BIOMASS TORREFACTION - GRINDABILITY AND DUST EXPLOSIBILITY

by

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DEDICATION PAGE

I dedicate this dissertation to my parents, Sanja and Davor Boskovic and to the love of my life, Fariba Davoody.

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ABSTRACT

Torrefaction, a thermo-chemical process, improves properties such as energy density, grindability, hydrophobicity of the biomass. As a result of the altered properties, the biomass behaves more like coal increasing the feasibility of co-firing.

The first part of the work examined how torrefaction affects dust explosiblity characteristics. Both the minimum ignition temperature (MIT) and the minimum explosible (MEC) concentration for a given particle size distribution were measured. Two extremes cases were tested, both under-torrefied samples (200°C) and over-torrefied samples (300°C) as well as a common torrefaction temperature of 250 °C. Three different particle size distributions were tested. Torrefaction temperatures showed minimal to no impact on MEC and MIT.

The second part of the study examined how torrefaction changed the grindability of biomass. Experiments were performed for torrefaction temperature ranges between 200-300 °C using a Hardgrove Grinding Index (HGI) Machine. For co-firing it is necessary to grind coal and torrefied biomass together. Varying volume percentages of coal and biomass were mixed and their overall HGI value was measured. This value was compared with that predicted using individual HGI values of coal and biomass. The predicted values showed reasonable correlation to the actual values.

LIST OF ABBREVIATIONS USED

| ASTM | American Society for Testing and Materials |
|-----------------|--|
| BFB | Bubbling fluidized bed |
| С | Carbon |
| CCS | Carbon Capture and Sequestration |
| CO_2 | Carbon Dioxide |
| CO | Carbon Monoxide |
| °C | Celsius |
| daf | Dry Ash Free |
| db | Dry Basis |
| ED | Energy Density |
| EY | Energy Yield |
| FC | Fixed Carbon |
| MJ | Mega Joule |
| HGI | Hardgrove Grinding Index |
| HPGR | High Pressure Grinding Rollers |
| HHV | Higher Heating Value |
| H_2 | Hydrogen |
| H_2O | Water |
| kWhr/t | Kilo Watt hour per ton |
| kg | Kilogram |
| m | Meter |
| CH ₄ | Methane |
| mm | Millimeter |
| MEC | Minimum explosible concentration |
| MIT | Minimum ignition temperature |
| MY | Mass Yield |
| min | Minutes |
| N_2 | Nitrogen |
| 0 | Oxygen |
| PC | Pulverized coal |
| VS. | Versus |
| VM | Volatile Matter |
| wt | Wet Basis |

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CHAPTER 1 INTRODUCTION

1.1 BACKGROUND

In the next three decades the worlds energy demand will increase by 56%, primarily driven by developing countries including but not limited to China and India. [IEA, 2013] Given that fossil fuels account for approximately 80% of the world's energy demand, as shown in Figure 1, the increase in demand will inevitably have a taxing burden on the remaining supply of the world's fossil fuels.





Figure 1 A look at world energy consumption by fuel type in 2010 [BU Today, 2013]

Figure 2 shows how the annual electrical generation has increased by more than two fold in the last thirty years. It also shows that while renewable sources compromise a larger percentage of the net annual electric load the total fossil fuel consumption continues to increase.



Figure 2 Net Global Electrical Generation [EIA, 2015]

The combination of the increase in energy demand and the decline in fossil fuel reserves, as shown in Figure 3, creates an increasing need for alternative sources of energy. One such abundant source is biomass.

For the work presented biomass will be considered as any and all organic matter that is not fossilized. This includes all organic materials created from plants, animals, and microorganisms [UNFCCC, 2005]. Given that the time required for most biomass species to grow or produce is relatively short, biomass can be considered a renewable source of energy.



Figure 3 Fossil Fuel Reserve Estimates [Ecotricity, 2015]

It is important to understand the origins of the energy source that is stored in all biomass. Biomass can be summarized primarily as a combination of hydrogen, oxygen and carbon. These three elements make up, by weight, about 95% of all woody and herbaceous biomass. The following equations describe the photosynthesis process that is involved in creating biomass. The production of glucose is used for this example. Note that chlorophyll serves as the catalyst.

$$6CO_2 + 6H_2O (+ radiant (solar) energy) \rightarrow C_6H_{12}O_6 + 6O_2$$
(1.1)

The majority of the world's energy resources are directly provided by the sun's rays. Solar energy may be stored as fossil fuels, biomass sources, alternation in wind currents providing wind energy as well as more direct measures through the use of photovoltaic cells. While fossil fuels are the result of anaerobic decomposition of dead organisms, and this is an ongoing process, in order to produce large scales of fossil fuels it can take up to 650 million years. It is for this reason that fossil fuels cannot be considered renewable. This is not the case for many species of biomass. Through the process of photosynthesis, solar energy is stored within biomass and is available for release through the process of combustion. The energy released during the combustion of biomass is an indirect release of solar energy. The process of photosynthesis requires the presence of both CO_2 and H_2O . The CO_2 absorbed from the environment during this process is the same amount that is released during the combustion process. Therefore, biomass can be considered as a greenhouse gas (GHG) neutral and a natural source of energy.

The key difference in the production of fossil fuels and the production of biomass is that biomass is solely formed from living and recently dead biological species. Fossil fuels are a product of the decomposition of biological species over millions of years. The following list is a sample of sources of biomass.

- Wood, plants, grass, algae
- Municipal waste, bio solids, sewage, landfill gas
- Bark, leaves, sawdust

These sources can be placed into two main categories, virgin and waste biomass and then virgin biomass can be divided into four further subcategories. These are as follows: woody biomass, herbaceous biomass, fruit biomass and blends and mixtures. This thesis primarily focuses on the use of woody biomass, poplar. Herbaceous biomass pertains to

those plants that have very short life spans, and cycle through on a yearly basis. These include wheat straws, grasses, cereal crops, etc.

Poplar was used as a sole source of biomass for all experiments in this thesis due to it being readily available in a uniform dowel shape that could be used to produce consistent results. Poplar is a lignocellulosic biomass. Lignocellulosic biomass is not digestible by human beings and is formed of three primary constituents. These major polymers are lignin, cellulose, and hemicellulose. The availability of biomass throughout the world is abundant and relatively well distributed. The plethora of biomass can be used as a local energy source for countries lacking fossil fuel reserves. It can therefore alleviate some of the issues surrounding foreign dependence on energy sources.

In order for biomass to be used as a fuel it must be converted into a more suitable form of solid, liquid, or gaseous fuel. The differences in chemical composition of biomass and coal presents a significant obstacle for coal based boilers. Coal contains about 75-90% carbon while biomass is normally around 45-50%. This means that the heating value of raw biomass is lower. This is well described by H/C and O/C ratios. Biomass has a higher H/C ratio and O/C ratio than coal, as can be seen in Figure 4. This difference means that for specific combustion conditions the design characteristics for coal will not be applicable to biomass. A large percentage of modern day boilers rely on the use of coal as its fuel source. It would be expensive to redesign these boilers so that they could operate under designed conditions using raw biomass as its fuel. Hence, the use of untreated biomass in current boilers would be expensive, unreliable and unrealistic for the following reasons:

1. Lower heating value requiring higher feed rates.

- 2. Difficult to grind and transport.
- 3. Unstable storage requirements.

4. High tar concentration causing buildups and plugging, due to the much higher volatile content of biomass as compared to coal



Figure 4 Composition, O/C and H/C Ratios of Different Species [Prins, 2006]

Cofiring can use up to 20% biomass in a coal-fired boiler and if implemented correctly

can produce the following benefits:

-potential lower fuel costs

-reduction in sulfur oxide and NOx emissions

-decrease in fuel gas opacity

It should be noted that in order for the plant to have lower fuel cost it must use biomass fuels that cost at least 20% less than coal on a thermal basis. This can be achieved by using waste biomass that is locally abundant.

1.1.1 Economic aspect of Torrefaction Process

Torrefaction greatly increases the feasibility and practicality of co-burning biomass with coal [Bergman et al, 2005; Basu, 2013], which in turn helps produce sustainable power with reduced greenhouse gas emission but without the massive extra investment required for carbon capture & storage. Since torrefaction makes biomass more brittle, the grinding or milling of torrefied biomass is likely to produce considerably more amounts of fine particles than that by raw biomass. Such fine dust is advantageous for combustion of the fuel in a co-fired pulverized coal boiler due to the increased overall exposed surface area of fuel particles, but for the same reason the fine dust could pose explosion hazards. Presently, the commercial use of torrefied biomass is in its early stage. Not much information is available on its economic viability. The energy conversion efficiency of commercial torrefaction process is expected to be in the range of 95-97% [Batidzirai et al. 2013]. This accounts for minor energy loss in this pretreatment process. The cost of torrefied biomass depends significantly on the price of biomass but it is estimated in the range of 3.3 to 4.8 \$/GJ_{LHV} [Batidzirai et al., 2013]. Although torrefied wood pellet brings a large number of added benefits its cost of production is higher than that of wood pellet [Ehrig et al., 2013], but the potential of achieving higher cofiring ratios which in turn will result in further reduction in CO2 emission. This will also benefit the economic value and could justify the extra price for torrefied biomass pellet [Koppejan et al., 2012].

Not much information is available on incidences of explosion in commercial plants that use torrefied wood.

One potential solution to the limitations of using raw biomass is a heat treatment process called torrefaction. The following presents an overview of torrefaction and an introduction to the main aspects studied in this thesis. An overview of grinding is presented as well as an introduction to dust explosibility.

1.2 INTRODUCTION

Torrefaction is a pretreatment process where biomass is slowly heated (50°C/min) by an external source in an oxygen limited environment, so as to avoid or minimize oxidation, at temperatures of about 200-300°C. The biomass is held at that temperature for varying periods of time, in the range of 20-180 minutes. This results in a product that has near complete degradation of its hemicellulose content and an increase in energy density. The process of torrefaction can be split into three parts: initial heating, drying and torrefaction (heating at a constant temperature). The torrefaction process improves many properties (energy density, grindability (ease of grinding), hydrophobicity) of the biomass so as to make it behave more like coal while still producing a potentially carbon-neutral fuel. Torrefaction greatly increases the feasibility and practicality of co-burning a mixture of coal and biomass. Torrefied biomass is a carbon rich solid, with significantly lower H/C and O/C ratio. Figure 5 summarizes the process.



Figure 5 Torrefaction Mass and Energy Schematic

Torrefaction can be considered as mild pyrolysis as it exhibits the same decomposition reactions as the early onsets of pyrolysis. The following is a summary of the torrefaction process:

-Initial heating from room temperature to the boiling temperature of the moisture content ($\sim 100 \ ^{\circ}$ C)

-Drying Process, this is the most energy intensive process due to the high moisture content of biomass and the high latent heat of vaporization of water. Moisture content can range from 5% to as high as 60%.

-Post Drying, the temperature is increased from 100 °C to approximately 200 °C upon which mild pyrolysis begins.

-Torrefaction. An endothermic process below temperatures of about 280 °C, where volatile gasses are driven off, resulting in biomass with a lower mass yield and higher

energy density. Above temperatures of 280 °C, torrefaction becomes mildly exothermic where core temperatures will exceed that of the reactor temperatures.

The maximum temperature of the torrefaction process should be defined as 300°C. This is to limit the degradation of lignin and cellulose. Figure 6 shows how the constituents of lignocellulosic biomass degrade at varying temperatures. Torrefaction, unlike pyrolysis, aims to maximize solid yield which in turn forces a process that uses a slow heating rate. The overall goal of torrefaction is to produce a solid fuel that maximizes energy and mass yield. By balancing the loss in mass yield and energy yield one can obtain a final product that is up to 30% higher in energy density. While carbonization, charcoal production, produces a more energy dense product it also has a very low energy yield. A summary is shown in Tables 2 and 3. The following describes these three terms in detail.

Mass yield on dry ash free basis:

$$MY_{daf} = \frac{mass \ torrefied \ biomass \ (daf)}{mass \ orginial \ biomass \ (daf)}$$
(1.2)

Energy Yield:

$$EY = \frac{net \ energy \ torrefied \ biomass}{net \ energy \ orginial \ biomass}$$
(1.3)

Energy density on dry ash free basis:

$$ED_{daf} = \frac{EY}{MY_{daf}} = HHV_{daf}$$
(1.4)

During torrefaction, low energy dense gases are driven off, primarily carbon dioxide (due to decarboxylation), acetic acid, formic acid, and some methanol and carbon monoxide. In order to better understand the torrefaction process it's important to look at the composition of biomass. Raw biomass is typically 70% volatile, 25% fixed carbon and about 5% ash on a dry basis.



Figure 6: Degradation of Hemicellulose, Cellulose and Lignin at Different Temperature [Basu, 2013]

A summary is shown in Tables 1, 2 and 3. The volatile gases contain up to 400 different species; however, they primarily contain carbon dioxide, carbon monoxide, water, formaldehyde, acetic acid, furfural, methanol and formic acid.

| Table 1 Proximate Composition of Different Types of Biomass [Forschungszentrum Kansrune, 2007] | | | |
|--|-------|-----|------|
| Dry (%) | Wheat | Hay | Wood |
| Volatiles | 69 | 65 | 84 |
| Fixed Carbon | 23 | 21 | 16 |
| Ash | 8 | 14 | 0.5 |

Table 1 Proximate Composition of Different Types of Biomass [Forschungszentrum Karlsruhe, 2007]

Table 2 Proximite Composition Comparison between Charcoal, Coal and Torrefied Wood

| | Torrefied | Charcoal | Coal (Bituminous) |
|------------------------|-----------|----------|-------------------|
| | Wood | | |
| Moisture (%wb) | 2-5 | 1-5 | 3-20 |
| Volatiles (%db) | 55-65 | 10-12 | 28-45 |
| Fixed Carbon (%db) | 28-35 | 85-87 | 45-60 |
| Mass Yield | 80% | 30% | N/A |
| Energy Density (MJ/kg) | 20-24 | 30-32 | 24-33 |

Table 3 Summary of carbonization and torrefaction of a 1kg raw sample

| | Total Mass | Energy Density | Total Energy |
|----------------|------------|----------------|---------------------|
| Raw Wood | 1kg | 18 MJ/kg | 18 MJ |
| Charcoal | 0.3 kg | 30 MJ/kg | 9 MJ |
| Torrefied Wood | 0.8kg | 22 MJ/kg | 17.6MJ |

Lignocellulosic biomass, or feedstock, refers to plant biomass that is composed of three primary components, cellulose, hemicellulose, and lignin. The cellulose network is embedded in a matrix of hemicellulose and lignin. The hydrogen bonds and Van der Waals forces between the cellulose chains are what results in crystalline structures. Figure 7 shows in detail this cell structure. Cellulose fibers are responsible for the fibrous structure and anisotropic properties of (woody) biomass and they are bound together through a matrix of mainly hemicellulose and, to a lesser extent, lignin [Bergman et al., 2005]. Both hemicellulose and lignin are considered to be responsible for the tenacity of the biomass.



Figure 7 Schematic of Cell Wall Structure [Bergman, 2005]

A major part of this thesis examines at the effect torrefaction has on grinding. It is believed the crystalline structures are likely altered during the grinding conditions and their alterations may depend on the intensity of the breaking mechanism used. It is believed that the polymer constituents of biomass (hemicellulose, cellulose, lignin) degrade separately [Chen et al., 2011]. The degradation and the intensity of degradation is a function of temperature. In fact, the degradation of each of the constituents occurs within distinct range of temperature as summarized in Table 4 below. Here we note that within the torrefaction temperature range the most reactive fraction of biomass (hemicellulose) degrades while others remain stable [Arias et. al., 2008]. Phanphanich and Mani (2011) noted that hemicellulose in pine decreased steadily from 12% to about

0.5% as the torrefaction temperature was raised from 225 to 300 °C. Owing to the progressive degradation of the cell wall of the wood, which is made of the above polymers, the wood becomes more brittle [Repellin et al., 2010]

Table 4 Degradation Temperatures of Biomass Constituents

| Constituent | Temperature (°C) |
|---------------|------------------|
| Hemicellulose | 225-300 |
| Cellulose | 305-375 |
| Lignin | 250-500 |

Lignocellulosic biomass can be summarized as a piece of reinforced concrete. In this analogy:

Cellulose: the framework – the thick steel rods

Hemicelluloses: the connecting agents – the cement paste

Lignin: the encrusting substance

Figure 6 shows that at temperatures above 250°C, over 60% of hemicellulose will degrade. At temperatures reaching 300 °C it is seen that nearly all (~80-85%) of the hemicellulose has degraded. Notice that at torrefaction temperatures, even above 250°C, lignin and cellulose have depolymerized by about 15-20%. Using the analogy above and the data presented in this paragraph one can infer that because torrefaction causes the degradation of hemicellulose, due to torrefaction, the grinding characteristics of torrefied biomass will be significantly improved. This is a significant advantage of torrefaction and is a major topic of this thesis.



Figure 8 Degradation of Biomass as a Result of Torrefaction [Kumar, 2009.]

Before continuing on with the work in this thesis it is important to get a better understanding of what biomass is and how its composition can be described.

Different types of biomass will have very different properties but they may all be described using a common terminology. This terminology will now be introduced in the following section.

• The *as received composition (ar)* includes the moisture content of the biomass. This is typically reported either at the point of harvesting or at delivery of the fuel. It is the most valid composition to be used in terms of performing combustion calculations and estimating efficiencies. However, the exact as received composition is affected by the moisture content and therefore all factors which affect overall moisture content. As a result, the moisture of a sample may vary between the sampling point, the delivery point and the final analysis in the lab. Although extremely useful for actual applications, the as

received composition is not typically a valid indication for comparisons between biomass types.

• The *dry basis composition (db)* refers to the composition of the biomass excluding all water content. The dry basis is practically unobtainable in real life scenarios as all forms of industrial dryers will leave some residual moisture. This state can only be applicable for laboratory samples. Since in the dry basis state all of the moisture is removed, and this parameter is very difficult to control even between samples of the same batch, different types of biomass can now be directly compared. The dry basis is a good starting point for comparing the properties of different fuel types and is the typical format in which most laboratories report their results.

• *Ash* makes up about 1-5% of biomass. Ash encompasses all inorganic constituents of biomass, including metals and minerals such as potassium and phosphorus.

• The *dry, ash free basis (daf)* refers to the composition of biomass excluding all water and ash content. The dry, ash free basis is an ideal case since the separation of the ash from the organic part of biomass is impossible – in the laboratory and combustion applications, it is the organic part that is separated from the ash. However, this basis allows for the exclusion of all influences of the supply chain and for the direct comparison of the properties of different types of biomass fuels. [Zethraeus, 2013] This terminology is common to all biomass types. It also describes all forms of solid fuels, including coal. In summary, the typical breakdown of the main components of biomass

into over-all categories is: moisture content, organic (or combustible) content and inorganic (or ash) content.



Figure 9 Various ways of describing biomass composition, valid for other solid fuel as well [Zethraeus, 2013]

1.2.1 Proximate Analysis

One way of describing a fuel is by breaking its composition into volatiles, char (fixed carbon) content and ash. This is known as a proximate analysis.

The content of fixed carbon, "char", is calculated by subtracting from 100% of the weight composition of the other two compounds. This is often done in a controlled laboratory furnace.

Most biomass will have much higher volatile content than coals. Herbaceous biomass also tends to have slightly higher volatile content compared to woody biomass or certain agro-industrial residues; a general trend would be that the lower the lignin content, the higher the volatiles. With waste biomass, depending on the fraction, the volatile content can be as high as 90 % of *daf*, with herbaceous it is usually in the range 70-85% and with woody biomass it is usually about 60-80 % of *daf*.

1.2.2 Cellulose, Hemicellulose, Lignin and Extractives

Being a product of the photosynthetic process the dry matter content of herbaceous biomass resources are also typically composed of carbohydrate polymers (cellulose and hemicellulose), phenolic polymers (lignin) and, in lesser quantities, other substances, such as resins, fats and fatty acids, commonly known as extractives.

The measurement of the cellulose, hemicelluloses and lignin content of biomass is not a standard analysis, especially for combustion applications.

One key difference of herbaceous biomass and sewage sludge as compared to woody biomass is the lower weight percentage of lignin and the increased presence of cellulose and hemicelluloses, also fats in the case of sewage sludge.

Since lignin is less oxidized than hemicelluloses, it has a higher heating value and this typically translates to lower heating values of herbaceous biomass as compared to woody biomass or some agro-industrial residues, such as olive press cakes. The lower lignin content also affects, to some extent, the combustion speed. Higher heating value (**HHV**) (also known as gross calorific value (GCV)) is defined by returning all the products of combustion back to the original pre-combustion temperature, and in particular

condensing any vapor produced. Lower heating value (LHV) (*also known as net calorific value (NCV)*) is determined by subtracting the heat of vaporization of the water vapor from the higher heating value.

1.2.3 Ultimate Analysis

The <u>elemental or ultimate analysis</u> is the second typical way to present the components in the organic part of fuels. Instead of grouping compounds based on the chemical structure or the combustion behavior, the ultimate analysis presents directly the main elements present in the organic part of biomass. The main components of biomass are hydrogen, oxygen and carbon. These three elements typically make up over 95% of the total composition.

The ultimate analysis is also commonly referred to as the CHNS analysis on the basis of the most commonly measured elements; for herbaceous biomass, as for waste fractions, chlorine and sulfur are also of major importance. Large presence of chlorine leads to the formation of hydrochloric acid (HCl) during combustion. HCl is highly temperature sensitive and can be very corrosive. The following key points can be made for each element:

<u>*Carbon (C)*</u> is the most important constituent of biomass fuels. It mostly comes from the atmospheric CO_2 that became part of the plant matter during photosynthesis. Carbon represents the major contribution to the overall heating value. During combustion, it is mainly transformed back into CO_2 , which is again released in the atmosphere.

In any combustion application, a part of the carbon is not combusted completely and leads to emissions of unburned gases, typically carbon monoxide or polycyclic aromatic hydrocarbons (PAH). However, this does not correlate to the overall carbon content but rather to combustion conditions and equipment.

The carbon content of the fuel is directly related to its content of lignin, hemicellulose and cellulose. A low lignin content, like with herbaceous biomass, leads to a lower carbon content as compared to woody biomass. Typical values would be between 44 – 50% wt db. Fuels rich in lignin, such as olive kernel, have carbon contents higher than 50% wt db.

<u>Hydrogen (H)</u> is another major constituent of biomass, as can be expected from the chemical structure of the carbohydrate and phenolic polymers. During combustion, hydrogen is converted to H₂O, significantly contributing to the overall heating value. Hydrogen content affects the calculation of the lower heating value from the experimentally measured higher heating value. The weight content of hydrogen, on a dry basis, is usually slightly lower in herbaceous biomass (5.5 – 6 %) than in woody biomass (6 - 8%).

<u>Nitrogen (N)</u> is the most important nutrient for plants. It is absorbed via the soil or the applied N-fertilizers by the plant during its growth. Due to their high growth rate and the application of fertilizers, herbaceous biomass species have a higher N content (0.4 - 1.0 % wt db) compared to woody biomass types – even higher values have been reported for some grains. In some waste fractions, the content of nitrogen may make up a significant

percentage, a fact that contributes significantly to the degradability in biochemical processes like digestion or fermentation.

During combustion and for all practical purposes, nitrogen does not oxidize in any significant quantities and is released in the gas phase as N_2 – therefore, its contribution to the overall heating value is zero. Depending on the combustion conditions, the high nitrogen content of herbaceous biomass may result in high emissions of nitrogen oxides (NOx).

<u>Sulphur (S)</u> is incorporated in several organic structures like amino-acids, proteins and enzymes. With waste fractions, where a mixture of organic substances forms the main part of the fuel, the content of sulphur may in some cases be significant. Along with nitrogen, phosphorus and potassium, it is an important nutrient for plant growth.

The high growth rate of most herbaceous crops means that the sulphur concentration in plant biomass is typically higher than those in woody biomass: while the concentration of sulphur in wood can be as low as 0% (which means below the detection limit of most laboratory devices) and reaches up to 0.1% on a dry basis in exceptional cases, herbaceous biomasses have a sulphur content ranging from 0 to 0.2% or even higher. In waste fractions, values up to approximately 1 % have been reported. Still, the sulphur content of these fuels is lower compared to most coals and certain types of liquid fossil fuels.

During combustion, sulphur is typically oxidized and has a minor contribution to the overall heating value. However, its most important impact relates to gaseous emissions, syngas cleaning in gasification processes and corrosion issues.

<u>Chlorine (Cl)</u> is the most important differentiation between herbaceous biomass and waste biomass on the one side and woody biomass or coals on the other side. While chlorine is typically found in negligible amounts in coals and in wood (< 0.05 % on a dry basis), herbaceous biomass species have a chlorine content ranging from less than 0.1% to 2% or more. Chlorine is absorbed via the plants through a variety of environmental sources and plays a role in certain plant functions. In waste fractions, the main part of the chlorine comes from salt present in food scrapings and from plastic (PVC) that has accidentally been sorted into the organic fraction.

During combustion, chlorine is almost completely vaporized, forming HCl, Cl₂ and alkali chlorides. The problems associated with chlorine stem from issues related to emissions (dioxins, facilitation of aerosol formation) and operation issues, namely fouling and corrosion of metallic surfaces.

<u>Oxygen(O)</u> is a major element in all biomass fuels, as is evident from the nature of the photosynthetic process and the chemical composition of the biomass constituents. Fuel oxygen reduces the amount of air needed for combustion and is found in the combustion products chemically bound in the molecules of CO₂ and H₂O. It should be noted that oxygen is not measured directly – its weight concentration is estimated by subtracting from 100% the concentrations of all other elements (C, H, N, S, Cl) and of the ash content in the dry fuel.

1.3 INTRODUCTION TO GRINDING

Pulverized coal (PC) fired boilers require the fuel to undergo a reduction in particle size to about 75 micron. When biomass is co-fired with coal in a PC boiler it must be ground to comparable sizes. The grinding of fibrous biomass is, however, a very energy intensive process because the fibrous structure and the tenacity nature of woody biomass. A possible solution is to pretreat this biomass using torrefaction to degrade the hemicellulose fractions in the biomass that gave it the fibrous nature. Torrefied biomass significantly reduces the energy required for grinding and can achieve coal like grinding characteristics.



Figure 10: Size Reduction Mechanism, Milling and Grinding

There are many types of grinding mills and pulverizes available in the industrial market. These types include the following:

• The tumbling reservoir of a **ball**, **tube**, **roller**, **media**, **or vertical mill** uses the impact and friction of the feed material, often supplemented by the action of stone or metal shapes.

- Hammer and impactor pulverizers use large hydraulic steel plungers or dropdown arms, either repeatedly or with stead force. Some use cages or chains instead.
- **Ring or disc mills** use both inside and outside surfaces of a rotating circle for grinding.
- **High Pressure Grinding Rollers (HPGR), or roller mills** pulverize material as it moves between two large rollers or a roller and a flat surface. The rolls can be serrated, toothed, or smooth.
- A granulator, cutting, knife, or shredder pulverizer uses numerous evenly spaced blades to finely mince material. Some devices contain both vertically and horizontally blades, producing a confetti-like output. Wood hogs use blades to produce wood chips.
- Rotor, pin, or universal mills use high speed and centrifugal force.
- Jet or fluid energy mills project a stream of feed particles against another jet or a chamber wall.
- **Buhrstone or attrition mills** rotate a grooved stone or metal plate against a stationary one of similar substance.

Figure 11 shows the differences in the material output sizes that can be expected from the different types of reduction tools.
When one is specifying a grinding mill or a pulverizer they must include at least some of the following specifications:

- The **size** of the mill. This can range from pilot/lab to production, e.g., 3.5 to 1600 cu. ft.
- Feed size, material, and hardness of feed must be considered.
- Output size ranges.

Notice that the output must be specified as a range and not as one dimension. No size reduction tool is perfect and simply cannot produce only one size of final product.



Figure 11 Type of Mill and Expected Output Size Range [Bauermeister USA Inc.]

Pulverizers are used to crush glass, aluminum, concrete, plastic, coal, rock, resin, tires, waste, and other materials. They are used in the ceramics, chemical/fertilizer, construction, food processing, pharmaceutical, metallurgy, paint/adhesives, pulp/paper, coal, and recycling industries.

The heart of a pulverized coal-fueled plant is the pulverizer. Problems including but not limited to excessive furnace gas temperatures, poor furnace combustion, overheated superheater tube metals, high desuperheating water flows, and water wall wastage are often traced back to poorly performing pulverizers. Up to 75% of the controllable or correctable efficiency improvements in coal-fired power plants can be attributed to the pulverizers and closely related coal fineness, fuel distribution, fuel-line balance and primary airflow issues.

Improved fuel fineness, achieved only when the pulverizers are in top-notch shape, leads to improved fuel distribution and more surface area of each coal particle for the fuelbound nitrogen to be released in the burner devolatilization zone. Larger coarse coal particles have higher momentum when entrained in air at a certain velocity and are more easily stratified than finer coal particles that have less mass thus lower momentum. Moreover, as coal particle size is reduced the available furnace residence time is more effectively used to complete carbon char burnout before the actively burning products of combustion entering the superheater section of the boiler.

"The prerequisites for optimum pulverizer performance are good grinding element condition, satisfactory spring pressure, and of course, excellent mechanical condition. When these conditions are satisfied, the performance of the mill can then be optimized. The key to good combustion in the furnace is a pulverizer that produces coal with the right fineness." (Storm Technologies Inc.) Fineness and hardness have a more profound effect on pulverizer performance than moisture or feed size. This fact illustrates an important point: the common link for good furnace combustion and good pulverizer performance is fuel fineness. This is why it is important to have a properly tuned pulverizer that is capable of delivering rated fuel flow with satisfactory fuel fineness. The optimum air/fuel ratio and optimum fuel fineness is essential for optimum burner belt combustion. Pulverizer optimization is critical for optimum plant performance, lowest NOx emissions, reliability and maximum unit capacity.

1.5 HARDGROVE GRINDABILITY INDEX

Material properties, such as strength, elasticity and hardness, reflect the ability of a material to be ground and the ease at which this grinding occurs. R. N Hardgrove developed a method in which this ease could be quantified and it is known as the Hardgrove grindability test. The purpose of this test is to measure how different coals behave in commercial sized pulverizers. The test produces what is known as the Hardgrove Grindability Index (HGI). A sample of coal is placed in a ball mill, rotated for a set number of rotations and then the fines are measured and sieved. After the test an HGI value is assessed to the coal. A coal with a higher HGI is considered to be easier to grind. Easier refers to lower energy consumption and higher percentage of finer grinds. Coals that are easiest to grind (having highest grindability index) are those of about 14-30 per cent volatile matter content on the dry mineral-matter free basis. The increase in volatile combustible content of coal sample leads to higher HGI values up until about 30% at which point the HGI begins to deteriorate.

Sengupta (2002) noted the following correlation between statistical grindability index (SGI) and proximate analysis of coal. It was given as;

SGI = 93.25 + M (0.256 + 0.196M) + 3A (1.097 - 0.009A) - 3 VM (1.165 - 0.029 VM)- 5 FC (1.103 - 0.0166 FC) (1.5) where M, A, VM, and FC are percentages of moisture, ash, volatile matter and fixed

carbon respectively, determined on air-dried basis.

Similar to this another correlation was proposed to relate HGI with ultimate analysis of coal [Mathews et al., 2014]:

$$HGI=77.162+3.994*ln[S]-10.920[H]+1.904[M]-0.424[ASH]-11.765*ln([O+N]/[C])$$
(1.6)

1.6 DUST EXPLOSIBILITY

The explosibility behavior of torrefied biomass dust has not been extensively studied. Understanding the explosion characteristics of a particular dust is essential for a safe operating environment.

A combustible dust, air dispersion, and concentrations above the flammable limit, presence of a sufficiently energetic ignition source and some form of confinement are the requirements for a dust explosion. These five requirements form the pentagon of dust explosion as shown in Figure 12.



Figure 12 Dust Explosion Pentagon

How does dust explosion differ from combustion? Consider a larger piece of dry wood. Under an oxidizing environment and in the presence of a heat source the wood will begin to combust and do so in a slow manner. This is due to its minimal surface area. If the wood is chopped into pieces, as would be done for a camp fire, the increase in surface area results in faster combustion. If this division occurs until the size of wood is a particle, .1mm or less, then the wood combusts instantly and this is called an explosion.



Figure 13 Rate of combustion and how it relates to explosions

When a flammable dust is dispersed in air and an ignition source is present the rapid oxidation that results leads to a rapid increase in both temperature and pressure. The resulting increase in pressure can destroy structures and pose as a serious danger to personnel.



Figure 14 Industrial Dust Explosion

Ignition sources can include any of the following:

- Smoldering dust
- Open flames
- Hot surfaces (moving parts, dryers, heaters, etc)
- Heat from mechanical impact
- Electrical arcs

Two parameters that give an overview of the likelihood of a dust explosion are the minimum ignition temperature of a dispersed cloud (MIT) and the minimum explosible concentration (MEC). The severity of a dust explosion is determined by the size-normalized maximum rate of pressure rise (KSt) and the maximum explosion pressure (Pmax). By better understanding the properties of a dust material one can create inherently safer designs and attempt to prevent explosions from occurring in the first place. Risk management is a balance between the likelihood of a disaster occurring and the severity of the damage that may occur as a result of said disaster. Inherently safer designs are quintessential for better risk management.

With the desire to use torrefied biomass for co-firing purposes it is imperative that explosiblity characteristics of said biomass be understood. Co-fired plants require the transport of finely ground, dust like, particles of biomass and coal to be transported throughout the plant. In order to implement safe operating conditions plant designer must take into account the properties of torrefied biomass and how those properties effect dust explosion. These effects are presented and discussed in Chapter 4.

The objective of this thesis is two folded. The first section of this thesis will explore the effect of torrefaction on dust explosibility. This is critical for understanding what kind of precautions must be taken when using finely ground torrefied biomass in a cofired plant. The second half will consider what kind of gains can be obtained by grinding coal and torrefied biomass simultaneously. Obtaining properly sized particles is essential for proper combustion and is therefore vital in operating a cofired plant. The results will be presented in their respective chapters as well as a discussion of the results.

CHAPTER 2 LITERATURE REVIEW ON GRINDABILITY, PHYSICAL PROPERTIES AND DUST EXPLOSIBILITY OF TORREFIED BIOMASS

This chapter entails a critical review of current studies on grindability, physical properties, and dust explosibility as they pertain to torrefied biomass. The dust explosibility section primarily focuses on coal and metal dust explosions as torrefied biomass has not been extensively studied.

2.1 GRINDABILITY OF TORREFIED BIOMASS

Co-firing of biomass and coal has become a topic of great interest. Raw biomass, due to its tenacious fibrous nature, is difficult to reduce to an appropriate size for both transportation and combustion. Grinding raw biomass is energy intensive and itis difficult to obtain smaller particle sizes. This may be a result of the plastic behavior of biomass. In order to obtain coal like properties torrefaction pretreatment of biomass is required. During the process of torrefaction the hemicellulose that binds cellulose fibers in biomass degrades and thereby the biomass becomes dry, dark and brittle especially at temperature ranges exceeding 250 °C. Photo-optical micrographs (Figure 15) have shown that certain types of raw biomass exhibit a highly fibrous nature. The surface fibers make links between individual particles causing the handling, flow transportation, and the grindability of untreated biomass difficult.



Left: Raw Fibrous BiomassRight: Torrefied Biomass at 240 °CFigure 15 Photomicrograph of biomass before and after torrefaction [Arias, 2008]

Torrefied samples show no such fibers. By looking at the right hand side of Figure 15 one can appreciate that the problems of flow transportation and the handling of torrefied biomass are reduced as a result of torrefaction. Without the presence of the fibrous exterior the friction created by the interlocking of these fibers during transportation is minimized.

The following three parameters, temperature, residence time and original particle size, are used to determine the effect torrefaction has on grinding energy and particle size distribution. Studies have shown that all three play a role in the reduction of the required energy for grinding and the final particle size distribution. The parameters are most influential in the following order: temperature > residence time > original particle size. Torrefaction temperature is the most influential parameter. The higher the torrefaction temperature, the lower the energy requirement for grinding is and the smaller the particles are after grinding. Not only were particles found to be smaller but also the particle distribution was found to be more uniform.

After grinding and sieving, Repellin (2008) obtained the results shown in Figure 16 for four different torrefaction temperatures and the raw material.



Figure 16 Particle Distribution for Various Temperatures [Repellin, 2008]

Figure 17 summarizes a particular range of size, 100µm or less, using Figure 16. It shows that the higher the torrefaction temperature the more particles in range of 100µm or less there are. There is nearly double the amount of particles in the 100µm or less range for samples torrefied at 280°C than there is for the raw material. Fine particles are essential for proper combustion in coal based boilers and this graph proves that torrefied wood will produce a larger percentage of finer grinds.



Figure 17 Percent of Particles Less than 100micron vs Torrefaction Temperature



Figure 18 Particle Distribution for Various Temperatures, Particle Sizes, and Residence Times [Bridgeman, 2010]

Figure 18 shows the importance of residence time on the particle distribution. Shorter residence times, even at higher torrefaction temperatures, produce poor particle distributions especially when compared to coal. We note that raw Willow has nearly no particles of 200µm size or less. Willow that has been torrefied at high temperatures (290°C) and for a higher residence time (60 minutes) will produce a particle distribution similar to that of coal with an HGI value of 66.

Figure 19 shows that torrefaction can reduce the energy required for grinding of biomass (kWh/t) by as much as five times when compared to raw biomass, 245 kWh/t to 45kWh/t. To grind a ton of coal to a fineness of d_{50} ~500µm it would take 7-36 kWh of energy [Esteban et al., 2006]. Note that torrefied biomass requires nearly the same amount of grinding energy as coal. One can see that no two types of biomass will have the exact same grinding characteristics, in this example this is due to the difference in composition between Beech and Spruce. However, and more importantly, it can be seen that both species show a significant improvement in grinding characteristics post torrefaction.



Figure 19 Grinding Energy Required for Various Temperatures and Biomass Types [Repellin, 20010]

Grinding is a parasitic load on a coal based power plant. Assume a 150MWt plant plans to switch to a co-firing option and would like to use 30% biomass by weight. The following table shows an analysis of energy required for grinding. Here we note a substantial rise in grinding energy when 30% biomass is raw compared to that when it is torrefied

| 150 MWt | | | | | |
|-------------|------|----------|--------------|-----------------|----------------|
| | LHV | Required | Required | Grinding Energy | Grinding Power |
| | (MJ/ | Amount, | Amount, mass | Required, kWh/t | Required, kW |
| | kg) | % | (t/hr) | | |
| Coal | 21 | 70% | 18.5 | 25 | 463 |
| Torrefied | 19 | 30% | 7.94 | 45 | 357 |
| Biomass | | | | | |
| (~280°C) | | | | | |
| | | | | | |
| Coal | 21 | 70% | 19.7 | 25 | 492 |
| Raw Biomass | 15 | 30% | 8.44 | 245 | 2068 |

Table 5 150 MWt Case Scenario - Grinding Energy Requirement for Co-Fired Situations

Notice that to grind the raw biomass, at 30% of the total composition of fuel, takes up about 1.5% of the net thermal output of the plant. This is a very high parasitic load and is simply not economical. This aspect of mixing and grinding effects will be further explored in Chapter 4.

| 150 MWt | | | | | | | |
|-----------|------|----------|----------|-----------|----------|---------------|---------|
| | LHV | Required | Required | Grinding | Grinding | Energy | Total |
| | (MJ/ | Amount, | Amount, | Energy | Power | Required for | Power |
| | kg) | % | mass | Required, | Required | Torrefaction, | Require |
| | | | (t/hr) | kWh/t | , kW | kWh/t | d, kW |
| | | | | | | [CENER, 2013] | |
| Coal | 21 | 100% | 25.71 | 25 | 642.75 | N/A | 642.75 |
| Torrefied | 19 | 100% | 28.42 | 45 | 1278.9 | ~200 | 7026 |
| Biomass | | | | | | | |
| (~280°C) | | | | | | | |
| Raw | 15 | 100% | 36 | 245 | 8820 | N/A | 8820 |
| Biomass | | | | | | | |

Table 6 150 MWt Case Scenario - Grinding Energy Requirement for 100% raw biomass, coal, or torrefied biomass

Table 6 shows three scenarios of the same plant using only coal, raw biomass or torrefied biomass. While the switch to 100% torrefied biomass would double the parasitic load for grinding it is still significantly lower than the nearly 14 times increase in parasitic load for raw biomass. This simple case study is proof that a pretreatment of biomass is vital if coal based plants are looking at moving to a co-firing option. Improvement in grindability is only one benefit of many that torrefaction introduces.

In order to obtain coal like grindability, biomass should be torrefied at temperatures of at least 230 °C. Tensile strength and grindability of torrefied wheat straw were measured while studying the decomposition of the three major constituents of biomass. [Lei Shang, 2012] Spectroscopic information obtained from Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) indicated that below 200 °C there was no obvious structural change of the wheat straw. Within the temperatures range of 200 to 250 °C decomposition of hemicellulose began to occur. Torrefaction at 300 °C for two hours results in total degradation of hemicellulose, while cellulose and lignin began to

decompose at about 270 to 300 °C. Tensile failure strength and strain energy of oven dried wheat straw and torrefied wheat straw showed a clear reduction with increasing torrefaction temperature. In addition, Hardgrove Grindability Index (HGI) of wheat straw torrefied at different conditions was determined on a standard Hardgrove grinder. Both results showed an improvement of grindability in the torrefaction temperature range of 250 to 300 °C, which can be well explained by the findings from FTIR analysis. The FTIR analysis shows that there is a clear correlation between the removal of hemicellulose and the improvement in grindability of biomass within that temperature range. The study showed that at a torrefaction temperature of 260 °C and with a residence time of 2 hours, wheat straw samples produced similar HGI values to that of coal with 0% moisture content.



Figure 20: FTIR Analysis Used to Determine Hemicellulose, Cellulose and Lignin for Different Temperatures [Lei Shang, 2012]



Figure 21 HGI Values at Different Torrefaction Temperature for Wheat Straw [Lei Shang, 2012]

By combining data from the work by Shang, Figures 21 and 22 were produced. Figure 22 show HGI and grinding energy requirements as a function of the total hemicellulose content of a heat treated sample.

The five individual points represent four torrefaction temperatures (225 °C, 250 °C, 275 °C, 300 °C) and also the raw material. The hemicellulose content is directly related to the torrefaction temperature. The lower the hemicellulose content the higher the torrefaction temperature. It is evident that as hemicellulose decreases the HGI increases, Figure 22, and the required grinding energy decreases, Figure 23. Both are qualities of improved grinding characteristics.



Figure 22 HGI vs. Hemicellulose Content %



Figure 23 Grinding Energy vs Hemicellulose Content %

Studies show that a large decrease in energy requirement for the grinding of biomass is needed when torrefaction residence times are longer than five minutes under all temperature conditions. After the initial five minutes it was found that as the residence time increased only a small change in grinding energy requirement was seen. This suggests that after an initial period of time, changes in residence time do not play a significant role on the grindability factor.



Figure 24 Shows that after 5 Minutes Residence Time in No Longer Important [Repellin, 20010]



Figure 25 Mass Fraction of Particular Particle Size for Varying Residence Times (250°C) [Lei Shang, 2012]

Some differences arise when comparing particle size distribution and energy required for grinding as far as residence time is concerned. Figure 25 shows that while optimizing for grinding energy torrefaction may not require residence times of greater than five minutes, optimizing for particle size distribution requires a residence time of at least one hour. The degradation of hemicellulose is a time based process. A longer residence time, for a given torrefaction temperature will produce samples, which contain lower hemicellulose content. Samples with the least amount of hemicellulose produced the most amount of sample within a small particle size distribution. One can conclude that the reason why the residence time had such a large influence on the particle size distribution is due to the relationship between degradation of hemicellulose and residence time.

A linear relationship might exist between the specific grindability energy and temperature [Phanphanich, 2011]. A second order polynomial relationship may exist between the mean particle size after grinding and the temperature at which the biomass was torrefied.



Figure 26 Effect of Temperature on Grinding Energy [Phanphanich, 2011]



Figure 27 Effect of Temperature on Particle Size [Phanphanich, 2011]

Figure 28 summarizes the required energy for the grinding of various types of torrefied woody biomass. It also shows the amount of energy required for achieving a certain mean particle size. The required energy for grinding significantly increases with the decrease in the required particle diameter after grinding. From the graph it is evident that torrefied wood and coal require the least amount of energy. Untreated biomass requires the most.



Figure 28 Summary of Grinding Power Consumption for Varying Biomass Types [Bergman, 2005]

A knife cutting mill is typically used for size reduction of raw untreated biomass. Unfortunately these types of mills do not give a good indication of the pulverization of the torrefied biomass and may misrepresent the ease of co-milling. If one hopes to use biomass in a co-firing plant it is recommended that a ball milling apparatus be used for the determination of the ease of grindability.

The Hardgrove Grindability Index (HGI) has been used to assess the ease of grinding torrefied biomass [Bridgeman, 2010; Bergman, 2005]. The HGI is used to determine the capacity, performance and energy requirement of the mill as well as the typical particle size distribution. The HGI is widely used in determining the ease of pulverization of coals and is therefore directly applicable to torrefied biomass as it provides an excellent reference. The higher the HGI the lower the power requirements, the finer the particle

size and overall it represent a sample that is easier to grind. A small change is recommended in the way the HGI is performed. One should use a fixed volume of biomass and not a fixed mass to perform the HGI. By doing so, it is possible to avoid the fact that the HGI, based on fixed mass, favors more dense fuels. It should be noted, though, that the HGI is not without its limitations. It can be sensitive to heterogeneous properties and typically does not return repeatable results. As such Bridgeman suggests that particle size distribution gives a better understanding of the ease of grinding than the HGI. Bergman also suggests that the HGI has its limitations, mainly in that it is not a general technique. The test uses coarse particles in a ball-mill, created by a pre-grinding process, to determine the HGI score. These coarse particles represent the most difficult parts of the fuel to grind. The amount of these coarser particles produced for the HGI test was observed to be less for torrefied biomass than for coal. As a result, the HGI may produce a conservative result for torrefied biomass in comparison to coal.

The energy requirement for grinding is typically reported by monitoring the power consumption of the mill and integrating over the period of time during which the grinding had occurred. One problem that was observed was that no standard or common method was used to determine how one should define the power consumption of the mill. One set of experiments was performed by taking the difference between the power consumption during just the load scenario. Neither set of experiments took into account the efficiency of the motors used to operate the mills.

Overall energy reductions for grinding were found to be as high as a factor of 4-10 when torrefaction occurred between the temperature of 280°C and 300°C [Repellin et. al, 2010; Phanphanich et. al, 2011]. The type of biomass used played a significant role on the magnitude in energy reduction of the grinding. Different types of biomass (beech, spruce, logging residue, pine chips) show that there is a surprising similarity between the required grinding energy per ton for these different types of biomass including both untreated and torrefied biomass. Untreated biomass appears to require about 250 kWh/ton and torrefied biomass (280°C) requires about 25-50 kWh/ton [Repellin et. al, 2010]. The required grinding energy is significantly reduced as the temperatures are increased, especially at temperatures above 275°C. However, one must be careful to balance between the energy yield of the biomass and reduction in grindability energy. Higher temperatures will result in lower energy yields but will improve the grindability of biomass. An optimum has been suggested at 10% weight loss and 85% grindability reduction.

It can be concluded that torrefied biomass will produce two results as far as grinding is concerned. These two results are as follows, a lowered energy requirement and a reduced particle size. A proposed grindability criterion has been suggested where both particle size and energy requirement are combined into one result [Repellin et. al, 2010]. This criterion is shown as follows:

$$G = \frac{Energy \, Required \, for \, Grinding}{Volume \, Percentage \, of \, Particles \, Less \, than \, x \, \mu m}$$
(2.1)

The lower the "G" value the better the grindability of a material is. Equation 2.1 shows that in order to reduce the "G" value the energy requirement must be lower or the percentage of fine particles must be higher or a combination of the both.



Figure 29 Grindability Index vs. Anhydrous Weight Loss [Repellin et. al, 2008]



Figure 30 Ultimate Tensile Strength for Varying Torrefaction Temperature [Lei Shang, 2012]

Figure 30 shows that by increasing the torrefaction temperature the ultimate tensile strength of wheat straw decreases. However, it appears that the decrease occurs in ranges rather than in a linear or exponential fashion. Dried samples and torrefied samples at 150 °C have approximately the same tensile strength of about 50MPa. In the temperature range of 200-250 °C the wheat straw has a tensile strength of only half of its original value, 25MPa. Again, this has been related to the degradation of hemicellulose at these temperatures. While at a higher temperature, 300 °C, the tensile strength is nearly 10 times smaller at 5 MPa. At these higher temperatures there is a significant degradation of lignin and even some degradation of cellulose. This is likely the reason why there is a drastic decrease in ultimate tensile strength. By obtaining results for finer changes in temperature one would observe whether there truly are sharp transition points as is seen in the curve above or whether some form of decaying exponential curve could be obtained.

2.2 OTHER PHYSICAL PROPERTIES OF TORREFIED BIOMASS

2.2.1 Hydrophobicity of Torrefied Biomass

Raw woody biomass and, in particular, agriculture waste tends to have a high moisture content. The moisture content of woody biomass can range anywhere between 10-50%. This property is undesirable for transportation, handling and storage. Drying in itself is not a solution. Solely drying the biomass will not prevent it from future absorption of moisture from its surroundings while in storage (especially in an open air environment). The moisture within the biomass attracts fungal attacks and causes rotting while in

storage. Torrefaction promotes a hydrophobic nature of the biomass. Minimal moisture is therefore absorbed while in storage and as a result a more stable fuel is created. The fuel is now no longer susceptible to fungal attacks and can be safely stored outside in an open environment. Even in a moist environment only a limited amount of moisture is absorbed after torrefaction and decomposition is no longer a problem. This is not the case for raw biomass. Given the right temperature, raw biomass provides the perfect environment for fungus to grow and force decomposition. This is a major concern for storing untreated biomass in an open environment as is often done for coal.

The moisture that was absorbed from the humid air, over a long period of time, for torrefied bamboo was measured to be about 3-6% [ABETS, 2006]. An actual time frame of the storage period was not provided. In the case of sun-dried bamboo (not-torrefied) the moisture was found to increase by 10-12% over this same period of time. From this simple study one can conclude that torrefied woody biomass can be up to four times more resilient to the absorption of moisture while in storage.

Table 7 and 8 show the results of a proximate analysis performed by M. Pach, 2002. The proximate analysis shows the moisture of several samples measured prior to torrefaction as well as the moisture content after torrefaction and a 30-45 day storage period. The results show that the material absorbed only a limited amount of moisture. Even with this absorption the torrefied wood still had much lower moisture content than the raw products, again approximately four times less.

Table 7 Moisture Content of Raw Materials [M. Pach, 2002]

| Biomass | Ash | Moisture |
|---------|--------|----------|
| | wt% mf | wt% |
| Birch | 0.50 | 5.4 |
| Pine | 0.14 | 5.1 |
| Bagasse | 2.24 | 4.4 |
| | | |

Table Raw materials

mf: moisture free

Table 8 Moisture Content of Stored Torrefied Biomass [M. Pach, 2002]

| Biomass | Time, hours | Temperature, °C | Ash wt% mf | Moisture wt% |
|---------|-------------|-----------------|------------|--------------|
| Birch | 2 | 280 | 0.75 | 1.3 |
| Pine | 2 | 280 | 0.2 | 0.6 |
| Bagasse | 2 | 280 | 3.46 | 1.7 |

Hydrophobic characteristics of torrefied briquettes were analyzed by submerging several of the briquettes in water and then determining the moisture content by measuring the change in weight. [Felfli et al., 2006] Figure 31 shows four samples, one raw and three torrefied. For shorter periods of submersion time it appears that higher torrefaction temperatures have limited impact on the moisture absorption. This will later be shown not to be the case for longer periods of time.

The raw briquettes were found to disintegrate in less than 10 minutes. The change in moisture content did not exceed 10% in the 70 minute immersion test. In the 17 day immersion test the briquettes torrefied at 220°C allowed water to penetrate the solid matrix and as a result a significant weight change was measured. The final change in moisture for this sample was found to be 116%. One should note, however, that even

though such a large change was observed the briquette did not show signs of disintegration. The briquettes torrefied in the temperature range of 250-270°C only showed maximum moisture content of 28%. This would leave one to believe that once again temperature plays a significant role in the success of torrefaction. Higher temperatures of torrefaction appear to create superior hydrophobic properties. In conclusion, torrefaction at temperatures of about 250-270°C make briquettes hydrophobic significantly improving storage capability in humid locations.



Figure 31 Hydrophobic Properties with Varying Torrefaction Temperatures [Felfli et al., 2006]

Figure 32 shows how the equilibrium moisture content of wood varies with the torrefaction temperature. One explanation given for the lower equilibrium moisture is the result of tar condensation which clogs the pores preventing moist air to pass through the solid. As the temperature is increased one can observe an inflection point. This is likely due to the fact that as the temperature is increased the amount of volatiles released is also

increased. The release of volatiles creates pores, which now allow for the absorption of moist air.



Figure 32: Equilibrium Moisture Content vs. Torrefaction Temperature [Felfli et al., 2006]

The reason why torrefaction improves hydrophobic properties is because the dehydration reactions destroy many of the OH groups within the biomass. This destruction of OH groups reduces the ability of torrefied biomass to form hydrogen bonds with water. Also, unsaturated structures are formed which happen to be non-polar. The condensed tar after torrefaction may also block the pores of the biomass preventing capillary action and therefore the uptake of moisture. The combination of the above explanations results in a material that has significantly improved hydrophobic characteristics. By not being able to absorb moisture the torrefied biomass is essentially in a preserved state and hence is

capable of resisting biological degradation. Biomass with no moisture will not support any biological organism. This means that torrefied biomass can be stored outside, just like coal. This leads to significant cost reductions in storage.

Thus far only a limited number of studies have been performed on the hydrophobic nature of thermo-chemically treated woody biomass. A test protocol should be created for testing hydrophobicity so that a direct comparison can be made between different studies.

The level of torrefaction depends on many aspects such as biomass type, temperature, residence time, etc. and as a result it is difficult to determine an optimal torrefaction point. One suggested method is to use the level of hydrophobicity or equilibrium moisture content to determine what that optimal point may be. One could use the torrefaction temperature at which the equilibrium moisture content approaches a point of inflection. Again this inflection point may vary for different types of biomass. It would be useful to try and see at what temperature this inflection point resides for different types of biomass and whether the point is dependent on residence time. Then, determine whether the temperatures are in small enough range to conclude an optimal point. Another method would be to say that a torrefied sample shall not exceed x% moisture absorption after being submerged in water for a period of y time. This moisture percentage and time should correlate to outdoor storage periods and moisture requirement of a typical coal type power plant. The temperature at which that x and y are satisfied can be claimed as the optimal torrefaction temperature for that particular type of biomass.

2.3 EXPLOSIBILITY OF TORREFIED BIOMASS

There is a lack of studies on dust explosibility for torrefied biomass and as so, coal and metal dust studies have been used instead. The general behavior and concepts of dust explosibility are applicable to most dusts.

Understanding the explosion hazards and characteristics of dust explosion is essential for a safe operating environment. The extent of the dust explosion is dependent on the rate of energy release due to the chemical reaction relative to the space confinement and the rate of heat dissipation. Although confinement is typically required for a large build up in pressure an explosion can be destructive even in an open environment if the pressure within the dust cloud builds up faster than it can drop (release) at the outer edge of the cloud.

The combustion properties of dust depend on its chemical and physical properties. Particle size distribution and volatile content is most influential. The flame propagation for most dusts is twofold, direct surface oxidation and/or combustion of volatiles. Both of the aforementioned mechanisms propagate faster for finer sized particles. Dust particle size and shape are of primary concern when explosibility is concerned. The finer the particle size, the larger the risk and therefore finer particles are considered most hazardous. This is because they have a larger surface area and therefore react faster. They are easily dispersed in the air and have a tendency to remain airborne for longer periods of time. The following are the main parameters of dust explosibility: maximum explosion pressure, the maximum rate of pressure rise, the minimum ignition temperature, the minimum explosible concentration and the minimum ignition energy. The reactivity of dust can be estimated either from peak explosion pressure or the maximum rate of pressure rise. The higher the P_{max} and the dP/dt_{max} the more reactive a dust is and the more dangerous it can be. Dust are categorized by their K_{st} (bar m s⁻¹) values.

$$K_{st} = \left(\frac{dP}{dt}\right)_{max} V^{1/3} \tag{2.2}$$

Where d/dt_{max} (bar s⁻¹) is the maximum rate of pressure rise and V (m³) is the volume of the vessel. The vessel must either be a 1m³ vessel of a 20L sphere.

| Dust Explosion Class | K _{st} (bar m s ⁻¹) | Characteristic |
|-----------------------------|--|-------------------------------|
| | | |
| St 0 | 0 | Non-explosible |
| St 1 | 0-200 | Weak to moderately explosible |
| St 2 | 200-300 | Strongly explosible |
| St 3 | 300-800 | Very strongly explosible |

Table 9 Dust Explsion Classifications [Barton, 2002]

Dusts are characterized by their K_{st} values. The higher the K_{st} the more explosive the dust. Table 9 shows the different classes and the associated characteristics of each class.

Table 10 presents a small summary of varying dusts and shows which category they fit. Notice how much more reactive wood dusts are than coal dusts. They are an entire class higher. This is of serious concern when considering the implementation of woody biomass for co-firing purpose

| Sample | Kst value (bar m/sec) | Pmax (bar) | ST class |
|---------------|--------------------------|---------------|----------|
| Grain dust | 89 | 9.3 | 1 |
| Coal dust | 85 | 6.4 | 1 |
| Flour | 63 | 9.7 | 1 |
| Sugar | 138 | 8.5 | 1 |
| Wood dust | 224 | 10.3 | 2 |
| Aluminum dust | 515 | 11.2 | 3 |
| Sewage sludge | 102 | 8.1 | 1 |
| GRP dust | 216 | 7.6 | 2 |

Table 10 Dust Explosibility Characteristics of Varying Materials [Explosiontesting.co, 2015]

Figure 33 shows typical pressure data for a moderate explosion. The less vertical the rise in pressure is, the smaller the K_{st} value, the less reactive the dust is and the weaker the explosion is. In Figure 33 the pressure rise is relatively slow and is therefore classified as a moderate explosion. Figure 34 represent what a typical explosion would like while Figure 35 shows a non-explosion. Figure 35 is representative of an experiment containing a small enough concentration of dust to cause no explosion even under ideal conditions. Figure 36 shows the explosion pressure of various dusts and one can observe from the direction of the arrow how the reactivity is related to maximum pressure and rate of pressure rise.



Figure 33 Pressure Data for Moderate Explosion [Cashdollar, 1996]



Figure 34 Explosion, 300 °C, 45-75 μ m, 100 g/m³

Figure 35 No explosion, 300 °C, 45-75 $\mu m,$ 50 g/m 3



Figure 36 Pressure Data for Various Types of Dusts [Cashdollar, 1996]

Figure 37 shows the effect dust concentration and particle size have on the pressure, rate of pressure rise, and temperature. The figure shows that finer dusts (Fe-1), of the same iron species, will produce higher temperatures and larger explosion pressures. The combination of higher pressures and temperatures will create more impacting and dangerous explosions.


Figure 37 Effect of Concentration on Pressure and Temperature [Cashdollar, 1996]

Figure 38 shows that as the concentration of dust is increased there is a large drop in the required ignition temperature. Higher concentrations of dust will require lower ignition temperatures, although, this appears to be true only to a certain extent of concentration. The lower the ignition temperature the more dangerous the dust becomes as it is more likely that minimal energy sources, such as a static charge, could set of an explosion. If

this were to occur in small confined space the extent of this explosion could be hazardous to an operator.



Figure 38 Effect of Concentration on Ignition Temperature [Cashdollar, 1996]



Figure 39 Effect of Pre-Ignition Temperature on Flammability [Cashdollar, 1996]

Dusts that are high in volatile content generally tend to be more explosible. Therefore, if possible, one should avoid using a fuel high in volatile content because that way the explosion hazards can be reduced. This is why woody biomass is of particular concern. Pretreatment processes, like torrefaction, can be used to reduce the volatile content and potentially alter the reactivity of the final product. Comparison of dust explosion characteristics, between raw and torrefied biomass, will be further explored in Chapter 3.

Another form of limiting the hazard is by limiting the maximum pressure. Mixing an inert dust, such as limestone, with the combustible dust is one example. The inert dust acts as a heat sink and as a result reduces the flame temperature bellow its limit value. The first graph from Figure 40 shows how increasing the relative percentage of inert dust decreases the explosion pressure. From the figure it appears that in order to achieve any significant results a high concentration of inert dust is required, above 70%.



Figure 40 Effect of Inert Dust on Pressure [Cashdollar, 1996]

A more obvious method of preventing dust explosion is by limiting the oxygen concentration, typically by diluting the air with an inert gas (most likely nitrogen). Figure 41 shows how much the oxygen concentration must be reduced, from the standard air concentration of 20.95%, to prevent explosion in relation to the dust concentration. For this particular coal type the oxygen concentration had to be reduced by nearly 90% when the concentration increased above 150 g/m^3 .



Figure 41 Effect of Oxygen Concentration on Explosibility [Cashdollar, 1996]

Dust explosibility is a serious subject as it directly relates to the safety of both personnel and equipment. If torrefied biomass is to become a mainstream energy source studies must be done on the explosibility of torrefied biomass. It is known that due to the brittle nature of torrefied biomass there is a tendency for dust to form when the biomass is being handled.

CHAPTER 3 DUST EXPLOSIBILITY AND TORREFIED POPLAR BIOMASS

As has been previously mentioned, torrefaction greatly increases the feasibility and practicality of co-burning biomass with coal. [Basu, 2013; Bergman et al., 2005] This in turn will help produce sustainable power with reduced greenhouse gas emission but without the extra required capital, typically needed for carbon capture and storage or other forms of greenhouse gas reduction. Torrefaction makes biomass more brittle, the grinding or milling of torrefied biomass is likely to produce considerably greater amounts of fine particles than raw biomass. Such fine dust is advantageous for combustion of the fuel in a co-fired pulverized coal boiler due to the increased overall exposed surface area of fuel particles, but for the very same reason the fine dust could pose as an explosion hazards. The explosibility behavior of torrefied biomass dust has not been studied in depth. Understanding the explosion characteristics of a particular dust is essential for a safe operating environment, and development of safe operating protocol of a torrefied wood plant.

Presently, the commercial use of torrefied biomass is in its early stage. Little information is available on the incidences of explosion in commercial plants that use torrefied wood. However, there are large numbers of industrial biomass plants that have had dust explosions occur. The Chemical Safety Board reported in its 2006 Combustible Dust Hazard study that, in a 25-year period in the United States, from 1980 to 2005, there were a total of 281 explosion incidents, 24% of which were attributed to wood and paper dust [S.J Luzik, 2012]. One can however speculate the magnitude of the risk from the

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incidence of explosion in plants working with raw or untorrefied biomass. The following are some examples of such occurrences:

a) In June, 2011 – explosion occurred at the world's largest pellet manufacturing facility in Georgia, USA [Renewables-International-Magazine 2011].

b) In December 1994, ignition of dusty cotton waste from an electricity leak started a fire at a textile mill of the Shinko Seishoku Company at Okaharu, Japan. This fire destroyed the factory. In the same year, a large dust explosion at the Kanaya Shoe making factory, near Tokyo, killed 5 and injured 22. The cause of the explosion was static electricity generated in the fine rubber waste dust [Vijayraghavan, 2004].

c) On 14 December 1970, a severe dust explosion, shattered the grain silos at Kiel-Nordhafen on the Kaiser Wilhelm shipping canal, connecting the North and the Baltic seas. Six men died and 17 were injured. The damage to plant, building and machinery is estimated at 10 million dollars [Abassi, 2007].

d) On 25 May 1955 a corn dust explosion occurred in the Wayne Feeds at Waynesboro, the USA, killing 3 and injuring 13. The violence of the explosion caused extensive property damage.

e) On 24 September 1952, a grain dust explosion ripped through the grain elevator in a grain pool in Saskatchewan, Canada killing 6 and injuring 14 people. The primary explosion occurred in a shipping bin, and it was followed by a secondary explosion involving large quantities of dust, which had been allowed to accumulate in the building [Theimer, 1973].

Nifuku et al (2000) reports 567 explosions in Japan between 1952-1995. About 160 incidences per year are recorded in Germany. More than 1000 incidents are known to have occurred in the USA between1900 and 1956 [Proust, 1996]. Comparable number exists in other industrialized countries.

It may be noted that only a small fraction (about 15%) of the incident of explosion gets recorded [Jeske & Beck, 1989]. Statistics in less developed countries are not easily available, but one can guess that incidence of dust explosion could be much higher due to less stringent safety regulations. Consequences of dust explosion in a biomass plant can be extremely costly both in terms of lives and money. Abassi (2007) summarized the incidences of dust explosion, wherefrom it is apparent that a good number of incidences occurred with dust from materials that can be classified as biomass. This underlines the importance of studying the explosion of dusts in biomass treatment plants.

Biomass plants, particularly those with fine dust are especially vulnerable for dust explosion. Owing to the more brittle nature of torrefied biomass, one expects greater amounts of dust produced during its handling. This could in principle make plants

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handling torrefied biomass more vulnerable to explosion hazards. This inference is speculative at best at the time of writing this thesis because amongst the very small number of torrefied biomass plants no incident of explosion is reported to date. Therefore, it is important that this major safety threat to torrefied biomass be examined closely before an incident occurs.

Research on the explosion of torrefied wood is scarce in open literature. One literature from Huescar et al, (2013) proposed minimum explosible concentration (MEC) as a means for measurement of explosion potential of raw and thermally treated wood.

3.1 BACKGROUND

To assess the risk with a new material it is worth examining the factors that influence the occurrence of explosion. Followings are five primary requirements for a dust explosion to occur [Amyotte, 2013]

- a) Combustible dust,
- b) Air dispersion,
- c) Dust concentrations above the flammable limit,
- d) Presence of a sufficiently energetic ignition source and
- e) Some form of confinement

When a flammable dust is dispersed into the air and an ignition source is present the dust may ignite. If the mixture is in a confined space its combustion leads to a rapid increase in both temperature and pressure. A confined space permits the buildup of pressure due to the compression of the air molecules within the confined space. As a result of that there is a faster increase in flame speed, which eventually turns into explosion. The exceptionally rapid increase in pressure during explosion can destroy the confinement and structures nearby. This is the called the primary explosion, which can also disturb the dust settled on surfaces nearby. This disturbance can then form a cloud which may then be ignited by the heat released from the primary explosion causing secondary explosion. In many cases the secondary explosion causes more serious damage to personnel and property.

For the dispersed dust cloud to ignite the ambience in the confinement must reach the minimum ignition temperature of the dust cloud. Furthermore for ignition to sustain the cloud must have a minimum dust concentration. Thus, two parameters that give an assessment of the likelihood of a dust explosion are:

- a) Minimum ignition temperature of a dispersed cloud (MIT) and
- b) Minimum explosible concentration (MEC).

The severity of an explosion after it occurs is determined by the maximum rate of pressure rise (K_{St}) and the maximum explosion pressure (P_{max}) [Cashdollar & Harazberg, 1987]. The purpose of this work is to examine if there is possibility that an explosion could occur, not what might be the impact of the explosion be after it occurs. Therefore, measurement of P_{max} and K_{St} was kept outside the scope of this study.

The volatile content of a dust has a strong relation with its explosibility [Cashdollar, 1996]. In an explosion the volatiles of the solid are released and are then ignited. In the case of metal-dust only the molten and vaporized phase participate in the reaction. The volatile matter content of the dust is the dominant parameter that affects its explosion potential.

Biomass of a given species would have a defined amount of volatile matter and fixed carbon, but for torrefied biomass that is not the case. The volatile content as well as fixed carbon content of the torrefied biomass could vary depending on the torrefaction temperature and reaction or residence time of torrefaction [Basu, 2013]. These two parameters qualitatively define the severity of torrefaction. Higher torrefaction temperature (within 200-300°C range) and longer residence time produces more severely torrefied biomass and vice versa. Thus one can speculate that there could be a link between the explosibility of the dust of torrefied biomass and severity of its torrefaction.

The effect of torrefaction temperature on dust explosibility, in particular the MIT and MEC, is therefore analyzed in the present work. By better understanding how such properties of a dust affect the explosion, one can create inherently safer designs and reduce the risk of explosion occurring in the first place [Echkoff, 2009]

Risk management is a balance between the likelihood of a disaster occurring and the severity of the damage that may occur as a result of the disaster. Inherently safer designs are quintessential for better risk management. The full picture of explosion characteristics

of a torrefied biomass is admittedly inconclusive without the data on P_{max} and K_{St} results. The present study being exploratory in nature, attempts are made to study the first part of the risk management, which is to examine the explosibility of a mixture of torrefied dust. This will provide an understanding whether or not current protocols used in handling and transporting biomass dust, in particular that of wood dusts; can be applied for torrefied samples.

3.2 METHODOLOGY

The objective of the work does not include the severity or the impact of explosion, the work is limited to the measurement of minimum explosible concentration (MEC) and minimum ignition temperature (MIT) of the dust. The following willdescribe the process used to prepare the material and determine the MEC and MIT.

Cylindrical pieces of Poplar wood, 19 mm diameter and 63 mm length, were torrefied by heating them in an oxygen free bubbling fluidized bed (BFB) heater at specified temperatures for a fixed residence time of 30 minutes. The samples were immersed in a fluidized bed of sand, where the fluidizing gas was nitrogen. This avoided exposure to oxygen providing an inert environment as necessary for torrefaction. The fluidized bed was electrically heated, and its temperature was maintained at the desired value using a temperature controller. The excellent heat transfer characteristic of a fluidized bed ensured uniform heating of the biomass, and it allowed production of torrefied samples precisely at 200 °C, 250 °C, and 300 °C. Additionally, air-dried untreated raw samples were used as reference. Both torrefied and raw samples were then crushed, pulverized

and sieved. The sieved dust was sorted in the following particle size ranges: $< 45 \mu m$, 45-75 μm , 75-106 μm .

Proximate analysis was performed on each sample to determine their gross composition. Table 11 shows results of the proximate analysis. Thereafter, higher heating values of the samples were measured in a bomb calorimeter (Parr 6100). It is apparent from Table 11 that as torrefaction temperature increased the percentage of volatile matter reduced while the fixed carbon percentage increased. This happened because at higher temperatures, greater amounts of the volatiles decomposed, forming char. This observation is consistent with those observed by many [Pimchua et al., 2010, Basu et al., 2013]. Figure 42 shows the relationship between fixed carbon, volatile content and torrefaction temperature. It is clear that as torrefaction temperature increases volatile content decreases and fixed carbon increases. The absolute value of the ash in the biomass does not change during torrefaction. As mass of the biomass reduces when torrefied at higher temperature, one would expect a rise in ash fraction in the sample with severity of torrefaction. This was observed.



Figure 42 Fixed Carbon and Volatile % of Torrefied Bamboo at Varying Temperatures [ABETS, 2006]

Torrefaction results in a net mass loss of the biomass. The mass loss is mainly due to loss in low energy-dense volatiles rather than high energy-dense fixed carbon. As a result, the net energy of the sample does not decrease in proportion to the mass loss. The energy density (heating value) of the biomass therefore increases after torrefaction. The energy density of the samples, as measured in a bomb calorimeter is shown in Table 12. It shows that the energy density or HHV increased after torrefaction, and it continued to increase when the torrefaction temperature increased from 200 to 300 °C. A gain of 19% in heating value is noted between raw biomass and torrefied sample (300 0 C).

| | Raw untreated | Torrefied at | | |
|----------------|---------------|--------------|--------|--------|
| | | 200 °C | 250 °C | 300 °C |
| Fixed Carbon % | 6.84 | 10.94 | 16.95 | 25.38 |
| Volatile % | 92.41 | 88.29 | 82.20 | 73.56 |
| Ash % | 0.75 | 0.77 | 0.85 | 1.06 |

Table 11 Proximate Analysis of Torrefied Samples

- All values are reported on a dry basis.

- 45-75 µm particle distribution was used

Table 12 Comparison of Higher Heating Values of Torrefied Samples with that of the raw sample

| | HHV (MJ/kg) |
|--------------------|-------------|
| Raw sample | 18.35 |
| Torrefied at 200°C | 18.47 |
| Torrefied at 250°C | 19.42 |
| Torrefied at 300°C | 21.84 |

3.2.1 Minimum Explosible Concentration

To determine the minimum explosible concentration (MEC) of the torrefied dust experiments were conducted in a Siwek 20L chamber details of which can be found on the manufacturer's website. (http://www.kuhner.com). The MEC experimental procedure followed the ASTM E1515 standard. These experiments were conducted in a 20 L explosion chamber. For the measurement of MEC, a minimum of 1-bar overpressure was taken as evidence that an explosion had occurred. For example, Figure 43 shows the pressure-time plot of a recorded explosion, where the pressure rose well above 1 bar. Figure 44, on the other hand shows a non-explosion situation as here the peak pressure did not rise above 0.8 bar.

Experiments were conducted for a specific particle size distribution of poplar wood torrefied at a specific temperature. The initial concentration of dust started with 100 g/m³. The dust concentration was then reduced in 10 g/m³ in steps until no explosion was recorded. The final concentration was repeated for verification purposes.



Figure 43 Explosion, 300 °C, 45-75 μm, 100 g/m³



Figure 44 No explosion, 300 °C, 45-75 µm, 50 g/m³

3.2.2 Minimum Ignition Temperature

A BAM-Oven was used to determine the minimum ignition temperature (MIT) values of torrefied and raw biomass samples. Dust with volumes 0.5 mL, 1 mL, and 2 mL were dispersed as a cloud in this oven-like environment. The cloud struck a hot wall whose temperature could be set at desired values. The minimum temperature of the wall at which the mixture ignited was taken as the minimum ignition temperature. Ignition of the cloud was visually detected. Temperatures of the wall were decreased in 10 °C increments until an ignition was no longer visible.

3.3 **RESULTS AND DISCUSSION**

A dust explosion can be summarized as a three-step process: devolatilization of the dust, followed by the mixing of gases (oxidant and volatiles), and then combustion of the mixed gas phase. Volatility and particle size are two main factors in determining explosibility of a dust [Abbasi, 2007]. In the present experiment, both parameters were varied. The volatility of the fuel is related to its volatile content, which in turn depends on the torrefaction temperature of the torrefied product as has been described earlier. Experiments of Phanphannch & Mani, (2011), Airas et al., (2008) and Wannapeera et al., (2011) show the definite effect of temperature on the volatile content of the torrefied biomass. Additionally, it can be noted from Table 11 that volatile content decreases with torrefaction temperature. For the MEC and MIT tests, it was possible to vary the volatile content of the sample by simply changing the torrefaction temperature while keeping torrefaction residence time unchanged. The residence time was kept fixed because it is

another parameter that could affect the volatile fraction in the torrefied product, though to a lesser extent. The particle size of the dust was changed by sieving the crushed and ground raw and torrefied samples.

Abassi (2007) analyzed the effects of particle size and volatile matter on the MEC and MIT values for a range of untorrefied biomass and other materials. Their work shows that minimum explosible concentration (MEC) increases when the moisture in the dust increases but MEC decreases when the dust particle size decreases or volatile matter in the dust material increases. Similar observations are made for the minimum ignition temperature. Since these observations were made for untorrefied biomass or metals, it is uncertain if the same dependence could be expected of torrefied biomass.

Table 13 Behavior of dusts of untorrefied or raw material [Abassi, 2007]

| | Increases With: | Decreases With: |
|-----|----------------------------|--|
| | | |
| MEC | Increased moisture content | Decreased particle size, increased volatile matter |
| MIT | Increased moisture content | Decreased particle size, increased volatile matter |

Tables 15 and 16 present the findings of the present experiments on MIT and MEC with torrefied samples of poplar wood, except for the data from Torrent (2011) presented for comparison for which the type of wood is unknown.

| | Particle Size | \rightarrow | | |
|--------------------|------------------|--|-------|--------|
| | (µm) | <45 | 45-75 | 75-106 |
| | Volatile content | | | |
| | on dry basis (%) | Minimum Ignition Temperature (MIT) (°C) | | |
| Raw sample of | 92.4% | | | |
| Poplar wood | | 410 | 410 | 420 |
| Torrefied at 200°C | 88.3% | 410 | 410 | 420 |
| Torrefied at 250°C | 82.2% | 420 | 420 | 440 |
| Torrefied at 300°C | 73.3% | 410 | 430 | 430 |
| Raw pellet wood | NA | | | |
| dust [Torrent, | | | | |
| 2011] | | 460 (unknown size) | | |
| Wood pellet dust | NA | | | |
| torrefied at 245 C | | | | |
| [Torrent, 2011] | | 420 (unknown size) | | |

Table 14 Experimental Findings of MIT of Raw and Torrefied Poplar Dust

Table 15 Experimental Findings of MEC of Raw and Torrefied Poplar Dust

| Particle Size | Particle Size | \rightarrow | | |
|---------------|------------------|--|-------|--------|
| (µm) | (µm) | <45 | 45-75 | 75-106 |
| | Volatile content | | | |
| | on dry basis (%) | Minimum Explosible Concentration (MEC) (g/m ³) | | |
| Raw sample | 92.4% | 60 | 60 | 60 |
| Torrefied at | 88.3% | | | |
| 200°C | | 60 | 50 | 60 |
| Torrefied at | 82.2% | | | |
| 250°C | | 50 | 60 | 60 |
| Torrefied at | 73.3% | | | |
| 300°C | | 60 | 60 | 60 |

3.3.1 Effect of Torrefaction Temperature

During torrefaction biomass loses volatile matter. The higher the torrefaction temperature or duration of torrefaction (residence time) the greater the reduction in volatile content [Dhungana et al, 2012]. Therefore, higher torrefaction temperature at a given residence time would lead one to expect lower volatile content of the torrefied product. A biomass with lower volatile content is expected to be less reactive in nature and would naturally have higher MEC and higher MIT values according to Table 13 developed for untorrefied biomass. In this table note that both MEC and MIT decreased when volatile matter increased. This dependence on volatile matter was not observed for torrefied biomass. In the present experiments with torrefied wood, there is no effect of volatile content or the torrefaction temperature on the measured values of either MEC or MIT for torrefied biomass. It does not show any evidence of torrefied biomass being more or less explosive than dust from raw biomass.

Table 11 shows that when torrefaction temperature was increased from 200 to 300 °C the volatile matter decreased from 88.29 to 73.56% but MIT remained close to 410 °C for less than 45 micron size. There is a slight increase with temperature for coarser particle, but they are no more than 2.5% above the value for untorrefied or raw biomass. We note similar trend (Table 15) for MEC. Here minimum concentration did not show much sensitivity to the change in torrefaction temperature. All MEC values were in the neighborhood of 60 g/m³. Results in Table 10 and 11 shows little effect of torrefaction on the explosibility of dust.

The above difference in observation between raw wood and torrefied wood may be explained as below. Dust explosion is a kinetically driven reaction due to its exceptionally short reaction times. It is too short for the char to burn. The explosion of dust cloud may be taken as volatile driven. Dust made from higher torrefaction temperature (300 °C for example) has lower volatile content [Dhungana et al, 2012], but the quality of its volatile matter is superior because during the torrefaction process low or zero energy carrying components of the biomass, like CO_2 , are released first leaving the higher energy containing hydrocarbon of the volatile in the biomass. As a result of this a torrefied sample prepared at higher temperature would have smaller amount but more reactive volatile. While lower amount of volatile tends to deter explosion, more energy-dense volatile tends to help the onset of explosion. Due to this balance of two opposing factors in a torrefied biomass one does not note the decrease in MEC with rise in volatile as noted by Abassi (2007) and others for non- torrefied biomass.

For the same reason as above no clear effect of torrefaction temperature on the MIT was observed. These are unique explosion related properties of torrefied biomass.

3.3.2 Effect of Particle Size Distribution

Huescar et al. (2013) studied the effect of particle size distribution on MEC for three different sizes, < 38 micron, 38-75 micron and 75-150 micron of biomass. For sizes less than 75 micron, they noted negligible effect of particle size, but they found that MEC increased above 75 micron. This increase was higher for torrefied biomass and smaller for raw biomass. Present experiment shows a similar trend. A negligible effect of particle size is observed on explosivity of raw biomass dust though for torrefied biomass, a slight increase was observed, but only above 75 micron for torrefied biomass (200 $^{\circ}$ C). These

findings suggested that MEC was less dependent on particle size for smaller particle size ranges. Husar et al (2013) noted that the reactivity of the raw biomass is slightly higher than that of the torrefied product. Their study found that particle sizes above 150 μ m, torrefied biomass showed a lower reactivity. Minimal changes in MEC were observed at particles sizes below 150 μ m.

The observations of the present work and that of Huescar et al. (2013) are compared in Figure 45. These suggest that the effect on MEC and MIT appears only above a certain critical characteristic length. A study on coal by Huescar et al (2013) also showed this exact behavior. It is evident that below the critical characteristic length, decreasing the particle size (in the range of 2 to 100 μ m) does not dramatically decrease the MEC [Cashdollar, 1996]. Cashdollar and Hertzberg (1987) also noted such independence of particle size for finer particles of coal. It should be noted that a large increase in MEC was observed after 100 μ m particle size (Figure 46).



Figure 45 Effect of Particle Size of on MEC [Huescar et al., 2013]



Figure 46 Effect of Particle Size on MEC in a Pittsburgh Coal Study [Cashdollar, 1996]

Figure 47 shows a sample SEM photograph of a torrefied wood. It shows that the opened pores as a result of the torrefaction process. Such opening of pores could make torrefied biomass particles more reactive, but that enhanced reactivity did not influence its explosion characteristics. This happened because of reduced volatile content of biomass due to torrefaction. Two opposing effect muted the net effect of torrefaction on explosion potential. When the particle size increases the volatiles takes finite time to come out to the surface for reaction. Thus the effect of particle size becomes recognizable in larger particle sizes.



Figure 47 Scanning Electron Microscope Picture of Poplar Wood (45-75 $\mu m)$ Torrefied at 300 $^\circ C$ Showing Pore Openings

3.4 PREVENTION OF EXPLOSION IN PLANTS HANDLING TORREFIED BIOMASS

Amyotte et al, (2003) listed the following major options for reduction in risks of dust explosion:

- Effectively modifying the process to reduce dust handling hazards (examples include enclosed and sealed conveyors, sealed openings, operating process under partial vacuum, etc.)
- 2. Preventing suspension of flammable dusts
- 3. Complete removal or minimization of the presence of any ignition source
- 4. Inerting

Modification of the torrefaction process to reduce dust handling hazard is very difficult to achieve, as the whole essence of a torrefaction plant is to use torrefied wood. One can

however make efforts to reduce the formation of suspended flammable dusts through proper house-keeping. For example the dust settling on the floor may not be allowed to exceed a certain particle size. For cleaning use of steam or air blowing can be replaced with suction that will take the dust away from the plant. Window seals or overhead structures may be designed such that dust does not settle there from the air. Good housekeeping and proper design can reduce presence of ignition source though accidental ignition cannot be avoided.

Based on the limited data collected it can be concluded that torrefaction does not appear to increase the risk of explosion. Torrefaction appears to have limited effect on the explosibility of poplar biomass-dust especially when particle sizes are below 150 μ m. Above 150 µm the MEC is expected to increase but further study is required. While many studies have shown that torrefaction temperature alters the physical and chemical properties most significantly, the current study noted that this was not the case for the dust explosion potential. While one can infer that the ignitability of the material is not significantly affected by the torrefaction process, it is not clear what effect torrefaction may have on the severity of an explosion. As far as the likelihood of an explosion is concerned, it appears that current biomass handling protocol is probably adequate for design of handling, storing, and transporting systems for torrefied biomass. A recommendation for future studies is to obtain larger sample quantities and perform a full Pmax and K_{St} study. This will give the full characteristics of the dust and allow a designer to determine what measures must be taken to prevent any harm or damage if an explosion was to occur.

CHAPTER 4 TORREFIED POPLAR BIOMASS & COAL MIXING, GRINDABILITY CHARACTERISTICS

As has been mentioned previously torrefied biomass exhibits significantly improved grinding characteristics. This is extremely important when considering biomass as a cofired source of fuel. Grinding of raw biomass can be a highly energy intensive process and therefore creates demands for high parasitic loads. Ground raw biomass will not have desirable particle distribution and could result in particles sizes that are too large for a pulverized coal fired plant. This will result in reduction in efficiency and an increase in capital cost in order to improve the overall operation of the plant. Torrefaction can be the solution to this problem. The purpose of this chapter is to show the extent of improvements in grinding characteristics that can be obtained from torrefaction and the results of mixing torrefied biomass and coal and measuring Hardgrove Grindability Indices of the mix.

4.1 METHODOLOGY

As with Chapter 3 cylindrical pieces of Poplar wood, 19 mm diameter and 63 mm length, were torrefied by heating them in an oxygen free bubbling fluidized bed (BFB) heater at specified temperatures but for a fixed residence time of 60 minutes. The samples were immersed in a fluidized bed of sand, where the fluidizing gas was nitrogen. This avoided exposure to oxygen providing an inert environment as necessary for torrefaction. The fluidized bed was electrically heated, and its temperature was maintained at the desired value using a temperature controller. The excellent heat transfer characteristic of the fluidized bed ensured uniform heating of the biomass, and it allowed production of

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torrefied samples precisely at 210 °C, 230 °C, and 250 °C and 270 °C. Additionally, airdried untreated raw samples were used as reference.

The following is a summary of the ASTM D409/D409M standard that defines the standard test method for grindability of coal by the Hardgrove-Machine Method. Figure 46 shows the HGI machine used to perform these tests.



Figure 48 HGI Machine Used for Testing

Normally 50 g of air dried coal featuring a grain size in the range between 0.6 and $1.18 \text{ mm} (1.18 \times 0.60 \text{ mm} (\text{No. } 16 \times 30))$ are evenly distributed amongst the grinding balls in the cylindrical sample holder. It should be noted this same sizing was used for the preparation of the biomass. A standardized weight is put on the mill's grinding stone to create the required pressure. After exactly 60 rounds the grinded coal is put on a sampling sieve. Any material that falls below the 75µm is retained and measured. Factor *X* equals

the fraction of the coal passing through the sieve. HGI is then calculated from *X* as follows:

$$HGI = 5.679X + 3.321 \tag{4.1}$$

The above equation was obtained by calibrating the machine used and is valid only for that particular machine. In order to calibrate the machine coals with pre-determined HGI values were used. The coal samples were certified to have the following HGI values (*Y*): 38, 56, 88, and 101. Since the HGI values were known, by performing the HGI test and determining how many grams of sample were less than $75\mu m$ a correlation could be made.

Table 16 summarizes the data obtained from the calibration test. *Y* represents the standardized HGI value. *X* represents how many grams were less than 75 μ m in size. Notice that as the HGI values increases more of the original 50g sample is less than 75 μ m. This is what is to be expected. Using sum of least squares fit method the y-intercept is found to be 3.321 (a) and the slope is 5.679 (b). That is how equation 4.1 was obtained. Values *a* and *b* are calculated as shown below using the data from Table 16.

Table 16 HGI Calibration Data

| Y | X | X ² | XY |
|-----|---------|----------------|----------|
| 38 | 5.5722 | 31.04941 | 211.7436 |
| 56 | 10.1526 | 103.0753 | 568.5456 |
| 88 | 15.0265 | 225.7957 | 1322.332 |
| 101 | 16.7443 | 280.3716 | 1691.174 |

$$a = \frac{\sum Y \sum X^2 - \sum X \sum XY}{n \sum X^2 - (\sum X)^2}$$
(4.2)

$$b = \frac{n\sum XY - \sum X\sum Y}{n\sum X^2 - (\sum X)^2}$$
(4.3)



Figure 49 HGI Calibration Curve

A 50g sample of coal, with a density of 816 kg/m³, will have a total volume of 62 mL. A 50g sample of poplar biomass, with a density of about 400 kg/m³, will have a total volume of 125 mL. Due to the fact that biomass is half as dense as coal it would require twice the volume of material to perform an HGI experiment. This would in turn mean that the chamber used for the HGI machine would be filled to twice the height. The HGI machine was designed for measuring grindability of coal and therefore the spacing between the balls, used to crush the coal, and the housing where the balls are placed in was designed for volumes of around 60-70 ml. Using 50g samples of poplar biomass would require too large of a volume of material and would not expose a significant amount of the material to the grinding balls creating disproportional grinding. The amount of surface exposed to grinding balls is important in defining the grindability of the material. Therefore, all HGI experiments with biomass and biomass/coal mixtures

were performed using volume of samples same as that of coal i.e., 65 mL, instead of using same weight but higher volume. Bridgman et al. (2010) also adopted this strategy of volume based HGI measurement.

In order to use the calibration equation to determine the HGI of all experiments performed only with the poplar biomass the measured mass of material less than $75\mu m$ in size had to be referenced to that of coal. This was done as follows.

$$X = \frac{50}{z} * Y \tag{4.4}$$

Where X: Mass value used in determining HGI

Y: Measured mass (g) of less than 75µm post HGI experiment

z: Measured mass (g) of material used to perform HGI experiment

Experiments with mixtures of biomass and coal were performed in volumetric ratios rather than weight ratios. The biomass to coal volume ratio considered were: 20:80, 50:50, 80:20, 5:95, 10:90, and 15:85. When samples where less than 20% in volume of biomass the overall mass of the sample was always close to 50g. However, this wasn't the case when the sample had higher volume fraction of biomass. Again, in these situations the above method of using Equation 4.4 had to be used.

The present study involved determination of HGI values of 100% coal. Two such samples of coal was tested and found to have HGI values of 33 and 88. Next HGI value

of 100% torrefied biomass was measured following the above procedure. Torrefaction temperature affects the properties of torrefied biomass. Therefore, biomass torrefied at varying torrefaction temperatures was tested and it was found to have varying HGI values. After this, torrefied biomass was mixed with the aforementioned coals and tested for determination of overall HGI value of the mixture. The mixture ratio was also varied as described above. The results of these experiments is discussed in detail in section 4.2

The following section will consider how the varying volume ratios of coal and torrefied biomass influence the grindability of the mixture. Here we assume that the grindability of coal and torrefied biomass are unique properties and they are not influenced by mixing. Thus this will result in an arithmetic relationship based on experimental HGI values individual constituents and their mixing ratio.

The predicted values are calculated as follow:

$$HGI = HGI_{coal} * \% mass coal + HGI_{biomass} * \% mass biomass$$

(4.5)

When testing blends some anomaly may appear because HGI is not necessarily an additive property. Studies have shown that the samples will normally move towards the lower HGI of the two different materials. [ACARP Report, 1998].

It should be noted that the above predictive equation uses percentage mass instead of percentage volume. The HGI is based on a sample of 50g of coal. Since the volume of 50g of coal is approximately 65cm³ the experiments were performed using 65 mL volume of sample, but the mixture ratios were based on volume.

For example, consider the case of 80:20 biomass to coal volume ratio. This mixture will have 80% by volume of biomass which is (0.80 * 65) or 52 mL, and (0.20 * 65) or 13 mL of coal. The mixture will contain (52 * 0.48) or 24.96 g of biomass and (13 * 0.82) or 10.66 g of coal. Total mass of the mixture will be (z = 10.66 + 24.96 = 35.62g)

Upon creating the mixture an HGI experiment would be performed and the measured weight that was less than 75 micron (Y) would then use the following to obtain mixture's HGI value:

$$X = (50/z) * Y$$
 (4.6)

$$HGI = 5.679 * X + 3.21 \tag{4.7}$$

Using the above example the HGI would be calculated as follows:

$$HGI = 24.96/(24.96+10.66) HGI_{bm} + 10.66/(24.96+10.66) HGI_{coal}$$
 (4.8)

4.2 **RESULTS & DISCUSSION**

In order to perform any experiments with mixtures of both coal and torrefied biomass it was first necessary to determine what effect torrefaction temperatures had on the HGI values of the torrefied biomass. Since it is difficult to measure HGI values for every single mixture of biomass and coal for the purpose of cofiring, an attempt was made to investigate if one could predict the HGI value of the mixture from known HGI values of each component as discussed in Chapter 2. Accuracy and reliability of such prediction is examined here by comparing them with the HGI values measured for specified mixtures.

4.2.1 Effect of Torrefaction Temperature on HGI

Figure 49 shows that as torrefaction temperature increased the measured HGI values of torrefied biomass increased as well. This follows what was explained in Chapter 2 that cellulose fibers are responsible for the fibrous structure and anisotropic properties of (woody) biomass and they are bound together through a matrix of mainly hemicellulose and, to a lesser extent, lignin. The higher the degradation of hemicellulose the higher is loss of tenacity and fibrous structure of the biomass and the easier it is for grinding. During torrefaction, hemicellulose, one of the main constituents of biomass, experiences a significant decomposition. This decomposition typically does not begin until temperatures exceeding 220 °C. As the hemicellulose content begins to decrease, with increasing torrefaction temperature, the grinding characteristics improve and the HGI value increases. Note that there is a sharp rise in HGI above 260 °C. This clearly coincides with highest degradation of hemicellulose as seen from Figure 6. Experiments with wheat straw [Lei Chang, 2012], showed this increase to start at a lower temperature of about 240 C. This could be an effect of composition of the hemicellulose of the biomass. Wheat straw is an herbaceous biomass whereas poplar is a woody biomass.

Figure 50 shows strong indication that at torrefaction temperatures above 280 °C one can expect Poplar wood to obtain coal like grindability. This is very much due to the fact that at above 280 °C the biomass will have undergone nearly 80% degradation of its hemicellulose polymer and will involve partial decomposition of both cellulose and lignin. Mild torrefaction, at temperatures of 200-250 °C, showed minimal to no improvements in the grinding characteristics of the Poplar wood.



Figure 50 HGI vs Torrefaction Temperature for Poplar



Figure 51 Effect of Residence Time on HGI of Torrefied Poplar

4.2.2 Effect of Torrefaction Residence Time

Reaction time, or residence time, spent in a torrefier is another important parameter that affects the quality of the torrefied product. Longer residence time makes torrefaction more severe as does higher temperature. It was important to examine if longer residence times improves the HGI values. Experiments were conducted with one batch of samples torrefied at temperatures of 260 and 290 °C for residence times of 15, 30, and 45 minutes. These were subjected to the grindability test.

Figure 51 shows the effect of residence time. Here it should be noted that longer residence time did improve grindability but not to the extent that was observed for torrefaction temperature. As is seen in Figure 51 at a given temperature when the

residence time is increased HGI increased, but above 30 minutes the HGI values show minimal improvement. It is reasonable to conclude that as residence time increases above one hour the effect residence time has on the HGI is minimal.

For the above reason the poplar samples prepared for the HGI values used in the mixed coal and biomass experiments were all prepared using a 60 minute residence time.



Figure 52 Volatile Content vs Residence Time of Torrefied Polar
4.2.3 Effect of Volatile Matter on HGI

These same samples were then used during a proximate analysis and their volatile content was determined. As is expected, at higher torrefaction temperatures the volatile content will be lower and as the residence time increased the volatile content continued to decrease. Both factor increased the HGI. Thus there is a correlation between volatile content and higher HGI values. The lower the volatile content the higher the HGI value will be. This effect is similar to that observed for coals [Kuyumcu, 2010] and is summarized in Figure 53.



Figure 53 Effect of Volatile Content on HGI using 6 Samples of Coal [Kuyumcu, 2010]

4.2.4 Effect of Cofiring Ratio on HGI

Torrefied biomass has many beneficial characteristics. As has been shown, one of these improvements is grindability. This benefit drastically improves the likelihood of co-firing biomass and coal. In particular it presents an opportunity to increase the amount of biomass used in these co-fired plants. "Though 15 large coal-fired power plants in the UK have co-fired biomass, all but two have co-fired at co-firing ratios of less than about 6%." [IEA Coal Clean Center] It is normal to have co-firing ratios of only 5-15% : 95-85% of coal to biomass in these co-fired plants.



Figure 54 Grindability characteristics of mixtures using different volume percentages of biomass and 88 HGI coal (50:50, 80:20, 20:80)



Figure 55 Grindability characteristics of mixtures using different volume percentages of biomass and 88 HGI coal (5:95, 10:90, 15:85)

The first set of experiments consisted of using coal with an HGI value of 88. With each associated torrefaction temperature there is a measured HGI for the biomass. Table 17 summarizes the poplar HGI values at different torrefaction temperatures. These HGI values were used in the prediction formula, 4.8, for the biomass portion and this table should be referred to when interpreting the co-mixture graphs that will follow.

| Torrefaction Temperature | HGI |
|--------------------------|-----|
| (°C) | |
| 210 | 8 |
| 230 | 11 |
| 250 | 21 |
| 270 | 47 |

Table 17 HGI values of biomass used for co-mixing experiments

Next, the HGI of the mixture was measured. In preparing this mixture the same numerical value of the ratio, but in volume, was used as explained in in section 4.1.

Figure 54 and Figure 55 show the HGI of mixtures of varying volume ratios between biomass and coal (20/80, 50/50, 80/20, 95/5, 90/10, 85/15 of coal to biomass) and varying biomass HGI values, and therefore the corresponding torrefaction temperatures, using only 88 HGI coal. It may be noted that the difference in HGI from one condition to another is rather small when small volumes of biomass are used. Thus for small changes one could easily get data that is inconsistently high or low. For that reason it was necessary to revisit the measurement noting the calculated values. If it was inconsistent without any valid scientific reason the value was adjusted by interpolating from the value above and below that point. When the volume fraction of biomass in the mixture is high the torrefaction temperature plays a major role in determining the HGI of the mixture. This is to be expected since the influence of the coal on the overall HGI is less, and HGI of torrefied biomass is greatly affected by torrefaction temperature. If the biomass makes up between 5 to <50% of the overall volume of the composition the actual HGI values always exceeds that of the predicted HGI values. The opposite is true for when the volume of biomass exceeds that of coal in the overall mixture. This can be seen in Figure 57 which shows that the ratio between actual to expected is above 1 for smaller concentrations of biomass and below 1 for larger concentrations.

Figure 56 and 57 show that when the HGI of the coal is high, 88, the worst predictions occur either for high concentration of biomass or at low concentrations of biomass, but only when the torrefaction temperatures are high. This relation does not hold true when the HGI value of coal is small. Therefore, as far a designer may be concerned, for coals that have an HGI exceeding 88, it is recommended that the prediction formula only be used for torrefied biomass concentration of <20% except for when torrefaction temperatures exceed 270 °C.

The overall impact on the HGI of the mixture is minimized when the concentration of biomass decreases and/or when the torrefaction temperature increases. A co-fired plant looking at increasing their overall usage of biomass should consider using torrefied biomass with torrefaction temperatures of about 270 °C. While biomass that is torrefied at higher temperatures exhibits better grinding characteristics it also has a lower energy yield. It is for this reasons mixtures with torrefaction temperatures exceeding 270°C were not tested. When using coal with a high HGI value, ratios exceeding 80% biomass, by volume, are not recommended unless the biomass will be torrefied at above 270 °C. Biomass ratio of about 50% should be torrefied at least to temperatures of 250 °C before being used for co-firing.

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Figure 56 Variation in ratio of actual to predicted values of HGI for different volumetric mixtures of biomass and coal with HGI 88 (50:50, 80:20, 20:80)



Figure 57 Variation in ratio of actual to predicted values of HGI for different volumetric mixtures of biomass and coal with HGI 88 (5:95, 10:90, 15:85)

Figure 59 and Figure 61 show the HGI of mixtures of varying volume ratios between biomass and coal (20/80, 50/50, 80/20, 95/5, 90/10, 85/15 of coal to biomass) and varying biomass HGI values, and therefore the corresponding torrefaction temperatures, using only 38 HGI coal. When the volume fraction of biomass in the mixture is high the torrefaction temperature once again plays a major role in determining the HGI of the mixture. This is to be expected since the influence of the coal on the overall HGI is less, and HGI of torrefied biomass is greatly affected by torrefaction temperature. The only case where the HGI of the mixture increased when the biomass content was high (>80%) by volume) was when the poplar was torrefied above 270 °C. This is due to the higher HGI of the biomass than the HGI of the coal (47 vs 38). If the biomass makes up between 5 to <50% of the overall volume of the composition the actual HGI values always exceeds that of the predicted HGI values. The opposite is true for when the volume of biomass exceeds that of coal in the overall mixture. This can be seen in Figure 57 which shows that the ratio between actual to expected is above 1 for smaller concentrations of biomass and below 1 for larger concentrations.

Figure 60 and 62 show that when the HGI of the coal is low, 38, the worst predictions occur primarily for very high concentrations of biomass (80%) and for biomass concentrations of >50% at low torrefaction temperatures. For design purposes, for coals that have an HGI below 38, the prediction formula may be used for almost all circumstances except those where the biomass content exceeds 80%.

The overall impact on the HGI of the mixture is minimized when the concentration of biomass decreases, except for when torrefaction temperatures exceed 270°C, and/or when the torrefaction temperature increases. When torrefaction temperatures increase above 270°C the HGI values of torrefied biomass exceeds 38. This implies that it is actually beneficial to use large quantities of torrefied biomass (with torrefaction temperatures exceeding 270 °C) when mixing with low HGI coal in order to increase the overall HGI of the mixture. When using coal with a low HGI value, ratios exceeding 80% biomass, by volume, are highly recommended as long as the biomass is torrefied at above 270 °C. Use of a large ratio of biomass is not recommended below torrefaction temperatures 270 °C. This is the biggest difference observed between high and low HGI coal. While with high HGI coal torrefied biomass, at any ratio, will maintain or reduce the overall HGI of the mixture, with low HGI coal high percentages of biomass, at high torrefaction temperatures will actually increase the overall HGI. Biomass ratio of about 50% should be torrefied at least to temperatures of 250 °C before being used for co-firing.



Figure 58 Grindability characteristics of mixtures using different volume percentages of biomass and 38 HGI coal (50:50, 80:20, 20:80)



Figure 59 Variation in ratio of actual to predicted values of HGI for different volumetric mixtures of biomass and coal with HGI 38 (50:50, 80:20, 20:80)



Figure 60 Grindability characteristics of mixtures using different volume percentages of biomass and 38 HGI coal (5:95, 10:90, 15:85)



Figure 61 Variation in ratio of actual to predicted values of HGI for different volumetric mixtures of biomass and coal with HGI 38 (5:95, 10:90, 15:85)

CHAPTER 5 CONCLUSION AND RECOMMENDATIONS

This chapter will present the overall concluding remarks of this thesis and will suggest several recommendations for future works.

- Torrefaction greatly increases the feasibility and practicality of co-burning biomass with coal. This in turn will help produce sustainable power with reduced greenhouse gas emission but without the extra required capital, typically needed for carbon capture and storage or other forms of greenhouse gas reduction.
- Torrefaction makes biomass more brittle, the grinding or milling of torrefied biomass is likely to produce considerably greater amounts of fine particles than raw biomass. Such fine dust is advantageous for combustion of the fuel in a co-fired pulverized coal boiler due to the increased overall exposed surface area of fuel particles, but for the very same reason the fine dust could pose as an explosion hazards.
- Consequences of dust explosion in a biomass plant can be extremely costly both in terms of lives and money.
- Biomass plants, particularly those with fine dust are especially vulnerable for dust explosion. Owing to the more brittle nature of torrefied biomass, one expects greater amounts of dust produced during its handling.

- The volatile content of a dust has a strong relation with its explosibility. In an explosion the volatiles of the solid are released and are then ignited. In the case of metal-dust only the molten and vaporized phase participate in the reaction. The volatile matter content of the dust is the dominant parameter that affects its explosion potential.
- Biomass of a given species would have a defined amount of volatile matter and fixed carbon, but for torrefied biomass that is not the case. The volatile content as well as fixed carbon content of the torrefied biomass could vary depending on the torrefaction temperature and reaction or residence time of torrefaction. These two parameters qualitatively define the severity of torrefaction. Higher torrefaction temperature (within 200-300°C range) and longer residence time produces more severely torrefied biomass and vice versa.
- As torrefaction temperature is increased the percentage of volatile matter reduced while the fixed carbon percentage increased. This happened because at higher temperatures, greater amounts of the volatiles decomposed, forming char. This observation is consistent with those observed by many (Pimchua et al., 2010, Basu et al., 2013).

- It is clear that as torrefaction temperature increases volatile content decreases and fixed carbon increases. The absolute value of the ash in the biomass does not change during torrefaction.
- Torrefaction results in a net mass loss of the biomass. The mass loss is mainly due to loss in low energy-dense volatiles rather than high energy-dense fixed carbon. As a result, the net energy of the sample does not decrease in proportion to the mass loss. The energy density (heating value) of the biomass therefore increases after torrefaction.
- A dust explosion can be summarized as a three-step process: devolatilization of the dust, followed by the mixing of gases (oxidant and volatiles), and then combustion of the mixed gas phase. Volatility and particle size are two main factors in determining explosibility of a dust [Abbasi, 2007].
- A biomass with lower volatile content is expected to be less reactive in nature and would naturally have higher MEC and higher MIT values according to Table 13 developed for untorrefied biomass. This dependence on volatile matter was not observed for torrefied biomass.
- There is no effect of volatile content or the torrefaction temperature on the measured values of either MEC or MIT for torrefied poplar wood. There was no

evidence of torrefied biomass being more or less explosive than dust from raw biomass.

- When torrefaction temperature was increased from 200 to 300 °C the volatile matter decreased from 88.29 to 73.56% but MIT remained close to 410 °C for < 45 micron size. All MEC values were in the neighborhood of 60 g/m³.
- Dust made from higher torrefaction temperature (300 °C for example) has lower volatile content [Dhungana et al, 2012], but the quality of its volatile matter is superior. As a result of this a torrefied sample prepared at higher temperature would have smaller amount but more reactive volatile. While lower amount of volatile tends to deter explosion, more energy-dense volatile tends to help the onset of explosion. Due to this balance of two opposing factors in a torrefied biomass one does not note the increase in MEC or MIT with the decrease in volatile content.
- A negligible effect of particle size is observed on explosivity of raw biomass dust though for torrefied biomass, a slight increase was observed, but only above 75 micron for torrefied biomass (200 °C).
- Based on the limited data collected it can be concluded that torrefaction does not appear to increase the risk of explosion. Torrefaction appears to have limited effect on the explosivity of biomass-dust especially when particle sizes are below

150 μ m. While one can infer that the ignitability of the material is not significantly affected by the torrefaction process, it is not clear what effect torrefaction may have on the severity of an explosion. It is recommended that a future study be conducted where K_{st} and P_{max} values are determined for torrefied poplar for varying torrefaction temperatures. By determining the aforementioned parameters one can form a complete conclusion on the effect of torrefaction on torrefied poplar dust explosibility.

- As far as the likelihood of an explosion is concerned, it appears that current biomass handling protocol is probably adequate for design of handling, storing, and transporting systems for torrefied biomass.
- Grinding of raw biomass can be a highly energy intensive process and therefore creates demands for high parasitic loads. Ground raw biomass will not have desirable particle distribution and could result in particles sizes that are too large for a pulverized coal fired plant.
- As torrefaction temperature increased the measured HGI values of torrefied poplar biomass increased as well. Cellulose fibers are responsible for the fibrous structure and anisotropic properties of (woody) biomass and they are bound together through a matrix of mainly hemicellulose and, to a lesser extent, lignin. The higher the degradation of hemicellulose the higher is loss of tenacity and fibrous structure of the biomass and the easier it is for grinding.

- During torrefaction, hemicellulose, one of the main constituents of biomass, experiences a significant decomposition. This decomposition typically does not begin until temperatures exceeding 220 °C. As the hemicellulose content begins to decrease, with increasing torrefaction temperature, the grinding characteristics improve and the HGI value increases.
- There is a sharp rise in HGI above 260 °C torrefaction temperature. This clearly coincides with highest degradation of hemicellulose as seen from Figure 6.
- At torrefaction temperatures above 280 °C one can expect poplar wood to obtain coal like grindability. This is very much due to the fact that at above 280 °C the biomass will have undergone nearly 80% degradation of its hemicellulose polymer and will involve partial decomposition of both cellulose and lignin. Mild torrefaction, at temperatures of 200-240°C, showed minimal to no improvements in the grinding characteristics of the poplar wood.
- Reaction time, or residence time, spent in a torrefier is another important parameter that affects the quality of the torrefied product. Longer residence time makes torrefaction more severe as does higher temperature.
- Longer residence time did improve grindability but not to the extent that was observed for torrefaction temperature. As is seen in Figure 51 at a given temperature when the residence time is increased HGI increased, but above 30 minutes the HGI values show minimal improvement. It is reasonable to conclude

that as residence time increases above one hour the effect residence time has on the HGI is minimal.

- When the volume fraction of biomass in the mixture, using coal with a large HGI, is high the torrefaction temperature plays a major role in determining the HGI of the mixture. This is to be expected since the influence of the coal on the overall HGI is less, and HGI of torrefied biomass is greatly affected by torrefaction temperature.
- If the biomass makes up between 5 to <50% of the overall volume of the composition the actual HGI values always exceeds that of the predicted HGI values. The opposite is true for when the volume of biomass exceeds that of coal in the overall mixture.
- When HGI of the coal used for the mixture is high, 88, the worst predictions occur either for high concentration of biomass or at low concentrations of biomass, but only when the torrefaction temperatures are high. This relation does not hold true when the HGI value of coal is small.
- For coals that have an HGI exceeding 88, it is recommended that the prediction formula only be used for torrefied biomass concentration of <20% except for when torrefaction temperatures exceed 270 °C.

- The overall impact on the HGI of the mixture is minimized when the concentration of biomass decreases and/or when the torrefaction temperature increases. A co-fired plant looking at increasing their overall usage of biomass should consider using torrefied biomass with torrefaction temperatures of about 270 °C.
- When using coal with a high HGI value, ratios exceeding 80% biomass, by volume, are not recommended unless the biomass will be torrefied at above 270
 °C. Biomass ratio of about 50% should be torrefied at least to temperatures of 250
 °C before being used for co-firing.
- When the volume fraction of biomass in the mixture is high, using coal with a small HGI, the torrefaction temperature once again plays a major role in determining the HGI of the mixture. This is to be expected since the influence of the coal on the overall HGI is less, and HGI of torrefied biomass is greatly affected by torrefaction temperature. The only case where the HGI of the mixture increased when the biomass content was high (>80% by volume) was when the poplar was torrefied above 270 °C. This is due to the higher HGI of the biomass than the HGI of the coal (47 vs 38).
- If the biomass makes up between 5 to <50% of the overall volume of the composition the actual HGI values always exceeds that of the predicted HGI

values. The opposite is true for when the volume of biomass exceeds that of coal in the overall mixture.

- When the HGI of the coal is low, 38, the worst predictions occur primarily for very high concentrations of biomass (80%) and for biomass concentrations of >50% at low torrefaction temperatures. For design purposes, for coals that have an HGI below 38, the prediction formula may be used for almost all circumstances except those where the biomass content exceeds 80%.
- The overall impact on the HGI of the mixture is minimized when the concentration of biomass decreases, except for when torrefaction temperatures exceed 270°C, and/or when the torrefaction temperature increases. When torrefaction temperatures increase above 270°C the HGI values of torrefied biomass exceeds 38. This implies that it is actually beneficial to use large quantities of torrefied biomass (with torrefaction temperatures exceeding 270 °C) when mixing with low HGI coal in order to increase the overall HGI of the mixture.

• When using coal with a low HGI value, ratios exceeding 80% biomass, by volume, are highly recommended as long as the biomass is torrefied at above 270 °C. Use of a large ratio of biomass is not recommended below torrefaction temperatures 270 °C. This is the biggest difference observed between high and low HGI coal. While with high HGI coal torrefied biomass, at any ratio, will maintain or reduce the overall HGI of the mixture, with low HGI coal high percentages of biomass, at high torrefaction temperatures, will actually increase the overall HGI. Biomass ratio of about 50% should be torrefied at least to temperatures of 250 °C before being used for co-firing.

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