TORREFACTION OF BIOMASS

by

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I dedicate this dissertation to my parents:

Sharada Dhungana and Bishnu P. Dhungana.

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ABSTRACT

Torrefaction is a thermo-chemical pre-treatment of biomass within a narrow temperature range from 200°C to 300°C, where mostly the hemicellulose components of a biomass depolymerise. This treatment is carried out under atmospheric conditions in a non-oxidizing environment at low heating rates (< 50°C/min) and for a relatively long reactor residence time. Torrefaction increases the energy density of a biomass and reduces its O/C and H/C ratio, so its properties approach to that of coal.

Biomass is usually referred to as lignocellulose, as its major mass constituents are cellulose, hemicelluloses and lignin. Research on torrefaction carried out to date deals solely with lignocellulose biomasses, and their degradation mechanism is explained primarily in terms of hemicellulose. However, there are biomasses which are non-lignocellulosic, have a small fraction of fibres in them or could possibly benefit from torrefaction. These include municipal solid waste, sewage sludge, animal waste, etc. Experiments were conducted on three non-cellulose biomasses (poultry waste, digested sludge, and undigested sludge) along with three typical lignocellulose biomasses (wood pellet and switchgrass and an agricultural waste – coffee bean husks). Results showed that non-lignocellulose biomasses torrefy similarly to their lignocellulose counterparts.

Due to the immense potential of the torrefaction process, numerous manufacturers have developed their own patented technology for torrefying. Nevertheless, choosing the right torrefaction technology has become exceptionally difficult because of a near absence of a comparative assessment of different types of reactors. An experimental work was conducted to review the major generic types of reactors such as rotating drum, convective bed, fluidized bed and microwave, delineating the essential features of generic types of reactors. According to the results of this study, biomass torrefaction in a rotating drum gave the highest energy dense product, followed by fluidized bed and convective bed; the microwave reactor showed over-torrefaction at the core, while leaving the exterior green.

To help effective design of a torrefier, several systematic experiments were conducted to investigate the effects of some of the more important operating parameters, such as torrefaction temperature, residence time and biomass particles size on the torrefaction yield. Although the mass yield decreased with the torrefaction temperature, energy density increased with it. Moreover, torrefaction yield varied for different biomass particle sizes depending on the type of reactor used, but the particle size did not have any clear effect on the energy density of the torrefied product.

LIST OF ABBREVIATIONS AND SYMBOLS USED

$	United States of America Dollar
¢	Cents
°C	Degree Celsius
ASTM	American Society for Testing and Materials
BE	Belgium
BSE	Bovine spongiform encephalopathy
C	Carbon
CA	Canada
CCME	Canadian Councils of Ministers of Environment
CCS	Carbon Capture and Sequestration
CH_4	Methane
CO	Carbon Monooxide
CO_2	Carbon Dioxide
CWWA	Canadian Water and Wastewater Association
DAF	Dry Ash Free
db	Dry Basis
dia	Diameter
DTA	Differential Thermal Analysis
DTG	Differential Thermogravimetry
ECN	Energy Research Centre of the Netherlands
ESRU	Energy System Research Unit
FC	Fixed Carbon
FR	France
GJ	Giga Joule
GR	Germany
H	Hydrogen
H_2	Hydrogen
HHV	Higher Heating Value

kg	Kilogram
KW_e/h	Kilo Watt (electric) per Hour
m	Meter
mins	Minutes
mm	Millimeter
N_2	Nitrogen
NL	Netherlands
NS	Nova Scotia
NSAC	Nova Scotia Agricultural College
O	Oxygen
PC	Pulverized Coal
QWM	Quartz Wool Matrix
S	Spain
UK	United Kingdom
USA	United States of America
VM	Volatile Matter
vs.	Versus
WPAC	Wood Pellet Association of Canada
wt	Wet Basis

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CHAPTER 1: INTRODUCTION

1.1 Background

Biomass energy is currently sought as a major source of alternative energy. In this context biomass is defined as non-fossilized organic matter of recent biological origin. Some people exclude items with food value from this definition to discourage their use for energy. Biomass is an alternative source of energy whose sustainability depends upon the rate of consumption over the production. Photosynthesis takes energy from the sun and stores five to eight times more energy in biomass annually than our current energy consumption [Prins, 2005]. Biomass energy is thus an indirect means of utilizing of solar energy. Moreover, a major advantage of using biomass as fuel is that, it is a carbon neutral source of energy. Any addition of CO_2 to the atmosphere from biomass combustion is offset by new batch of biomass growth [Basu, 2010, p. 4-5] absorbing equivalent amounts of CO_2. As a replacement for fossil fuels, biomass is one of the most environmentally benign and affordable options. Unlike fossil fuels and other alternative energy sources such as wind, geothermal and tidal power, biomass is a distributed source of energy, meaning it is available near the point of use. Hence, it is one of the key resources for energy security in many countries.

Biomass can be used in virtually any energy application where fossil fuel is used. However, in doing so, it has to be converted into a convenient solid, liquid or gaseous fuel. There are two main routes for energy conversion from biomass - biological and thermo-chemical. This thesis is concerned only with the thermo-chemical route for the production of solid biofuel.

Substitution of fossil fuel with carbon neutral biomass is a much more effective carbon abatement option than carbon capture and sequestration (CCS), which is currently being considered for major coal-fired power plants around the world. A typical CCS plant can reduce the overall energy conversion efficiency of the pulverized coal (PC)-fired power plant by 40% and increase the electricity generation cost by 4.84 to 7.79 ¢/KW_eh [MIT, 2007]. Furthermore, the earliest possibility for the development of CCS at the utility scale is not expected until 2026 [WBCSD, 2006]

On the other hand, substituting coal with carbon-neutral biomass in existing power plants to reduce CO_2 emissions with practically no increase in generation costs is an option that is available right now. Ontario Power Generation, a premier utility in Canada, has for this reason decided to switch over their Nanticoke coal fired power plant to 100% biomass. Although biomass is a carbonaceous fuel like coal, it has a much higher H/C and O/C ratio, as seen in the van Krevelen diagram (Figure 1-1). Coal is significantly lower in these ratios. This basic difference makes the combustion characteristics of biomass dissimilar from those of coal. Thus, even if it is possible to make up for the lower heating value of biomass with a higher feed rate, a boiler designed for coal cannot maintain the steam output when fired on biomass due to its different combustion air requirement, gas mass per unit heat released, volumetric heat release rate, and flame emissivity characteristics. In addition, there are several other characteristics that make it difficult to maintain the output of a coal-fired power plant when fired with biomass. These are as follows:

1. A mill designed for coal will produce a much lower amount of pulverized biomass due to its fibrous and tenacious nature.
2. When stored like coal, biomass absorbs significant amounts of moisture and is susceptible to biological degradation.
3. Handling and pneumatic transport of fibrous biomass is more difficult than for coal.
4. The ignition temperature of biomass is lower than that of coal.

The major differences in the aforementioned properties of biomass and coal can be reconciled at least to some extent by torrefying the biomass. Figure 1-1 shows that the H/C and O/C come closer to that of coal after torrefaction.

Furthermore, torrefied biomass is found to be a valuable feed stock for gasification [Prins, 2005] and production of superior pellets [Bergman, 2005].

This chapter presents a broad overview of the torrefaction process and its reactors, and will also delineate the organization of this thesis

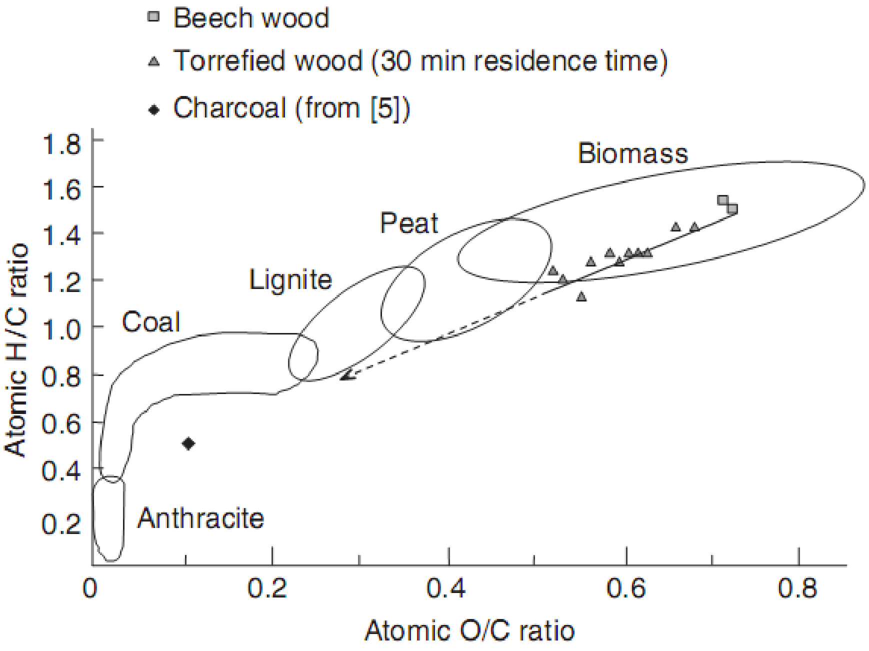

Figure 1-1: Composition of beech wood and torrefied wood (obtained at temperature from 220 to 280°C) in van Krevelen diagram [Prins, 2005].

1.2 Introduction

Torrefaction is a thermo-chemical treatment, in a narrow temperature range from 200 °C to 300 °C, where mostly hemicellulose components of a biomass depolymerise. This treatment is carried out under atmospheric conditions in a non-oxidizing environment at low heating rates (< 50 °C/min) and for a relatively long reactor residence time (typically 1 hour) [Bourgois and Doat, 1984; Pentananunt et al., 1990; Girard and Shah, 1991; Lipinsky et al. 2002, Bergman et al. 2005^{a}]. During the process, the biomass partly decomposes giving off various condensable and non-condensable gases. The final product is a carbon rich solid, which is referred to as **torrefied biomass**.

In the literature, the torrefaction process also goes by several names, such as roasting, slow and mild pyrolysis, wood-cooking and high-temperature drying [Bergman et al., 2005[a]]. Torrefaction science is easier to understand by relating it to the pyrolysis process, as torrefaction reactions are essentially the first step of decomposition reactions of pyrolysis; although the process conditions are similar, the heating rate is much lower in torrefaction. The name 'torrefaction' is a French word that means 'roasting', which generally refers to the roasting of coffee beans performed in the presence of air (oxygen).

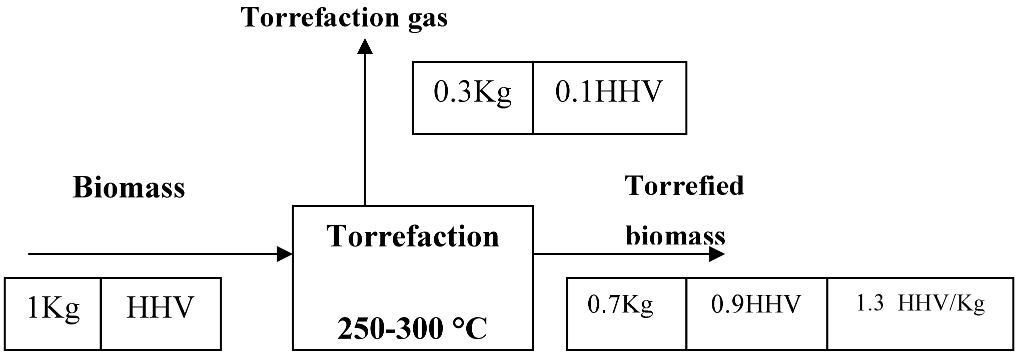

Figure 1-2: Typical mass and energy balance of the torrefaction process, HHV is Higher Heating Value of raw biomass.

Figure 1-2 shows a typical mass and energy balance of torrefaction. In the torrefaction process, biomass loses mass due to the escape of moisture, light hydrocarbon volatiles, and some gases. However, as the energy density of the released items is less than that of the biomass, the latter loses a lower fraction of its energy content than of its mass content. This is illustrated in Figure 1-2, where 1 kg of biomass is torrefied to produce 0.3 kg of volatiles and 0.7 kg of torrefied solids. If the energy content of 1 kg of biomass is HHV (kJ/kg), the volatiles carry away 10% of the energy content (0.1 HHV) of the biomass, leaving 90% of the energy (0.9 HHV) in the torrefied biomass. Thus, there is a rise in energy density of the biomass, which is 30% higher than the original value. The pyrolysis process that takes place at much higher temperatures is characterized by an energy yield of 55-65% in advanced concepts and down to 20% in traditional ones [Pentananunt et al., 1990], while for low-temperature torrefaction, it is in the neighbourhood of 90%.

The principal characteristics of torrefied products are as follows:

1. High Energy Density:

   Torrefied biomass contains 70-80% of the original weight while retaining 80-90% of original energy of the biomass. In effect, there can be an increase of around 30% in its energy density.

2. Hydrophobicity:

   Torrefied biomass becomes hydrophobic, i.e., it does not absorb moisture or its equilibrium moisture percentage drops. The equilibrium moisture content of torrefied biomass is very low (from 1 to 3%) [Lipinsky et al., 2002].

3. Increased Fixed Carbon:

   The fixed carbon content of torrefied biomass is high. For example, depending on the treatment temperature and duration, it is between 25% and 40%, while the ash content is low. This property makes the torrefied wood a very attractive reducing agent [Bergman, 2005].

4. Reduced Oxygen:

   Torrefaction reduces the O/C ratio through reduction in oxygen. This makes a biomass better suited for gasification due to its lower O/C ratio [Prins, 2005]. In addition to its higher heating value, torrefied biomass also produces less smoke when it burns. This is because the smoke-causing volatiles are already driven off during the torrefaction process and the biomass is also dry.

5. Improved Grindability:

Torrefied biomass grindability is superior to that of raw biomass. The output of a pulverizing mill can increase by 3-10 times [Bergman et al, 2005^{b}]

6. Combustion Properties:

   Torrefied biomass takes less time for ignition due to less moisture and it burns longer due to larger percentage of fixed carbon compared to raw biomass [Bridgeman et al., 2008].

1.3 Torrefaction Mechanism

The major mass constituents of a biomass are cellulose, hemicelluloses and lignin, which together are called lignocellulose. These sugar-based polymeric structures comprise the cellular structure of plants and also form the foundation of their cell wall. In this wall, hemicellulose binds macro-fibrils (cellulose) and lignin binds adjacent cells [Bergman et al., 2005^{b}]. The function of hemicellulose is like the function of concrete in a reinforced concrete cement structure, which holds the steel rods (cellulose) together to give the strength to the biomass [Basu, 2010, p. 94].

Within the torrefaction temperature range, the hemicellulose undergoes a depolymerisation reaction (Figure 1-3). This torrefaction temperature zone, bordered by two vertical lines in the figure, has an insignificant effect on the cellulose and only a minor effect on lignin in comparison to hemicellulose.

During these reactions, smaller hydrocarbons molecules (volatiles and gases) with low-energy density escape, which in turn increases the energy density of the remaining carbon-rich solids.

Biomass absorbs moisture because it has higher potential locations for hydrogen bonding. The removal of OH groups from the hemicellulose during torrefaction together with newly formed unsaturated structures (which are non-polar) reduces the biomass's ability to form a hydrogen bond with water. This renders biomass hydrophobic. Hence, torrefied biomass resists biological degradation and therefore can be preserved for long periods of time in outdoor storage [Bergman, 2005].

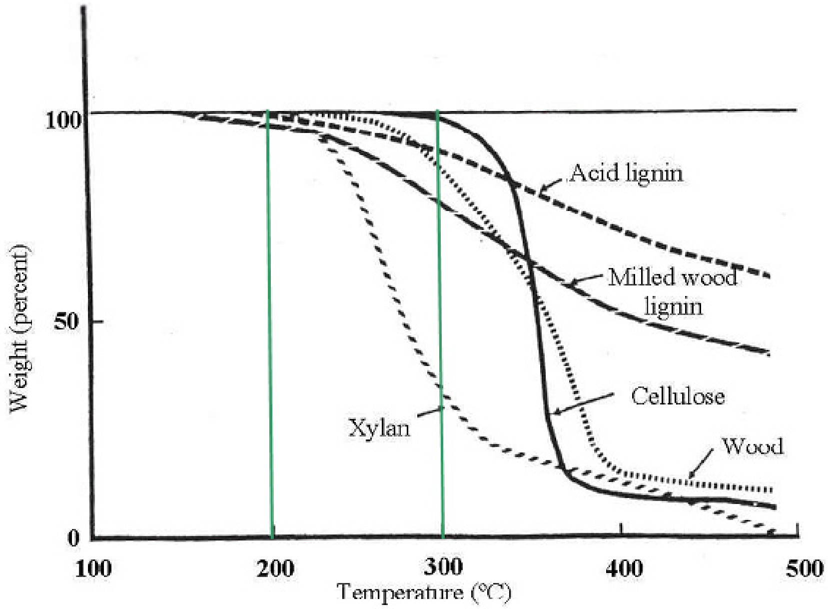

Figure 1-3: Weight loss of lignocellulosic biomass components [Bergman et al., 2005[b]].

1.4 Torrefaction Reactors

Many types of reactors are currently in use and under development. Based on their mode of heating, they can be classified as either directly- or indirectly-heated reactors (Figure 1-4), as described below:

I. **Directly-heated.** In this type of reactor, biomass is brought in direct contact with a gaseous heat carrier. The heat carrier can be hot flue gases, recirculated gases, or superheated steam. Some of the directly-heated reactors include moving bed, fluidized bed, rotary drum and entrained spiral types (Figure 1-4). Here, the heating is primarily through convection. These reactors heat quickly and uniformly compared to indirectly-heated reactors.

Reactors like fluidized bed, microwave and hydrothermal reactors are also included in the direct heating group but in a separate category, as their heating medium is not gas, as with the others. Although these reactors are still in the early stages of development, research indicates that they show distinct advantages in terms of heat transfer, chemical reactions, and so on.

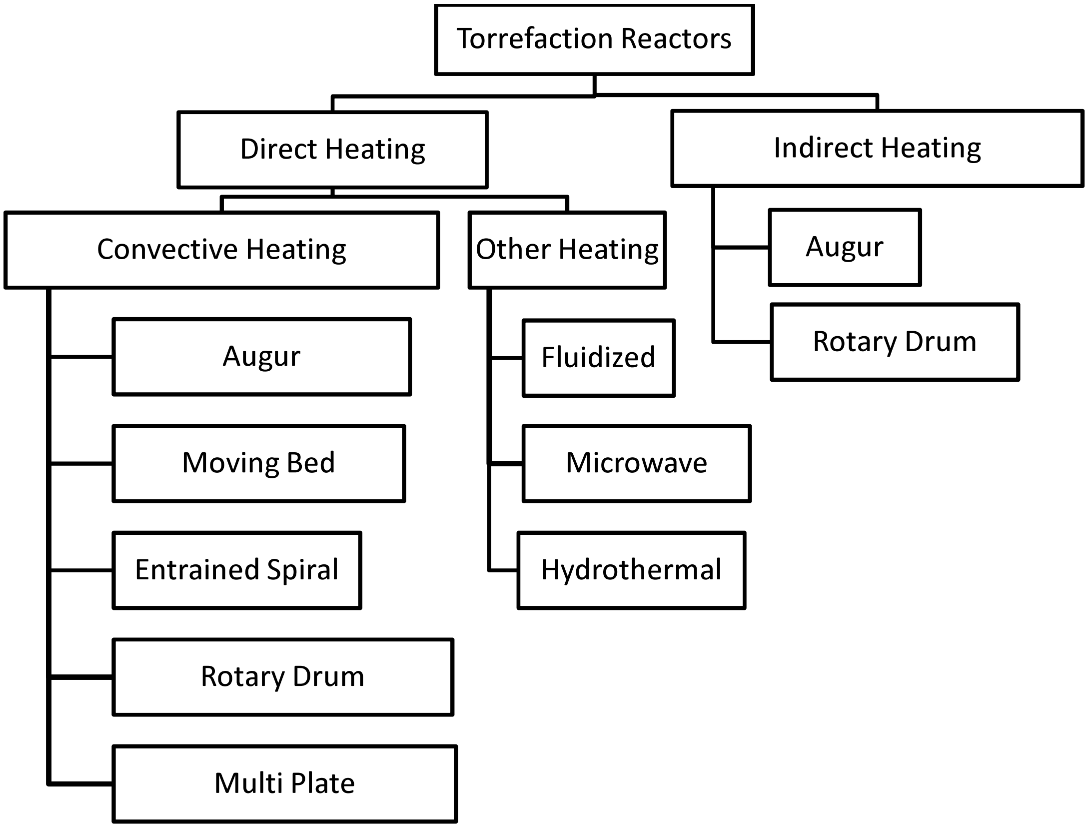

Figure 1-4: Torrefaction reactor type [Dhungana and Basu, 2011].

I. **Indirectly-heated**. In this type of reactor, heat is exchanged between the heat source and the biomass through a hot surface. Most of the carbonization and slow pyrolysis reactors are based on this mode of heating (e.g., rotary kilns and indirectly-heated screw reactors). They are simplistic and can handle a wide range of sizes and types of biomass. Moreover, as thermal recovery from the combustion of volatiles during torrefaction is simpler, they can be easily turned into thermally self-sufficient reactors. The main challenge of this type of reactor is its low heat transfer and non-uniform heating of the feedstock.

Currently, the large number of designs and patents on torrefaction has led to a frenzied race in the market, with each group claiming their design is best suited for commercial use. Hence, for investors, it is very hard to make an objective choice of a reactor for a commercial application. This makes an objective evaluation of major reactor types a priority issue.

1.5 Problem Statement

Torrefaction is a relatively new area in scientific research. The torrefaction of biomass may be explained by the degradation of its polymeric constituent (hemicellulose, cellulose, lignin, xylan and dextran). Such degradation is influenced by time, temperature, constituents and many other factors. While some work has been done already, the field is relatively unexplored, especially from the design standpoint. Furthermore, all biomasses are not lignocellulosic in nature. Some waste biomasses, like municipal solid waste, sewage waste and agricultural animal waste, are made up of fats, proteins and other organic matter, with very little lignocellulose content. Due to wide-scale urbanization, the production of such wastes has substantially increased, and the torrefaction process may help utilize this large volume of non-lignocellulose biomass. The current absence of direct research in this particular area renders torrefaction decidedly under-utilized.

The previous section discussed a few of the torrefaction reactors presently being offered by more than 50 technology suppliers [Madrali et al., 2011], with each reporting data in their respective set of conditions. Within this niche market, many groups are proposing different designs and claiming superiority. The choice of the best torrefaction technology for a particular project developer for its set of conditions thus proves to be very difficult, as there is no independent assessment of these reactors.

The torrefaction technology is therefore, at the time of writing this thesis, at a very critical stage. Owing to very attractive financial returns (especially for co-firing), many investors are poised to pour millions of dollars into building new plants. While the market is ready and eager to accept torrefied products, technology is not yet ready, due to a lack of in-depth and objective research in this field. For example, some partially-ready technology used for a scale-up faced major setbacks. This underscores the dire need for systematic research in the general field of torrefaction, which this present research proposes, in part, to do.

1.6 Objectives of the Thesis

The major objectives of this thesis are:

- To examine the effects of particle size and operating parameters (e.g., temperature, residence time, etc.) on the torrefaction of woody biomass;
- To explore the torrefaction of non-lignocellulose biomass; and,
- To examine how reactor type could influence the yield of torrefaction.

1.7 Scope and Structure of the Thesis

Because torrefaction is a relatively new technology, whose research stretches back only to the early 2000s, many areas in the subject remain unexplored. This thesis will investigate some of those areas to fill the knowledge gap in the current science. Hence, it has three distinct area of focus: non-lignocellulose biomass, effect of reactor types and effect of different parameters in torrefaction. Nonetheless, the sole intent of this work is to help improve design and selection of torrefaction reactors.

This work is presented in six chapters. The first chapter introduces the thesis topic, and the second chapter outlines the current state of knowledge on torrefaction in relations to the scope of this thesis. Later chapters on actual experimental works are organized in paper fashion. They have their own introductory remarks, objective and conclusion.

Hence any reader wishing to concentrate on only one of the aspects of the work do not need to go through all the chapters.

The third chapter presents an experiment on torrefaction of non-lignocellulose biomass compared with that of lignocellulose biomass. The comparison is based on the physical properties as well as mass and energy yield. Similarly, the fourth chapter presents the effect of torrefaction reactor types on the properties of torrefied biomass.

Chapter 5 deals with the effects of the size of the biomass in a torrefaction yield. Finally, Chapter 6 summarises the conclusions drawn from the work and offers future recommendations.

CHAPTER 2: LITERATURE REVIEW ON TORREFACTION

This chapter presents a critical review of current torrefaction technology based on the research objective focus. To that end, fundamental aspects of torrefaction are presented towards detailed understanding of its science.

2.1 Biomass Structural Components

Torrefaction is a thermo-chemical process for biomass conversion to achieve a set of desirable chemical and physical properties. Hence it is imperative to know in detail the chemical and physical properties of biomass.

Woody and herbaceous biomasses are referred to as lignocellulose biomasses, as their major organic mass fraction consists of cellulose, hemicellulose and lignin. These components are responsible for the structural strength of such biomasses. Biomass also contains some non-structural organic compounds referred to as extractives. These materials are soluble in either water or ethanol, and are thus known as water soluble extractives and ethanol soluble extractives [Sluiter et al, 2005]. They include resins, fats and fatty acids, phenolics, phytosterols, and other compounds. Finally, all inorganic contents are termed as ash. The mass percentage of ash is typically less than 1% in woods to 15% in herbaceous biomass and agricultural residues [Diaz, 2006].

Table 2-1: Organic components of biomass (soft wood and hard wood) [Sjostrom, 1981]

Constituent	Soft Wood (Scots Pine)	Hard Wood (eucalyptus)
Cellulose (%)	40	41
Hemicellulose (%)	28.5	19.2
Lignin (%)	27.7	31.3
Total extractives (%)	3.5	2.8

Table 2-1 shows an example of the percentage of these components in soft wood and hard wood. As illustrated, the major constituent of the organic fraction of biomass is cellulose, at around 40%, followed by hemicellulose and lignin and a small fraction of extractives (Table 2-1). The mass fraction of the hemicellulose is higher in soft wood and lower in hardwood. The percentage of hemicellulose is very important in torrefaction process, as explained later in section 2.2.

Cellulose is the most abundantly available organic matter on Earth [Basu, 2009, p. 36]. It consists of long straight chains of glucose molecules $(C_6H_{10}O_5)_n$, also called Cellobiose (Figure 2-1) and forms the skeleton of the plant cell wall.

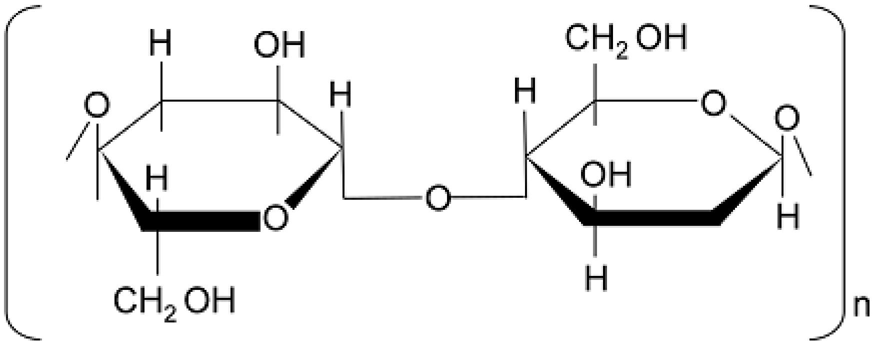

Figure 2-1: Repeating unit of cellulose (Cellobiose) [Diaz, 2006].

Hemicelluloses are short branched chains of glucose and other sugar molecules $(C_5H_8O_4)_n$ that are matrix substances between cellulose microfibrils. Hemicellulose, in general, is in higher concentration in hardwood [Diaz, 2006]. There are numbers of distinct types of hemicellulose of variable composition such as xylose, arabinose, galactose, glucose, and mannose [Diaz, 2006]. The most abundant monomeric unit of hemicelluloses is xylan. Figure 2-2 illustrates the structure of xylan and glucamannan.

Lignin is a three-dimensional phenolic polymer network whose structure can be represented by $[C_9H_{10}O_3.(OCH_3)_{0.9-1.7}]_m$. In addition, there are extractives, whose composition has already been explained.

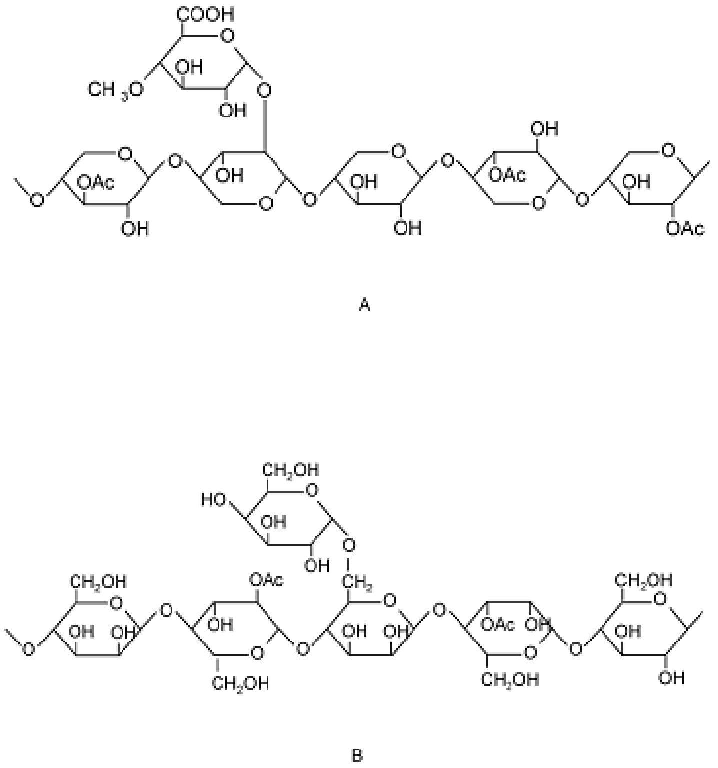

Figure 2-2: Molecular structures of the principal hemicelluloses monomers in wood. A) O-acetyl-4-O-methylglucuronoxylan from hardwood and B) O-acetyl-galactoglucomannan from softwood. Ac=acetyl group [Diaz, 2006].

These structural organic compounds are arranged together in cell walls. However, they do not occur randomly but are arranged in a very specific fashion to provide maximum strength and tenacity to the biomass structure. Long cellulose polymers arrange themselves to form micelle, which continues in a similar fashion to create micro-fibril and then macro-fibril (Figure 2-3). In many regards, this arrangement resembles the pultrusion manufacturing process. However, instead of resin, cellulose macro-fibrils are held together mechanically by the matrix of disoriented and branched hemicellulose structure. Hydrogen bonding also assists in this process. Lignin usually is present in middle lamella and holds different cellular structure together.

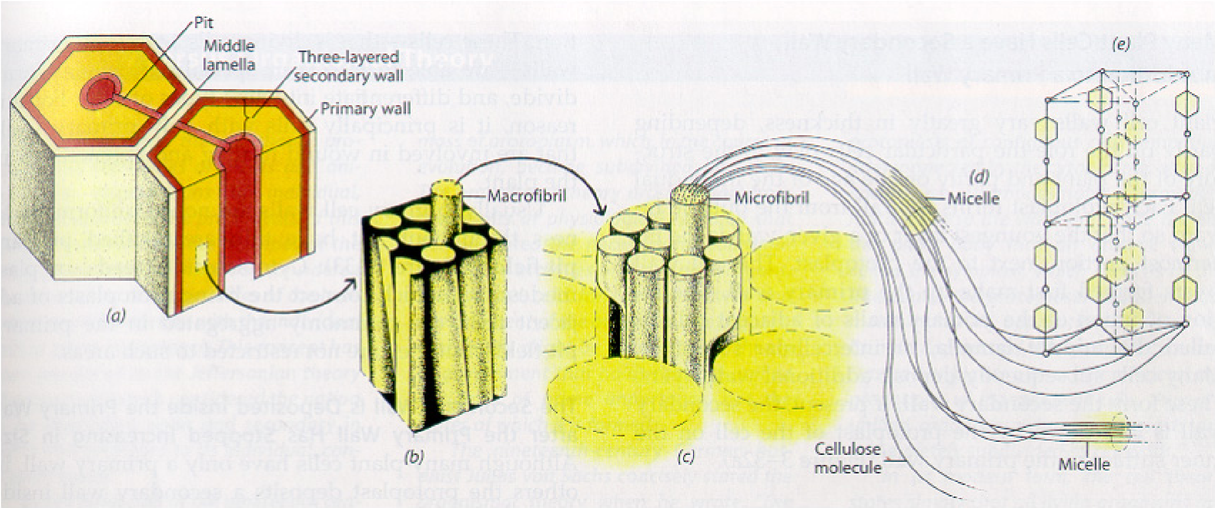

Figure 2-3: Detailed schematic of the cell wall structure. a) cell diagram showing different cell wall i.e. middle lamella, primary wall and secondary cell wall, b) bands of macro-fibril that makes the wall structure, c) micro-fibril inside the macro-fibril structure, d) bands of cellulose polymers including micelles, and e) detailed arrangement of individual cellulose polymer on a micro level [Bergman et al., 2005^{b}]

2.2 Torrefaction Thermal Decomposition Mechanism

During torrefaction, individual polymers behave differently within a given temperature. There are numerous reactions and pathways for degradation of these polymers. Details of such reactions are not fully known. Therefore, instead of discussing the chemical reactions, one can view them as five physical steps as proposed by Bergman et al. (2005^{a})

1. Drying
2. Glass transition and softening
3. Depolymerisation and recondensation:
4. Limited devolatilisation and carbonization:
5. Extensive devolatilisation and carbonization

Figure 2-4 graphically presents the progress of these reactions for the three major biomass constituents. It can be seen that hemicellulose undergoes the greatest degradation amongst all within the torrefaction temperature of 200-300°C. This is followed by lignin and then cellulose. Decomposition of lignin and cellulose generally occurs at higher end of torrefaction temperatures but to a lesser degree than hemicellulose.

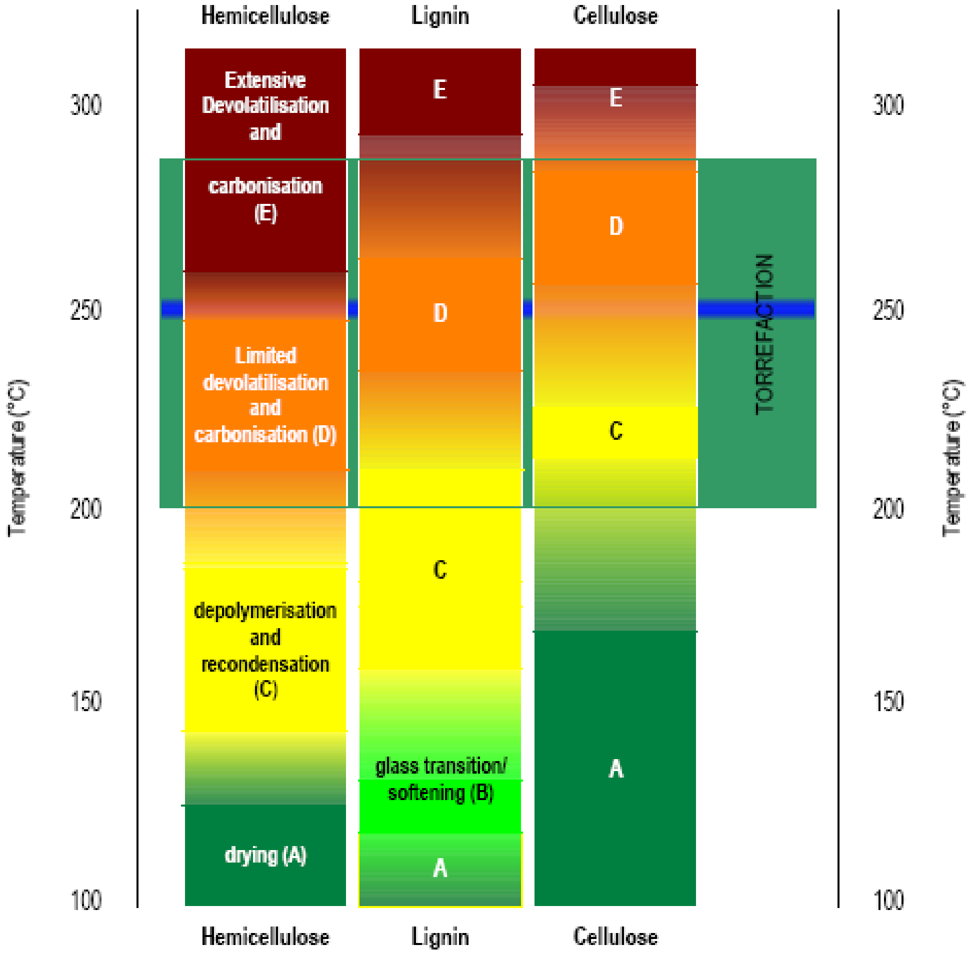

Figure 2-4: Main physio-chemical phenomena during torrefaction [Bergman et al., 2005^a].

Most of the literature defines 200 to 300°C as the range for torrefaction temperature but currently there is no stipulation on this temperature range, because there is no strict definition of the degree of torrefaction. The upper limit 300°C is chosen, perhaps, hemicellulose undergoes excessive degradation within reasonable time. It is hemicellulose that gives the tenacious nature of biomass, which must be altered for convenient use of torrefied biomass.

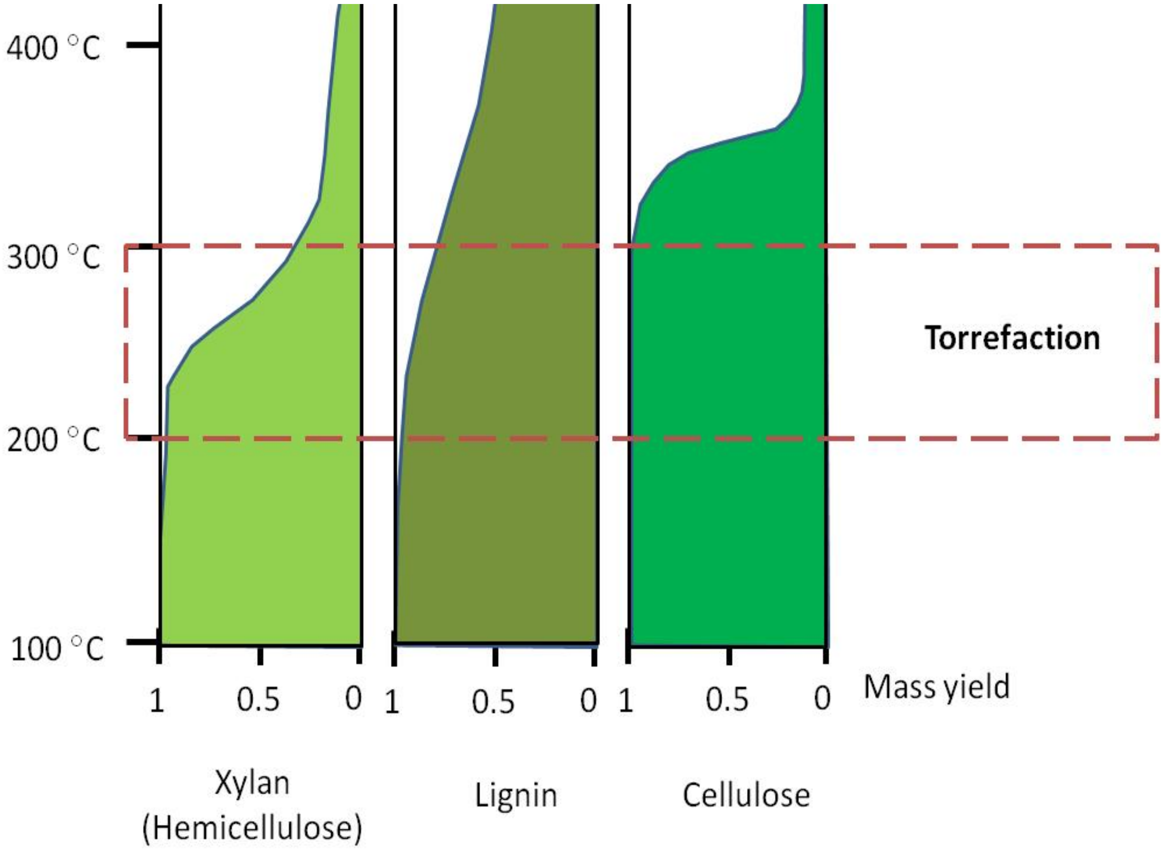

Figure 2-5: Relative thermal decomposition of the lignocellulose components (based on Figure 1-3).

Figure 2-5 shows the relative degradation of the lignocellulose components of the biomass. If any line is drawn across the temperature axis, fraction of the line on the coloured zone gives the mass yield of that polymer at that particular temperature when torrefied for a very long time.

Though hemicellulose is primarily responsible for the decomposition of biomass, its percentage does not help in predicting the relative degree of decomposition in torrefaction for various types of biomass. This is because the composition of the polysugars that forms the hemicellulose is substantially different in different in each biomass [Prins et al., 2006^{a}].

Table 2-2: Composition of the hard wood (deciduous), soft wood (conifer) [Bergman et al., 2005^b] and Straw [Lee et al., 2007]

	Type of Biomass		
Polymer	Hard Wood (Deciduous)	Soft Wood (Coniferous)	Straw (Switchgrass)
Cellulose (wt %)	40-44	40-44	31-45
Hemicellulose (wt %)	15-35	20-32	31-38
Lignin (wt %)	18-25	25-35	18-22
Composition of Hemicellulose (wt %)			
4-O methyl glucuronoxylan (Xylan)	80-90	5-15	70-92
4-O methyl glucuronoarabinoxylan	<1	15-30	13-16
Glucomannan	1-5	60-70	1-2
Galactoglucomannan	<1	1-5	-
Arabinogalactan	<1	15-30	3-5
Other galactose polysaccharides	<1	<1	-
Pectin	1-5	<1-5	-

Table 2-2 shows composition of major polysugars of typical hardwood, softwood and straw (Switchgrass), along with the composition of their hemicelluloses. It can be observed that the percentage range of hemicellulose content in hardwood (e.g., Beech and Willow), softwood (Larch) and straw (Switchgrass) are comparable. However, their mass loss curve (shown in Figure 2-6) is distinctly different. Table 2-2 also shows major differences among hemicellulose constituents when the biomass type is considered. Hardwood has the highest concentration of 4-O methyl glucoronoxylan, commonly referred to as xylan. It is the most thermally unstable polymer of all; thus, biomasses with higher amounts of xylan tend to breakdown more rapidly [Ciolkosz and Wallace, 2011]. In Table 2-2, we can see that hemicellulose in hardwood and straw has the highest amount of xylan. Hence, these biomasses experience faster degradation reactions during torrefaction. This can be seen in Figure 2-6, where straw has the fastest degradation followed by Beech and Willow (Hardwood) and Larch (Softwood). After 5000 seconds, Larch looses around 20% of its mass, Beech and Willow loses around 25% of their mass, and straw looses approximately 35%. Here, the mass loss curve of straw is the most rapid among other biomasses although the xylan percentage is not as high as in hardwood. This might be due to the presence of a larger percentage of hemicellulose. Mass loss of all types of lignocellulose biomass lies within two extremes of cellulose and xylan.

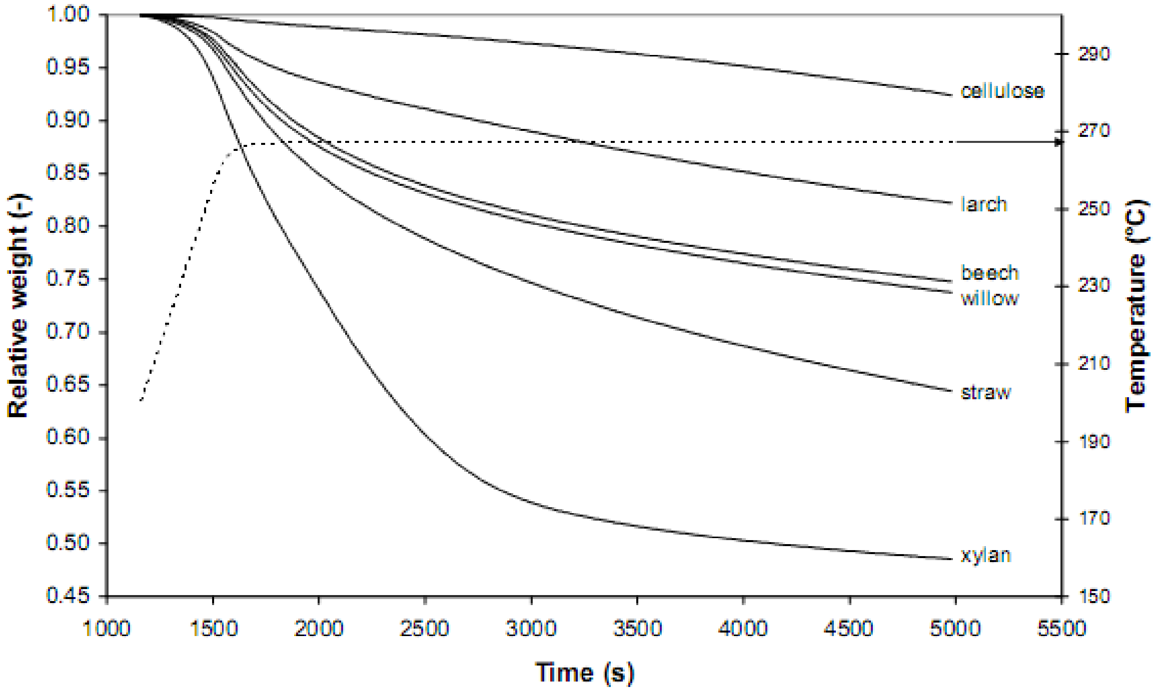

Figure 2-6: TGA of various biomass compounds at 267°C. Heating rate 10°C/min, particle size 0.5-2 mm; the dotted line is the heating curve. [Prins, 2006[a]].

All of these polymers (hemicellulose, cellulose, lignin, including xylan) when individually torrefied and in a mixture were found to exhibit a superposition effect. Therefore, the torrefaction yield of any type of biomass with a known mixture of polysugars can be closely predicted [Chen and Kuo, 2011].

However, not all biomasses are lignocellulose in nature. Waste biomasses, such as municipal solid waste, animal waste, food processing waste and sewage waste, have very little or no lignocellulose content. They are mainly made of proteins, fat, carbohydrate and a relatively tiny fraction of cellulose fibre. Thus the science of torrefaction based on lignocellulose only limits its knowledge and application.

2.3 Torrefaction Heating Process

Torrefaction involves the treatment of biomass within a temperature range of 200 to 300ºC in an inert atmosphere. To improve for better mass yield, heating should occur slowly (below 50ºC/min). Faster heating will increase the liquid yield at the expense of solid char. Thus, biomass temperature is raised slowly from room temperature to the torrefaction temperature (Figure 2-7) and left there for sufficiently long time to ensure the reaction. Depending on the temperature effect on biomass, the temperature curve is divided into different zones [Bergman et al., 2005^{a}]. This assists in many ways in designing a torrefaction setup, because an ideal torrefaction reactor should provide the required amount of heat efficiently during the process. Figure 2-7 demonstrates 5 temperature zones, which are explained below:

- Initial Heating: At first, the biomass is heated from room temperature to the drying temperature (i.e. 100ºC). Here, the reactor should provide a small fraction of heat for a sensible rise in temperature. This is be accompanied by a steady drop in mass (wet mass) due to moisture loss. Since the temperature is measured at the core of the biomass, the outer layer heats faster and starts to get dried.

- Pre-Drying (Drying): As biomass starts to lose moisture, the temperature profile flattens and an almost a horizontal line is observed until all the surface moisture or free water is driven off. When the critical moisture constant is reached, the rate of evaporation starts to decrease and the temperature starts to climb. Depending on the moisture of the biomass, this stage requires the largest fraction of the total heat load. As can be seen in Figure 2-7, there is a sharp increase in cumulative heat demand.

- Post-Drying: This stage again involves raising the sensible temperature of the biomass until the torrefaction process starts (i.e. 200ºC). In this stage, all physically bound moisture is released along with some light organic compounds such as terpenes [Bergman et al., 2005[a]]. As seen in Figure 2-7, the energy demands of this stage are not a large fraction of the total heat energy demand.

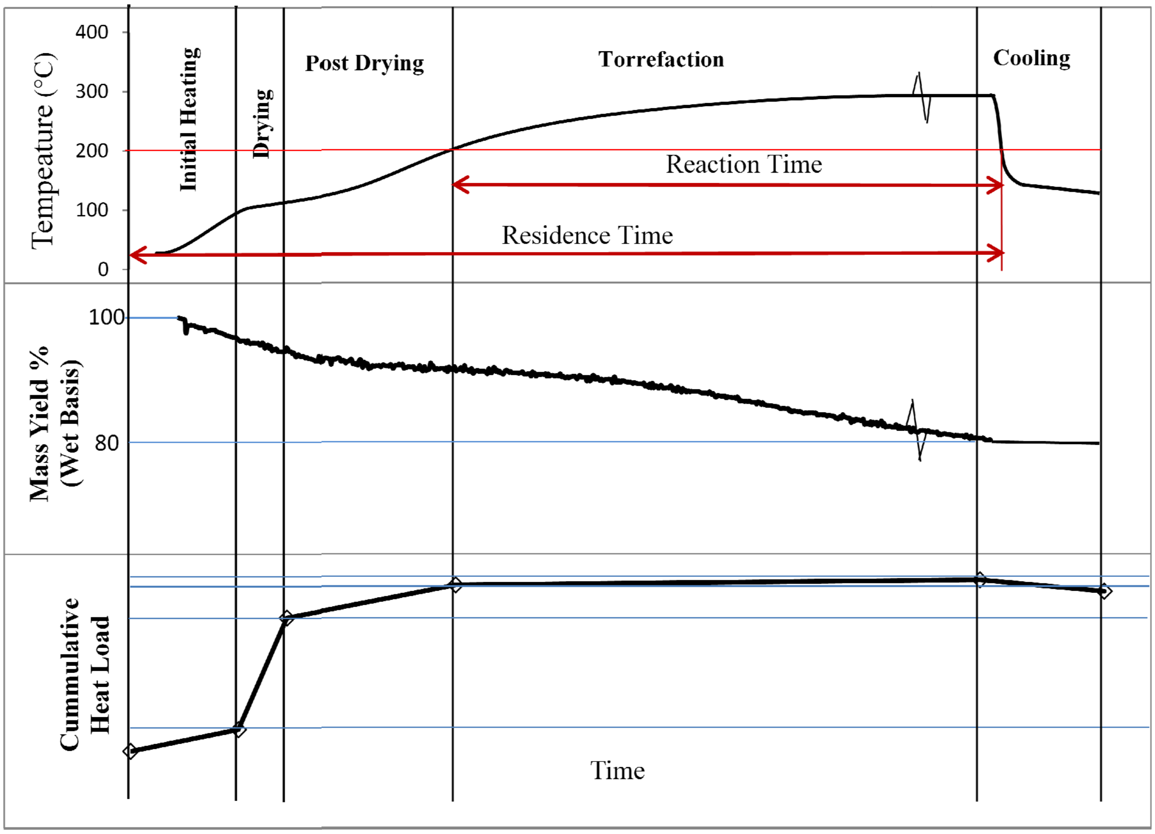

Figure 2-7: Stages in the heating of a moist biomass (50% moisture) particle from ambient temperature to the desired torrefaction temperature (280°C) and subsequent cooling of the torrefied product projected in the temperature, mass yield (experimental) and cumulative heat load (theoretical) profile. (assuming 140°C as drying temperature and 20% moisture remains after drying). (data taken from author's experiment)

- **Torrefaction:** The torrefaction process occurs in this stage. Here, the biomass still requires sensible heat to raise it to the specified torrefaction temperature. A gestation period is needed to allow the depolymerisation reactions to continue until the desired severity of torrefaction is achieved. This stage requires very little amount of energy (Figure 2-7), but this does not imply that torrefaction is an endothermic process, as it still needs a sensible heat. Prins (2005) concluded that torrefaction is mildly endothermic within the range of 250 to 300ºC. On the contrary, Knezevic et al. (2009), Felfli et al. (2004), Chen and Kuo (2011) and Englisch (2011) have suggested that torrefaction is endothermic at lower temperature and exothermic at higher temperature (greater than 230 - 250ºC). Turner et al. (2010) proved that the exothermic reaction is not dependent only on temperature but on the size of the biomass as well. However, this represents a very small fraction of energy compared to the amount of energy being supplied for the entire process. Nevertheless, in situations involving large-sized biomasses or in a fixed bed torrefier of a large cross-section, this exothermic heat can build up and cause temperature runoff.

Another important parameter in torrefaction is residence time. With increasing residence time the biomass mass continues to fall. Not apparent in Figure 2-7, after a long time its mass starts to level. Figure 2-7 clearly defines the residence time and reaction time which are used often in this thesis. Residence time is the total time the biomass resides in the torrefier, while reaction time is defined as the time the biomass is above 200°C (Figure 2-7).

- **Solid Cooling.** Biomass is then cooled down from the torrefaction zone to the desired final temperature for further processing or storage. This process releases heat and can be recycled back to the torrefaction process.

Figure 2-7 is much useful in the design of the torrefaction unit. The heat load for drying is much higher than that for torrefaction, and drying can be performed at lower temperatures; any innovative ideas of utilization of low-grade waste heat could make the system more efficient. For the torrefaction process, energy demand can be met by combusting the volatiles generated during the torrefaction process.

2.4 Product Yield and Factors Affecting It

Biomass generally contains a large amount of surface moisture that depends upon how the biomass is stored and the humidity of the surroundings. Furthermore, the ash percentage of biomass varies depending upon the section of the biomass. Hence, torrefaction product yields are generally expressed on dry and ash free (daf) basis. The quality of the torrefaction product is generally defined by the two product yields and the energy density, as defined below.

$$\text{Mass Yield (daf)} = \frac{\text{Mass (daf) of torrefied biomass}}{\text{Mass (daf) of raw biomass}} \tag{2-1}$$

$$\text{Energy yield (daf)} = \frac{\text{Mass (daf) of torrefaction product x Heating value of torrefied product}}{\text{Mass (daf) of raw biomass x Heating value of raw biomass}} \tag{2-2}$$

$$\text{Energy density of product (daf)} = \text{HHV(daf)}_{product} \tag{2-3}$$

Bergman et al. (2005^{a}) also applied similar definitions; however, they used LHV instead of HHV upon the argument that LHV is the amount of recoupable energy from biomass in combustion. Measurement of HHV is much easier than for LHV, HHV-based design and operation of power plant is common [Basu, 2006, p. 92].

The mass yield in equation 2-1 gives the fraction of the initial dry ash free mass of the biomass that remains after torrefaction, while the energy yield gives the fraction of the total chemical energy in the original dry biomass that remains in the torrefied biomass. It is desirable to have both the lowest mass yield and the highest energy yield because that will result in the highest energy density of the torrefied biomass.

Several factors affect the torrefaction yield. Some of the major factors reported in the literature are described below.

2.4.1 Torrefaction Temperature

Much research has been devoted in examining the effects of temperature on torrefaction yield and the products' properties. Bergman et al. (2005^{a}) varied torrefaction temperatures in the range of 250 to 300°C using three different types of biomass: Willow, woodcuttings and demolition wood. The results (Figure 2-8) show that torrefaction temperature has a pronounced effect on both mass and energy yield.

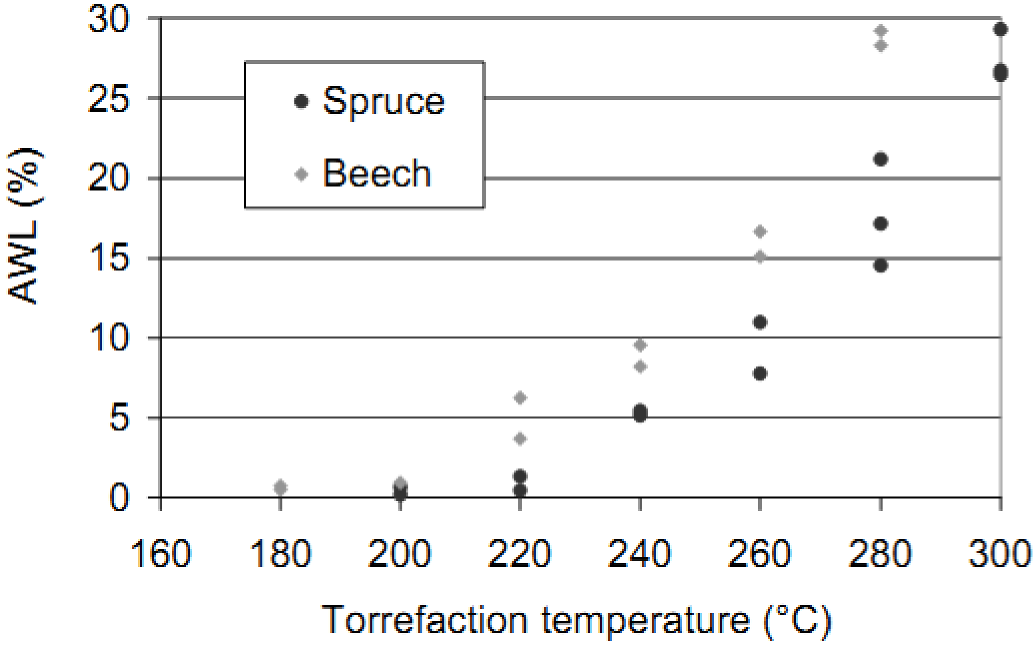

Figure 2-8: Anhydrous Weight Loss (AWL) or mass loss on a dry basis as a function of torrefaction temperature for Spruce and Beech [Repellin et al., 2010].

Several other study [Ciolkosz and Wallace, 2011; Bridgeman et al., 2008; Pimchuai et al, 2010; Ferro et al., 2004; Repellin et al., 2010] showed that temperature is the most influential parameter of all. Figure 2-8, plotted by Repellin et al. (2010), shows the effect of torrefaction temperature on the mass yield of biomass (residence time of 5 mins). One can see that the mass loss at 220°C was around 5%, which significantly increased to around 30% when torrefied at 300°C. Mass loss of Beech was higher than for Spruce due to the fact that Beech (deciduous or hardwood) contains a higher percentage of xylan than Spruce (coniferous or softwood). Prins et al. (2006^{a}) also observed the same relation.

Ferro et al. (2004) suggested that after drying (above 160°C), new water is formed from the chemical reaction through the thermo-condensation process. Within the temperature range of 180-270°C exothermic reactions with degradation of hemicellulose take place, releasing acetic acid, CO and phenol. The reaction becomes entirely exothermic at about 280°C, releasing CO and other hydrocarbons [Ferro et al., 2004].

The energy density increases with torrefaction temperature because C/H and C/O ratios increase with rising temperatures. As well, longer residence times and higher temperatures increase the percentage of CO in the non-condensable product gas [Ferro et al., 2004]. Thus, energy yield decreases with temperature but energy density increases with it because the O/C ratio reduces at higher temperatures.

2.4.2 Residence Time

Residence time is another important parameter that affects the yield of torrefaction. Although it influences the torrefaction yield to a lesser degree than temperature, it has a significant effect on the design of the torrefaction plant: A longer residence time will necessarily require a larger torrefier. Observations of many researchers regarding different types of biomass show that mass yield decreases with longer residence times (e.g., rice husk [Kargbo et al, 2009]; wood [Nimlos et al, 2003]; wood, birch and bagasse [Pach et al., 2002]; rice husk, sawdust, peanut husks, bagasse, and water hyacinth [Pimchuai et al., 2010]. However, the effect of residence time eventually tapers off, as can be seen in Figure 2-9. When the residence time for the torrefaction of Beech at 260°C was increased from 5 minutes to 60, weight loss increased only by 10%.

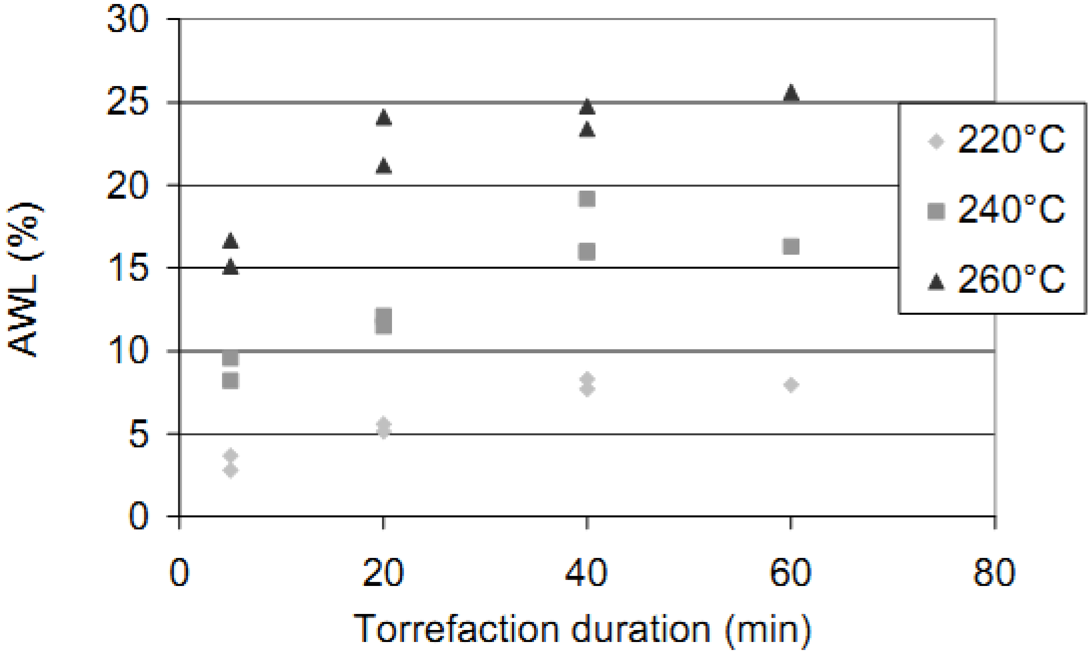

Figure 2-9: Anhydrous Weight Loss (AWL) of Beech chips as a function of torrefaction residence time. [Repellin et al., 2010].

For industrial designs, it is important to know the minimum residence time, as a reduction in residence time will reduce the size of the reactor, which reduces the investment cost [Bergman et al., 2005^{a}]. To identify the shortest required torrefaction time by convective heating, Nimlos et al, (2003) torrefied sawdust for 5 and 10 minutes. Five minutes of residence time did not bring any noticeable change in the heating value of biomass, even at a high torrefaction temperature. Some changes were visible at 10 minutes of residence time, but at higher temperatures. For an acceptable level of torrefaction yield, Bergman et al. (2005^{a}) suggested torrefaction for 17.5 minutes at 280˚C for co-firing application. As stated previously, the required residence time may depend upon the particle size and reactor type, but this aspect has yet to be adequately researched.

Reaction time also depends upon the quality of the product required. At a short residence time also, biomass grindability is significantly improved, which is a basic requirement in biomass co-firing [Bergman et al., 2005^{a}]. However, for other applications requiring higher heating value, increased devolatilisation may be required, prompting longer residence time. Thermal conduction within the biomass being an issue, an efficient biomass heating mechanism can reduce residence time.

2.4.3 Biomass Particle Size

Torrefaction is a relatively slow process due to the following two reasons:

i. Reaction kinetics of biomass is slow at temperatures typical for torrefaction.
ii. Slow heat transfer within biomass: For torrefaction to occur heat has to travel from the outside to the surface of a biomass particle. It is then conducted from the surface to its interior, where the thermal degradation, which is a function of temperature, takes place. During the first stage, the surface heat transfer coefficient is important and it is affected by the surface area. Heat diffusion into the interior is a function of size as well as biomass conductivity. The thermal conductivity of biomass being low, heating of its interior takes longer.

Woodchips as large as 20 mm in thickness can be torrefied without heat transfer limitations [Bergman and Kiel, 2005]. However, if the particle size is much larger, it takes longer for uniform heat distribution and homogeneous reaction. This limitation can be eliminated by the use of a volumetric heating mechanism, such as microwave heating, whereby large biomasses can be torrefied and then reduced in size as per the end use application requirements.

Bergman et al. (2005[b]) torrefied Willow of different sizes (0-10, 10-30, 30-50 mm) to examine the differences in yield. They observed that the mass yield of solids were similar, despite the size differences, but could not provide an explanation as to why this was. Nonetheless, they did speculate that, at this temperature level, the effect of particle size and heating rate may be very low. Turner et al. (2010), in their experiment to model the torrefaction found that exothermic reaction in biomass is definitely affected by the size of the biomass.

Particle size is rarely uniform in a commercial plant. Thus, to ensure a proper design, it is necessary to know the effect of particle size. With current information being limited and conflicting, there is an urgent need to explore the effects of particle size on biomass torrefaction.

2.4.4 Heating Rate

One of the major differences between pyrolysis and torrefaction is that, in the latter process, the heating rate of biomass is preferably kept low during the initial heating period. Once the torrefaction temperature is reached, heating (if required) is governed by the rate of exothermic/endothermic reaction and heat losses from the reactor. As the temperature of the biomass must be kept constant in the torrefaction reactor, it should provide only as much heat as is needed to maintain the torrefaction temperature.

If the initial heating rate could be increased, then the total residence time of biomass in a reactor could be reduced. For fine particles, this constitutes a small fraction of the total time. However, little information on the effects of varying heat rate during the initial temperature rise is currently available.

In carbonization reactions, the heating rate is generally kept low, but biomass is heated to higher temperatures. This is because, at lower heating rate, char yield is higher, and at higher temperatures, the energy density of the product is higher. In torrefaction, energy density is not the only criterion. Energy yield, which is very low in carbonization, is also an important consideration and is always desired to be at maximum. For that reason, torrefaction generally uses slow heating to a low temperature that gives high energy yield with moderate energy density.

Almost all the literature states the need of lower heating rate for torrefaction. Bergman et al. (2005[a]) suggested limiting the heating rate at 50°C/min. However, no quantitative effects of heating rates have been identified to date.

2.5 Product Distribution

In a torrefaction plant, biomass experiences loss in mass due to the loss of moisture and volatiles. These volatiles are classified as condensable volatiles and gases (non-condensable volatiles) depending on their state at room temperature. Volatiles comprise a number of hydrocarbons, as shown in Figure 2-10. Torrefied biomass comprises numerous newly-formed polymeric structures as well as modified sugar and char, along with some original polymers. Its properties are thus generally assessed by physical and combustion properties instead of chemical constituents. Liquid or condensed volatiles contain a large fraction of water, and short organic acids, alcohols, furans and ketones are present (Figure 2-10), which are combustible. The gas consists of CO_2, CO, H_2, CH_4 and other gaseous hydrocarbons.

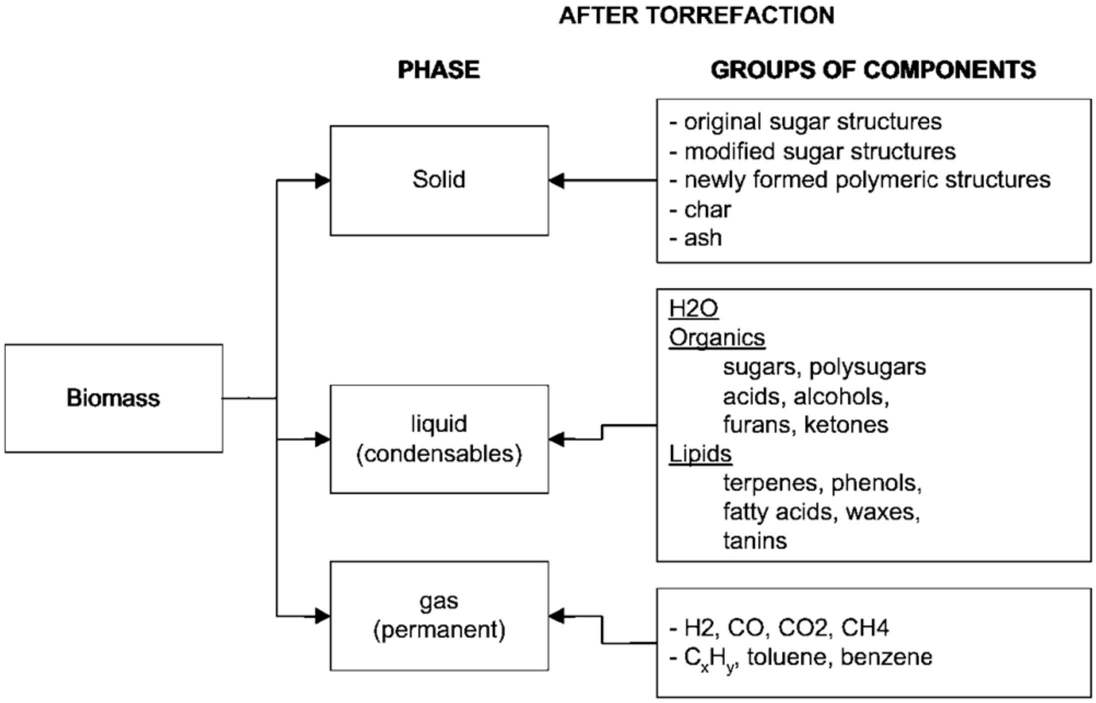

Figure 2-10: Products formed during torrefaction of biomass [Bergmann et al., 2005[a]].

Relative mass and composition of the product depends on the torrefaction conditions (e.g., temperature and time) [Bergman et al., 2005[a]]. Figure 2-11 and Figure 2-12 illustrate an example of product breakdown, with their mass fraction and energy content for torrefaction conditions of 280°C and 17.5 mins reaction time. In this example, 12.5% mass of the dried biomass is transformed into volatiles, of which 64% is water (Figure 2-11). Again the ratio of non-condensable (permanent) gas to volatiles is almost 30:70%, and most of the energy of the volatiles is conserved in condensables (organics and lipids). The permanent gases in this case consist mainly of CO_2 and CO with traces of other components. Since the CO2 is non-combustible, almost all the energy in the gases is with CO. Figure 2-12 shows the extended composition of organic components of the volatiles. Dominant fractions of the organics are acetic acid (~65%), methanol (~15%) and 2-furaldehyde (~5%), which dominates in energy fraction as well.

Figures 2-11 and 2-12 plot the relative Energy and Mass of volatile torrefaction products. They are expressed in terms of the energy of the raw biomass. From Figure 2-12, it is apparent that acetic acid has a lower energy density, while the methanol has a higher energy density. Thus, biomass that releases higher amounts of acetic acid will lose a lower energy dense mass and hence will retain a greater fraction of its energy in solids after torrefaction. For this reason Willow and Birch had an increase in energy density of 17% and 20% respectively, while Larch, with its lower acetic acid fraction in volatiles, had an increase in energy density of only 7% [Prins et al., 2006[b]]

These volatiles and permanent gases contain some parts of the energy of biomass. They are combustible and can be utilized to supplement the thermal load of the entire torrefaction process [Bergman et al., 2005[a]].

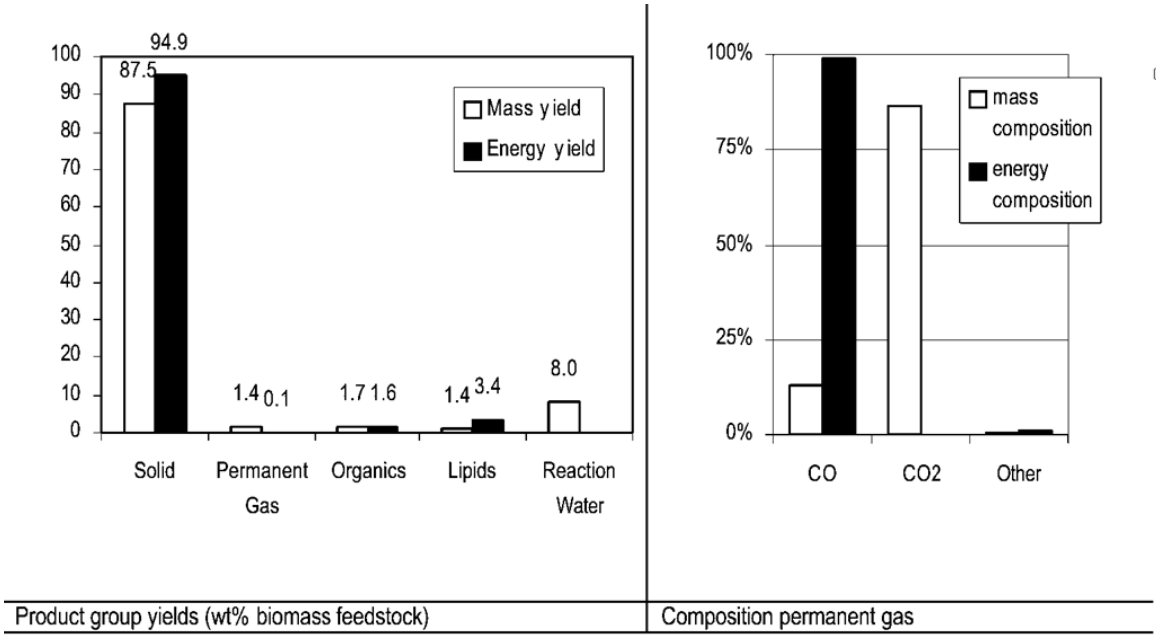

Figure 2-11: Overall mass and energy distribution in major products of torrefaction (woodcuttings at 280°C and 17.5 min reaction time) [Bergman et al., 2005[a]].

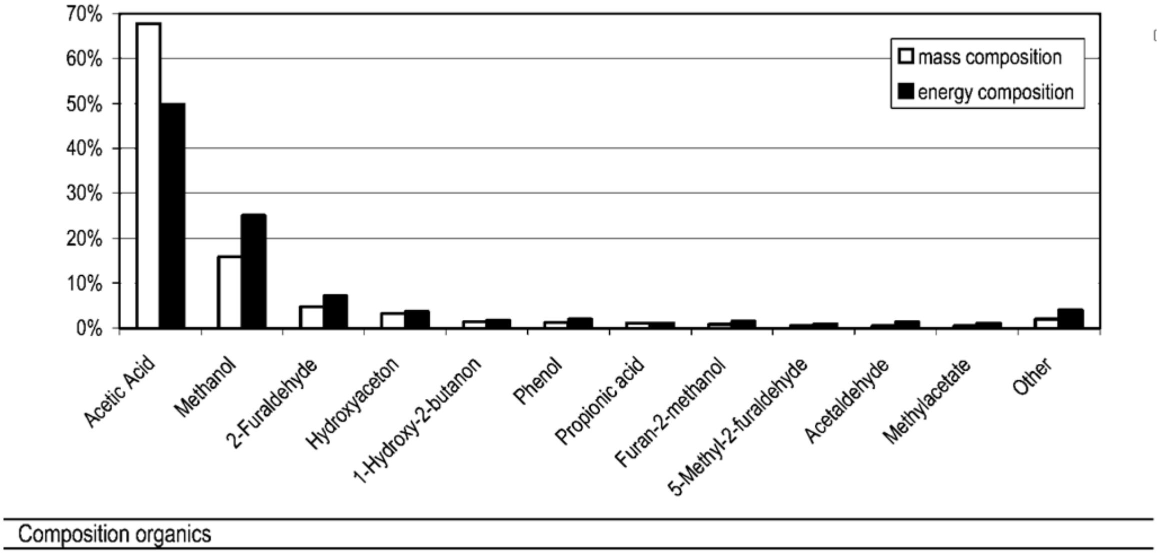

Figure 2-12: Mass and energy yield distribution in condensable volatiles from torrefaction of woodcuttings at 280°C and 17.5 min reaction time [Bergman et al., 2005[a]].

2.6 Properties of Torrefied Biomass (Fuel Quality)

In this section, properties of torrefied biomass are discussed in some detail, with reference to different studies carried out in these areas.

2.6.1 Physical Appearance

After torrefaction, biomass colour changes to anything from brown to black, depending on the severity of the torrefaction. This distinct change in colour helps determine if the biomass is torrefied or not. Even the degree, severity or uniformity of the torrefaction can be roughly determined by the colour. Torrefied biomass also appears dry and friable to the touch.

2.6.2 Energy Density

Significant portion of the released volatiles, acetic acid, is less energy dense than biomass, as a result, the remaining char-rich torrefied biomass attains high energy density i.e., higher heating value per unit mass. From another perspective, during torrefaction, biomass loses relatively more oxygen and hydrogen than carbon. This increases the heating value of the product. Depending upon the severity of torrefaction, energy density can increase up to 102- 120% of the original energy density [Ciolkosz and Wallace, 2011].

Physically torrefaction makes biomass less dense and porous, but it can be compressed into pellets or briquettes. Pellets are attractive end products due to their high volumetric energy density and simplicity in handling. This significantly reduces the transportation and handling cost of the biomass [Bergman et al., 2005]. Additionally uniform size makes handling convenient and reliable.

2.6.3 Proximate Analysis

A good database of proximate analysis of torrefied biomass of different feedstock is available in the published literature [Bergman et al., 2005[a]; Prins, 2005; Bridgeman et al., 2008]. In general, torrefaction reduces the moisture and volatile components of the raw biomass. Due to charring of biomass and cracking of volatiles, the amount of fixed carbon in biomass also increases after torrefaction [Dhungana et al., 2011].

Table 2-3: Proximate analysis of raw and torrefied biomass [Bridgeman et al., 2008]

	Raw	Torrefaction Temperature (^{0}C)			
Biomass & Its Components		230	250	270	290
Reed Canary Grass					
Moisture Content (wet basis) (%)	4.7	-	1.9	1.3	1.2
Volatile Matter (dry basis) (%)	82.5	-	80.3	76.6	70.5
Ash Content (dry basis) (%)	5.5	-	6.4	7.3	8.3
Fixed Carbon (dry basis) (%)	12.1	-	13.3	16.1	21.3
Wheat Straw					
Moisture Content (wet basis) (%)	4.1	-	0.9	0.3	0.8
Volatile Matter (dry basis) (%)	76.4	-	77.0	65.2	51.8
Ash Content (dry basis) (%)	6.3	-	7.4	8.4	10.2
Fixed Carbon (dry basis) (%)	17.3	-	15.6	26.5	38.0
Willow					
Moisture Content (wet basis) (%)	2.8	0.5	0.1	0.2	0.0
Volatile Matter (dry basis) (%)	87.6	82.1	79.8	79.3	77.2
Ash Content (dry basis) (%)	1.7	1.8	1.9	2.1	2.3
Fixed Carbon (dry basis) (%)	10.7	16.1	18.4	18.6	20.5

Torrefaction at higher temperatures causes a large increase in the fixed carbon percentage. For example, Bergman et al. (2005[a]) noted that at 280°C, the decrease in volatile matter (VM) may ranges between 10-15% of its original mass, and the increase in fixed carbon (FC) content ranges between 25-60% of to its original mass. Table 2-3 lists changes in FC and VM for several biomass torrefied at different temperatures.

The absolute amount of Fixed Carbon is increased after torrefaction due to conversion of hemicellulose into more thermally stable compounds [Ciolkosz and Wallace, 2011].

2.6.4 Grindability

Many utility companies are considering using torrefied biomass as a substitute for coal in existing power plants. One of the major challenges of introducing biomass for direct co-firing is matching the power demand on the existing milling machine. Being less brittle and fibrous, biomass requires considerably greater efforts to be ground to an appropriate fineness. To do so, energy density and grindability of the biomass must be close to that of coal. Bergman (2005[a]). Figure 2-13 shows that power consumption of a mill for torrefied biomass reduces significantly around 70-90% compared to that for raw biomass, depending upon the biomass and torrefaction condition.

In the conventional pelletisation production process hammer mills are used for biomass, while for torrefied biomass a simpler type of equipment can be applied (e.g., cutting mill or jaw crusher) or size reduction can be established during densification itself.

While the potential exists for minimizing operational and investments costs for the production of torrefied biomass pellets, very little research has yet examined potential equipment or process modifications to suit torrefied biomass.

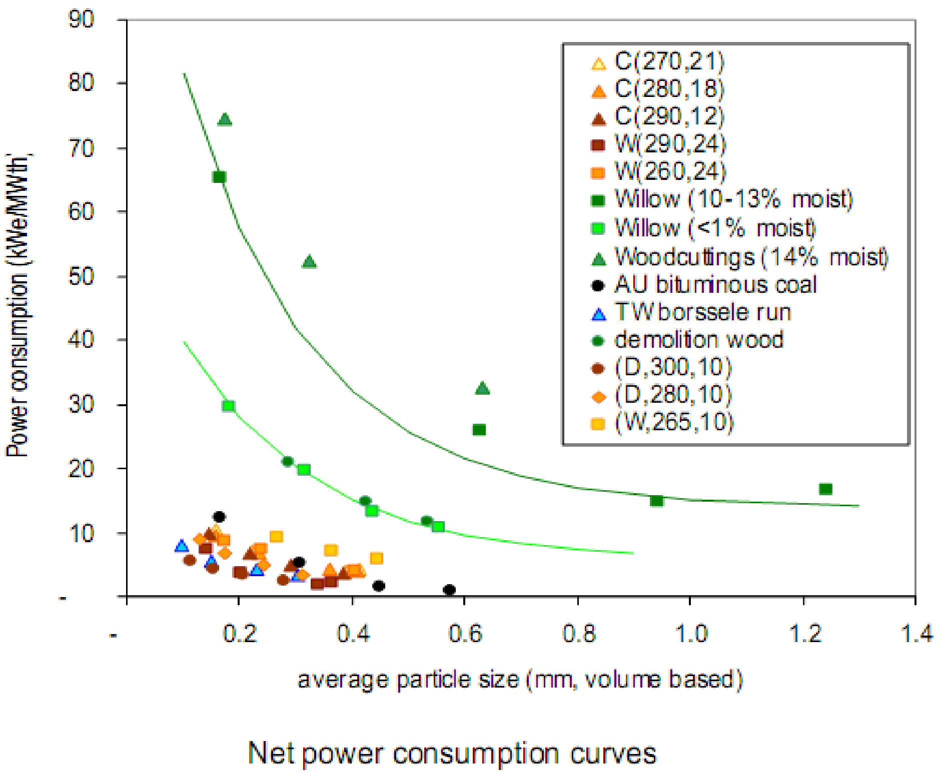

Figure 2-13: Size reduction results of coal, biomass feedstock, and various torrefied biomasses. (C- Coal, W- Wood, D- Demolition wood and (270, 21) – temperature of 270°C and residence time of 21 minutes) [Bergman, 2005].

2.6.5 Hydrophobicity

Biomass absorbs moisture due to the presence of the OH (hydroxyl) group in biomass [Tumuluru et al., 2010]. The torrefaction process removes this group in hemicellulose, and newly-formed molecules are also hydrophobic [Sadaka and Negi, 2009; Ciolkosz and Wallace, 2011]. Again, these new molecules and condensed tar might block the pores so as not to allow capillary uptake of water vapour and subsequent condensation [Felfli, 2005].

Bergman (2005) performed a qualitative assessment of the hydrophobic nature by immersing raw and torrefied biomass pellets in water for 15 hours. It was found that raw biomass pellet quickly disintegrated into original particles while torrefied biomass only took around 7-20% moisture by its weight.

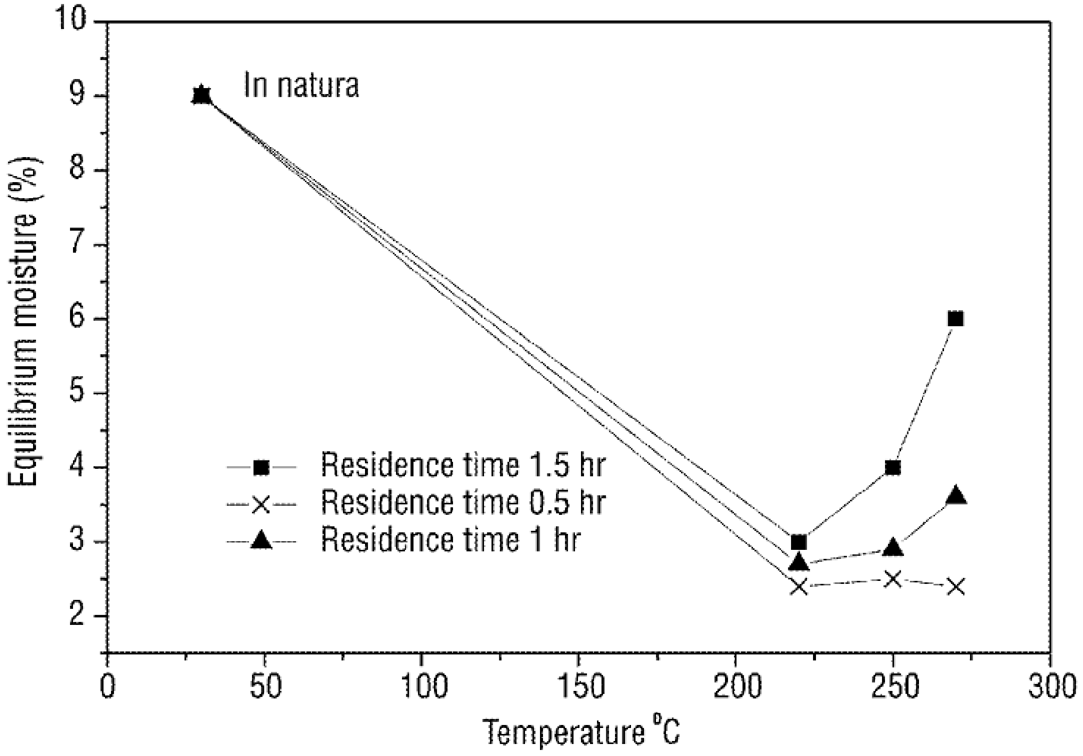

Figure 2-14: Equilibrium moisture content of raw biomass and torrefied biomass briquette at different temperature and residence time [Felfli et al. 2005].

Felfli et al. (2005) quantified this property by calculating the equilibrium moisture of biomass at different torrefaction times. Figure 2-14 shows that, with increased torrefaction temperatures, the equilibrium moisture of the biomass decreased drastically from 9 to 3-4%. However, with further increase in torrefaction temperature (increased severity of torrefaction), equilibrium moisture started to increase. This was predicted due to increase in porosity. In a further extended test, where briquettes were dipped for 16 days, it was found that torrefied biomass briquettes were stable, with only minor addition of moisture. However, the process of calculating the equilibrium moisture is not presented by Felfli et al. (2005). Moreover, there seems to be a lack of a standard methodology in calculating the hydrophobicity of torrefied biomass.

Biomass with no moisture will not support any biological organism. Hence, unlike raw biomass, it will not degrade when stored for an extended period. Because of this property, biomass, like coal, can be stored in an open ground, avoiding the cost of an indoor storage facility.

2.6.6 Combustion Properties

In their study on the reactivity of torrefied biomass, Bergman et al. (2005^{a}) found a small decrease in the reactivity due to the increase in fixed carbon. This means, torrefied biomass could take longer for the complete combustion than raw biomass. This could adversely affect the volumetric heat release rate of a boiler furnace and combustion efficiency or unburnt carbon loss. Nevertheless, it is comparable with that of low-volatile coal, and that could make torrefied biomass more suitable for replacing coal in an existing furnace.

Bridgman et al. (2008) studied the combustion time for torrefied char and volatiles. As, anticipated, due to the increase in the amount of char, the combustion time for the torrefied biomass was longer than that for raw biomass. The burning rate of volatiles is an order of magnitude faster than that of fixed carbon. So, the increase in the combustion period was due to higher fixed carbon amounts in torrefied biomass. This phenomenon becomes more pronounced with increasing torrefaction temperatures, which reduces the volatile content. It was interesting to note that the combustion time for coal is longer than biomass. This may result in a shorter flame, which may affect flame stability, an important issue for co-firing.

Ignition time is another important combustion property of biomass. It defines the time required for biomass to reach a self-sustained combustion at a certain temperature. Bridgeman et al. (2008) found that torrefaction reduces the ignition time for both char and volatiles. This compensates for the increase in the combustion time for torrefied biomass.

One important issues of torrefied biomass related to combustion is the dust explosion hazard [Bergman et al., 2005^{a}; Madrali et al., 2011; Ontario Power Generation, 2010].

Biomass can self-ignite at temperature as low as 150ºC -170ºC [Englisch, 2010]; hence, handling biomass just after torrefaction and its storage offers immense challenges. The explosion potential depends on concentration and size of fines, the flammability limit of torrefied fuels, volatile matter in fuel, and ignition temperature of dust, among other considerations (Basu, 2003).

2.6.7 O/C and H/C ratio

Upon torrefaction, biomass loses various compounds with high Oxygen and Hydrogen contents such as chemically-bound moisture (H_2O), CH_3COOH, CH_3OH and CO_2, so the remaining product has lower O/C and H/C ratios. This is particularly beneficial for gasification of biomass that contains a large amount of oxygen [Prins, 2005; Couhert et al, 2008]. Raw biomass gasified at 950°C suffers from significant over-oxidation; this negatively influences the gasification efficiency, which is alleviated by torrefaction [Prins, 2005].

Furthermore, the increase in the carbon fraction causes increased energy density of the biomass [Bergman et al., 2005^a].

This decrease of O/C and H/C ratio is depicted in the van Krevelen diagram (Figure 1-1) in comparison with other solid fuels. It can be seen that, with increased severity (temperature) of torrefaction, biomass approaches the O/C ratio of low grade coal - Peat.

2.7 Torrefaction vs. Carbonization

Table 2-4 illustrates the properties of torrefied biomass compared among wood, charcoal and coal. Torrefied pellet stands in between wood and charcoal in terms of volatile matter, fixed carbon content and energy density. Due to densification its bulk density and volumetric energy density is very high. Most importantly most of its properties like energy density and volumetric energy density are closer to the lower end of coal. This makes torrefied pellets a close substitute of low grade coal for energy production purpose. Though charcoal energy density is higher than that of coal, it is not economical as energy source, because of excessive mass loss during its production process.

Table 2-4: Comparative fuel properties of torrefied biomass, wood, charcoal and coal [Kleinschmidt, 2011] (wt = wet basis, db = dry basis)

	Wood	Torrefied Pellet	Charcoal	Coal
Moisture (% wt)	30-45	1-5	1-5	10-15
Volatile (% db)	70-75	55-65	10-12	15-30
Fixed Carbon (% db)	20-25	28-35	85-87	50-55
Energy density (db) (MJ/kg)	9-12	20-24	30-32	23-28
Volume energy density (GJ/m^3)	2-3	15-18.7	6-6.4	18.4-23.8
Bulk density (kg/m^3)	200-250	1500-1870	600-640	1840-2380

2.8 Torrefaction Reactors

At the time of writing this thesis, very few commercial plants were reported to have started operations. Nevertheless, within a relatively short period of time (around five years), significant developmental progress has been made. Technology has now entered the commercial demonstration phase [Kleinschmidt, 2011]. Madrali et al. (2011) report 10 projects slated to be in production by the end of 2011, with a few front runners testing with torrefaction units of capacities greater than 5 tonnes per hour. Table 2-5 shows the various reactors currently being developed by parties all around the globe.

Table 2-5: Torrefaction reactors under development [Madrali et al., 2011; WPAC, 2011; Kleinschmidt, 2011 and respective companies' websites]. (CA-Canada, BE-Belgium; FR-France; NL- Netherands; GR-Germany; S- Spain, UK-United Kingdom, USA-United States of America)

S. N.	Party (Developers)	Reactor name	Country	Heating mode	Reactor Technology	Target date	Capacity (t/h)
1	Torr-coal	Torr-coal	NL	Indirect	Rotary Drum	2010/11	4.5
2	4 Energy	Stramproy	NL	Direct	Belt conveyer	2010/11	5.5
3	Torrsys	Torrsys	USA	-	-	2011/12	5
4	EBES	ACB	GR	Direct	Rotating Drum	2012	1.5
5	Integro	Wyssmont	USA	Direct	Multiple hearth	2010/11	2
6	West Creek Energy	Konza	USA	Direct	Rotary drum	2012	10
7	Topell	Torbed	NL	Direct	Toroidal Fluidized Bed	2011	8
8	ETPC	BioEndev	S	Indirect	Rotary Drum	2012/13	4.3
9	BTG	BTG	NL	Indirect	Screw Conveyer	2014	5
10	Foxcoal	Foxcoal	NL	Indirect	Screw Conveyer	2010/11	4.2
11	Biolake	ECN	NL	Direct	Moving Bed	2011	5
12	Agritech	Torre-tech	USA	Indirect	Screw Conveyer	2011	5
13	RFT	RFT	USA	Indirect	Screw Conveyer	2012	5
14	Stramproy	Stramproy	NL	Direct	Oscillating Belt Conveyer	2010/11	5.5
15	New Earth	ECO-PYRO	USA	Direct	Oscillating Belt Conveyer	2012	2
16	ECN	BO_2	NL	Direct	Moving bed	2012	5
17	IDEMA	Thermya	FR	Direct	Moving Bed	2011	2.5
18	Atmosclear	Airless	UK	Direct	Belt	2011	5
19	Diacarbon	Diacarbon	-	-	-	2014	8
20	CanBiocoal	Rotawave	UK	Direct	Microwave	2011	12

S. N.	Party (Developers)	Reactor name	Country	Heating mode	Reactor Technology	Target date	Capacity (t/h)
21	C2SKY	-	-	-	-	2011	5
22	WPAC	WPAC	CA	unknown Technology	unselected	2012	5
23	CDS	CDS	UK	Direct	Rotating Drum	-	-
24	BIO3D	BIO3D	FR	Direct	Rotating Drum	-	-
26	CMI-NESA	CMI-NESA	BE	Direct	Multiple Hearth	-	-
27	Airex	Airex	CA	-	-	-	-
28	Allied Blower	-	-	Indirect	Augers	-	-
29	Alterna	Alterna	CA	Direct	Tunnel	-	-
30	Thermya	-	FR	Direct	Moving bed	-	-
31	Terradyne	-	CA	Direct	Not disclosed	-	-
31	Torrfuels	SVI	CA	Direct	Rotary drum	-	-
32	Buhler	Buhler	USA	Direct	Compact Moving Bed	-	-

In Table 2-5, we can see that most of the developers are from Europe and are leading the development effort. The Netherlands (NL), in particular, is quite aggressively working on this technology. On the other hand, the Canadian presence in this technology race is slight, due to its late entry into the field. At this stage, torrefaction technology is close to commercial demonstration, which is still not the end of the development process. The reactors need to be optimized for the most economical process while meeting the requirements of the end use. Hence, the product still requires a substantial amount of testing on end applications. Moreover, the demand of the end users cannot be easily assessed, as none of the users are experienced with this product. A concerted effort from both sides (i.e., producer and end user) is necessary to put this technology into action [Kleinschmidt, 2011].

2.8.1 Choice Of Reactor

The majority of the developers are companies with extensive backgrounds in biomass processing and conversion technology, such as carbonization and drying. Thus, the reactors they are developing are reactors they are most familiar with. In other words, little has been done to develop an optimal reactor from the ground up.

The technology proposed by the developers (Table 2-5) can be broadly classified as indirect and direct heating reactors, based on the mode of heating [Dhungana and Basu, 2011; Bergman et al., 2005[a]]. Bergman et al. (2005[a]) attempted theoretically to assess the performance of the reactors technology and select the best one. For this assessment, only three reactors were shortlisted for comparison, based on assumptions that these three were the most promising types of reactors and covered both types of heating mechanism, namely direct and indirect heating. The selected reactors types were the indirectly-heated screw reactor, the directly-heated rotating drum and the directly-heated moving bed. Upon further evaluation based on energy efficiency and heat transfer coefficients, the directly heated moving bed reactor was selected as the best technology. It had the best heat transfer coefficient and energy efficiency while being the cheapest. However, other qualitative aspects can also be decisive in the choice of reactor technology. Table 2-6 presents qualitative comparison of major reactor technologies.

In conclusion, there is no universal best reactor technology as all of them have their pros and cons. However, for the given properties and application of the biomass, the proper technology can be selected. Nevertheless, to date, experimental observations comparing these reactors are lacking.

Table 2-6: Pros and cons of torrefaction technology currently being developed [adapted from WPAC, 2011]

Technology	Pros	Cons
Rotating Drum	• Can be both direct and indirect heating. • Uniform heat transfer. • Takes large variation of size and wastes biomass.	• Lower heat transfer. • Difficult temperature control. • Scalability unproven. • Large footprint and cost.
Moving Bed	• Simple and economical. • High heat transfer.	• Selective biomass size and type only due to pressure drop limitations. • Channelling of gas. • Difficult temperature control. • Scalability unproven. • Non-uniform temperature distribution especially for indirect heating.
Screw Conveyer	• Better biomass flow. • Takes wide range of size.	• Hot spots. • Lower heat transfer. • Scalability unproven.
Belt Conveyers	• Better temperature control. • Can take wide size of biomass.	• Weak upsizing possibilities. • Non-homogeneous product. • Numerous mechanical parts.
Multiple Hearth	• Good heat transfer. • Good temperature control. • Wide range of size acceptable. • Proven scalability.	• Large size.
Fluidized Bed	• Good heat transfer. • Proven scalability.	• Particle size limitations. • Attrition of biomass and loss of fines. • Slow temperature response. • Separation of bed solids and biomass.

Technology	Pros	Cons
Microwave	- High heat transfer. - Can take large size of biomass also. - Modular. - Fast torrefaction. - Good temperature control.	- Electric energy required. - Needs to be integrated with other conventional heater for uniform heating. - Non-uniform heating of biomass particles' interior. - Effect of rapid heating of biomass unknown.

2.9 Applications

Torrefaction is a biomass upgrading process that converts biomass into a superior product. Without original constraints on the biomass, it can easily be used in many applications, such as co-firing, pellets, reducing agent and gasifier fuel [Prins, 2005]. As well, the optimized production of torrefied biomass will eventually reduce the cost of electricity generated from biomass [Bergman and Kiel, 2005]. This can be the most economic CO_2 abatement option which can be applied in a relatively short term. Gerard and Shah (1991) studied the application of the torrefied biomass in several processes. The actual evaluation or testing of these products remains, some of the applications of the torrefied biomass are explained below.

2.9.1 Torrefied Biomass Pellet

As a fuel, torrefied biomass pellets are superior to conventional pellets with regards to technology and economics [Bergman, 2005; Zwart et al., 2006]. Torrefaction not only makes the biomass pellets cheap but also increases their quality through high energy density, hygroscopic property, absence of biological activity, and high strength. Torrefied biomass pellet is an appropriate biomass intermediate product, which can be used for conversion of biomass to energy, liquid or gas (BtE, BtL & BtG).

2.9.2 Co-Firing in PC-Fired Boilers

Torrefaction can alleviate many constraints of biomass co-firing. It is particularly effective for direct co-feeding of biomass and it significantly improves biomass handling and combustion properties. For direct co-firing of biomass in a pulverized coal fired (PC) boiler, biomass has to be grounded to a fine size, similar to coal. Green biomass takes about seven times more energy for pulverizing than by coal. Torrefaction significantly improves this property and bridge this problem in co-firing of biomass. Biomass percentage mixed to coal can also be raised after torrefaction (20% to 40% by energy basis) [Kleinschmidt, 2011]. However, one still needs to address the uncertainty regarding the quality of the torrefied biomass.

2.9.3 Gasifier Fuel (BtL and BtG)

Girard and Shah (1991) explained advantages of torrefied biomass as a fuel for gasification. Based on the results of a number of experiments, they concluded that a higher heating gas can be produced, especially at the very low moisture content of torrefied biomass. Moreover, torrefied biomass gasification allows higher gasification temperature, yields a cleaner gas of constant quality increasing the fix-bed capacity and decreases the dust content of the gas when substituting charcoal.

Prins (2005, p. 134) found that torrefied biomass is a better feedstock for fluidized bed gasification. Bergman et al. (2005^b) discovered that torrefaction solved the feeding problems in entrained flow gasifier. This finding is important, as efficient gasification of biomass can lead to economical production of liquid fuel by the Fischer Tropsch process.

2.9.4 Reducing Agent

High fixed carbon in torrefied product renders it useful as a reducer. The Pechiney plant was constructed in France in the 1980s as a demonstration plant for the purpose of producing a reducing agent. Although the project was technically sound, it was dismantled in the early 1990s for economic reasons. This chemical application of torrefied biomass is good for diversifying the market of the torrefied biomass.

2.9.5 Domestic Fuel

Torrefied wood can be used as an excellent alternative to coal or raw wood for domestic application. It generates less smoke and has high heating value. It can be used in many countries where charcoal is used for cooking.

2.9.6 Chemical Production

Production of chemical by-products during torrefaction or supplying torrefied biomass as a feedstock to chemical industries may alter the economics of biomass torrefaction to a great extent.

2.10 Torrefaction Patent

Publication of a large number of patents within a short period of time signifies the strong interest of business in this field. Table 2-7 presents published patents in various jurisdictions. As can be seen, a significant portion of the patents are registered in the USA. This does not necessarily mean that the technology originated in USA but that developers from different jurisdictions also registered patents in US for potential marketing there.

Table 2-7: Torrefaction patents from various jurisdictions

Jurisdiction	Valid Patents	Application	Expired/Abandoned	Total
Canada	0	7	2	9
US	1	13	2	16
Europe	0	6	2	8
Rest of the World	0	12	3	15

Table 2-8: Lists of some of the patents on torrefaction

SN	Title	Publication date	Country	Application number
1	Autothermal and mobile torrefaction devices	10/08/2009	US	US12418381
2	Process for converting ligneous matter of vegetable origin by torrefaction and product obtained there by	11/19/1985	France.	4553978
3	System and method for drying and torrefaction	04/08/2010	US	12/456427
4	Process and device for treating biomass	04/02/2009	Netherlands	12/160106
5	Method and system for roasting a biomass feedstock	03.01.2008	France.	FR2007/001086
6	Process and apparatus for making a densified torrefied fuel	2003/04/12	US	US2003221363
7	Method and system for the torrefaction of raw materials	2005/06/23	Netherlands	PCT/NL 2004/000873
8	Method and apparatus for biomass torrefaction, manufacturing a storable fuel from biomass and producing offsets for the combustion products of fossil fuels and a combustible article of manufacture	2007/11/22	US	US2007266623
9	Method for the preparation of solid fuels by means of torrefaction as well as the solid fuels thus obtained and the use of these fuels	2009/02	Netherlands	EP2027233
10	Method and system for roasting a biomass feedstock	2008/01/03	France	FR2007001086
11	Thermo-condensed lignocellulose material, and a method and an oven for obtaining it	1989/03/28	US	US 4954620
12	Method for producing torrefied wood, product obtained thereby, and application to the production of energy	1988/11/29	US	US 4787917

As can be seen in Table 2-7, there are around 50 patents. Table 2-8 lists some of these patents. Lebouttee (2009) has summarized the most comprehensive lists of around 45 patents.

2.11 Conclusion

1. Research into torrefaction is still at an early stage of development. Most of the knowledge and related technology is adapted from drying, carbonization and pyrolysis. Since the beginning, the most intense drive for the technology was to produce an optimized torrefaction reactor. Interest in torrefaction is growing tremendously, but the development in science has not been able to keep pace. There are still many parameters whose effect on torrefaction is not very clear, such as heating rate and particle size. Nevertheless, some solid research has been done on the fundamental science of torrefaction, though further investigations are urgently needed.
2. As different biomasses behave differently in the torrefaction process, an optimum production recipe for individual or groups of biomass might be different. This issue needs further investigations.
3. Torrefaction reactors are now in the commercial demonstration stage, but the fundamental challenge is still to identify the optimum production process. This is difficult because the properties of the product should come from the demand side. For example, co-firing may simply require acceptable grindable and hydrophobic biomass, but long-distance transportation of biofuel may require a more energy dense product. Hence, the process should be optimized based on the end use. The irony here is that end users cannot give specific requirements, since there is no past experience of what exactly is required. Hence, team work with input from both sides is required to push this technology from demonstration into application. This requires further work in the quantification of torrefied biomass quality.
4. Issues like dust explosibility, emissions from the torrefaction production and storage and other safety aspects need to be studied.

5. Torrefaction science is based on the behaviour of the major lignocellulose material of the biomass (i.e., cellulose, hemicellulose and lignin) with hemicellulose undergoing major thermochemical degradation. However, there are many types of biomass which are not lignocellulose such as sewage sludge, municipal waste and food processing waste. These biomasses could benefit the most from this process, but no attempts in this direction have been tried to date.
6. The selection of the most suitable reactor according to size and type of biomass is essential for optimum efficiency and quality of the product, as there is no single perfect reactor. Theoretical comparisons are currently being made based on pre-existing knowledge of these reactors used in processes like drying and pyrolysis. A comparative study of these reactors in actual torrefaction process has not yet been published.

CHAPTER 3: TORREFACTION OF NON-LIGNOCELLULOSE WASTE BIOMASS[1]

In this chapter torrefaction of some non-lignocellulose waste biomass are presented, which examines if such materials could benefit from this process as conventional lignocellulose biomass does. Experiments were conducted on Poultry waste, digested sludge, and undigested sludge from a municipality in Canada together with other common lignocellulose biomass: wood pellet and switchgrass and an agricultural residue: coffee husk for a comparative analysis.

3.1 Background

In Canada, approximately 660,000 dry tonnes of bio-solid is produced every year (CCME, accessed in 2011). Majority (around 50%) of it is incinerated and other half is used for land application as fertilizer, the rest is used for landfilling (CWWA, accessed in 2011). Incineration and landfill disposal have much environmental concerns including release of large amount of GHG gas. Land application is often under pressure due to leaching and runoff issues. Common waste-to-energy practice in sewage sludge is incineration. This is a good commercial option, but is often energy negative i.e. energy required for the process is more than what it produces (ESRU, accessed in 2011). Some attempts have been made to produce fertilizer or soil remediation compounds from sludge by mixing lime, but the market for fertilizer is unstable and rather limited due to environmental concerns. Some other non-lignocellulose wastes such as poultry litter has major disposal problems. The use of poultry litter in cattle feed is no longer viable because of the threat of bovine spongiform encephalopathy (BSE).

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1 This chapter is based on the paper: Dhungana, A., Dutta, A., Basu, P., 2011. Torrefaction of non-lignocellulose biomass waste., Canadian Journal of Chemical Engineering, Wiley Online Library. The copyright of this journal is attached in Appendix A.

A novel technology like torrefaction may effectively deal with these kinds of waste where the traditional method of disposal is no longer is suitable or desirable. The torrefaction process in woody biomass is explained as the depolymerisation reactions of the lignocellulose components (Section 2.2). However, non-lignocellulose biomass contains significantly different components. Table 3-1 shows the composition of poultry waste and sewage sludge. The fibre is termed as ‘crude fibre’, which is indigestible fibres, majorly cellulose (Matrone et al., 1946). Depending upon the species of the bird, fibre content may be around 15% (Martin et al, 1983). Nitrogen Free Extracts is an estimate of crude starch and sugar content. It is important to note that poultry waste means the manure only, while poultry litter is a mixture of bedding, manure, feathers, and spilled feed. Hence, the actual fibre content on poultry litter can vary significantly depending upon the type and percentage of the bedding material. The percentage of fibre in sewage sludge is even less than in poultry waste (Table 3-1).

Table 3-1: Typical chemical composition of dry poultry waste (El-Sabban et al., 1970) and dried sewage sludge [Beaudouin et al, 1980]

	Moisture (air dried) (%)	Crude Protein (%)	Crude Fibre (%)	Ether Extract (%)	Nitrogen Free Extracts (NFE) %	Ash (%)
Dried Poultry Waste (no litter)	8.83	24.88	10.43	2.23	35.3	27.17
Dried Sewage sludge	8.1	25.9	4.3	0.46	40.6	28.8

Thermal behaviour of materials like crude protein, NFE and ether extract are unknown. Their torrefaction for pre-treatment of sewage sludge has been discussed in several publications (Leckner, 2007, Veringa et al., 2004), but no comprehensive research on this waste is reported in published literature. Thus no data on torrefaction of non-lignocellulose biomass like sludge or poultry litter is available. The present research attempts to fill this important gap in the present body of knowledge on torrefaction. If torrefaction proves viable for such difficult biomass, it could potentially be one of the most preferable means of handling such waste. Biomass with relatively high lignin content can be blended with sludge to form a new type of biofuel that can be pelletized for burning of gasification in a wide range of systems.

3.2 Objective

The main objective of this work is to investigate into the torrefaction of waste non-lignocellulose biomass (poultry litter and sewage wastes). The properties of the torrefied biomass are assessed by mass yield, energy yield and the heating value. Specific objectives of this work are:

1. To perform a mass and energy balance of a typical woody biomass
2. To observe the effects of torrefaction temperature and residence time on non-lignocellulose biomass in comparison with some known lignocelluloses biomasses such as wood pellet and switchgrass pellet along with an agricultural waste: coffee husk. Properties of the product are assessed using proximate analysis and higher heating value.

3.3 Materials and Methods

3.3.1 Biomass Samples

Digested sewage sludge (treated after anaerobic digestion) along with undigested or raw sewage sludge were collected from the Municipality of Truro, Nova Scotia, Canada. As these wastes undergo biological degradation with time, long-term storage is not recommended for them. Hence within one month of collecting the samples, they were dried and stored for further experiments. Poultry litter is a mixture of poultry waste and bedding material (wood chips) 50% each by weight. Switchgrass pellets (from NSAC, Truro, NS), commercial wood pellets and coffee husks were also used. The physical properties of these samples are shown in Table 3-2. A change in any of these properties can impact the results, owing to their effects on heat transfer.

Table 3-2: Physical properties of biomass samples

S.N.	Biomass	Solid Size	Bulk Density (Dry) (kg/m3)
1	Poultry Waste	Generally flakes of 1 -2 mm thickness and 1 cm length as well as small particles of less than 2 mm diameter	150-250
2	Digested Sludge	Porous 3D flakes when dried	150-250
3	Undigested Sludge	Porous 3D flakes when dried	150-250
4	Switchgrass Pellets	¼” diameter, ½” to 1” long	500-700
5	Wood Pellets	¼” diameter, ½” to 1” long	600-800
6	Coffee Husk	< 0.5 cm	200-300

3.3.2 Mass and Energy Balance in Torrefaction (for Sawdust)

As shown in Figure 3-1, a simple arrangement was prepared to investigate the basics of the torrefaction process and its products. Half the length of a 6.35 mm diameter and 305 mm long reactor was filled with Pine sawdust (75-600μm) and then heated for an hour in a muffle furnace at 280°C. After loading the biomass, the reactor was flushed with nitrogen a few times. During torrefaction, the volatiles traveled through an ice bath and finally into a gas bag (Figure 3-1). All of the condensable volatiles and moisture were collected in the ice bath and the non-condensable gases in the gas bag (Figure 3-1). Figure 3-2 shows a photograph of the arrangements for the collection of volatiles and gases in this experiment. Following this procedure, the torrefied biomass and condensed volatiles were weighed and respective HHV was calculated by a bomb calorimeter (model 1360 Plain Jacket, by Parr Instruments). In the case of collected gases, a proxy method was used. First the gas composition was measured from a gas chromatograph. Then, from the known properties of those respective gases, mass and HHV of the product was mathematically calculated (Equation 3.1 and 3.2).

$$\text{Mass of the gas} = \sum \text{Volume fraction x density of the corresponding gas} \qquad (3.1)$$

$$\text{HHV of the gas} = \sum \text{Volume fraction x density x HHV of the corresponding gas} \quad (3.2)$$

Error analyses of the results are performed in Appendix E.

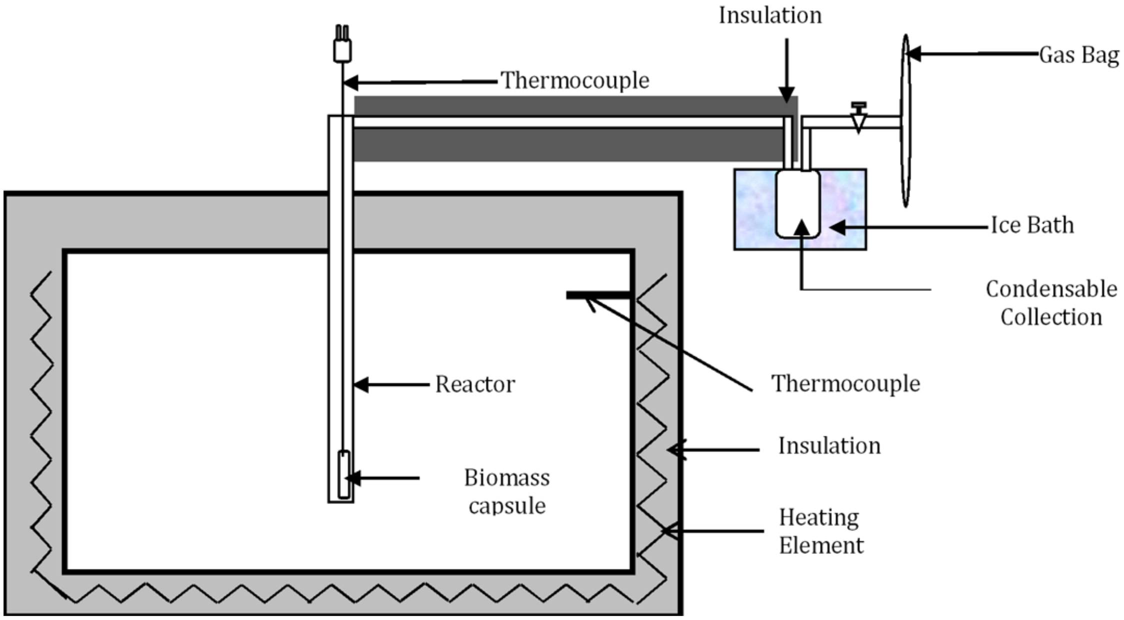


Figure 3-1: Schematics of the reactor arrangement to collect the products of torrefaction.

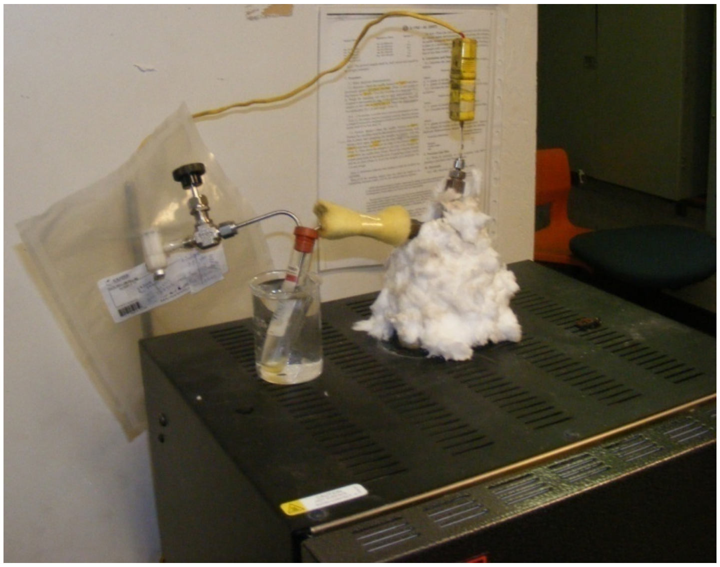


Figure 3-2: Photograph of the actual experimental arrangement to collect the products of torrefaction.

3.3.3 Torrefaction of the Non-lignocellulose Biomass

A second set-up was fabricated to examine the mass and energy yield of waste biomass torrefaction. Prior to torrefaction, all of the samples were dried according to ASTM standard (D1762-84) procedure. The samples, around 1-2 gm in mass, were kept in a muffle furnace for two hours at 105°C. They were then cooled down in a desiccator and weighed, after which they were again placed in the muffle furnace for another hour and weighed. This was repeated until the two consecutive masses were almost same. The change in mass per unit original mass of raw biomass is calculated as the moisture percentage. These dried samples were then torrefied in the muffle furnace. The arrangement of the reactor is shown in Figure 3-3. Multiple samples on their respective crucible, 2±0.2 gm in mass, were heated in the muffle furnace. No attempts were made here to collect the gases and condensable, as only the properties of the torrefied biomass were studied. The muffle furnace was maintained O_2-free by continuously flushing with an inert gas (Argon). A built-in thermocouple controlled the temperature of the furnace, while a separate thermocouple monitored the actual temperature in the furnace.

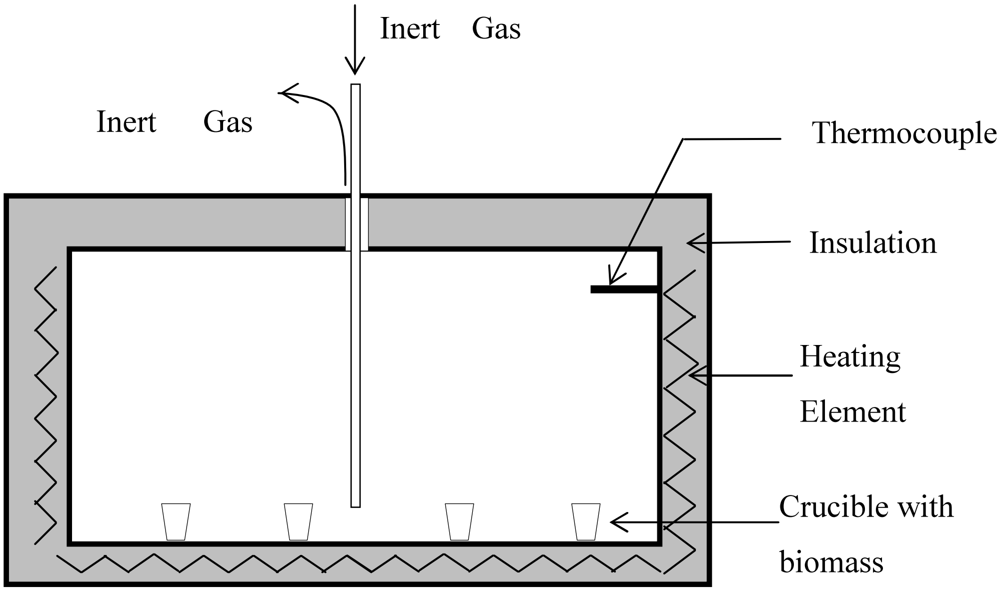


Figure 3-3: A schematic of the experimental set-up to study torrefaction in different types of biomasses.

The flow rate of the Argon was maintained to prevent infiltration of air inside the oven. The furnace temperature was increased slowly to the required temperature at a rate of 20°C/min. The residence time for torrefaction was measured after the temperature inside the reactor (oven) crossed 200°C. This does not correspond to the temperature of the biomass; hence this is not the reaction time.

To examine the effect of residence time and temperature on the properties of the torrefied biomass waste, two different torrefaction temperatures (250°C and 280°C) and three different residence times (15, 30 and 60 mins) were chosen. The products were allowed to cool in a vacuum desiccator. After 60 minutes of cooling, the weight of the samples were measured and then subjected to proximate analysis and bomb calorimetry. The yields of torrefaction were measured in terms of mass yield, energy yield and energy density. Mass yield and energy yield are defined in equation 2-1 and 2-2. Equation 3-3 below defines the energy density ratio. All the values are presented on a dry and ash free (daf) basis. .

$$\text{Energy density ratio} = \frac{\text{Higher heating value(daf) of torrefied biomass}}{\text{Higher heating value(daf) of raw biomass}} \tag{3-3}$$

The mass yield is the fraction of the original mass that remains in the torrefied biomass, while energy yield indicates the percentage of the original thermal energy retained in the biomass after torrefaction and the energy density ratio gives the ratio of the increase in heating value of the torrefied biomass compared to raw biomass. Error analyses of the results are performed in Appendix E

3.4 Results and Discussion

Results and discussion of this experimental work are presented below.

3.4.1 Drying

Table 3-3 shows the moisture content of each sample. We can see that the moisture content of the sludge is extremely high and that only 10% by weight of the sample is solid. This indicates that, a large amount of energy is required to drive off this quantity of moisture. Wet torrefaction (heating in pressurized water) may be a preferable torrefaction route for these types of biomasses, but this process is still in conceptual stage. Coffee husks also showed a significant proportion of moisture, followed by poultry waste. Wood pellets and switchgrass pellets, have lower moisture content.

Table 3-3: Biomass and its moisture content and time for drying

S.N.	Type of Biomass	Biomass	Moisture Content (%)	Drying Time (hrs)
1	Non-lignocellulose	Digested sludge (bio-solid)	89.2 %	7
2	Non-lignocellulose	Undigested sludge (Sewage)	92.97%	8
3	Non-lignocellulose	Poultry waste	28.36%	2
4	Lignocellulose	Switchgrass pellets	7.94%	2
5	Lignocellulose	Wood pellets	7.70%	2
6	Lignocellulose	Coffee husks	60.21%	2

Table 3-3 also lists the total time required for each biomass type to dry (according to the ASTM standard D1762-84). Digested sludge and undigested sludge took an extremely long time to dry. This may be attributed to the relatively large moisture content (~90%) in sludge samples, but this alone cannot explain the phenomenon. The coffee husk sample also had a large (~60%) moisture content, yet its drying time was about the same as the biomass containing less than 10% moisture. Formation of a solid shell around the sludge biomass was visible during intermittent weighing stages. Hence, one can speculate this to be responsible for reduced heat and mass transfer to and from the interior of the sludge causing an extensive drying period. An investigation into the drying process not being the main objective of the work, no additional exploration into this cause was conducted.

3.4.2 Torrefaction

This section discusses the results obtained on ligno- and non-ligno-cellulose biomass separately.

3.4.2.1 Torrefaction of a Lignocellulose Biomass (Mass and Energy Balance)

A generic description of the torrefaction process will be provided here first, using sawdust as an example of a typical lignocellulose biomass. After that, a detailed description of the effects of biomass type and operating parameters on torrefaction yields is presented.

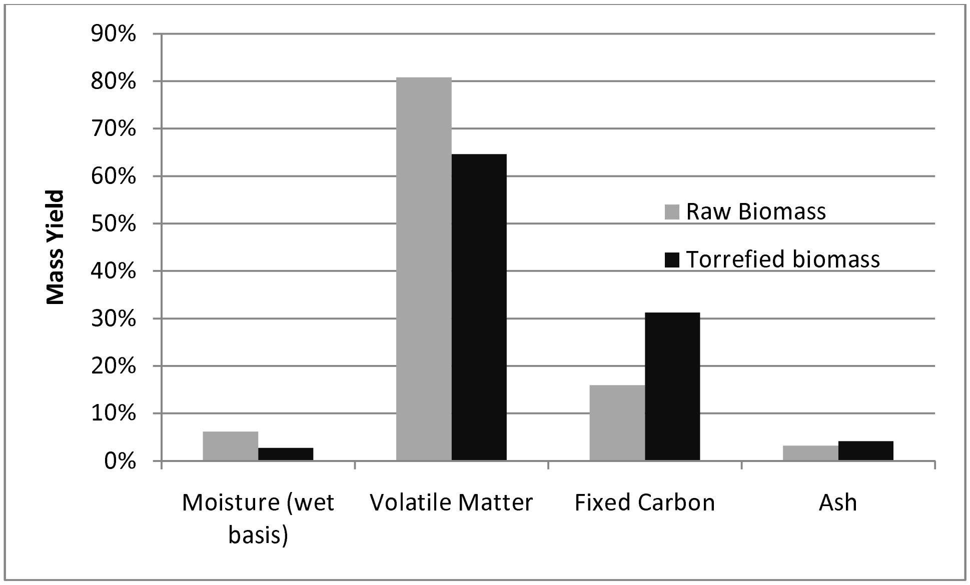


Figure 3-4: Proximate analysis of raw and torrefied biomass (sawdust).

Figure 3-4 compares the proximate analysis of raw sawdust with that of torrefied sawdust. It also shows that the solid product of torrefaction is not pure char, as one would have expected of the carbonization process. This is because volatile and moisture content have only been reduced (compared to the parent biomass), not eliminated. The torrefaction process does not remove any part of the fixed carbon (FC) and ash content of a biomass, but these parameters instead increase in percentile owing to the reduction in other constituents of the biomass. However, upon closer observation, one notes a significant increase in the absolute amount of FC (about 42% above the original amount), calculated by multiplying the FC percentage of torrefied biomass with the mass yield of the solid. This might be due to cracking of volatiles into char.

A typical mass balance of the torrefied product of sawdust is shown in Figure 3-5. It can be observed that the major portion of the volatiles generated is condensable. In the figure, 73% of the torrefaction product is solid, 22% is condensable volatiles, and about 6% is a non-condensable gas mixture. Pach et al. (2002) reported a similar observation in their study of torrefaction of Pine, where, torrefaction at 280˚C for an hour produced 77.3% solids, 19.6% condensable volatiles and 2.1% gases. Ferro et al. (2004) reported an 88.1% solid yield, 8.5% liquid yield and 2.9% gas yield. Figure 3-5 also shows the distribution among the products. Most of the energy (94%) is still in the solid biomass while losing a large percentage of mass, indicating that biomass experiences energy densification. Ferro et al. (2004) also reported solid's energy yield of 92% in similar tests.

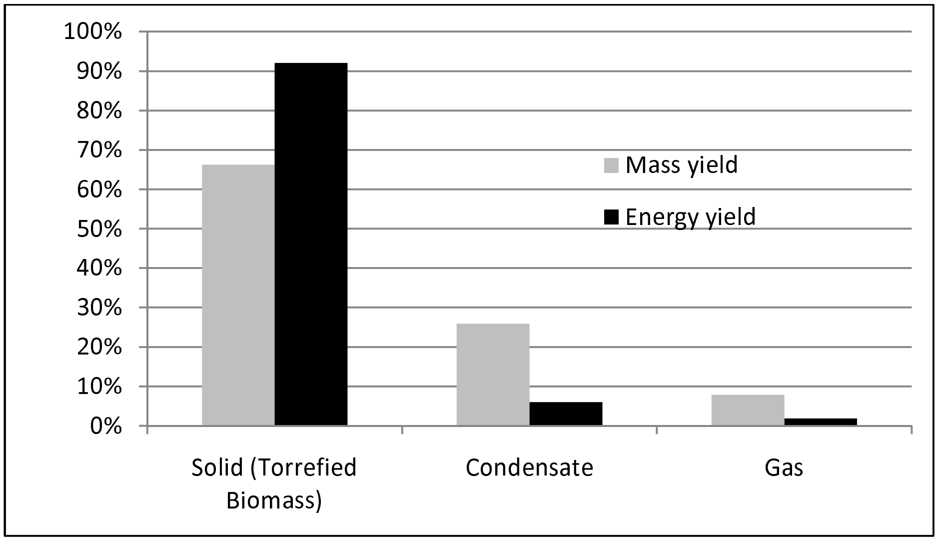


Figure 3-5: Mass and heat balance of the torrefaction of sawdust.

Among the volatiles generated, condensates hold the majority of the energy (75%). Condensates can be easily separated from the gas stream and used for energy recovery, though condensates contain large fraction of water (Bergman et al., 2005). The bomb calorimeter showed that the heating value of solid biomasses increased from 18.4 MJ/kg to 23.12 MJ/kg, and that the heating value of condensable volatiles generated was 4.12 MJ/kg. A gas chromatography of the remaining gases revealed that CO and CO_2 were major constituents and H_2 in trace amounts. About 64% (by mass) of the non-condensable gas was CO_2 and 36% CO (Figure 3-6). This result is consistent with a study by Pach et al. (2002), where Pine torrefied at 280 ^{0}C for 1 hour produced gases with 68.2% of CO_2 and 31.4% of CO, with traces of other gases (C1 and C2). Taking heating value of CO as 10.11 MJ/kg, the heating value of the non-condensable gas can be calculated as 3.6 MJ/kg.

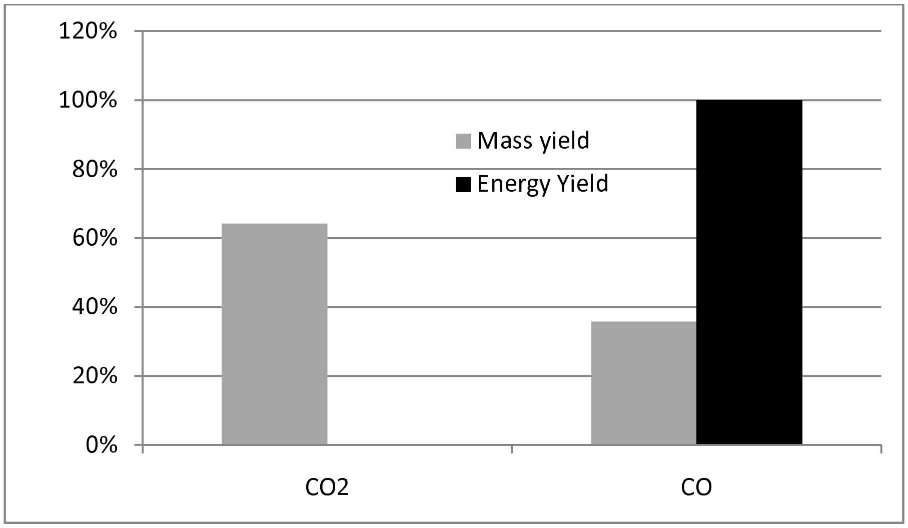


Figure 3-6: Mass and energy share of the components in gas from sawdust.

3.4.2.2 Torrefaction of Non-lignocellulose Biomass

Here, results of torrefaction of the three types of non-lignocellulose along with other three type of lignocellulose biomass are presented and discussed. Table 3-4 lists proximate analysis and higher heating value of the samples studied. It can be observed that fixed carbon contents in both types of sewage sludge are very small compared to that of others, while the ash content is higher. Coffee husk had a very high percentage of ash because it was mixed with some inert soil material, which could not be separated. All these biomass were torrefied at different set of temperatures and residence times and their properties studied.

Table 3-4: Proximate analysis and heating value of the different biomasses studied

	Proximate Analysis				HHV (MJ/kg) (db)
Biomass	Moisture (wt)	Volatile Matter (db)	Ash (db)	Fixed Carbon (db)	
Poultry waste	28.36%	69.17%	13.49%	17.35%	16.59
Digested sludge	89.20%	71.52%	20.57%	7.90%	21.59
Undigested sludge	92.97%	76.28%	15.15%	8.56%	20.53
Switchgrass	7.94%	78.07%	3.27%	18.67%	19.24
Wood pellets	7.70%	81.37%	1.01%	17.61%	18.91
Coffee husk	60.21%	47.09%	32.01%	20.90%	14.19

a) Visual Observation

The most distinctive property of a torrefied biomass is the change in its visual appearance. The biomass changes its colour into anything from brown to black, depending upon the severity of torrefaction. Severely torrefied biomass appears totally black like carbonized biomass. However, the torrefaction and carbonization are two distinct thermal treatments. Figure 3-7 shows photographs of biomasses before and after torrefaction. It can be seen that all of the torrefied biomasses are either black or dark brown. Moreover, they felt more dry and friable touch.

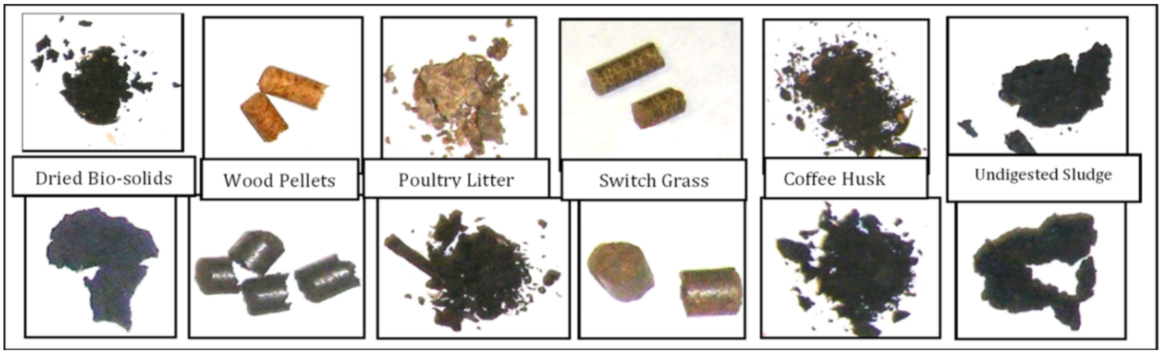


Figure 3-7: Color changes in biomass due to torrefaction. Top row shows photograph of the biomass before torrefaction and the lower row shows that after torrefaction.

b) Increase in Energy Density

The heating values of the raw and torrefied biomasses were first measured. Then, using results from the proximate analyses, dry and ash free heating values were calculated. These numbers were fed into Eq. 3-3 to calculate the energy density ratio. Table 3-5 lists the energy density ratios of the tested biomasses along with the values obtained by other investigators in other biomass types. All the tests were performed under the same temperature and residence time (i.e. at 280°C for 30 minutes).

From Table 3-5 it is apparent that at 250^0C, all three non-lignocellulose biomasses (digested sludge, undigested sludge and poultry litter) gained in energy density in the range of 7-16%. Digested sludge had the highest HHV (daf), but its percentage rise in HHV (daf) was the lowest of all three. Experimental values at 280°C showed an even greater (12-24%) rise in HHV, with digested sludge having the lowest (12%) rise. These values are comparable with wood pellets, which had 7% and 20% rises in energy density at 250°C and 280°C, respectively. This is an important finding, as it proves that the energy density of waste biomass can be significantly increased even though it contains a tiny amount of hemicellulose, if not any. The rise in energy density of these non-lignocellulose biomasses is likely due to the decomposition of other organic components of the biomass. These results suggest that the presence of hemicellulose is not essential for raising the energy density of biomass through torrefaction.

Table 3-5: Comparison of experimental energy density ratio with data in literature

	HHV (MJ/kg) daf Raw Biomass	Temperature (°C)	At 30 mins residence time
			Energy density ratio (daf)
Lignocellulose Biomass			
Wood pellet	19.1	250	1.07
		280	1.20
Willow[a]	20.0[e]	250	1.03
		270	1.07
Willow[b]	19.85	280 (18mins)	1.09
Sawdust[d]	19.63	250	1.04
		285	1.10
Wood briquette[c]	20.02[e]	250	1.06
		270	1.14
Switchgrass	19.89	250	1.06
		280	1.27
Coffee husk	20.16	250	1.05
		280	1.21
Wheat straw[a]	18.90[e]	250	1.05
		270	1.07
Reed canary grass[a]	19.50[e]	250	1.03
		270	1.07
Non-Lignocellulose Biomass			
Poultry waste	19.18	250	1.16
		280	1.24
Digested sludge	26.91	250	1.07
		280	1.12
Undigested sludge	24.20	250	1.14
		280	1.16

a) Bridgeman et al., 2008, b) Felfli et al., 2007, c) Bergman and Kiel, 2005, d) Nimlos et al., 2003 e) Data calculated from correlation with ultimate analyses by respective authors.

Table 3-5 also compares the energy density ratio of three lignocellulose biomass samples with those of additional six biomasses measured by other researchers [Bridgeman et al., 2008, Felfli et al., 2007, Bergman and Kiel, 2005, Nimlos et al., 2003]. Data from Bridgeman et al (2008) and Bergman and Kiel (2005) are calculated from a correlation from elemental analyses. One notes that the increase in energy density of all lignocellulose biomasses is of the order of 3-7%. This rise is smaller than that observed for the non-lignocellulose biomass. Experimental data at a higher temperature (280^{0}C) shows an even higher (7-27%) rise in energy density. These results are similar to those observed for non-lignocellulose biomasses at 280^{0}C. The volume of data is, however, not sufficiently large for a definitive conclusion to be drawn, only three types of non-lignocellulose biomasses have been studied. Nevertheless, it can at least be inferred that such biomasses could experience a rise in energy density similar to what is expected of most lignocellulose biomasses.

c) Effect of Residence Time

Residence time is an important design parameter in torrefaction because it determines the size of the reactor and the quality of the product. Hence, it is important to know the optimum residence time for a biomass. A longer residence time gives higher energy density but lower energy yields. The appropriate choice of residence time depends upon the specific demands of the consumers.

In this experiment, all biomass samples were torrefied over a wide range of residence times (15 – 60 mins). Table 3-6 illustrates a comparison of proximate analyses of three non-lignocellulose biomasses and their torrefied products with other lignocellulose biomasses. Analyses are based on the dry mass of raw and torrefied biomasses (except for the moisture content, which is a percentage of the wet biomass). As expected, the moisture content (on a dry basis) of biomass was reduced to a negligible amount after torrefaction. Indeed, torrefaction results in a drop in the volatile matter (VM) percentage (on a dry basis), because a part of the volatile is depolymerised. The drop in VM percentage is higher for longer residence time. For example, at 250 ^{0}C, the VM of undigested sludge decreased from 72.68% to 61.39% when residence time in the torrefier increased from 15 to 60 minutes. At a higher temperature (280 ^{0}C), the trend of variation of VM with residence time is similar to that at lower temperature, though the absolute value is lower. Figures 3-8 and 3-9 compare the change in VM at different residence times for undigested sludge and wood pellets.

Table 3-6: Proximate analysis of raw and torrefied biomass

`	Poultry litter											
	Residence time (min)											
	15	30	60	15	30	60	15	30	60	15	30	60
Temperature	Moisture			Volatile matter			Ash Content			Fixed Carbon		
250 ^{0}C	0.61%	0.40%	0.21%	69.38%	63.67%	58.59%	14.16%	15.98%	16.39%	16.46%	20.35%	25.02%
280 ^{0}C	-	-	-	70.40%	60.19%	47.12%	12.96%	17.14%	30.13%	16.64%	22.67%	22.75%
Raw biomass	28.36%			69.17%			13.49%			17.35%		
	Digested Sludge											
	Residence time (min)											
	15	30	60	15	30	60	15	30	60	15	30	60
Temperature	Moisture			Volatile matter			Ash Content			Fixed Carbon		
250 ^{0}C				70.81%	63.42%	61.60%	19.28%	23.95%	24.35%	9.91 %	12.63%	14.05%
280 ^{0}C	0.16%	0.35%	0.20%	65.90%	56.54%	54.26%	21.27%	26.08%	26.27%	12.83%	17.38%	19.48%
Raw biomass	89.20%			71.52%			20.57%			7.90%		
	Undigested Sludge											
	Residence time (min)											
	15	30	60	15	30	60	15	30	60	15	30	60
Temperature	Moisture			Volatile matter			Ash Content			Fixed Carbon		
250 ^{0}C	-	-	-	72.68%	67.29%	61.39%	16.25%	18.97%	20.52%	11.07%	13.74%	18.09%
280 ^{0}C	-	-	-	68.61%	65.27%	57.86%	16.36%	17.63%	21.06%	15.03%	17.10%	21.08%
Raw biomass	92.97%			76.28%			15.15%			8.56%		

	Switchgrass											
	Residence time (min)											
	15	30	60	15	30	60	15	30	60	15	30	60
Temperature	Moisture			Volatile matter			Ash Content			Fixed Carbon		
250 ^{0}C	0.35%	0.41%	0.16%	78.92%	76.69%	67.65%	3.30%	3.63%	4.35%	17.78%	19.68%	28.00%
280 ^{0}C	-	-	-	77.94%	66.81%	55.92%	3.17%	4.33%	5.79%	18.89%	28.86%	38.29%
Raw biomass	7.94%			78.07%			3.27%			18.67%		
	Wood Pellet											
	Residence time (min)											
	15	30	60	15	30	60	15	30	60	15	30	60
Temperature	Moisture			Volatile matter			Ash Content			Fixed Carbon		
250 ^{0}C	0.16%	0.26%	0.15%	81.06%	80.31%	77.09%	0.93%	0.87%	1.02%	18.01%	18.82%	21.89%
280 ^{0}C	-	-	-	80.97%	75.46%	66.16%	0.81%	1.24%	1.46%	18.22%	23.30%	32.38%
Raw biomass	7.70%			81.37%			1.01%			17.61%		
	Coffee Husk											
	Residence time (min)											
	15	30	60	15	30	60	15	30	60	15	30	60
Temperature	Moisture			Volatile matter			Ash Content			Fixed Carbon		
250 ^{0}C	0.23%	0.28%	0.17%	47.70%	42.61%	41.53%	30.17%	33.70%	36.09%	22.14%	23.68%	22.38%
280 ^{0}C	0.23%	0.38%	0.39%	47.26%	38.99%	37.01%	29.90%	38.62%	36.21%	22.83%	22.39%	26.78%
Raw biomass	60.21%			47.09%			32.01%			20.90%		

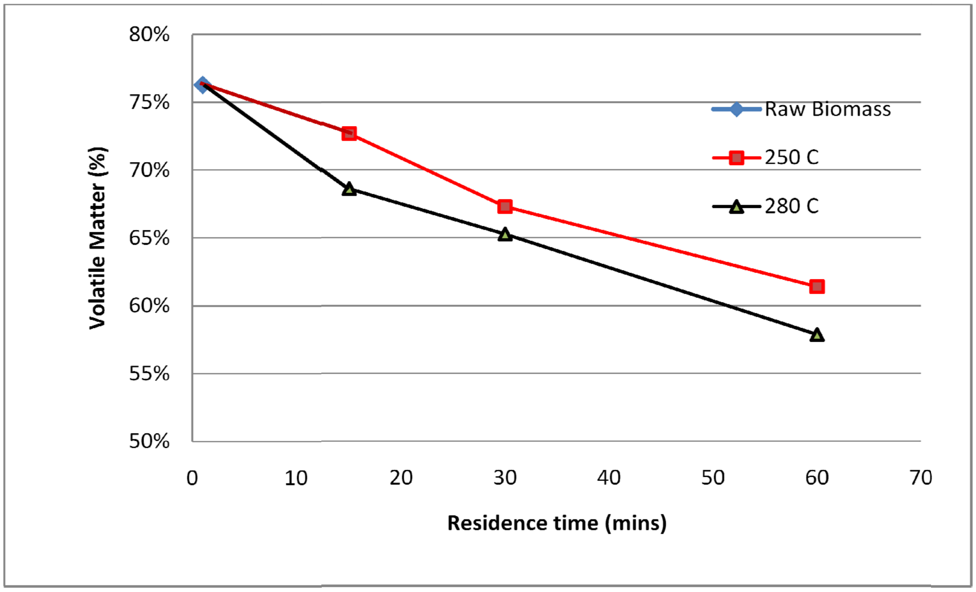


Figure 3-8: Change in volatile matter before and after torrefaction of undigested sludge.

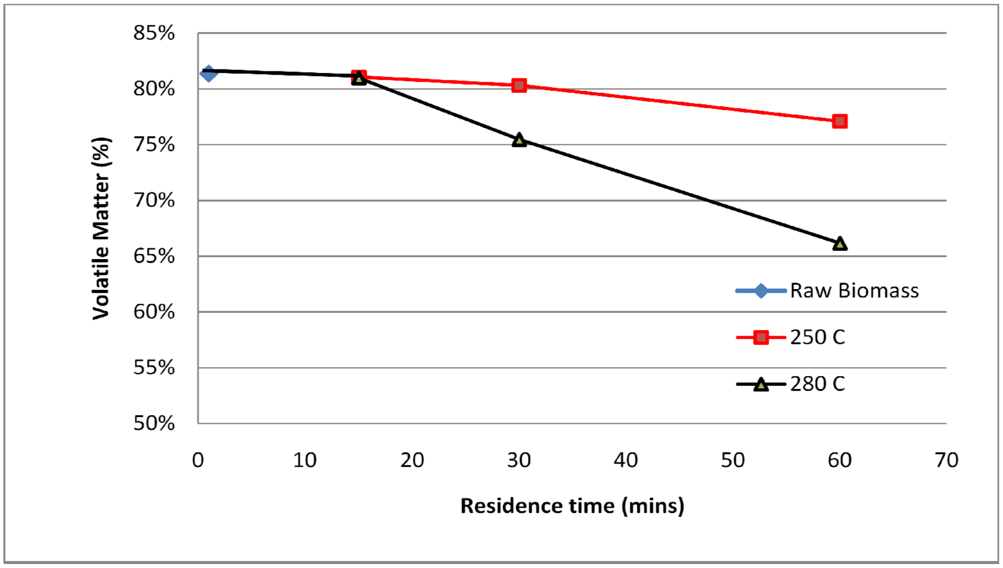


Figure 3-9: Change in volatile matter before and after torrefaction of wood pellets.

As the values in Table 3-6 are mass specific, analyses regarding a change in the absolute amount of the components cannot be inferred from these data. As can be seen, fixed carbon (FC) of undigested sludge increased from 8.56% to 21.08% when torrefied at 280°C for 60 minutes, partly due to the loss of volatiles, as is often the case for increases in ash percentage. Thus, a proper way would be to compute the change in the percentage of FC of the raw biomass. Table 3-7 shows absolute FC percentage per unit raw biomass (daf), computed by multiplying the FC percentage in the torrefied biomass with its mass yield. Figures 3-10 and 3-11 show the change in absolute amount of FC per unit raw biomass, where it is slowly increasing with increase in residence time and temperature.

Table 3-7: Change in fixed carbon per unit raw biomass upon torrefaction for different biomasses.

Undigested Sludge			
	Residence time (min)		
	15	30	60
Temperature	Absolute Fixed carbon/ mass of raw biomass (daf)		
250°C	10.08%	10.74%	12.62%
280°C	12.41%	12.94%	13.50%
Raw biomass	8.56%		
Digested Sludge			
	Residence time (min)		
	15	30	60
Temperature	Absolute Fixed carbon mass		
250°C	9.72%	10.59%	11.26%
280°C	12.37%	13.12%	14.39%
Raw biomass	7.90%		
Wood Pellet			
	Residence time (min)		
	15	30	60
Temperature	Absolute Fixed carbon mass		
250°C	17.39%	17.62%	18.90%
280°C	16.37%	18.35%	20.33%
Raw biomass	17.61%		

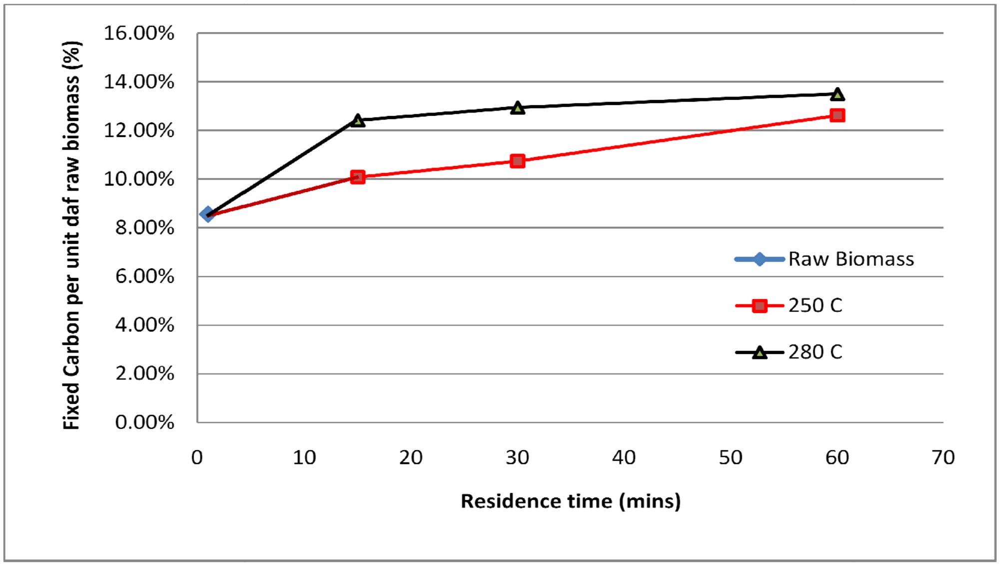


Figure 3-10: Change in absolute percentage of fixed carbon per unit raw biomass (daf) in undigested sludge.

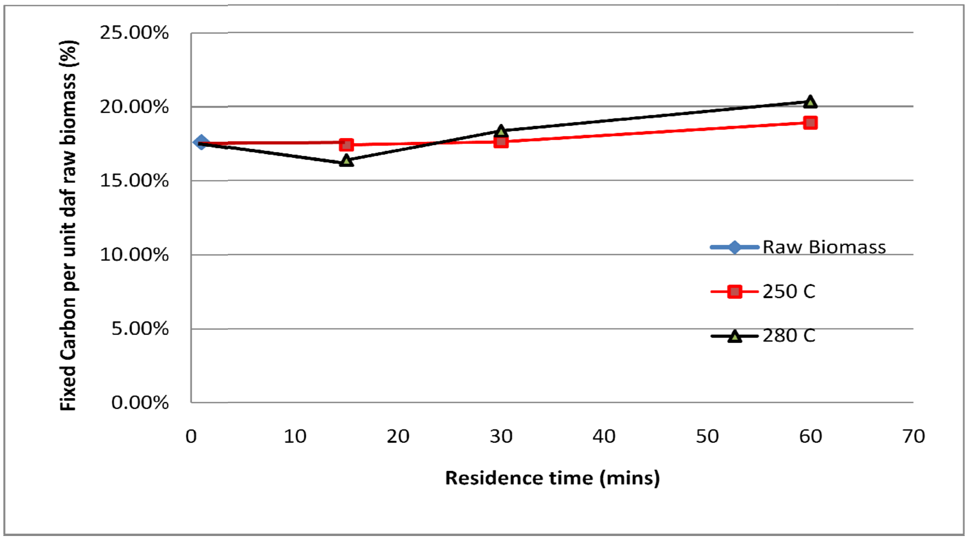


Figure 3-11: Change in absolute percentage of fixed carbon per unit raw biomass (daf) in wood pellets.

Table 3-7 shows the increase in the absolute value of FC per unit raw biomass (daf) in two non-lignocellulose biomass compared with wood pellet. It can be observed that the absolute FC has almost doubled after being torrefied at 280°C for 60 minutes. However, this increase in wood pellet is comparatively small and shows that a large amount of volatiles of non-lignocellulose gets charred into FC upon torrefaction. Such effects of residence time on the fixed carbon (FC) were also observed by Felfli et al. (2005). Absolute mass of fixed carbon in a unit weight of briquette is calculated to increase from 19.38% to 21.16% by increasing residence time from 30 to 90 minutes at 270˚C. This conversion of volatile matter to FC highlights a significant positive feature of torrefaction

d) Effect of Temperature

To examine the effect of temperature on torrefaction, experiments were conducted at two torrefaction temperatures typically used by many other researchers; 250 ^{0}C and 280 ^{0}C. Table 3-8 shows that the mass of the torrefied biomass decreases with increasing temperature at each residence time. Though the change in temperature was a modest 30 ^{0}C, the effect of temperature is decidedly more pronounced than that of residence time. It can be clearly seen in Figures 3-8, 3-9, 3-12 and 3-13 that the change in volatile matter and fixed carbon follow a steeper path for high temperatures.

Table 3-8: Mass yield and energy yield of biomass after torrefaction

	Poultry Litter								
	Residence time (min)								
	15	30	60	15	30	60	15	30	60
Temperature	Mass Yield (daf)			Heating Value (MJ/kg) (daf)			Energy Yield (daf)		
250 ^{0}C	90.60%	84.97%	77.84%	21.06	22.25	24.06	99.5%	98.6%	97.6%
280 ^{0}C	75.48%	59.61%	39.92%	21.64	23.69	24.56	85.2%	73.6%	51.1%
Raw biomass				19.18					
	Digested Sludge								
	Residence time (min)								
	15	30	60	15	30	60	15	30	60
Temperature	Mass Yield (daf)			Heating Value (MJ/kg) (daf)			Energy Yield (daf)		
250 ^{0}C	98.04%	83.88%	80.16%	27.25	28.67	29.64	99.3%	89.3%	88.3%
280 ^{0}C	96.41%	75.48%	73.90%	27.40	30.25	30.58	98.2%	84.9%	84.0%
Raw biomass				26.91					

	Undigested Sludge								
	Residence time (min)								
	15	30	60	15	30	60	15	30	60
Temperature	Mass Yield (daf)			Heating Value (MJ/kg) (daf)			Energy Yield (daf)		
250 ^{0}C	91.07%	78.15%	69.75%	25.71	27.50	29.16	96.8%	88.8%	84.1%
280 ^{0}C	82.60%	75.69%	64.05%	25.82	28.11	30.32	88.2%	87.9%	80.3%
Raw biomass				24.20					
	Switchgrass								
	Residence time (min)								
	15	30	60	15	30	60	15	30	60
Temperature	Mass Yield (daf)			Heating Value (MJ/kg) (daf)			Energy Yield (daf)		
250 ^{0}C	94.53%	87.36%	74.84%	20.55	21.14	22.85	97.7%	92.8%	86.0%
280 ^{0}C	88.88%	69.19%	56.84%	20.62	25.32	25.89	92.1%	88.1%	74.0%
Raw biomass				19.89					
	Wood Pellet								
	Residence time (min)								
	15	30	60	15	30	60	15	30	60
Temperature	Mass Yield (daf)			Heating Value (MJ/kg) (daf)			Energy Yield (daf)		
250 ^{0}C	96.60%	93.61%	86.35%	19.78	20.45	22.11	98.0%	98.2%	98.0%
280 ^{0}C	89.85%	78.77%	62.80%	20.31	22.85	23.93	93.7%	92.4%	77.1%
Raw biomass				19.48					
	Coffee Husk								
	Residence time (min)								
	15	30	60	15	30	60	15	30	60
Temperature	Mass Yield (daf)			Heating Value (MJ/kg) (daf)			Energy Yield (daf)		
250 ^{0}C	98.68%	90.57%	86.06%	20.20	21.24	22.06	98.8%	95.4%	94.1%
280 ^{0}C	97.73%	76.78%	73.71%	20.38	24.43	24.95	98.8%	93.0%	91.2%
Raw biomass				20.16					

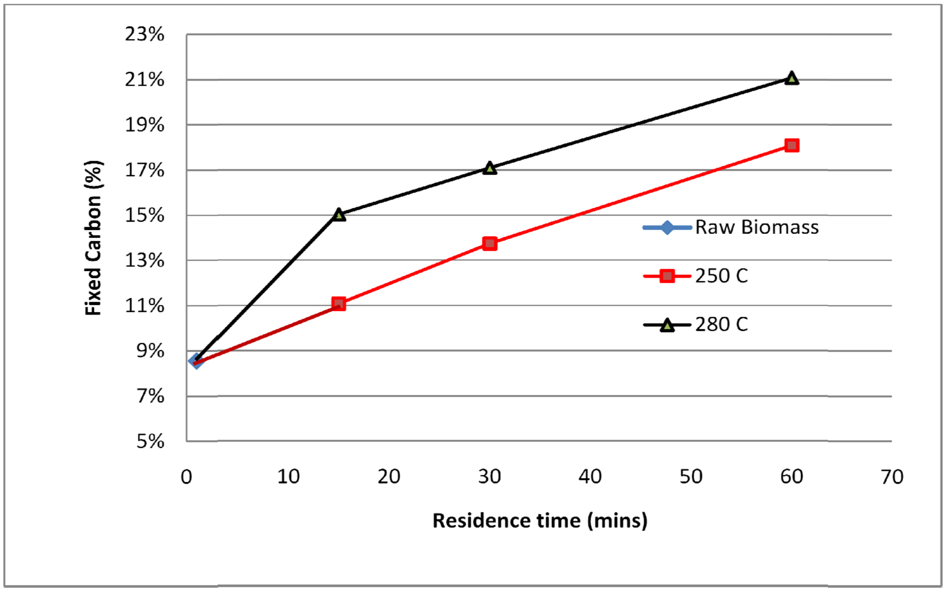


Figure 3-12: Change in fixed carbon before and after torrefaction of undigested sludge.

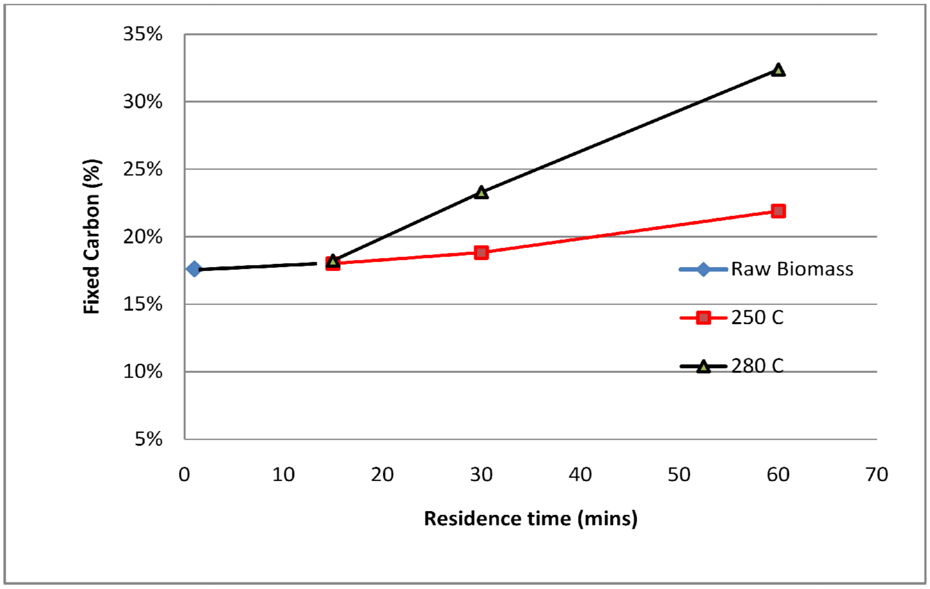


Figure 3-13: Change in fixed carbon before and after torrefaction of wood pellets.

e) Effect on Heating Value

The heating value (or energy density) is one of the most important parameters in assessing the quality of torrefaction. The more energy dense the product is, the lower are the transportation and handling costs. Together with mass yield, the heating value presents nearly the full picture of the torrefaction process and its product. It is always desirable to have a high energy density biomass while keeping the mass yield maximum. Hence, mechanical volume reduction through compaction or pelletization is an attractive option together with torrefaction.

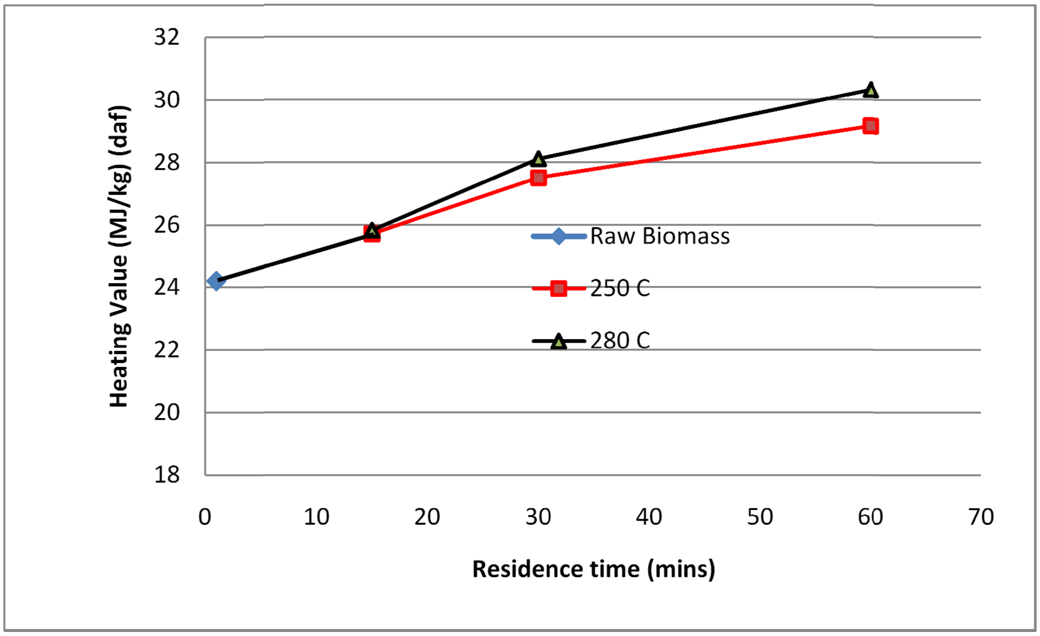


Figure 3-14: Effect of residence time and temperature on heating value of undigested sludge.

Figure 3-16 shows both mass yield and energy density of of the Undigested sludge, where it is evident that the mass and the energy yield decreases with increasing residene time and tempeature. Table 3-8 lists similar results for all the three non-lignocellulose waste biomasses (poultry litter, digested sludge and undigested sludge) along with other non-lignoclellulose biomass. Figures 3-14 and 3-15 plots the heating value of undigested sludge and wood pellets against residence time for both torrefaction temperatures. They show that the heating value is consistently higher for higher temperatures. They also show that the increase in energy density is higher in non-lignocellulose than in lignocellulose biomass, which is apparent in (Table 3-7) in the energy density ratio analysis.

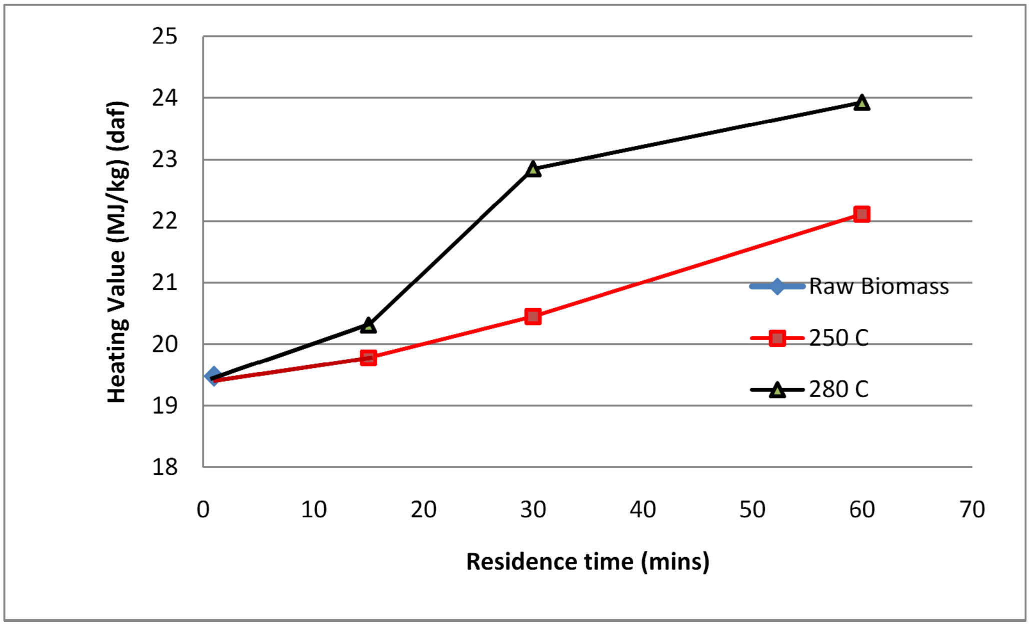


Figure 3-15: Effect of residence time and temperature on the heating value of wood pellets.

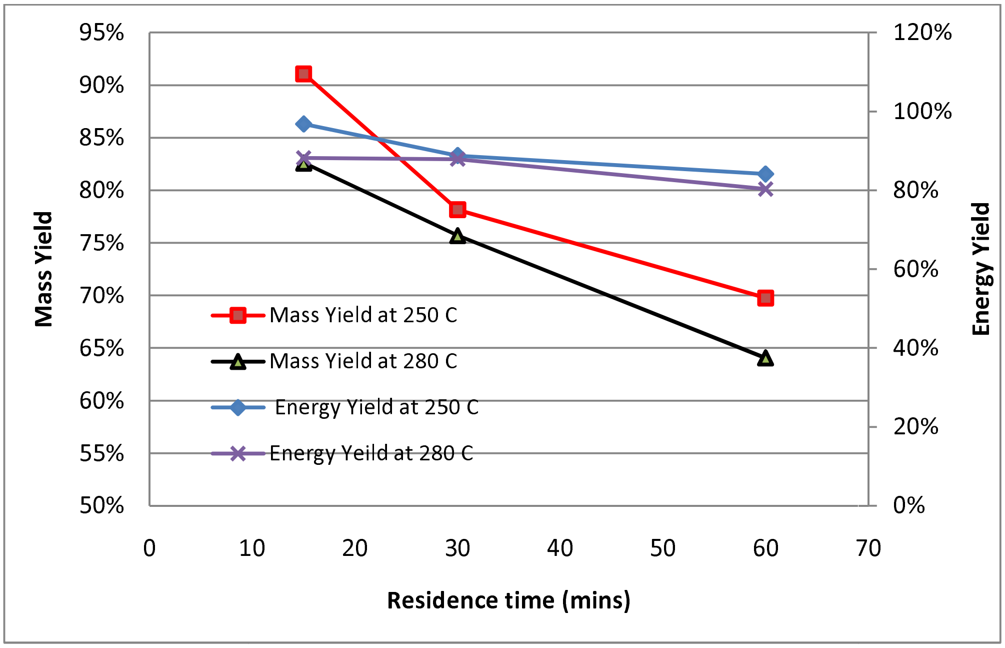


Figure 3-16: Change in Mass Yield and Energy Yield of Undigested sludge torrefied at various temperatures and residence times.

Table 3-8 also presents measured values of mass yield, energy density and calculated values of energy yield, all expressed on a dry ash free basis. Here, undigested sludge retained between 80 to 97% of the energy content after torrefaction, while digested sludge retained 84 to 99%. All figures are subjected to an experimental error of ± 5%. So, a 99.3% retention should not be taken as an indication of no loss in energy during torrefaction. This error is very high for coffee husk (±30% on HHV) because the biomass, as received, was mixed with inseparable inert material (soil).

Table 3-8 also lists experimental values of three lignocellulose biomasses: wood pellet, switchgrass and coffee husk for comparison. From these values, we can see that the energy yield and increase in HHV are of the same order as that for non-lignocellulose biomass. For example, coffe husk had an energy yield of 91.2-98.8%, wood pellet of 77.1-98.2%, and switchgrass of 74-97.7%. All three lignocellulose biomasses showed increases in heating value and decreases in energy yield with increasing residence time, a trend similar to that observed for non-lignocellulose biomass. A similar increase in HHV was noted for other lignocellulose (e.g., Williow, Wood briquette, Wheat straw, Reed Canary Grass) studied by other researchers (Table 3-5).

Of these non-lignocellulose biomasses, sludge has the highest percentage of ash content, while woody biomass has only negligile ash content (Table 3-6). Hence, a comparison based on an increase in HHV on a daf basis may not give a real picture of the actual HHV (dry basis). Upon calculation of HHV on a dry basis of undigested sludge (Table 3-9), it becomes apparent that the increase in HHV of the undigested sludge is not particularly high, as observed in Table 3-8. Furthermore, the relative increase in heating value (dry basis) with a change in residence time or temperature is much lower than in the case of wood pellets. There was a 17 % increase in energy density (dry basis) when torrefied at 280C for 60 mins (Table 3-9), which was 25% when considering the dry and ash free basis (Table 3-8). Nevertheless, 17% is a substantial increase and the value of HHV (dry basis) of 23.93 MJ/kg makes it an attractive fuel. This value is comparatively high than that in the literature, which is partly due to lower amounts of ash in raw dried sludge (15.15%) and the properties of the sludge being very specific to location and time. However, higher heating values in the literature can be found ranging from 13 to 21

MJ/kg (dry basis) [Thipkhunthod et al., 2005]. Hence, tests on similar waste from different sources needs to be performed to confirm these quantitative claims.

Table 3-9: Energy density (dry basis) of undigested sludge and wood pellet

	Undigested Sludge			Wood Pellet		
	15	30	60	15	30	60
Temperature	Heating Value (MJ/kg) (dry)			Heating Value (MJ/kg) (dry)		
250°C	21.53	22.28	23.18	19.60	20.27	21.88
280°C	21.60	23.15	23.93	20.15	22. 57	23.58
Raw biomass	20.53			19.28		

3.5 Conclusion

1. Torrefaction of three non-lignocellulose waste biomass shows that although such biomasses are low or free from hemicellulose they also undergo an increase in energy density similar to that experienced by lignocellulose biomass.
2. The extent of increase in energy density in non-lignocellulose is similar to those measured for the lignocellulose biomasses, switchgrass, coffee husk, wood pellet and poultry waste.
3. With an increase in torrefaction time the energy density increases but the energy yield decreases. Absolute values and trends are similar for both non-lignocellulose and lignocellulose biomasses.
4. Temperature has a greater effect on torrefaction than does residence time. With a rise in torrefaction temperature the energy density increased greatly for non-lignocellulose and lignocellulose biomass.
5. Torrefaction is, therefore, an option for waste materials such as sewage sludge for an upgrade in handling and combustion properties.

CHAPTER 4: EFFECTS OF REACTOR TYPE ON TORREFACTION OF BIOMASS

This chapter deals with experimental works on understanding the effects of reactor type on the torrefaction of biomass. Four common types of reactors (convective heating, fluidized bed, rotating drum and microwave reactor) were studied. Convective and fluidized beds are direct heating reactors, rotating drum is an indirect heating reactor, and microwave is a volumetric heating reactor.

4.1 Background

The development of the torrefaction process has progressed from prototype testing to the commercial demonstration phase [Kleinschmidt, 2011]. While many torrefaction reactors are currently under development, most have simply been adapted from other processes, such as drying, pyrolysis and high temperature heating. Hence, a proper study of the reactors and their comparisons is lacking.

Bergman et al. [2005^{a}] broadly classified all the reactors as direct and indirect heating reactors. In a direct heating reactor, the heating medium (fluid) comes in direct contact with the biomass. However, with indirect heating, the heat is transferred to a biomass via conduction (i.e. the heating medium does not come in contact with the biomass). Each type of technology has distinct features and advantages over the others [WPAC, 2011]. The most distinct one is that the direct heater has better and more uniform heat transfer, while in the indirect heater, the volatiles are not diluted by the heating fluid and can be easily used for combustion.

However, most promising reactors types in large-scale developments are now, according to Ontario Power Generation [2010]:

1. Entrained bed torrefier
2. Moving bed torrefier

3. Multiple hearth
4. Rotating drum
5. Indirect heated screw type.
6. Microwave torrefier

In addition to these, two other types of reactors are under study:

a) Fluidized bed torrefier
b) Superheated steam or heat carrying fluid based torrefier

The correct choice of a reactor for torrefaction is crucial, as each reactor has distinct properties and can handle specific types of biomass. At present, there is no published comparative analysis in the literature of any torrefaction reactors. Instead, torrefaction reactor developers champion their own designs, claiming superiority over other designs. The science of torrefaction thus lacks an independent comparative analysis of torrefaction reactors [Ciolkosz & Wallace, 2011].

To examine the reactors' effects on biomass torrefaction, four types of torrefaction reactors were chosen for study: moving (convective) bed, rotating drum, fluidized bed heaters and microwave. Among these, convective bed, fluidized bed, and microwave are directly-heated reactors, whereas rotating drum is an indirectly heated reactor. An overview of the reactors is presented below.

4.1.1 Convective Bed

In this reactor, hot inert gases pass through a packed or moving bed, transferring heat to the bed material, which is a biomass. The biomass could move in a vertical reactor under gravity, or it could be carried by a moving grate, like in a grate-fired combustor.

The primary characteristic of this reactor is that there is no back-mixing of biomass. Heating can also be done on the packed bed by indirect means (i.e., by heating the wall of the bed). Heat transfer in indirect heating is poor compared to direct heating. Bergman et al. [2005^a] estimated a gas-to-particle (biomass) heat transfer coefficient on a directly heated packed bed to be 200 W/m^{2}K. Which is comparatively high, but the pressure drop in the biomass bed is quite significant.

4.1.2 Rotating Drum

These types of reactors consist of a rotating drum, which tumbles the biomass in an environment of hot inert gas. Rotating drums can be heated directly by passing hot gas through it or by heating the wall (indirect heating). In some cases, it can also involve a hybrid design combining both modes of heat transfer [Amos, 1998]. The reactor used in the experiment is a hybrid design, but during torrefaction, it was found that heat transfer is primarily through hot walls. Hence, it can be considered an indirectly heated reactor. Heat transfer in a rotating drum is high due to the constant mixing of biomass. Bergman et al. [2005] reported the 'volumetric heat transfer coefficients' in a directly heated rotating drum to be around 40 W/m^{3}K upon solid fill percentage of 10-15%.

4.1.3 Fluidized Bed

Fluidized bed is a bed of heat carrying granular particles blown by a fluid wherein solid particles behave like fluid. As the particles are vigorously mixed together, fresh biomass feed will take the least time to reach torrefaction temperature. The main advantage of this reactor is the high heat transfer coefficient and the uniform temperature over the entire bed. It produces a high quality uniformly torrefied biomass. Some of the major challenges in this reactor are –

A) Fluidization of biomass particles
B) Separation of bed material, if used, from biomass
C) Entrainment of fine particles.

4.1.4 Microwave

Microwave is an electromagnetic radiation (300 MHz to 300 GHz) which makes polar molecules in biomass to rotate in the frequency of the microwave, causing friction and heating within the matrix of biomass. Hence, it is referred as a volumetric heating reactor. Compared to conventional heaters, it is advantageous in terms of uniform heating, shorter heating time, higher heating efficiencies, compact design and greater control [Budarin et al., 2010]. Although this reactor cannot be easily classified into direct and indirect heated reactors (since the heating is volumetric), it will for our purpose be considered here as a directly heated reactor.

4.1.5 Liquid Heated Torrefier

One potential means of heating biomass is by bringing it directly in contact with heat-carrying liquid. This technique, though still in the conceptual or developmental stage, has the advantage of being totally free from oxygen and enjoying the benefit of high heat capacity of heat transfer liquid. For this, one could use compressed high-temperature water, a thermal liquid which remains liquid at 200-300°C. Superheated steam (a gas) could also be used, but it has a low heat capacity.

4.2 Objective

The major objective of this work is to compare different types of torrefaction reactors based on three common properties of torrefied biomass: mass yield, energy yield and energy density.

4.3 Materials and Method

The following section presents a description of the experimental methodology applied to various ranges of studies comparing reactors. Details on the experimental set-up are also provided.

4.3.1 Physical Properties of Biomass

In order to compare the performance of chosen reactors, one standard biomass sample should be chosen. As biomass is generally slender in shape, the choice of a cylindrical sample could appropriately represent the branch or twigs of trees. A long (1.8 m) Poplar biomass cylindrical bar with longitudinally-oriented fibres was transversely cut into 75mm long cylinders. Three diameters of such cylinders were used viz 25.4mm, 19mm and 12.7 mm. This size corresponds with the typical size of raw biomass intake in biomass and conversion facilities, which are slender and measure approximately 20-50mm in diameter and 50-300 mm in length.

The density of the sample biomass was measured at 500 kg/m^3, and the energy density of the sample was measured at 19.71 MJ/kg. The proximate and ultimate analyses of the samples are shown in Appendix B.

4.3.2 Description of Reactors Used For Torrefaction of Single Piece of Biomass

The torrefaction of biomass depends on its physical properties, such as size, shape, density and orientation of fibres [Turner et al., 2010]. Hence, to simplify the task of comparing reactors, a standard biomass sample (a cylinder of Poplar wood of a fixed length) was torrefied individually in each reactor. The effects of different diameters (12.7, 19.2 and 25.4 mm) of the biomasses and of different temperatures (250, 280, and 300ºC) were observed for a fixed residence time on various reactors (Table D-1, Appendix D). To achieve the objective and fair results, the reactor residence time was varied according to torrefaction temperature and particle size to keep the mass and energy yield within a certain range (60-90% for mass yield and 70-95% for energy yield). If the residence time is too short or too long, the effects may be skewed. In any case, the temperature and residence time were kept unchanged between reactors except in the microwave reactor, where the biomass temperature during torrefaction could not be precisely measured.

Because of symmetry and a large aspect ratio of the biomass, heat transfer at the midsection of the cylinder was assumed to be radial. As well, the orientations of the fibres were longitudinal to the biomass cylinders for all the samples. Error analyses of the experimental data are done in Appendix E.

Details on the arrangement of the experimental reactors and the methodology of torrefaction in each of them are described below. Photographs of these reactors are shown in Appendix C.

4.3.2.1 Convective Bed Reactor

This reactor consists of a 60mm diameter column electrically heated from the outside. The biomass sample is suspended into the column, which is continuously flushed by N_2 at a flow rate of 1.0 lpm (litres per minute). The temperature of the biomass is measured by a thermocouple inserted into its core, which also supports the biomass from the electronic mass balance (Figure 4-1). This set-up, known as Thermogravimetric (TG), continuously measures the mass of the biomass. To maintain uniform temperature inside the reactor, N_2 was first heated by passing it around the reactor before releasing it from the bottom (Figure 4-1). Photograph of this unit is in Appendix C. Nonetheless, it was found that there was a significant temperature gradient along the length of the reactor. Indeed, even along the height of the biomass sample (64 mm) there was a temperature gradient of 8°C., a circumstance that might create discrepancy between the temperatures set on the controller and those experienced by the biomass. To minimize this error, the reactor temperature was adjusted with the temperature measured by the suspended thermocouple, which otherwise measures the biomass core temperature.

Initially, the reactor was operated for half an hour until an equilibrium temperature or steady state was attained. Then the sample of biomass cylinder of known mass, diameter, height and moisture content was placed into the reactor and the residence time was recorded. During torrefaction, the temperature of the gas passing through the biomass and the temperature of the core of the biomass were continuously recorded and logged into the computer. The mass of the biomass was also continuously recorded by the electronic balance.

After the torrefaction was completed, the biomass was air-cooled and weighed. Such cooling by air does not work for torrefaction of large mass, which because of its high thermal inertia will ignite in contact with air. Because of this low inertia of the single particle the temperature immediately dropped below its ignition temperature. Its properties were then assessed with proximate analysis (ASTM E870-82, 2006) and a bomb calorimeter (model 1360 Plain Jacket, by Parr Instruments). In these analyses, only the segment along the mid-plane was studied.

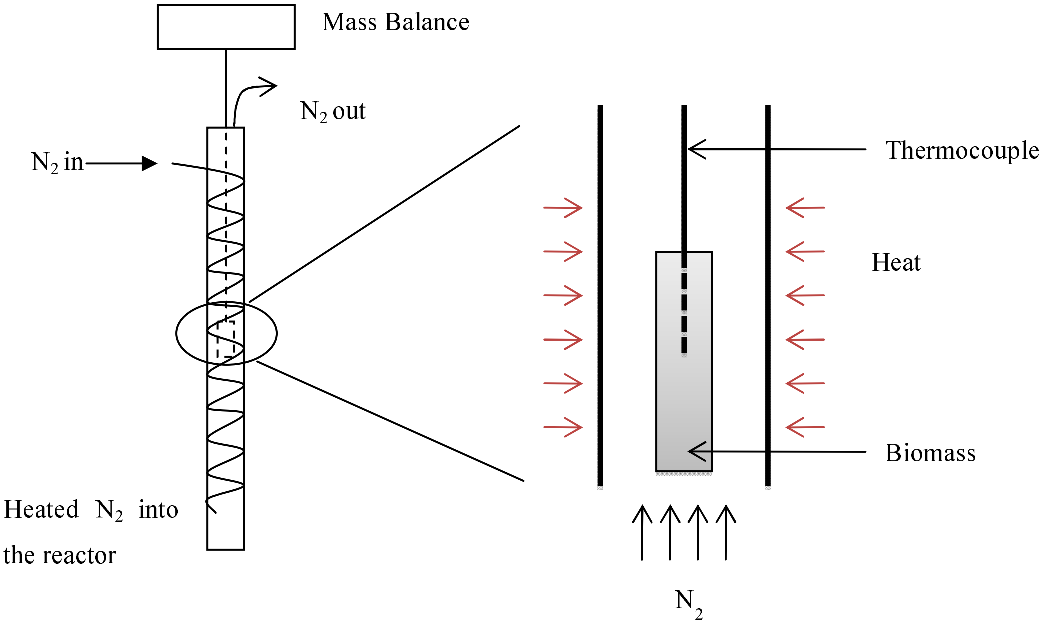


Figure 4-1: Schematic of the convective reactor.

4.3.2.2 Fluidized Bed Reactor

The fluidized bed reactor was a 89 mm wide and 230mm deep bubbling bed of sand (less than 300µm) fluidized by N_2 at a superficial velocity of 6 mm/s (Figure 4-2). Photograph of this unit is in Appendix C. The bed was heated by a set of annular electrical heaters encased by insulating refractory. A temperature controller maintained the fluidized bed at a uniform temperature. Except for the 20 mm entrance section above the grid, the bed remained at a uniform temperature. Care was taken so that samples were always above this height. While measuring core temperature, the biomass cylinder was supported by a 1.6 mm diameter thermocouple inserted into the biomass centre, as shown in Figure 4-2. During this test, the cylinder could move freely in a horizontal plane only. The reactor temperature was measured by another thermocouple at the same height adjacent to the biomass.

Residence time recording was started right after placing the biomass into the reactor. The reaction or torrefaction time is the amount of time that the biomass is above 200°C, and can be measured by deducting the residence time by the time required for it to reach 200°C.

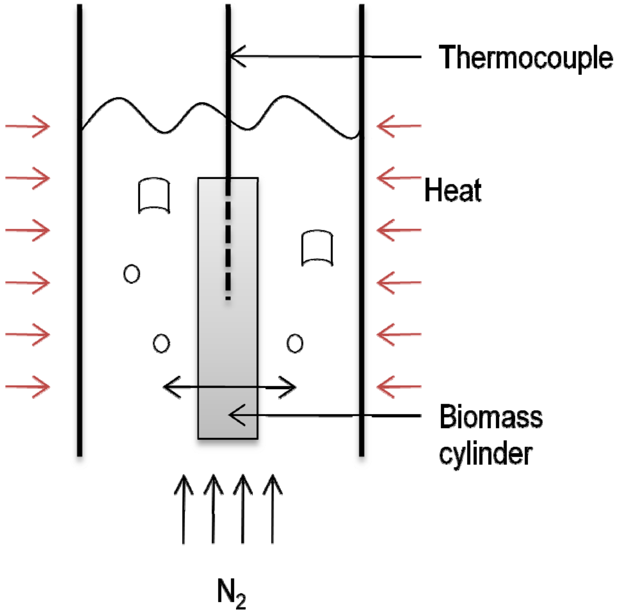


Figure 4-2: Schematic of the fluidized bed.

4.3.2.3 Rotating Drum

A simple set-up is constructed to functionally simulate the rotating drum heating. It consists of a small-sized drum of 10 cm diameter and 20 cm length. Photograph of this unit is in Appendix C. It has 3 fins (risers) of 2 cm length at equiangular position inside the drum for better tumbling action. The drum is rotated inside a convection heater (modified rotisserie) at a fixed speed of 2.9 rpm. To maintain the inert atmosphere, nitrogen is supplied to the heater near the bottom and is allowed to leak by itself. Both ends of the drum are covered by a 1 mm mesh, so that the volatile generated can easily diffuse into the heater chamber and the hot air can diffuse into the drum. Figure 4-3 shows a schematic of the unit. This is a low-cost innovative set-up and can be scaled to a larger size.

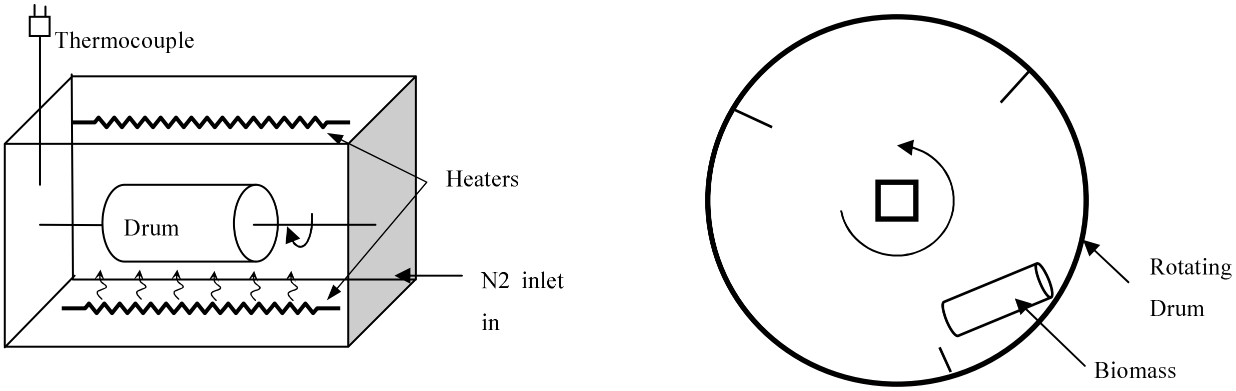


Figure 4-3: Schematic of rotating drum arrangements.

Biomass in this rotary drum is heated by both surface and convective heating. The surface temperature of the drum is taken as the temperature of the reactor. As it was difficult to measure the surface temperature of the drum while it was rotating, it was calibrated to the temperature of environment inside the reactor at a fixed flow rate of N_2 (2 lpm). The surface temperature of the drum and the environment in the heater chamber were measured while the drum was stationery. The surface temperature of the drum was noted to be 16 ºC higher than that of the gas inside the reactor for all torrefaction temperatures. This is probably due to the radiative heating of the drum.

Before starting the experiment, the reactor was heated to the desired temperature and held there for half an hour. Then the biomass sample was placed inside the drum, which was then mounted inside the reactor. In doing so, the temperature of the drum and the reactor dropped well below the torrefaction temperature. However, in the case of other reactors, reactor temperature does not change to the same extent while loading the biomass. To compensate for this effect, the temperature of the drum was allowed to rise to 200ºC before the residence time was counted. Note that it takes a couple of minutes for the drum to rise to the torrefaction temperature.

In this rotary arrangement, it was almost impossible to measure the temperature of the centre of the biomass in a tumbling motion. A proxy method was employed to assess the temperature of the core of the biomass. The sample biomass was kept in the heated drum without rotating it and its core temperature was recorded. Later, the mass yield measured in this state was compared with that measured for the freely tumbling similar biomass sample. The difference in mass yield, which is a strong function of core temperature, was very small between these two experiments. So, the temperature of the tumbling biomass core can be assumed to be close to that measured in the stationery drum.

4.3.2.4 Microwave

A domestic microwave heater was modified for use as a torrefaction reactor. An air circulation chamber was closed and small ports for inserting a thermocouple and an inert gas line were added (Figure 4-4). Photograph of this unit is in Appendix C. The biomass sample was placed in the centre of the reactor, with the thermocouple inserted into the biomass. Nitrogen gas was continuously flushed into the reactor at a flowrate of 5.0 lpm.

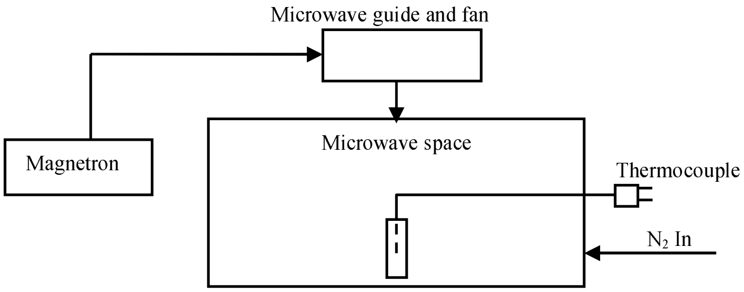


Figure 4-4: Schematic diagram of microwave torrefaction.

This reactor presented a number of challenges in continuously measuring the mass. Initially, biomass was kept on a platform inside the microwave. The platform's legs passed through the bottom plate of the microwave, where it rested on an electronic balance at the bottom of the microwave. However, as legs the legs were metallic, they produced sparks and got stuck on the bottom plate of the microwave. Hence, this idea was scrapped and only initial and final measurements were taken. Measuring the temperature of the biomass also proved difficult. The thermocouple element would heat up itself and sometimes produced an arc inside the microwave, resulting in erroneous temperature. To get around this difficulty, the microwave was turned on and off intermittently for about 20 seconds so as to allow the thermocouple to be isothermal with the biomass. Though this method was not perfect, it at least offered some idea of the temperature rise within the biomass. The current experiment on microwave reactors thus remained qualitative in nature.

4.3.3 Method Employed for Experiments with Sawdust

The previous section described the experimental methods used for torrefying a single piece of standard biomass sample in four types of torrefaction reactors. The sample left in isolation in the reactor did not simulate any effect of neighbouring biomass particles on heat transfer during torrefaction. To examine this, experiments were conducted with a bulk of particles (sawdust) made by chipping and then grinding the same parent biomass (Poplar wood cylinders). Sawdust in sizes ranging from 0.5-1.12 mm diameter was prepared. Sawdust finer than these measurements was considered unsuitable.

The amount and arrangement of the biomass samples depended on reactor type and size. With the convective bed, a hollow copper tube was packed with the sawdust. The bulk density of the packed biomass was 50 kg/m^3. To be able to compare this test with the torrefaction of a biomass cylinder, the inside diameter of the tube was chosen to be the same as the standard Poplar wood sample (25.4 mm diameter and 64 mm long). Similar to previous experiments, a 1.6 mm diameter thermocouple was inserted into the centre of the sample and its mass was continuously measured.

For experiments in the rotating drum, a 10% volume of the drum was filled with sawdust, and an experimental procedure similar to that used for single cylindrical biomass was followed. With the fluidized bed, fine particles were poured into the sand bed. Here also, 10% of the volume of the sand was mixed. Finally, with the microwave reactor, a 75 mm diameter glass beaker was filled with particles up to a depth of 75 mm and was torrefied inside the microwave oven, which was continuously flushed by N_2.

4.4 Results & Discussion

The present section discusses experimental results comparing the effect of reactor type on torrefied biomass. Mass yield, energy yield and energy density of the product are used as markers of quantitative quality parameters to define the performance of a torrefaction reactor. They are defined by Equations 2-1, 2-2 and 2-3.

4.4.1 Torrefaction of Single Piece of Biomass in the Convective Bed

The convective reactor used for this test is referred to as QWM (Quartz Wool Matrix) reactor. This versatile reactor can simulate a number of other types of gas-solid reaction as well. Figure 4-5 shows the thermal history of a typical biomass particle subjected to convective heating for torrefaction in the QWM reactor. It shows how the mass of the biomass, its temperature at the centre and that of the furnace changed with time. The furnace was operating at a steady temperature of 250°C. When the cold biomass particle is dropped into the furnace, there was a sudden drop in temperature, which then slowly increased back to the set value. The rate of mass change varied as the biomass passed through different temperature zones that are associated with different thermochemical processes occurring on it.

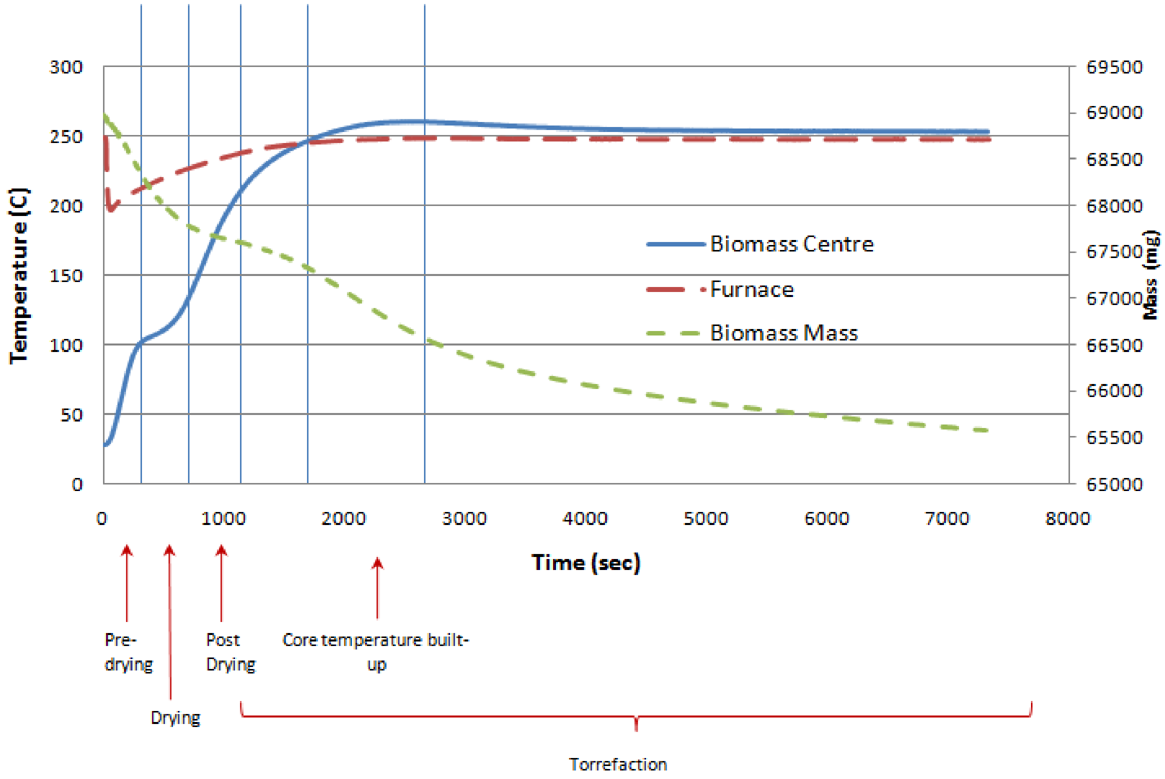


Figure 4-5: Experimentally measured temperature history of biomass core and reactor (convective furnace) and the mass of the biomass (25.4 mm diameter and 64 mm long poplar cylinder at 250°C furnace temperature).

During the course of heating the sample went through different stages of torrefaction. As explained in Section 2.3 using Figure 2.7. The sample passed through four heating stages:

1. Pre-drying
2. Drying
3. Post-drying
4. Torrefaction

On Figure 4-5, one notes temperature hump in the temperature profile of the biomass core. The temperature of the biomass core rises above the reactor temperature, which is discussed more in the following section.

4.4.2 Effect of Reactor Type on Torrefaction of Single Piece of Biomass

4.4.2.1 Effect of Reactor Type on Mass Yield

The present body of knowledge on torrefaction suggests that the following parameters influence the basic qualities (mass yield, energy yield, energy density) of a torrefied product:

1. Torrefaction or furnace temperature
2. Residence time
3. Biomass type, and
4. Particle size

A standard cylinder of Poplar wood was chosen for torrefaction in each of the various reactors, keeping all of the above parameters fixed for comparative tests. To observe the consistency of the results, a number of unique sets of these parameters were organized, as seen in Table 4-1. As explained earlier (section 4.3.2), with each set of size and reactor temperature, residence times were varied to prevent over- and under-torrefaction.

In a given reactor, the mass yield varies with the chosen set of parameters, as shown in Appendix D. For a given set parameters, the mass yield also varies from one reactor to other. Thus, a comparison between different reactors becomes difficult. Consequently, these yields were arranged in terms of the yield of one reactor. For example, for each set of experiments, the mass yield of all the reactors was divided by the mass yield of the convective bed and plotted against reactor types (Figure 4-6). Although values for convective bed is a single point (Figure 4-6), it represent a range of values for each set of experimental set of conditions as shown in Appendix D. Although the plot shows some scatter, the trend is obvious. The mass yield in the convective bed was the highest, followed by that in the fluidized bed and then that in the rotating drum. The average value of mass yield over the entire range of operating parameters was 80.5% for the convective bed, 78.9% for the fluidized bed and 69.3% for the rotating drum.

Table 4-1: Experimental conditions for torrefaction of cylinders of Poplar wood of various diameters (but the same length of 64 mm)

Test #	Legend in Figure 4-6 and 4-7	Reactor Temperature (°C)	Size (dia mm)	Residence time (mins)
1	♦	300	25	23
2	x	300	19	18
3	+	300	13	16
4	■	280	25	33
5	*	280	19	35
6	–	280	13	27
7	▲	250	25	60
8	●	250	19	44
9	▬	250	13	30

These results shows some stark differences in the yields of samples torrefied in different reactors, even though operating parameters such as size, type, temperature and residence time were kept constant. Compared to combustion, gasification and pyrolysis, torrefaction is a very slow process. Indeed, in such slow processes, reaction kinetics become the main influencing parameter, leaving very little influence of the gas-solid contacting mode that is dictated by the reactor design. However, the results prove otherwise. Some explanations for this are offered in section 4-5.

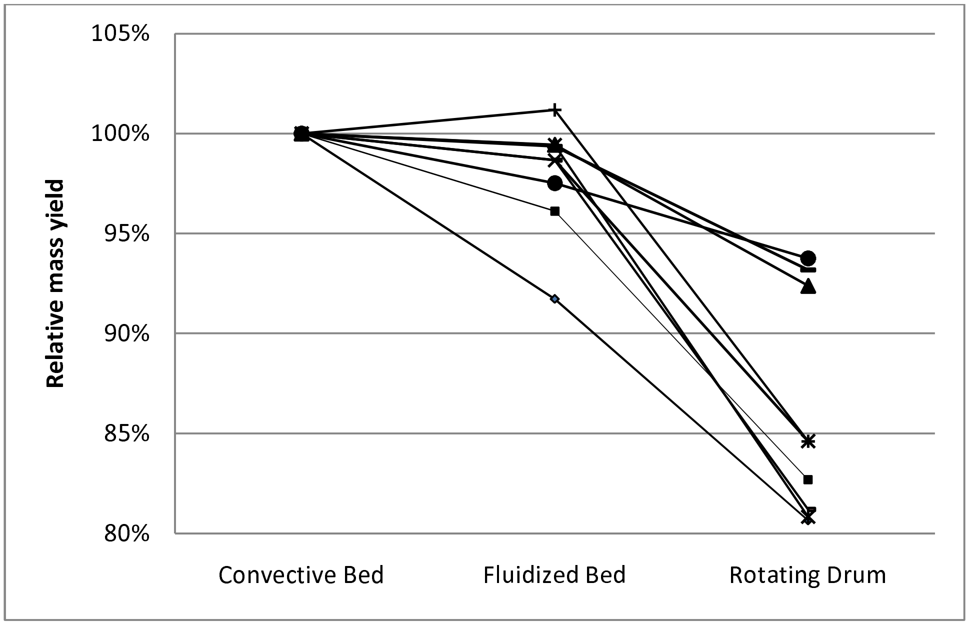


Figure 4-6: Relative mass yield in different reactor types with respect to convective bed. Legends correspond to test parameters as shown in Table 4-1.

4.4.2.2 Effect of Reactor Type on Energy Yield

Energy yield is another important property of the torrefied biomass. Energy yield and mass yield together provides the total picture of the torrefaction yield. Similar to mass yield, the energy yields of the biomass samples are plotted in a non-dimensional form in Figure 4-7. It also shows a similar trend. The relative energy yields for convective and fluidized bed reactors are close, while for that of the rotating drum, they are lower. The average values measured over the full range of particle size, residence time and torrefaction temperature showed a similar trend. They were 87.9%, 86.1% and 77.9% for convective, fluidized bed and rotating drum reactors, respectively.

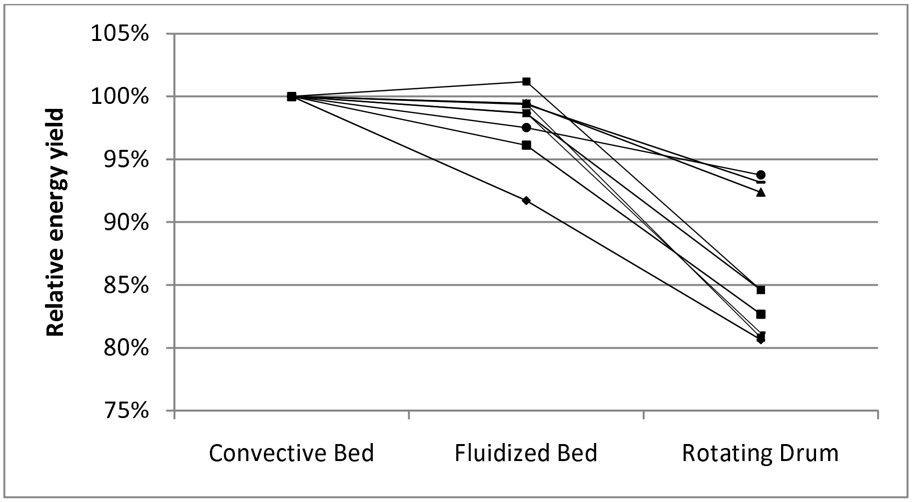


Figure 4-7: Effect of reactor type on energy yield of 25 mm diameter x 64 mm long Poplar cylinder. Legends correspond to test parameters as shown in Table 4-1

In the case of a representative size of biomass (i.e., 25 mm diameter biomass torrefied at 250°C for 60 minutes), the energy yield was 91.8%, 91.8% and 77.9% for convective, fluidized bed and rotating drum reactors, respectively. A complete set of data for mass and energy yield is given in Appendix D.

4.4.2.3 Effect on Energy Density

The energy density or higher heating value of the torrefied product is of primary concern for most applications. The value of energy density on dry and ash-free (DAF) basis for torrefied wood averaged over the full range of particle sizes (25.4 – 12.7 mm, 250 – 300°C, 23-60 minutes) was 21.58 MJ/kg for the convective bed reactor. Interestingly, this was similar in fluidized bed reactors, but much higher (at 22.23 MJ/kg) in rotating drums. While there is some variation in individual values, the trend is similar, which shows only slight differences between fluidized bed and convective reactors and lower values for rotating drums (Figure 4-7).

Here, one may note that the energy density is highest for the rotating drum reactor while lower for convective and fluidized bed reactors, values for the latter two types of reactors being similar.

4.4.3 Effect of Reactor Type on Torrefaction of Sawdust:

Previous experiments dealt with the torrefaction of a single piece of biomass without any influence of neighbouring biomass particles that might constrain heat transfer to the biomass cylinder.

Experiments on fluidization of sawdust mixed in a sand (75-250 micron) bed showed a good mixing and uniform torrefaction of biomass. However, due to excessive entrainment of biomass, results did not allow quantitative comparison. Hence, a comparison of torrefaction of sawdust only in a convective bed and rotating drum could be presented. In the case of microwave, as mentioned earlier, only qualitative observations are made, as is explained later in section 4.7.

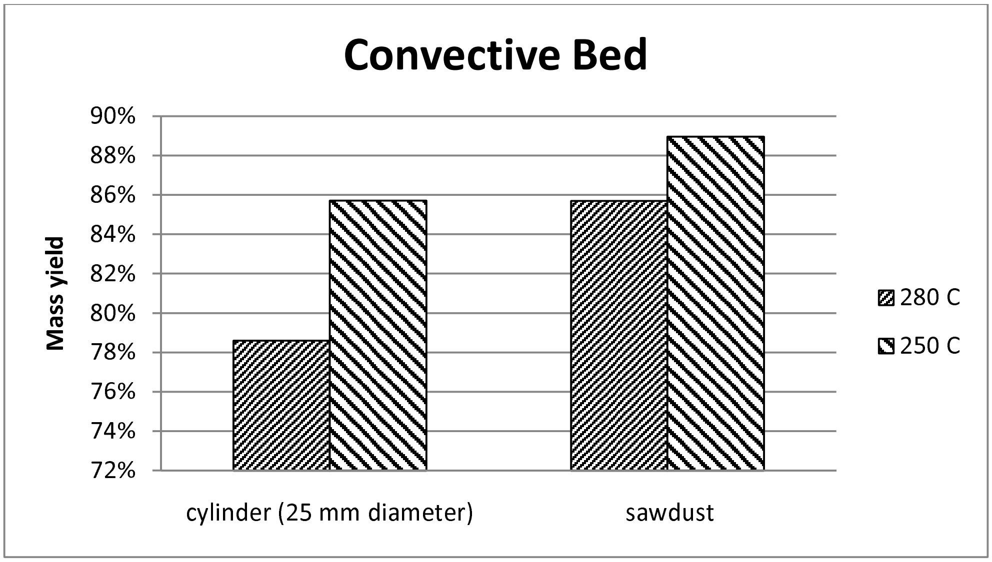


Figure 4-8: Comparison of mass yield of biomass cylinder and saw dust torrefied in convective bed.

Figure 4-8 shows the yield of torrefaction of sawdust compared to that of a single 25 mm diameter cylinder at the same residence time in the convective bed reactor. Mass yields of sawdust were 85.7% and 89.4% for the 280°C (33 min) and 250°C (60 min), which are higher than those for the cylinder (78.6% and 85.7%). Figure 4-9 shows the temperature profile of the sawdust centre and the temperature of the reactor. It is apparent that there is no peak (excess) temperature phenomenon with sawdust. Figure 4-10 shows a similar curve for 25.4 mm biomass cylinder, yet here we see a distinct peak temperature phenomenon. Moreover, heat transfer in sawdust seems to be better than that in the cylinder, which took 22 minutes to reach the reactor temperature, while sawdust achieved it in only 10 minutes. Even though heat transfer in sawdust is better due to the convection current, the mass yield of the cylinder is lower. This is due to the core temperature build-up from exothermic influences. The mass yield here is more correlated to the core temperature than the heat transfer. At a given furnace temperature, a higher core temperature results in higher depolymerisation and hence a lower mass yield. The reasons for the core temperature to be higher with large solid particles of biomass are explained in section 4-5.

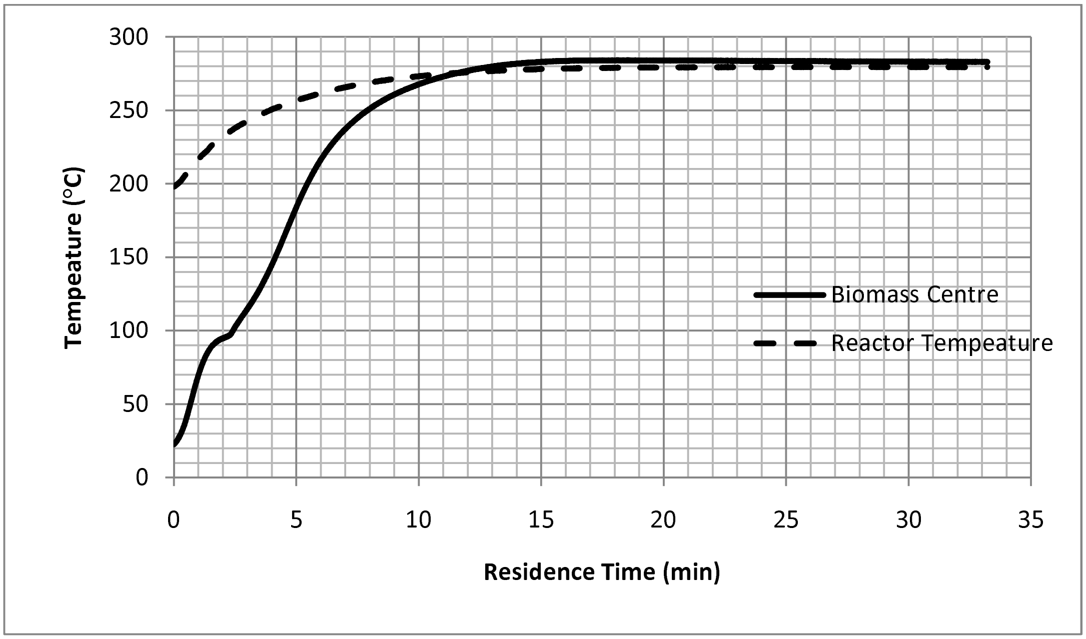


Figure 4-9: Temperature profile of the sawdust in convective bed (280°C 33 mins).

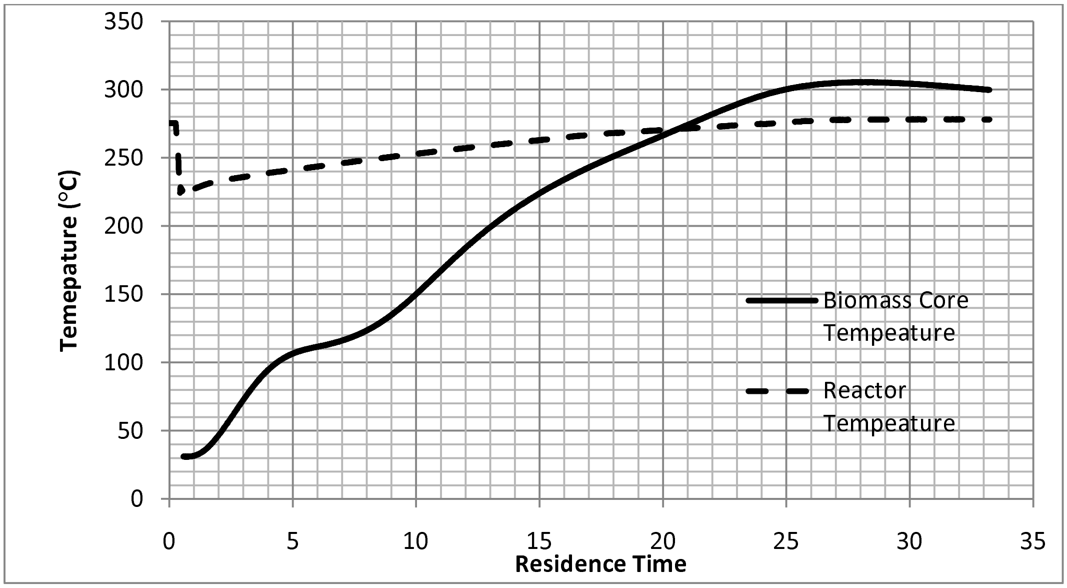


Figure 4-10: Temperature profile of the solid biomass in convective bed (280°C, 33 min).

In the rotating drum, it was observed that the mass yield for sawdust was 38.7% at 280°C (33 min), which increased to 76.3% at 250°C (60 min). These values were lower than those measured in the convective bed reactor, likely due to the fact that during tumbling action, biomass contacts the hot wall frequently, which is not the case with a packed bed (convective bed). However, quantitative comparisons cannot be made between the packed bed and the rotating drum as these values are very specific to the amount of biomass torrefied and the geometry of each reactor.

The energy yield of sawdust in different reactors also followed similar trends as mass yield. Sawdust torrefied in a rotating drum had an energy yield of 47.7% (280C, 33mins) and 78.1% (250 C, 60 mins), while that for a convective bed was 85.7% (280 C, mins) and 89.4 % (250C, mins).

4.5 Heat and Mass Transfer Phenomenon:

All effects of reactor type on the biomass torrefaction revolve around the heat and mass transfer phenomenon. Hence, an attempt is made here to explain this transport phenomenon behind torrefaction. Figure 4-11 schematically shows the parameters involved in the heat and mass transfer in a biomass particle. The ambient heat flows to the surface of the biomass particle, overcoming the thermal resistance around it. Then, the heat enters the interior of the particle, overcoming the resistance inside. Similarly, when the volatile travels from the biomass interior, it overcomes mass transfer resistance inside as well as outside the particle.

Heat and mass transfer are affected by four factors, as explained below.

i) **Internal mass transfer resistance:** This property resists the flow of volatiles, generated in the biomass, from travelling outward to its surface. The longer the path of travel, the greater is the resistance. This naturally allows volatiles to reside longer inside the biomass where they have the opportunity to react with biomass, creating an exothermic reaction. Such reactions increase the temperature of the interior, which in turn increases the volatile release rate. This process continues until a dynamic equilibrium with heat loss is reached.

ii) **External mass transfer resistance:** External mass transfer resistance is also important. If the medium surrounding the biomass does not allow easy dissipation of volatiles, the concentration of the volatile would rise around the biomass, which makes it difficult for the volatiles to come out of the biomass, again increasing its temperature. The external mass transfer is a function of reactor type. Thus, the type of reactor could influence the temperature rise in the biomass interior.

iii) **Internal heat transfer resistance:** The thermal resistance of the biomass interior is a function of its thermal property and size. It resists the propagation of heat from the biomass interior to its surface and increases with the size of the biomass. Thus, one could expect the highest core temperature in a larger biomass particle.

iv) **External heat transfer resistance:** It is again dependent upon the heat transfer properties of the surrounding of a biomass and is heavily influenced by reactor type and mode of operation.

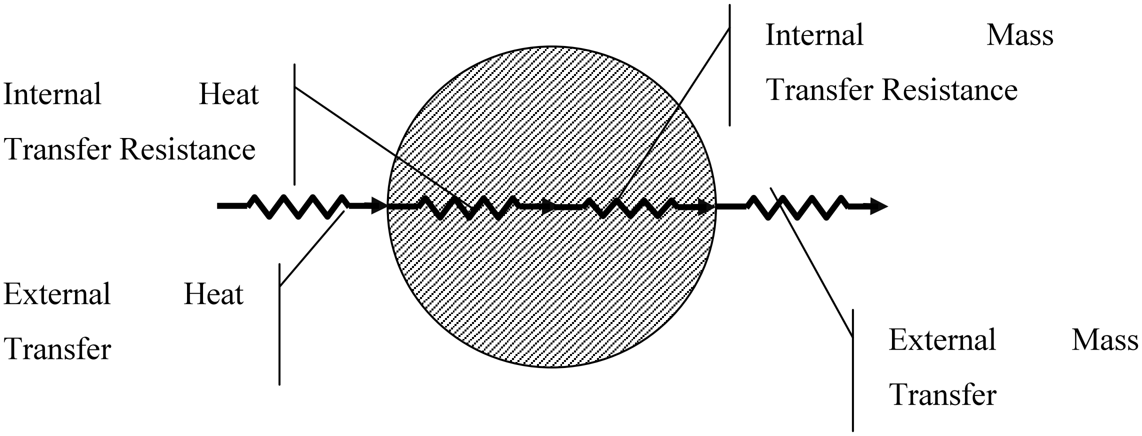


Figure 4-11: Diagram showing heat and mass transfer resistance along the mid-plane of a biomass cylinder.

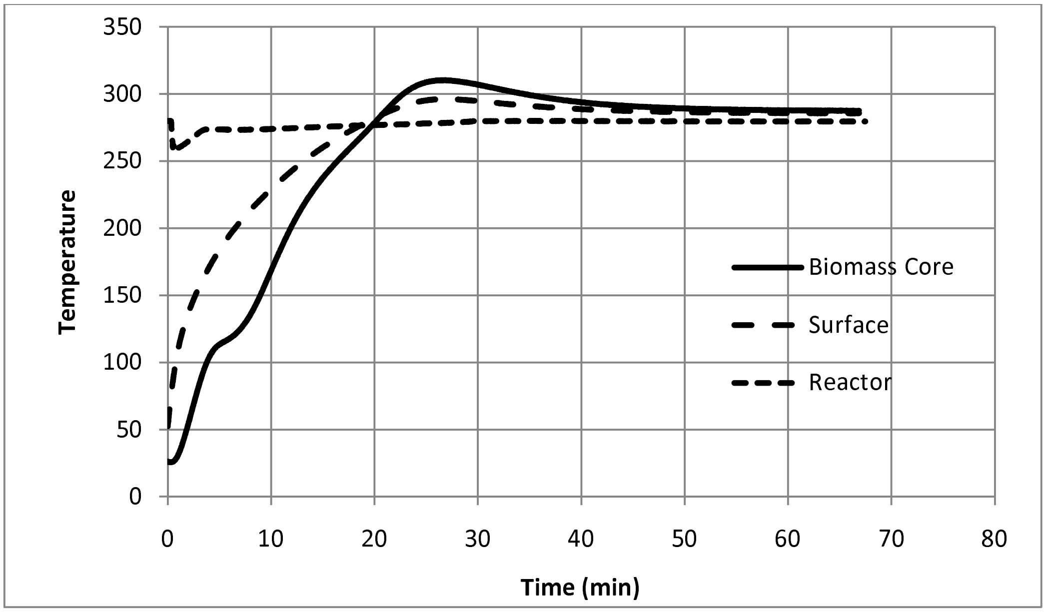


Figure 4-12: Temperature profile of the biomass core, surface and reactor during torrefaction of a 25.4 mm diameter biomass at 280°C on a convective bed reactor.

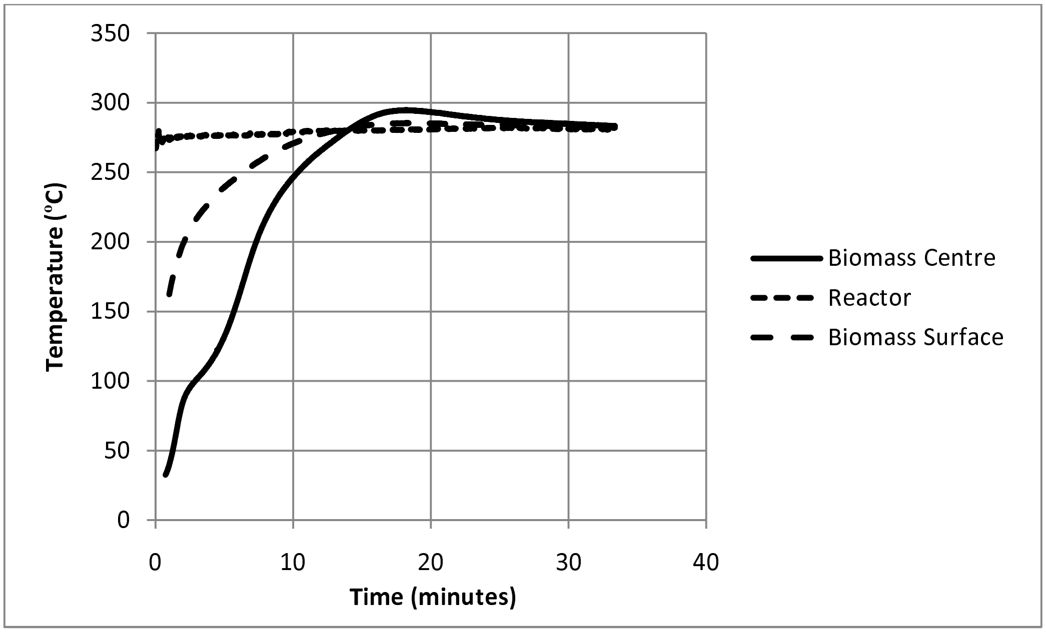


Figure 4-13: Temperature profile of the biomass core, surface and the reactor during torrefaction of a 25.4 mm diameter biomass at 280°C on the fluidized bed reactor.

When examining the results of torrefaction of the 25.4 mm diameter cylinder torrefied on different reactors (Figure 4-6 and Figure 4-7), we see that the fluidized and convective beds have similar mass yields, while the rotating drum has a much lower one. Further, if we look at the heat transfer coefficient, the fluidized bed has the highest one of all. This is evident from Figures 4-12 and 4-13, which show the surface and core temperature profiles of the biomass cylinder torrefied at the same temperature and residence time on convective and fluidized beds. There, it can be seen that, in the fluidized bed, the temperature of the biomass reached close to the reactor temperature in a relatively short time (10 minutes), while in the convective reactor, it took almost twice that amount of time. Hence, an increase in the heat transfer coefficient (or a decrease in the heat transfer resistance) increases the reaction time (defined in Figure 2-7). This explains the lower mass yield of the biomass in the fluidized bed than that in the convective bed. Similar data on the temperature of the tumbling biomass in the rotating drum was not recorded. But, it is known that the rotating drum (indirect heater) has a lower heat transfer coefficient. This should result in the highest mass yield of the biomass in rotating drum, but the result, quite the opposite. Hence, the heat transfer coefficient alone does not explain the results in Figure 4-6.

One instance of Figure 4-6 is plotted in Figure 4-14, which presents a 25 mm diameter Poplar cylinder torrefied at 280°C and 33 minutes. It also plots the set reactor temperature and the maximum biomass core temperature. We can see that the biomass in the rotating drum has the highest core temperature, followed by those in the convective and fluidized beds. This new information explains the excessive loss of biomass mass in rotating drums. With convective and fluidized beds, data on the maximum core temperature for all test specimens are listed in Table D1 (Appendix D), which shows that the core temperature of biomass in a convective bed is slightly higher than that in a fluidized bed.

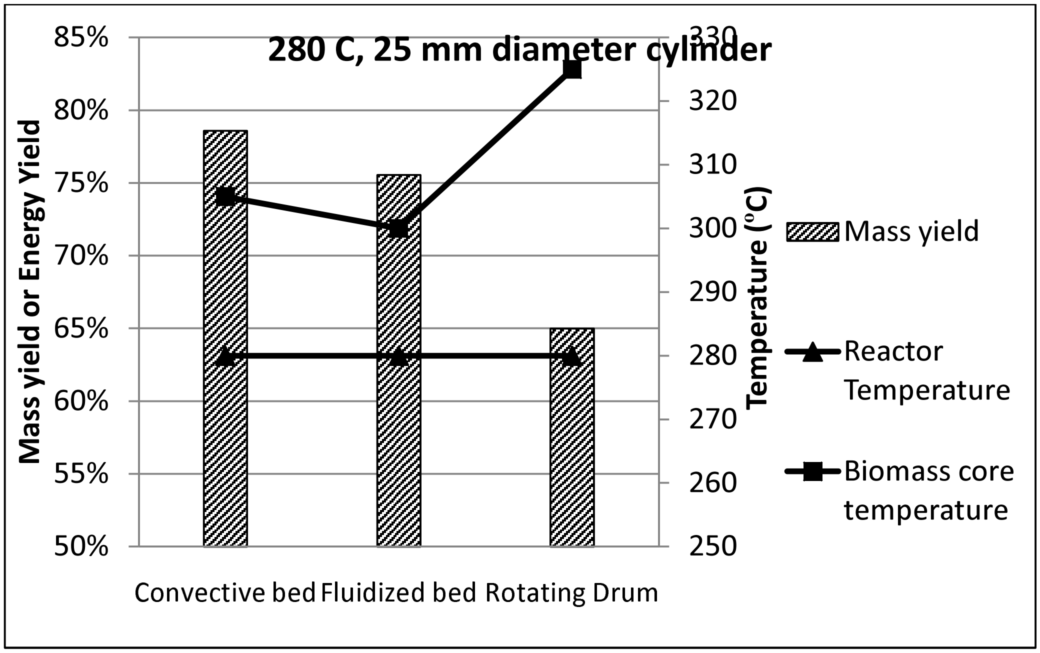


Figure 4-14: Mass and Energy yield of 25 mm diameter cylinder torrefied at 280°C on different reactor in relationship with peak core temperature.

The information presented above demarcates two parameters: heat transfer coefficients causing change in residence time and exothermic reactions causing change in torrefaction temperature, responsible for the yield of biomass in different reactors. Any yields are the mixed effect of these two parameters. However, it is not known why there is an excessive increase in core temperature in the rotating drum compared to the other two. As well, biomass in the convective bed had a slightly higher core temperature than that in the fluidized bed. Two hypotheses are given below to explain this phenomenon.

a) A better heat transfer coefficient or less external heat transfer resistance allows for faster heat transfer to the biomass. It also allows any internally generated heat to quickly dissipate to the surrounding environment. This reduces the core temperature of the biomass in reactors like fluidized and convective beds but not that in rotating drum. Hence, a biomass torrefied in a reactor with a high heat transfer coefficient has a lower core temperature than that torrefied in another type of reactor. However, one may note that, in a rotating drum, the temperature of the fluid inside the reactor was 16°C lower than the torrefaction temperature (drum surface temperature). Hence, biomass should lose its heat more rapidly, which is not the case.
b) The exothermic reaction is caused by secondary charring reaction of volatiles [Prins, 2005]. This depends upon the residence time of volatiles inside the biomass. Due to differences in the construction of reactors, the external mass transfer resistance is not the same across all reactors. In directly heated reactors, the volatiles are continuously flushed by the carrier gas. Because of this, the partial pressure of volatiles outside the biomass is less, and the mass transfer resistance drops. Conversely, in an indirectly heated reactor, the concentration of volatiles around the biomass is high, causing higher mass transfer resistance.

4.6 Practical Implications

From the study above, some of the important effects of reactors on torrefaction yields of biomass are uncovered. This work does not intend to identify the best reactor, but to identify the fundamental parameters that affect torrefaction. These parameters can be easily related to various types of reactors as well, and would thus facilitate the selection of a reactor for a particular set of conditions, such as feedstock properties, transportation and storage costs, intended use of the product, etc. As an example, a case will be considered here to select a best reactor allowing shortest residence time.

From the above findings, it is evident that a directly heated reactor with a high heat transfer coefficient requires less amount of time to increase the biomass temperature to torrefaction temperature. Hence, if it is intended to have a higher mass and energy yield, one would choose this type of reactor. If it is intended to have a high energy density product at the expense of mass and energy yield, one should choose an indirectly heated reactor. An indirectly heated reactor with a lower heat transfer coefficient takes a longer time to reach torrefaction temperature. However, once it reaches the torrefaction temperature, due to excess heat, the rate of depolymerisation is very fast. It would thus take less time for indirectly heated reactors.

Once a type of reactor is decided upon, a specific reactor can be chosen based on the flexibility of the reactor, cost, and other parameters. Similarly, one can analyse different issues related to reactor types in torrefaction.

4.7 Microwave Torrefaction

Microwave torrefaction was tested on both a single piece of biomass cylinder and a bulk of sawdust. This reactor is considered to be distinctly effective in heating biomass uniformly in significantly less time and in producing uniform torrefied biomass [Budarin et al., 2010]. However, such results were not observed in this test. Figure 4-15 shows the surface and split-up section of the cylinders torrefied in the microwave for different lengths of time.

Figure 4-15: Microwave Torrefaction of a 19 mm diameter poplar wood (5.4% moisture) at 280 C, (a) for 5 minutes, Mass yield obtained 94%. (b) for 10 minutes, Mass yield obtained 91.9%. The figure shows photograph the exterior of the cylinder after torrefaction and after splitting

We can see that the torrefaction occurred at the centre of the biomass only, while the surface of the biomass remained unaltered. This is due to the selective heating property of the microwave. Microwave heats the biomass only, not the air around it. So, the surface of the biomass transfers heat to the surrounding inert gases and cannot be raised to the torrefaction temperature. However, the central part of the biomass remains insulated and can reach torrefaction temperature. That is why dark patches of torrefied biomass in the central region are observed in Figure 4-15.

With sawdust, similar observations were made. The microwave also showed a directional nature, whereby only a certain side of the biomass was torrefied while the rest remained unaltered.

4.8 Conclusion

1. It was observed that reactor type has a significant influence on the yield of torrefaction.
2. The exothermic reaction and heat transfer coefficient of the reactors play a major role in affecting the yield of biomass. An increase in the heat transfer coefficient of the reactor increases the time (reaction time) that the biomass stays inside the

torrefier at temperatures higher than 200°C. Meanwhile, an increase in exothermic reaction increases the core temperature of the biomass.

3. Directly heated reactors have lower exothermic heat generation and higher heat transfer coefficients. Hence, they will torrefy biomass faster if higher mass and energy yield is desired. This is exactly opposite to indirectly heated reactors, which have higher exothermic reactions and take longer to reach torrefaction temperature, effectively reducing the reaction time. However, once the biomass temperature reaches torrefaction temperature, exothermic reaction increases the core temperature of the biomass. At this point, it is not clear why there is more exothermic reaction in an indirectly heated reaction, and therefore further study is recommended.
4. Torrefaction in a microwave, qualitatively analyzed, showed that only the core was torrefied, leaving the surface largely green.

CHAPTER 5: PARAMETRIC STUDY OF TORREFACTION

This chapter explores the effects of some important operating parameters such as temperature and particle size on torrefaction product quality. This chapter also investigates the core temperature phenomenon in greater details.

5.1 Background

Torrefaction is affected by many parameters. Some are external to biomass, like reactor type, torrefaction temperature and residence time [Dhungana and Basu, 2011], while others are related to biomass itself, like polymeric composition of biomass [Ciolkosz and Wallace, 2011], particle size, shape, density and orientation of fibres [Turner et al, 2010]. Another important phenomenon identified during torrefaction is the exothermic reaction of biomass. Chapter 4 discussed the significant effect of exothermic reaction on torrefaction yields (section 4.5). The effect of these parameters must be clearly identified in order to design an optimal torrefier or select among the various choices.

Extensive headway has been made in understanding the effects of temperature and residence time (Antal and Gronli, 2003; Prins, 2005; Pimchuai et al., 2010 Dhungana et al. 2011), showing that temperature is a more important factor than residence time. However, the impact of temperature on mass and energy yields as well as on the optimization of the process has not been definitively studied. This chapter will address those aspects of torrefaction.

5.1.1 Exothermic Reaction

Exothermic reaction is an important phenomenon that has significant consequence in the design and operation of a torrefier. Torrefaction was previously considered as an entirely endothermic process [Prins, 2005]. Heat from the exterior of biomass moves into the solid during torrefaction. DTG (Differential Thermogravimetry) and DTA (Differential Thermal Analysis) data provided by Chen and Kuo (2011) shows endothermic peaks of hemicellulose, cellulose and lignin torrefaction at 230, 260 and 290°C, respectively. Several researchers, including Turner et al. (2010), Ferro et al. (2004), Knezevic et al. (2009), Chen and Kuo (2011) and Englisch (2011) measured the temperature at the centre of a biomass rising above the temperature of the heating medium outside the biomass. This proves the presence of exothermic reaction at least at sometime during the operation.

Chen and Kuo (2011) suggest that this exothermic reaction is due to consumption of oxygen present in hemicellulose by the heated biomass. Turner et al. (2010) proposes the presence of a secondary reaction, where volatiles react to produce char and lighter gases, for causing exothermic reactions. However, Felfli et al. (2004) states that torrefaction temperature is not high enough for secondary reactions. Our own study on non-lignocellulose biomass as well as the study by Felfli et al. (2004) shows that the increase in the absolute amount of char mass could be due to secondary reactions. Knezevic et al. (2009) also supports the suggestion of a secondary breakdown mechanism at higher temperatures.

In any event, this effect is real and can be considered beneficial, as it increases the temperature of the biomass accelerating the torrefaction process. More volatiles are converted into char increasing the heating value of the solid product. In the pyrolytic process, exothermic reaction is considered beneficial for the same reason [Antal and Gronli, 2003]. However, runaway temperature can cause severe torrefaction with excessive loss in mass and energy in the product. Hence, a controlled exothermic reaction should be aimed for in any design.

5.1.2 Effect of Particle Size

The study on exothermic reaction by Turner et al. (2010) indicated that it depends on the particle size. Their simulated results (Figure 5-1) show that with increasing biomass size, the core temperature of the biomass likewise increases and lasts longer. Since the effect of temperature on the product yield is profound, this phenomenon might cause distinct reduction in mass and energy yields. However, with increasing size, internal heat transfer resistance (Figure 4-11) also increases, causing slower heating of biomass and reducing the reaction time. This will increase the mass and energy yields. The combined effect of exothermic reaction and heat transfer resistance on different sizes of biomass has not yet been studied in the literature.

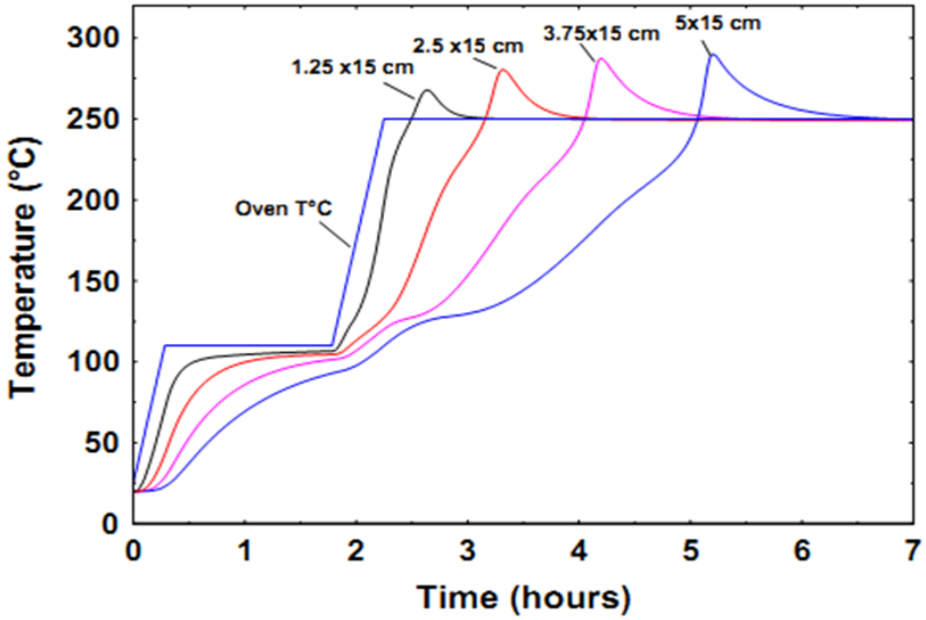


Figure 5-1: Simulated temperature profile of the biomass of different sizes on torrefaction [Turner et al., 2010].

Nevertheless, there are numerous studies that identify the effect of particle size on torrefaction yield. Bergman et al. (2005^b) presented a preliminary study on the effect of biomass size on torrefaction yield in Willow particles of different size bins (0-10, 10-30, 30-50 mm), torrefied at around 260°C for 30 minutes. The results of this experiment showed no measurable differences on mass yield. Almeida et al. (2010) also did not detect any effect of particle size, but Demirbas (2004) did note some influence.

Though pyrolysis is not the same process as torrefaction, both belong to the same family of thermochemical reaction qualitatively. With that in mind, it is worth examining how pyrolysis of biomass is affected by particle size. Several researchers who studied pyrolysis at higher temperatures have reported that size did not have any effect on the yield. Sensoz et al. (2000) studied pyrolysis of rape seed across five particle sizes in the range of 0.224 to 1.85 mm at 500°C. Hanson et al. (2002) pyrolysed coal particles at 900°C the size range of 0.5 to 2.8 mm. They did not find an appreciable effect of particle size on char yield. Encinar et al. (1996) studied the effect of particle size (0.5 to 1.8 mm) while pyrolyzing grape bagasse at 500°C. Coal pyrolysis was reported to be affected by particle size, with both theory and experimental work showing that the particle size had only a minor effect on the total liquid yield up to a diameter of 20 mm (Wang, 2004). As torrefaction is also considered as mild pyrolysis, the effects may be similar.

Thus, from this, we can see that there is inadequate research and conflicting views on this matter. An experimental evaluation is therefore necessary to observe the effect of size on biomass torrefaction yield. An analysis of these results based on heat transfer of torrefied biomass could help in discerning the different parameters that affect torrefaction.

5.2 Objective:

i) To study the effect of temperature of torrefaction on mass and energy yield of torrefied biomass in view of optimizing the process.

ii) To study the temperature overshoot phenomenon in relation to torrefaction temperature and biomass size.

iii) To study the effect of biomass size on torrefaction yield, measured by mass yield, in an indirectly heated reactor (rotating drum) and in convective reactors.

5.3 Materials and Methods

The experimental work is divided into two parts. The first part studies the temperature overshoot of different sizes of biomass, while the second section investigates the effect of the size of biomass on mass yield. Errors expected in experimental results are discussed in details in Appendix E.

5.3.1 Effect of Torrefaction Temperature

A series of Oak wood samples, 22 mm dia x 64 mm long, were torrefied individually at different temperatures for a reaction time of 60 minutes on a convective bed (QWM) reactor. The proximate analysis and higher heating value (HHV) is shown in Appendix B. The experimental methodology explained in section 4.3.2.1 was employed. After torrefaction, pictures of the individual biomass were taken to observe the change in colour. Finally, the mass yield and energy yield of the products were measured.

5.3.2 Exothermic Reaction (Excess Temperature)

This study examines the relation of exothermic reaction with different biomass sizes and torrefaction temperatures. Poplar biomass cylinders, 65 mm in length and two diameters (13 and 25 mm) were chosen for this study. These samples are similar to the biomass used for the comparison of reactor types (Chapter 4). The properties of these biomasses are shown in Table B-1, Appendix B. The methodology employed for the torrefaction of these particles on a convective bed (QWM) reactor is identical to that explained in section 4.3.2.1. Three different torrefaction temperatures were selected (220, 250 and 280°C) to study excess temperature relation with the torrefaction temperature.

From the temperature profile of the biomass core recorded in the computer, the maximum temperature of the biomass core can be identified. Its difference in relation to reactor temperature is called excess temperature or peak temperature [Antal and Gronli, 2003]. In our analysis, temperature difference is calculated between the maximum temperature and the final steady state temperature of the biomass as the reactor temperature does not precisely represent the temperature at the zone of torrefaction (see section 4.3.2.1). The excess temperature gives a rough measure of the exothermic reaction. Nonetheless, excess temperature also depends on the size of the biomass. Larger biomass insulates the core and allow for higher core temperature.

5.3.3 Effect of Biomass Particle Size

The effects of biomass size were studied in all three reactor types. Seven sizes (4.76, 6.35, 10, 12.7, 15, 22 and 25.4 mm diameter) of poplar biomass at a length of 64mm were torrefied in a convective bed (QWM) and a fluidized bed reactor. These reactors are similar to those used in Chapter 4 and similar experimental methodologies were employed. In these experiments, in place of residence time, reaction time (Section 2-3) was fixed. Finally, their mass yield and energy yield are plotted vs. their diameter, and analyzed.

A similar study was also done on the rotating drum, but three different diameters (5, 6.5 and 11 mm) and shorter (25.4mm) biomass samples were chosen. Also, Birch was chosen instead of Poplar (the proximate analysis and heating value of Birch is presented in Appendix B). The reactor is the same as that used in the experiment described in Chapter 4. Proceeding with the experiments, a single piece of biomass of various diameters was torrefied under same temperature and residence time. Subsequently, bulks of same-sized biomass occupying about 10% volume of the drum were torrefied under the same set of temperature and residence time. Due to difficulties in measuring the temperature of the biomass core in a rotating drum, the total residence time was fixed, unlike in the previous experiments, where reaction time was fixed. Since biomass of a larger diameter takes longer to reach torrefaction temperature, using residence time instead of reaction time reduces the torrefaction reaction time for larger biomasses compared to smaller ones. Hence, the effect of size becomes more pronounced. In scientific studies, the use of reaction time makes comparison easy, while in actual practice residence time is more practical, as the reactor size is designed based upon the total residence time.

5.4 Results and Discussion

5.4.1 Effect of Temperature on Mass Yield

Figure 5-2 shows the picture of all the biomass samples torrefied at various temperatures for a fixed reaction time of 60 minutes on a convective bed torrefier. It can be clearly seen that the colour of the biomass changes with the severity of torrefaction. Simply from observing the colour of the torrefied biomass, one can roughly assess the degree of torrefaction. The biomass torrefied at 310°C broke during handling of it, which shows how brittle it is.

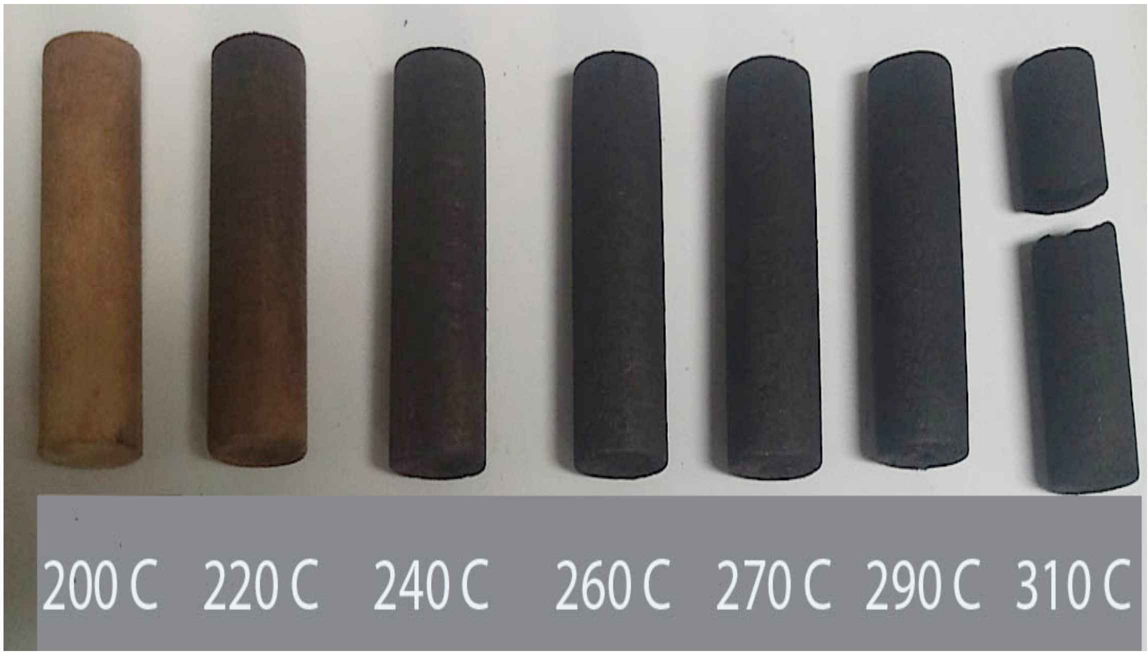


Figure 5-2: Picture of Oak cylinders (22mmx64mm) torrefied at various temperatures for a 60 minutes reaction time.

Mass yield (daf) and increase in energy density of these biomass samples are plotted in Figure 5-2. The figure shows two opposite exponential curves, where mass yield continuously drops while energy density continuously rises. Biomass torrefied at 200°C did not show any change in mass yield (daf) and HHV (daf). This suggests that below 200°C, there is no effective torrefaction of biomass.

Here, the most important and fundamental questions about on torrefaction are raised: What quality makes biomass torrefied and what are the quantitative parameters that describe the quality of torrefied biomass?

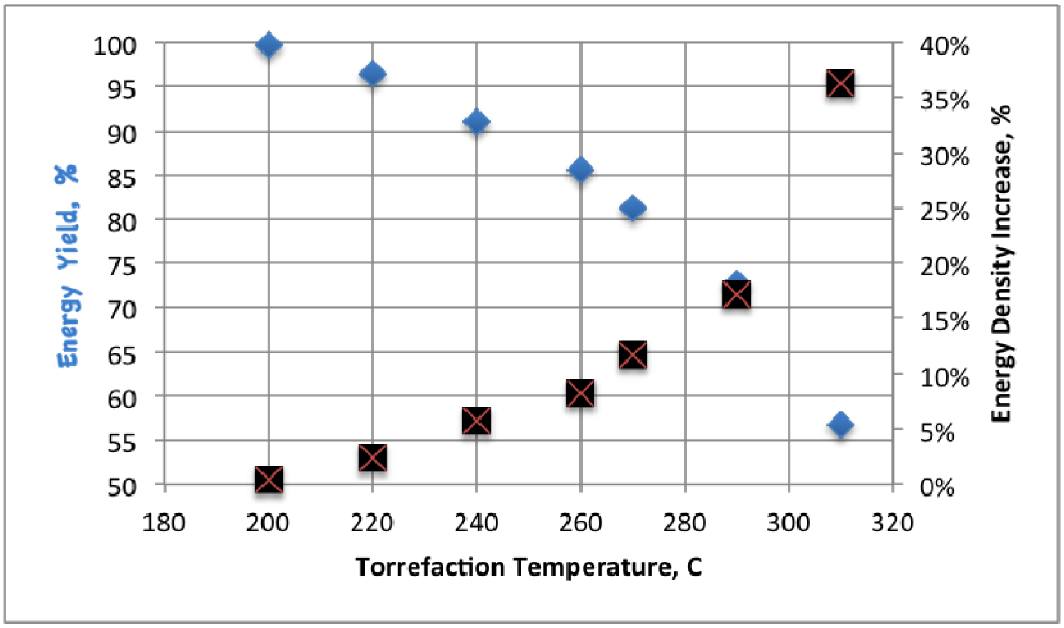


Figure 5-3: Effect of torrefaction temperature on mass yield. Data gathered for 22 mm dia x 64 mm Oak cylinders torrefied for 60 minutes at various temperatures on a convective oven.

Some basic characteristics other than mass yield and energy density (or energy yield) are hydrophobicity and grindability. From the literature, we know that the grindability of biomass continuously improves with the severity of torrefaction (Figure 2-13). Section 2.6.5 describes the hydrophobic properties of biomass, where severe torrefaction was shown to increase the equilibrium moisture. However, under operational range, the change is not significant and these properties do not allow optimization of the process.

End users prefer to have the most energy dense product, but the cost of the product will be very high as most of the raw materials (biomass) would be lost as volatiles. Hence, an economic optimization parameter like GJ/$ can be used. The per-unit costs involved in delivering this energy depends on the cost of raw materials (biomass) and the transportation mode, as well as the customer's least acceptable values of energy density, hydrophobicity and grindability by the customer. When the transportation distance is long, its cost is significant compared to other aspects. In this scenario, one might wish to severely torrefy the biomass to achieve high energy density, while in other scenario, the consumer is very near to the production facility, in which case it is desirable to have a high mass and energy yield with acceptable hydrophobicity and grindability. Hence, the whole economics of the production and distribution specific to an end use application is needed to determine the optimal recipe of torrefaction.

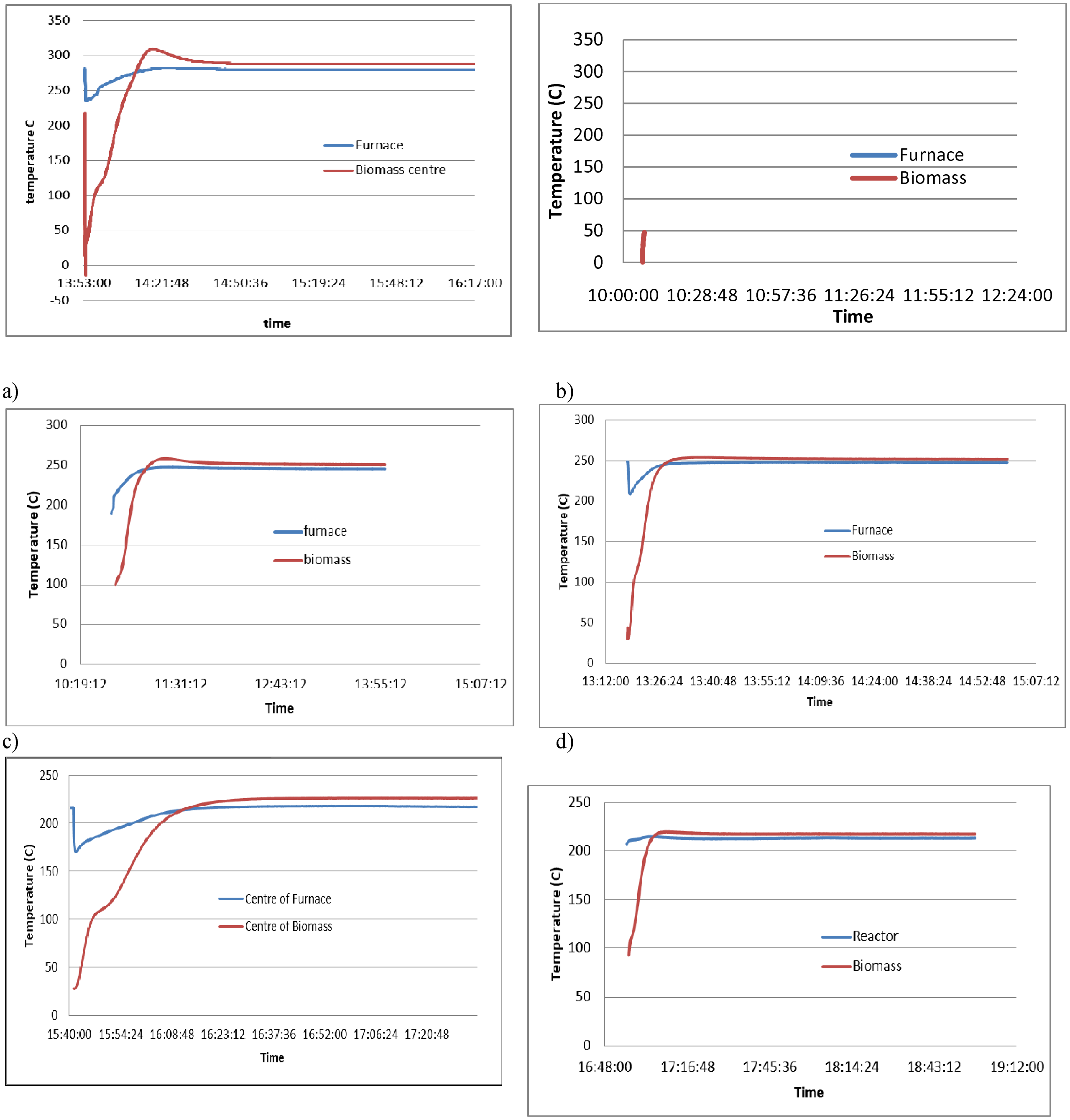
Furthermore, there is a need to develop quantitative parameters which measure the quality of the torrefied biomass. An ideal parameter would be a single proxy value that is easily assessable and relates to all the properties of the torrefied biomass.

5.4.2 Biomass Core Temperature Built-Up (Excess Temperature)

Figure 5-4 shows the temperature history of the biomass core and the reactor. The experiment was continued until a steady state temperature was observed. Figure 5-4 shows that temperature of the core of the biomass continues to increase beyond the reactor temperature and falls back. The temperature offshoot is determined from the difference of the maximum value of this temperature recorded by the core thermocouple and the reactor temperature (Table 5-1).

We can observe that, for higher furnace temperatures, the peak temperature is also higher. Table 5-1, shows that larger biomasses have higher exothermic temperature rise than the smaller ones. However, the excess temperature is affected both by exothermic reaction and heat transfer resistance, as explained in section 5.3.2.

Furthermore, this result validates the simulated results of Turner et al. (2009) (Figure 5-1). In Table 5-1, larger-sized biomasses have higher excess temperatures, while smaller biomasses have lower excess temperatures that last only a short time. Though this temperature difference is not significant in a single piece of biomass, it is definitely noteworthy in bulk biomasses in a large cross-section torrefier. In such cases, temperature runoff may be a serious issues and needs to be controlled.



a)

b)

c)

d)

e)

f)

Figure 5-4: Temperature profile of the biomass and the furnace for different biomass size and torrefaction temperature on a convective bed reactor. a) 280°C, 25 mm ; b) 280°C, 13mm; c) 250°C, 25mm; d) 250°C, 13mm; e) 220°C, 25mm; and f) 220°C, 13 mm.

Table 5-1: Maximum temperature of biomass core in excess of that of the furnace

	Excess Temperature (°C)	
Furnace Temperature↓	Diameter 25.4mm	Diameter 12.7 mm
280°C	20.5	10.7
250°C	7.24	1.88
220°C	0.2	0

5.4.3 Effect of Size of Biomass on Mass Yield

5.4.3.1 Directly Heated Reactors (Fluidized Bed and Convective Bed)

Poplar wood cylinders 64 mm in length and 3.17 to 25.4 mm in diameter were torrefied at 250°C for 60 minutes of reaction time in the directly heated reactors. The mass yield is plotted against diameter in Figure 5-5.

Figure 5-5 shows that mass yields in the convective bed reactor are higher than those in the fluidized bed reactor. This is due to a better heat transfer coefficient in the fluidized bed reactor. However, as data from these reactors were random and the error band was also very high, no definitive conclusions could be drawn. It was later identified that the errors were mostly due to human error in temperature control. Data obtained from the convective bed reactor appear to show some trend, but the difference is not significant and the small amount of data prevents any definitive conclusions. Hence, the effect of biomass size has neither been affirmed nor denied. Further experiments should be repeated at higher temperature and with a larger range of biomass sizes if definitive patterns emerge.

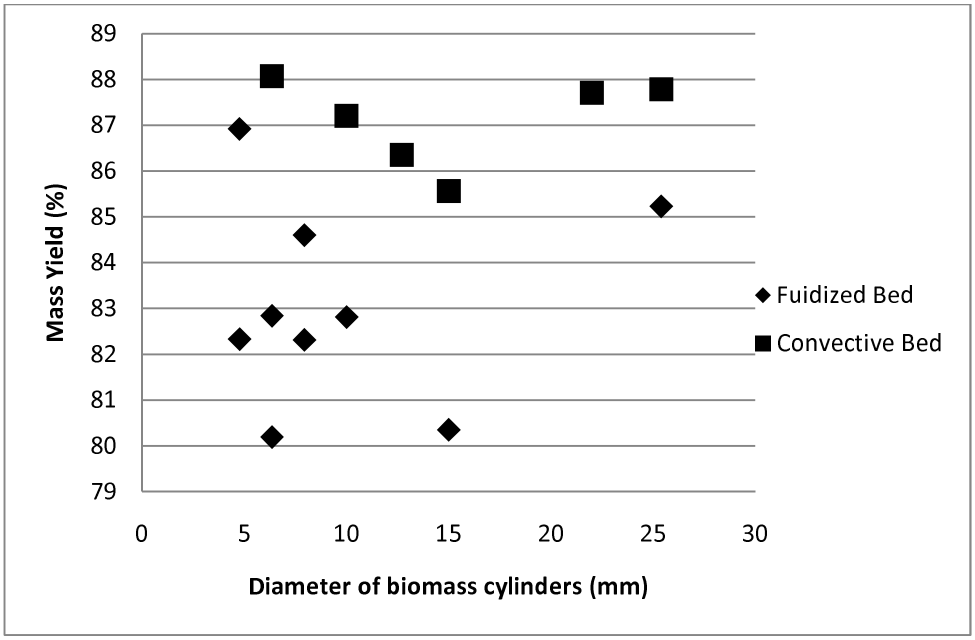


Figure 5-5: Mass yield of several Poplar cylinders with different diameters but same 64 mm lengths, torrefied at 250°C for a 60 mins reaction time on the convective bed.

5.4.4 Indirectly Heated Reactor (Rotating Drum)

5.4.4.1 Torrefaction of Single Particles

Figure 5-6 show the mass yields of three biomasses of different sizes, torrefied individually at 280°C for 15 minutes in a rotating drum reactor. One notes that for biomasses 5, 6.5 and 11 mm diameter, the mass yield drops as the diameter increases.

Smaller biomasses have a greater heat transfer surface area per unit mass and thus should give lower mass yields compared to larger ones. However, the results (Figure 5-6) indicate the opposite. This is possibly due to exothermic reactions. The larger the diameter, larger is the excess temperature as seen in section 5.4.2. When exothermic reaction is inhibited, mass yield is only dependent on heat transfer resistance. Hence with an increase in size of biomass, the mass yield should correspondingly increase. This argument produces a general picture of the effect of biomass size on mass yield, as shown in Figure 5-7. Heat transfer resistance has a tendency to bring down the mass loss (increase the mass yield), while the increasing exothermic reaction will increase the mass loss. Hence a combined effect would be a valley shaped mass loss curve with respect to biomass size. However, this argument needs experimental validation. The data obtained from the experiment only lies on the right side of the curve i.e., increasing mass loss with increasing size.

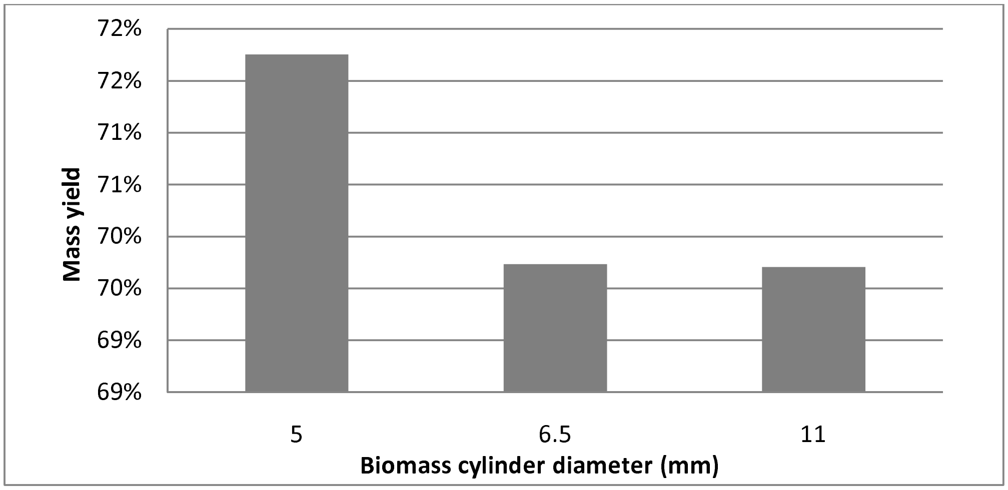


Figure 5-6: Mass yield of single biomass (Birch) particles in a rotating drum at 280°C for 15 minutes residence time.

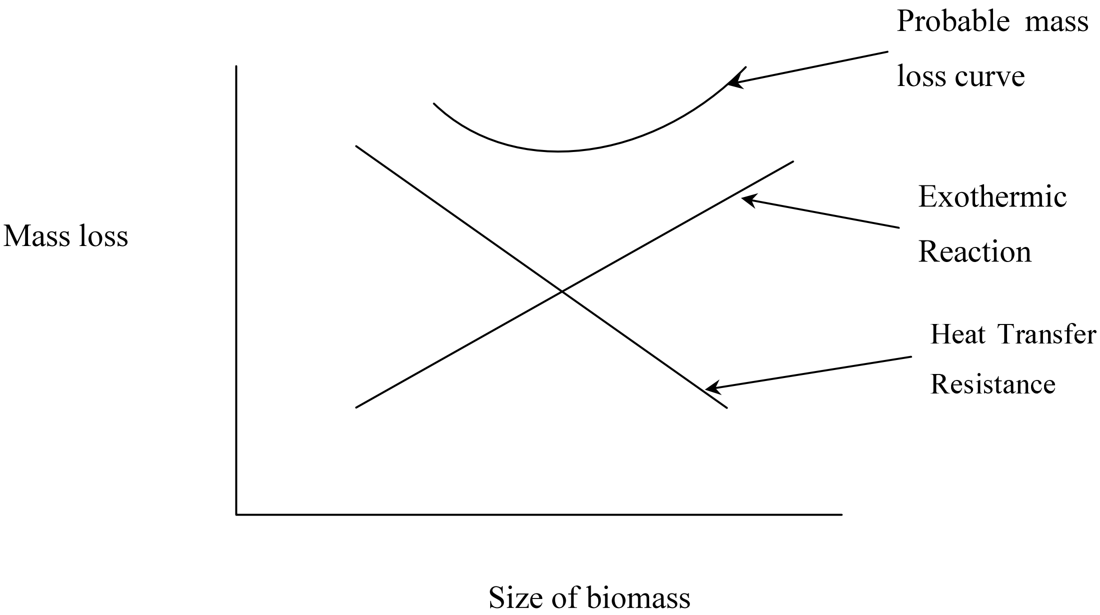


Figure 5-7: Conceptual variations of heat and mass transfer with particle size.

In previous experiments on effect of particle sizes on directly heated reactors however, exothermic reaction was not significant as the excess temperature measured were comparatively lower Hence, their mass yields were primarily dependent upon heat transfer resistance. However, by using of reaction time instead of residence time, the effect of the heat transfer resistance is also inhibited. There is thus no apparent effect of biomass size while torrefied on directly heated reactors. With this in mind, experiments with a larger spectrum of sizes of biomass torrefied at higher temperatures on directly heated reactors may reveal a more pronounced effect of biomass size.

5.4.4.2 Torrefaction of Bulk Of Biomass

Some interesting observations were made while torrefying several biomass particles together. Two sets of experiments were done in the rotating drum reactor. The first one was torrefied for 15 minutes and the second for 33 minutes under similar conditions.

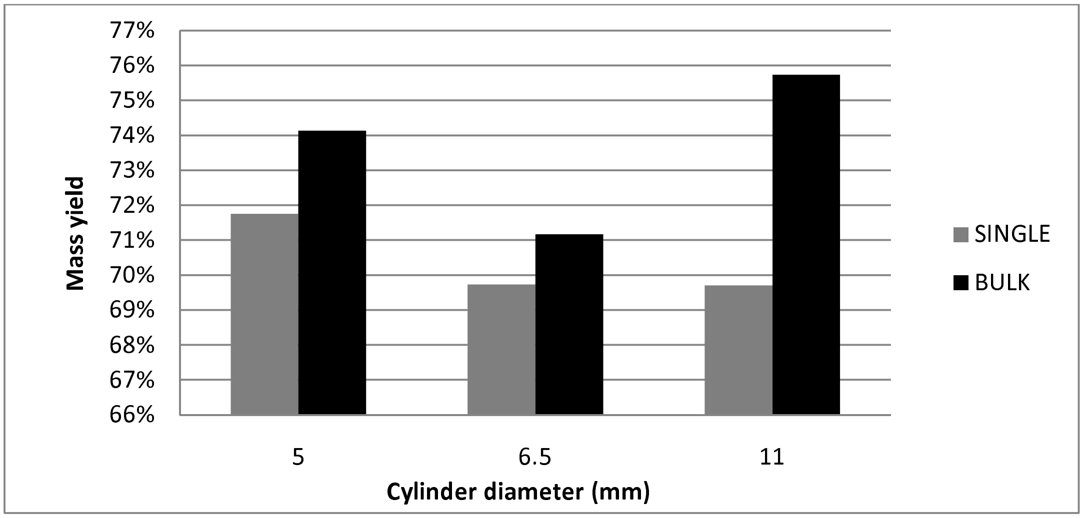


Figure 5-8: Mass yield of single and bulk of biomass in a rotating drum at 280°C for 15 minutes.

Results plotted in Figures 5-8 and 5-9 show that for both residence times, the mass yields of bulk particles are larger than those of single particles. This is because of the reduced heat transfer to each particle when packed together in the reactor

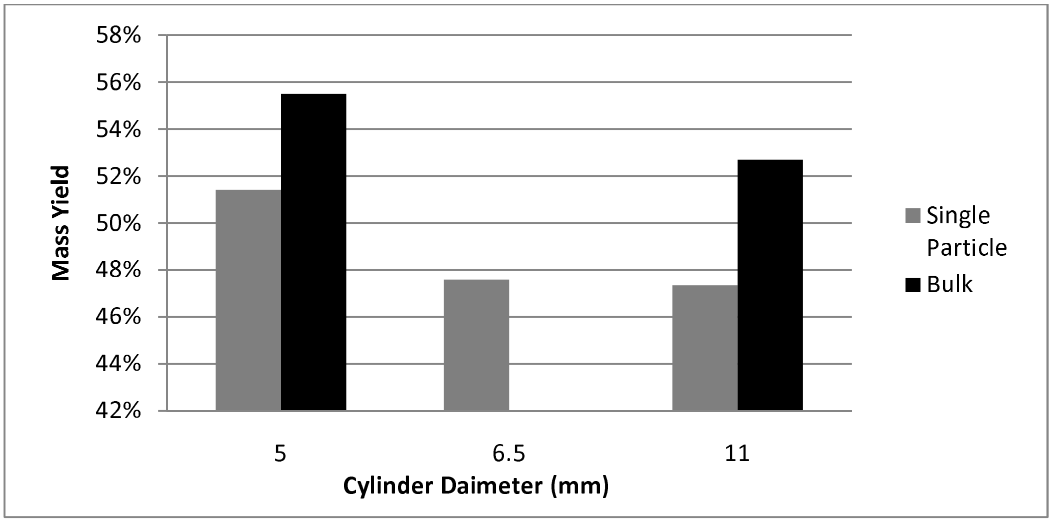


Figure 5-9: Mass yield of single and bulk of biomass in a rotating drum at 280°C for 33 minutes.

Furthermore, mass yields in relation to biomass size follow the same pattern as for individual particles, except for the 11 mm diameter particle. One may identify that Figures 5-8 and 5-9 are the results at that particular point in time. Since the bulk of large particles need a longer time to reach torrefaction temperature, larger pieces of biomass cannot reach torrefaction temperature at 15 minutes and get enough reaction time compared to others, and hence its yield is higher. However at 33 min residence time, its mass dropped sharply due to a higher core temperature.

5.4.4.3 Torrefaction of Single Particle vs. Bulk

Qualitative nature of the results of torrefaction of bulk biomass essentially shows the same behaviour as for torrefaction of single particles (Figure 5-8 and 5-9). Absolute values in single particle and bulk are different due to difference in heat transfer to the individual particles. Analyses performed on single particles of biomass relate qualitatively with those done on bulk amounts of the same particles. Hence, results obtained on single particle torrefaction could be applied to commercial units where large numbers of particles are packed together. Since control of different variables (like temperature and residence time) and their measurement are relatively much easier in single particles, any new method of heating or behaviour of biomass can be tested for single particles and later projected to bulk material. This will save a lot of time and effort in solving problems in large torrefiers.

5.4.5 Effect Of Particle Size On Energy Density

Energy density or heating values of different sizes of torrefied biomass was measured on a dry basis. All of the samples were Poplar wood, torrefied at 250°C for 60 minutes in a convective reactor. The heating values were measured in a bomb calorimeter using standard procedure. Figure 5-10 shows that the measured energy density of the torrefied biomass is higher than that of the raw biomass on a dry basis, but no discernable effect of particle size on the energy density is evident here. Only the smallest particle (4.76 mm diameter) showed a high heating value. This could be an experimental error as the next sizes (7.9 mm and 10 mm) show much lower heating values. Each particle had a thermocouple wire drilled into its core. As the size of this thermocouple (1.6mm) is comparable to a 4.76 mm diameter cylinder, the result obtained here in comparison with those of other sizes may not be reliable.

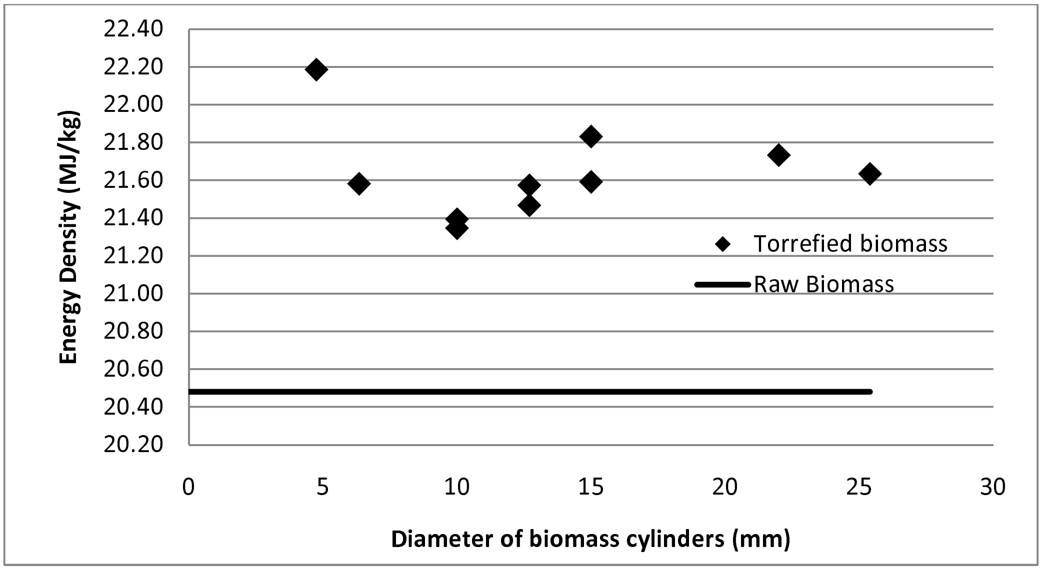


Figure 5-10: Effect of particle size on energy density measure for 22 mm diameter Poplar wood, 64 mm in length, torrefied at 250°C for 60 minutes.

5.5 Conclusion

1. Mass yield decreases with rising torrefaction temperatures, and energy density increases. It was observed that there were no optimization parameters in the process, nor were there any parameters to assess the degree of torrefaction. Hence, the optimization of the process needs to consider the economics of the whole production as well as transportation factors.
2. Exothermic reaction depends mainly on torrefaction temperature and moderately on biomass size.
3. The mass yield of biomass is guided by the combined effect of heat transfer resistance and exothermic reaction. However, the relative change in these factors upon changing biomass size (3.5 - 25.4 mm) may not be adequate to observe the distinct effect. Further experiments on a larger spectrum of biomass as well as torrefaction at higher temperatures should be conducted.
4. Results of single particle torrefaction can qualitatively reflect the results one would expect when bulk amounts of same particles are torrefied together.

CHAPTER 6: CONCLUSION AND RECOMMENDATION

This chapter presents overall concluding remarks of this study and makes recommendations for future works. Conclusions of the individual works are presented in the respective chapters.

6.1 Conclusions

1. Torrefaction product, measured in terms of mass yield, energy yield and energy density, is influenced by the following parameters (in order of importance): torrefaction temperature, biomass size and torrefaction time.
2. During the torrefaction process the temperature of the biomass core under some circumstances exceeds that of the furnace. This confirms the presence of an exothermic reaction during torrefaction, as suggested by some researchers. The excess temperature depends on torrefaction temperature and particle size.
3. Torrefaction of three non-lignocellulose waste biomasses shows that although these biomasses are low or free from hemicellulose, they not only benefit from higher energy density on a gross mass basis, but also undergo an increase in dry and ash free (daf) energy density similar to that experienced by lignocellulose biomass. These biomasses have larger ash content (15-30%) and hence their actual increase in dry energy density is low compared to lignocellulose biomass, which has a negligible fraction of ash (0.1-5%).
4. The effects of temperature and residence time on torrefaction yields are similar in both types of biomass (lignocellulose and non-lignocellulose).
5. Torrefaction produces a stable and relatively high energy density fuel from waste non-lignocellulose biomass such as sewage sludge. This technology offers a potential avenue for utilization of non-lignocellulose biomass. However, further study is needed to determine its many challenges and opportunities. Another attractive commercial option is to pelletize such waste with conventional

lignocellulose biomass, and torrefy them together, to make a high energy dense and low-cost fuel.

6. The comparative study of different reactor technologies (i.e., packed bed, fluidized bed, rotating drum and microwave) regarding torrefaction yields showed differences in yields from different reactors. Indirectly heated reactors, though having lower heat transfer coefficients, produced products with higher energy density but lower mass yield than directly heated reactors, probably due to higher exothermic reactions.
7. Torrefaction in microwave produced a patch of over-torrefied section in the core instead of a uniformly torrefied biomass like in the other reactors. This was likely due to the microwave torrefaction selectively heating the biomass, while the temperature outside the biomass remained at a low temperature, hence the temperature of the surface could not rise to the torrefaction temperature, without excessive temperature at the core.
8. Mass yield decreases with increase in torrefaction temperature, while energy density increases.
9. Biomass mass yield is guided by the combined effect of heat transfer resistance and exothermic reaction. However, the effect of size of the particles in torrefier was not evident.
10. Results of single particle torrefaction can qualitatively reflect the results one would expect, when bulk amounts of same particles are torrefied together.

6.2 Recommendations and Future Works

1. The science of torrefaction remains relatively unexplored. There is no comprehensive quantitative definition of torrefaction or a measure of the degree of torrefaction. Degradation of hemicellulose, hydrophobicity and increase in energy density are some of the properties of the product. There is a lack of knowledge in explicit requirements in the properties of torrefied biomass for a specific application and how to attain it in the most efficient manner by

controlling the torrefaction parameters. Hence, there is still a major knowledge gap in the fundamental science of torrefaction.

2. The work on the torrefaction of non-lignocellulose biomass was of a preliminary nature. Further study is needed to explore the option for the production of inexpensive bio-coal from wastes. Combustion properties, heavy metal and chlorine contents, the agglomeration effect, and the ability to make a mixed pellet with biomass are to name few areas where further research can be carried out.
3. Further works is needed on the effect of the exothermic reactions on torrefaction.
4. Quantitative results produced in the comparison of reactors are very specific to the size and construction of the reactors used in the experiment. These results might be different in industrial-sized reactors. Hence, it is recommended to scale-up these experiments into meaningful sizes. Studies on other common reactors such as indirectly heated moving screw, multiple hearth, microwave, and entrained bed needs to be undertaken.
5. Current work on the effect biomass size remained largely inconclusive. This issue needs to be examined in-depth with the help of a mechanistic model to predict the mass yield of different biomass sizes in various reactors.

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APPENDIX B: PROPERTIES OF BIOMASS

Table B 1: Proximate analysis of various types of biomass used in the study

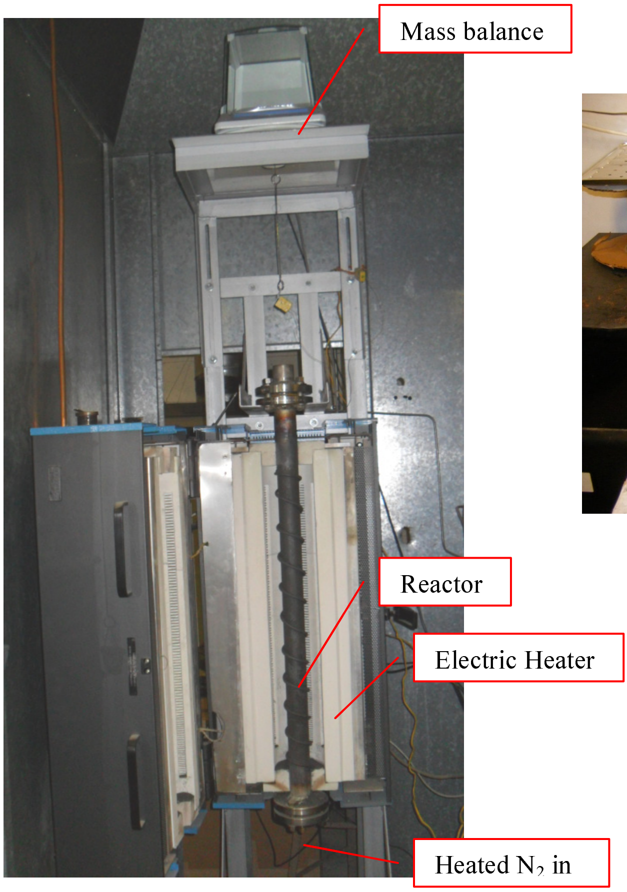
Proximate Analysis	Poplar	Oak	Birch
Moisture (%) - wet basis	3.95	8.65	9.97
Volatiles (%) – dry basis	74.66	86.65	91.9
Fixed carbon (%) - dry basis	20.47	12.82	8.03
Ash (%) – dry basis	4.88	0.53	0.11

Table B 2: Elemental (ultimate) analysis of the Poplar biomass

	Carbon %	Hydrogen %	Nitrogen %	Oxygen %	Sulphur %	Ash %	Moisture %
Ultimate Analysis	46.47	7.18	0.05	32.3	2.74	5.35	3.78

APPENDIX C: PHOTOGRAPHS

Picture of reactors used in this study are shown below:



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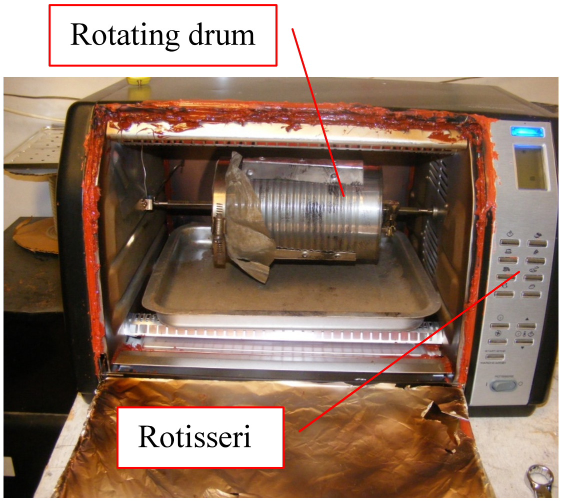

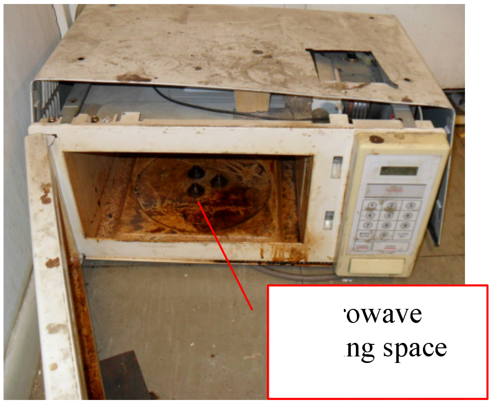

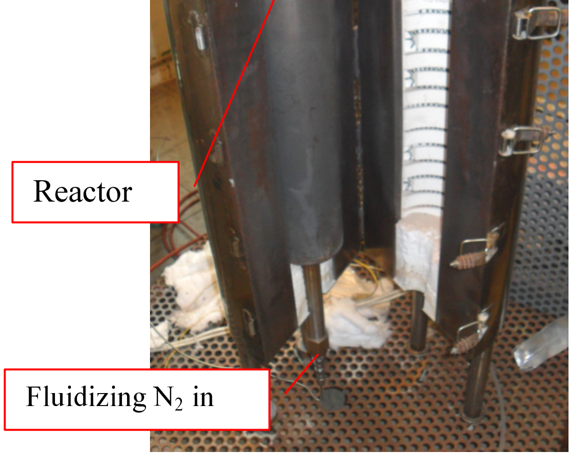

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APPENDIX D: DATA ON COMPARISON OF REACTORS

Table D-1: Experimental data on the comparison of reactors for a single piece of Poplar biomass cylinder

Reactor	Diameter (inch)	Temperature (°C)	Res time (min)	Mass yield (%) (daf)	Core temperature (°C)	Heating value (daf)	Energy yield	Proximate (Fixed carbon)
Convective bed	1	300	23:14	73.97%	327	22.22	83.41%	21.43%
	1	280	33:14	78.59%	305	22.02	87.79%	19.73%
	1	250	60:00	85.71%	269	21.12	91.86%	17.10%
	0.75	300	17:44	75.84%	322	22.16	85.29%	18.38%
	0.75	280	35:26	79.96%	297	21.87	88.73%	16.80%
	0.75	250	44:28	90.91%	253.5	20.59	94.98%	12.46%
	0.5	300	15:32	70.00%	325	22.57	80.18%	21.57%
	0.5	280	26:50	79.04%	291	21.37	85.69%	-
	0.5	250	30:00	91.04%	254	20.28	93.70%	-
Fluidized bed	1	300	23:14	67.84%	329	22.95	79.01%	24.21%
	1	280	33:14	75.54%	300	21.84	83.71%	19.42%
	1	250	60:00	85.23%	260	21.24	91.85%	16.21%
	0.75	300	17:44	74.83%	317	21.78	82.70%	18.76%
	0.75	280	35:26	79.50%	287	21.44	86.51%	15.51%
	0.75	250	44:28	88.65%	256	20.87	93.86%	10.59%
	0.5	300	15:32	70.83%	319	22.24	79.93%	20.87%
	0.5	280	26:50	77.99%	290	21.41	84.71%	19.57%
	0.5	250	30:00	90.45%	254	20.45	93.85%	15.81%
Rotating Drum (RD)	1	300	23:14	59.65%		23.75	71.88%	28.00%
	1	280	33:14	64.98%		22.77	75.07%	24.78%
	1	250	60:00	79.18%		21.19	85.12%	21.13%
	0.75	300	17:44	64.17%		22.62	73.67%	19.89%
	0.75	280	35:26	64.63%		22.45	73.63%	23.63%
	0.75	250	44:28	85.23%		21.29	92.07%	14.87%
	0.5	300	15:32	59.22%		23.32	70.08%	24.79%
	0.5	280	26:50	64.17%		22.28	72.55%	25.54%
	0.5	250	30:00	84.82%		20.38	87.73%	18.09%
Core temp on RD	1	280		67.18%	325	22.62	77.10%	21.69%
Raw biomass	1	-				19.71		10.25%

Table D 2: Experimental data on the comparison of reactors for sawdust.

Reactor	Temperature (°C)	name	Mass yield	Heating Value (daf)	Energy yield	Proximate (Fixed Carbon)
Convective Bed	280	SD11	81.75%	20.66	85.69%	53.94%
	250	SD10	88.96%	19.81	89.41%	22.15%
Rotating Drum	280	SD9	38.71%	24.28	47.69%	15.15%
	250	SD8	76.35%	20.16	78.11%	14.23%

APPENDIX E: ERROR ANALYSIS

E1. Systematic Error

The systematic errors for all the parameters used to assess the properties of biomass are presented below. The calculation methodology is shown in Table E-1. Generally, these values of errors are minor less due to the use of high precision equipments. The maximum amount of systematic errors found in the calculations is listed in Table E-2.

Table E- 1: Procedure to calculate systematic error (ΔZ) of a derived value Z from independent values A and B (http://teacher.pas.rochester.edu/PHY_LABS/AppendixB/AppendixB.html)

	Relation between Z And (A,B)	Relation between errors ΔZ and (ΔA, ΔB)
Eq [1]	$Z = A + B$	$(\Delta Z)^2 = (\Delta A)^2 + (\Delta B)^2$
Eq [2]	$Z = A - B$	$(\Delta Z)^2 = (\Delta A)^2 + (\Delta B)^2$
Eq [3]	$Z = AB$	$\left(\frac{\Delta Z}{Z}\right)^2 = \left(\frac{\Delta A}{A}\right)^2 + \left(\frac{\Delta B}{B}\right)^2$
Eq [4]	$Z = A/B$	$\left(\frac{\Delta Z}{Z}\right)^2 = \left(\frac{\Delta A}{A}\right)^2 + \left(\frac{\Delta B}{B}\right)^2$
Eq [5]	$Z = A^n$	$\frac{\Delta Z}{Z} = n\frac{\Delta A}{A}$
Eq [6]	$Z = \ln A$	$\Delta Z = n\frac{\Delta A}{A}$
Eq [7]	$Z = e^A$	$\frac{\Delta Z}{Z} = \Delta A$

The following is a list of equipment used and their systematic errors from their respective equipment specifications.

1. Analytical Balance – Least count (Δm) = 0.1 mg
2. Bomb Calorimeter – manufacturer suggested error (ΔHHV) = 17.6 J
3. Temperature sensor – least count (ΔT)= 1 °C
4. Water volumetric flask - Error (Δv) – 1 ml.

Table E- 2: Calculated maximum systematic error

	Maximum Error (%)
Proximate Analysis	
Fixed Carbon	0.11
Volatile Matter	0.01
Ash	8.0
Mass Yield	0.2
Energy Yield	0.1

Systematic error in Ash is very high because the absolute mass of the measured ash is also very low and comparable to the least count. This error is again not significant due to the same reason, percentage ash in the biomass studied were as low as 0.1% of the biomass mass.

E2. Repeatability

To control the error in analysis, larger numbers of tests were conducted and their patterns were observed relative to each other. Some of the tests were repeated to see the repeatability.

a. Proximate analysis

Table E-3 shows the proximate values of two samples A and B, repeated twice under identical conditions. Mostly the data are consistent with each other; however ash percentage is high in Sample B. This is due to the implicitly high systematic error. So the repeatability of the proximate analysis of the biomass is acceptable.

Table E- 3: Repeatability test on proximate analysis results

	Sample A			Sample B		
Proximate Analysis ↓	A1 (%)	A2 (%)	Error (%)	B1(%)	B2 (%)	Error
Moisture	3.40	3.24	4.7	3.89	3.85	1.03
Volatile Matter	78.83	77.57	1.6	78.73	78.33	0.5
Fixed Carbon	20.53	21.79	6.14	20.52	20.85	1.6
Ash	0.64	0.65	1.6	0.75	0.82	9

b. Heating value (bomb calorimeter)

The repeatability in heating value is also very good, with an error of maximum 3%.

Table E- 4: Repeatability test on the results of the bomb calorimeter

	Sample C			Sample D		
	C1 (MJ/kg)	C2 (MJ/kg)	Error (%)	D1 (MJ/kg)	D2 (MJ/kg)	Error (%)
HHV (MJ/kg)	22.53	21.91	2.8	21.33	20.91	2.0

c. Torrefaction in a convective bed

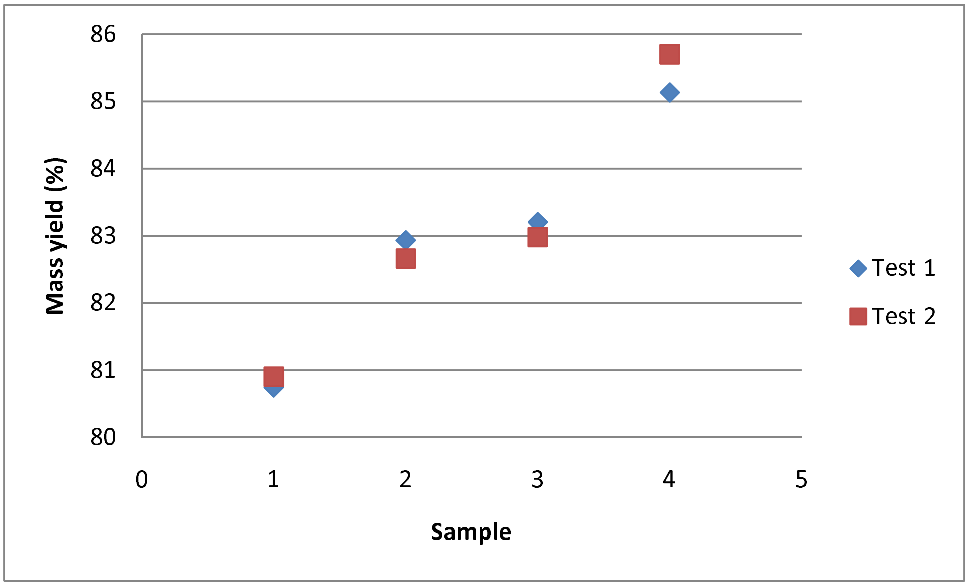

Figure E- 1: Repeatability test on the mass yield of biomass torrefied in a convective bed.

d. Torrefaction in a fluidized bed

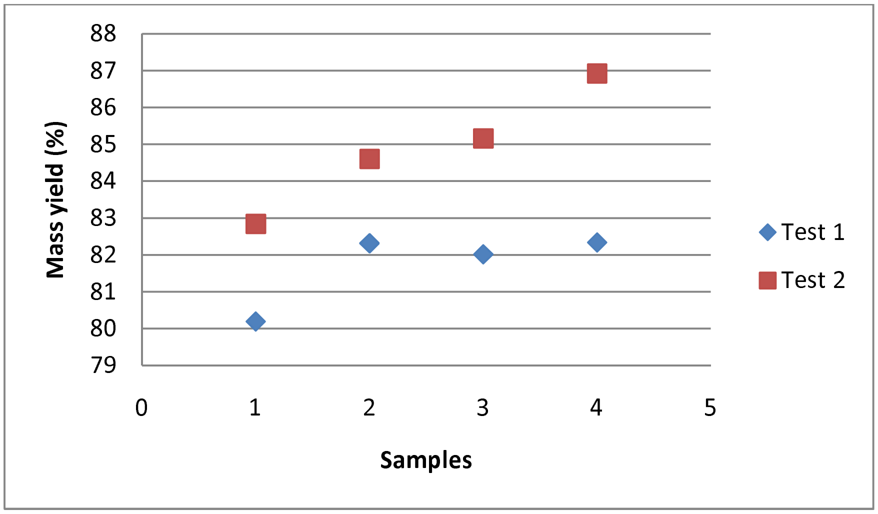

Figure E- 2: Repeatability test on the mass yield of biomass torrefied in a fluidized bed.

Although the error relating to the fluidized bed is high, the trend is obvious. This is probably due to change in set temperature. Hence, during the actual test, the fluidized bed was continuously run for all the samples in succession.

e. Torrefaction in a rotating drum

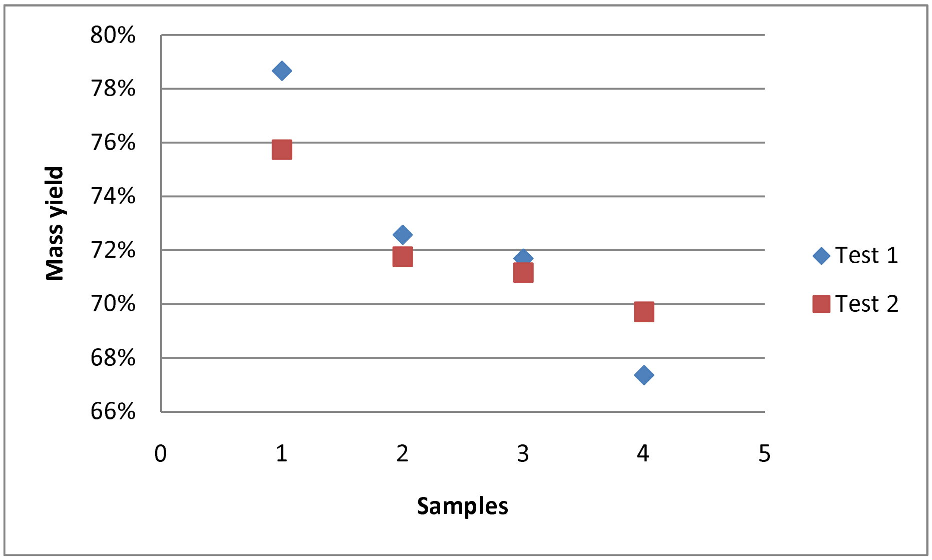

Figure E- 3: Repeatability test on the mass yield of biomass torrefied in a rotating drum.