	8.63		
		5.29	6.50	7.10	7.10	7.69	7.69	8.84	8.84		
250	45	5.46	7.67	7.67	7.67	8.20	8.74	9.78	9.26	9.04	0.19
		6.03	7.22	7.22	7.80	8.38	8.38	8.95	8.95		
		5.15	5.80	6.44	6.44	7.07	7.07	8.31	8.92		
275	15	3.75	5.36	6.40	6.91	7.41	7.41	8.90	8.41	8.35	0.07
		2.61	4.95	6.09	6.64	6.09	7.19	8.27	8.27		
		3.99	6.24	6.24	7.32	6.78	7.85	8.38	8.38		
275	30	4.13	5.83	6.39	6.39	5.83	6.39	8.01	8.01	8.16	0.14
		4.28	6.04	6.61	6.61	6.61	7.18	8.29	8.29		
		4.95	6.59	7.12	6.59	6.59	7.65	8.17	8.17		
275	45	5.48	7.13	7.13	7.66	7.13	7.66	8.72	8.72	8.44	0.26
		5.75	7.36	8.40	7.88	8.40	8.40	8.40	8.40		
		5.14	6.39	7.60	7.60	7.60	7.60	7.60	8.20		

Table A.9: Moisture absorption of switchgrass at 25°C and 90% RH

		MC% (w.b.)									
Temp	Time	Initial	1 hr	2 hr	3 hr	4 hr	5 hr	24 hr	48 hr	Mean	Std. dev.
Untreated		5.82	9.97	11.92	12.55	13.78	14.38	16.71	16.14	15.92	0.34
		5.47	9.77	10.45	12.42	13.06	14.31	16.71	15.53		
		6.22	10.18	12.04	12.64	13.24	14.97	17.18	16.09		
225	15	4.89	9.06	9.85	10.63	11.39	11.39	12.88	12.88	12.52	0.48
		5.12	9.07	10.01	10.01	11.83	11.83	12.71	12.71		
		4.19	7.47	9.02	9.78	9.78	9.78	11.98	11.98		
225	30	4.25	6.86	8.52	8.52	8.52	8.52	9.33	9.33	9.54	0.22
		4.19	7.06	8.89	8.89	9.77	8.89	9.77	9.77		
		3.98	7.75	7.75	8.64	8.64	7.75	8.64	9.52		
225	45	4.13	7.79	7.79	8.66	8.66	8.66	9.51	9.51	9.54	0.22
		6.21	8.91	9.78	9.78	9.78	9.78	10.63	9.78		
		5.56	8.42	8.42	8.42	9.34	9.34	10.24	9.34		
250	15	4.88	6.69	7.57	8.43	8.43	9.28	9.28	9.28	9.44	0.16
		4.57	6.58	8.51	7.55	8.51	8.51	9.44	9.44		
		4.53	7.13	7.13	7.97	7.97	7.97	9.60	9.60		
250	30	5.28	7.12	7.12	8.01	8.01	8.01	8.01	8.89	8.94	0.18
		4.25	7.06	7.06	7.06	6.14	7.97	8.85	8.85		
		4.06	6.63	7.46	8.27	6.63	8.27	9.07	9.07		
250	45	5.36	7.33	8.29	9.22	8.29	9.22	9.22	10.14	10.59	0.49
		6.13	8.69	9.51	9.51	9.51	10.32	10.32	11.11		
		6.29	8.87	9.70	9.70	9.70	9.70	9.70	10.51		
275	15	1.89	6.02	7.00	7.00	7.00	7.96	8.90	8.90	8.80	0.23
		1.44	5.12	6.86	6.86	6.86	6.86	7.71	8.54		
		4.42	7.20	7.20	8.09	8.09	8.09	8.09	8.97		
275	30	5.74	8.27	8.27	9.08	8.27	9.08	9.08	9.08	9.26	0.20
		7.34	8.29	9.23	9.23	9.23	9.23	9.23	9.23		
		5.93	8.62	7.74	7.74	8.62	7.74	8.62	9.48		
275	45	6.88	9.96	9.96	9.96	9.96	9.96	10.69	11.42	11.05	0.59
		6.06	8.69	9.54	9.54	9.54	9.54	10.37	10.37		
		8.34	10.62	10.62	10.62	10.62	10.62	11.35	11.35		

Table A.10: Ash and volatile contents (dry basis) of pine

Temp (˚C)	Time (min)	Ash %	Mean	Std. dev.	Volatile %	Mean	Std. dev.
Untreated		0.68 0.77 0.70	0.72	0.05	81.06 80.24 81.07	80.79	0.47
225	15	0.70 0.55 0.64	0.63	0.08	81.58 81.71 78.30	80.53	1.93
225	30	0.84 0.79 0.99	0.87	0.10	76.62 76.08 76.42	76.37	0.27
225	45	0.94 0.85 1.02	0.94	0.09	63.81 66.05 66.50	65.45	1.44
250	15	0.88 1.01 1.11	1.00	0.12	75.77 77.18 76.75	76.57	0.72
250	30	1.00 0.99 0.89	0.96	0.06	71.07 69.69 69.32	70.03	0.92
250	45	1.09 0.98 1.15	1.08	0.09	58.20 62.96 58.10	59.75	2.78
275	15	0.97 0.80 1.03	0.94	0.12	70.23 72.45 70.02	70.90	1.35
275	30	0.88 0.87 1.18	0.98	0.18	57.01 56.63 55.94	56.53	0.54
275	45	1.11 1.40 1.70	1.40	0.30	45.29 42.76 41.47	43.17	1.94

Table A.11: Ash and volatile contents (dry basis) of sweetgum

Temp (˚C)	Time (min)	Ash %	Mean	Std. dev.	Volatile %	Mean	Std. dev.
Untreated		1.41	1.39	0.10	81.41	81.41	0.02
		1.41			81.40		
		1.35			81.43		
225	15	1.11	1.09	0.30	82.74	82.24	1.15
		0.79			83.06		
		1.38			80.93		
225	30	1.42	1.35	0.11	79.41	78.43	1.46
		1.41			79.14		
		1.22			76.75		
225	45	1.78	1.65	0.14	72.30	73.27	1.00
		1.51			74.29		
		1.67			73.22		
250	15	1.43	1.46	0.14	78.41	78.40	0.77
		1.33			79.16		
		1.61			77.62		
250	30	1.66	1.87	0.18	69.47	71.54	1.82
		1.96			72.89		
		1.98			72.27		
250	45	2.43	2.18	0.21	56.32	60.02	3.29
		2.06			62.63		
		2.07			61.10		
275	15	1.84	1.79	0.06	70.72	70.87	0.72
		1.73			71.66		
		1.80			70.24		
275	30	2.34	2.53	0.21	59.09	59.64	0.50
		2.48			59.76		
		2.76			60.06		
275	45	3.80	3.08	0.64	40.51	44.27	3.42
		2.81			47.20		
		2.61			45.11		

Table A.12: Ash and volatile contents (dry basis) of switchgrass

Temp (˚C)	Time (min)	Ash %	Mean	Std. dev.	Volatile %	Mean	Std. dev.
Untreated		2.68	2.71	0.02	79.32	79.18	0.26
		2.72			78.88		
		2.71			79.33		
225	15	3.00	2.77	0.23	78.92	79.38	0.73
		2.55			80.22		
		2.76			79.00		
225	30	3.79	3.75	0.07	66.47	67.45	0.86
		3.78			67.81		
		3.67			68.07		
225	45	5.29	5.39	0.09	48.64	48.25	1.60
		5.46			46.50		
		5.41			49.62		
250	15	3.78	3.67	0.22	69.45	69.85	0.86
		3.81			69.26		
		3.41			70.84		
250	30	5.58	5.37	0.29	46.37	49.37	3.65
		5.04			53.43		
		5.50			48.32		
250	45	6.20	6.62	0.40	39.80	39.00	0.71
		6.99			38.75		
		6.67			38.46		
275	15	4.44	4.21	0.28	59.45	60.03	2.13
		3.90			62.39		
		4.30			58.25		
275	30	5.92	6.40	0.42	42.16	38.68	3.07
		6.67			37.50		
		6.63			36.38		
275	45	7.44	7.24	0.20	35.29	34.82	2.39
		7.23			32.23		
		7.05			36.95		

Table A.13: Ultimate analysis (dry basis) of pine

Temp (˚C)	Time (min)	C %	Mean	Std. dev.	H %	Mean	Std. dev.	N %	Mean	Std. dev.
Untreated		50.91	50.90	0.20	6.07	6.11	0.04	0.37	0.48	0.11
		50.70			6.15			0.49		
		51.09			6.12			0.58		
225	15	51.44	51.15	0.37	5.91	5.99	0.07	0.59	0.61	0.03
		51.28			6.05			0.59		
		50.73			6.02			0.64		
225	30	54.57	53.67	0.77	5.73	5.70	0.09	0.77	0.78	0.01
		53.18			5.77			0.77		
		53.27			5.59			0.78		
225	45	58.97	58.63	0.37	4.72	4.88	0.18	0.89	0.88	0.01
		58.23			4.86			0.87		
		58.70			5.07			0.89		
250	15	53.81	53.02	0.84	5.99	5.95	0.18	0.79	0.78	0.02
		52.13			6.11			0.76		
		53.13			5.76			0.80		
250	30	56.86	57.14	0.32	5.42	5.27	0.13	0.84	0.84	0.02
		57.06			5.19			0.82		
		57.48			5.21			0.86		
250	45	63.18	62.26	1.15	4.53	4.68	0.19	0.91	0.87	0.03
		60.97			4.89			0.86		
		62.65			4.61			0.85		
275	15	57.41	56.59	1.04	5.42	5.49	0.08	0.75	0.74	0.01
		55.42			5.49			0.74		
		56.93			5.58			0.74		
275	30	64.13	64.17	1.22	4.91	4.81	0.14	0.83	0.81	0.02
		62.97			4.86			0.79		
		65.41			4.65			0.80		
275	45	70.05	71.48	1.27	3.67	3.47	0.02	0.91	0.92	0.01
		71.91			3.27			0.93		
		72.49			3.47			0.90		

Table A.14: Ultimate analysis (dry basis) of sweetgum

Temp (˚C)	Time (min)	C %	Mean	Std. dev.	H %	Mean	Std. dev.	N %	Mean	Std. dev.
Untreated		49.88	49.76	0.18	5.87	5.96	0.08	0.40	0.36	0.04
		49.84			6.03			0.33		
		49.55			5.97			0.35		
225	15	49.30	49.20	0.10	5.91	5.96	0.06	0.32	0.34	0.02
		49.19			5.95			0.35		
		49.11			6.02			0.33		
225	30	51.98	52.16	0.44	5.58	5.57	0.10	0.39	0.41	0.02
		51.84			5.65			0.43		
		52.65			5.46			0.42		
225	45	55.03	54.27	0.67	5.00	5.19	0.18	0.56	0.49	0.07
		53.79			5.36			0.47		
		53.98			5.20			0.44		
250	15	51.55	51.70	0.14	5.71	5.76	0.05	0.45	0.47	0.02
		51.80			5.75			0.49		
		51.76			5.82			0.47		
250	30	56.21	55.77	0.44	5.24	5.17	0.06	0.60	0.55	0.06
		55.33			5.14			0.58		
		55.77			5.13			0.48		
250	45	61.08	59.68	1.36	4.50	4.71	0.20	0.58	0.63	0.08
		58.35			4.89			0.57		
		59.61			4.75			0.72		
275	15	56.10	55.70	1.68	5.26	5.37	0.10	0.55	0.55	0.02
		54.92			5.44			0.53		
		56.09			5.40			0.56		
275	30	60.93	60.61	0.37	4.88	4.92	0.04	0.64	0.66	0.02
		60.20			4.96			0.67		
		60.71			4.92			0.67		
275	45	69.61	68.39	1.69	3.59	3.89	0.26	0.89	0.76	0.11
		66.45			4.06			0.68		
		69.10			4.01			0.73		

Table A.15: Ultimate analysis (dry basis) of switchgrass

Temp (˚C)	Time (min)	C %	Mean	Std. dev.	H %	Mean	Std. dev.	N %	Mean	Std. dev.
Untreated		48.25	48.26	0.04	5.97	5.98	0.05	0.65	0.62	0.03
		48.23			5.93			0.60		
		48.31			6.04			0.62		
225	15	48.59	49.11	0.54	5.77	5.78	0.02	0.63	0.56	0.06
		49.06			5.76			0.54		
		49.67			5.81			0.52		
225	30	54.55	54.27	0.29	5.32	5.36	0.06	0.77	0.76	0.05
		53.97			5.43			0.70		
		54.29			5.34			0.80		
225	45	63.10	62.29	0.91	4.18	4.32	0.13	0.97	0.83	0.31
		62.46			4.37			1.04		
		61.31			4.41			0.47		
250	15	55.13	54.40	0.68	5.25	5.33	0.07	0.43	0.40	0.03
		54.27			5.39			0.38		
		53.79			5.33			0.40		
250	30	63.15	61.04	1.88	4.34	4.65	0.29	0.68	0.63	0.04
		59.54			4.91			0.61		
		60.44			4.69			0.61		
250	45	69.94	69.73	1.12	3.75	3.34	0.36	0.57	0.65	0.11
		70.72			3.21			0.61		
		68.52			3.07			0.77		
275	15	58.09	58.05	0.21	4.94	4.94	0.03	0.48	0.50	0.02
		57.83			4.92			0.52		
		58.24			4.98			0.48		
275	30	68.23	70.73	2.28	3.80	3.55	0.24	0.62	0.61	0.01
		71.25			3.53			0.62		
		72.70			3.32			0.60		
275	45	74.50	74.04	0.72	2.92	2.93	0.08	0.60	0.63	0.04
		74.39			3.01			0.67		
		73.21			2.85			0.63		

Table A.16: Energy content (dry basis) of biomass samples

		Pine			Sweetgum			Switchgrass		
Temp (˚C)	Time (min)	HHV	Mean	Std. dev.	HHV	Mean	Std. dev.	HHV	Mean	Std. dev.
		20.13			19.71			19.54		
Untreated		20.41	20.18	0.21	19.50	19.65	0.12	19.43	19.50	0.06
		19.99			19.73			19.52		
		20.42			20.39			19.30		
225	15	20.47	20.50	0.10	20.26	20.43	0.19	19.37	19.39	0.10
		20.61			20.63			19.50		
		21.22			21.01			21.65		
225	30	21.04	21.11	0.10	20.75	20.91	0.14	21.11	21.41	0.28
		21.07			20.98			21.46		
		22.51			22.48			24.01		
225	45	22.73	22.50	0.23	22.68	22.46	0.23	24.28	23.99	0.31
		22.27			22.23			23.67		
		21.26			19.67			21.08		
250	15	21.14	21.28	0.15	19.89	19.92	0.26	21.16	21.02	0.18
		21.44			20.19			20.81		
		22.33			21.75			24.92		
250	30	22.19	22.40	0.25	21.44	21.61	0.16	23.66	24.34	0.64
		22.67			21.64			24.45		
		24.18			22.97			25.38		
250	45	23.66	24.01	0.31	22.36	22.67	0.31	25.24	25.45	0.25
		24.19			22.68			25.73		
		21.91			21.69			22.78		
275	15	21.70	21.91	0.20	21.32	21.57	0.22	21.99	22.63	0.58
		22.11			21.71			23.11		
		24.74			23.40			25.68		
275	30	24.42	24.72	0.29	23.21	23.37	0.15	26.48	26.25	0.50
		24.99			23.50			26.59		
		26.12			26.47			25.59		
275	45	27.01	26.68	0.49	25.20	25.86	0.63	26.26	25.95	0.34
		26.91			25.91			26.00		

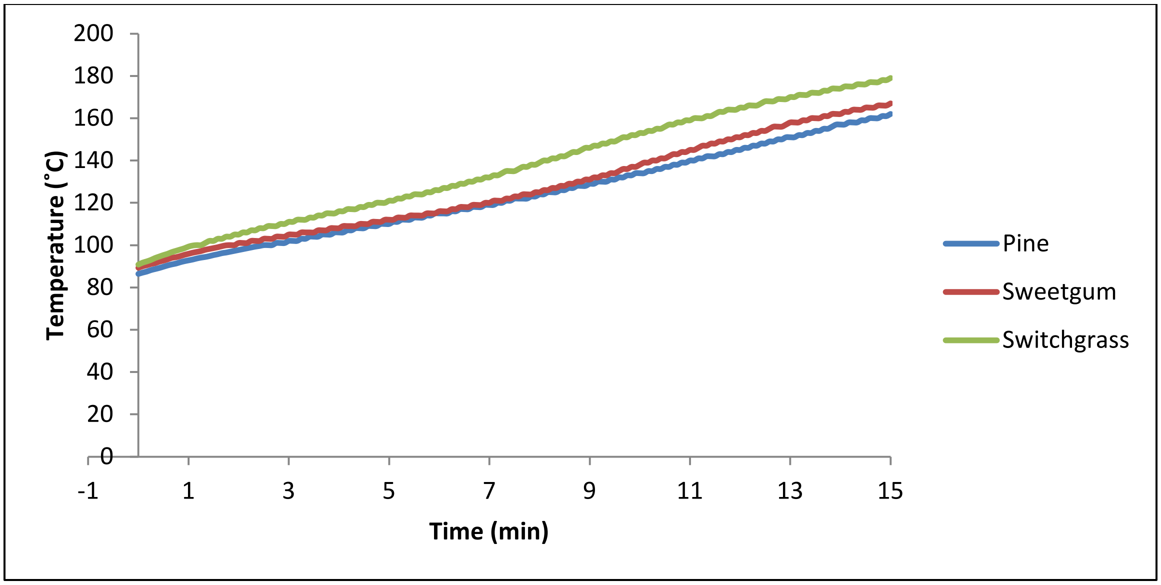

Figure A.1: Sample temperature for torrefaction at 225°C, 15 minutes

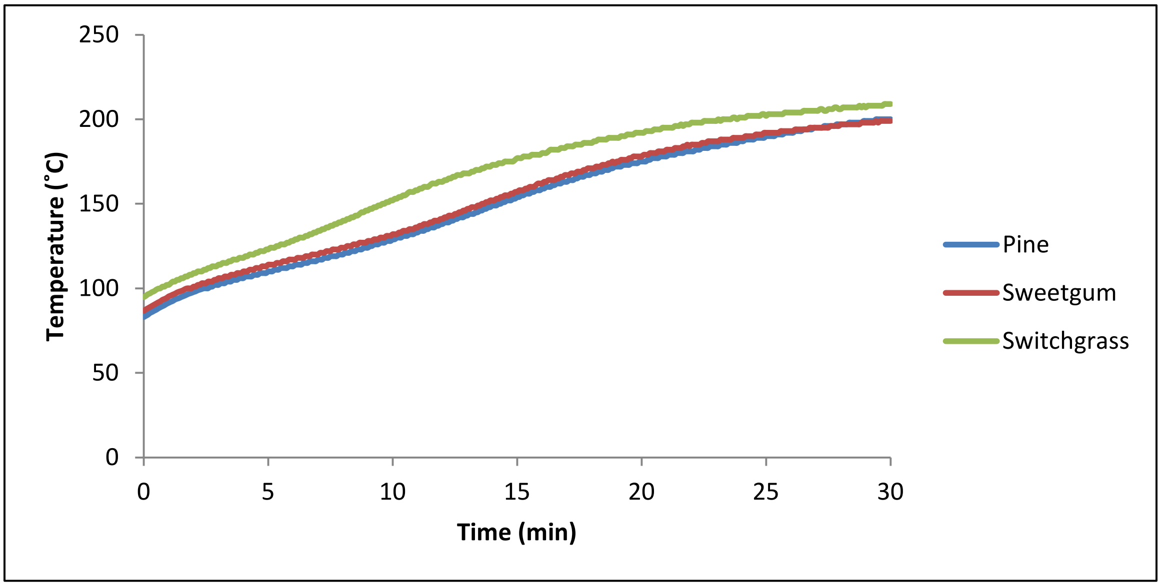

Figure A.2: Sample temperature for torrefaction at 225°C, 30 minutes

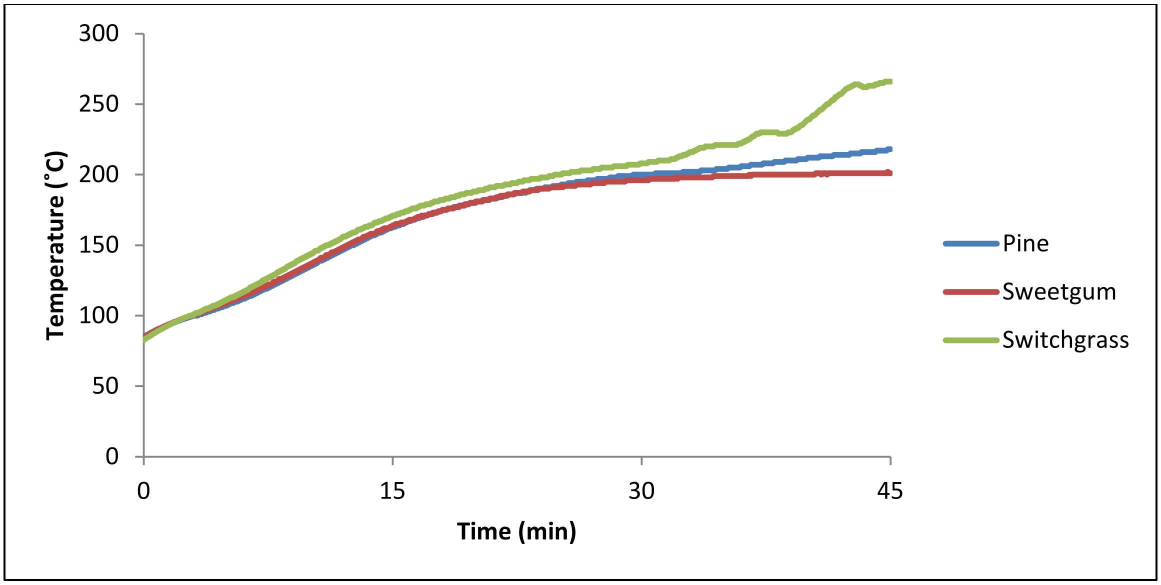

Figure A.3: Sample temperature for torrefaction at 225°C, 45 minutes

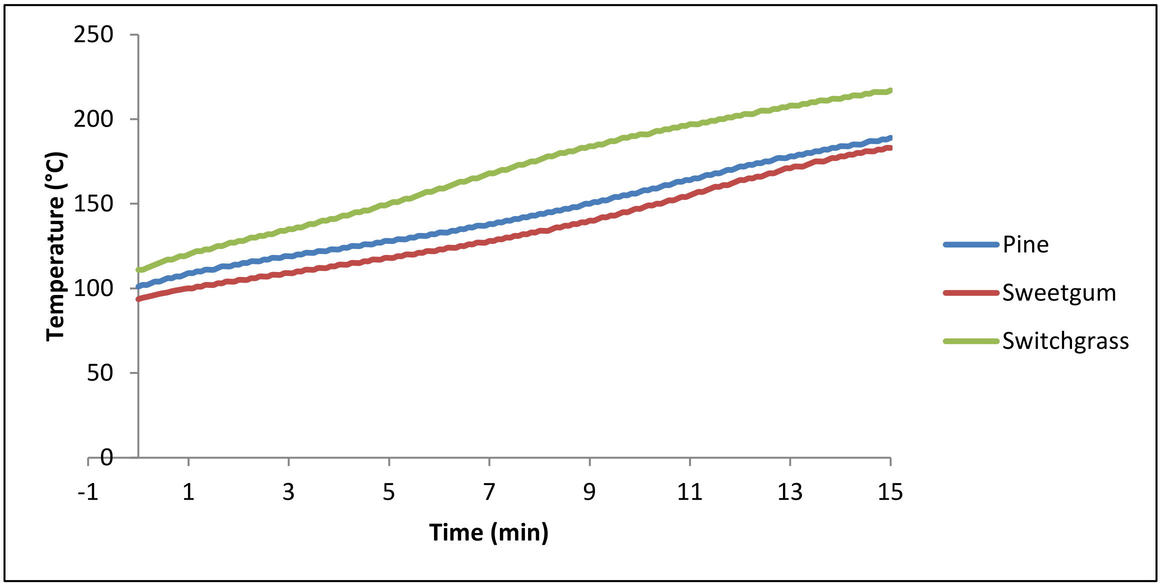

Figure A.4: Sample temperature for torrefaction at 250°C, 15 minutes

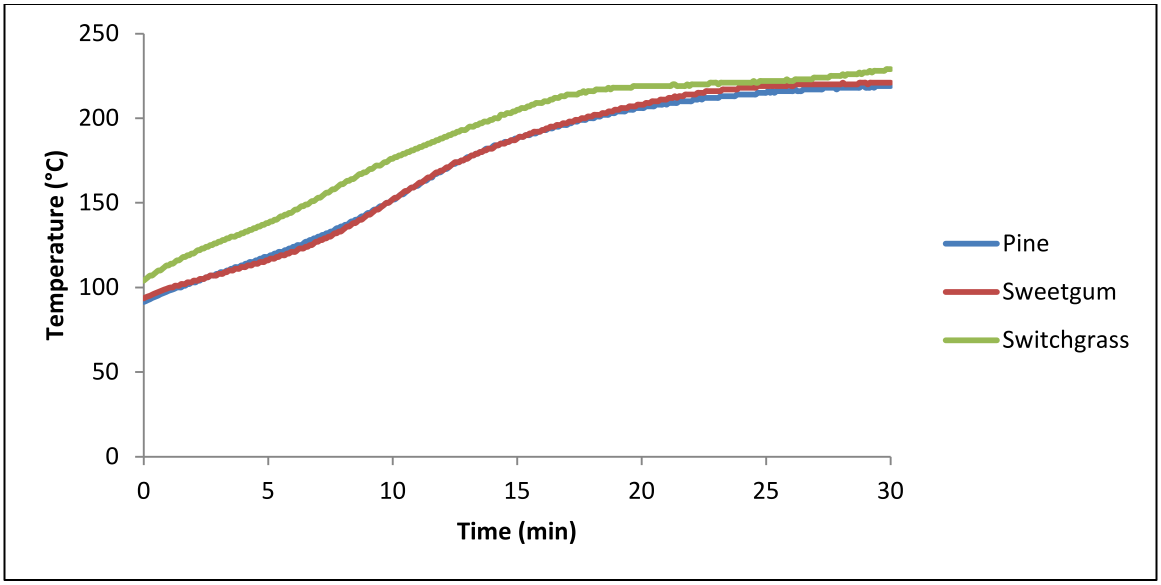

Figure A.5: Sample temperature for torrefaction at 250°C, 30 minutes

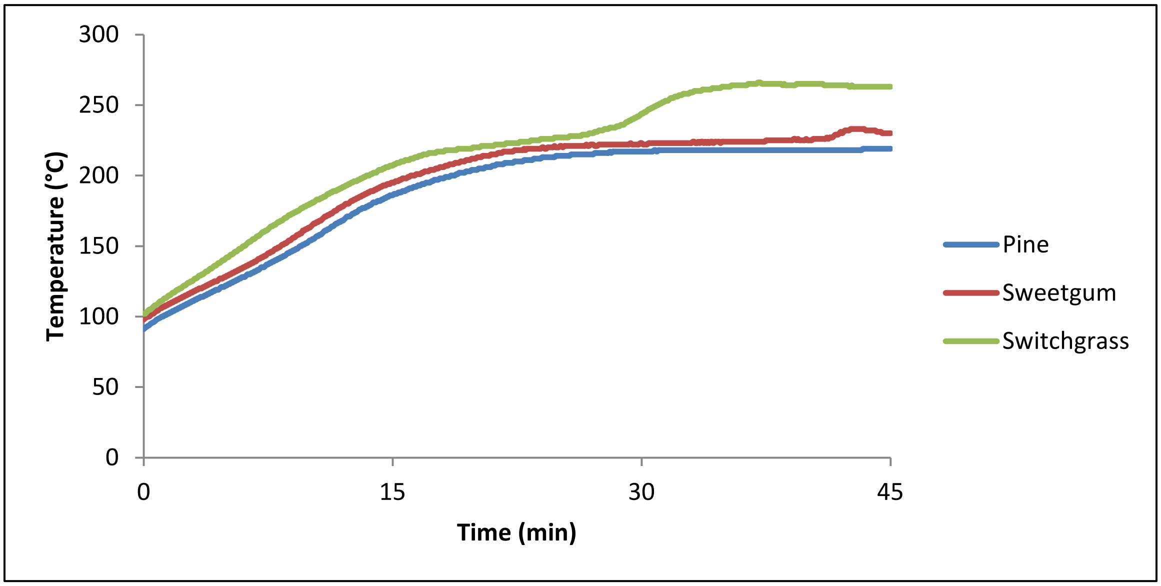

Figure A.6: Sample temperature for torrefaction at 225°C, 45 minutes

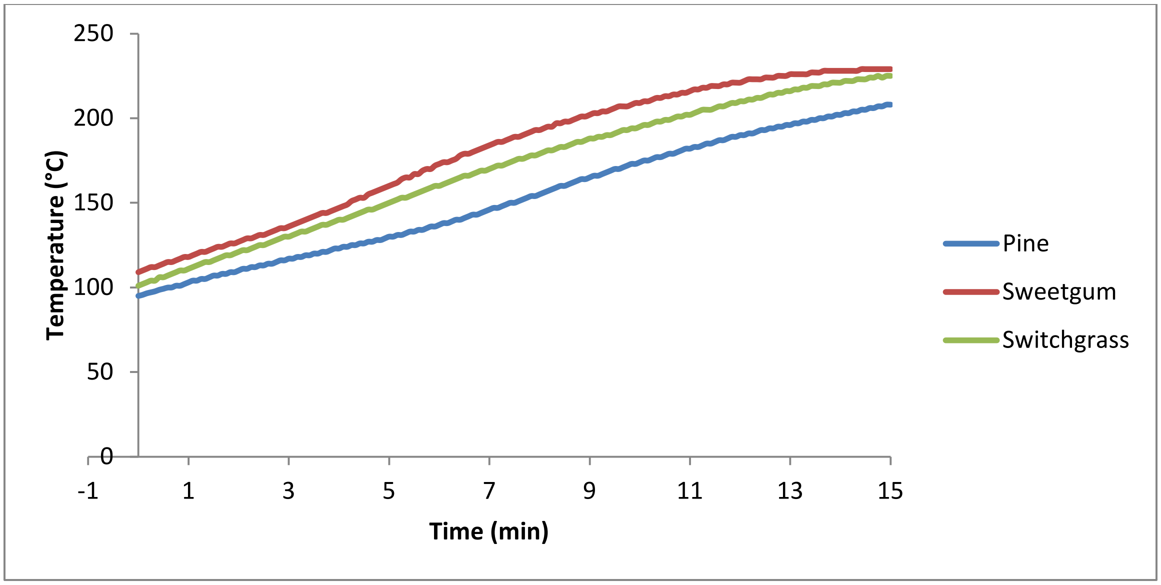

Figure A.7: Sample temperature for torrefaction at 275°C, 15 minutes

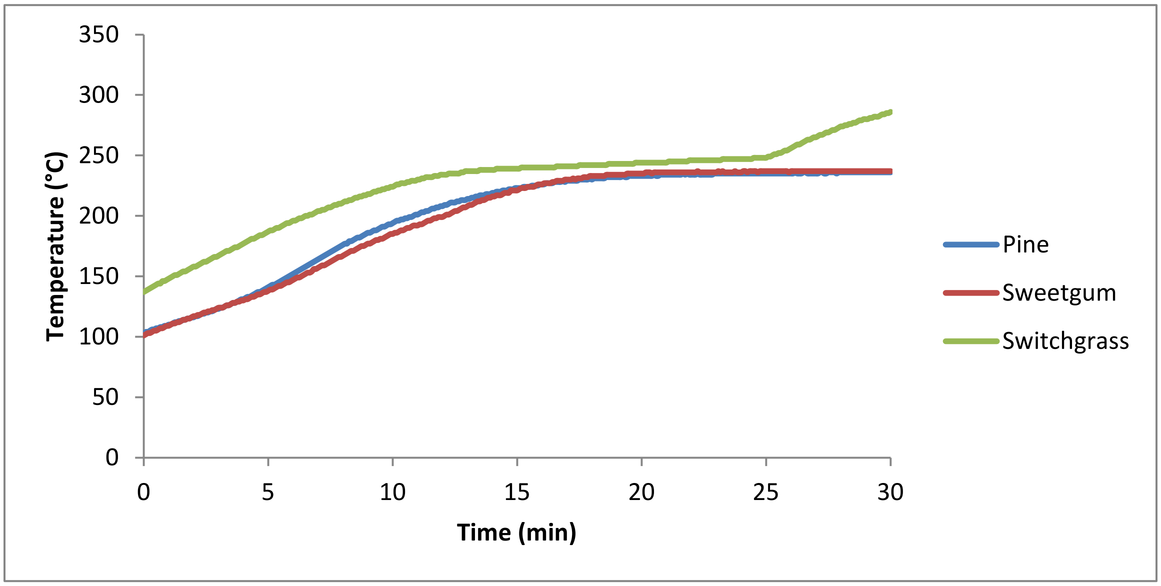

Figure A.8: Sample temperature for torrefaction at 275°C, 30 minutes

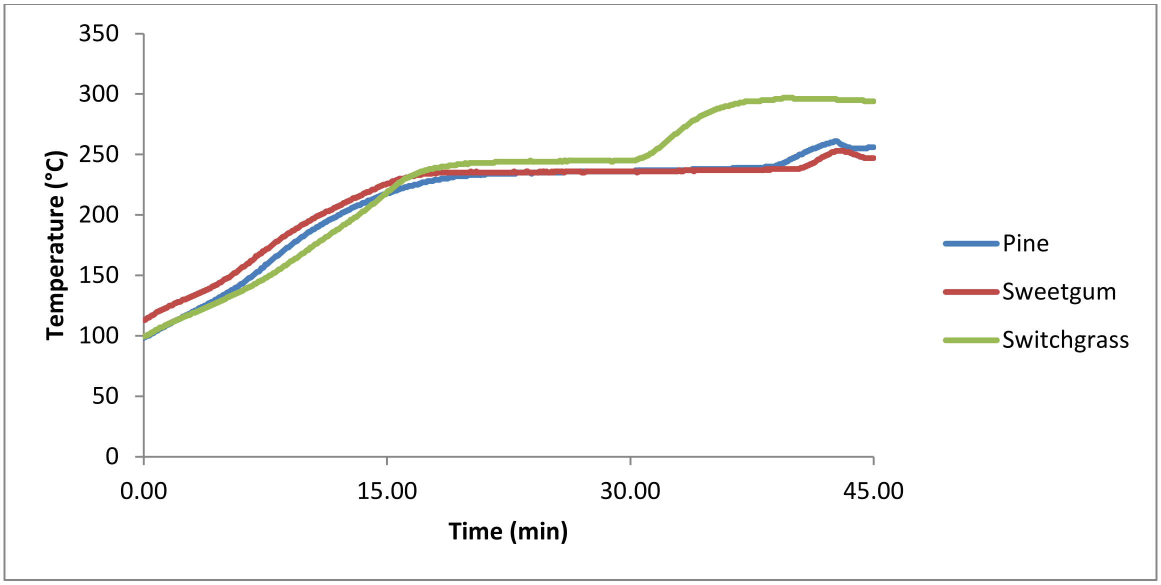

Figure A.9: Sample temperature for torrefaction at 275°C, 45 minutes

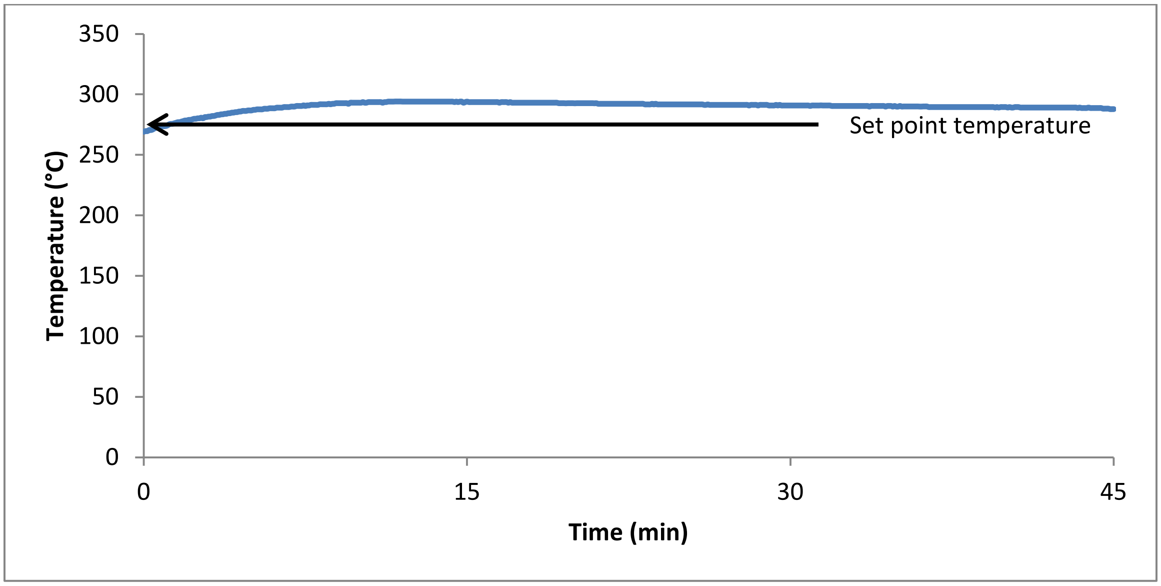

Figure A.10: Thermocouple temperature in furnace without sample, 275°C, 45 minutes

Appendix B. Thermal Analysis

Table B.1: Pre-exponential factors (1/s) for pyrolysis of untreated pine

	Reaction order, n			
α	0	1	2	3
0.1	3.04E+10	3.38E+10	3.76E+10	4.18E+10
0.2	1.45E+10	1.81E+10	2.26E+10	2.83E+10
0.3	5.63E+08	8.04E+08	1.15E+09	1.64E+09
0.4	2.34E+08	3.90E+08	6.50E+08	1.08E+09
0.5	8.59E+07	1.72E+08	3.44E+08	6.87E+08

Table B.2: Pre-exponential factors (1/s) for pyrolysis of treated pine

	Reaction order, n			
α	0	1	2	3
0.1	3.11E+11	3.46E+11	3.84E+11	4.27E+11
0.2	4.53E+10	5.66E+10	7.08E+10	8.85E+10
0.3	1.69E+10	2.41E+10	3.44E+10	4.92E+10
0.4	2.95E+08	4.92E+08	8.20E+08	1.37E+09
0.5	3.71E+12	7.41E+12	1.48E+13	2.96E+13

Table B.3: Pre-exponential factors (1/s) for pyrolysis of untreated sweetgum

	Reaction order, n			
α	0	1	2	3
0.1	2.96E+11	3.29E+11	3.66E+11	4.06E+11
0.2	1.93E+12	2.41E+12	3.01E+12	3.77E+12
0.3	1.06E+12	1.51E+12	2.16E+12	3.08E+12
0.4	2.03E+11	3.38E+11	5.64E+11	9.39E+11
0.5	2.27E+10	4.54E+10	9.08E+10	1.82E+11

Table B.4: Pre-exponential factors (1/s) for pyrolysis of treated sweetgum

	Reaction order, n			
α	0	1	2	3
0.1	1.01E+12	1.12E+12	1.25E+12	1.38E+12
0.2	9.06E+10	1.13E+11	1.42E+11	1.77E+11
0.3	2.13E+09	3.04E+09	4.34E+09	6.20E+09
0.4	3.93E+08	6.55E+08	1.09E+09	1.82E+09
0.5	9.95E+10	1.99E+11	3.98E+11	7.96E+11

Table B.5: Pre-exponential factors (1/s) for pyrolysis of untreated switchgrass

	Reaction order, n			
α	0	1	2	3
0.1	1.16E+10	1.29E+10	1.44E+10	1.60E+10
0.2	1.56E+10	1.95E+10	2.43E+10	3.04E+10
0.3	3.05E+11	4.35E+11	6.22E+11	8.89E+11
0.4	3.15E+10	5.25E+10	8.75E+10	1.46E+11
0.5	1.63E+11	3.25E+11	6.50E+11	1.30E+12

Table B.6: Pre-exponential factors (1/s) for pyrolysis of treated switchgrass

	Reaction order, n			
α	0	1	2	3
0.1	2.86E+11	3.18E+11	3.54E+11	3.93E+11
0.2	3.34E+12	4.17E+12	5.21E+12	6.52E+12
0.3	5.95E+11	8.49E+11	1.21E+12	1.73E+12
0.4	6.83E+11	1.14E+12	1.90E+12	3.16E+12
0.5	3.05E+20	6.09E+20	1.22E+21	2.44E+21

Table B.7: Pre-exponential factors (1/s) for combustion of untreated pine

	Reaction order, n			
α	0	1	2	3
0.1	4.14E+11	4.60E+11	5.12E+11	5.68E+11
0.2	1.23E+11	1.53E+11	1.92E+11	2.40E+11
0.3	1.77E+11	2.52E+11	3.61E+11	5.15E+11
0.4	9.38E+09	1.56E+10	2.61E+10	4.34E+10
0.5	8.49E+11	1.70E+12	3.39E+12	6.79E+12
0.6	2.53E+16	6.33E+16	1.58E+17	3.95E+17

Table B.8: Pre-exponential factors (1/s) for combustion of treated pine

	Reaction order, n			
α	0	1	2	3
0.1	5.32E+08	5.92E+08	6.57E+08	7.30E+08
0.2	8.25E+10	1.03E+11	1.29E+11	1.61E+11
0.3	2.60E+11	3.71E+11	5.31E+11	7.58E+11
0.4	6.93E+10	1.16E+11	1.93E+11	3.21E+11
0.5	6.69E+17	1.34E+18	2.68E+18	5.35E+18
0.6	3.42E+10	8.55E+10	2.14E+11	5.35E+11

Table B.9: Pre-exponential factors (1/s) for combustion of untreated sweetgum

	Reaction order, n			
α	0	1	2	3
0.1	1.07E+10	1.19E+10	1.32E+10	1.47E+10
0.2	1.07E+13	1.34E+13	1.68E+13	2.10E+13
0.3	7.60E+13	1.09E+14	1.55E+14	2.22E+14
0.4	3.11E+10	5.19E+10	8.64E+10	1.44E+11
0.5	1.10E+10	2.19E+10	4.38E+10	8.76E+10
0.6	7.47E+18	1.87E+19	4.67E+19	1.17E+20

Table B.10: Pre-exponential factors (1/s) for combustion of treated sweetgum

	Reaction order, n			
α	0	1	2	3
0.1	1.84E+10	2.05E+10	2.28E+10	2.53E+10
0.2	7.27E+11	9.09E+11	1.14E+12	1.42E+12
0.3	3.99E+11	5.70E+11	8.15E+11	1.16E+12
0.4	1.20E+10	2.00E+10	3.34E+10	5.56E+10
0.5	5.81E+14	1.16E+15	2.32E+15	4.65E+15
0.6	1.55E+19	3.88E+19	9.69E+19	2.42E+20

Table B.11: Pre-exponential factors (1/s) for combustion of untreated switchgrass

	Reaction order, n			
α	0	1	2	3
0.1	1.84E+09	2.04E+09	2.27E+09	2.52E+09
0.2	6.80E+10	8.50E+10	1.06E+11	1.33E+11
0.3	8.98E+10	1.28E+11	1.83E+11	2.62E+11
0.4	3.15E+12	5.25E+12	8.76E+12	1.46E+13
0.5	7.92E+10	1.58E+11	3.17E+11	6.33E+11
0.6	1.42E+17	3.56E+17	8.90E+17	2.22E+18

Table B.12: Pre-exponential factors (1/s) for combustion of treated switchgrass

	Reaction order, n			
α	0	1	2	3
0.1	1.82E+13	2.02E+13	2.25E+13	2.50E+13
0.2	1.14E+10	1.42E+10	1.78E+10	2.22E+10
0.3	4.37E+13	6.24E+13	8.92E+13	1.27E+14
0.4	1.80E+15	3.00E+15	4.99E+15	8.32E+15
0.5	2.77E+14	5.55E+14	1.11E+15	2.22E+15
0.6	1.90E+10	4.74E+10	1.19E+11	2.96E+11

Table B.13: Pre-exponential factors (1/s) for combustion of 30% pine and 70% coal

	Reaction order, n			
α	0	1	2	3
0.1	7.90E+08	8.78E+08	9.76E+08	1.08E+09
0.2	6.70E+06	8.37E+06	1.05E+07	1.31E+07
0.3	3.47E+03	4.96E+03	7.09E+03	1.01E+04
0.4	1.74E+05	2.89E+05	4.82E+05	8.03E+05

Table B.14: Pre-exponential factors (1/s) for combustion of 20% pine and 80% coal

	Reaction order, n			
α	0	1	2	3
0.1	1.13E+12	1.25E+12	1.39E+12	1.55E+12
0.2	3.93E+09	4.92E+09	6.15E+09	7.68E+09
0.3	5.12E+06	7.32E+06	1.05E+07	1.49E+07
0.4	4.59E+01	7.66E+01	1.28E+02	2.13E+02

Table B.15: Pre-exponential factors (1/s) for combustion of 10% pine and 90% coal

	Reaction order, n			
α	0	1	2	3
0.1	3.89E+08	4.32E+08	4.80E+08	5.33E+08
0.2	2.73E+07	3.41E+07	4.26E+07	5.33E+07
0.3	1.06E+04	1.52E+04	2.17E+04	3.10E+04
0.4	8.55E+00	1.42E+01	2.37E+01	3.96E+01

Table B.16: Pre-exponential factors (1/s) for combustion of 100% coal

	Reaction order, n			
α	0	1	2	3
0.1	1.46E+12	1.62E+12	1.81E+12	2.01E+12
0.2	2.54E+04	3.18E+04	3.97E+04	4.97E+04
0.5	3.74E+02	5.35E+02	7.64E+02	1.09E+03
0.4	5.84E-01	9.73E-01	1.62E+00	2.70E+00

Table B.17: Enthalpy of torrefaction for pine

	Run #	MC% (w.b.)	$\dot{Q}$ (J/g)	Mean	Std. dev.
Des 1	1	4.54	258.4	310.0	48.0
	2	4.86	318.3		
	3	4.56	353.4		
Des 3	1	6.94	351.5	362.3	26.6
	2	6.99	342.9		
	3	7.19	392.6		
Des 6	1	12.68	435.6	434.4	23.4
	2	12.40	410.5		
	3	12.72	457.2		
Des 8	1	18.57	492.6	509.8	15.3
	2	18.49	521.6		
	3	18.54	515.3		

Table B.18: Enthalpy of torrerfaction for sweetgum

	Run #	MC% (w.b.)	$\dot{Q}$ (J/g)	Mean	Std. dev.
Des 1	1	4.19	247.5	277.3	26.0
	2	4.15	288.9		
	3	4.43	295.4		
Des 3	1	6.53	366.5	328.4	33.2
	2	6.45	305.6		
	3	6.49	313.1		
Des 6	1	12.50	463.8	446.8	14.8
	2	12.00	440		
	3	12.04	436.7		
Des 8	1	18.16	531.1	574.7	40.1
	2	17.74	582.9		
	3	17.75	610		

Table B.19: Enthalpy of torrefaction for switchgrass

	Run #	MC% (w.b.)	$\dot{Q}$ (J/g)	Mean	Std. dev.
Des 2	1	3.75	280.1	259.1	18.3
	2	4.09	246.3		
	3	4.26	250.9		
Des 4	1	5.96	284.5	300.6	16.0
	2	6.19	316.5		
	3	6.22	300.8		
Des 7	1	10.10	410.4	410.3	11.6
	2	11.77	421.9		
	3	11.65	398.7		
Des 9	1	18.90	609.6	609.9	5.0
	2	18.80	615		
	3	18.83	605.1		

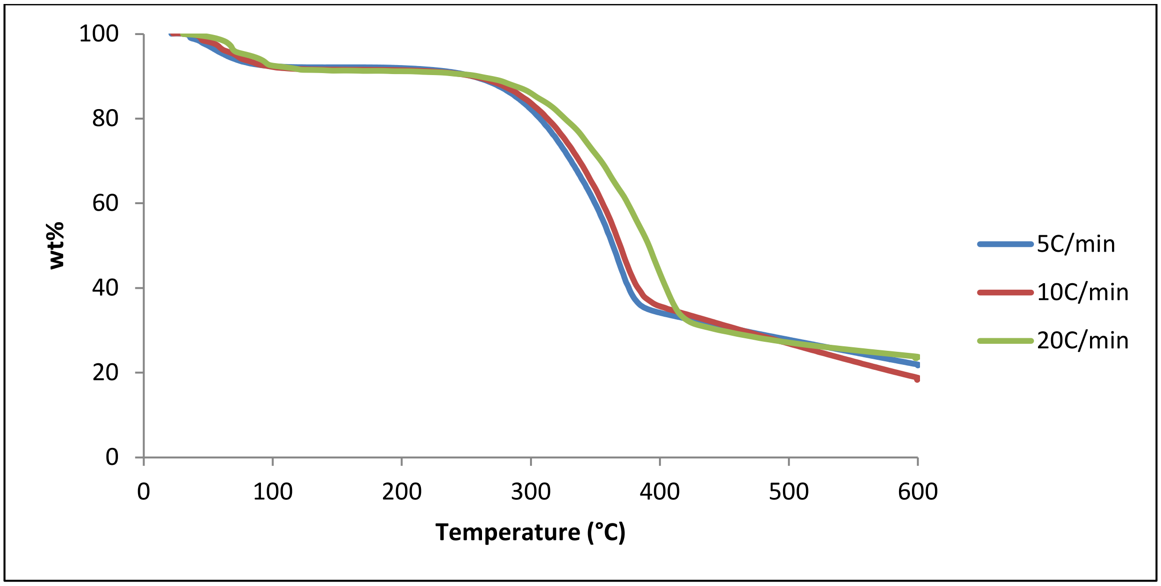

Figure B.1: TG pyrolysis profile of untreated pine

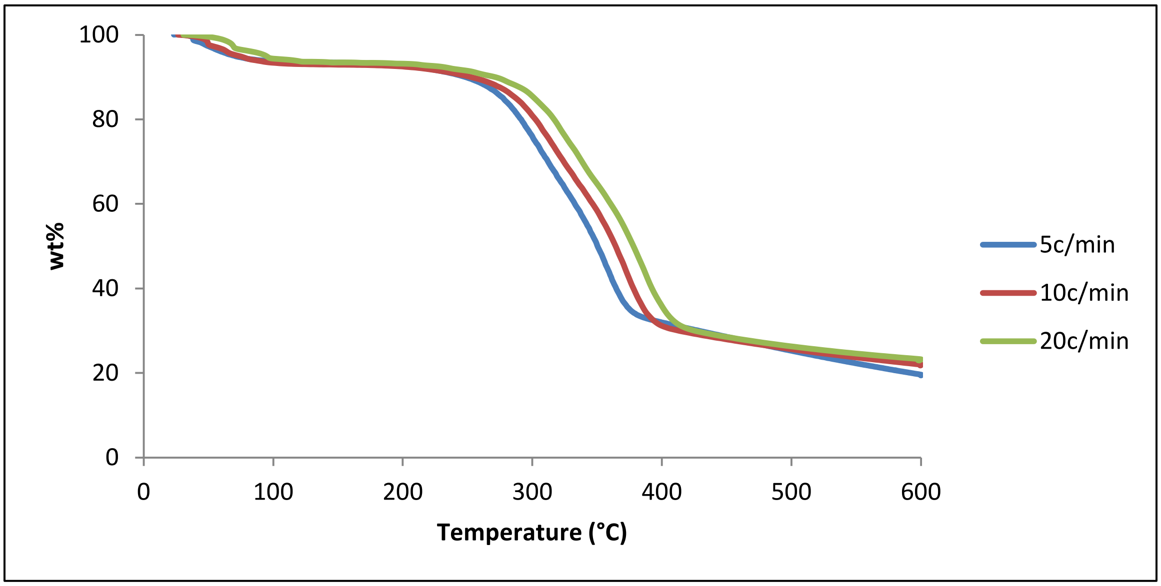

Figure B.2: TG pyrolysis profile of untreated switchgrass

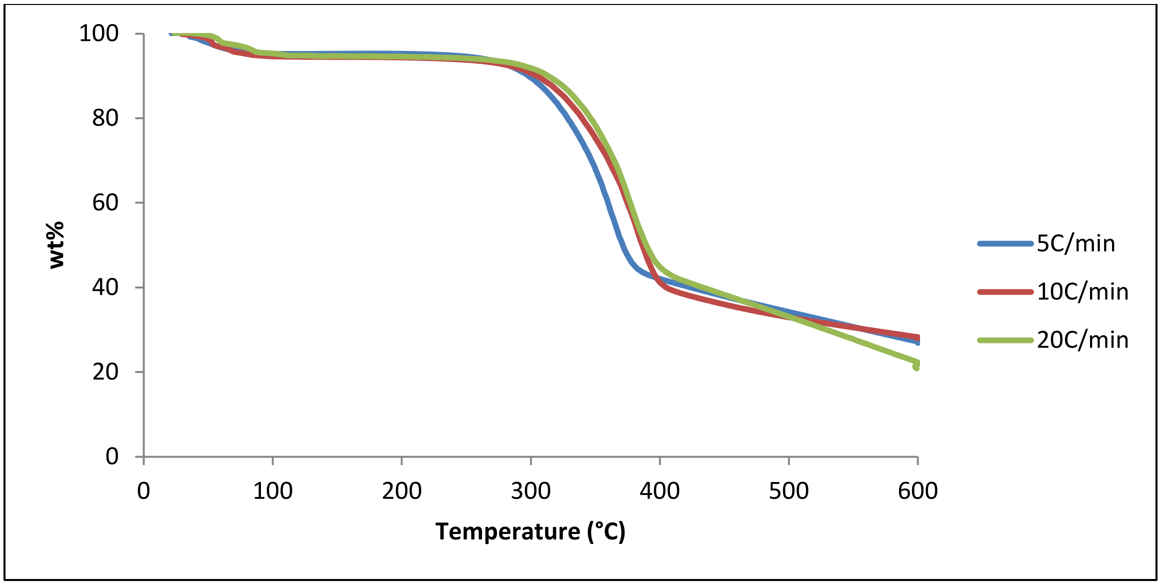

Figure B.3: TG pyrolysis profile of treated pine

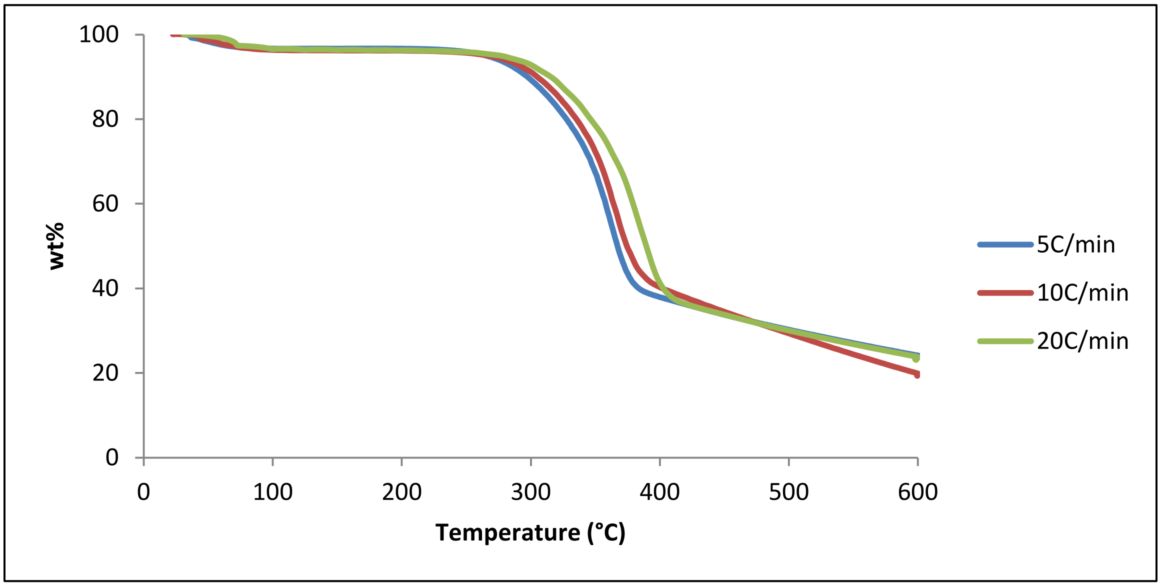

Figure B.4: TG pyrolysis profile of treated sweetgum

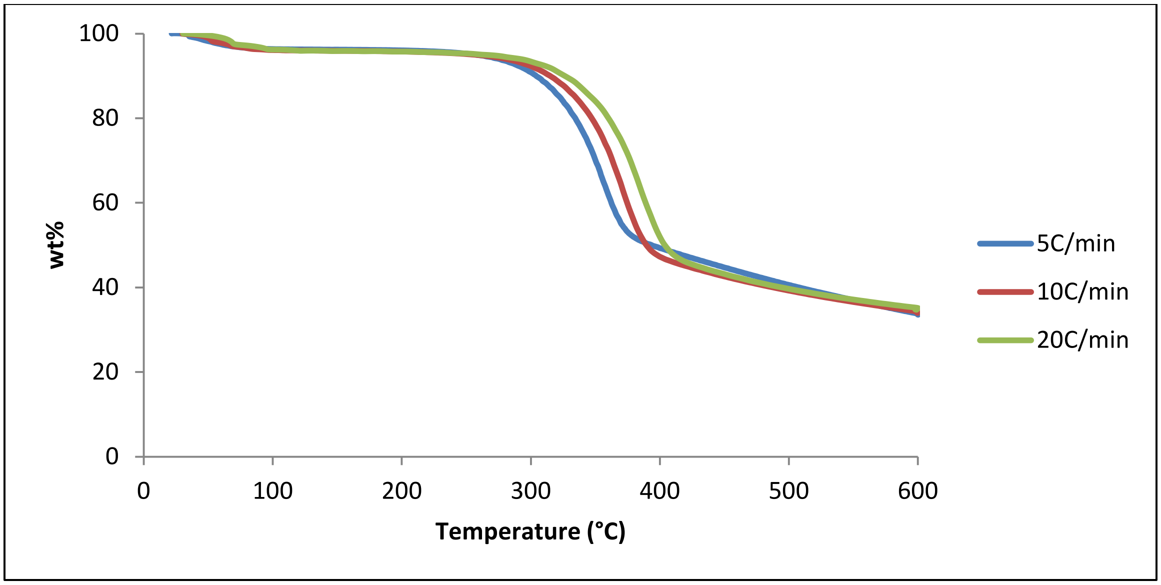

Figure B.5: TG pyrolysis profile of treated switchgrass

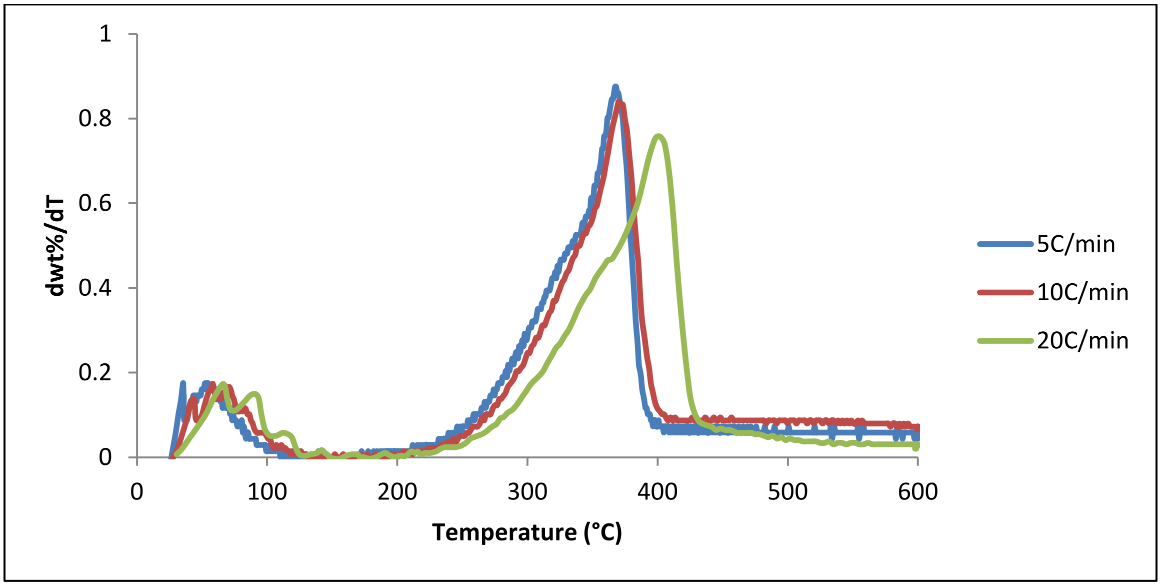

Figure B.6: DTG pyrolysis profile of untreated pine

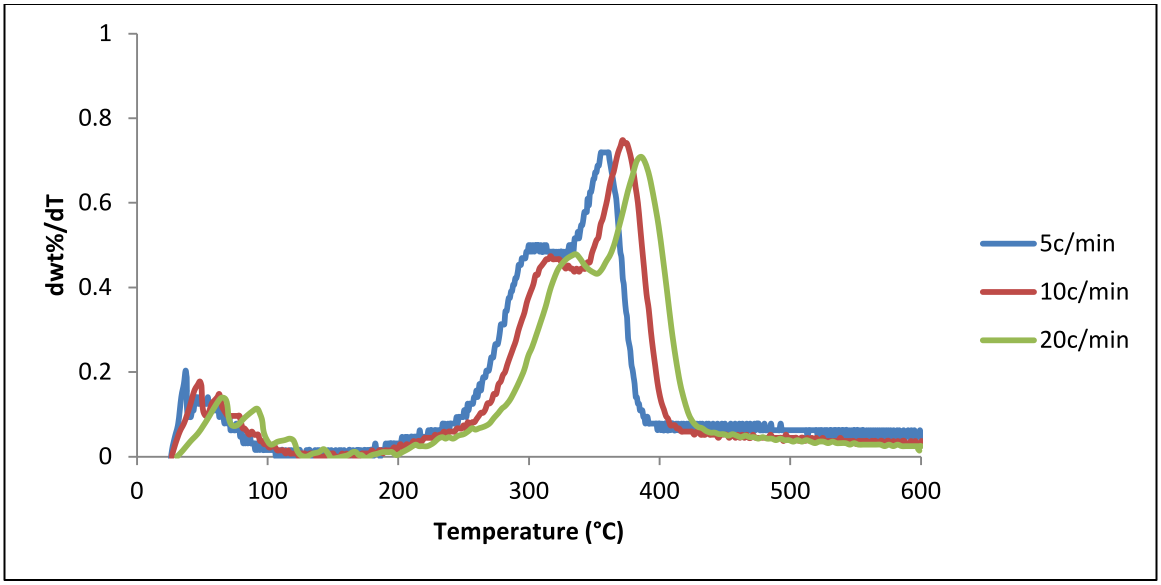

Figure B.7: DTG pyrolysis profile of untreated switchgrass

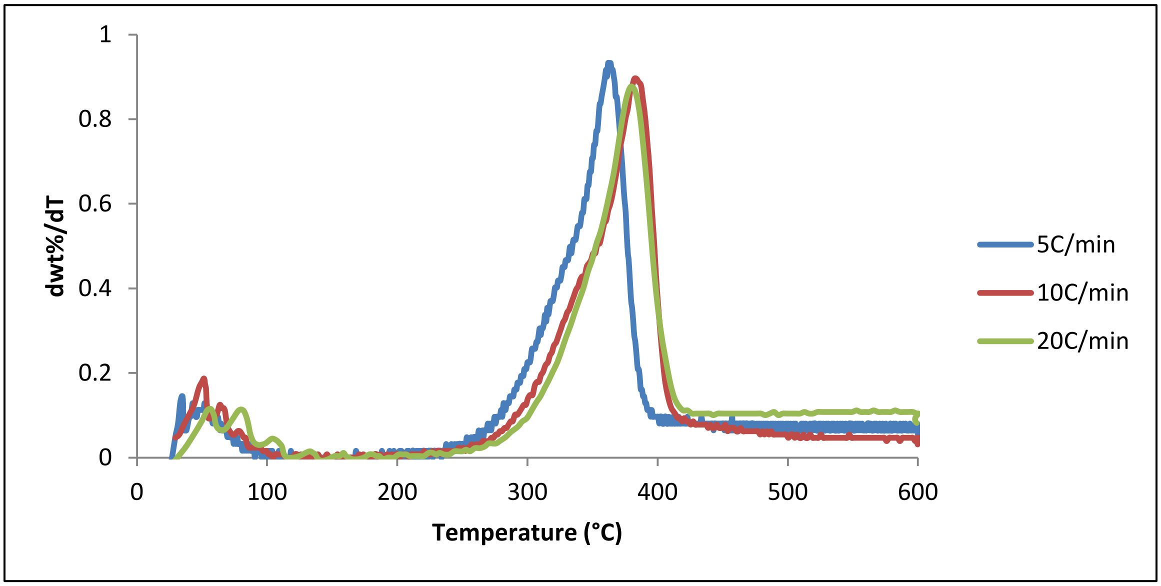

Figure B.8: DTG pyrolysis profile of treated pine

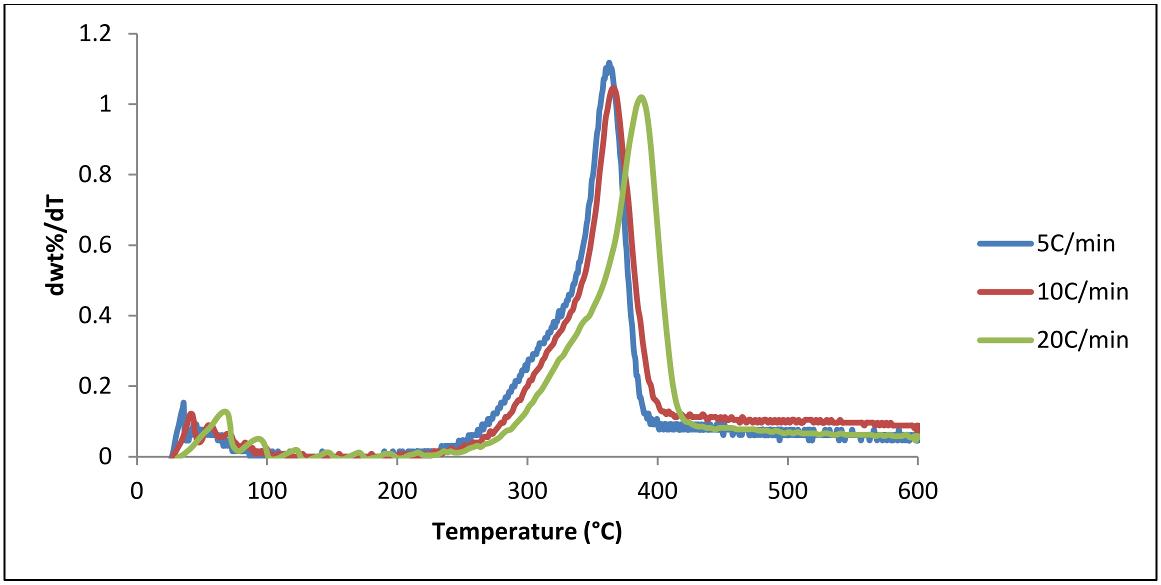

Figure B.9: DTG pyrolysis profile of treated sweetgum

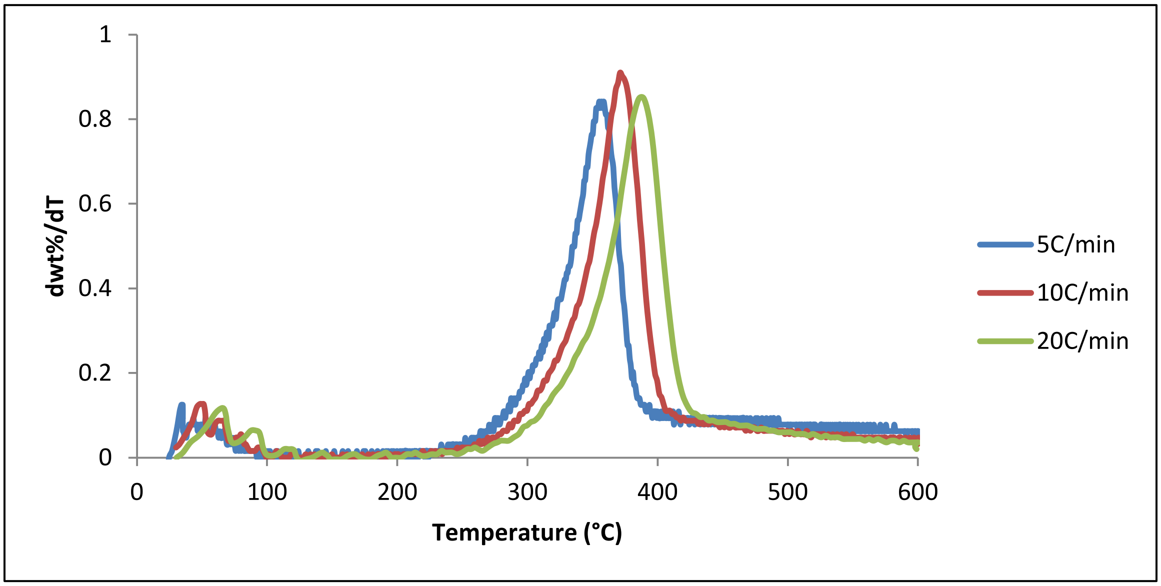

Figure B.10: DTG pyrolysis profile of treated switchgrass

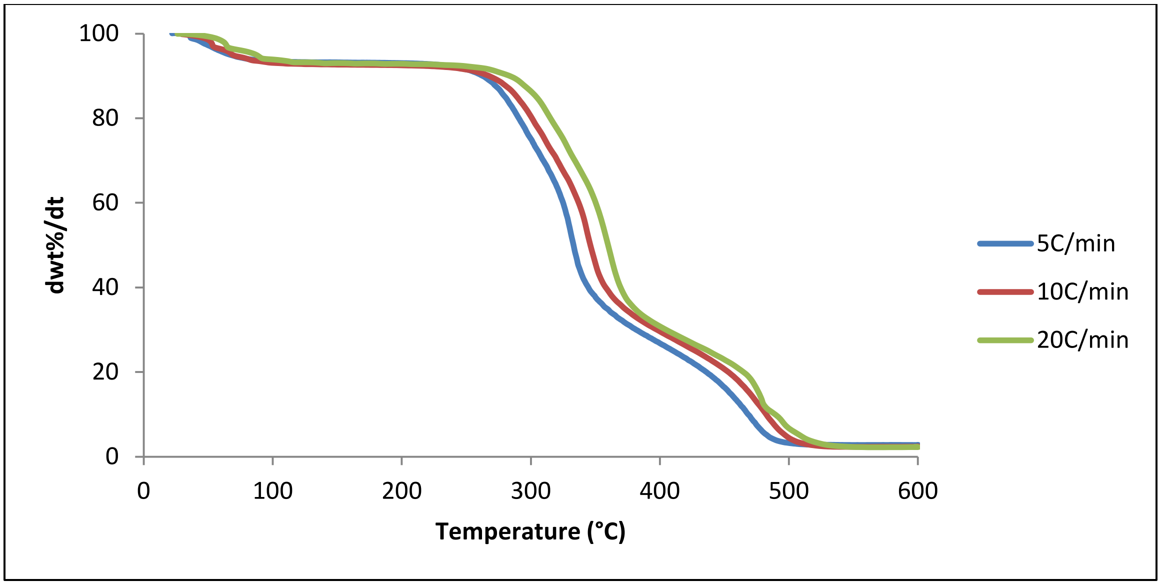

Figure B.11: TG combustion profile of untreated sweetgum

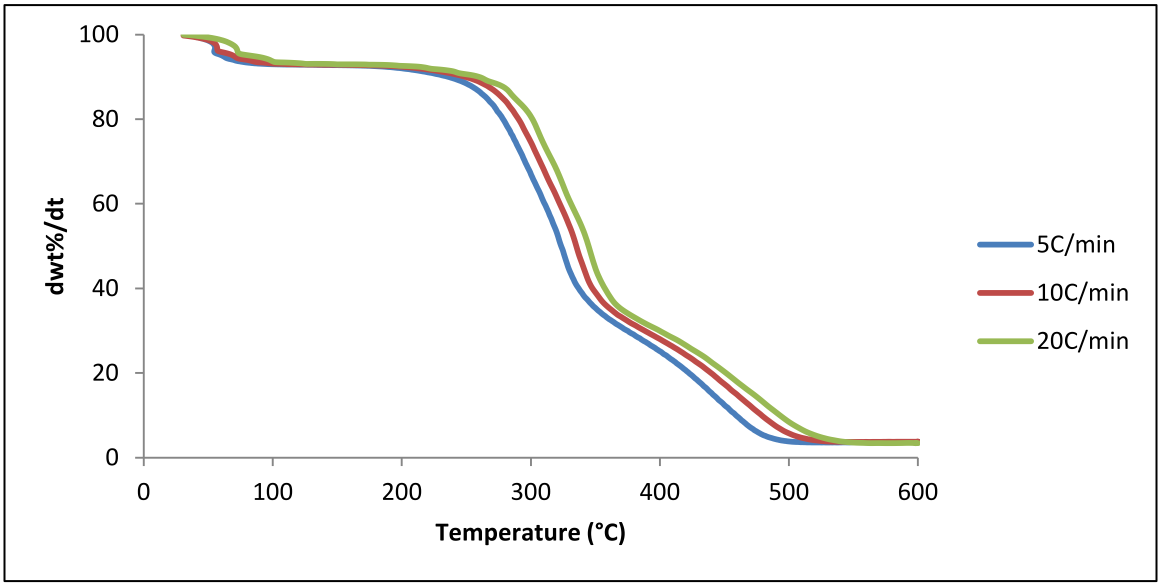

Figure B.12: TG combustion profile of untreated switchgrass

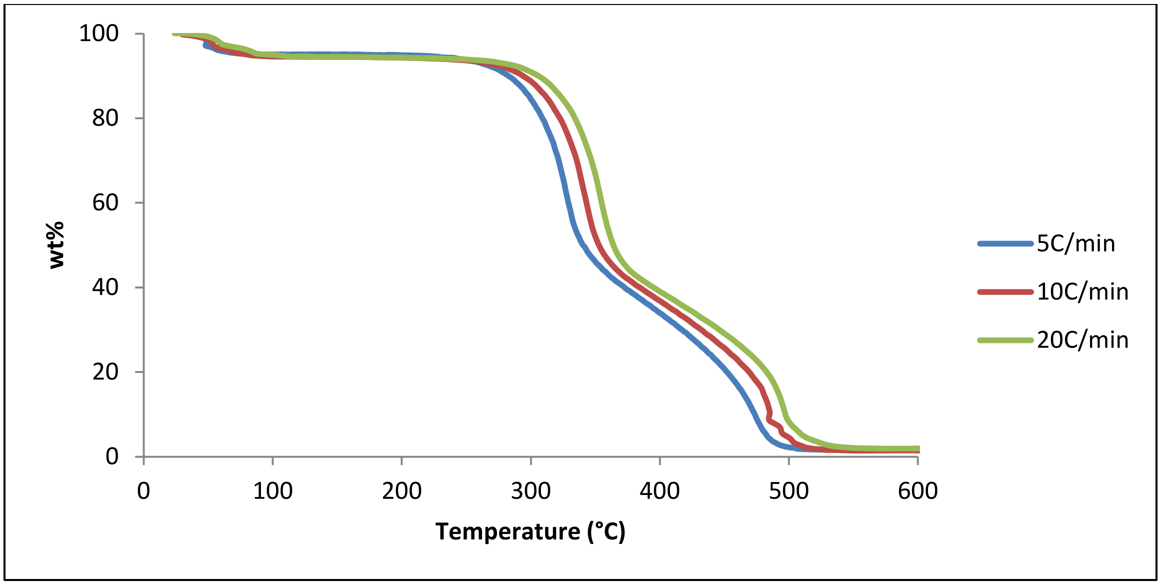

Figure B.13: TG combustion profile of treated pine

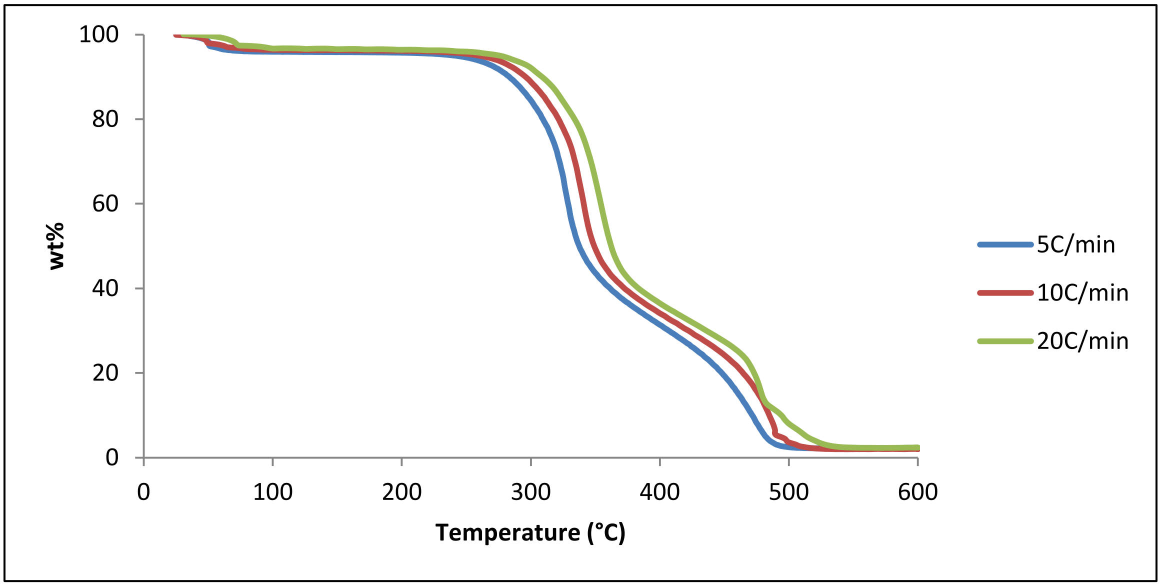

Figure B.14: TG combustion profile of treated sweetgum

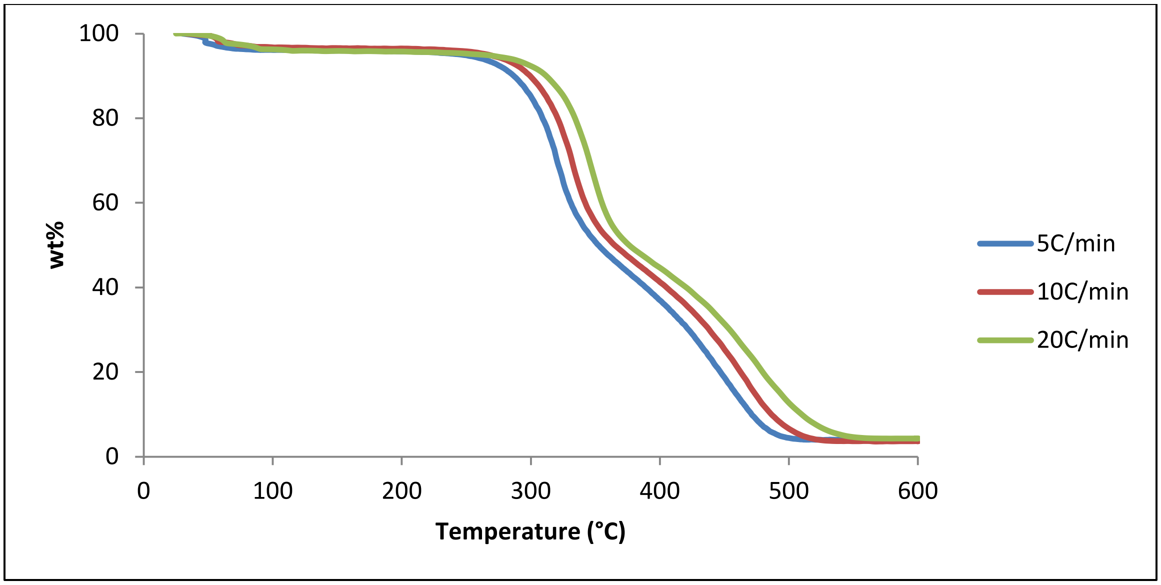

Figure B.15: TG combustion profile of treated switchgrass

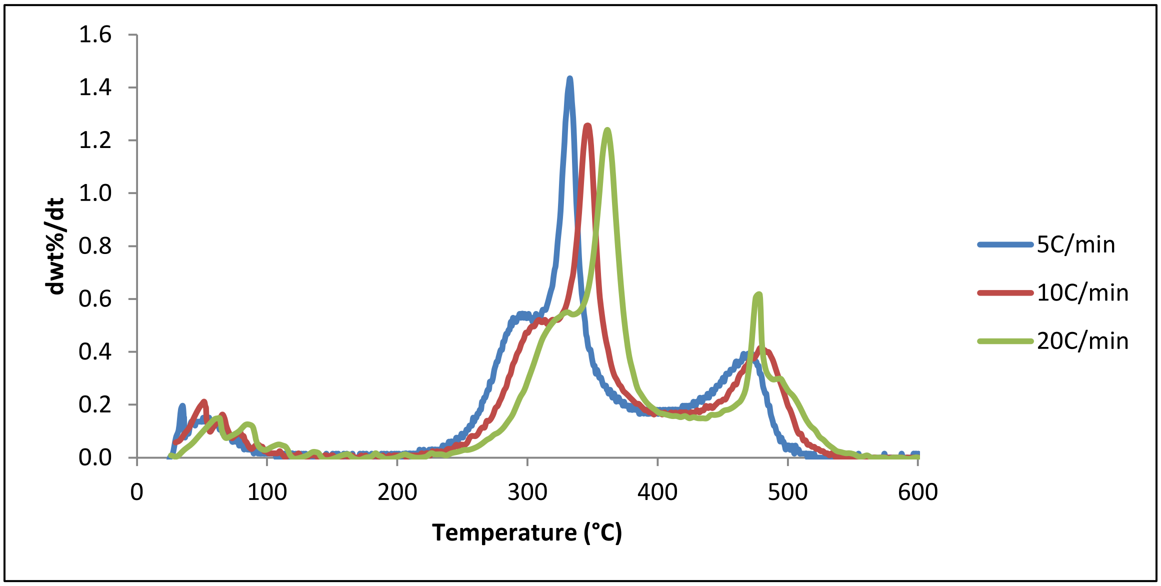

Figure B.16: DTG combustion profile of untreated sweetgum

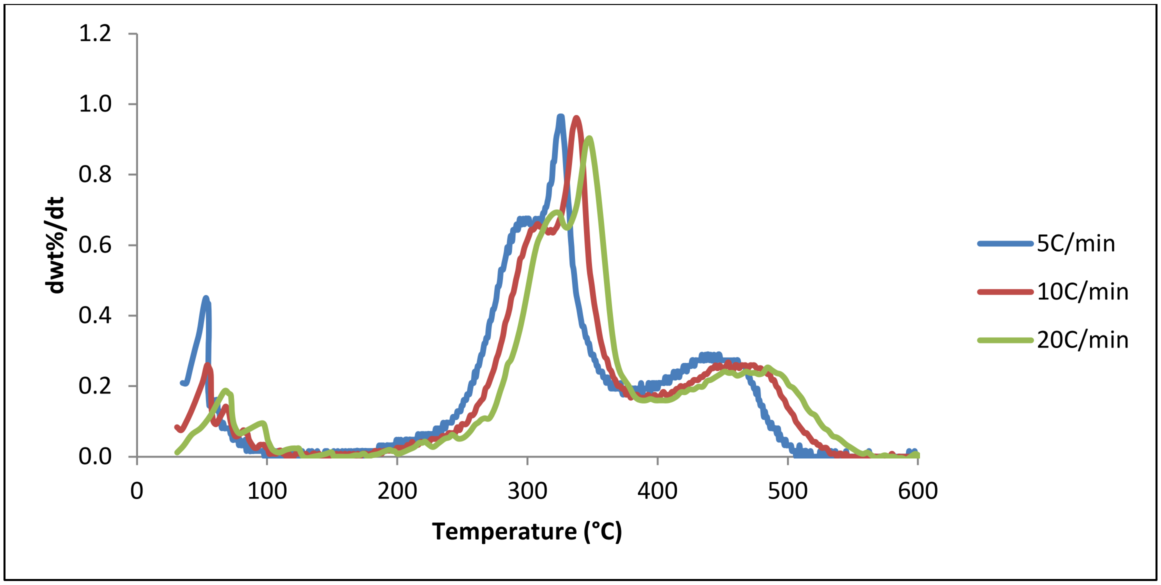

Figure B.17: DTG combustion profile of untreated switchgrass

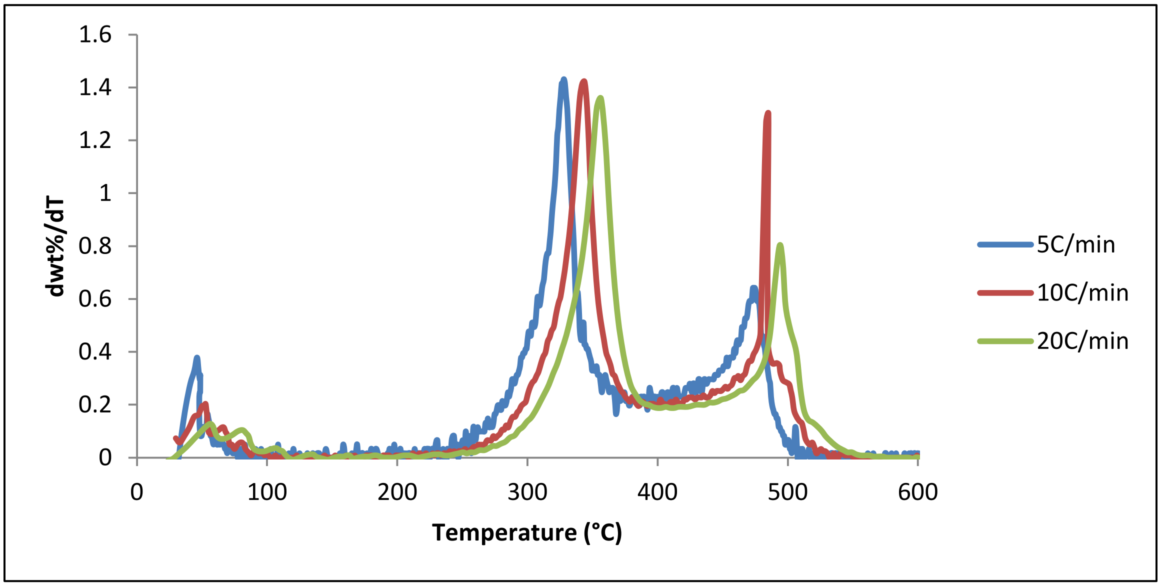

Figure B.18: DTG combustion profile of treated pine

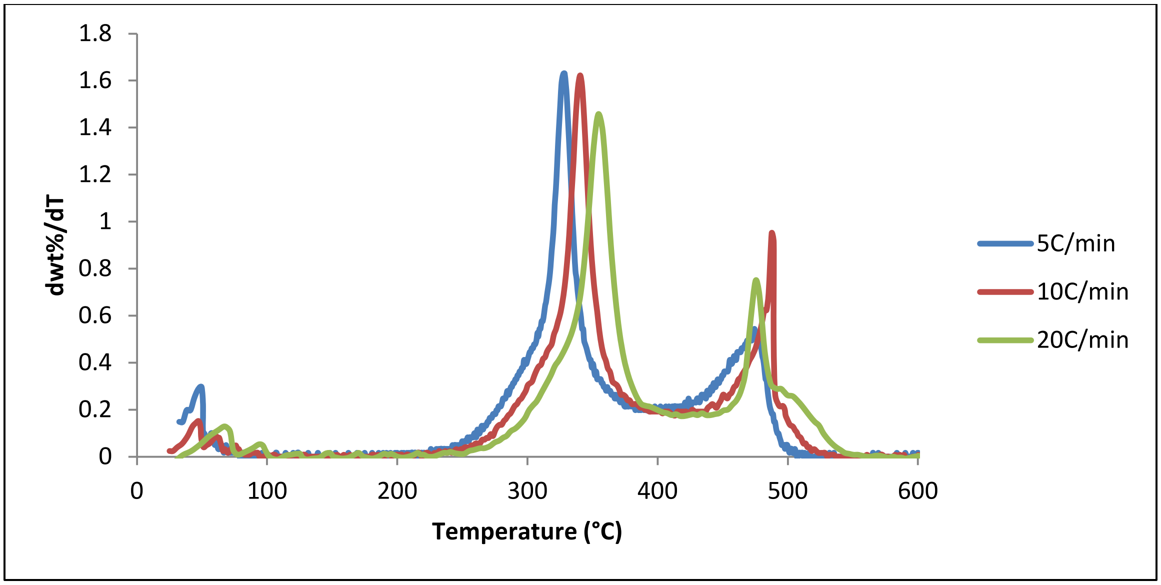

Figure B.19: DTG combustion profile of treated sweetgum

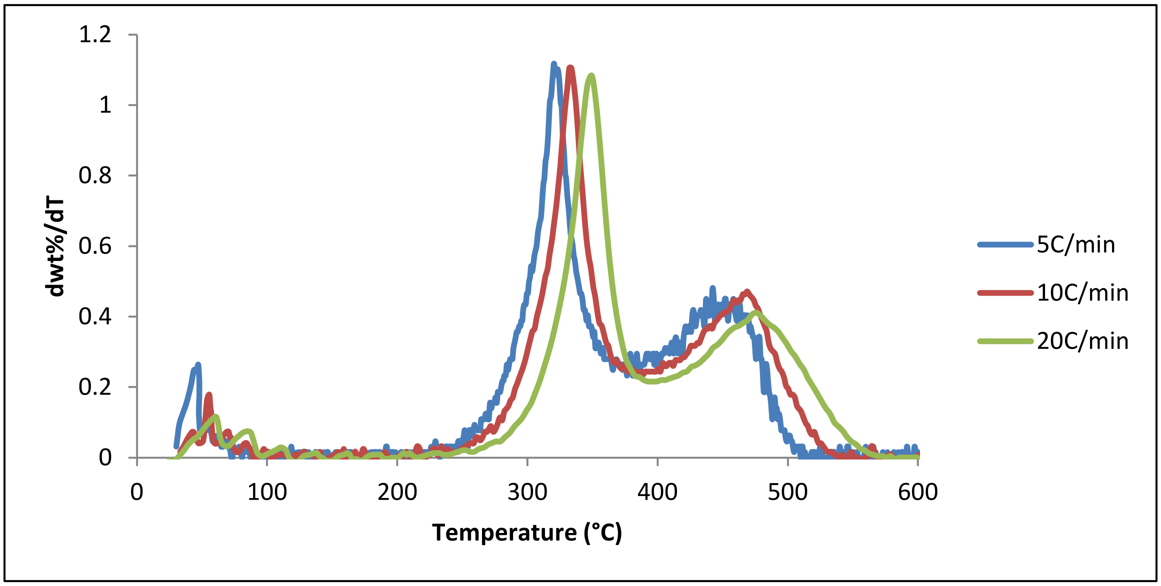

Figure B.20: DTG combustion profile of treated switchgrass

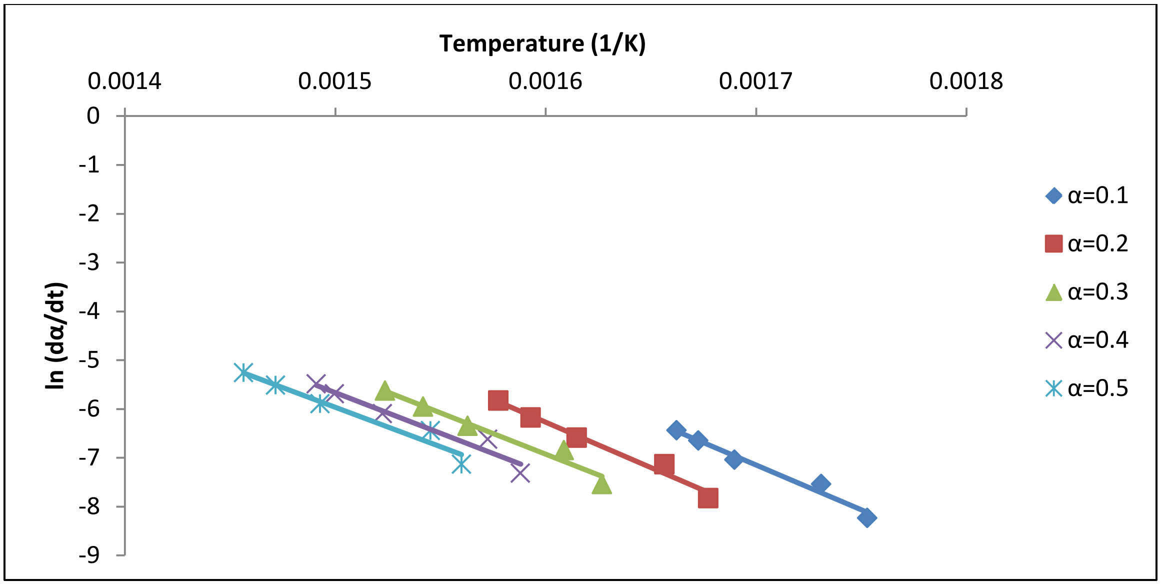

Figure B.21: Isoconversional plot for pyrolysis of untreated pine

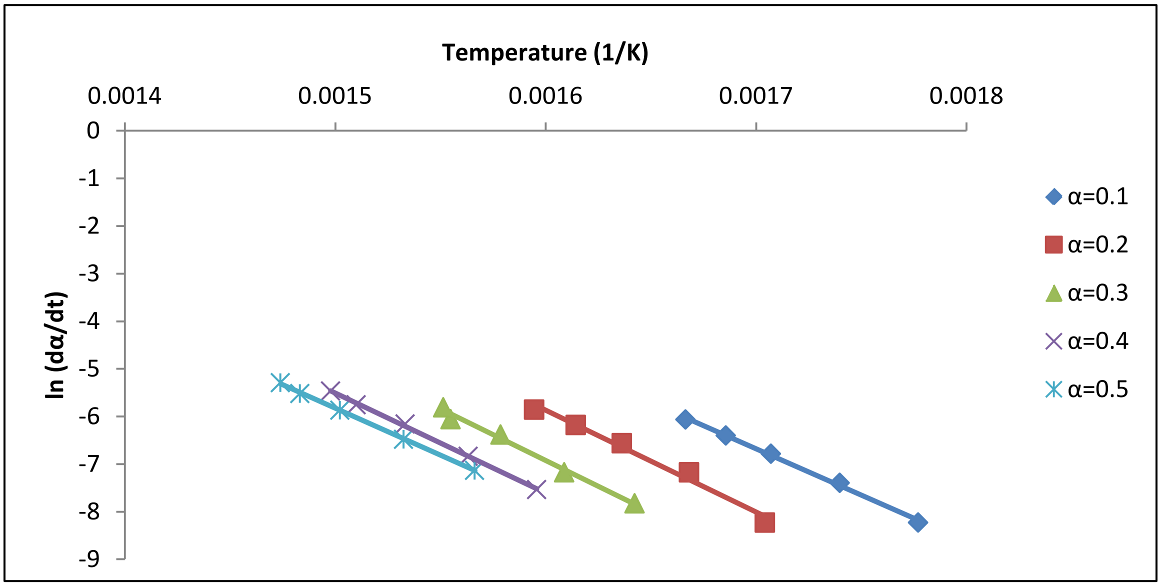

Figure B.22: Isoconversional plot for pyrolysis of untreated sweetgum

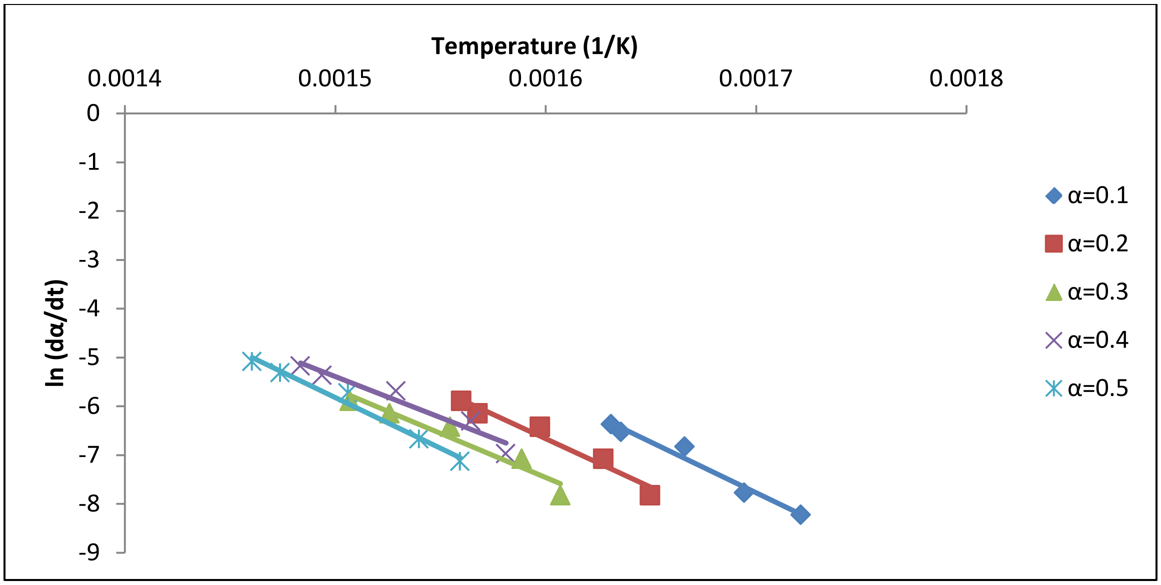

Figure B.23: Isoconversional plot for pyrolysis of treated sweetgum

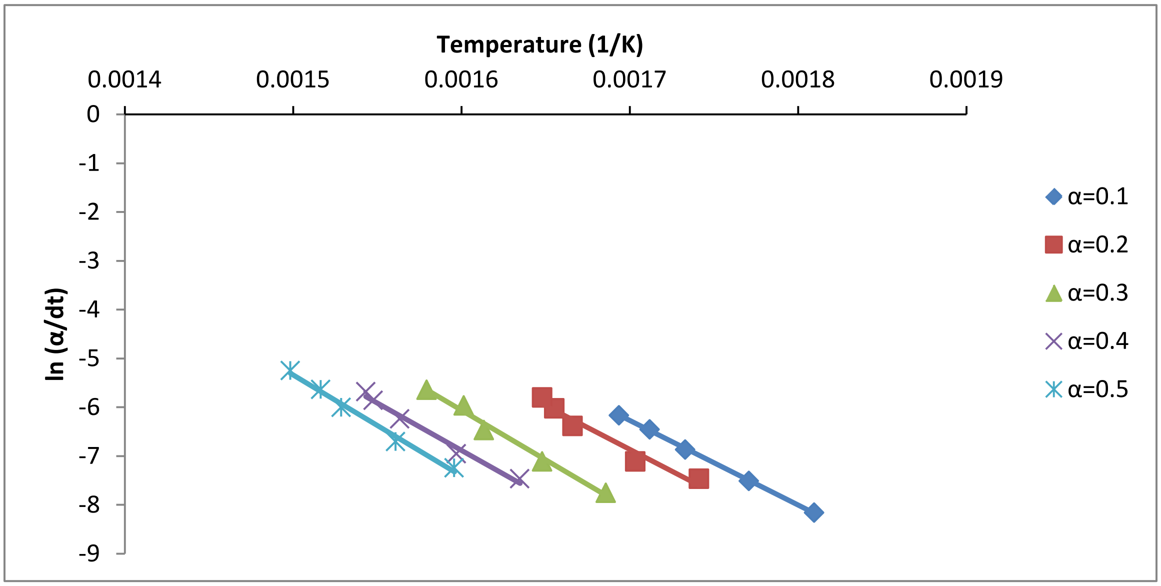

Figure B.24: Isoconversional plot for pyrolysis of untreated switchgrass

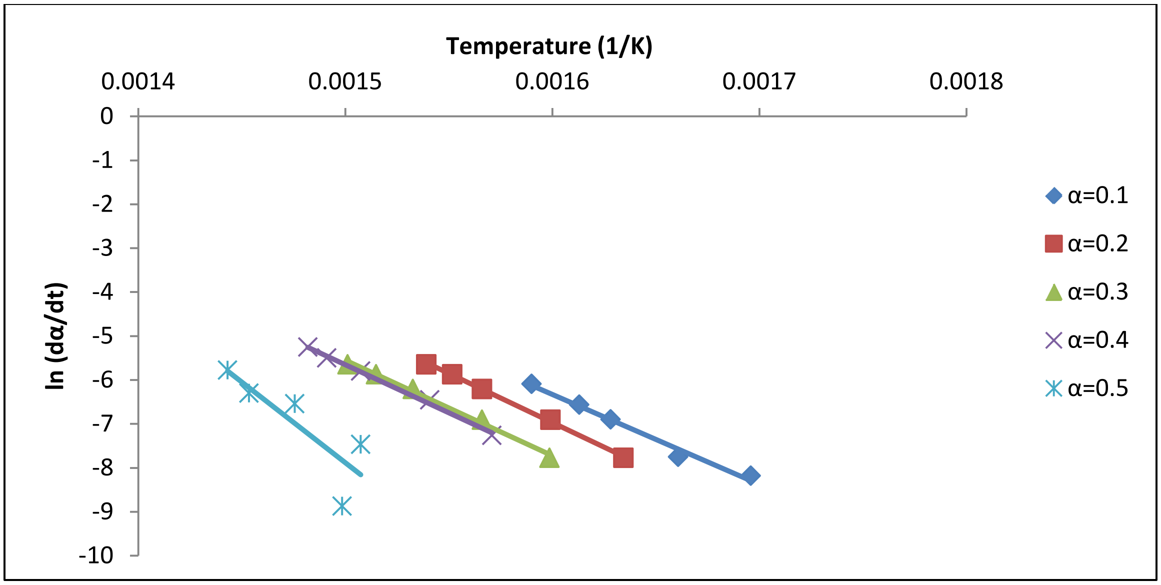

Figure B.25: Isoconversional plot for pyrolysis of treated switchgrass

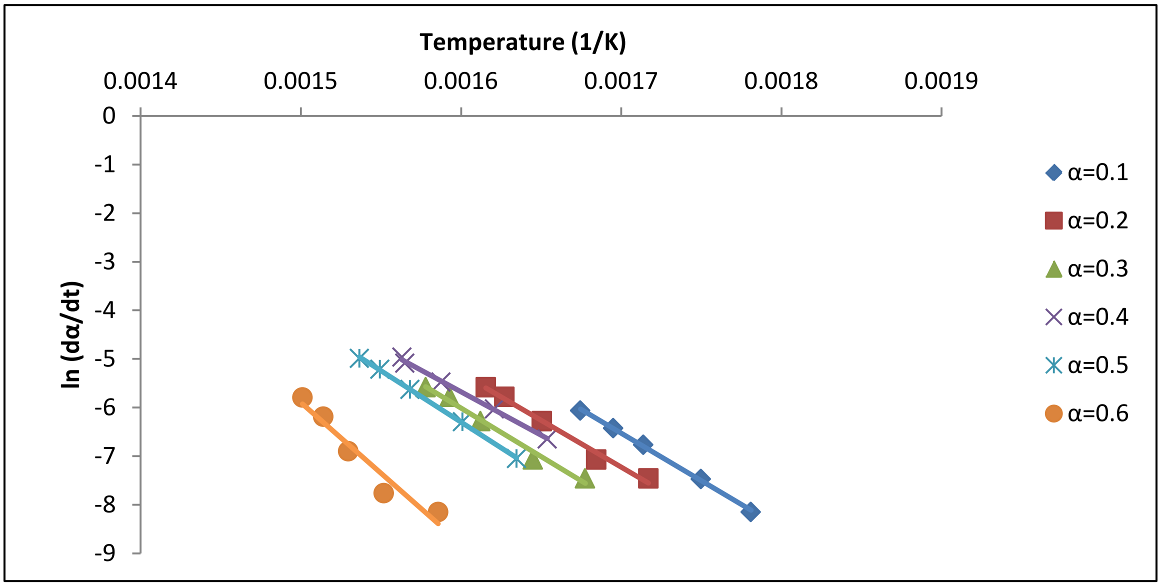

Figure B.26: Isoconversional plot for combustion of untreated pine

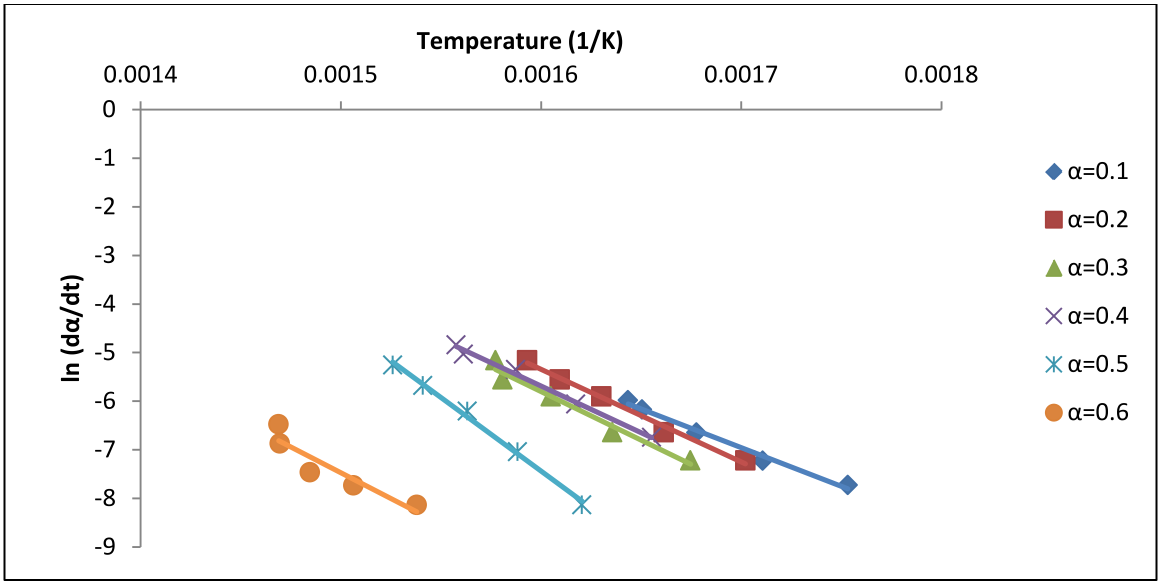

Figure B.27: Isoconversional plot for combustion of treated pine

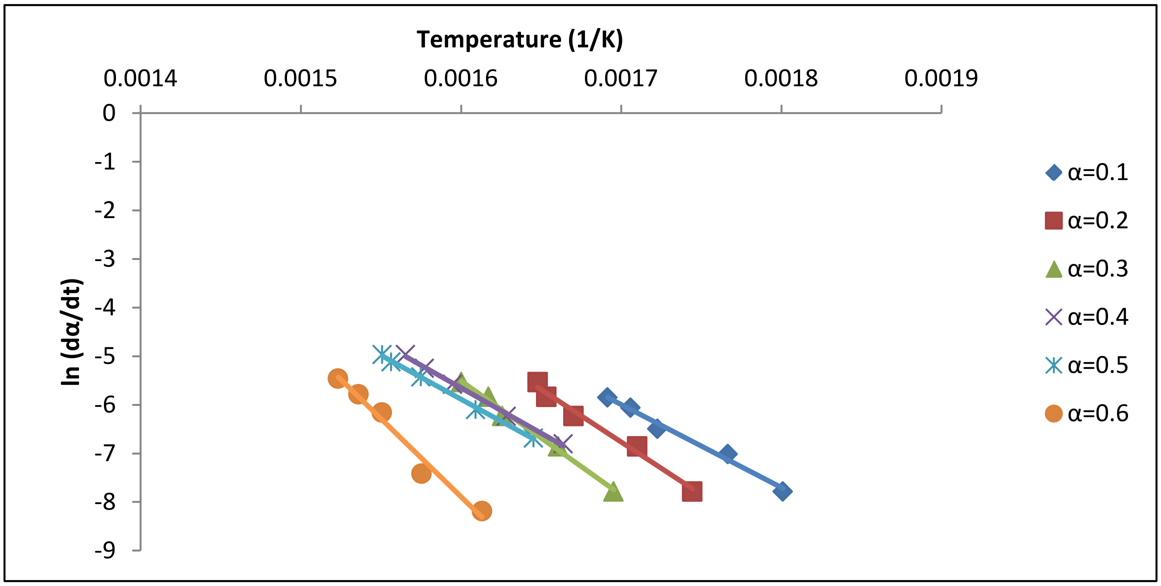

Figure B.28: Isoconversional plot for combustion of untreated sweetgum

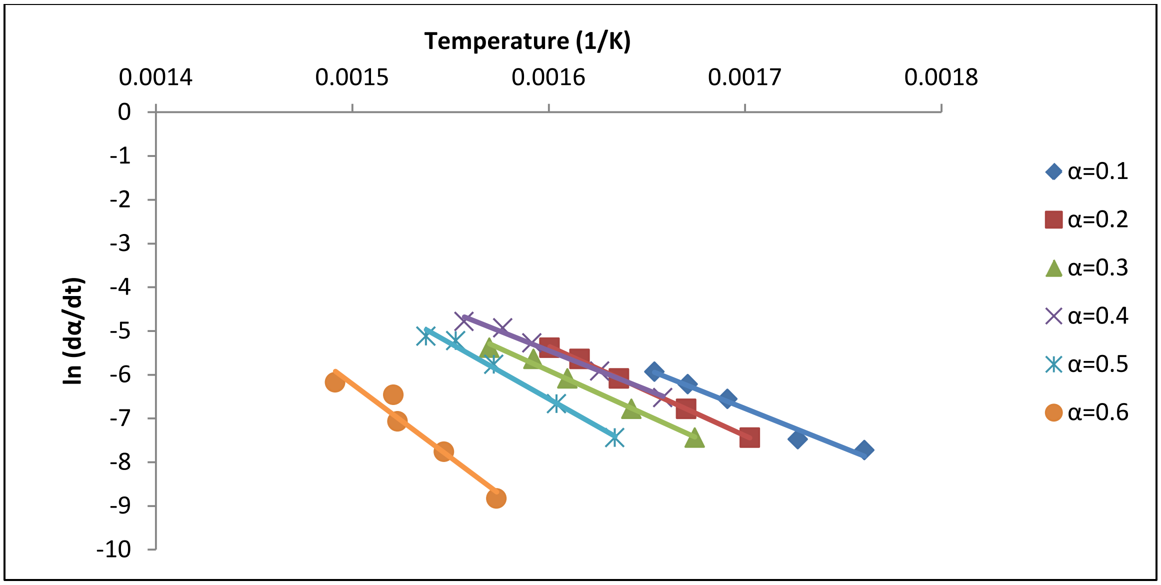

Figure B.29: Isoconversional plot for combustion of treated sweetgum

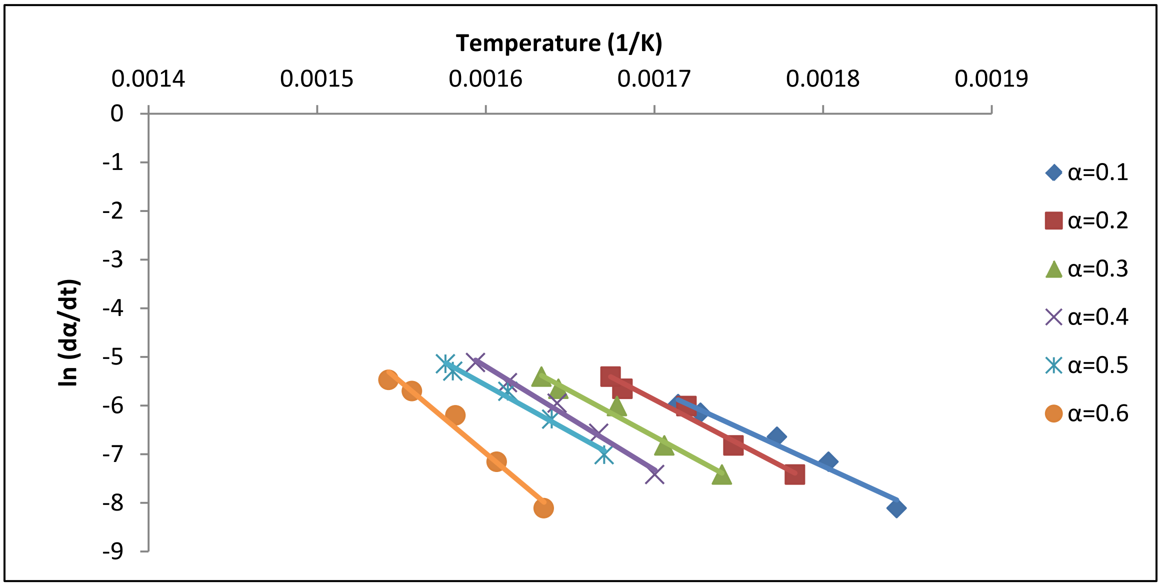

Figure B.30: Isoconversional plot for combustion of untreated switchgrass

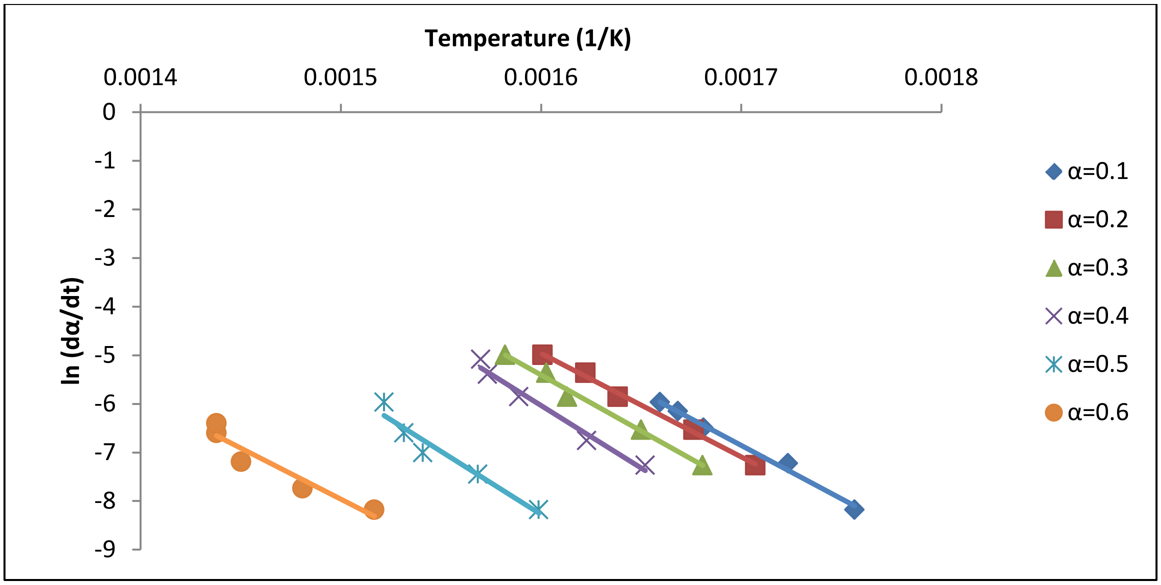

Figure B.31: Isoconversional plot for combustion of treated switchgrass

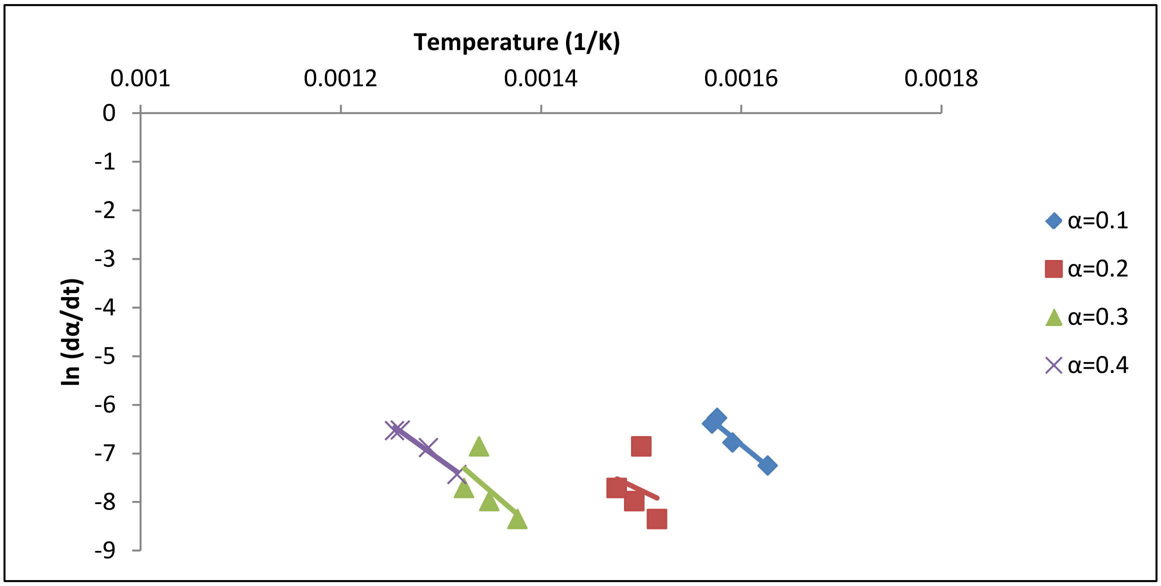

Figure B.32: Isoconversional plot for combustion of 30% pine and 70 % coal

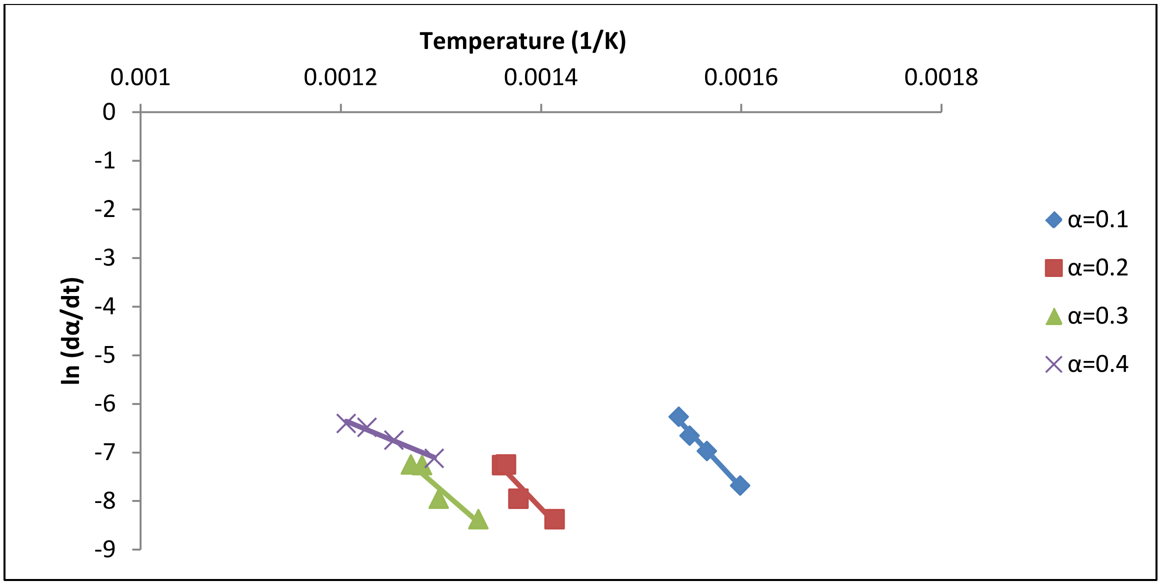

Figure B.33: Isoconversional plot for combustion of 20% pine and 80% coal

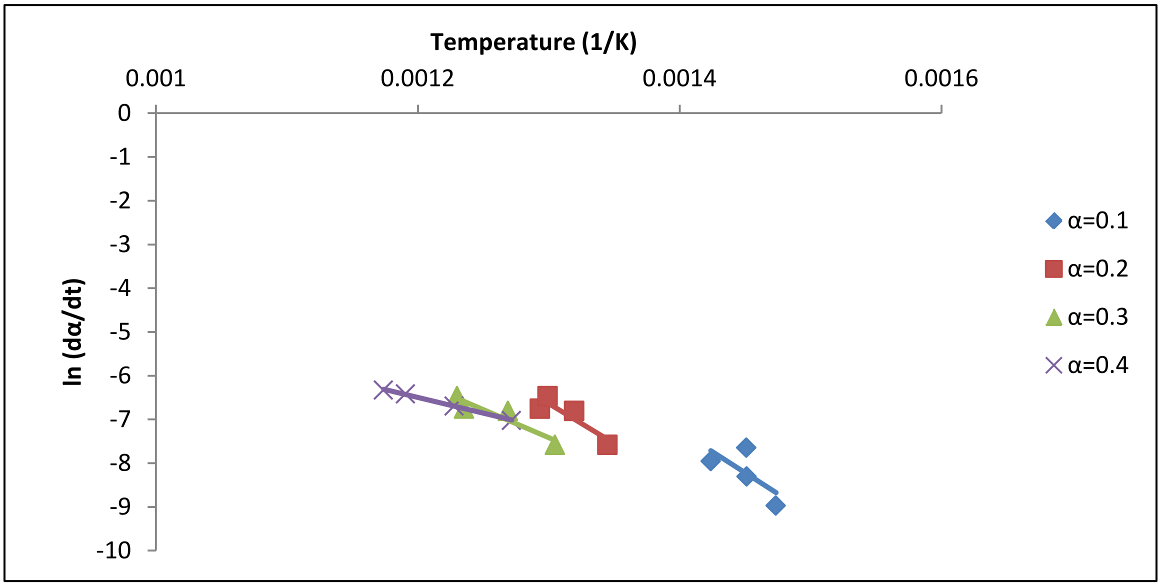

Figure B.34: Isoconversional plot for combustion of 10% pine and 90% coal

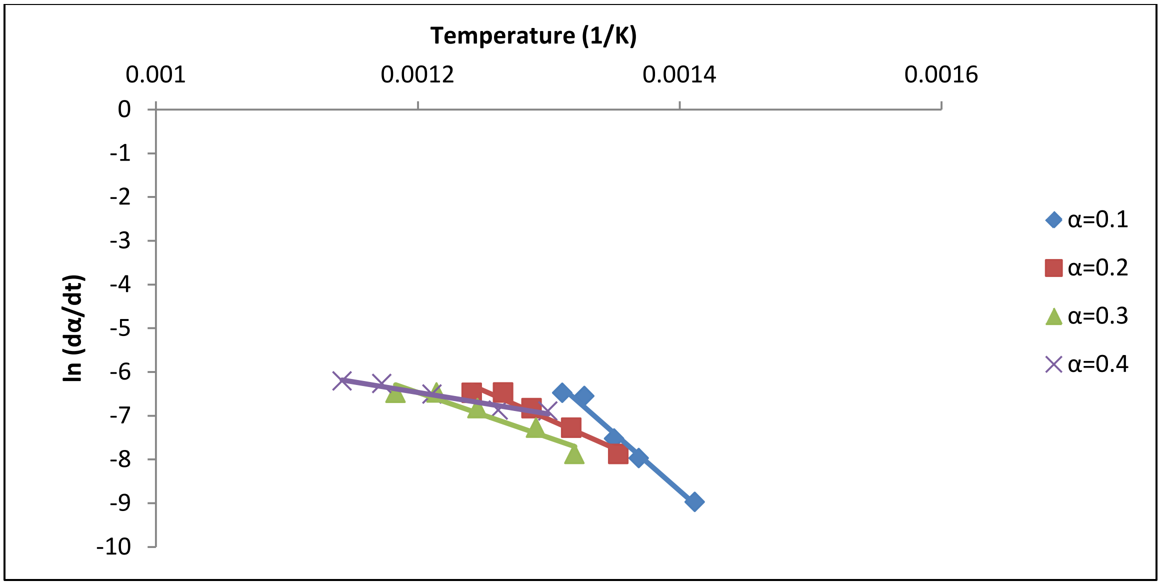

Figure B.35: Isoconversional plot for combustion of coa

Appendix C. Instrument Photos

Figure C.1: Kason vibrating screen separator

Figure C.2: C.S. Bell Hammer Mill

Figure C.3: Wiley Mill

Figure C.4: Omega HH147U datalogger

Figure C.5: A&D balance

Figure C.6: Hamilton Beach Coffee Grinder

Appendix D. SAS Codes and Output

D.1: Example SAS code and output for physical properties analysis

```
data pinesolids;
input sol comb $ temp time;
datalines;
0.9791      A      225    15
0.9814      A      225    15
0.9782      A      225    15
0.8877      B      225    30
0.9130      B      225    30
0.9038      B      225    30
0.7189      C      225    45
0.7589      C      225    45
0.7467      C      225    45
0.9005      D      250    15
0.9246      D      250    15
0.8961      D      250    15
0.7803      E      250    30
0.7914      E      250    30
0.7747      E      250    30
0.6349      F      250    45
0.7060      F      250    45
0.6488      F      250    45
0.8040      G      275    15
0.8235      G      275    15
0.7923      G      275    15
0.6155      H      275    30
0.6307      H      275    30
0.5979      H      275    30
0.4910      I      275    45
0.4639      I      275    45
0.4451      I      275    45
;
run;

ods html;
ods graphics on;

proc anova data = pinesolids;
class temp time;
model sol = temp time temp*time;
run;
```

```
proc anova data = pinesolids;
class comb;
model sol = comb;
means comb / lsd;
run;

proc means data = pinesolids mean std;
class comb;
var sol;
run;

ods html close;
ods graphics off;
```

The SAS System

The ANOVA Procedure

Class Level Information		
Class	**Levels**	**Values**
temp	3	225 250 275
time	3	15 30 45

Number of Observations Read	27
Number of Observations Used	27

The SAS System

The ANOVA Procedure

Dependent Variable: sol

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	8	0.62797735	0.07849717	209.95	<.0001
Error	18	0.00672999	0.00037389		
Corrected Total	26	0.63470735			

R-Square	Coeff Var	Root MSE	sol Mean
0.989397	2.535722	0.019336	0.762552

Source	DF	Anova SS	Mean Square	F Value	Pr > F
temp	2	0.27611282	0.13805641	369.24	<.0001
time	2	0.33787604	0.16893802	451.84	<.0001
temp*time	4	0.01398850	0.00349712	9.35	0.0003

The SAS System

The ANOVA Procedure

Class Level Information		
Class	**Levels**	**Values**
comb	9	A B C D E F G H I

Number of Observations Read	27
Number of Observations Used	27

The SAS System

The ANOVA Procedure

Dependent Variable: sol

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	8	0.62797735	0.07849717	209.95	<.0001
Error	18	0.00672999	0.00037389		
Corrected Total	26	0.63470735			

R-Square	Coeff Var	Root MSE	sol Mean
0.989397	2.535722	0.019336	0.762552

Source	DF	Anova SS	Mean Square	F Value	Pr > F
comb	8	0.62797735	0.07849717	209.95	<.0001

The SAS System

The ANOVA Procedure

t Tests (LSD) for sol

Note: This test controls the Type I comparisonwise error rate, not the experimentwise error rate.

Alpha	0.05
Error Degrees of Freedom	18
Error Mean Square	0.000374
Critical Value of t	2.10092
Least Significant Difference	0.0332

Means with the same letter are not significantly different.

t Grouping	Mean	N	comb
A	0.97957	3	A
B	0.90707	3	D
B			
B	0.90150	3	B
C	0.80660	3	G
C			
C	0.78213	3	E
D	0.74150	3	C
E	0.66323	3	F
F	0.61470	3	H
G	0.46667	3	I

The MEANS Procedure

Analysis Variable : sol			
comb	**N Obs**	**Mean**	**Std Dev**
A	**3**	0.9795667	0.0016503
B	**3**	0.9015000	0.0128059
C	**3**	0.7415000	0.0205007
D	**3**	0.9070667	0.0153429
E	**3**	0.7821333	0.0084996
F	**3**	0.6632333	0.0376835
G	**3**	0.8066000	0.0157617
H	**3**	0.6147000	0.0164146
I	**3**	0.4666667	0.0230747

D.2: SAS code and output for bulk density hypothesis testing

```
data bulkcomp;
input pinetrue pinepred gumtrue gumpred grasstrue grasspred;
datalines;
154.1 155.8 171.1 180.1 113.6 111.3
142.5 156.2 169.9 180.7 109.1 111.4
142.7 155.7 170.6 179.2 112.9 109.4
141.8 141.3 164.5 160.4 92.3  84.5
145.3 145.3 172.0 162.9 85.1  87.6
135.2 143.8 161.9 154.3 95.6  87.5
…………
;
```

The SAS System

The REG Procedure
Model: MODEL1
Dependent Variable: pinepred

Number of Observations Read	27
Number of Observations Used	27

Analysis of Variance					
Source	**DF**	**Sum of Squares**	**Mean Square**	**F Value**	**Pr > F**
Model	1	14645	14645	255.15	<.0001
Error	25	1434.93791	57.39752		
Corrected Total	26	16080			

Root MSE	7.57611	**R-Square**	0.9108
Dependent Mean	121.37037	**Adj R-Sq**	0.9072
Coeff Var	6.24215		

Parameter Estimates							
Variable	**DF**	**Parameter Estimate**	**Standard Error**	**t Value**	**Pr > |t|**	**95% Confidence Limits**	
Intercept	**1**	-77.85285	12.55719	-6.20	<.0001	-103.71487	-51.99083
pinetrue	**1**	1.56267	0.09783	15.97	<.0001	1.36119	1.76416

The SAS System

The REG Procedure
Model: MODEL2
Dependent Variable: gumpred

Number of Observations Read	27
Number of Observations Used	27

Analysis of Variance					
Source	**DF**	**Sum of Squares**	**Mean Square**	**F Value**	**Pr > F**
Model	1	20359	20359	298.17	<.0001
Error	25	1706.98050	68.27922		
Corrected Total	26	22066			

Root MSE	8.26312	**R-Square**	0.9226
Dependent Mean	136.13333	**Adj R-Sq**	0.9195
Coeff Var	6.06988		

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	t Value	Pr > |t|	95% Confidence Limits	
Intercept	**1**	-142.34178	16.20526	-8.78	<.0001	-175.71713	-108.96642
gumtrue	**1**	1.85006	0.10714	17.27	<.0001	1.62940	2.07072

The SAS System

The REG Procedure
Model: MODEL3
Dependent Variable: grasspred

Number of Observations Read	27
Number of Observations Used	27

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	10725	10725	124.36	<.0001
Error	25	2156.06185	86.24247		
Corrected Total	26	12881			

Root MSE	9.28668	**R-Square**	0.8326
Dependent Mean	68.36667	**Adj R-Sq**	0.8259
Coeff Var	13.58364		

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	t Value	Pr > |t|	95% Confidence Limits	
Intercept	**1**	-62.15177	11.83955	-5.25	<.0001	-86.53578	-37.76776
grasstrue	**1**	1.50540	0.13499	11.15	<.0001	1.22738	1.78343

D.3: SAS code and output for heating value of torrefied biomass

```
data hhvanal;
input c h n m a v hhv;
datalines;
0.47   0.0646 0.0034 0.0768 0.00624756  0.74834592 18.582
0.4681 0.0653 0.0045 0.0768 0.007082414 0.74077568 18.843
0.4717 0.065  0.0054 0.0768 0.00648952  0.74843824 18.459
0.4848 0.0621 0.0056 0.0575 0.006619733 0.7688915  19.25
0.4843 0.0633 0.0056 0.0556 0.00516203  0.77166924 19.334
0.4835 0.0626 0.0061 0.0469 0.006061208 0.7462773  19.645
0.5217 0.0597 0.0074 0.0439 0.008032915 0.73256382 20.292
………
;

ods html;
ods graphics on;

proc reg data = hhvanal;
model hhv = c h n m a v / selection = stepwise;
model hhv = c h n m a v / selection = cp;
run;

ods html close;
ods graphics off;
```

Stepwise Selection: Step 4

Variable a Entered: R-Square = 0.9649 and C(p) = 3.9753

Analysis of Variance					
Source	**DF**	**Sum of Squares**	**Mean Square**	**F Value**	**Pr > F**
Model	4	332.42073	83.10518	584.17	<.0001
Error	85	12.09227	0.14226		
Corrected Total	89	344.51300			

Variable	**Parameter Estimate**	**Standard Error**	**Type II SS**	**F Value**	**Pr > F**
Intercept	24.52895	3.29608	7.87863	55.38	<.0001
c	11.10214	3.41923	1.49985	10.54	0.0017
m	-31.85336	4.37066	7.55624	53.11	<.0001
a	-25.76696	4.99145	3.79107	26.65	<.0001
v	-11.54325	1.99125	4.78070	33.60	<.0001

Bounds on condition number: 48.998, 348.85

All variables left in the model are significant at the 0.1500 level.

No other variable met the 0.1500 significance level for entry into the model.

Summary of Stepwise Selection

Step	Variable Entered	Variable Removed	Number Vars In	Partial R-Square	Model R-Square	C(p)	F Value	Pr > F
1	c		1	0.9363	0.9363	66.4826	1292.74	<.0001
2	m		2	0.0145	0.9508	33.7465	25.67	<.0001
3	v		3	0.0031	0.9539	28.3025	5.80	0.0181
4	a		4	0.0110	0.9649	3.9753	26.65	<.0001

D.4: Example SAS code for enthalpy of pyrolysis analysis and regression

```
data pinedsc;
input des mc rh ljpg;
datalines;
1     4.54  11    258.4
1     4.86  11    318.3
1     4.56  11    353.4
3     6.94  33    351.5
3     6.99  33    342.9
3     7.19  33    392.6
6     12.68 75    435.6
6     12.4  75    410.5
6     12.72 75    457.2
8     18.57 94    492.6
8     18.49 94    521.6
8     18.49 94    515.3
;

proc anova data = pinedsc;
class des;
model ljpg = des;
means des / lsd;
run;

proc means data = pinedsc mean std;
class des;
var ljpg;
run;

proc reg data = pinedsc;
model ljpg = mc;

run;
```

The SAS System

The ANOVA Procedure

Class Level Information		
Class	**Levels**	**Values**
des	4	1 3 6 8

Number of Observations Read	12
Number of Observations Used	12

The SAS System

The ANOVA Procedure

Dependent Variable: ljpg

Source	**DF**	**Sum of Squares**	**Mean Square**	**F Value**	**Pr > F**
Model	3	68077.88250	22692.62750	23.94	0.0002
Error	8	7583.90667	947.98833		
Corrected Total	11	75661.78917			

R-Square	**Coeff Var**	**Root MSE**	**ljpg Mean**
0.899766	7.618158	30.78942	404.1583

Source	**DF**	**Anova SS**	**Mean Square**	**F Value**	**Pr > F**
des	3	68077.88250	22692.62750	23.94	0.0002

The SAS System

The ANOVA Procedure

t Tests (LSD) for ljpg

Note: This test controls the Type I comparisonwise error rate, not the experimentwise error rate.

Alpha	0.05
Error Degrees of Freedom	8
Error Mean Square	947.9883
Critical Value of t	2.30600
Least Significant Difference	57.972

Means with the same letter are not significantly different.

t Grouping	**Mean**	**N**	**des**
A	509.83	3	8
B	434.43	3	6
C	362.33	3	3
C			
C	310.03	3	1

The SAS System

The MEANS Procedure

Analysis Variable : ljpg			
des	**N Obs**	**Mean**	**Std Dev**
1	**3**	310.0333333	48.0364792
3	**3**	362.3333333	26.5620657
6	**3**	434.4333333	23.3718492
8	**3**	509.8333333	15.2533057

The SAS System

The REG Procedure
Model: MODEL1
Dependent Variable: ljpg

Number of Observations Read	12
Number of Observations Used	12

Analysis of Variance					
Source	**DF**	**Sum of Squares**	**Mean Square**	**F Value**	**Pr > F**
Model	1	67886	67886	87.30	<.0001
Error	10	7775.82972	777.58297		
Corrected Total	11	75662			

Root MSE	27.88517	**R-Square**	0.8972
Dependent Mean	404.15833	**Adj R-Sq**	0.8870
Coeff Var	6.89957		

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	**1**	253.84770	17.98855	14.11	<.0001
mc	**1**	14.04444	1.50310	9.34	<.0001