ANALYSIS OF TORREFACTION OF BIG BLUESTEM AND MIXED GRASS FROM THE
CONSERVATION RESERVE PROGRAM

By

KYLE HENRY LINNEBUR

A THESIS

submitted in partial fulfillment of the requirements for the degree

MASTER OF SCIENCE

Department of Biological and Agricultural Engineering
College of Engineering

KANSAS STATE UNIVERSITY
Manhattan, Kansas

2013

Approved by:

Major Professor
Dr. Donghai Wang

Abstract

Biomass torrefaction is an important preprocessing step in improving biomass quality, specifically in terms of physical properties and chemical composition. The objective of this research was to study effects of torrefaction as a pretreatment method on chemical and elemental compositions and thermal properties of Conservation Reserve Program (CRP) biomass. Most CRP grasslands are a mixture of native grasses, and in the state of Kansas, species including indiangrass, big bluestem, little bluestem, sideoats grama, and switchgrass comprise a majority of CRP grounds. Pure forms of big bluestem biomass were analyzed and compared with a mixture of the species that make up CRP lands. Two strategies for torrefaction were tested: one with a pre-dry step and one without. After torrefaction, big bluestem and CRP biomass showed an increase in energy density, making the biomass more attractive as a biofuel source than raw biomass. Big bluestem also showed slightly higher calorific values than that of CRP biomass. The torrefaction process had a significant effect on chemical composition and elemental composition of the biomass. Carbon content increased and oxygen content decreased as torrefaction temperature increased. Glucan and xylose decreased and lignin increased as torrefaction temperature increased. Pre-drying biomass before torrefaction is beneficial to torrefaction of biomass with high moisture content because moisture removal leads to less dry matter loss while maintaining the same calorific value.

Table of Contents

List of Figures

List of Tables

Acknowledgements

Dedication

I would like to dedicate this thesis to my grandfathers, Cecil Phillips and Francis Linnebur, whose devotion to agriculture and farming life style inspired this research.

Chapter 1 - Need for an Alternative Fuel

Fossil fuels have been the primary source of fuels in the United States. The energy value and cost effectiveness of fossil fuels have made them ideal for fuel sources for increasing energy demand. However, fossil fuels are nonrenewable and are being consumed faster than the Earth can replenish them. Petroleum and coal are currently the main fossil fuel sources of energy, supplying liquid fuel and electricity demand. Alternative sources, such as biomass, are currently being researched to supply the energy demand so as to reduce demand for fossil fuels and prevent complete fossil fuel depletions. However, in its current form, biomass is inadequate because of high moisture content and low calorific value. Pretreatment, such as torrefaction, may improve the quality of the biomass, potentially making it an ideal alternative to fossil fuels.

1.1 Future of Petroleum Oil

Petroleum oil has been the dominate source of energy over the past century. According to the US Department of Energy, oil supplies 40% of US energy demand and provides a majority of fuel used for transportation needs. Petroleum has become a popular source of fuel because it is simple and inexpensive to produce (US Department of Energy, 2010). Alternative sources of energy have attempted to compete with oil, but no alternative has come close to achieving the efficiency of petroleum oil. Even with political pressures on the US government to become a more energy independent and environmentally friendly nation, petroleum still controls the energy market. Some experts believe that current oil demands and lack of new oil discoveries will lead to the complete depletion of petroleum.

1.1.1 Current Oil Demands

In 2011, over 88 million barrels of oil were consumed worldwide each day (EIA, 2012), and this demand is expected to increase. China's industry is growing rapidly and their oil consumption is expected to increase at a rate of 7.5% per year (G.Luft, 2004). The United States and Europe's demands are expected to slightly decrease over the coming years but only by a few million barrels less per day. Appendix A - shows predicted changes in oil demand over the next 25 years.

1.1.2 Worldwide Oil Discoveries

Since the 1960s when over 350 million barrels of oil were discovered, worldwide oil discoveries have declined each decade. In the 1990s, only approximately 100 billion barrels were discovered. Dr. Hunter Herron, president of Petroleum Equities Inc., predicts that if oil discoveries continue to decline at the current rate, only 165 billion barrels of oil will remain to discover throughout the world (H. Herron, 2000). Figure 1-1 shows the decline of oil discoveries over the past 40 years in billion barrels per year (Gb/a).
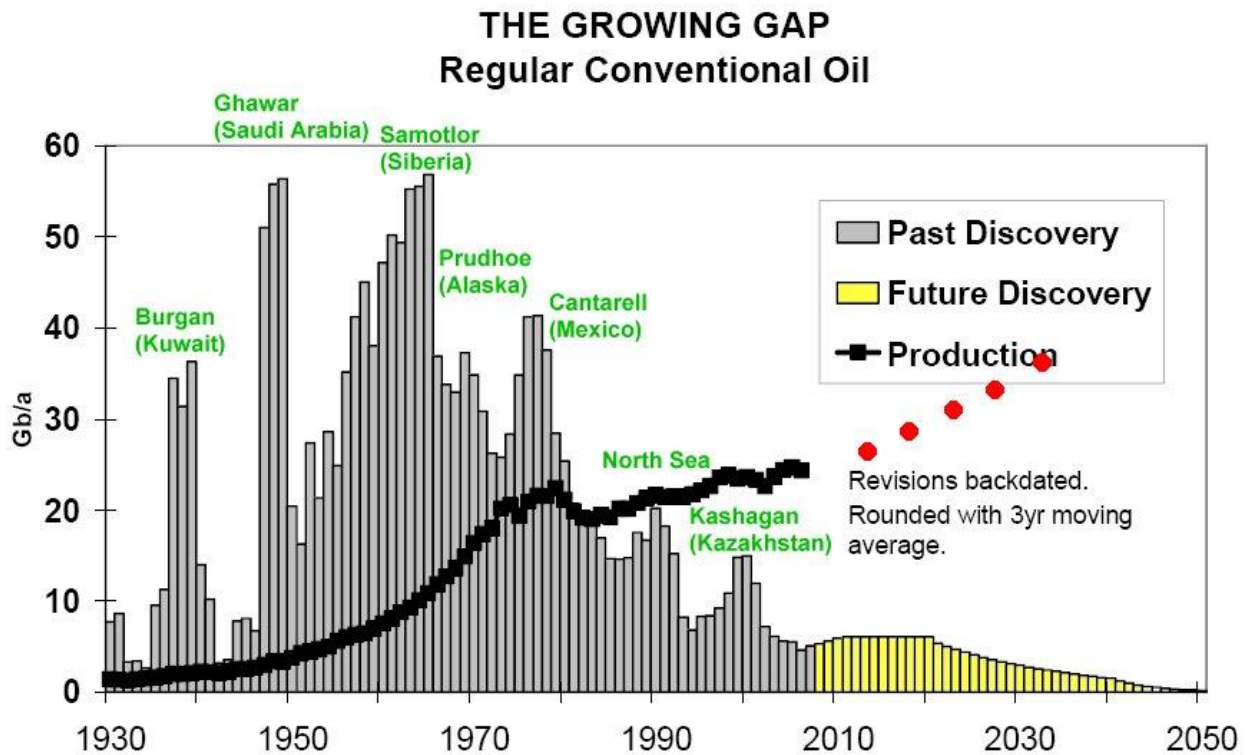
Figure 1-1: Oil Discoveries and Production

Source: "The Growing Gap." 2008. Planet for Life. 2010 < http://planetforlife.com/images/growinggap.jpg>

This graph predicts that by 2050 all of the oil fields on the planet will have been discovered.

1.1.3 Amount of Petroleum Left

The exact amount of remaining oil in current fields is difficult to estimate because companies like OPEC keep production numbers private. Estimates report approximately 1.35 trillion barrels of oil in reserves across the world; with roughly 50% of these reserves in the

Middle East. Currently, the United States has 22.5 billion barrels in reserve, only about 1.7% of the total reserves (EIA, 2012). In 2000, Dr. Herron predicted there were approximately 830 billion barrels left in oil fields. Adding to his calculation 165 billion barrels to be discovered, approximately 995 billion barrels of oil not being stored in oil reserves are left today. In 2008, the world crude oil consumption was just over 31 billion barrels (EIA, 2012). If Herron's estimation is correct and the world's current consumption rate of oil continues, the oil supply not stored in reserves could fail in less than 35 years, posing a serious threat to the United States. In 35 years, the United States' source of transportation fuel could rest in the fate of foreign countries that have a high supply of oil in their reserves.

1.2 Future of Coal

The United States is the leading producer of coal and accounts for the highest reserves in the world. Coal is the most abundant fossil fuel in the US and the primary source for electricity production, totaling almost 45% of total production.
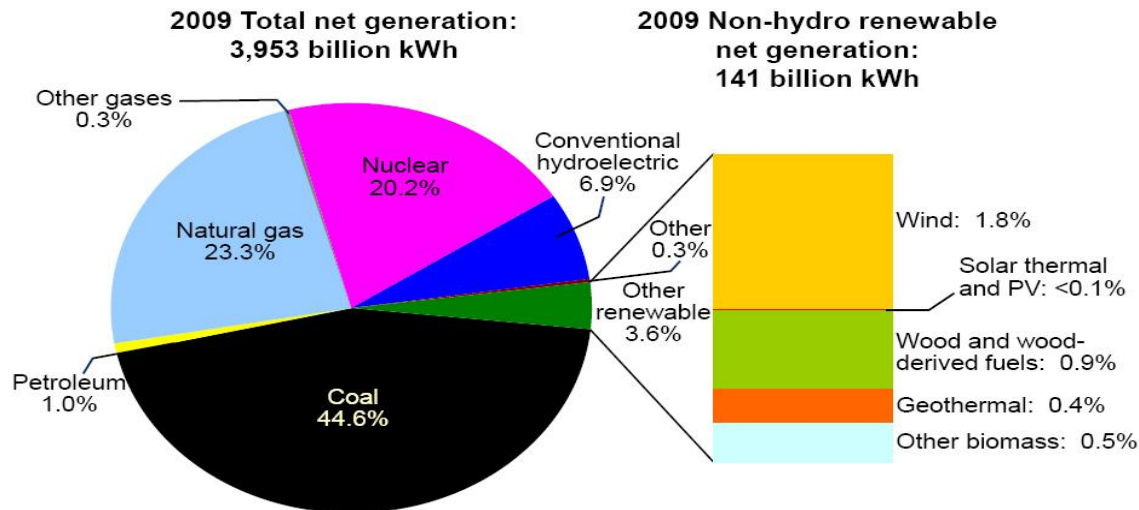
Figure 1-2: Sources of U.S. Electricity Generation

Source: http://www.cleantechblog.com/2011/10/what-if-every-residential-home-in-the-u-s-had-a-solar-rooftop.html/us-electricity-generation-mix-2009

Coal is an inexpensive and efficient fuel source, rivaled only by natural gas, that is readily available and shipped to power plants across the United States. However, many environmental issues have been attributed to coal fire plants, such as their contribution of 25% of all CO_2 emissions. In addition, the emission of CO_2 and other greenhouse gases, such as NO_x, has been linked to rising global temperatures. Coal fire plants are also responsible for 50% of

mercury, 60% of SO_2, and 62% of arsenic pollutants in the United States, which have been linked to several health related issues. The Environmental Protection Agency (EPA) has issued regulations and standards regarding the reduction of power plant emissions. Enacted in December 2011, the Mercury and Air Toxics Standard (MATS) is the latest standard enforced by the EPA aimed at reducing mercury and other toxins released by coal fired plants (EPA, 2011). It has been responsible for the close of at least six power plants due to high cost of installing scrubbers needed to remove the pollutants (First Energy, 2012). Although most coal fire plants are designed to meet EPA standards, the environmental impacts will remain a concern for future power production.

1.3 Cellulosic Biofuels

Despite their many advantages, fossil fuels pose a time and environmental problem, as they will eventually be depleted and other sources will have to supplement energy demand. Cellulosic ethanol and co-firing biomass with coal are two alternatives that could be the future of energy production.

1.3.1 Cellulosic Ethanol

Cellulosic ethanol is an alternative fuel that could supplement petroleum fuels. Most ethanol currently produced in the United States is first generation biofuel. First generation biofuel is any biofuel that is derived from the sugars, starches, or grain oils. Ethanol in the United States is largely produced from the starches of corn and grain sorghum where enzymes are used to break down the starches into glucose which are then converted into ethanol via fermentation. Even though grain based ethanol provides a renewable alternative to gasoline, competition for corn and grain sorghum has sparked some controversy. Arguments have developed from the ethical debate over whether or not food sources should be used for fuel production. To avoid this dilemma, the United States government and the EPA created the Energy Policy Act of 2005, and developed Renewable Fuel Standard. The Renewable Fuel Standard was then later revised under the Energy Independence and Security Act of 2007. The Revised Renewable Fuel Standard (RFS2) aims to increase production of biomass derived biofuels. By 2022 the RFS2 calls for the production of 16 billion gallons of cellulosic ethanol (EPA, 2007).

Year	Cellulosic Biofuel	Biomass-Based Diesel	Other Advanced Biofuel	Total Advanced Biofuel	Other Biofuel	Total Renewable Fuel
2006					*4.00*	4.00
2007					*4.70*	4.70
2008					*9.00*	9.00
2009		0.50	*0.10*	0.60	*10.50*	11.10
2010	0.10	0.65	*0.20*	0.95	*12.00*	12.95
2011	0.25	0.80	*0.30*	1.35	*12.60*	13.95
2012	0.50	1.00	*0.50*	2.00	*13.20*	15.20
2013	1.00	1.00	*1.75*	2.75	*13.80*	16.55
2014	1.75	1.00	*2.00*	3.75	*14.40*	18.15
2015	3.00	1.00	*2.50*	5.50	*15.00*	20.50
2016	4.25	1.00	*3.00*	7.25	*15.00*	22.25
2017	5.50	1.00	*3.50*	9.00	*15.00*	24.00
2018	7.00	1.00	*4.00*	11.00	*15.00*	26.00
2019	8.50	1.00	*4.50*	13.00	*15.00*	28.00
2020	10.50	1.00	*4.50*	15.00	*15.00*	30.00
2021	13.50	1.00	*4.50*	18.00	*15.00*	33.00
2022	16.00	1.00	*5.00*	21.00	*15.00*	36.00

Table 1-1: Revised Renewable Fuel Standard (Billons of Gallons)

Note: Values in italics calculated from RFS values as found in the 2007 Act.

Other Advance Biofuel= Advance Biofuel- Cellulosic Biofuel- Biomass-Based Diesel

Other Biofuel= Total Renewable Fuel- Total Advanced Biofuel

Source: United States Environmental Protection Agency: Energy Independence and Security Act of 2007: Key Provisions Affecting Combined

Heat and Power

Corn stover is a common source expected to supply the biomass for cellulosic biofuel production. When corn is harvested for grain, a combine collects the grain while leaving the stover in the field. The corn stover benefits the health of the soil by replenishing organic matter in the soil and providing the soil with cover which can reduce wind and water erosion. Removing corn stover may have a negative impact on future corn yields and the environment. Studies have shown that organic matter and erosion losses can be minimized if farmers implement no-till practices; however, most farmers currently use conventional tillage, resulting in greater loss in organic matter and soil erosion (J. Sheehan, 2008). If a maximum rate of corn stover is removed from a conventionally tilled field, a farmer must replace lost nutrients with additional fertilizer or

encounter a reduction in corn yields. If corn yields are reduced, then the use of corn stover for cellulosic ethanol production renews the fuel versus fuel debate.

Although corn stover is an ideal source for cellulosic ethanol production, the effect on organic matter in the soil has to be considered. Other types of cellulosic biomass, such as biomass from the Conservation Reserve Program, should play a role in cellulosic ethanol production, thus easing demand for corn stover.

1.3.2 Co-firing Biomass with Coal in Coal Fire Plants

Recently, Sandra Broekema of the Spiritwood Industrial Park in North Dakota prepared a feasibility study of co-firing biomass in Spiritwood coal fire power plant (S.Broekema, 2009). The study was conducted in response to the rising cost, enacted by the EPA, of releasing carbon dioxide (CO_2) emissions into the atmosphere. Using biomass as a fuel source in a coal fire plant is considered carbon neutral, meaning that CO_2 released by burning biomass is later sequestered by a biomass source, therefore adding no CO_2 to the carbon cycle. In the study, several feedstocks were evaluated based on the availability, calorific value, cost to acquire, and energy cost of each feedstock.

Biomass	TPY (% available)		BTU/lb	Delivered Cost $/dry ton	$/MMBTu
Corn Cobs	400,000	(17.5 %)	6,900	50	3.60
Grasses CRP	3,500,000	(2%)	7,500	50	3.80
Corn Stover	1,200,000	(5.8%)	6,600	50	3.60
Wheat Straw	690,000	(10%)	7,000	50	3.35
Beet Foliage	100,000	(70%)	7,000	42	3.00

Table 1-2: Top 5 Biomass Sources for Spiritwood North Dakota

Biomass (per dry ton)	Nutrient Value	Harvesting	Transportation (up to 50 miles)	Grinding	Total Cost ($)
Corn Cobs	0	31	14	4	49
Grasses CRP	16	16	14	4	50
Corn Stover	8	23	14	4	49
Wheat Straw	16	16	14	4	50
Beet Foliage	8	16	14	4	42

Table 1-3: Cost and Comparison for Top 5 Biomass

Source: Broekema, Sandra. Feasibility Study of Biomass Supply for the Spiritwood Industrial Park. June 30,2009

Further studies were conducted on biomass processing. In raw form, biomass has many drawbacks, such as a high moisture content which adds to unnecessary shipping and storage cost. To reduce shipping cost, biomass can be grinded and pelleted in order to increase density, thus increasing the amount of biomass that can be shipped. However, the grinding cost of biomass with high moisture content is considerably higher than biomass with low moisture content or dry biomass. High moisture content also leads to a lower calorific value per unit mass than dry biomass. Even when dry, however, biomass has a relatively low calorific value as compared to coal. CRP biomass had the highest energy value in the study with an energy value of 7,500 BTU/lb or 17,445 kJ/kg, as compared to coal which averages around 25,000 kJ/kg. Raw biomass is also heterogeneous, meaning that different parts of the biomass have dissimilar energy values. In order to achieve a predictable and steady stream of power production, the biomass must be processed and homogenized (S.Broekema, 2009). Biomass is also hydrophilic and absorbs moisture during storage if exposed to wet environments, leading to biomass decomposition at a faster rate than if the biomass was kept in a dry environment. If biomass is to be co-fired with coal in power plants, then pretreatment processing needs to improve these drawbacks in order to make biomass as efficient as coal.

Chapter 2 - Conservation Reserve Program

2.1 History of the Conservation Reserve Program

The Conservation Reserve Program (CRP) began as an effort to prevent soil erosion and enhance ground water recharge from highly erodible lands. The program was first introduced in the 1985 Farm Bill as an incentive for farmers to convert row crop ground into perennial vegetative crop, such as native grasses or trees. Farmers volunteering for the program signed a 10-15 year contract relinquishing rights to farm a section of crop ground and instead planting the section according to the Farm Service Agency (FSA). The incentives offered by the FSA include rental payments based on the value of the land, 50 percent of establishing cost, and maintenance payments (FSA, 2013).

CRP has been a key asset in the prevention of soil erosion. According to the United States Department of Agriculture (USDA), the thick vegetation the CRP provides conserves 325 million tons of top soil, 600 million pounds of nitrogen, and 100 million pounds of phosphorous each year from water and wind erosion (USDA, 2012). Reducing runoff and wind erosion not only aids in soil quality of the ground dedicated to the CRP, but also benefits downstream water and air quality. Air quality is also benefited by carbon that is sequestered and the removal of CO_2 from the air by vegetation. The USDA estimates that CRP lands sequestered an amount of carbon equivalent to removing 10 million cars from the roads. The thick vegetation also offers wildlife benefits by providing cover and habitat to many species, including quail, pheasant, waterfowl, and deer (USDA, 2012).

Many different contracts are offered to farmers by the CRP and each has different regulations as to what the farmer is able to do with the land. Most contracts state that the farmer cannot profit from the land that was converted to CRP by grazing or bailing forage due to the fact that subsidies were provided by the World Trade Organization. Subsidies for the CRP fall under the Uruguay Round's Agreement on Agriculture's "Green Box" long-term resource retirement policy, which states the land receiving subsidies could be disqualified if used for agriculture production, excepting when the US drought monitor has declared that a county is a natural disaster area. A county must experience eight consecutive weeks of drought conditions during the growing season to be considered a natural disaster area (FSA, 2012). Farmers can then

choose to take a cut in rental payments and bail the forage with which they can feed their own livestock but not sell it to another farmer. Once CRP forage is established, a farmer continues to be responsible for maintaining the ground. Depending on the contract, a farmer must burn or mow the land in order to control noxious weeds and tree seedlings. Depending on the contract, the number of times a farmer must maintain the land varies, but it is typically three times every 10 years. Farmers who mow as a control method generally cut the forage and let it lie because they cannot bail it as a livestock food source due to violation of the "Green Box" policy.

Approximately around 30 million acres are currently enrolled in the CRP, with 6.5 million acres on contract ending September 30, 2012 (USDA, 2012). Farmers with expiring contracts can choose to reenroll in the program or can convert the CRP lands back to row crops. With recently recorded high prices in corn and soybeans, CRP lands are expected to be converted back to row crops. If more incentives were available to farmers, they may be more inclined to continue with the CRP.

2.2 Sustaining Benefits of the Conservation Reserve Program

One way to keep current CRP lands from being converted to row crops when contracts expire is to offer farmers more benefits. Each year, thousands of acres of CRP are burned or mowed and farmers are not allowed to utilize this biomass. Because pressure is building on the United States to become an environmental, sustaining, independent nation, the FSA could utilize thousands of acres of biomass as an alternative to fossil fuels.

A possible way to utilize the biomass from the CRP and get around the "Green Box" retirement policy is to enroll the land in the Biomass Crop Assistance Program (BCAP). The BCAP was introduced in the 2008 Farm Bill to encourage production of perennial or annual bioenergy crops for advanced biofuel production. Farmers can enroll their land in the program for five years and receive incentives that include annual payments for production of the crop, cost-share payments for perennial crop establishment, and matching payments up to $45 per ton of biomass for harvesting, bailing, storage, and shipping cost of biomass to a processing facility (NSAC, 2008).

Officially, the farmers' land would no longer be enrolled in the CRP, but the same environmental benefits resulting from the CRP may not continue with the BCAP. Since annual crops can be established on lands enrolled in the program, possible soil erosion could result from

reestablishing a new crop year after year. Concerns could arise from those who are interested in using CRP lands for wildlife habitat and water conservation. Removing all biomass from the land every year eliminates any biomass used to form snow drift and wildlife cover during winter months. In order for benefits of both programs to occur, reasonable management practices allowing for some remaining biomass must be practiced.

2.3 Biomass Potential from the CRP

Recent studies have analyzed potential biomass yield of CRP lands and increased yields because of nitrogen applications. According to studies, biomass yields depend on a number of variables, including biomass species, location, precipitation, harvest timing, and fertilizer rate. The study involved six test sites across the United States. North Dakota, Kansas, and Oklahoma CRP plots contained warm season grasses while Missouri, Montana, and Georgia established cool season grasses. Figure 2-1 shows how nitrogen application affects biomass yield across the six sites (D. Lee, 2012).
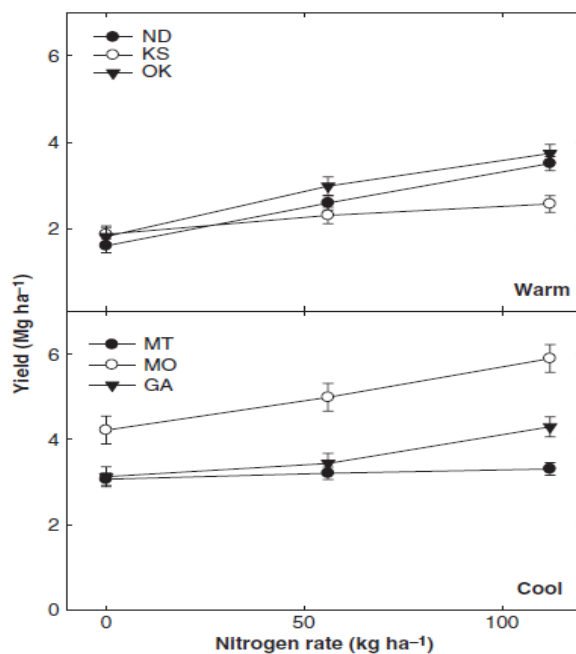
Figure 2-1: Effect of Nitrogen on CRP Yields

Source: Nitrogen and harvest management of Conservation Reserve Program grasslands for sustainable biomass feedstock production. 9 March

2012

In most cases, nitrogen application increased biomass yield from the CRP. Whether the CRP plot contained warm or cool season grasses, the species also showed yield differences. Minimum yields occurred with warm season grasses when no nitrogen was applied. Since farmers are not allowed to harvest biomass from CRP lands, they have no need to apply fertilizers. Using the data above, if a minimal yield rate of 2 Mg/ha was harvested from CRP lands across the United States, then slightly more than 24 million metric tons of biomass could potentially be used for bioenergy production every year (D.Lee, 2012). However, as stated earlier, reasonable management practices which allow for some biomass to be left over is advised. If a farmer was allowed to maintain and harvest 1/3 of CRP every year, the entire field would be maintained three times every nine years, consistently leaving biomass for wildlife habitat and water conservation and maintaining environmental benefits already provided by the CRP, while adding benefits by allowing biomass to be harvested as a biofuel source. If this scenario was practiced, roughly eight million metric tons of CRP biomass per year could be implemented into biofuel production.

Chapter 3 - Torrefaction

Torrefaction, often referred to as mild pyrolysis, is a thermal pretreatment of biomass between 200 ˚C and 300 ˚C in an oxygen free environment. It is essential that the environment is free of oxygen because of the high temperature that may cause the biomass to spontaneously combust. In this temperature range, the hemicellulose in biomass starts to degrade. If temperatures exceed 300 ˚C, pyrolysis effects begin and decomposition of cellulose and lignin shows a greater effect (W. Chen, 2010).
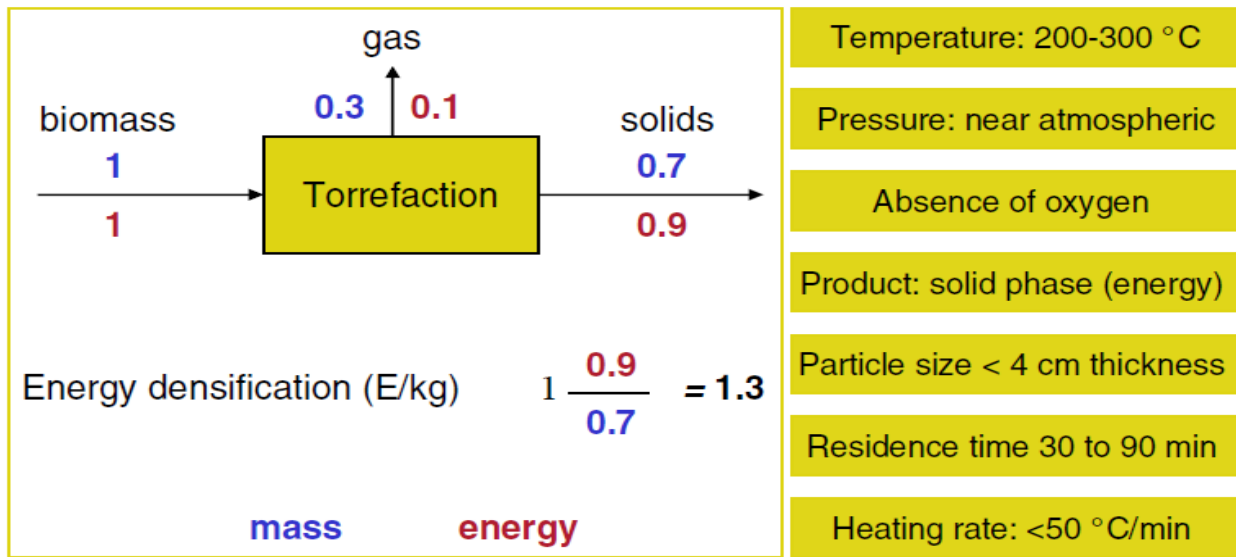
Figure 3-1: Schematic of Torrefaction

Source: Energy research Centre of the Netherlands. Biomass Pre-treatment by Torrefaction

3.1 Properties of Torrefaction

The biomass characteristics changes due to the intense heat experienced during torrefaction, many of which improve the quality of the biomass. As a result, drawbacks of raw biomass are reduced, thus reducing cost involved in distributing and storing biomass.

3.1.1 Reduction in Moisture Content

Torrefaction is capable of reducing moisture content of the initial biomass to less than five percent. With higher temperatures and longer residence times, moisture content of woody biomass can be reduced to less than 3% after torrefaction (H. Boerrigter, 2006). Reducing moisture content has many benefits, such as slowing down the rate of decay which allows the

biomass to be stored and processed over a longer time frame instead of all at once. Removing moisture also reduces the weight and volumetric size of the biomass, resulting in lower shipping and storage cost.

3.1.2 Increase in Energy Density

Another characteristic of torrefaction is an increase in energy density. Not only does energy density increase from moisture loss but also from dry matter losses. Most dry matter losses results from decomposition of hemicellulose but some cellulose and little lignin begin to add to the dry matter losses at higher torrefaction temperatures. The hemicellulose in the biomass begins to breakdown when exposed to temperatures between 130 and 260 ˚C while the cellulose and lignin do not begin to degrade until 240 and 280˚C, respectively (J. Tumuluru). The hemicellulose devolatizes and results in gas products, mostly CO_2 and CO and a few hydrocarbons (J. Tumuluru, 2011). The higher the temperature, the more the hemicellulose degrades, leading to higher dry matter loss. Residence time also contributes to the amount of dry matter loss, though not as significantly as temperature. In 2004, Ferro et al. studied the effects of torrefaction temperature and time on biomass dry mater loss, liquid yield, gas yield, and ash content (D. Tito, 2004). Table 3-1 illustrates how increasing temperatures and times reduces solid dry matter products and increases liquid and gas yields.

Biomass	Treatment Conditions		Yield of Products			
	T °C	time hour	Solid yield wt%maf	Liquid yield wt%maf	Gas yield wt%maf	Ash wt% mf
Pine	230	1	95.5	3.4	0.8	0.23
	230	2	94.4	4.6	1.0	0.23
	250	1	93.5	4.9	1.2	0.23
	250	2	92.5	6.1	1.3	0.23
	280	1	88.1	8.5	2.9	0.24
	280	2	84.9	11.3	3.4	0.24
Lucern	230	1	87.0	11.5	1.5	7.60
	230	2	85.0	13.0	1.7	7.80
	250	1	81.6	16.0	1.9	8.10
	250	2	81.0	16.4	2.1	8.20
	280	1	71.6	24.1	3.9	9.20
	280	2	70.0	25.9	4.1	9.50
Bagasse	230	1	87.5	9.9	2.6	2.41
	230	2	85.0	10.0	5.0	2.66
	230	3	83.7	10.3	6.0	2.46
	250	1	78.9	10.7	10.4	2.84
	250	2	77.5	10.9	11.6	2.89
	250	3	75.4	12.6	12.0	2.97
	280	1	68.6	18.5	12.9	3.27
	280	2	64.7	20.5	14.8	3.46
	280	3	63.8	21.0	15.2	3.51
Straw pellets	230	1	95.0	5.0	0.1	4.75
	230	2	93.6	6.2	0.2	4.81
	230	3	92.4	8.3	0.3	4.89
	250	1	90.0	9.8	0.3	5.00
	250	2	89.1	10.5	0.4	5.07
	250	3	86.9	12.2	0.6	5.18
	280	1	79.9	19.1	1.0	5.60
	280	2	76.5	21.1	1.6	5.80
	280	3	74.9	22.5	2.0	5.93
Wood pellets	230	1	96.5	3.5	0.06	0.23
	230	2	95.5	4.4	0.10	0.23
	230	3	94.6	5.3	0.15	0.23
	250	1	94.4	5.5	0.15	0.23
	250	2	93.3	6.5	0.20	0.24
	250	3	92.5	7.2	0.30	0.24
	280	1	89.4	10.0	0.60	0.25
	280	2	86.7	12.3	1.00	0.25
	280	3	85.8	12.9	1.30	0.26

Table 3-1: Mass Yields for Different Biomass Sources

Source: Torrefaction of agricultural and forest residues. D. Tito Ferro, V. Vigouroux , A. Grimm, and R. Zanzi.

biomass[a]	T	time	C	N	H	O diff[b]	CV	$\frac{CV_p}{CV_b}$ [c]	Energy recovery	H/C atomic Ratio[f]	O/C atomic Ratio[g]
	°C	hour	wt% maf[d]	wt% maf[d]	wt% maf[d]	wt% maf[d]	MJ/kg		% [e]		
Pine, raw	raw	raw	47.9	6.5	0.07	45.53	18.10			1.63	0.71
Pine	230	1	48.7	6.3	0.08	44.92	18.19	1.00	0.96	1.55	0.69
	230	2	48.9	6.3	0.08	44.72	18.29	1.01	0.95	1.55	0.69
	250	1	50.0	6.0	0.09	43.91	18.37	1.02	0.95	1.44	0.66
	250	2	50.3	5.9	0.09	43.71	18.37	1.01	0.94	1.41	0.65
	280	1	52.5	5.6	0.09	41.81	19.00	1.05	0.92	1.28	0.60
	280	2	52.7	5.5	0.14	41.66	18.95	1.05	0.89	1.25	0.59
Lucern, raw	raw	raw	47.7	6.5	2.7	43.1	18.42	1.01	0.88	1.64	0.68
Lucern	230	1	48.7	6.3	3.2	41.8	18.69	1.02	0.86	1.55	0.64
	230	2	49.0	6.2	3.3	41.5	18.70	1.02	0.83	1.52	0.64
	250	1	50.7	5.7	3.2	40.4	18.75	1.02	0.82	1.35	0.60
	250	2	50.9	5.6	3.3	40.2	18.71	1.08	0.77	1.32	0.59
	280	1	54.1	5.3	3.6	37.0	19.89	1.09	0.76	1.18	0.51
	280	2	55.1	5.1	3.9	35.9	20.13	1.01	0.88	1.11	0.49
Bagasse, raw	raw	raw	44.8	0.25	5.8	49.10	15.50			1.55	0.82
Bagasse	230	1	48.6	0.25	5.6	45.50	17.08	1.10	96.47	1.38	0.70
	230	2	48.8	0.26	5.6	45.30	17.18	1.11	94.26	1.38	0.70
	230	3	49.2	0.28	5.7	44.90	17.49	1.13	94.47	1.39	0.69
	250	1	50.6	0.30	5.6	43.50	18.08	1.06	92.04	1.33	0.64
	250	2	50.6	0.30	5.6	43.50	18.08	1.05	90.45	1.33	0.64
	250	3	51.5	0.32	5.7	42.50	18.69	1.07	90.94	1.33	0.62
	280	1	52.8	0.39	5.3	41.50	18.73	1.04	82.93	1.20	0.59
	280	2	54.7	0.41	5.4	39.50	19.84	1.10	82.83	1.18	0.54
	280	3	55.4	0.44	5.5	38.70	20.34	1.09	83.76	1.19	0.52
Straw pellets	raw	raw	47.5	6.4	0.63	45.5	17.8			1.62	0.72
Straw pellets	230	1	47.8	6.3	0.66	45.2	17.90	1.00	0.95	1.59	0.71
	230	2	47.9	6.3	0.69	45.1	17.9	1.00	0.94	1.57	0.71
	230	3	48.1	6.2	0.69	45.0	17.9	1.00	0.93	1.55	0.70
	250	1	49.0	6.1	0.79	44.1	18.21	1.02	0.92	1.50	0.67
	250	2	49.6	6.1	0.80	43.5	18.43	1.03	0.92	1.48	0.66
	250	3	49.6	6.1	0.80	43.5	18.46	1.04	0.90	1.48	0.66
	280	1	52.8	6.1	0.85	40.3	20.02	1.12	0.90	1.38	0.57
	280	2	53.8	6.0	0.92	39.3	20.40	1.14	0.88	1.34	0.55
	280	3	55.5	5.9	0.95	37.7	21.04	1.18	0.88	1.26	0.51
Wood pellets	raw	raw	48.5	6.6	0.05	44.9	18.58	--	--	1.64	0.69
Wood pellets	230	1	49.8	6.3	0.09	43.8	18.77	1.01	0.98	1.52	0.66
	230	2	50.4	6.3	0.09	43.2	19.02	1.02	0.98	1.49	0.64
	230	3	50.6	6.2	0.11	43.1	19.03	1.02	0.97	1.47	0.64
	250	1	50.7	6.2	0.12	43.0	19.05	1.03	0.97	1.47	0.64
	250	2	50.8	6.2	0.12	42.9	19.12	1.03	0.96	1.47	0.63
	250	3	51.0	6.2	0.12	42.6	19.24	1.04	0.96	1.46	0.63
	280	1	52.5	6.2	0.12	41.3	19.87	1.07	0.96	1.41	0.59
	280	2	53.0	6.2	0.13	40.7	20.13	1.08	0.94	1.40	0.58
	280	3	54.1	6.2	0.14	39.6	20.68	1.11	0.96	1.36	0.55

Table 3-2: Properties of Torrefied Biomass

Source: Torrefaction of agricultural and forest residues. D. Tito Ferro, V. Vigouroux , A. Grimm, and R. Zanzi.

In the same study, calorific value was also analyzed. Table 3-1 and Table 3-2 display how dry matter loss and calorific value of biomass increase with increased time and temperature. Increase in the energy value is a result of CO_2 produced by the devolitization of the hemicellulose. CO_2 is a noncombustible gas, therefore, like water, it was no energy value. The production of CO_2 also affects the overall elemental composition of the biomass. The more CO_2 that is produced, the more O_2 is removed, therefore lowering the overall oxygen composition while increasing the carbon composition. This theory is also supported by data in Table 3-2.

The other gas that formed, CO, is a result of a reaction of CO_2 and moisture with the bio-char produced from torrefaction (J. Tumuluru, 2011). CO is a combustible gas and does carry energy value. As a result of CO production, some energy is lost from the biomass during the torrefaction reaction. Table 3-2 also shows that with increasing time and temperature, energy recovery of the biomass decreases.

Even though some biomass energy was lost, even more dry matter was removed during torrefaction. Using results of the Lucern test at 280 ˚C for two hours as an example, removal of hemicellulose, small amounts of cellulose, and other volatile matter led to a 30% reduction in total mass, while only losing 12% of total energy (H. Boerrigter, 2006). The reaction resulted in an energy densification of 1.26, which reduces shipping and storage costs.

3.1.3 Hydrophobic Biomass

Another torrefaction benefit is turning biomass into a hydrophobic substance because of the destruction of OH bonds and the release of organic volatiles. As a result, chemical reactions occur which fix carbon and hydrogen bonds, turning the biomass into a non-polar hydrophobic substance (J. Tumuluru, 2011) (W. Chen, 2010). If the biomass is hydrophobic, it retains a higher quality by keeping consistent moisture content and not degrading as quickly as raw biomass. The ability to resist water also reduces storage cost because the biomass does not need to be stored in special environments to keep out moisture.

3.1.4 Homogeneous Biomass

Torrefaction reestablishes the biomass as a homogenous substance partly by providing a lower consistent moisture content. The resulting compositional breakdown turns the biomass hydrophobic. Homogeneous biomass provides a consistent fuel source, allowing for a more predictable biofuel production.

3.1.4 Grinding and Pelletization

Due to the breakdown of hemicellulose and alteration of the cellulose structure, torrefaction makes the biomass friable and can lead to a 90% reduction in energy consumption when grinding. Pelletization is also easier because of increases in lignin fraction, thus increasing the strength and durability of the pellet (A. Dutta).

3.2 Pilot Scale Torrefaction

Torrefaction pretreatment is still primarily in the research stage. Currently, no large scale commercial torrefaction plants exist, but a few pilot scale systems are being evaluated. The following diagram describes the overall pilot scale process.
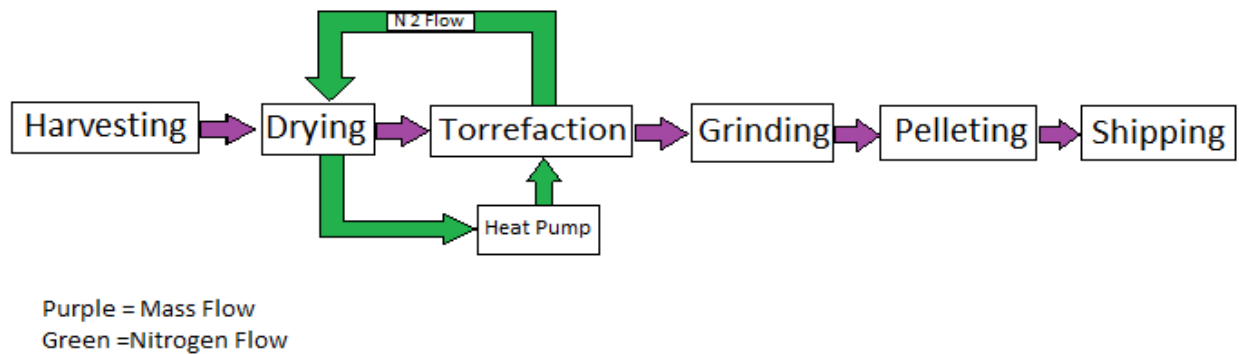
Figure 3-2: Pilot Scale Torrefaction

The biomass is dried before it enters the torrefaction reactor. Reducing the moisture content lowers the amount of CO produced, consequently lowering the energy loss from the biomass. The biomass is then fed into the torrefaction reactor. After torrefaction, the biomass is grinded and pelletized, and finally, the torrefied biomass is shipped out for further processing (J. Tumuluru, 2011).

3.3 Torrefaction Applications

      Torrefied biomass is suitable for syngas production through gasification, bio-oil production through pyrolysis, ethanol through gasification and the Fischer-Tropsch process, and co-firing agent with coal. Extra processing ultimately leads to additional costs which hinder biofuel's competiveness with petroleum gasoline. However, using torrefied biomass as bio-coal requires no additional processing in order to be co-fired with coal. Like coal, bio-coal does have to be pulverized before entering the reactor, but the cost is comparable so, therefore, neither source has a cost advantage.

Chapter 4 - Hypothesis and Methods

The objective of this research was to study the effects of torrefaction as a pretreatment method on chemical and elemental compositions and thermal properties of Conservation Reserve Program (CRP) biomass. Most CRP grasslands are a mixture of native grasses. In Kansas, species such as indiangrass, big bluestem, little bluestem, sideoats grama, and switchgrass comprise a majority of CRP grounds. The percentage of each species vary upon location. Pure forms of big bluestem were analyzed and compared with a mixture of species found in CRP lands. Different strategies of torrefaction procedures were tested. For the first strategy, torrefaction treatment was performed immediately after harvesting. The second strategy included biomass drying before torrefaction was implemented.

4.1 Hypothesis

If torrefaction is an effective pretreatment method that induces CRP forage to be a cost effective source of biomass useful for co-firing in coal fire power plants and increases biofuel production efficiency through gasification and pyrolysis, then the FSA may promote the use of CRP biomass for biofuel production, allowing farmers to profit more from CRP lands. In addition, using biomass from CRP lands for biofuel production relieves pressure from crop lands that are used in the food and feed industry as well as biomass used to replenish organic matter in the soil of row crop lands.

The following two strategies were tested:

Purple = Mass Flow
Green = Nitrogen Flow
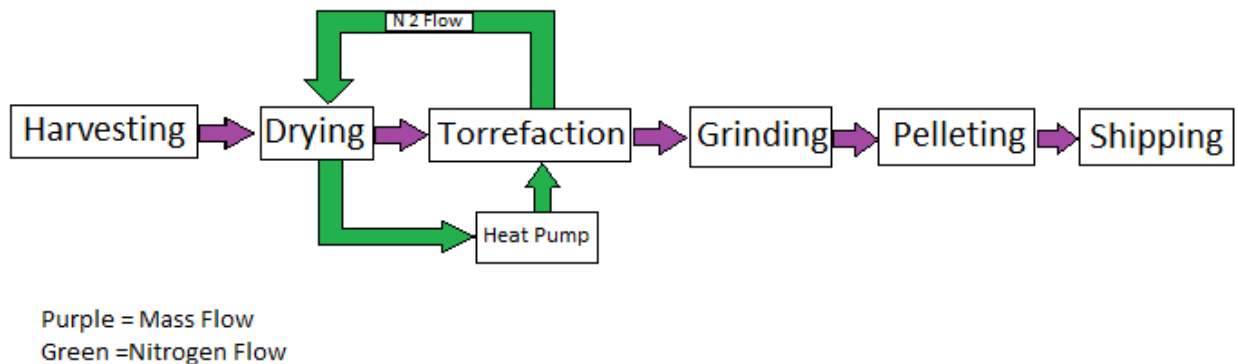
Figure 4-1: Pre-Dry Strategy

Purple = Mass Flow
Green = Nitrgoen Flow
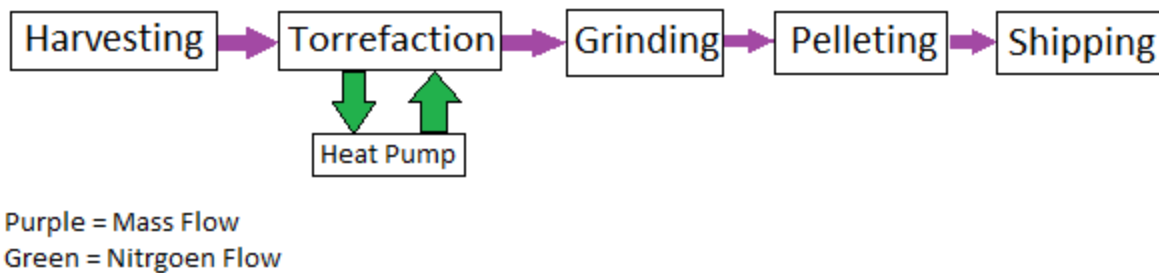
Figure 4-2: Non Pre-Dry Strategy

Figure 4-1 represents current pilot scale models, where, after the biomass is harvested, it is dried in order to achieve significantly lower moisture content than before torrefaction. The nitrogen flows in a closed loop was used for drying and torrefaction with energy source provided by a heat pump. Figure 4-2 illustrates a strategy used to study the effects of using wet biomass directly (without pre-drying) on the properties of torrefied biomass. An additional drying step added to the overall processing procedure would suggest higher operational and maintenance cost. If the additional pre-drying stage does not produce a superior final product that justifies the additional cost, then, in order to make the biomass as cost effective as possible, future torrefaction pretreatment strategies should not incorporate a pre-drying phase.

4.2 Methods

Biomass harvesting, biomass pretreatment via torrefaction, biomass pre-drying, and analysis of chemical and elemental composition and thermal properties of both control and torrefied biomass were conducted in this research. Controls of each biomass were grinded and analyzed for moisture content and calorific value, along with compositional and elemental analysis. The effects of torrefaction on chemical composition, thermal properties, dry matter, and energy loss of torrefied biomass were studied.

4.2.1 Harvesting

Big bluestem and a random mix of additional species were harvested October 20, 2012 from a CRP section outside of Valley Falls, KS. A majority of additional species found and harvested on the CRP land were Indian grass, yellow foxtail, and giant foxtail. The forage was cut four to eight inches long with scissors and stored in paper bags with proper labeling. The biomass was then stored outside for two days, leaving the biomass exposed to the environment, simulating conditions of cutting and bailing hay. This exposure reduced the moisture content of

20

the biomass from 40%-60% down to approximately 20%. The biomass was then stored in a refrigerator and kept at a constant temperature of 4 ˚C.

4.2.2 Torrefaction Pretreatment

Two different variables, resident time (15, 30, and 45 minutes) and temperature (200, 250, and 300 ˚C), were used to study effects of torrefaction on big bluestem and CRP biomass. Parr 4570 vertical pressure reactor was used as torrefaction reactor. All experiments were duplicated and average values reported. In order to ensure an oxygen free environment during the torrefaction process, air was vacuumed out of the reactor alternating with a continuous flushing of the reactor with nitrogen (N_2). A step by step procedure is described in Appendix B -

4.2.3 Pre-Drying

Another variable tested was examining whether or not drying the biomass before torrefaction impacts the final product. One hundred twenty grams of big bluestem and CRP biomass were placed in labeled test pans.

Figure 4-3: Pre-Drying

The test pans were then transferred to an air-oven drier and dried over night at 60 ˚C. The biomass was then removed from the drier and stored for future use in a refrigerator at 4 ˚C. After drying, 1 gram of the biomass samples was used for determination of moisture content. The pre-

drying process lowered the moisture content of the big bluestem and CRP biomass from 17-22% to 7-8% (wb). Torrefaction pretreatment of the pre-dried biomass was conducted at 250 ˚C for time periods of 15, 30 and 45 minutes. Results from pre-dried torrefied biomass were compared with results from torrefied biomass without pre-drying to determine if pre-drying benefits the torrefaction process.

4.2.4 Grinding

Both control samples and torrefied samples were first grinded with a Retsch SM 2000 grinder, which reduced the particle size of the samples to 1 mm. After the biomass was grinded down to 1 mm, a small amount (<0.5 grams) of each sample was milled to 0.5 mm using a UDY cyclone mill. Biomass with a particle size of 1 mm was used to analyze moisture content, dry matter loss, calorific value, chemical composition, and thermal stability. Biomass with a particle size of 0.5 mm was used for elemental composition analysis.

Figure 4-4: Retsch SM 2000 Grinder / UDY cyclone mill

4.2.5 Analysis

4.2.5-1 Moisture Content

Moisture content is a major disadvantage of raw biomass, and removal of moisture content is essential to reduce shipping and storage cost. Controls of big bluestem and CRP biomass, along with all torrefied biomass samples, were analyzed for moisture content following the NREL Determination of Total Solids in Biomass and Total Dissolved Solids in Liquid Process Samples procedure (A. Sluiter, 2008). Aluminum weighing dishes were dried in an air dry oven at 105 ˚C for four hours. The dishes were then cooled in a desiccator and weighed to the nearest 0.1 mg (Weight $_{dish}$). Approximately 0.5 grams of each control and tested sample were added to the dishes. The initial weight of the biomass and dish was weighed and recorded to the nearest 0.1 mg (Weight $_{Initial}$).
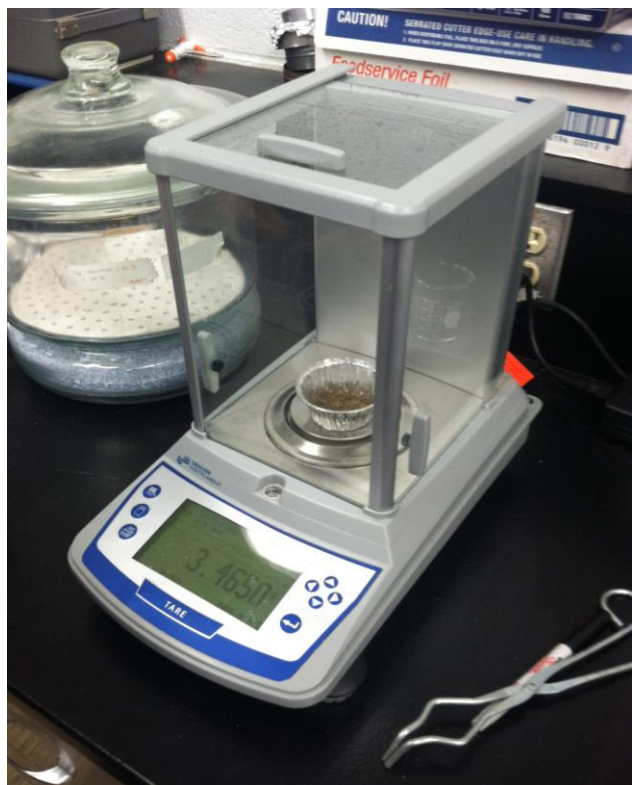
Figure 4-5: Initial Measurement of Dish and Biomass

The samples were then placed in an air dry oven at 105 ˚C for a minimum of four hours.

Figure 4-6: Samples in Air Dry Oven

The samples were then transferred to a desiccator for cooling. Once the samples had cooled, the final weight of the dry biomass and weighing dish were recorded to the nearest 0.1 mg (Weight $_{Final}$). Moisture content was calculated by the following equation:

$$\% \, Moisture = 100 - \left| \frac{(Weight_{Final} - Weight_{Dish})}{(Weight_{Initial} - Weight_{Dish})} \times 100 \right|$$

Equation 4-1: Moisture Content (Wet Basis)

4.2.5-2 Dry Matter Loss due to Torrefaction

Determining the amount of dry matter loss is essential to maximize the effects of torrefaction. The goal of torrefaction should be to maximize calorific value of the biomass while minimizing the dry matter loss required to achieve that value. The percentage of dry matter loss is found using the following equations:

$$Initial\ Dry\ Matter\ (g) = Initial\ Mass\ (g) * \left(1 - \frac{Control\ MC\%_{wb}}{100}\right)$$

$$Final\ Dry\ Matter\ (g) = Final\ Mass\ (g) * \left(1 - \frac{Final\ MC\%_{wb}}{100}\right)$$

$$\%\ Dry\ Matter\ loss = \left[\frac{(Initial\ DM - Final\ DM)}{Initial\ DM}\right] * 100$$

Equation 4-2: Percentage of Dry Matter Loss

4.2.5-3 Calorific Value

The calorific value (CV), also referred to as the energy or heating value, determines how much energy is released during combustion per gram or kg of substance. Torrefaction maximizes the calorific value of biomass by removing the moisture and some dry matter while retaining energy in the biomass. Calorific value was measured using an IKA C 200 calorimeter.
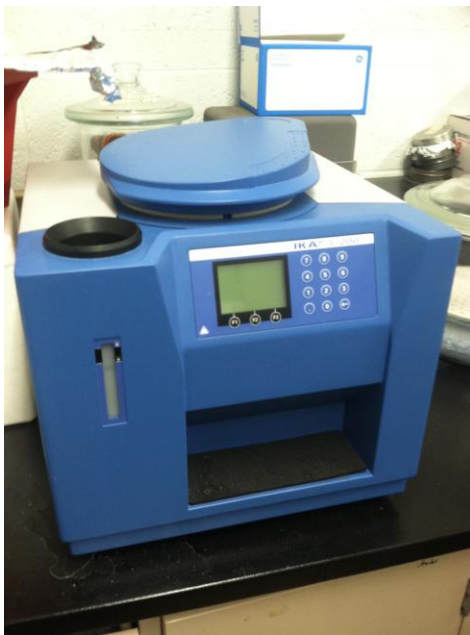
Figure 4-7: IKA C 200 calorimeter

Between 0.3 and 0.5 grams of biomass of each control and torrefied samples were loaded into a pellet press chamber. After pelletizing the sample, the pellet was loaded into a decomposition vessel. The decomposition vessel was then loaded into a combustion crucible and injected with oxygen to a pressure of 30 Barr for 30 seconds.
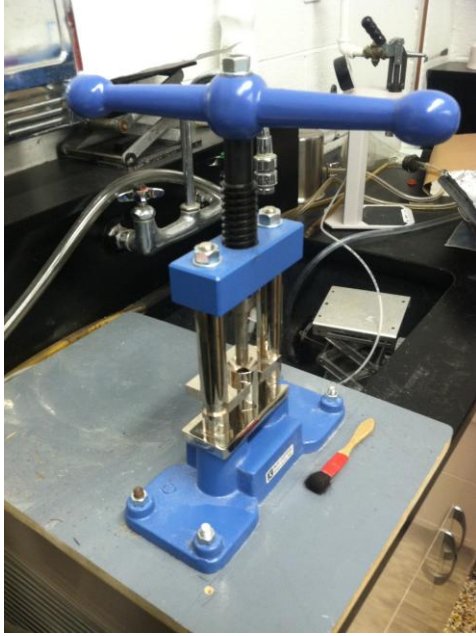
Figure 4-8: IKA Pellet Press

The sample was then loaded into the calorimeter and the calorific value was recorded. In addition, a dry calorific value was also calculated. The dry calorific value was slightly higher than the measured calorific value due to the small percentage of moisture still retained in the biomass. From the dry calorific value, the percentage of energy recovered and energy density can then be calculated. The increase in energy density is the key factor in determining how beneficial torrefaction is for biomass. The following equation was used to determine dry calorific value, energy recovery, and energy density of the biomass samples.

$$Dry\ Calorific\ Value\ (J/g) = \frac{Calorific\ Value\ (J/g)}{(1 - MC_{wb})}$$

$$Energy\ Recovery\ \% = \frac{Calculated\ CV_{Sample} * (100 - Dry\ Matter\ Loss\ \%_{Sample})}{Calculated\ CV_{Control}}$$

$$Energy\ Increase = \frac{Energy\ Recovery\ \%}{(100 - Dry\ Matter\ Loss\ \%)}$$

Equation 4-3: Calorific Value Equations

4.2.5-4 Elemental Analysis

The carbon, hydrogen, nitrogen, sulfur, and oxygen contents in each of the biomass samples before and after torrefaction were analyzed. The samples tested were 0.5 mm in size to ensure homogeneity.

Figure 4-9: (0.5 mm) Big Bluestem Biomass

Approximately 3 mg of each sample was used for elemental analysis. The samples were loaded into small aluminum dishes and weighed on a balance that was accurate to the thousandth milligram.
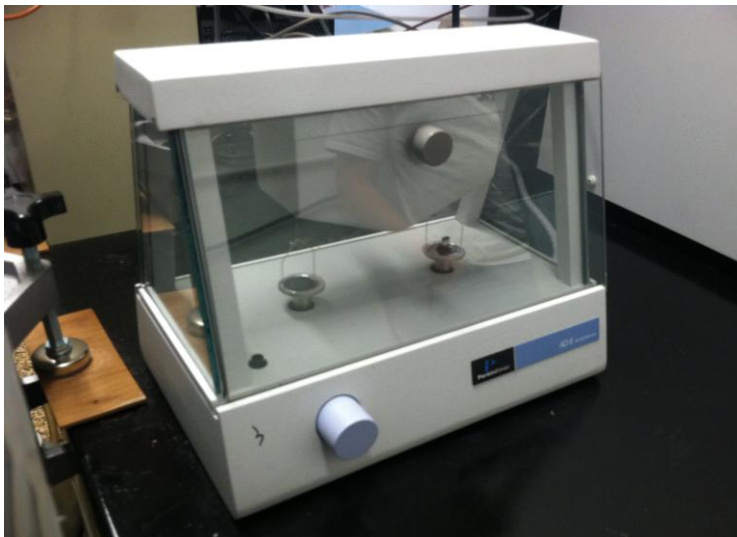
Figure 4-10: Perkin Elmer AD 6 Autobalance

The weight of the sample was recorded in the elemental analyzer. The sample was then removed from the scale, enclosed in the aluminum dish, and loaded in the elemental analyzer. The analyzer was unable to calculate oxygen percentage, but since oxygen is the only other major element in the biomass, the oxygen percentage was assumed to be 100% minus the sum of the other elements.
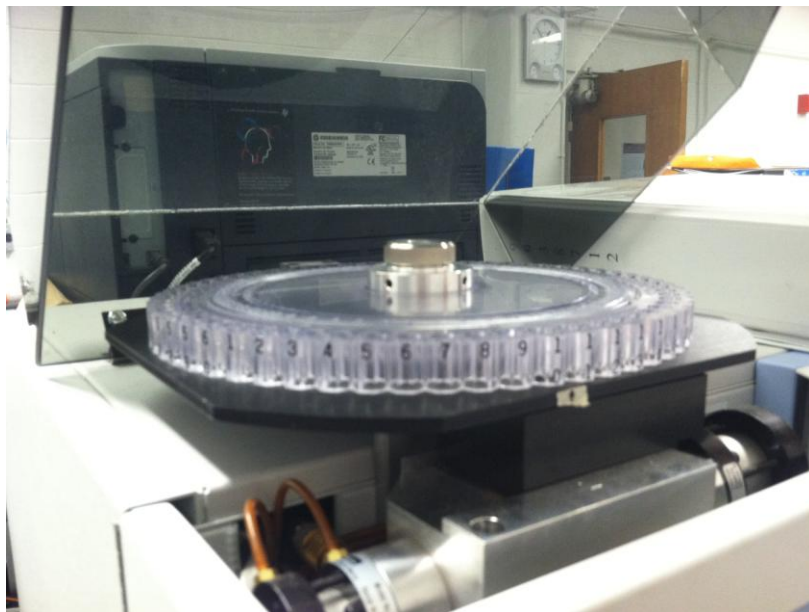
Figure 4-11: Elemental Analyzer

4.2.5-5 Thermogravemetic Analysis (TGA)

TGA was used to study the thermal stability of pre-dried and non-dried big bluestem and CRP control samples. TGA provides thermal decomposition temperature for hemicellulose, cellulose, and lignin in the biomass. The data from TGA can be used to determine the temperature range of the torrefaction process.

4.2.5-6 Compositional Analysis

Control and torrefied samples that were processed at 200, 250 and 300 ˚C for 30 minutes were analyzed for overall composition. The samples were prepared by first performing water and ethanol extraction. After extraction, lignin, ash (acid insoluble), glucan, xylose, and arabinose contents of extract free biomass were analyzed by HPLC. The compositional analysis helps with understanding effects of thermal treatment on composition change. Glucan is a sugar that represents the percentage of cellulose, while xylose and arabinose are sugars that comprise the hemicellulose composition. The percentage of each component as received is the actual

percentage in the sample because it accounts for biomass that was dissolved in the extraction process. A step by step procedure of the composition analysis can be found in Appendix C - (A. Sluiter, 2005a) (A. Sluiter, 2005b) (B. Hames, 2008).

Chapter 5 - Results and Discussion

5.1 Characteristics of Control Biomass

Control biomass samples were analyzed for both big bluestem and CRP biomass using NREL standard methods. The samples were used to determine whether or not torrefaction improves biomass quality.

	Initial MC % (wb)	Actual CV (Before Dry) (kJ/kg)	Calculated Dry CV (Before dry) (kJ/kg)	Final MC % (wb)	Actual CV (After dry) (kJ/kg)	Calculated Dry CV (After dry) (kJ/kg)
Big Bluestem		15,167	18,769	0.78	18,266	18,410
		15,080	18,661	0.67	18,465	18,590
Average	**19.19**	**15,124**	**18,715**		**18,366**	**18,500**
CRP		15,003	18,364	1.17	18,102	18,316
		14,995	18,354	1.25	18,157	18,387
Average	**18.30**	**14,999**	**18,359**		**18,130**	**18,352**

Table 5-1: Moisture Content and Calorific Values of the Control Biomass Samples

High moisture content and low calorific value are two known disadvantages of using raw biomass as a biofuel feedstock. The initial moisture content of the raw big bluestem and CRP biomass were 19.19% and 18.3%, respectively. The calorific value of raw big bluestem and CRP biomass was analyzed before and after drying at 105 ˚C for at least four hours. As moisture decreased, actual calorific value of the dried biomass increased roughly by the moisture percentage that was found in the raw biomass. The calculated dry calorific value shows the theoretical calorific value that raw biomass can achieve from removing the moisture content. Big bluestem and CRP samples were able to achieve theoretical calorific values of 18,769 and 18,387 kJ/kg, respectively.

5.2 Effects of Torrefaction on Properties of Biomass

5.2.1 Dry Matter Loss

Both torrefaction temperature and time affected dry matter loss of big bluestem and CRP biomass during torrefaction, but temperature had the greater impact. At a constant temperature, the dry matter loss of big bluestem biomass showed a steady trend slightly increasing between 15 and 45 minute intervals, usually by less than 2%. Temperature exhibited the same increasing

trends; however, the trends were much greater. An approximate 10% increase in dry matter loss occurred when the temperature increased from 200 to 250 ˚C, and an additional 7% rise in dry matter loss transpired between 250 and 300 ˚C. After torrefaction, it was expected that final moisture content of the samples would be lower than 5% (wb). For all of the big bluestem samples the final moisture content was below 2%, but time and temperature did not seem to show a steady trend among different treatments.

When comparing the dry matter loss between pre-dried samples and non-pre-dried samples, the pre-dried biomass had less dry matter loss. The moisture content after torrefaction in the pre-dried samples was lower with respect to the non-pre-dried samples, and a slightly decreasing trend in moisture content occurred with respect to time. Table 5-2 and Table 5-3 display the average dry matter loss from the big bluestem torrefaction samples. For the results of the entire big bluestem torrefaction samples, reference Appendix D -

˚C, min.	Mass Initial (g)	Initial Dry Matter (g)	Mass Final (g)	Final Dry Mass (g)	Total loss %	Dry Matter Loss %	Final MC % (wb)	Final MC % (db)
200, 15	12.10 ±1.6	9.78 ±1.3	8.60 ±0.8	8.43 ±0.8	28.79 ±2.1	13.61 ±2.5	1.96 ±0.2	2.00 ±0.2
200, 30	14.00 ±3.4	11.31 ±2.7	10.10 ±2.4	9.94 ±2.4	27.82 ±0.3	12.17 ±0.1	1.67 ±0.6	1.70 ±0.6
200, 45	11.80 ±2.3	9.54 ±1.8	8.50 ±1.8	8.35 ±1.8	28.16 ±1.8	12.71 ±2.3	1.84 ±0.2	1.87 ±0.2
250, 15	11.60 ±0.6	9.37 ±0.5	7.40 ±0.3	7.29 ±0.3	36.19 ±0.7	22.26 ±0.6	1.55 ±0.2	1.58 ±0.2
250, 30	12.60 ±0.3	10.18 ±0.2	8.00 ±0.6	7.92 ±0.6	36.55 ±3.0	22.30 ±3.9	1.06 ±0.3	1.08 ±0.3
250, 45	13.30 ±1.0	10.75 ±0.8	8.30 ±0.7	8.21 ±0.7	37.60 ±0.7	23.67 ±0.5	1.12 ±0.4	1.13 ±0.4
300, 15	14.60 ±0.3	11.80 ±0.2	8.50 ±0.7	8.41 ±0.6	41.80 ±3.7	28.75 ±4.0	1.02 ±0.7	1.03 ±0.7
300, 30	18.30 ±3.0	14.79 ±2.4	10.70 ±2.4	10.57 ±2.4	41.81 ±3.7	28.89 ±4.9	1.22 ±0.5	1.24 ±0.5
300, 45	16.20 ±0.8	13.09 ±0.7	8.60 ±1.1	8.49 ±1.1	47.02 ±4.2	35.24 ±5.0	1.21 ±0.3	1.23 ±0.3

Table 5-2: Effect of Torrefaction Condition on the Dry Matter Loss of High Moisture Content Big Bluestem   *Initial Moisture Content (wb):19.19%*

°C, min.	Mass Initial (g)	Initial Dry Matter (g)	Mass Final (g)	Final Dry Mass (g)	Total loss %	Dry Matter Loss %	Final MC (wb)	Final MC (db)
250, 15	10.90 ±0.4	10.10 ±0.4	8.60 ±0.0	8.49 ±0.0	21.05 ±3.0	15.84 ±3.2	1.24 ±0.1	1.25 ±0.1
250, 30	10.50 ±0.4	9.73 ±0.4	8.30 ±0.4	8.22 ±0.4	21.00 ±0.8	15.50 ±1.1	0.93 ±0.2	0.95 ±0.2
250, 45	12.80 ±0.3	11.86 ±0.3	9.20 ±0.3	9.12 ±0.3	28.10 ±3.8	23.06 ±4.2	0.87 ±0.1	0.88 ±0.1

Table 5-3: Effect of Torrefaction on the Dry Matter Loss of Pre-dried Big Bluestem

Initial Moisture Content (wb):7.3%

Dry matter loss in CRP biomass showed much of the same trends as the pre-dried torrefied big bluestem biomass. A slight increase existed in dry matter loss with increasing time, but a much larger increase took place in dry matter loss with increasing temperatures. Pre-dried CRP biomass samples did not demonstrate a significant difference between non-dried samples, but they did show a slight increase in dry matter loss. Table 5-4 and Table 5-5 display the average percentage of dry matter loss from the CRP torrefaction samples. For the results of all the CRP torrefaction samples, reference Appendix E - .

°C, min.	Mass Initial (g)	Initial Dry Matter (g)	Mass Final (g)	Final Dry Mass (g)	Total loss %	Dry Matter Loss %	Final MC % (wb)	Final MC % (db)
200, 15	11.50 ±0.4	9.40 ±0.3	8.70 ±0.4	8.52 ±0.5	24.35 ±0.9	9.34 ±1.8	2.08 ±0.8	2.13 ±0.8
200, 30	12.50 ±2.7	10.21 ±2.2	9.30 ±1.8	9.12 ±1.7	25.45 ±1.3	10.47 ±2.2	1.88 ±0.7	1.98 ±0.7
200, 45	11.50 ±0.1	9.40 ±0.1	8.40 ±0.3	8.27 ±0.2	26.93 ±3.4	11.97 ±3.7	1.56 ±0.3	1.59 ±0.3
250, 15	13.33 ±2.2	10.89 ±1.8	9.33 ±1.3	9.17 ±1.3	31.94 ±5.3	15.53 ±2.6	1.73 ±0.5	1.77 ±0.5
250, 30	11.90 ±0.4	9.72 ±0.3	8.20 ±0.0	8.05 ±0.0	31.05 ±2.5	17.13 ±2.6	1.81 ±0.4	1.84 ±0.4
250, 45	11.90 ±0.4	9.72 ±0.3	8.30 ±0.1	8.15 ±0.1	30.19 ±3.7	16.09 ±3.9	1.79 ±0.6	1.82 ±0.6
300, 15	12.50 ±2.1	10.21 ±1.7	7.20 ±2.0	7.12 ±1.9	42.92 ±6.2	30.91 ±7.2	1.09 ±0.4	1.10 ±0.4
300, 30	12.50 ±1.0	10.21 ±0.8	7.10 ±1.0	6.97 ±0.9	43.33 ±3.4	31.92 ±3.6	1.82 ±0.8	1.86 ±0.8
300, 45	13.30 ±0.1	10.87 ±0.1	7.10 ±0.1	6.99 ±0.1	46.62 ±0.5	35.63 ±0.7	1.48 ±0.1	1.51 ±0.1

Table 5-4: Effect of Torrefaction Condition on the Dry Matter Loss of High Moisture Content CRP Biomass   *Initial Moisture Content (wb):18.3%*

°C, min.	Mass Initial (g)	Initial Dry Matter (g)	Mass Final (g)	Final Dry Mass (g)	Total loss %	Dry Matter Loss %	Final MC % (wb)	Final MC % (db)
250,15	10.20 ±0.3	9.34 ±0.3	7.70 ±0.1	7.55 ±0.1	24.50 ±0.7	19.14 ±0.9	1.90 ±0.2	1.94 ±0.2
250,30	11.80 ±0.8	10.81 ±0.8	8.70 ±0.4	8.59 ±0.4	26.20 ±1.7	20.45 ±2.2	1.26 ±0.5	1.27 ±0.5
250,45	11.90 ±1.3	10.90 ±1.2	9.60 ±1.1	9.48 ±1.2	19.38 ±0.9	13.14 ±1.4	1.32 ±0.5	1.34 ±0.5

Table 5-5: Effect of Torrefaction on the Dry Matter Loss of Pre-dried CRP Biomass

Initial Moisture Content (wb):8.4%

Changes in temperature had a greater effect on dry matter loss than time in both big bluestem and CRP samples. The increase in dry matter loss can be attributed to high amounts of emitted CO_2 due to decarboxylation as a result of increasing temperatures, but the increase in dry matter loss can also be related to the beginnings of pyrolysis. Pyrolysis usually takes place in biomass at temperatures above 300 °C, and it was observed that bio-oil began to develop in the torrefied samples, meaning that the biomass was reaching temperatures above 300 °C. This can be attributed to the vertical conduction design of the reactor. Figure 5-1 illustrates what occurred in the Parr 4570 vertical pressure reactor. In order for gas in the reactor to reach the desired temperature, the steel drum that makes the reactor must be heated to a temperature much greater than the desired gas temperature. The top half of the biomass sample was exposed to the desired N_2 temperatures and finished was a light brown color. The bottom half of the sample most likely made contact with the reactor beaker. The heat could then be conducted through the beaker, raising the beaker temperature higher than the measured gas temperature where heat is transferred via convection. These results suggest that a conduction heating system is not ideal for torrefaction. Another problem the samples displayed was the mixing capabilities of a vertical reactor. If the samples had been free to mix, they likely would have been pushed to the walls or bottom of the beaker where the temperature could not be accurately controlled resulting in further pyrolysis. An ideal reactor to be used in response to these issues is a horizontal revolving drum reactor with a convection heating system in which the N_2 is heated in a heat pump outside the reactor and flushed inside the reactor. The horizontal drum, with fins attached to the outer wall of the reactor, uses gravity to evenly mix the samples, resulting in a more uniformed product.

Figure 5-1: Pre-Dried CRP Torrefaction (250 ˚C, 30 min.)

5.2.2 Calorific Value (CV)

Like dry matter loss, the calorific value of the biomass escalated with increasing time and temperature partly as a result of compositional breakdown and formation of CO_2 which removes dry matter without losing energy. The energy loss is a result of CO production, and the amount of recovered energy decreased when temperature increased but had varied results with time. Energy density is a ratio that compares energy loss to dry matter loss. To fully utilize the value of biomass, torrefaction needs to minimize the amount of energy loss while maximizing dry matter loss. The higher the energy density, the more the biomass is improved. Biomass energy density increased with both torrefaction time and temperature. Table 5-6 and Table 5-7 show the average calorific value, energy recovery percentage and energy density of big bluestem and CRP biomass. Full results can be found in Appendix F - and Appendix G - .

˚C, min.	Dry Matter Loss %	Final MC % (wb)	Actual CV (kJ/kg)	Calculated CV (dried) (kJ/kg)	Energy Recovery %	Energy Density
Control	0	19.2	15,124 ±62	18,715 ±76.1	100 ±0.0	1.00 ±0.00
200,15	13.61 ±2.5	1.96 ±0.2	18,454 ±169.0	18,823 ±143.2	86.89 ±1.8	1.01 ±0.01
200,30	12.17 ±0.1	1.67 ±0.6	18,586 ±86.3	18,902 ±24.4	88.71 ±0.0	1.01 ±0.00
200,45	12.71 ±2.3	1.84 ±0.2	18,768 ±125.2	19,119 ±161.2	89.18 ±1.6	1.02 ±0.01
250,15	22.26 ±0.6	1.55 ±0.2	19,613 ±705.7	19,921 ±672.4	82.75 ±2.1	1.06 ±0.04
250,30	22.30 ±3.9	1.06 ±0.3	19,798 ±10.6	20,010 ±40.0	83.07 ±4.1	1.07 ±0.00
250,45	23.67 ±0.5	1.12 ±0.4	20,252 ±77.1	20,480 ±1.1	83.53 ±0.6	1.09 ±0.00
300,15	28.75 ±4.0	1.02 ±0.7	20,666 ±662.6	20,876 ±515.8	79.48 ±2.5	1.12 ±0.03
300,30	28.89 ±4.9	1.22 ±0.5	20,853 ±364.2	21,112 ±470.7	80.22 ±3.7	1.13 ±0.03
300,45	35.24 ±5.0	1.21 ±0.3	21,435 ±120.9	21,698 ±177.5	75.08 ±6.4	1.16 ±0.01
Pre-Dry						
250,15	15.84 ±3.2	1.24 ±0.1	19,704 ±429.9	19,951 ±413.9	89.71 ±1.5	1.07 ±0.02
250,30	15.50 ±1.1	0.93 ±0.2	19,554 ±18.4	19,738 ±21.6	89.12 ±1.0	1.05 ±0.00
250,45	23.06 ±4.2	0.87 ±0.1	19,943 ±142.8	20,117 ±116.1	82.71 ±5.0	1.07 ±0.01

Table 5-6: Effect of Torrefaction Condition on Calorific Value and Energy Density of Big Bluestem Biomass

˚C, min.	Dry Matter Loss %	Final MC % (wb)	Actual CV (kJ/kg)	Calculated CV (dried) (kJ/kg))	Energy Recovery %	Energy Density
Control	0	18.3	14,999 ±5.7	18,359 ±7.1	100 ±0.0	1.00 ±0.00
200,15	9.34 ±1.8	2.08 ±0.8	18,413 ±87.7	18,804 ±58.5	92.86 ±1.6	1.02 ±0.00
200,30	10.47 ±2.2	1.88 ±0.7	18,518 ±96.9	18,874 ±234.1	92.04 ±1.2	1.03 ±0.01
200,45	11.97 ±3.7	1.56 ±0.3	18,591 ±258.8	18,886 ±197.1	90.55 ±2.9	1.03 ±0.01
250,15	15.53 ±2.6	1.73 ±0.5	19,155 ±327.9	19,493 ±426.0	89.69 ±2.5	1.06 ±0.02
250,30	17.13 ±2.6	1.81 ±0.4	19,061 ±630.7	19,410 ±569.7	87.61 ±0.2	1.06 ±0.03
250,45	16.09 ±3.9	1.79 ±0.6	19,075 ±277.9	19,422 ±166.9	88.76 ±3.4	1.06 ±0.01
300,15	30.91 ±7.2	1.09 ±0.4	20,188 ±101.1	20,410 ±183.9	76.81 ±8.8	1.11 ±0.01
300,30	31.92 ±3.6	1.82 ±0.8	20,748 ±139.3	21,131 ±33.1	78.36 ±4.3	1.15 ±0.00
300,45	35.63 ±0.7	1.48 ±0.1	21,364 ±287.8	21,685 ±268.0	76.03 ±1.8	1.18 ±0.01
Pre-Dry						
250,15	19.14 ±0.9	1.90 ±0.2	18,998 ±206.5	19,366 ±255.1	85.29 ±0.1	1.05 ±0.01
250,30	20.45 ±2.2	1.26 ±0.5	19,369 ±170.4	19,614 ±81.3	84.99 ±2.8	1.07 ±0.00
250,45	13.14 ±1.4	1.32 ±0.5	19,208 ±230.5	19,464 ±128.3	92.09 ±2.1	1.06 ±0.01

Table 5-7: Effect of Torrefaction Condition on Calorific Value and Energy Density of CRP Biomass

Torrefaction had similar effects on the energy density of big bluestem and CRP biomass. On average, big bluestem had slightly higher calorific value than CRP biomass, but CRP biomass had an advantage in energy density. Overall, the results were too similar to distinguish advantages between one biomass source over another probably because CRP biomass is a mixture of native grass including big bluestem. In addition, other grasses in the CRP biomass are very similar to big bluestem.

The pre-dried big bluestem and CRP biomass had calorific values and energy densities very comparable to the non-dried samples on dry basis. Pre-dried big bluestem samples had an advantage over non-dried samples in terms of energy value and energy density; pre-dried samples exhibiting lower dry matter loss is ideal. Pre-dried CRP biomass, on the other hand, had higher dry matter loss therefore demonstrating a slight advantage of non-pre-dried over pre-dried biomass.

5.2.3 Elemental Analysis

Elemental analysis of big bluestem and CRP biomass showed an increase in carbon content in direct correlation to increase in torrefaction time and temperature. This increase is due to the production and release of CO_2, CO, and other hydrocarbons. If CO_2 production from decomposition of the biomass occurs during torrefaction, then the overall carbon content of the biomass increases and the oxygen content decreases. Table 5-8 and Table 5-9 show the decreasing trend in the atomic ratio between oxygen and carbon over time and temperature for both biomasses. Figure 5-2 and Figure 5-3 display the increasing trend of carbon content of the biomass. Hydrogen, nitrogen and sulfur were also analyzed; however, torrefaction had only a slight effect on these elements, varying with time and temperature, and the overall increase was less than 1%. Appendix H - and Appendix I - display full results of elemental analysis of big bluestem and CRP biomass. When comparing the two biomasses, big bluestem is slightly favored over CRP due to a higher carbon content and lower O/C atomic ratio. When comparing the pre-dried to non-dried samples, results were very similar and not distinguishable.

˚C, min.	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen	O/C Atomic Ratio
Control	47.35	4.89	1.40	0.97	45.39	0.72
200, 15	48.49 ±0.36	5.68 ±0.23	1.49 ±0.33	1.67 ±0.21	42.68 ±0.67	0.66 ±0.02
200, 30	48.78 ±1.23	5.58 ±0.42	1.52 ±0.19	1.47 ±0.10	42.66 ±1.56	0.66 ±0.04
200, 45	48.94 ±0.24	5.46 ±0.16	1.66 ±0.15	1.42 ±0.05	42.54 ±0.12	0.65 ±0.00
250, 15	51.09 ±0.40	5.60 ±0.06	1.68 ±0.21	1.48 ±0.04	40.17 ±0.52	0.59 ±0.01
250, 30	50.75 ±1.42	5.49 ±0.07	1.61 ±0.11	1.45 ±0.04	40.69 ±1.20	0.60 ±0.03
250, 45	52.54 ±0.80	5.39 ±0.11	1.97 ±0.17	1.41 ±0.03	38.70 ±0.83	0.55 ±0.02
300, 15	52.86 ±0.93	5.36 ±0.16	1.73 ±0.00	1.44 ±0.06	38.62 ±0.71	0.55 ±0.02
300, 30	52.83 ±1.91	5.32 ±0.05	1.86 ±0.18	1.40 ±0.02	38.61 ±2.02	0.55 ±0.05
300, 45	55.07 ±0.28	5.48 ±0.35	1.93 ± 0.16	1.50 ±0.13	36.03 ±0.60	0.49 ±0.01
Pre-Dry						
250, 15	50.91	5.96	1.82	1.62	39.69	0.58
250, 30	51.62 ±0.85	5.82 ±0.3	1.63 ±0.05	1.59 ±0.08	39.35 ±1.27	0.57 ±0.03
250, 45	52.19 ±0.76	5.69 ±0.15	1.66 ±0.13	1.55 ±0.05	38.93 ±1.10	0.56 ±0.02

Table 5-8: Effect of Torrefaction on Elemental Composition of Big Bluestem

˚C , min.	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen	O/C Atomic Ratio
Control	46.55	5.37	1.70	1.41	44.97	0.72
200, 15	47.87 ±0.37	5.57 ±0.04	2.00 ±0.03	1.45 ±0.04	43.12 ±0.42	0.68 ±0.01
200, 30	48.30 ±0.19	5.63 ±0.01	1.83 ±0.07	1.49 ±0.03	42.76 ±0.25	0.66 ±0.01
200, 45	48.26 ±0.46	5.98 ±0.22	1.86 ±0.10	1.65 ±0.04	42.25 ±0.82	0.66 ±0.02
250, 15	49.34 ±0.11	5.71 ±0.19	1.95 ±0.17	1.55 ±0.06	41.45 ±0.19	0.63 ±0.00
250, 30	49.84 ±0.66	5.44 ±0.04	2.12 ±0.07	1.43 ±0.04	41.18 ±0.66	0.62 ±0.02
250, 45	49.94 ±0.95	5.25 ±0.24	1.79 ±0.17	1.39 ±0.08	41.63 ±0.46	0.63 ±0.02
300, 15	51.39 ±0.45	5.28 ±0.24	2.07 ±0.40	1.40 ±0.08	39.87 ±0.53	0.58 ±0.01
300, 30	52.91 ±0.52	5.07 ±0.04	2.06 ±0.11	1.35 ±0.03	38.62 ±0.69	0.55 ±0.02
300, 45	55.51 ±0.45	5.48 ±0.13	2.33 ±0.13	1.47 ±0.07	35.22 ±0.77	0.48 ±0.01
Pre-Dry						
250, 15	49.46 ±1.27	5.96 ±0.49	1.93 ±0.18	1.63 ±0.16	41.02 ±2.11	0.62 ±0.05
250, 30	49.40 ±0.08	5.43 ±0.25	1.88 ±0.06	1.37 ±0.23	41.94 ±0.49	0.64 ±0.01
250, 45	49.60	5.57	1.93	1.60	41.30	0.62

Table 5-9: Effect of Torrefaction on Elemental Composition of CRP Biomass
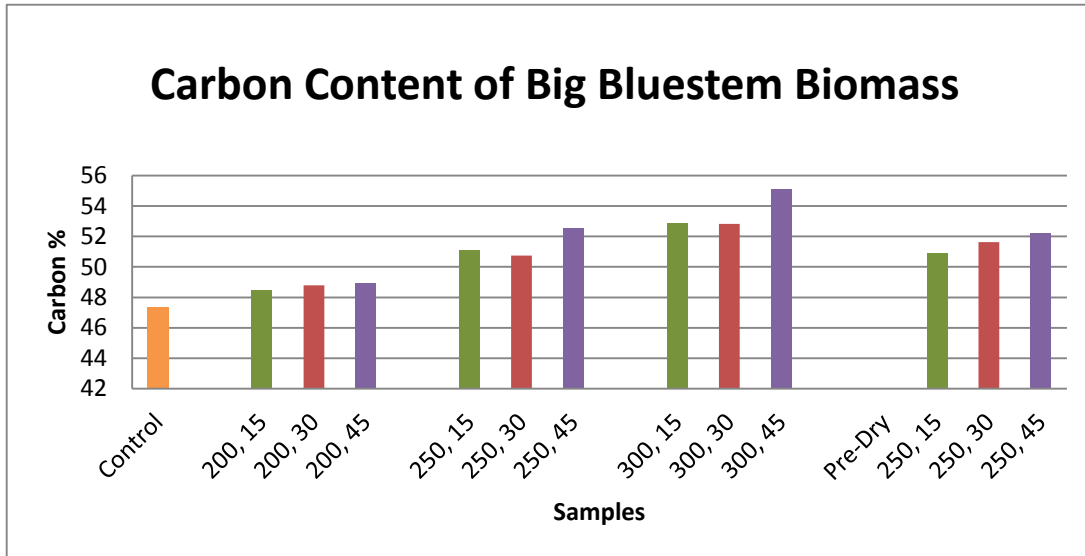
Figure 5-2: Effect of Torrefaction on Carbon Content of Big Bluestem
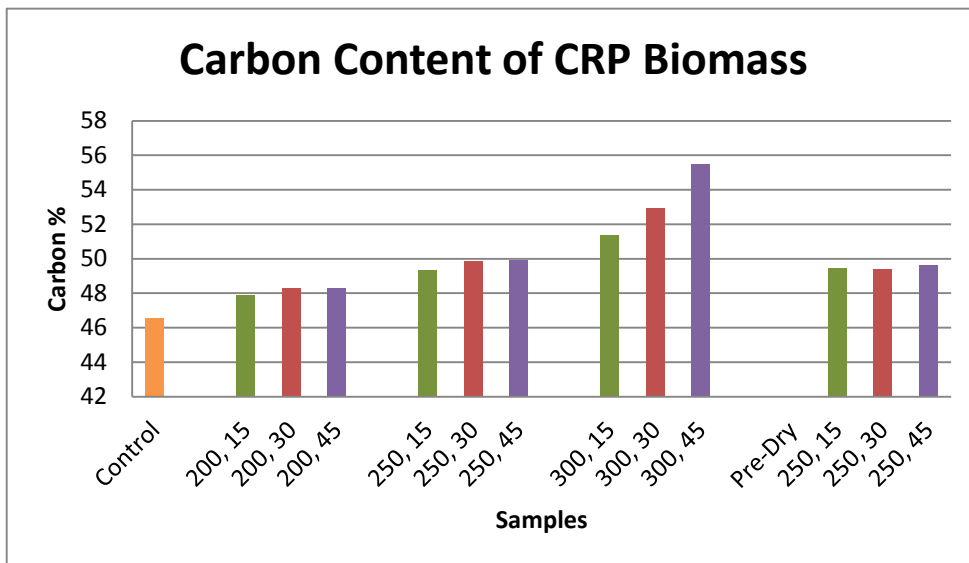
Figure 5-3: Effect of Torrefaction on Carbon Content of CRP Biomass

5.2.4 Thermogravemetric Analysis

Thermogravemetric analysis was performed on non-dried and pre-dried big bluestem and CRP control samples. Derivative gravimetric analysis (DGA) was also conducted. TGA and DGA determine the temperature at which biomass starts to decompose and the range of

temperatures displaying significant weight loss during the heating process. Figure 5-4, Figure 5-5, Figure 5-6, and Figure 5-7 display the TGA and DGA curves. The results show that both non-dried and pre-dried samples had similar decomposition temperatures. The DGA curve shows that the hemicellulose decomposition temperature begins near 160 ˚C. The cellulose was estimated to start decomposing at temperatures around 250 ˚C. Maximum weight loss occurred at temperatures near 344 ˚C with the exception of pre-dried big bluestem which experienced maximum weight loss at 350 ˚C. The temperature at which maximum weight loss occurs suggests that hemicelluloses, cellulose, and lignin were decomposing, therefore, the lignin was estimated to decompose at temperatures just before 340˚C.
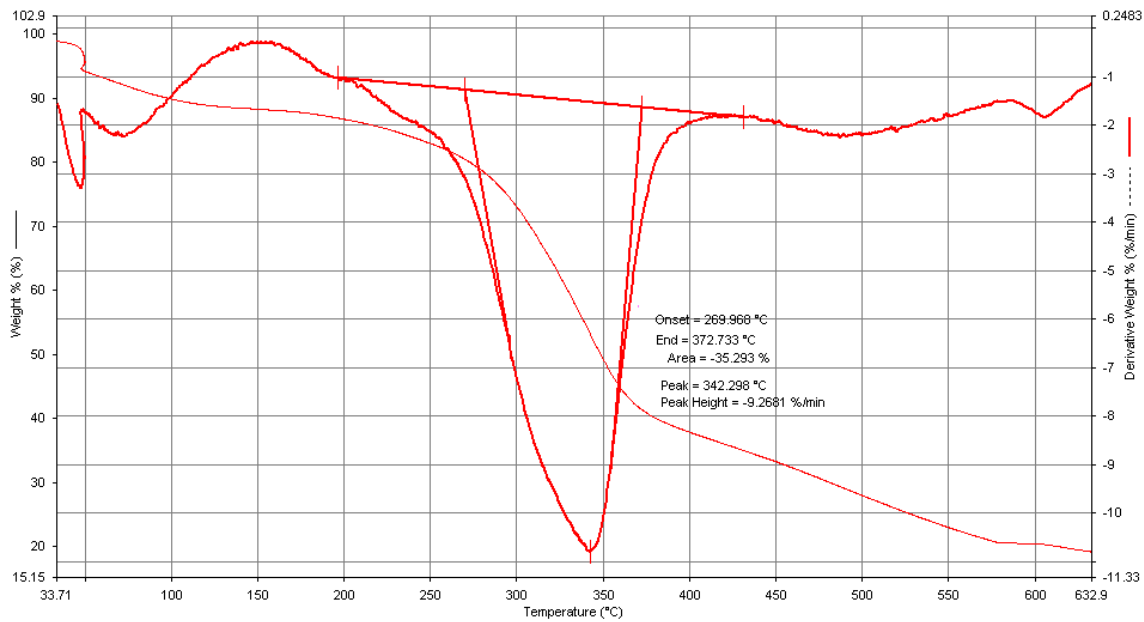
Figure 5-4: Big Bluestem (TGA and DGA)
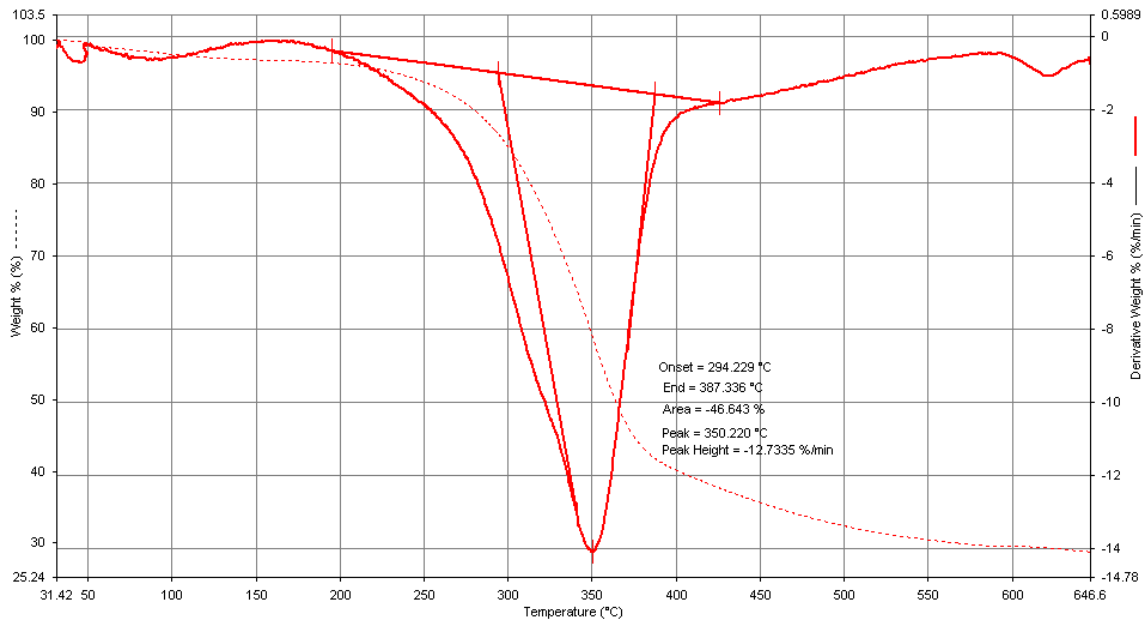
Figure 5-5: Big Bluestem Dried (TGA and DGA)

40
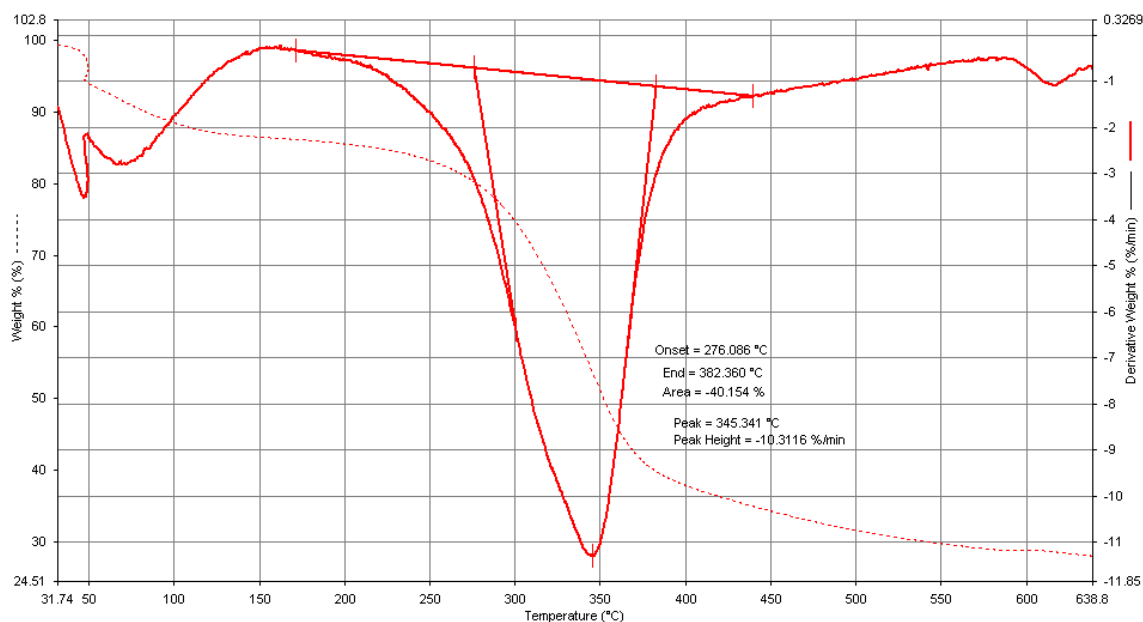
Figure 5-6: CRP (TGA and DGA)
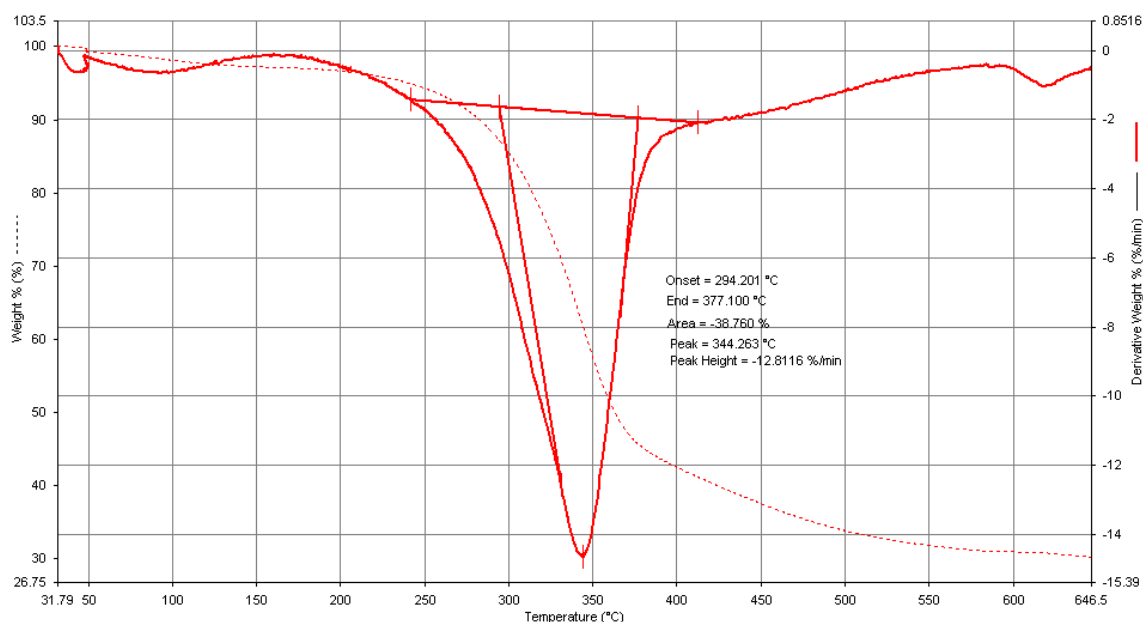
Figure 5-7: CRP Dried (TGA and DGA)

5.2.5 Compositional Analysis

Compositional analysis determined the effects of torrefaction on chemical composition of biomass such as hemicellulose, cellulose, and lignin content of the biomass. The compositional analysis also determined the extractives extracted by water and ethanol.

As torrefaction temperatures increased to 300 ˚C, the xylose content, a major component of the hemicellulose, decreased by as much as 50 and 60% for big bluestem and CRP biomass,

respectively. The other hemicellulose component, arabinose, decreased by approximately 30 and 60% for big bluestem and CRP biomass, respectively. The decomposition of xylose and arabinose was observed at 200 ˚C. This is supported by the data from the TGA which discovered the hemicellulose in big bluestem and CRP biomass started to devolitize at temperatures around 160˚C. Overall composition of the xylose and arabinose was initially lower in big bluestem biomass, but it finished with a higher composition than CRP biomass as temperatures reached 300˚C. The pre-dried samples differed from non-dried biomass in both big bluestem and CRP biomass. Pre-dried samples had a less arabinose decomposition for both biomasses, while big bluestem samples had less oxygen decomposition.

Glucan, a sugar which makes up cellulose, remained steady in big bluestem biomass until reaching 300˚C, at which time the total mass loss was 20%. Glucan in CRP biomass slowly decreased between 200 to 250˚C before similarly decreasing as temperatures reached 300 ˚C. The slight decrease of glucan in CRP samples at 200 and 250 ˚C could be due to varying species in which celluloses decompose at lower temperatures. The data analyzed in the compositional analysis was also supported by TGA results where it was estimated that cellulose in big bluestem and CRP biomass would start to decompose around 250 ˚C. Pre-dried samples seemed to have a slight effect on the glucan decomposition, which is slightly higher than non-dried samples.

Glucan, xylose, and arabinose decreased as temperature increased, while the lignin content steadily increased, suggesting that the lignin only decreased slightly or not at all as temperatures approached 300 ˚C. The TGA results suggested that lignin in biomass probably did not start to decompose until temperatures reached above 300 ˚C. However, the acid insoluble lignin percentage seemed to increase at a rate unsupported by mass balance equations. The results could be explained by the carbonization of sugars due to the high temperatures the biomass experiences during torrefaction. The carbonized sugar could not have dissolved during the acid treatment of the compositional analysis which would have increased the resulting acid insoluble lignin, therefore increasing the apparent lignin content. Hence forth in the data, the acid insoluble lignin was assumed to have not degraded and compositional percentage was based on mass balance of dry matter lost. The pre-dried samples contained higher lignin content than the non-dried samples and can be explained by significant decomposition of xylose and arabinose.

The acid insoluble ash content (Ash (AI)) was also analyzed. The results showed that torrefaction temperature did not have a significant effect on the ash content; however, ash content increased slightly with increasing temperatures.

Sample	Extraction %	Lignin %	Glucan %	Xylose %	Arabinose %	Ash (AI) %
BB Control	32.15	12.85	28.32	16.97	3.48	0.40
BB 200, 30	30.34 ±3.21	14.95	29.12 ±0.10	16.51 ±1.86	3.91 ±0.69	0.72 ±0.46
BB 250, 30	26.06 ±0.08	17.74	28.21 ±3.46	14.71 ±1.90	3.65 ±0.03	0.47 ±0.08
BB (Pre-Dry) 250, 30	24.75 ±0.14	16.82	28.86 ±1.10	13.61 ±0.25	2.65 ±1.33	0.51 ±0.07
BB 300, 30	24.67 ±1.11	19.41	22.77 ±3.96	8.35 ±3.80	2.53 ±1.43	0.62 ±0.51

Table 5-10: Effect of Torrefaction on Chemical Composition of Big Bluestem

AI=Acid Insoluble

Sample	Extraction %	Lignin %	Glucan %	Xylose %	Arabinose %	Ash (AI)%
CRP Control	29.46	13.01	30.18	17.43	5.69	0.20
CRP 200, 30	32.12 ±0.68	14.08	27.62 ±1.28	15.66 ±0.69	4.39 ±0.85	0.46 ±0.01
CRP 250, 30	28.60 ±0.06	15.84	26.95 ±2.74	12.45 ±2.51	3.54 ±0.26	0.57 ±0.21
CRP (Pre-Dry) 250, 30	26.40 ±0.71	16.94	28.21 ±0.29	13.19 ±0.52	3.38 ±0.29	0.76 ±0.19
CRP 300, 30	26.28 ±5.33	19.25	22.49 ±5.93	6.63 ±1.96	2.24 ±0.01	1.19 ±0.20

Table 5-11: Effect of Torrefaction on Chemical Composition of CRP Biomass

AI=Acid Insoluble

Chapter 6 - Conclusion

Torrefaction pretreatment improved the calorific value and energy density of big bluestem and CRP biomass, thus making the grass biomass more attractive as a biofuel production source. The improvements resulting from torrefaction potentially raise the calorific value of the big bluestem and CRP biomass to 21,500 kJ/kg, which is more comparable to coal (25,000 kJ/kg) than untreated biomass (18,500 kJ/kg). If the conservative amount of 8 million metric tons of CRP biomass mentioned in the literature review is harvested, undergoes torrefaction at 300 ˚C for 45 minutes, and is utilized as a co-firing product with coal, then approximately 4.47 million metric tons of coal could be conserved every year. The torrefied CRP biomass can also be converted into ethanol via the Fischer-Tropsch process although further research is needed to determine ethanol yields.

Torrefaction, however, does not greatly improve energy density of big bluestem and CRP biomass. The greatest increase in energy density was only 18%, occurring at torrefaction conditions of 300 ˚C for 45 minutes. This increase is fairly low when compared with other forms of biomasses such as the Lucern example in the literature review, where energy density increased 26%.

After analyzing results between big bluestem and CRP biomass, big bluestem generally had a slightly higher energy value than CRP biomass. This supports the idea that contamination of a pure species of biomass lowers the energy potential. However, the results were not significant in difference. Trying to maintain a field in which big bluestem is the only species would be ill-advised because the cost of managing foreign species would be more than the energy loss of using mixed species like that in CRP lands.

The results also determined the effect of pre-drying on the properties of torrefied biomass. Although there was no significant difference in calorific value between pre-dried biomass and non-pre-dried biomass after torrefaction, the pre-dried biomass had much less dry matter loss.

The results from this research support the belief that torrefaction is an effective method to improve the physical quality of the biomass. However, a cost analysis must be completed in order to determine whether or not torrefaction should be implemented on a large scale. If the operational cost of torrefaction exceeds the amount that torrefaction biomass can save on

shipping and storage cost then torrefaction of big bluestem and CRP biomass should not be pursued.

Suggestions

After completing the research, it was determined that using a vertical conduction reactor is not ideal when using torrefaction to pretreat grassy biomass. The vertical reactor resulted in non-uniformed biomass which does not improve the quality of the biomass. Using a horizontal convection reactor would evenly mix the biomass while exposing the biomass to uniform temperatures, leading to a uniform final product.

Future Endeavors

Further testing is needed in order to determine whether torrefaction of CRP biomass is beneficial. Future testing will include cost analysis of the torrefaction process, including the cost of torrefaction and the savings in shipping, storage, and additional processing. Future testing should also be conducted in a horizontal convection reactor with gravitational mixing in order to achieve a more uniformed product. Testing will be used to confirm uniformity. Additional pre-drying before torrefaction testing could also be researched at varying temperatures and times, thus maximizing calorific value with less dry matter loss. The effect of torrefaction on hydrophobic property of torrefied biomass should be studied, which will help to understand moisture absorption during storage which related to biomass degradation. Future testing should also extend to ethanol production from torrefied biomass via the Fischer-Tropsch process to determine if torrefaction is a viable pretreatment to lower ethanol cost.

References

A. Dutta, M. Leon. Pros and Cons of Torrefaction of Woody Biomass. University of Guelph
School of Engineering. Available at:
http://www.agrireseau.qc.ca/references/32/presentations_guelph/2Torrefaction%20-
%20Pros%20and%20Cons%20By%20Mathias%20Leon%20UoG.pdf. Accessed 27
January 2013.

A. Sluiter, B. Hames, D. Hyman, C. Payne, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton, J.
Wolf. 2008. Determination of Total Solids in Biomass and Total Dissolved Solids in
Liquid Process Samples. National Renewable Energy Laboratory. Available at:
http://www.nrel.gov/biomass/pdfs/42621.pdf. Accessed 10 October 2012.

A. Sluiter, B. Hames. R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton, D. Crocker. 2005a.
Determination of Structural Carbohydrates and Lignin in Biomass. Available at:
http://www.nrel.gov/biomass/pdfs/42618.pdf. Accessed 10 October 2012.

A. Sluiter, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton. 2005b. Determination of Extractives in
Biomass. National Renewable Energy Laboratory. Available at:
http://www.nrel.gov/docs/gen/fy08/42619.pdf. Accessed 10 October 2012.

B. Hames, R. Ruiz, C. Scarlata, A. Sluiter, J. Sluiter, D. Templeton. 2008. Preparation of
Samples for Compositional Analysis. National Renewable Energy Laboratory. Available
at: http://www.nrel.gov/biomass/pdfs/42620.pdf. Accessed 10 October 2012.

D. Lee, E. Aberle, C. Chen, J. Egenolf, K. Harmoney, G. Kakani, R. Kallenbach, J. Castro.
2012. Nitrogen and harvest management of Conservation Reserve Program (CRP)
grassland for sustainable biomass feedstock production. GCB Bioenergy. Vol. 5. Issue 1.
Available at: http://onlinelibrary.wiley.com/doi/10.1111/j.1757-1707.2012.01177.x/pdf.
Accessed 28 February 2013.

D. Tito Ferro, V. Vigouroux, A. Grimm, R. Zani. 2004. Torrefaction of Agricultural and Forest
Residues. Cubasolar. Available at: http://hem.passagen.se/alealfa/c4.pdf. Accessed 1
March 2013.

EIA. 2012. International Energy Statistics. U.S. Energy Information Administration. Available
at: http://www.eia.gov/cfapps/ipdbproject/IEDIndex3.cfm?tid=5&pid=5& aid=2.
Accessed 1 April 2013.

EPA. 2007. Energy Independence and Security Act of 2007: Key Provisions Affecting
Combined Heat and Power. Environmental Protection Agency. Available at:
http://www.epa.gov/chp/documents/chp_energybill.pdf. Accessed 2 March 2013.

EPA. 2011. Reducing Toxic Pollution from Power Plants. Environmental Protection Agency.
Available at: http://www.epa.gov/mats/actions.html. Accessed 17 July 2012.

First Energy. 2012. FirstEnergy, Citing Impact of Environmental Regulations, Will Retire Six
Coal-Fired Power Plants. FirstEnergy. Available at:
https://www.firstenergycorp.com/content/fecorp/newsroom/featured_stories/Coal_Plant_R
etirements0.html. Accessed 16 July 2012.

FSA. 2012. USDA Announces Streamlined Disaster Designation Process with Lower Emergency
Loan Rates and Greater CRP Flexibility in Disaster Areas. Farm Service Agency. United
States Department of Agriculture. Available at:
http://www.fsa.usda.gov/FSA/printapp?fileName=nr_20120711_rel_
0228.html&newsType=newsreel. Accessed 18 July 2012.

FSA. 2013. Fact Sheet: Conservation Reserve Program. Farm Service Agency. United States
Department of Agriculture. Available at:
http://www.fsa.usda.gov/Internet/FSA_File/crpfactsheet0213.pdf. Accessed 2 March
2013.

G. Luft. 2004. Fueling the dragon: China's race into the oil market. Available at: http://www.iags.org/china.htm. Accessed 12 November 2010.

H. Boerrigter, J. Kiel, P. Bergman. 2006. Biomass Pre-treatment by Torrefaction. Energy research Centre of the Netherlands. Available at: http://www.agri-techproducers.com/upload/ECN_%20Torrefaction%20of%20Biomass%20as%20pretreatmentLille.pdf. Accessed 16 July 2012.

H. Herron. 2000. The looming crisis in worldwide oil supplies. Petroleum Equities Inc. Available at: http://www.petroleumequities.com/OilSupplyReport.htm. Accessed 1 November 2010.

J. Sheehan, A. Aden, K. Paustian, K. Killian, J. Brenner, M. Walsh, R. Nelson. 2008. Energy and Environmental Aspects of Using Corn Stover for Fuel Ethanol. Journal of Industrial Ecology. Vol. 7. Issue 3-4. Pg. 117-146. Available at: http://onlinelibrary.wiley.com/doi/10.1162/108819803323059433/pdf. Accessed 4 March 2013.

J. Tumuluru, S. Sokhansahj, C. Wright, R. Hess, R. Boardman. 2011 A Review on Biomass Torrefaction Process and Product Properties. Idaho National Laboratory. Available at: http://www.inl.gov/technicalpublications/Documents/5094547.pdf. Accessed 26 February 2013.

J. Tumuluru, S. Sokhansahj, C. Wright, T. Kremer. GC Analysis of Volatiles and Other Products from Biomass Torrefaction Process. Available at: http://cdn.intechopen.com/pdfs/32823/InTech-Gc_analysis_of_volatiles_and_other_products_from_biomass_torrefaction_process.pdf. Accessed 3 March 2013.

NSAC. 2008. Biomass Crop Assistance Program. Available at:
http://sustainableagriculture.net/publications/grassrootsguide/renewable-energy/biomass-
crop-assistance-program/. Accessed 24 February 2013.

S. Broekema. 2009. Feasibility Study of a Biomass Supply for the Spiritwood Industrial Park.
Great River Energy. Available at:
http://www.greatriverenergy.com/makingelectricity/newprojects/biomass_feasibility_rpt.p
df. Accessed 17 July 2012.

USDA. 2012. Agriculture Secretary Vilsack Announces New Conservation Reserve Program
Initiative to Restore Grasslands, Wetlands, and Wildlife. United States Department of
Agriculture. Available at:
http://www.fsa.usda.gov/FSA/newsReleases?area=newsroom&subject=landing&topic=ne
r&newstype=newsrel&type=detail&item=nr_20120302_rel_0076.html. Accessed 8 July
2012.

U.S Department of Energy. 2010. *Oil.* Energy.gov. Available at:
http://www.energy.gov/energysources/oil.htm. Accessed 12 November 2010.

W. Chen, P. Kuo. 2010. A study on torrefaction of various biomass materials and its impact on
lignocellulosic structure simulated by a thermogravimetry. Department of Greenergy.
National University of Tainan. Elsevier Ltd. Available at:
http://www.sciencedirect.com/science/article/pii/S0360544210001210. Accessed 19 July
2012.

Appendix A - Change In Oil Demand By Region

Change in oil demand by region in the 450 Scenario compared with 2008
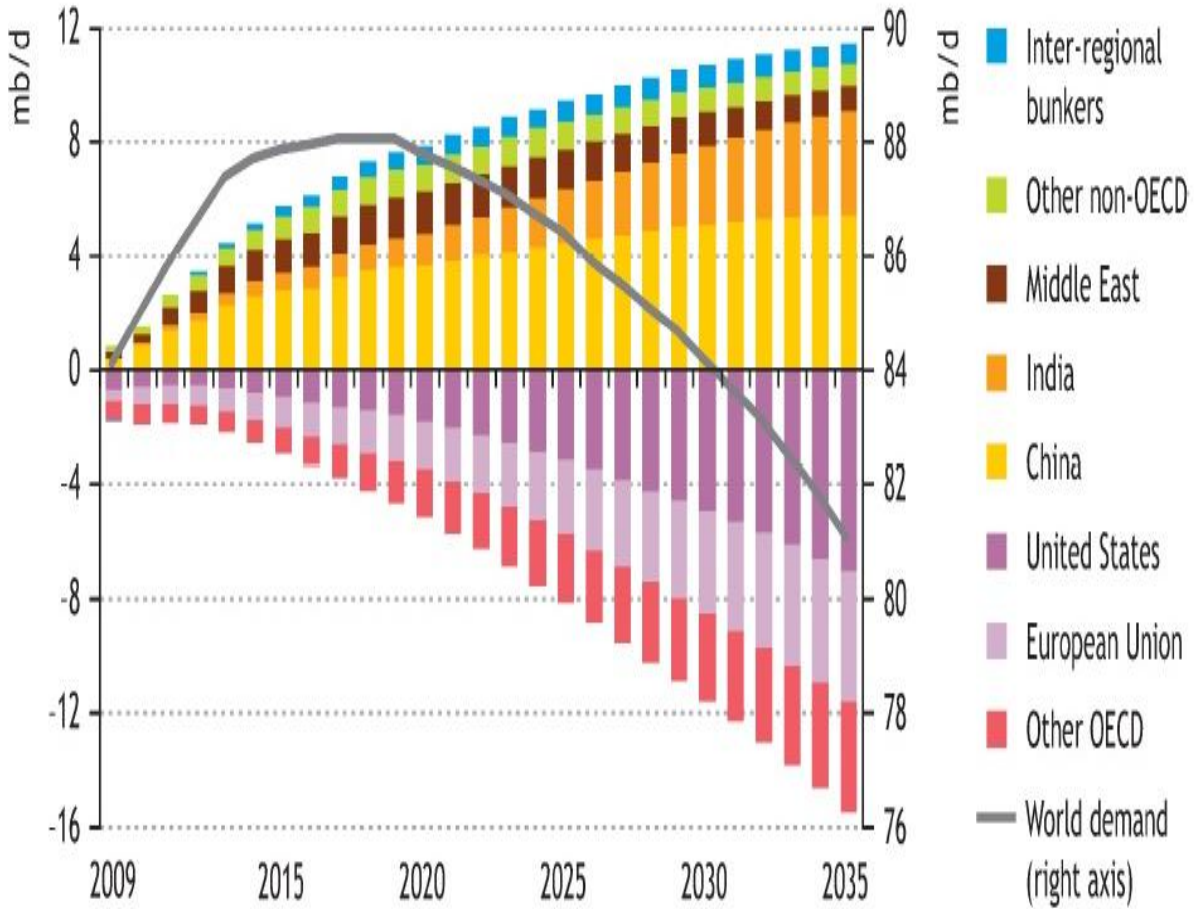
Source: "World Energy Outlook 2010" 2010. International Energy Agency. 2010
< http://www.worldenergyoutlook.org/docs/weo2010/key_graphs.pdf>

Appendix B - Procedure for Torrefaction Pretreatment

Materials

- Parr 4570 Pressure Reactor
- Parr 4570 Pressure Reactor Beaker
- Parr 4848 Reactor Controller
- Stop Watch
- ½" wrench
- Nitrogen (N_2) bottle
- Weighting Scale (accurate to .2g)
- Vacuum Pump
- 1 Pail (empty)
- 1 Pail (filled with water)

Maintenance

- Wire brush
- Soap and Water

Procedure

1. Turn on the Parr 4848 Reactor Controller. Turn the heat and motor to the off position. Make sure that the Parr 4570 Pressure Reactor is clean and that the N_2 tank is connected to the inlet flow.
2. Weigh and record the mass of a clean, empty Parr 4570 Pressure Reactor Beaker.
3. Collect a minimum of 11 grams of biomass for torrefaction
   - Bundle the biomass into bunches that weigh less than 5 grams. Take one blade of grass and tie a square knot around the middle of the bundle. Typically 4-6 bundles were used in each test

4. Collect the bundles and place in the reactor beaker. Record the initial mass of the biomass and beaker.

5. Take bundles out of beaker and load in between the propeller blades of the reactor. Place an empty pail beneath the reactor to catch loose blades of grass. Mix any loose blades that were caught in the pail with the bundles.

6. Once the bundles are secure in the blades, place the beaker in the reactor, and, using the lift, raise to the close position. Secure the reactor by tightening all the bolts with a ½" wrench. The beaker will surround the biomass and catch any biomass that may come loose during the reaction.
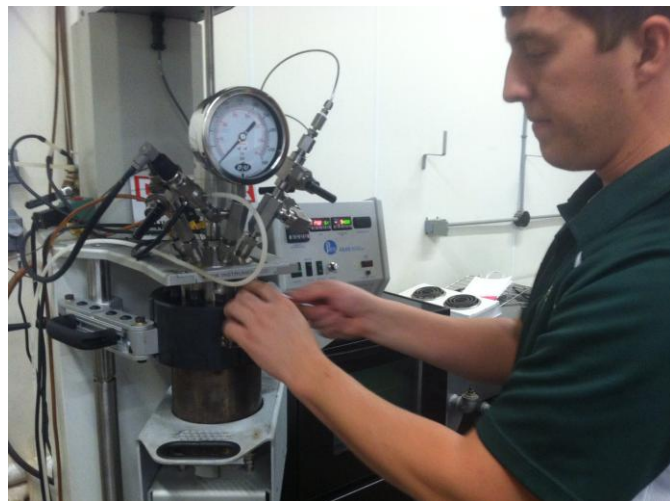
7. Connect a vacuum pump to the outlet valve. Close the inlet valve and open the outlet valve.

8. Turn on the vacuum pump.

9. Observe the pressure gauge on the Parr 4848 reactor controller and when the pressure has reached a constant pressure (usually between -21 to -16 psi), close the outlet valve. Open the valve on the N_2 tank and set the tank gauge at 5 psi or less. The N_2 pressure does not need to be high, just enough to fill the reactor with N_2. Open the inlet valve. Observe the pressure gauge again and when the pressure has reached the pressure that is set on the tank gauge, close the inlet valve. Open the outlet valve and repeat Step 9 five times. The objective of this step is to flush all oxygen out of the reactor so that biomass does not spontaneously combust.

10. After the final flush and the reactor is full of N_2, remove the vacuum pump and open the outlet valve. N_2 should be detected emerging from the outlet valve. This can be done by hearing the N_2 coming out of the outlet valve or by placing a thumb over the outlet valve and feeling pressure build up. Lower the pressure on the tank gauge as low as possible to where N_2 can still be detected coming out of the outlet valve. This will use the least amount of N_2, while keeping the reactor chamber filled with N_2.

11. Lift and lock the heater around the reactor.

12. Adjust initial temperature 40 to 50°C below the desired test temperature. The Parr 4570 pressure reactor uses a conduction heating system. Heating elements transfer

heat into the stainless steel reactor, which then radiates into the reactor chamber. The cooling system will then engage once the air temperature reaches near the set temperature, but since N_2 has a lower thermal conductivity, the temperature inside the reactor chamber will overshoot the set temperature. By the time the cooling system brings the reactor into an equilibrium state, the N_2 temperature inside the reactor will be approximately 40 ˚C higher than the initial set temperature, which should be around the desired test temperature. When the rate of temperature increase drops to about 1˚C per minute, reset the temperature on the reactor controller to the desired temperature.

13. Begin time with a stopwatch when the temperature reaches within 5 ˚C of test temperature. Watch over the reaction and adjust the temperature gauge so that the temperature remains ±5 ˚C of the test temperature.

14. Before the desired test time is reached, begin cooling the reactor. This can be done by removing the heater and lowering the set temperature. The goal is to be 5 ˚C below test temperature when the test time is reached. When the test time is completed, using the lift, raise a pail full of water and submerge the reactor. The objective of this step is to lower the N_2 temperature as quickly as possible.

15. When the reactor temperature drops to 100 ˚C, close the N_2 tank valve. The biomass will not spontaneously combust at this temperature, therefore closing the tank valve will conserve N_2.

16. When the reactor temperature drops to a safe temperature to touch, lower the lift and remove the water pail. Raise the lift around the reactor. Open and remove the reactor. The majority of the biomass should still be entangled in the propeller. The rest of the biomass is inside the reactor beaker. Lift an empty pail up to the biomass and collect the biomass in the pail.

17. Transfer all the biomass into the reactor beaker. Weigh and record the mass of the beaker and final biomass.

18. Transfer biomass to the grinding process.

19. Clean beaker and reactor with wire brush, soap, and water.

Appendix C - Procedure for Compositional Analysis

NREL Preparation of Samples for Compositional Analysis

Materials

- Convection Oven
- Balance, accurate to 0.2 g
- Test Pans

Procedure

1. Place roughly 20 grams of control big bluestem and CRP biomass in separate labeled test pans. Factoring in losses, this should provide more than enough biomass for water and ethanol extraction.

2. Place the test pans in a convection oven set at 43 ˚C for 48 hours.
3. Remove the controlled samples and grind the samples with a 1 mm screen. Collect the grinded sample. Save 1 gram of each dried grinded control sample and analyze and record the moisture content (wet basis) using the procedure previously mentioned in the methods section. The rest of the biomass can be used for water and ethanol extraction.

Note: This procedure is only necessary for control samples because the moisture content of the controls is above 10%. Torrefaction samples have moisture content below 10% and are ready for water and ethanol extraction.

NREL Determination of Extractives

(Water and Ethanol Extraction)

Materials

- Balance, accurate to .1 mg
- Cotton cellulose thimble
- Heating mantle
- Glass Soxhlet extraction tube
- Condenser, with cooling water source
- 500 mL boiling flask
- 250 mL boiling flask

- 190 mL distilled water
- 125 mL ethanol (190 proof)
- Graduated cylinder
- Antifoam (Organic)
- Cookie sheet
- Convection oven
- Air-Oven dryer

Procedure

1. With a pencil, label a cotton cellulose thimble with what sample is being tested. Place the thimble on a balance. Weigh and record the weight of the thimble. Add roughly 4 grams of biomass to the thimble. Weigh and record the initial weight of the thimble + biomass to the nearest 0.1 mg.

2. Add 190 mL of distilled water and 1 drop of antifoam to a 500 mL boiling flask. Place the flask on the heating mantle.

3. Place the cellulose thimble inside the Soxhlet extraction tube. Connect the extraction tube to the condenser and boiling flask. Make sure the connections are sealed so that no water escapes. Turn the heating mantle up to high.

4. Allow the water extraction process to continue for 24 hours.

5. After 24 hours, turn off the heating mantle and allow the boiling flask to cool at room temperature for 1 hour.

6. Once cool enough to touch, remove the boiling flask and dispose of water and extractives. Remove as much water as possible from the extraction tube. Be observant as to make sure no biomass escapes the thimble during this process.

7. Add 125 mL of ethanol (190 proof) to a 250 mL boiling flask. Place the flask on the heating mantle. Connect the extraction tube (with the thimble still inside) to the condenser and boiling flask. Make sure the connections are sealed so that no ethanol escapes. Turn the heating mantle up to high.

8. Allow the ethanol extraction process to continue for 24 hours.

9. After 24 hours, turn off the heating mantle and allow the boiling flask to cool at room temperature for 1 hour.

10. Once cool enough to touch, remove the boiling flask and dispose of ethanol and extractives. Remove as much ethanol as possible from the extraction tube. Be observant as to make sure no biomass escapes the thimble during this process.

11. Remove the thimble from the extraction tube.

12. For thimbles containing control samples, place thimbles on a cookie sheet and dry in a convection oven set to 43 ˚C overnight. Turn the thimbles and mix the biomass periodically to achieve even drying. After drying, weigh and record the final weight of the thimble + biomass. Save 1 gram of biomass for moisture content analysis. The remaining biomass can be used for compositional analysis.

13. For thimbles containing torrefaction samples, place thimbles on a cookie sheet and dry in an air-oven dryer set to 105 ˚C overnight. Turn the thimbles and mix the biomass periodically to achieve even drying. After drying, weigh and record the final weight of the thimble + biomass. The biomass can then be used for compositional analysis.

Note: Control samples must be dried at temperatures below 45 ˚C because of potential sugar decomposition. Some moisture will still be left in control samples after extraction. This must be accounted for when determining the final oven dry weight (ODW) of the sample. Torrefaction samples can be dried at 105 ˚C after extraction because torrefaction temperatures would have already decomposed sugars that would have decomposed at 105 ˚C. Since torrefaction samples were dried at 105 ˚C for over 4 hours, the final biomass weight was considered the ODW.

Calculating Percentage Loss due to Extraction

$Initial\ Mass\ (biomass) = Int.\ Mass\ (biomass + thimble) - Int.\ Mass\ (thimble)$

$Final\ Mass\ (biomass) = Fin.\ Mass\ (biomass + thimble) - Int.\ Mass\ (thimble)$

$$ODW_{int.} = Initial_{biomass} * \left| \frac{(100 - Int.MC\%_{wb})}{100} \right|$$

$$(Control\ Samples)\ \ ODW_{Fin.} = Final_{biomass} * \left[\frac{(100 - Fin.MC\%_{wb})}{100} \right]$$

$$(Torrefaction\ Samples)\ \ ODW_{Fin.} = Final_{biomass}$$

$$Extractives\ (g) = ODW_{int.} - ODW_{Fin.}$$

$$\%\ Extractives = \frac{Extractives}{ODW_{int.}} * 100$$

Note: The initial moisture content of the control samples was the moisture content measured in the biomass before extraction. The initial moisture content of the torrefaction samples was the moisture content measured in the biomass after torrefaction was completed. The percentage of extractives will later be used to determine the total composition of lignin and sugars in the biomass.

NREL Determination of Structural Carbohydrates and Lignin in Biomass

Materials

- Balance, accurate to 0.1 mg
- Weighing paper
- Air-Oven Dryer
- Muffle Furnace
- Water Bath
- Autoclave
- Vacuum Filtration setup
- Desiccator
- HPLC system
- UV-Visible spectrophotometer
- Automatic burette
- Pressure tubes (glass, minimum 90 mL capacity)
- Teflon caps
- O-ring seals
- Stir rods
- Filtering Crucibles (25 mL, porcelain, medium porosity)
- Filtration flasks (250 mL)
- Filtration flask funnels
- Erlenmeyer flasks (50 mL)
- Adjustable pipettors
- pH paper
- Disposable syringes with .2 µm syringe filters
- Autosampler vial
- UV Cuvette
- Centrifuge
- Centrifuge
- Cookie sheet

Reagents

- 72% sulfuric acid
- Calcium Carbonate
- Distilled Water
- SRS sugar concentrations

Procedure

1. Obtain the needed amount of filtering crucibles. Make sure the crucibles are labeled with a permanent marker. Place the crucibles in a muffle furnace set at 575 ±25 ˚C for a minimum of 4 hours. Allowing time for the furnace to warm up, crucibles were left in the furnace overnight. Remove the crucibles and place in a desiccator until the crucibles are needed in Step 9.

2. Place a sheet of weighing paper on the balance. Tare the balance. Weigh 300.0 ± 10 mg of sample onto the weighing paper. Record the initial weight of the sample. Carefully transfer the biomass into a pressure tube. Place the weighing paper back onto the scale. Subtract the weight of any remaining sample on paper from the initial weight. Repeat this step for each sample.

3. Add 3 mL of 72% sulfuric acid to the pressure tubes. Stir the samples with a stir rod for one minute.

4. Place the pressure tubes in a water bath that is set at 30 ˚C for 60 ± 5 minutes. Stir the samples every 20 minutes to ensure even acid to particle contact.

5. After 60 minutes, remove the pressure tubes from the water bath. Using an automatic burette, add 84 mL of distilled water to the pressure tubes. Place a Teflon cap on the pressure tube, and cap with an O-ring seal. Mix the concentration by inverting the pressure tube numerous times.

6. Prepare a sugar recovery standard (SRS). This standard is used to correct for losses due to destruction of sugars during dilute acid hydrolysis. The SRS included D-(+)glucose, D-(+) xylose, and –L(+)arabinose because those are the main sugars found in big bluestem and CRP biomass. Weigh out the required (Ask Feng)

7. Place the SRS and the sample pressure tubes in an autoclave for 60 minutes at 121 ˚C. After the allotted time, slowly cool the pressure tubes to room temperature.

8. Add 420 mg of calcium carbonate into a 50 mL Erlenmeyer flask. Prepare a flask for each sample and the SRS. Empty the SRS into a flask.

9. Weigh the filtration crucibles and record the weight to nearest 0.1 mg. Be sure not to touch the crucibles before weighing due to potential error in ash weighing results.

10. Obtain UV cuvettes, one for each sample

11. Prepare the vacuum filtration system. Connect the filtration flask to the system. Place a filtration funnel and crucible on the flask. Turn on the pump. Uncap the pressure tube and slowly pour the sample into the crucible. Once the pressure tube is empty and the liquids are filtered, turn off the pump. Remove the funnel and crucible; be

observant as to make sure no biomass is lost from the crucible. Extract 5 mL of the filtered solution and dispense in a 50 mL Erlenmeyer flask that was prepared earlier. Extract an additional 1 mL and transfer to a UV cuvette. Repeat for each sample.

12. Place the funnel and crucible back on the filtration flask and turn on the pump. Remove the remaining solids in the pressure tube by washing with distilled water and pouring into the crucible. Continue washing until all solids are removed.

13. Once the liquids are filtered from the solids in the crucible, turn off the pump. Remove the crucibles and place on a cookie sheet. Transfer the crucibles to an air-oven dryer and dry at 105 ˚C for a minimum of 4 hours. After drying, remove the crucibles and cool in a desiccator. Once cool, weigh the crucible and the acid insoluble residue (AIR) and record the weight to the nearest 0.1 mg. This will later determine the acid insoluble lignin.

14. Analyze for ash content. Place the crucibles in the muffle furnace set at 575 ± 25 ˚C for 24 hours. Remove the crucibles and cool in a desiccator for 60 minutes. Weigh the crucible and ash. Record the weight to the nearest 0.1 mg. Be sure not to touch the crucibles before weighing due to potential error in ash weighing results.

15. Prepare the UV-Visible spectrophotometer. Place a cuvette with distilled water in the blank and calibrator the spectrophotometer. Analyze the samples in the cuvettes and record the absorbance wavelength.

16. Stir the liquid samples and SRS with the calcium carbonate in the Erlenmeyer flask from Step 11 with a stirring rod. Check the pH of the solution with pH paper. If the solution is below pH 5, add more calcium carbonate to neutralize the solution. Stop adding calcium carbonate when the solution is between pH 5-6.

17. Add 1 mL of solution of each sample to a centrifuge vial. Centrifuge for 3 minutes at 7000 rpm. Pour the liquid into a disposable syringes with a 0.2 μm syringe filters. Plunge the liquid into an autosampler vial. Repeat this step for each sample and the SRS. In addition, prepare another SRS sample by adding 0.5 mL into an autosampler vial to be analyzed. The difference between the SRS samples will provide a control of how the autoclaving and calcium carbonate affected the sugars. The samples are now ready for HPLC analysis.

18. Log and enter the samples into the HPLC analyzer. The results provided from this analysis will be used in the following equations to determine the concentration of glucose, xylose, and arabinose.

Equations Used For Compositional Analysis

1. The initial ODW must be calculated in order to determine the weight percentage of acid insoluble residue (% AIR), acid insoluble lignin (% AIL), acid soluble lignin (% ASL), and ash content (% ASH). For control samples, the initial moisture content of the biomass is equal to the moisture content calculated after drying following the extraction phase. Torrefaction samples can be assumed to have 0% moisture content since it was dried at 105 ˚C for more than 4 hours. Therefore, the ODW of torrefaction samples equals the initial weight.

$$(Control\ Samples)\ \ ODW_{Int.} = Initial_{biomass} * \left[\frac{(100 - Int.MC\%_{wb})}{100} \right]$$

$$(Torrefaction\ Samples)\ \ ODW_{Int.} = Initial_{biomass}$$

$$\%\ AIR = \frac{(Weight_{crucible+AIR} - Weight_{crucible})}{ODW_{Int.}} * 100$$

$$\%\ AIL = \left[\frac{(Weight_{crucible+AIR} - Weight_{crucible}) - (Weight_{crucilbe+ash} - Weight_{crucible})}{ODW_{Int.}} \right] * 100$$

$$\%\ ASL = \frac{UV_{abs} * Volume_{filtrate}}{\varepsilon * ODW_{Int.}} * 100$$

ε = 30 L/g cm (absorptivity of biomass at specific wavelength)

Volume $_{filtrate}$ = 87 mL

$$\%\ Lignin_{Extract\ Free} = \%\ AIL + \%\ ASL$$

$$\%\ Lignin_{As\ recieved} = \%\ Lignin_{Extract\ Free} * \frac{(100 - \%\ Extractives)}{100}$$

$$\%\ Ash = \frac{(Weight_{crucilbe+ash} - Weight_{crucible})}{ODW_{Int.}} * 100$$

2. The percentage of each sugar can be calculated using the HPLC results.

$$C_{Corr.} = \frac{C_{HPLC}}{\%\ R_{sugar} / 100}$$

C $_{Corr.}$= sugar concentration after hydrolysis correction

C $_{HPLC}$= sugar concentration determined by HPLC

% R $_{sugar}$= average recovery of a specific SRS component

$$C_{anhydro} = C_{Corr.} * Anhydro\ correction$$

$$\%\ Sugar_{Extract\ Free} = \frac{C_{anhydro} * Volume_{filtrate} * \frac{1\ g}{1000\ mg}}{ODW_{Int.}} * 100$$

$$\%\ Sugar_{As\ Recieved} = \%\ Sugar_{Extract\ Free} * \frac{(100 - \%\ Extractives)}{100}$$

Appendix D - Big Bluestem Torrefaction - Dry Matter Loss

˚C, min.	Date	Mass Initial (g)	Initial Dry Matter (g)	Mass Final (g)	Final Dry Mass (g)	Total % loss	% Dry Matter Loss	Final MC % (wb)	Final MC % (db)
200,15	1/14	11.0	8.89	8.0	7.83	27.27	11.87	2.07	2.11
	1/29	13.2	10.67	9.2	9.03	30.30	15.35	1.855	1.885
200,30	1/14	11.6	9.37	8.4	8.22	27.59	12.26	2.085	2.13
	1/29	16.4	13.25	11.8	11.65	28.05	12.08	1.26	1.275
200,45	1/14	10.2	8.24	7.2	7.06	29.41	14.36	1.96	2
	1/24	13.4	10.83	9.8	9.63	26.90	11.05	1.715	1.745
250,15	1/15	12.0	9.70	7.6	7.49	36.67	22.72	1.395	1.415
	1/28	11.2	9.05	7.2	7.08	35.70	21.80	1.705	1.735
250,30	1/25	12.4	10.02	7.6	7.51	38.70	25.10	1.24	1.26
	1/31	12.8	10.34	8.4	8.33	34.40	19.51	0.885	0.89
250,45	1/15	12.6	10.18	7.8	7.73	38.10	24.05	0.855	0.86
	1/25	14.0	11.31	8.8	8.68	37.10	23.29	1.38	1.405
300,15	1/15	14.4	11.64	8.0	7.96	44.40	31.60	0.5	0.5
	1/24	14.8	11.96	9.0	8.86	39.20	25.90	1.53	1.555
300,30	1/24	16.2	13.09	9.0	8.86	44.40	32.32	1.56	1.585
	1/29	20.4	16.49	12.4	12.29	39.22	25.45	0.885	0.89
300,45	1/24	16.8	13.58	9.4	9.27	44.04	31.72	1.39	1.41
	1/25	15.6	12.61	7.8	7.72	50.00	38.77	1.035	1.045
Pre-Dry									
250,15	2/1	11.2	10.38	8.6	8.50	23.2	18.10	1.165	1.175
	2/1	10.6	9.82	8.6	8.49	18.9	13.59	1.315	1.33
250,30	2/1	10.2	9.45	8	7.91	21.6	16.27	1.075	1.09
	2/1	10.8	10.01	8.6	8.53	20.4	14.74	0.79	0.8
250,45	2/1	12.6	11.68	9.4	9.33	25.4	20.11	0.77	0.775
	2/4	13	12.05	9	8.91	30.8	26.01	0.965	0.975

Appendix E - CRP Torrefaction – Dry Matter Loss

˚C, min.	Date	Mass Initial (g)	Initial Dry Matter (g)	Mass Final (g)	Final Dry Mass (g)	Total % loss	% Dry Matter Loss	Final MC% (wb)	Final MC% (db)
200,15	1/9	11.2	9.15	8.4	8.18	25	10.61	2.625	2.700
	1/16	11.8	9.64	9	8.86	23.7	8.08	1.535	1.560
200,30	1/8	14.4	11.76	10.6	10.35	26.39	12.05	2.380	2.560
	1/16	10.6	8.66	8	7.89	24.5	8.90	1.385	1.400
200,45	1/9	11.4	9.31	8.6	8.44	24.56	9.33	1.805	1.840
	1/16	11.6	9.48	8.2	8.09	29.3	14.62	1.320	1.335
250,15	1/7	15.4	12.58	10.6	10.37	37.66	17.62	2.215	2.280
	1/17	11	8.99	8	7.86	27.27	12.57	1.780	1.815
250,30	1/10	11.6	9.48	8.2	8.03	29.31	15.26	2.065	2.110
	1/17	12.2	9.97	8.2	8.07	32.78	19.00	1.545	1.570
250,45	1/9	11.6	9.48	8.4	8.21	27.59	13.32	2.205	2.250
	1/22	12.2	9.97	8.2	8.09	32.79	18.86	1.375	1.395
300,15	1/10	11	8.99	5.8	5.75	47.27	35.99	0.810	0.820
	1/22	14	11.44	8.6	8.48	38.57	25.84	1.370	1.385
300,30	1/10	11.8	9.64	6.4	6.32	45.76	34.44	1.240	1.260
	1/23	13.2	10.78	7.8	7.61	40.9	29.40	2.390	2.450
300,45	1/18	13.4	10.95	7.2	7.10	46.27	35.16	1.405	1.425
	1/23	13.2	10.78	7	6.89	46.97	36.10	1.560	1.585
Pre-Dry									
250,15	2/4	10	9.16	7.6	7.47	24	18.47	1.74	1.77
	2/4	10.4	9.53	7.8	7.64	25	19.81	2.06	2.46
250,30	2/4	11.2	10.26	8.4	8.32	25	18.88	0.93	0.94
	2/4	12.4	11.36	9	8.86	27.4	22.02	1.58	1.60
250,45	2/4	11	10.08	8.8	8.65	20	14.14	1.695	1.73
	2/4	12.8	11.72	10.4	10.30	18.75	12.13	0.94	0.95

Appendix F - Calorific Value of Big Bluestem Biomass

˚C, min.	Date	Dry Matter Loss %	Final MC (wb)	Actual CV (kJ/kg)	Calculated CV (dried) (kJ/kg)	Energy Recovery %	Energy Density
Control	1/28	0	19.2	15,167	18,771	100	1
	1/28	0	19.2	15,080	18,663	100	1
200,15	1/14	11.87	2.07	18,334	18,722	88.17	1.00
	1/29	15.35	1.86	18,573	18,924	85.59	1.01
200,30	1/14	12.26	2.09	18,525	18,919	88.70	1.01
	1/29	12.08	1.26	18,647	18,885	88.71	1.01
200,45	1/14	14.36	1.96	18,856	19,233	88.01	1.03
	1/24	11.05	1.72	18,679	19,005	90.33	1.02
250,15	1/15	22.72	1.40	20,112	20,397	84.22	1.09
	1/28	21.80	1.71	19,114	19,446	81.25	1.04
250,30	1/25	25.10	1.24	19,790	20,038	80.20	1.07
	1/31	19.51	0.89	19,805	19,982	85.94	1.07
250,45	1/15	24.05	0.86	20,306	20,481	83.12	1.09
	1/25	23.29	1.38	20,197	20,480	83.94	1.09
300,15	1/15	31.60	0.50	21,134	21,240	77.63	1.13
	1/24	25.90	1.53	20,197	20,511	81.21	1.10
300,30	1/24	32.32	1.56	21,110	21,445	77.55	1.15
	1/29	25.45	0.885	20,595	20,779	82.77	1.11
300,45	1/24	31.72	1.39	21,520	21,823	79.62	1.17
	1/25	38.77	1.035	21,349	21,572	70.58	1.15
Pre-Dry							
250,15	2/1	18.10	1.17	20,008	20,244	88.59	1.08
	2/1	13.59	1.32	19,400	19,659	90.76	1.05
250,30	2/1	16.27	1.08	19,541	19,753	88.38	1.06
	2/1	14.74	0.79	19,567	19,723	89.85	1.05
250,45	2/1	20.11	0.77	20,044	20,200	86.23	1.08
	2/4	26.01	0.97	19,842	20,035	79.21	1.07

Appendix G - Calorific Value of CRP Biomass

˚C, min.	Date	Dry Matter Loss %	Final MC% (wb)	Actual CV (kJ/kg)	Calculated CV (dried) (kJ/kg)	Energy Recovery %	Energy Density
Control	1/28	0	18.3	15,003	18,364	100	1.00
	1/29	0	18.3	14,995	18,354	100	1.00
200,15	1/9	11.87	2.625	18,351	18,846	90.47	1.03
	1/16	8.79	1.535	18,475	18,763	93.22	1.02
200,30	1/8	13.69	2.380	18,586	19,039	89.50	1.04
	1/16	9.77	1.385	18449	18,708	91.94	1.02
200,45	1/9	10.29	1.805	18,408	18,746	91.60	1.02
	1/16	17.12	1.320	18,774	19,025	85.89	1.04
250,15	1/7	21.38	2.215	19,532	19,974	85.53	1.09
	1/17	14.37	1.780	18,997	19,341	90.21	1.05
250,30	1/10	18.01	2.065	18,615	19,008	84.88	1.04
	1/17	23.46	1.545	19,507	19,813	82.60	1.08
250,45	1/9	15.37	2.205	18,878	19,304	88.99	1.05
	1/22	23.25	1.375	19,271	19,540	81.69	1.06
300,15	1/10	56.21	0.810	20,116	20,280	48.37	1.10
	1/22	34.85	1.370	20,259	20,540	72.89	1.12
300,30	1/10	52.53	1.240	20,846	21,108	54.58	1.15
	1/23	41.65	2.390	20,649	21,155	67.24	1.15
300,45	1/18	54.22	1.405	21,567	21,874	54.55	1.19
	1/23	56.50	1.560	21,160	21,495	50.93	1.17
Pre-Dry							
250,15	2/4	18.47	1.74	18,852	19,186	85.20	1.05
	2/4	19.81	2.06	19,144	19,547	85.38	1.06
250,30	2/4	18.88	0.93	19,489	19,672	86.92	1.07
	2/4	22.02	1.58	19,248	19,557	83.07	1.07
250,45	2/4	14.14	1.695	19,045	19,373	90.60	1.06
	2/4	12.13	0.94	19,371	19,555	93.59	1.07

Appendix H - Elemental Analysis of Big Bluestem biomass

˚C, min.	Date	Weight (mg)	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen
Control	1/28	5.00	47.35	4.89	1.40	0.97	45.39
200,15	1/14	4.80	48.74	5.52	1.72	1.82	42.2
	1/29	3.03	48.23	5.84	1.26	1.52	43.15
200,30	1/14	3.10	47.91	5.28	1.65	1.4	43.76
	1/29	2.65	49.65	5.87	1.38	1.54	41.56
200,45	1/14	4.36	49.11	5.34	1.55	1.38	42.62
	1/24	3.74	48.77	5.57	1.76	1.45	42.45
250,15	1/15	3.74	51.37	5.56	1.82	1.45	39.8
	1/28	3.16	50.80	5.64	1.53	1.5	40.53
250,30	1/25	4.03	51.91	5.39	1.55	1.4	39.75
	1/31	3.70	49.90	5.49	1.71	1.46	41.44
250,45	1/15	4.59	53.10	5.31	2.09	1.39	38.11
	1/25	3.70	51.97	5.46	1.85	1.43	39.29
300,15	1/15	4.10	53.51	5.24	1.73	1.4	38.12
	1/24	3.66	52.20	5.47	1.73	1.48	39.12
300,30	1/24	4.30	54.18	5.28	1.98	1.38	37.18
	1/29	4.08	51.48	5.35	1.73	1.41	40.03
300,45	1/24	3.75	54.87	5.23	2.04	1.41	36.45
	1/25	2.59	55.26	5.73	1.82	1.59	35.6
Pre-Dry 250,15	2/1	2.77	50.91	5.96	1.82	1.62	39.69
250,30	2/1	2.75	52.22	6.03	1.66	1.64	38.45
	2/1	3.15	51.02	5.61	1.59	1.53	40.25
250,45	2/1	2.75	52.73	5.79	1.75	1.58	38.15
	2/4	3.22	51.65	5.58	1.56	1.51	39.7

Appendix I - Elemental Analysis of CRP biomass

˚C, min.	Date	Weight (mg)	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen
Control	1/28	4.55	46.55	5.37	1.70	1.41	44.97
200,15	1/9	4.81	47.61	5.54	2.02	1.42	43.41
	1/16	4.23	48.13	5.59	1.98	1.48	42.82
200,30	1/8	3.63	48.43	5.64	1.88	1.47	42.58
	1/16	3.54	48.16	5.62	1.78	1.51	42.93
200,45	1/9	2.59	48.26	5.98	1.86	1.65	42.25
	1/16	2.85	47.61	5.67	1.72	1.59	43.41
250,15	1/7	3.20	49.38	5.62	2.08	1.51	41.41
	1/31	3.09	49.11	5.63	1.93	1.53	41.80
250,30	1/10	3.67	49.37	5.41	2.17	1.40	41.65
	1/17	3.82	50.31	5.46	2.07	1.45	40.71
250,45	1/9	3.19	48.60	5.59	2.03	1.50	42.28
	1/22	4.14	49.94	5.25	1.79	1.39	41.63
300,15	1/10	4.52	51.71	5.11	2.35	1.34	39.49
	1/22	3.39	51.07	5.45	1.78	1.46	40.24
300,30	1/10	3.56	53.28	5.09	2.13	1.37	38.13
	1/23	4.96	52.54	5.04	1.98	1.33	39.11
300,45	1/18	3.52	55.19	5.39	2.24	1.42	35.76
	1/23	2.92	55.82	5.57	2.42	1.52	34.67
Pre-Dry							
250,15	2/4	2.54	49.46	5.96	1.93	1.63	41.02
	2/4	3.83	47.66	5.26	1.67	1.40	44.01
250,30	2/4	3.14	49.45	5.60	1.83	1.53	41.59
	2/4	4.76	49.34	5.25	1.92	1.20	42.29
250,45	2/4	4.63	35.26	4.01	1.32	1.11	58.30
	2/4	3.06	49.60	5.57	1.93	1.60	41.30

Appendix J - CRP and Big Bluestem- *Water and Ethanol Extraction*

Sample	Initial (g)	MC (w) Initial %	ODW Int.(g)	Final (g)	MC (w) Final%	ODW Fin.(g)	Extraction %
CRP Control	5.52	3.83	5.31	3.85	2.75	3.74	29.46
BB Control	4.17	3.88	4.01	2.79	2.73	2.72	32.15

Sample	Date	Initial (g)	Final (g)	Extraction %
CRP 200,30	2/13	4.13	2.78	32.60
	2/20	4.43	3.03	31.64
CRP 250, 30	2/13	4.11	2.94	28.56
	2/20	5.04	3.59	28.65
CRP (Pre-Dry) 250,30	2/13	4.91	3.64	25.90
	2/13	4.26	3.11	26.90
CRP 300,30	2/13	3.80	2.94	22.52
	2/20	4.06	2.84	30.05
Big Blue 200,30	2/13	3.99	2.69	32.61
	2/20	6.27	4.51	28.07
Big Blue 250,30	2/20	4.53	3.35	26.00
	2/20	4.29	3.17	26.12
BB (Pre-Dry) 250, 30	2/13	4.28	3.22	24.84
	2/13	4.46	3.36	24.65
Big Blue 300,30	2/20	4.06	3.03	25.46
	2/20	4.40	3.35	23.88

Appendix K - CRP and Big Bluestem- *Acid Hydrolysis (Extract Free)*

Sample	Date	AIL %	ASL %	Glucan %	Xylose %	Arabinose %	Ash %
CRP 200,30	2/13	19.18	1.65	39.78	22.58	5.86	0.46
	2/20	19.18	1.49	41.76	23.67	7.10	0.47
CRP 250, 30	2/13	20.72	1.61	39.68	19.21	5.14	0.42
	2/20	20.72	1.31	35.95	15.74	4.79	0.71
CRP (Pre-Dry) 250,30	2/13	21.59	1.32	38.13	17.56	4.80	0.63
	2/13	21.59	1.54	38.54	18.30	4.39	0.90
CRP 300,30	2/13	25.22	1.13	26.31	10.38	3.03	1.05
	2/20	25.22	0.65	34.84	7.64	3.06	1.34
Big Blue 200,30	2/13	20.13	1.41	41.88	22.38	6.10	1.04
	2/20	20.13	1.25	41.91	25.12	5.16	0.40
Big Blue 250,30	2/20	22.76	1.24	40.77	21.34	4.94	0.53
	2/20	22.76	1.23	35.85	18.64	4.98	0.42
BB (Pre-Dry) 250 30	2/13	20.92	1.50	37.58	18.26	4.47	0.56
	2/13	20.92	1.37	39.13	17.90	2.58	0.46
Big Blue 300,30	2/20	24.86	0.77	27.54	8.44	2.35	0.98
	2/20	24.86	1.02	33.16	13.84	4.39	0.26

Sample	Date	AIL%	ASL %	Glucan %	Xylose %	Arabinose %	Ash %
CRP Control	2/20	17.17	0.58	42.79	24.71	8.07	0.20
BB Control	2/20	17.68	1.24	43.44	25.73	8.42	0.17

AIL= Acid Insoluble Lignin

ASL= Acid Soluble Lignin

Note: Acid insoluble lignin of torrefaction samples is an estimation based on mass balance of the control sample and the dry matter loss of the torrefaction sample.