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Investigation of Torrefaction Process Parameters on Biomass Feed-Stock and CO₂ Gasification of Torrefied and Pyrolysed Bio-char

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Investigation of Torrefaction Process Parameters on Biomass Feed-Stock and CO₂

Gasification of Torrefied and Pyrolysed Bio-char

by

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A THESIS

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Abstract

Torrefaction is a thermo-chemical process, carried out at a relatively low temperature ranging from 200-300°C. This research focuses on torrefaction of flax straw at laboratory scale. A Thermo Gravimetric Analyzer (TGA) was used to study the effect of temperature, particle size and residence time on the torrefaction of flax straw. Proximate analysis of the char showed a significant increase in fixed carbon and ash content, and a noticeable decrease in the moisture and volatile content with an increase in the temperature. Ultimate analysis was performed for the product char and from these results heating value of the torrefied char was calculated. The kinetic analysis showed an activation energy of $76.64 \text{ kJ mol}^{-1}$, for the particle size of $925 \text{ }\mu\text{m}$. The experimental results of the torrefaction of flax straw indicated that the temperature had greater effect on torrefaction process than the residence time and the particle size's chosen for this study.

CO_2 gasification of flax straw char produced by two different processes namely torrefaction and pyrolysis was investigated using a TGA. The objective of this research was to investigate the diffusion and surface reactions that occur during the CO_2 gasification of the torrefied and pyrolysed char particles. Gasification experiments were carried out at four different temperature range from 750 to 900°C and at different particle sizes ($<90 \text{ }\mu\text{m}$ to $925 \text{ }\mu\text{m}$). The effects of temperatures, particle sizes, and the char types on the rate of CO_2 gasification process were determined. The reactivity of the char particles at 50% conversion showed an increase in the reactivity values with a corresponding increase in the temperature and decreased with an increase in the particle sizes for both the char types. The diffusional parameters such as effective diffusivity, effectiveness factor, and Diffusion limitation index (DLI) were calculated from the experimental data for both the char types.

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Nomenclature

Notation

c = gas concentration (mol/m^3)

c_w = Weisz-Prater modulus (mol/m^3)

d_p = particle size (m)

d_t = crucible diameter (m)

M_g = gas molecular weight (kg/kmol)

M_C = carbon molecular weight (kg/kmol)

r_{obs} = observed gasification rate (kmol/s)

$r_{D,e}$ = maximum external diffusion (kmol/s)

$r_{D,i}$ = maximum internal diffusion (kmol/s)

r_p = pore radius (m)

R_g = universal gas constant ($\text{kJK}^{-1}\text{kmol}^{-1}$)

S_c = specific surface area of the char particle (m^2/g)

t = time (sec)

T = temperature (K)

w = instantaneous char weight (kg)

X = local particle conversion

X_p = global particle conversion

Greek letters

ε = char porosity

τ_t = tortuosity

η_R = effectiveness factor (Ramachandran)

ρ_c = apparent carbon density (kg/m³)

Subscripts

b = bulk diffusion mechanism

e = effective diffusion

K_n = Knudsen diffusion mechanism

i = instantaneous values

m = molecular diffusion

int=intrinsic

Chapter One: Introduction

1.1 Introduction

The use of renewable energy sources can reduce our dependence on energy from fossil fuels and thereby reduce greenhouse gas emissions. In Canada, about 540 petajoule of energy is derived from biomass sources and biomass provides more of Canada's energy supply than coal and nuclear power. About 100,000 Canadian homes use wood as their primary heating fuel. In some Canadian areas, such as British Columbia, Ontario and Quebec, the forest industries supply wood chips and pellets to nearby industries, residences and electricity generators from which they derive bio-energy to meet their regular needs. Canada is an endorser for the International Energy Agency Bio-energy Agreement and it promotes collaboration among 16 member countries to exchange information and develop new technologies to increase the potential for deriving energy from biomass sources (Cruickshank et al., 2012).

Biomass is a biodegradable material and is the only renewable source of carbon. This element plays an important role in the production of many chemicals and materials. Biomass is inexpensive and is available abundantly. The CANMET Energy Technology Center, Canada, is developing green power technologies in Canada. The main aim of this center is focused towards the development of bio-fuels and production of ethanol from forest and agricultural waste (Natural Resources Canada, 2009)

Flax straw is an agricultural biomass resource and it can be effectively used for the production of bio-energy, especially in Canada due to its immediate availability and abundance. It was estimated that Canada produced about 930,000 tonnes of flax straw in 2010. Flax straw

possesses similar heating value as that of soft coal and thus has a heating value higher than other crop residues (Flax Council of Canada, 2013). Table 1.1 shows the production rate of biomass for energy.

Table 1.1 Recoverable production of biomass for Energy (Tester et al., 2004)

Region	Forest (EJ/yr)	Crop (EJ/yr)	Dung (EJ/yr)
US and Canada	1.7	3.8	0.4
Europe	1.3	2.0	0.5
Japan	0.1	0.2	-
Africa	0.7	1.2	0.7
China	1.9	0.9	0.6
World Total	12.5	13.7	5.1

For the large scale production of bio-energy, significantly large amount of biomass feedstock has to be collected, transported, stored and processed in an economical and sustainable manner. Although biomass feedstock's are available in abundance, raw biomass possesses certain inferior characteristics such as high moisture content, low bulk density, low energy content, high oxygen content, heterogeneity, susceptibility to microbial degradation on storage and its disperse nature makes the use of raw biomass for energy production complex and expensive. These inferior characteristics of the raw biomass sources can be overcome by treating the raw biomass samples using different techniques under controlled conditions. The raw biomass can be treated thermo-chemically, biologically, or by catalytic processes (Tushar et al., 2010). Table 1.2 displays the various biomass conversion technologies.

Torrefaction is used to treat raw biomass samples to overcome their inferior properties. Torrefaction is a thermo-chemical, pre-treatment method carried out at a relatively low temperature range between 200 to 300°C, in the absence of oxygen and at atmospheric pressure. Treatment of raw biomass samples using torrefaction process results in the production of char that is rich in carbon content, has low moisture content, low oxygen content, low volatile content and high ash content. During the initial heating stage of the torrefaction process the unbound moisture is removed and continued heating of the raw biomass samples causes the removal of bound moisture along with the degradation of hemicelluloses. This degradation process causes the release of huge amounts of volatiles and the volatiles that are released majorly contains oxygen and hydrogen along with less significant amount of carbon in them, which in turn increases the carbon content of the resulting torrefied char. The char that is produced using the

torrefaction process resembles lignite which is a low grade charcoal (Tumuluru et al., 2010). There have been numerous studies conducted on the torrefaction process using different biomass samples such as torrefaction process on wood briquette has been conducted by Felfli et al., (2005), Pimchuai et al., (2010) studied torrefaction process on rice husks and four agricultural residues (saw dust, peanut husks, bagasse and water hyacinth), Prins et al., (2006(b)) studied torrefaction process on deciduous wood types (beech and willow) and on wheat straw and Pach et al., (2002) studied torrefaction on birch, pine and miscanthus. The impact of the torrefaction process on flax straw sample has not been investigated.

Table 1.2 Biomass conversion technologies (Biomass Energy, 2009)

Technology	Conversion process type	Major biomass feedstock	Energy/Fuel production
Direct Combustion	Thermo-chemical	wood, agricultural waste, municipal solid waste and residential fuels	heat, steam and electricity
Gasification	Thermo-chemical	wood, agricultural waste and municipal solid waste	producer gas
Pyrolysis	Thermo-chemical	wood, agricultural waste and municipal solid waste	synthetic fuel oil (bio-crude) and charcoal
Hydro-thermal conversion	Thermo-chemical	wood, agricultural waste and municipal solid waste	bio-oil
Anaerobic Digestion	Bio-chemical (anaerobic)	animal manure, agricultural waste, landfills and wastewater	methane
Ethanol Production	Bio-chemical (aerobic)	sugar or starch crops, wood waste, pulp sludge and grass straw	ethanol
Biodiesel Production	Chemical	rapeseed, soybeans, waste vegetable oil and animal fats	bio-diesel
Methanol Production	Thermo-chemical	wood, agricultural waste and municipal solid waste	methanol

The major product of torrefaction is the char and it has numerous applications. Torrefied char is used for generation of electricity, used as a fertilizer such as anhydrous ammonia and ammonia sulphate and for the production of synthetic natural gas.

The bio-char that is produced using the torrefaction has numerous agricultural benefits. Once the char is produced using the torrefaction process, the char is spread over the top layer of the soil. This helps in fertilizer runoff and leaching and thereby helps in less use of fertilizers and this in turn reduces the environmental pollution caused by agriculture. Biochar also helps the soil to retain moisture and thus helps the plants through a period of drought. The other important factor for using biochar in soil is that, the carbon that is present in the biochar can remain stable for millions of years and thus prevents carbon sequestration. All these properties of biochar that has been produced using the torrefaction process helps in an increase of agricultural crops (Biochar.info, 2013).

Torrefied char can be used as a superior quality fuel for cooking and for residential heating purposes, as a reducer in smelters and it can be co-fired with other fuels in boilers (Sridhar et al., 2007). Torrefaction process reduces the moisture content and increases the fixed carbon content in the torrefied char and this in turn increases the heating value of the char, which can be used as a suitable feedstock for combustion and gasification processes.

Gasification is a process of treating any carbonaceous materials at higher temperatures ($>700^{\circ}\text{C}$), without combustion and by supplying controlled amount of gasifying agents such as CO_2 , steam or oxygen. The resultant product of gasification process is a gaseous mixture of carbon-monoxide, hydrogen and carbon-dioxide. This gaseous mixture is called syngas, which is

a fuel by itself (Kannan et al., 1990). Gasification of biomass samples includes two important steps:

1. Thermo-chemical pre-treatment of the biomass samples (either pyrolysis or torrefaction process) during which moisture and volatiles are released and solid residue called char is left behind.
2. Reaction of the solid char with the gasification agents such as CO₂, water or oxygen respectively (Fisher et al., 2012).

Char conversion is the most important rate-limiting step during the biomass gasification process and hence successful design and operation of a gasifier requires reliable kinetic data. The rate of char gasification also depends on numerous process variables such as particle size, char porosity, gasification temperatures, mineral content of the char and the partial pressure of the gasifying agents. Physical effects such as diffusion and heat transfer also play a vital role in the determination of the gasification rates (Ollero et al., 2002). The diffusion and surface reaction phenomenon occurring during the biomass gasification of the torrefied and pyrolysed char have been investigated in this study.

1.2 Research objective

The major objective of this study is to better understand the torrefaction process and the characteristics of the torrefied flax straw biomass char. The objective of the first study was to perform the torrefaction process on the flax straw biomass and to investigate the effect of torrefaction temperature, particle sizes and residence time on the torrefaction of the flax straw. The effect of torrefaction on the ultimate and proximate analysis values of the torrefied biomass

char along with their kinetics was studied. The outcome also includes the calculation of the heating value of the torrefied flax straw char, which serves as a foundation for further optimization of the process. The objective of the second study is to make a comparative study on the CO₂ gasification of the torrefied and pyrolysed char. The effects of temperature and particles size of both the torrefied and pyrolysed char on the CO₂ gasification process were investigated. A mass-transfer effect that takes place during the CO₂ gasification of both the torrefied and pyrolysed char was examined. The results of this study compared the char quality that is produced by two different processes and may serve as a foundation for further investigations.

1.3 Dissertation organization

This Dissertation is organized into five chapters. The first chapter includes a brief introduction, research objectives and continues with the body of the dissertation organization in sections. The second chapter includes a comprehensive literature study on biomass, pyrolysis, torrefaction and gasification processes. The third chapter includes the torrefaction process of the flax straw biomass. The effect of different torrefaction process parameters and the kinetic analysis of the torrefied flax straw char are presented in this chapter. Chapter three is presented as a manuscript that has been accepted for publication in *Energy Sources-Part A* journal under the title "Torrefaction of flax straw biomass and its Kinetic studies". Chapter four consist of a comparative study on the CO₂ gasification of the torrefied and pyrolysed char. The important diffusion parameters and mass-transfer effects that take place during the CO₂ gasification of both the torrefied and pyrolysed char are calculated and presented in this chapter. Chapter four is also presented as a manuscript that has been submitted to the *Energy* journal for peer review under

the title "Mass transfer studies during CO₂ gasification of torrefied and pyrolysed char". General conclusion and recommendations for future work are given in chapter five.

Chapter Two: Literature survey

Currently the world is facing numerous challenges to reduce the dependence for energy on fossil fuels and to shift the interest towards renewable energy resources. The main reason for this change in energy utilization is because of the depletion of the fossil fuels and concern for global warming that is caused by the release of greenhouse gases while burning the fossil fuels. Although there are numerous renewable energy resources that are available, biomass has gained increasing amounts of attention in recent years. Biomass is biological degradable material from living organism that can be used as a source of energy either directly or indirectly. Deriving and utilizing energy from biomass is not a new technology for mankind. Wood is a biomass that has been used as a source of energy for heating and for cooking purposes throughout the evolution of mankind. Biomass is considered as carbon neutral, because the living organisms intake CO₂ to carry out their life cycle processes and when these organisms and biomass materials are burnt, they release CO₂ equal in amount to what they absorbed originally. This invaluable property of the biomass controls CO₂ emission and prevents global warming. As an energy source, biomass is readily available and sustainable.

2.1 Biomass sources and structure

2.1.1 Sources of biomass

The major sources of biomass are classified into the following groups (Tushar, 2010).

1. Wood waste
 - a. Sawdust
 - b. Wood chips

- c. Pallets
 - d. Crate discards
 - e. Wood yard trimmings
2. Agricultural residues
- a. Corn Stover
 - b. Sugarcane baggase
 - c. Animal waste
 - d. Straw
3. Energy crops
- a. Hybrid poplar
 - b. Switch grass
 - c. Willow

2.1.2 Structure of biomass

Biomass substances primarily consist of carbohydrate polymers with a small amount of inorganic and low molecular weight organic constituents. The amount of lignocelluloses materials (cellulose, hemicelluloses and lignin) that are present in the biomass varies depending upon the type of biomass materials being considered. Biomass usually consists of 18-35wt% of lignin, 65-75wt% of cellulose and about 10 wt% of low molecular weight compounds and inorganic compounds (Mohan et al., 2006).

Cellulose is a fibrous high molecular weight polymer. The micro fibrils that are present in the celluloses are connected together and form a carbohydrate matrix and this matrix provides

support to the plant structure. Cellulose is a rigid material and its degradation usually takes place at a temperature of about 240-350°C (Mohan et al., 2006).

Hemicelluloses are branched polymers that consist of smaller sugar units. In wood hemicelluloses account for about 25-35wt% and the degradation of hemicelluloses occurs at lower temperature range of about 130-260°C. During their thermal degradation, hemicelluloses are evolved as light volatile compounds and produce low tar compounds during their degradation (Demibras, 2009; Mohan et al., 2006).

Lignin is highly branched polyphenolic component and it is present in the cell wall of plants and fills the space between the celluloses, hemicelluloses and pectin. Lignin degradation begins at around 280-500°C and produces phenols during its degradation (Demibras, 2009; Mohan et al., 2006).

Raw biomass cannot be used directly as a source of energy because of its inferior properties like high moisture content and low bulk density. Due to these characteristics biomass possesses low heating value and undergoes biological degradation on storage. Transportation of the raw biomass with these inferior properties may create problems and challenges. There are several pre-treatment methods that have been adapted worldwide to treat the raw biomass. These pre-treatment methods help the raw biomass to overcome inferior properties and thereby increase the fuel properties. During the pre-treatment of raw biomass the lignocelluloses undergoes degradation at different degrees, depending on the temperature, residence time and the type of biomass used. The products formed as a result of biomass pre-treatment process are char, liquids and gaseous energy products at different levels.

2.2 Biomass conversion techniques

There are three main different conversion processes used to convert raw biomass into useful form of energy.

- a. Thermal Conversion: The processes under thermal conversion are direct combustion, pyrolysis, torrefaction, gasification and hydrothermal conversion
- b. Biological Conversion: The processes under biological conversion are aerobic, anaerobic digestion and fermentation processes
- c. Mechanical Conversion: The processes under mechanical conversion are hydrocarbon extraction and oil extraction (Hall and Kitani, 1989)

2.2.1 Thermal conversion process

Thermal pre-treatment is the primitive method for treating raw biomass. This process usually involves the heating of biomass sample to various temperatures and then deriving useful forms of energy from it. Thermal pre-treatment includes direct combustion, pyrolysis, torrefaction and hydrothermal conversion.

Direct combustion is the oldest method for producing energy from biomass. It includes burning of fuel or biomass directly with the help of an oxidizer, usually air, to a temperature where the biomass chemically react and combust. The major product of this conversion process is heat and it is used to run heat engines. The other products are CO₂, CO H₂O and N. The energy efficiency of this process can be improved by using a well designed combustor and by reducing the moisture content that is present in the biomass (Hall and Kitani, 1989).

Pyrolysis is a thermo-chemical pre-treatment of biomass in the absence of an oxidizing agent at higher temperature of about 500-800°C. Depending on the pyrolysis process conditions such as heating rate, temperature and residence time, pyrolysis is classified into three different categories namely, slow, mild and fast pyrolysis processes. Slow pyrolysis is usually carried out at a lower temperature and with slow heating rate. The major product formed during slow pyrolysis is the char. Liquid and gaseous products are formed in smaller amounts in comparison to the char. Mild pyrolysis is carried out at slightly higher temperature than the slow pyrolysis and at a slow heating rate. Mild pyrolysis yields a considerable amount of char, liquids and gaseous products. Fast pyrolysis is carried out at high temperature of about 800°C and at faster heating rate. Fast pyrolysis is gaining more attention than the slow and mild pyrolysis processes because it produced large amount of liquid product and this liquid product is called pyrolysis oil or bio-oil. When this oil is upgraded it can be used as a substitute for petroleum, for heating and as a transportation fuel (Patwardhan, 2010).

One of the major differences between pyrolysis and torrefaction is that, torrefaction is carried out at very low temperature at which pyrolysis process cannot take place. Pyrolysis process is primarily concerned with the production of liquid bio-oil. The torrefaction process is concerned with the production of solid bio-char. During torrefaction, hemicelluloses undergo maximum degradation with very little degradation of the celluloses and lignin. The primary reason for the maximum degradation of hemicelluloses is the torrefaction temperature. The maximum torrefaction temperature range is about 280-300°C and it is in this temperature range that hemicelluloses is the only lignocelluloses that can undergo complete degradation. The char

that is produced by the torrefaction process has high carbon content with low moisture and volatile content. This makes the biomass char hydrophilic and offers great resistance to biological activities on storage. The properties of the torrefied char also make the transportation process easier (Uslu et al., 2008).

Hydrothermal conversion is a thermo-chemical pre-treatment process. In this process the biomass sample is treated using water at a temperature of about 300-350°C and at higher pressure of 12-20MPa. Higher pressure is used in a hydrothermal pre-treatment process in order to maintain the water used for the process in the liquid state. The major products of hydrothermal conversion process is liquid (oil) with reduced oxygen and water (DOE, 2004).

2.2.2 Biological conversion process

Biological conversion is another kind of pre-treatment process, in this process the biomass samples are treated with different kinds of micro-organisms, in the presence or absence of oxygen and derive heat (biogas) from the waste biomass samples. Biological conversion process includes aerobic, anaerobic, and fermentation processes.

Aerobic conversion process is the degradation of waste biomass samples with the help of micro-organisms in the presence of oxygen. Traditionally, aerobic conversion process is used to treat the animal waste and obtain heat from the process. Aerobic conversion process is mainly used for the production of different kinds of fertilizers. The heat that is produced from the animal waste using aerobic conversion process is a low grade heat or energy. Hence, this process is not currently widely used (Hall and Kitani, 1989).

Anaerobic digestion is a process of treating waste biomass samples using micro-organisms in the absence of oxygen. Anaerobic micro-organisms do not make use of oxygen and any kind of wet biomass can be used as a raw material for this process. The major product formed as a result of anaerobic digestion process is biogas. Biogas is a renewable energy source and consists of a mixture of CO₂ and methane. It is used as a substitute for fossil fuels and thus reduces the emission of landfill gases into the atmosphere. The solid product that is formed as a part of the anaerobic digestion process can be used as a fertilizer (Tisdale, 2004).

Fermentation is one of the oldest methods that have been developed by mankind since ages. Traditionally, the fermentation process was used for the production of beverages from feedstock that had high sugar content. With the development of technologies, the fermentation process is used for the production of ethanol (bio-ethanol) from waste biomass samples. Biomass waste such as agricultural waste, forest residues, municipal solid waste, grasses and industrial waste can be used as a feedstock for the production of ethanol using the fermentation process. The conversion of raw biomass to bio-ethanol using fermentation process involves four different steps. First, the biomass feedstocks are treated with an acid or base to breakdown the tough and fibrous cell wall of the biomass samples. This enables easy hydrolysis of cellulose and hemicelluloses for further fermentation process to take and for the production of bio-ethanol (Energy Efficiency and renewable Energy, 2013). The second step is to convert the biomass samples into useful forms of sugar units. The third step is the fermentation of the biomass intermediates. This fermentation process is carried out by the addition of certain biocatalysts that includes yeast and bacteria. The resultant product of this fermentation process is bio-ethanol with

other additional by-products. The last step is the processing or purification of the bio-ethanol and further processing of the by-products to produce other types of fuel, chemicals, fertilizers, heat and electricity (DOE b, 2004).

2.2.3 Mechanical process

The Mechanical conversion process is primarily used for the production or extraction of vegetable oil. The feedstocks used for the production of vegetable oil are palm, coconut, peanut, sunflower, maize and soybean. The oil produced using the mechanical process requires further treatment processes in order to be used as a fuel. Another type of mechanical process is the hydrocarbon extraction. In this process, fuel is produced from biomass sources that naturally produce complex hydrocarbons. However, sustainable yield of hydrocarbons are not yet been determined, their potential to be used as fuel is not established (Hall and Kitani, 1989).

2.3 Comparison of biomass conversion techniques

There are various biomass conversion techniques that have been adapted worldwide to derive energy from various biomass sources. These techniques have been discussed briefly in the above sections. As discussed in section 2.2.2, biological conversion is one among the various conversion techniques that has been used to convert waste biomass into useful form of energy. This biological conversion method is not widely used because of the numerous disadvantages that are associated with the process. The biological conversion process (anaerobic digestion) requires a large area to setup the equipments and it needs continuous monitoring, which is labour intensive. Other disadvantages are the potential for water contamination challenges, and the technique is very time consuming.

Thermal conversion of biomass into useful forms of energy is one of the best conversion techniques that are been used worldwide today. Although this technique has some disadvantages the advantages overweight them. The disadvantages are, during the combustion of the biomass sample, nitrogen oxide is emitted and this emission must be controlled due to the negative impact it has on the environment. During the thermal conversion process huge amounts of ash are formed as a by-product. The agglomeration of ash and the fouling problems due to the phosphorus content and other inorganic compounds create operation challenges for the reactors and combustors. Regardless to these challenges, thermal conversion process is more economical and a faster process than any other conversion techniques and the energy obtained by this process is of high quality and it is renewable (Tisdale, 2004).

2.4 Pyrolysis of biomass

Pyrolysis is a process of thermal degradation of organic materials in the absence of oxygen or with a lack of the stoichiometrically needed amount of oxygen. The three main products that are formed during the pyrolysis process are gas, liquid and solid char. The proportion of the formation of pyrolysis products depends on various process parameters and the composition of the feedstock. The various process parameters that influence the product yields during the pyrolysis process are the operating temperature, operating pressure, heating rate, particle size of the feedstock and residence time. The various physical and chemical constituents of the biomass feedstock that influences the product yields during the pyrolysis process are moisture, volatiles and ash contents, along with the presence of catalysts. Among these parameters, the heating rate, pressure and operating temperature are believed to have most

important effect on the product yields from the pyrolysis process. Depending on the principle products that are desired (solid char, liquid or a gas) during the pyrolysis process, certain process conditions can be applied. At a low heating rate of about less than $1^{\circ}\text{C}/\text{sec}$ and at relatively low temperature of less than 600°C , the solid char, liquid and gaseous products are produced in equal amounts during the pyrolysis process. At a higher heating rate of about $100^{\circ}\text{C}/\text{sec}$, a moderate temperature range of about $450\text{-}600^{\circ}\text{C}$ and for a short residence time of $\sim 1\text{sec}$, the pyrolysis process yields a higher liquid product than solid char and gas. This type of pyrolysis process is called fast pyrolysis. If the pyrolysis temperature is above 650°C and if it is maintained at this temperature for a longer duration, the gas yield increases with a minimal yield of solid char and liquid products. At a low pyrolysis temperature of less than 400°C and at low heating rate and residence time, the solid char yield increases.

Depending on the process conditions, the pyrolysis process is divided into three groups namely, carbonization, slow or conventional pyrolysis and fast or flash pyrolysis. The Pyrolysis process is carried out at isothermal and at non-isothermal conditions (Tushar, 2010).

2.5 Torrefaction process of the biomass

Torrefaction is a pre-treatment method of biomass samples in a temperature range of about $200\text{-}300^{\circ}\text{C}$, in the absence of oxygen and at atmospheric pressure. Torrefaction process is considered a technically feasible method for converting the raw biomass samples into high energy density, hydrophobic, easily grindable and low oxygen-Carbon (O/C) ratio solid char particles that are used for commercial and residential combustion and for gasification processes.

Raw biomass contains high amounts of oxygen, nitrogen, sulfur, chlorine and fluorine compounds in them. The presence of these compounds in the raw biomass makes it unstable to be used as a fuel. During the combustion and gasification process of the raw biomass in the conventional equipments produces high amount of tars and oil and thus causes blocking of the equipment and is problematic (Tumuluru et al., 2010). Thus torrefactions helps to overcome these problems and the inferior properties such as high moisture content, low energy-density, hydrophilicity and low calorific value of the raw biomass samples.

2.5.1 Mechanism of torrefaction process.

The overall torrefaction process is divided into five different stages depending on the weight loss-time profile as proposed by Bergman (Bergman et al., 2005). Figure 2.1 shows different stages that occur during the torrefaction process.

Stage 1 is the initial heating stage during the torrefaction process and during this heating stage unbound water is removed and this happens at around 100°C. During stage 2, the biomass temperature remains constant and all the free water is removed. Stage 3 is the post-drying stage and during this stage heating of the biomass samples removes the bound moisture that is present in the biomass. This process occurs between 100-200°C and it results in the formation of CO₂. Stage 4 is the torrefaction stage during which further heating of the biomass sample is continued. The reaction becomes exothermic at temperature of about 280 °C due to the degradation of hemicelluloses (Yang et al., 2007). At this stage the biomass samples turns brown in colour due to the release of a large amount of water, CO₂, acetic acid and some amount of phenols that has low energy value (Zanzi et.al., 2002). This happens at around 200-270°C. Stage 4 is the most

important stage during the torrefaction process as it is responsible for the degradation of lignocelluloses materials that are present in the biomass samples and produce a dry product that can be preserved for months together. The last stage is the cooling zone and this stage starts when the temperature drops below 200°C.

During the torrefaction process of the lignocellulosic biomass samples, hemicelluloses undergo maximum degradation than celluloses and lignin. The lignocellulosic materials such as hemicelluloses undergo degradation in the temperature range of about 130-260°C, celluloses in the temperature range of about 240-350°C and lignin in the temperature range of about 280-500°C (Shafizedeh, 1985; Williams and Besler, 1996).

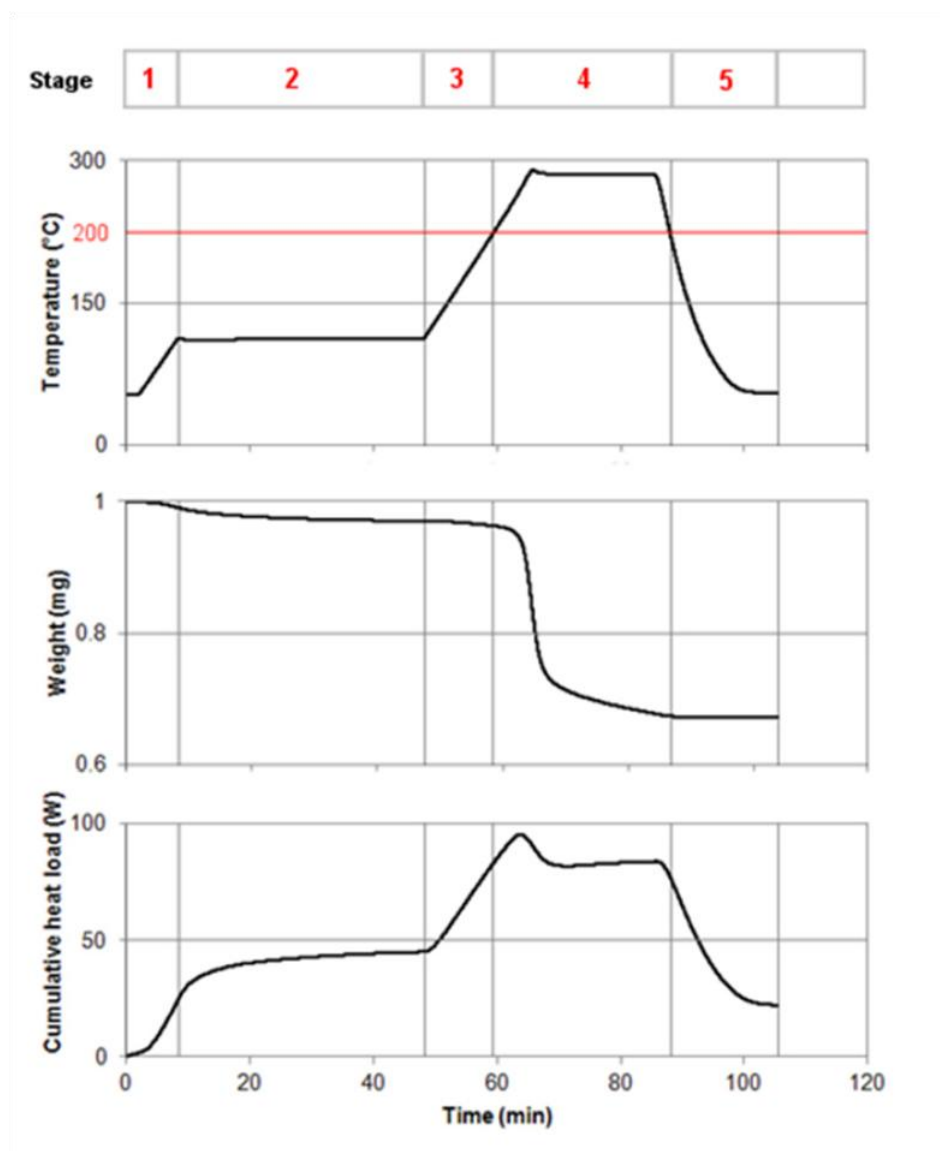


Figure 2.1 Different stages during the torrefaction process (Medic et al., 2012)

Figure 2.2 shows a graphical representation of the weight loss of lignocellulosic materials of a biomass sample. Note that the hemicelluloses show a sharp weight loss at around 250°C and a significant amount of weight loss between 250-300°C and thus the decomposition of the hemicelluloses can be divided into two major stages (Di Blasi et al., 1997). The first stage is the weight loss that occurs below 250°C. The weight loss that occurs during this stage is due to the depolymerisation reactions. The second stage is the weight loss that occurs between 250-300°C and produces a solid biomass char that is rich in carbon content. Most of the mass loss that occurs during the torrefaction process comes from hemicelluloses.

Lignin undergoes very little degradation in the torrefaction temperature range and also at much wider range. It can be noticed from the DTG curve that no larger significant weight loss peaks can be observed in the torrefaction temperature regime and above the torrefaction temperature. Cellulose is the most stable macromolecule among all the lignocelluloses that are present in the biomass samples. It can be noted from Figure 2.2 that only very moderate weight loss occurs at the end of the torrefaction process. The weight loss that occurs below 250°C is due to depolymerisation and heating above this temperature yields permanent and condensable gases. This distribution of torrefaction products was studied by Bergman et al., (2005)

This degradation of lignocellulosic materials causes degradation of hydroxyl group (OH^-) and thus makes the torrefied biomass hydrophobic in nature and increases the density and heating value of the torrefied biomass. Torrefaction process becomes exothermic at temperature of above 280°C due to the exothermic break down of the sugars at high temperature, and the gas

production increases and thus resulting in the formation of carbon monoxide, phenols, cresols and other heavier hydrocarbons (Tumuluru et.al., 2010). The torrefaction process yields higher amounts of solid char than liquid and gaseous products. A kinetic study on the thermal decomposition characteristics of hemicelluloses, celluloses, lignin and xylan has been studied and concluded that xylan and hemicelluloses are more sensitive to torrefaction temperature than celluloses and lignin (Chen et al., 2011).

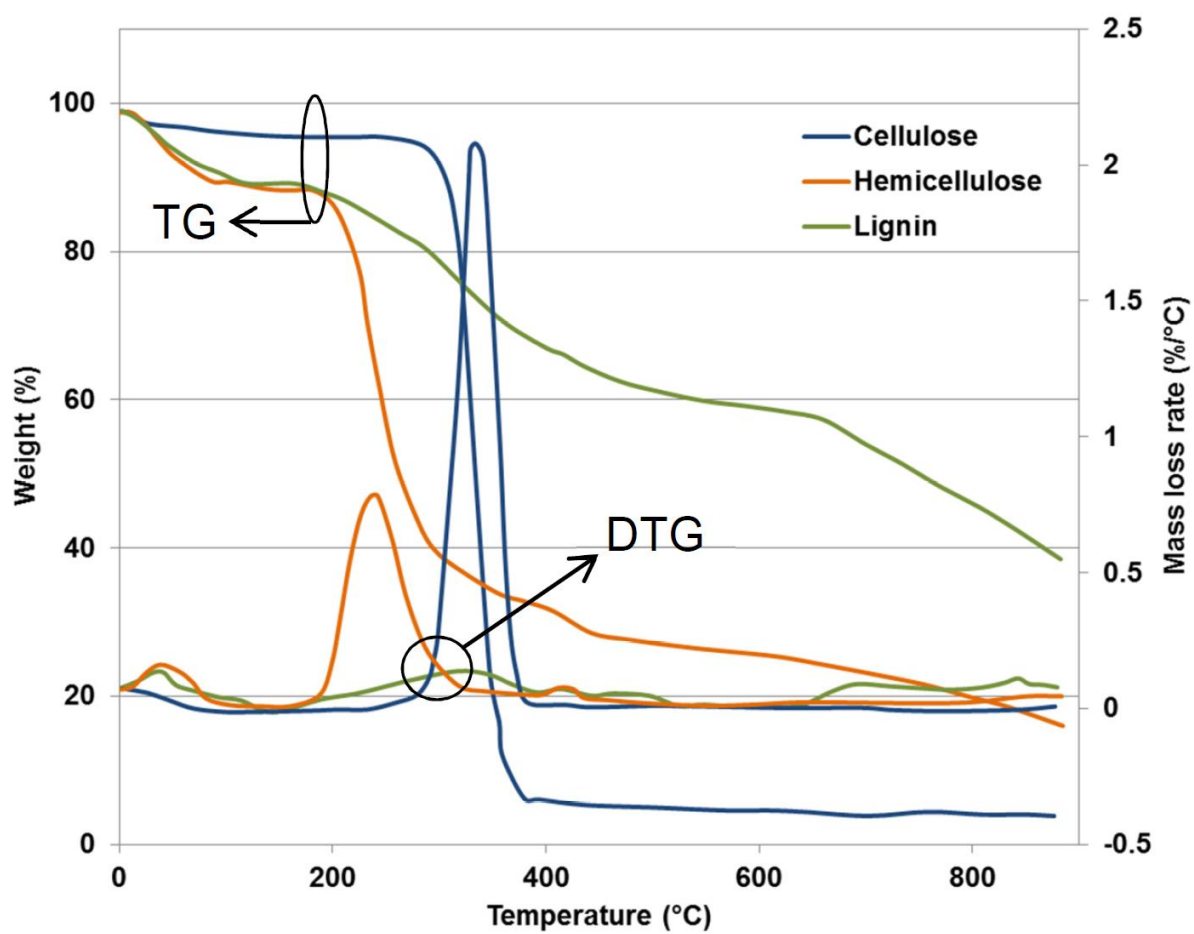


Figure 2.2. Weight loss of lignocelluloses materials during the torrefaction process (Yang et al., 2006)

2.5.2 Torrefaction products and its compositions

The major products of the torrefaction process are the solid torrefied biomass and the volatile matters. These volatile matters are further sub-divided into permanent and condensable gases, depending on their state at room temperature. The yield and the composition of the products during the torrefaction process are dependent on a number of factors such as temperature, residence time of the reaction and the various physical and chemical properties of the biomass sample.

Figure 2.3 shows the various products that are formed during the torrefaction process. About 30-40% of the biomass is composed of volatile matter and the energy content in these volatile matter accounts for only 10-15%. This is because the volatile matters consist of large amount of oxygen and thus have lower energy value. On the other hand, the solid products consist of polymer fractions that are less reactive at torrefaction conditions and consist of various products of reaction. In Figure 2.3, the solid products yields that are produced as a result of torrefaction process include the original sugar structure and the reaction products. The reaction products that remain as a solid includes modified sugar structure, char matter that is rich in carbon content and finally the mineral contents that were originally present in the biomass (Bergman et al., 2005; Prins et al., 2006).

The liquid products that are formed during the torrefaction process are water, acetic acid, methanol, furfural, lactic acid, formic acid and trace amount of other organic matter. Among these liquid products, water, acetic acid and methanol are the major constituents. Water is formed due to the release of the free and bound moisture that is present originally in the biomass

and water is also released during the thermal breaking of the biomass. Hemicelluloses contain acid and alcohol groups in them and during the thermal degradation of these hemicelluloses during the torrefaction process acetic acid and methanol are released (Prins et al., 2006)

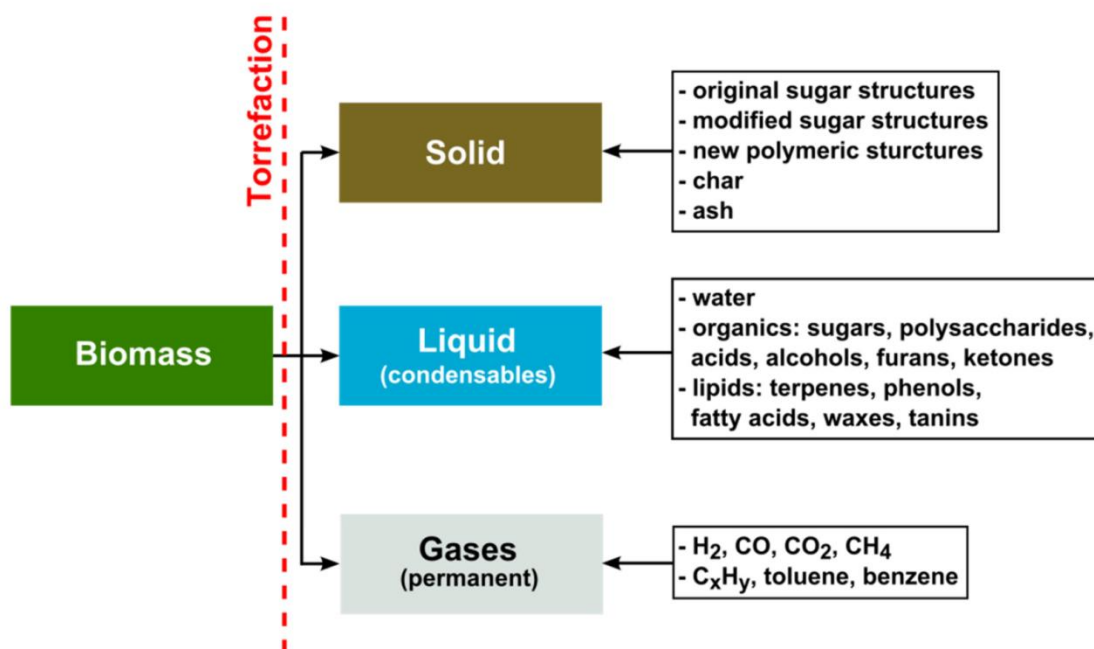


Figure 2.3. Major products that are formed during the torrefaction process (Bergman et al., 2005)

The gaseous products that are released during the torrefaction process includes CO₂, CO, CH₄, small amount of H₂ and traces of C₂ hydrocarbon (Pach et al., 2002; Prins et al., 2006). Among these, CO₂ is produced in greater amount and it is formed during the decarboxylation reactions of the organic acids. CO is the second largest gaseous product that is produced during the torrefaction process. CO is formed during the reaction of CO₂ with water and during the catalytic reaction of carbonized torrefied biomass.

Proximate and ultimate analysis of the solid product formed during the torrefaction process has been studied by Sridhar et al. (2007). The product description analysis by this researcher shows an increase in the fixed carbon content and decrease in the volatile content with an increase in temperature. Their result showed a decrease in the oxygen/carbon (O/C) ratio with an increase in the temperature and hence an increase in the carbon content and the energy density of the torrefied biomass.

The torrefaction process of deciduous wood type (beech and willow) and straw and coniferous wood (larch) have been performed by Prins et al. (2006). The solid product yields decreased with an increase in the torrefaction temperature and lower weight loss was observed for coniferous wood. While higher weight loss was observed for deciduous wood and straw. This is because the coniferous wood contains lower amount of the reactive component hemicelluloses (Xylan) compared to other deciduous wood and straw. The volatile products that are released were similar to those described in Figure 2.3.

2.5.3 Effect of temperature and residence time on the torrefaction process

The yield of a solid product decreases with an increase in the torrefaction temperature. This is due to the extensive degradation of hemicelluloses and to a lesser extent, the degradation of celluloses and lignin. The yield of liquid products is significantly greater than the yield of gaseous products as temperature increases (Zanzi et al., 2004; Bridgeman et al., 2008). Table 2.1 shows the product yields for different biomass types during the torrefaction process. It can be noted from Table 2.1 that the solid product yield dropped significantly from about 90% to about 75% as the torrefaction temperature increases from 230°C to 280°C. The liquid and the gaseous products yield increases as the temperature increases.

Residence time is another parameter that affects the product yields during the torrefaction process, to a much lesser extent than the torrefaction temperature. It is the most important factor in the design of the reactor for the process because it determines the volume of the reactor. Orfao et al. (1999) suggest that there is only a 1-5% increase in the weight loss with an increase in the reaction residence time from 20 to 40 minutes. Studies conducted by Arias et al. (2008) and Nimlos et al. (2003) concluded that an increase in the reaction residence time increases the grindability property of the torrefied biomass.

Table 2.1 Torrefaction product yields for different biomass types (Ciolkosz and Wallace, 2011)

Biomass	Temp. (°C)	Gas (%)	Liquid (%)	Solid (%)	Solids composition (%)			% energy retained
					C	H	O	
Pine	230	0.6	7.0	92.4	49.7	5.9	44.3	96.5
Pine	250	1.0	10.8	88.2	50.9	5.8	43.2	94.4
Pine	280	2.1	19.8	78.1	56.4	5.5	38.0	93.9
Bagasse	230	2.6	9.9	87.5	48.6	5.6	45.5	96.4
Bagasse	250	10.4	10.7	78.9	50.6	5.6	43.5	92.0
Bagasse	280	12.9	18.5	68.6	52.8	5.3	41.5	82.9
Birch	250	1.7	12.8	85.5	51.5	5.8	42.5	97.9
Birch	230	0.8	6.0	93.2	48.2	5.9	45.7	93.8
Birch	250	1.2	10.8	88.0	49.5	5.7	44.7	90.0
Birch	280	2.0	19.0	79.0	51.3	5.6	43.0	84.3
Salix	230	1.0	8.0	91.0	45.6	5.9	48.2	94.4
Salix	250	1.5	13.0	85.5	45.8	5.8	48.1	88.4
Salix	280	3.0	18.0	79.0	46.3	5.6	47.7	81.8
Miscanthus	230	1.0	10.0	89.0	44.4	6.1	48.7	87.7
Miscanthus	250	2.0	15.0	83.0	47.4	5.8	46.1	87.7
Miscanthus	280	7.0	24.0	69.0	51.3	5.7	42.4	80.0
Straw Pellets	230	0.1	5.0	95.0	47.8	6.3	45.2	95.1
Straw Pellets	250	0.3	9.8	90.0	49.0	6.1	44.1	91.6
Straw Pellets	280	1.0	19.1	79.9	52.8	6.1	40.3	89.8
Wood Pellets	230	0.06	6.5	96.5	49.8	6.3	43.8	97.5
Wood Pellets	250	0.15	5.5	94.4	50.7	6.2	43.0	96.9
Wood Pellets	280	0.6	10	89.4	52.5	6.2	41.3	96.0

*solids composition expressed on a dry ash-free basis

It is believed that temperature and residence time both play a vital role in the torrefaction process. They have significant impact on the physical and thermo-chemical properties of the raw biomass samples. Sadaka and Negi (2009) studied the effect of torrefaction temperature and residence time on three different biomass feedstock (wheat straw, rice straw and cotton gin waste). The torrefaction process was carried out at three different temperatures of about 200, 260 and 315°C, and at three different residence time of 60, 120 and 180 minutes, respectively. The results show a significant decrease in the moisture content by 70.5%, 49.4% and 48.6% for wheat straw, rice straw and cotton gin waste, at a torrefaction temperature of 260°C and for the residence time of 60 minutes. At a torrefaction temperature of 260°C and residence time of 60 minutes, an increase in the heating value by 15.3%, 16.9% and 6.3% was observed for wheat straw, rice straw and for the cotton gin waste, respectively. The result demonstrated that both, the moisture content and volatile content reduced by 10% and 0.9% with the increase in the torrefaction temperature and residence time. These authors concluded that temperature had greater effect on the torrefaction process than the residence time.

Torrefaction process also made a significant change in the ultimate analysis of the torrefied biomass samples. There is a large amount of research conducted, which examines the effect of the torrefaction process on the ultimate and proximate analysis of various biomass samples. Bridgeman et al. (2008) examined the torrefaction process on three energy crops namely, reed canary grass (RCG) and short rotation willow coppice and on a residue wheat straw. They conducted experiments at various torrefaction temperature ranges and at various residence times to optimize the torrefaction process conditions for these three fuels. The analysis

indicated a tremendous increase in the carbon content and a decrease in the hydrogen and oxygen content. The carbon content rose by 54.3%, 56.4% and 54.7% for RCG, wheat straw and willow, respectively. During the torrefaction process the volatiles released contained more hydrogen and oxygen compounds than carbon and thus increased the carbon content in the torrefied biomass char. This increase in the carbon content of the torrefied samples increased the energy content of all the biomass samples that have been investigated.

2.5.4 Physical properties of torrefied biomass

The most important physical properties of the torrefied biomass are density, grindability, hydrophobicity, combustion and gasification properties. Density of the torrefied biomass samples are measured in terms of their bulk density and energy density. Energy density is defined as the amount of energy present per unit mass of the sample. Rodriguez et.al. (2009) concluded that the bulk density of the torrefied sample remained unchanged with an increase in the torrefaction temperature and residence time, while the energy density increased significantly. Cielkosz and Wallace (2011) pointed out that the energy density of the torrefied samples increased from 102% to 120% and this increase in the energy density was due to the release of volatiles that contained huge amounts of oxygen and hydrogen, which reduced the O/C and H/C ratio in the torrefied biomass and increased the carbon content. Bridgeman et al. (2006) studied the Carbon (C), Hydrogen (H), Nitrogen (N) and calorific value of three different torrefied biomass and they used the Van Krevelen diagram to show changes in the O/C and H/C ratio during the torrefaction process and it is compared with different coal samples (Figure 2.4)

Research studies by Cielkosz and Wallace (2011) suggest that the torrefied biomass sample are more prone to aerial dispersion. Aerial dispersion increases the combustion hazards of the torrefied biomass than the raw biomass. To address this combustion hazard, the torrefied biomass are densified after the torrefaction process.

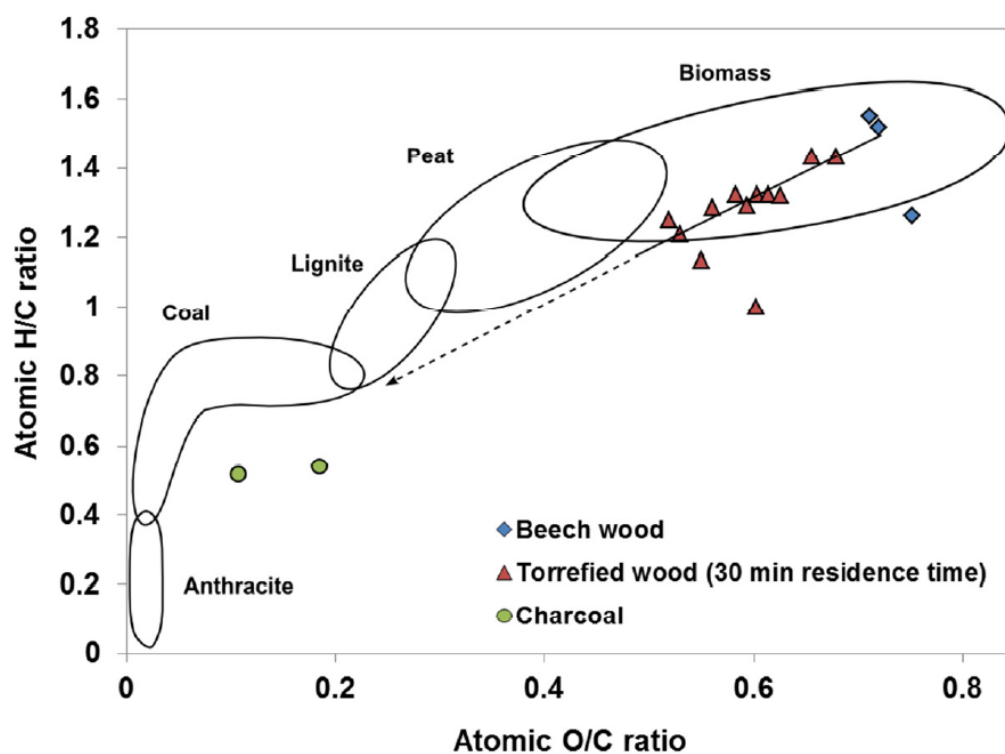


Figure 2.4. Van Krevelen diagram depicting the O/C and H/C ration in biomass during the torrefaction process (Prins et al., 2006)

Grindability is yet another important property of the torrefied biomass. The polysaccharides present in the biomass samples forms a long strand called micro-fibrils. These micro-fibrils are enclosed in the matrix of celluloses and lignin and are covered by an outer layer of hemicelluloses shell. The degradation of hemicelluloses during the torrefaction process disturbs the orientation of the micro-fibrils present in the celluloses and lignin matrix and thus makes the torrefied biomass samples more brittle and enhance its grindability property (Prins et al., 2006). The grindability property of the torrefied biomass sample is the most important factor to be considered, to be directly co-fired in exiting fired plant, and to be used in the pulverized and fluidized bed reactors for gasification and pyrolysis processes (Medic, 2012). Bergman et al. (2005) studied the grindability property of the raw and torrefied biomass and their results found that the power needed to grind the torrefied biomass was just 10-30% of that energy needed to grind the raw biomass. Figure 2.5 shows a relation between power consumption and cutting mill capacity during the grinding of the raw and torrefied biomass. The energy consumption is reduced dramatically for grinding the first torrefied biomass and depending on the torrefaction process conditions used, there is a resulting 70 to 90% reduction in power consumption. The cutting mill efficiency was increased by a factor of 7.5% to 15% (Bergman et al., 2005).

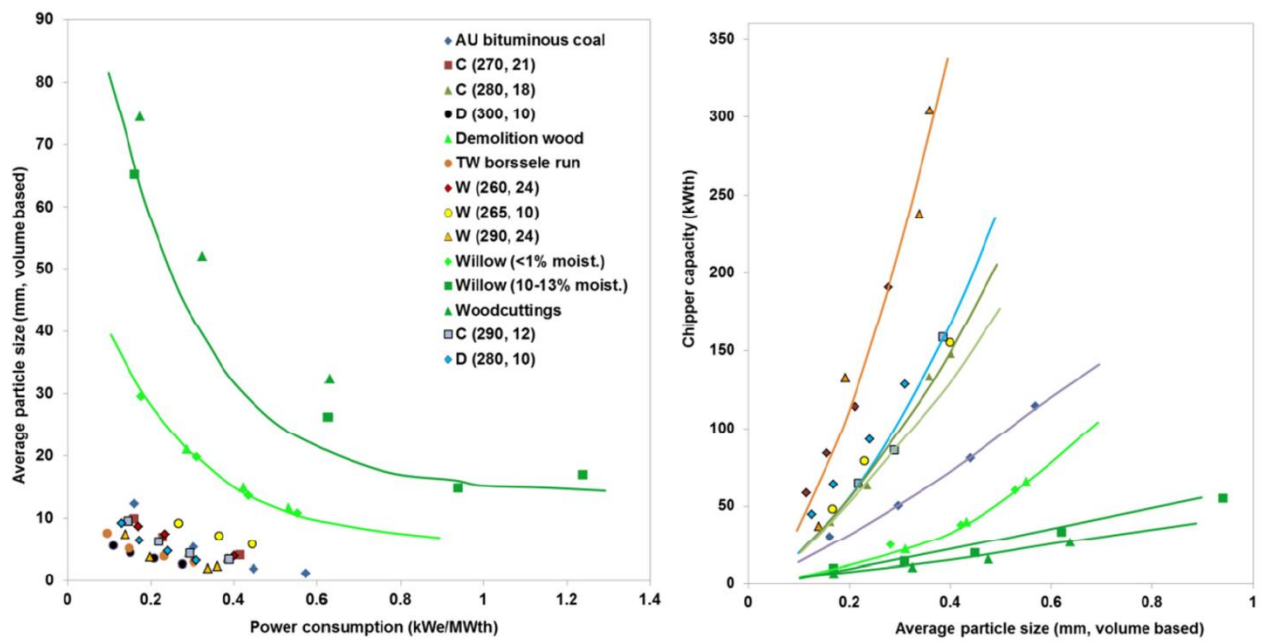


Figure 2.5. Power consumption and cutting mill capacity during the size reduction process of raw and torrefied biomass (Bergman et al., 2005)

Hydrophobicity is also an another important property of the torrefied biomass and this property helps in the storage of the biomass for year-around without any biological degradation and with a negligible amount of absorption of water. Hydrophobicity property also reduces the amount of moisture that has to be removed and transported from the biomass before the combustion steps (Sadaka and Negi, 2009; Acharjee et al., 2011). Torrefaction process increases the hydrophobic property of the biomass. During the torrefaction process the hydroxyl group that forms hydrogen bonding with the water molecules are eliminated and thus a non-polar compounds are formed and this improves the water repelling properties of the torrefied biomass (Acharjee et al., 2011; Kobayashi et al., 2009).

There are numerous studies conducted on the hydrophobicity property of both the raw and torrefied biomass. Bergman et al. (2005) conducted the hydrophobicity test on both the torrefied pellets and raw biomass pellets by immersing both types in water for 15 hours. The analysis of moisture uptake by both the sample types was analyzed by gravimetric method. From the hydrophobicity test it was concluded that the torrefied pellets did not undergo any significant physical changes (swelling and disintegration) when compared to the raw biomass pellets. There was just 7-20% of water uptake by the torrefied pellets, while, the raw biomass sample underwent swelling and disintegration. Felfli et al. (2005) conducted the hydrophobicity test on the torrefied wood briquette by immersing the wood briquette at different retention time. The briquettes remained intact and the moisture observed by the briquettes did not exceed 10% over a retention time of 70 minutes. Felfli et al., (2005) also studied the moisture and hydrophobic characteristics of the torrefied biomass samples and their results concluded that the equilibrium

moisture of the biomass sample reduced by 73% after the torrefaction process. The analysis results also conclude that this decrease in the moisture content was due to the condensation of the tar substances inside the pores of the solid torrefied char that obstructs the passage of moist air through the pore surface and thus preventing the condensation of water vapours (Felfli et al., 2005).

Torrefaction process also increases the carbon content and decreases the volatile content in the biomass thereby enhancing its combustion properties and thus possess high reactivity when compare to the raw biomass. Pimchuai et al. (2010) performed the combustion test in a spout fluid bed combustor using raw and torrefied rice husks as the fuel types. From their experimental results they concluded that the torrefied rice husks resulted in higher temperature than raw rice husks, in all the combustion zones. They also concluded that the higher fixed carbon content and low moisture content of the torrefied rice husks to be the main reason for the increase in the heating value of the torrefied biomass. Thus, the torrefied sample resulted in higher temperature during combustion. Bridgeman et al. (2005) also studied the combustion properties of the torrefied and raw biomass. They concluded that there exists a vast difference between the torrefied and untreated biomass samples, and the higher fixed carbon content of the torrefied biomass created higher heating values and thus it would provide an advantage during combustion.

Gasification is an important heterogeneous reaction which results in the production of a synthetic gas. Qing et al. (2011) studied the effect of a torrefied solid and gaseous product on the gasification process. They concluded that, different torrefaction temperatures and residence time

had a limited effect on the syngas composition. The cold gas efficiency was improved due to the torrefaction process and it increased with an increase in the residence time. Testing the effect of torrefaction gases on the gasification process showed that the gasification efficiency of the torrefied biomass was higher than the raw biomass. This was thought to be due to the energy loss that is caused by the release of gaseous and volatile products during the torrefaction process. Qing et al. (2011) concluded that in the practical application of the torrefaction process and to increase the overall gasification efficiency, the carbon and energy content of the torrefied sample must be utilized effectively.

Svoboda et al. (2009) have found that the torrefaction of the biomass size below 0.2mm helps to improve the gasification efficiency due to the minimization of the energy loss, easy feeding into the gasifiers and high specific energy of the torrefied biomass. The gasification of the torrefied biomass can be performed at higher pressure conditions. This may be useful for the downstream energy production or for the production of chemicals. However, this cannot be achieved with raw biomass sample due to its feeding issues such as high bulk volume, high moisture content and poor grindability (Deng et al., 2009).

2.6 Economic of the torrefaction process

Torrefaction process has the potential ability to improve both the physical and chemical properties of the raw biomass in a simpler and easier manner. Although torrefaction process has numerous advantages, its implementation as a new technology is justified only if the economics of the torrefaction process is competitive in the markets. Techno-economical analysis is one of the ways to determine whether the cost of adding an additional unit operation to the production

chain will increase the properties of the biomass or not. The techno-economical analysis conducted on the torrefaction process shows that there is no commercially available torrefaction unit presently (Medic, 2012).

Uslu et al. (2008) conducted an economic analysis on the overseas biomass supply chain to test the fuel and energy efficiency of biomass produced by the torrefaction process. They concluded that, the torrefaction process along with pelletization of the torrefied biomass improves the overall energy efficiency more than pelletization alone. Zwart et al. (2005) also conducted an economical analysis on the overseas supply chain of biomass. They concluded that pre-treating biomass significantly reduces the production cost and pre-treatment by torrefaction process is most promising. It is more efficient than the pre-treatment by pyrolysis or by traditional pelletization processes. In a study conducted by Bergman et al. (2005), they found that the torrefaction process combined with pelletization has significant economic potential when incorporated in the bio-renewable chain.

Chapter Three: Torrefaction of flax straw biomass and its kinetic studies

3.1 Introduction

In recent years, the use of biomass as a renewable energy source has gained significant attention since biomass is considered to be carbon neutral, cost effective and is readily available. Biomass sources include all agricultural waste, municipal solid waste, wood chips, forestry crops, and sewage, human and animal residues. Raw biomass as such cannot be used as the source of energy because of its inferior properties such as high moisture content, low bulk density, low calorific value and high energy consumption for grinding. Further, raw biomass is hygroscopic in nature and thereby causes storage and transportation problems (Felfli et al., 2005). Also, biomass has high oxygen to carbon ratio (O/C ratio) which makes it inferior to be used as fuel for industrial applications. Energy from biomass can be produced through different processes like chemical process, biological process and thermo-chemical process (Tumuluru et al., 2010). This study focuses on torrefaction, which is a thermo-chemical process.

Torrefaction is a mild pyrolysis which is carried out in a relatively low temperature range of about 250-300°C in the absence of oxygen. Biomass consist of lignocelluloses materials (hemicelluloses, celluloses and lignin) and the thermal degradation of hemicelluloses occurs in the range of 130-260°C, celluloses in the range of 240-350°C and lignin in the range of 280-500°C. Hence during the torrefaction process, hemicelluloses are more active and undergo degradation more extensively than cellulose and lignin (Tumuluru et al., 2010). The significant degradation of hemicelluloses during the torrefaction process makes the biomass soft in nature, which enables easy grinding. During the initially stage of the torrefaction process drying of the

biomass takes place followed by heating of the biomass to the required torrefaction temperature for a specified duration of time. During the initial drying temperature range of about 100 to 160°C, moisture is removed from the biomass and CO₂ is formed due to the thermo-chemical reaction. Further, at about 180 to 270°C, the torrefaction process becomes more exothermal and degradation of hemicelluloses occurs. At about 280°C, the reaction becomes exothermic due to the degradation of hemicelluloses (Yang et al., 2007). Further, during the torrefaction process, the hydroxyl (OH⁻) group in the structure of biomass is broken and becomes hydrophobic in nature, which enables storage of the torrefied biomass for a prolonged duration without biological degradation (Sadaka and Negi, 2009). Also, the moisture and carbon-dioxide are released during the torrefaction process and hence reduces the O/C ratio and hydrogen to carbon ratio (H/C ratio) and thus increases the gasification efficiency of the biomass. The major products formed during the torrefaction process are solids (torrefied biomass), with less significant amount of liquid and gaseous products (Tumuluru et al., 2010).

The torrefaction process increases the carbon content and decreases the hydrogen and the oxygen content of the torrefied biomass and thus resembles lignite (low grade charcoal) in its carbon content. Hence, the torrefied biomass can be used for electricity generation, fertilizer production such as anhydrous ammonia and ammonia sulphate and for the production of synthetic natural gas. The torrefaction process decreases the moisture content and increases the fixed carbon content of the torrefied biomass thereby increasing the heating value of the torrefied biomass and hence can be used as a suitable feed stock for combustion and gasification processes. Also, the torrefied biomass can be used as a superior quality fuel for cooking and

residential heating, reducer in smelters, and can be co-fired with other fuel in boilers (Sridhar et al., 2007).

Despite the information available on the torrefaction process in the open literature, there is a lack of comprehensive study that fully investigates the influence of different parameters on the torrefied char and its associated heating value and the kinetics of the reaction during the torrefaction process, especially on flax straw feedstock. Flax straw is used as a biomass source for the present research and this study reports the proximate, ultimate analysis of the torrefied flax straw and the effects of temperature, particle size and residence time on the torrefaction process are discussed along with the kinetic analysis.

3.2 Experimental methods

3.2.1 Torrefaction experiments

Sieve analysis of the raw flax straw was performed and an average particle size range of 225-1200 μm was chosen for the experiments. The sieve analysis process took about 10 minutes. About 10 mg of the raw flax straw sample was used to carry out all the experiments and the sample was placed in a ceramic crucible of the TGA (STA6000: Perkin Elmer). Figure 3.1 shows an experimental setup. The torrefaction procedure was carried out in two different steps. In the first step, the sample was heated from 30°C to 110°C during which the moisture loss occurs and the biomass sample was kept on hold at 110°C for about 5 min in order to remove any remaining moisture present. The second step was to raise the sample temperature from 110°C to the torrefaction temperature range of 250-300°C. The process was repeated for all the chosen particle sizes and for the residence time range of 60-180 min. The entire process was carried out

at an inert atmosphere (Nitrogen) and the heating rate used was $20^{\circ}\text{C min}^{-1}$. The weight loss data was recorded as a function of time by the TGA.

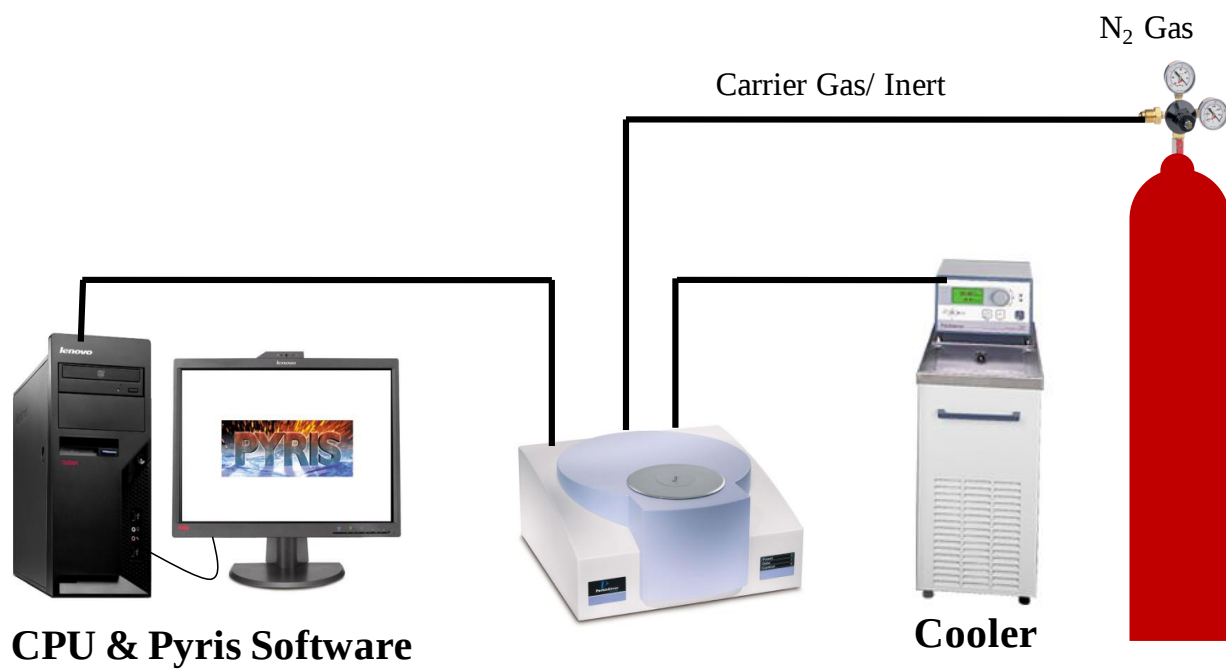


Figure 3.1. Schematic of the experimental setup

3.2.2 Proximate and ultimate Analysis

Proximate analysis of the torrefied flax straw sample was performed using a TGA. All though there are various methods that are available to perform the proximate analysis process, the method suggested by Beamish, (1994), Mayoral et al.,(2001)) has been followed for the present analysis as this method requires less amount of time to perform the proximate analysis . About 10 mg of the torrefied flax straw was heated from 25°C to 110°C in nitrogen atmosphere and was held at this temperature for 4 minutes. The weight loss at this stage represents the moisture content of the torrefied flax straw. The temperature of the sample was increased to 900°C and was held at this temperature for about 1 minute during which complete devolatilization occurs. The weight loss at this stage corresponds to the volatile loss of the torrefied flax straw. Further, the sample was held for 7 minutes at 900°C during which the carrier gas was switched from nitrogen to air. The weight loss at this stage represents the fixed carbon content and the remaining weight represents the ash content of the torrefied char. The entire proximate analysis process took about 30 minutes to complete. Ultimate analysis was performed for the torrefied flax straw using an Elemental Analyzer (Perkin Elmer 2400) to analyze the carbon, hydrogen, nitrogen, sulphur and the oxygen content.

3.3 Results and discussion

3.3.1 Effect of temperature, particle size and residence time on the torrefaction of flax straw

Figure 3.2 shows the weight loss for different particle sizes, for the residence time of 60 min, at torrefaction temperatures of 250, 275 and 300°C, respectively. Our experiments show that the weight loss observed during the torrefaction of flax straw increases with the increase in the temperature, and this observed weight loss is due to the degradation of the lignocelluloses materials, moisture loss and volatile loss that occur during the torrefaction process. Bergman et al., (2005), Pimchuai et al., (2010) and Prins et al., (2006) explained that, hemicelluloses undergo complete degradation at a temperature range of 200-280°C, cellulose decompose at 305-375°C and lignin decompose in the temperature range of 280-500°C. Thus, when the torrefaction temperature is increased to about 275 or 300°C, celluloses degradation also becomes predominant along with considerable degradation of lignin and thus, this was the reason for an increasing in the weight loss of the torrefied flax straw with the increase in the temperature. The torrefied flax straw was more brownish at higher torrefaction temperatures. Similar effect of temperature on the torrefaction process has been reported by Pimchuai et al. (2010), Prins et al. (2006), Sadak and Negi (2009). The particle size range chosen for this study had no significant effect on the weight loss for the torrefaction of flax straw.

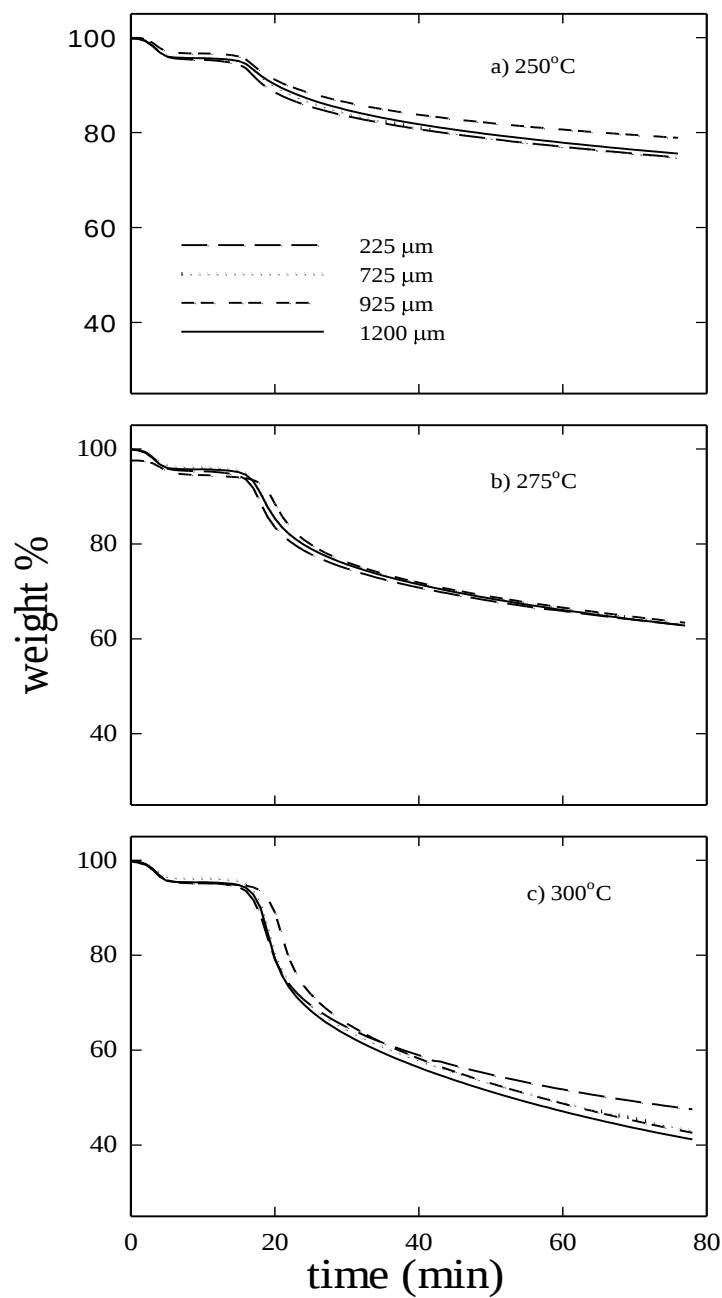


Figure 3.2. Weight loss plots for different particle size for a residence time of 60 min, and at a temperature of 250°C, 275°C and 300°C

Figure 3.3 shows the weight loss for different residence time, for a particle size of 925 μm , at the torrefaction temperature range of 250-300°C. Pimchuai et al., (2010) reported that at higher residence time the more reactive hemicelluloses components undergo degradation completely. Hence, from Figure 3.3 it can be noticed that with an increase in the residence time less significant increase in the weight loss of the flax straw is observed with respect to the residence time, while, again an increase in weight loss is observed with an increase in temperature during the torrefaction process. Similar effect of residence time on the torrefaction process has been reported by Prins et.al., (2006) and Arias et al. (2008).

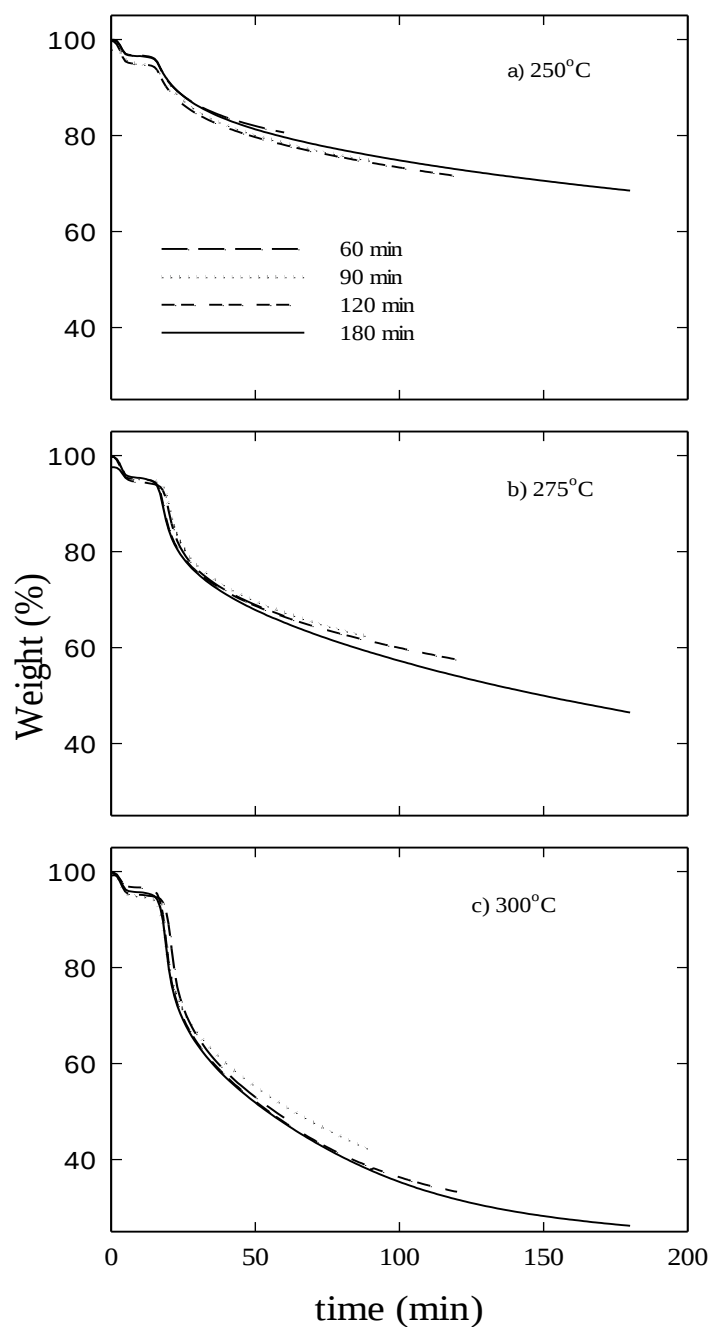


Figure 3.3. Weight loss plots for different residence time for a particle size of 925 μm , at 250°C, 275°C and 300°C

3.3.2 Ultimate analysis of the torrefied char

Table 3.1 shows the elemental analysis values for different particle sizes, for a residence time of 60min, at different torrefaction temperatures. The oxygen content of the torrefied sample was calculated by adding the carbon, hydrogen, nitrogen and sulphur values and then subtracting these values from a total of 100% for each of the torrefaction temperatures respectively. A significant increase in the carbon content and a decrease in the hydrogen and oxygen of the torrefied flax straw were observed with an increase in the torrefaction temperature. The volatiles released during the torrefaction process consist primarily of hydrogen and oxygen compounds and as the torrefaction temperature increases, the amount of volatiles released also increases and this causes an increase in the carbon content of the torrefied char (Bridgeman et al., 2008). Thus, an increase in the carbon value was observed with an increase in the temperature for the torrefied flax straw. A carbon value of 61% was observed for higher torrefaction temperature of about 300°C. Prins et al., (2006) reported that, a decrease in hydrogen content with an increase in temperature is due to the volatilization of H₂O and the release of hydrocarbons such as CH₄ and C₂H₆ at higher temperatures. The oxygen content decreases because the oxygen containing functional groups with low activation energy recombines to release CO and CO₂ (Qing et al., 2011) and thus reducing the concentration of the oxygen in the solid residue. A similar effect for the elemental analysis of the torrefaction process with respect to temperature was observed by Prins et al. (2006) and Pimchuai et al. (2010). The chosen particle size range had no significant change in the elemental composition.

Table 3.1 also shows the elemental analysis values for a particle size of 925 μm at different residence time and at different torrefaction temperatures. A significant increase in the carbon content from its initial value of 46% to a maximum of 61% was observed at a higher torrefaction temperature of about 300°C and at all chosen residence times. Lower torrefaction temperatures of about 250°C and 275°C had no noticeable increase in the carbon, hydrogen, nitrogen, and sulphur values with respect to particle size.

Table 3.1 Elemental analysis for different particle sizes at a residence time of 60 min, and for different residence time for a particle size of 925 μ m, for the torrefaction temperatures of 250, 275 and 300°C

Ultimate analysis												
particle size (μ m)	250°C				275°C				300°C			
	C (%)	H (%)	N (%)	S (%)	C (%)	H (%)	N (%)	S (%)	C (%)	H (%)	N (%)	S (%)
225	46.1	5.2	0.88	0.8	49.8	5.11	1.9	0.9	52.7	3.38	1.12	0.5
725	51.9	5.77	0.49	0.9	54.7	5.56	0.62	0.8	59.6	4.85	0.67	0.8
925	50.7	5.97	0.37	0.9	53.5	5.8	0.81	0.9	62.7	4.86	0.61	0.9
1200	51.9	5.72	0.41	0.9	54.2	5.66	0.35	0.9	61.4	4.82	0.57	0.8
residence time (min)	C (%)	H (%)	N (%)	S (%)	C (%)	H (%)	N (%)	S (%)	C (%)	H (%)	N (%)	S (%)
	C (%)	H (%)	N (%)	S (%)	C (%)	H (%)	N (%)	S (%)	C (%)	H (%)	N (%)	S (%)
60	50.7	5.97	0.37	0.9	53.6	5.8	0.81	0.9	62.7	4.86	0.61	0.9
90	52.2	5.86	0.42	0.9	56.1	5.58	0.4	0.8	62	4.99	0.71	0.7
120	52.8	5.82	0.38	0.9	56.3	5.51	0.45	0.8	60.9	4.03	0.61	0.6
Raw Flax straw	46.4	6.29	0.44	1.0								

C=Carbon, H=Hydrogen, N=Nitrogen and S=Sulphur

3.3.3 Proximate analysis of the torrefied char

Table 3.2 shows the proximate analysis of different particle sizes at different torrefaction temperatures for a residence time of 60 min. Proximate analysis data of the torrefied flax straw indicates a significant decrease in the moisture and the volatile content along with an increase in the fixed carbon and ash content with an increase in the temperature. The moisture content of the torrefied flax straw reduced from its initial value of 5% to about 0.1% and the volatile content reduced from 78% to an average of 52%. The fixed carbon content increased from its initial value of 16% to an average of 45%. The hemicelluloses devolatilization and carbonization are limited below 250°C and this was attributed to the reduction in volatile and moisture content during the torrefaction process (Sadaka and Negi, 2009) and an increase in the torrefaction temperature causes significant decrease in volatile content and this, in turn, increases the fixed carbon content. These results are in agreement with that of Pimchuai et al. (2010), Bridgeman et al. (2008) and Prins et al. (2006), while no significant pattern in the proximate analysis values were observed with an increase in the particle size.

Table 3.2 Proximate analysis for different particle sizes at a residence time of 60 min, for the torrefaction temperatures of 250, 275 and 300°C

Proximate analysis												
	250°C				275°C				300°C			
particle size (µm)	MC (%)	VC (%)	Ash (%)	FC (%)	MC (%)	VC (%)	Ash (%)	FC (%)	MC (%)	VC (%)	Ash (%)	FC (%)
225	0.42	72.6	2.83	24.1	0.37	61.9	6.24	31.5	0.02	48.5	8.76	42.7
725	0.29	75.0	0.61	24.1	0.26	70.8	1.55	27.4	0.13	51.7	1.15	46.9
925	0.37	75.0	1.59	18.5	0.27	72.1	0.19	27.4	0.14	48.6	0.26	51.0
1200	0.13	73.2	0.95	19.7	0.06	71.7	0.48	27.8	0.12	58.2	1.50	40.2

Raw Flax

Straw 5.04 78.6 0.15 16.2

MC= Moisture Content, VC = Volatile Content, FC = Fixed Carbon Content

3.3.4 Calorific value of the torrefied char

The heating value is calculated using the equations given by Friedl et al. (2005). Two methods, namely the Ordinary least square regression method (OLS) and the Partial least square regression method (PLS) are used.

$$\text{HHV (OLS)} = 1.87C^2 - 144C - 2802H + 63.8CH + 129N + 20147 \quad (3.1)$$

$$\text{HHV (PLS)} = 5.22C^2 - 319C - 1647H + 38.6CH + 133N + 21028 \quad (3.2)$$

Where, C= Carbon (%), H=Hydrogen (%) and N=Nitrogen (%)

Table 3.3 shows the heating value for different particle size at different torrefaction temperatures, for a residence time of 60 min. The heating values presented are the average values calculated by using equations 3.1 and 3.2. The heating value increases with an increase in the torrefaction temperature. The heating value increased from 18,411 kJ kg⁻¹ for lower torrefaction temperature of 250°C to 24,000 kJ Kg⁻¹ for higher torrefaction temperature of 300°C. The decrease in the volatile content and an increase in the carbon content in the resultant torrefied char was the reason for an increase in the heating rate with an increase in the temperature. Similar effect of temperature on heating rate was reported by Chen et al., (2010) and Bridgeman et al., (2008). However, for the chosen particle size range, less significant change in the heating value was observed. Table 3.3 also shows the heating values for different residence time at different torrefaction temperatures, for a particle size of 925µm. In the torrefaction temperature zone hemicelluloses undergoes maximum degradation and thus prolonged heating at a particular temperature has no noticeable change in the weight loss and thus less significant change in the heating values was observed with an increase in the residence time.

Table 3.3 Heating value for different particle sizes at a residence time of 60 min, and for different residence time for a particle size of 925 μm , for the torrefaction temperatures of 250, 275 and 300°C

Heating Value (kJ kg^{-1})			
particle size (μm)	250°C	275°C	300°C
225	18,271	19,762	16,725
725	20,717	21,834	23,499
925	20,159	21,379	24,760
1200	20,651	21,656	24,261
residence time (min)	250°C	275°C	300°C
60	20,159	21,379	24,760
90	20,779	22,337	24,559
120	21,004	22,356	23,200

3.3.5 Kinetics of flax straw torrefaction

Kinetic studies helps to scale up the torrefaction process and also provides the information on the thermal process that is involved in the torrefaction of flax straw. Prins et al., (2006) assumed the torrefaction process to be as first order. Hence, torrefaction of flax straw was considered as a first order reaction. The equation is as follow:

$$-r = -\frac{dw}{dt} = k * W \quad (3.3)$$

Where W=weight loss data

After solving the about equation mathematical, we get

$$-\ln\left(\frac{w_A}{w_{Ao}}\right) = kt \quad (3.4)$$

where, W_A = weight at any time t

W_{Ao} = weight at time t=0

k = rate constant at time t [s^{-1}].

t= time [s]

From the weight loss data, a plot of $-\ln\left(\frac{w_A}{w_{Ao}}\right)$ vs time (t) was plotted and the slope was taken as the rate constant of the reaction. From the rate constant data an Arrhenius plot of $\ln k$ vs T^{-1} was plotted for the chosen particle size range for a residence time of 60 min as shown in Figure 3.4a and for different residence time ranging from 60-120 min for a particle size corresponding to 925 μ m as shown in Figure 3.4b.

The activation energy was obtained from the slope of the Arrhenius plot and its intercept corresponded to the pre-exponential factor. The activation energy increased from 31.3-76.64 kJ

mol^{-1} for an increase in the particle size from 225-925 μm . The reason being, smaller particle size has larger surface area and lower heat loss and thereby requires less amount of heat for the reaction to occur and as the particle size increases, large amount of heat is lost and hence requires large amount of heat for the reaction to occur and thereby increases the activation energy. Also, the particle size chosen was an average particle size and hence the quantity of organic, inorganic and lignocellulosic materials that are present in the biomass samples differs and also the shape of each particles. This variation in the biomass sample is the result of the segregation process that occurs during the sieve analysis of the biomass feed stocks. Similar result of increase in activation energy with an increase in particle was reported by Zixiang et al., (2013). Prolong heating of the biomass causes degradation of some amount of cellulose and lignin with complete degradation of hemicelluloses and thus increases the activation energy with an increase in the residence time. The activation energy obtained for the particle size of 925 μm and for a residence time of 60 min was 76.64 kJmol^{-1} . Similar activation energy value was obtained by Prins et al. (2006a) for torrefaction of wood and by Branca and Blasi (2003) for thermal degradation of wood.

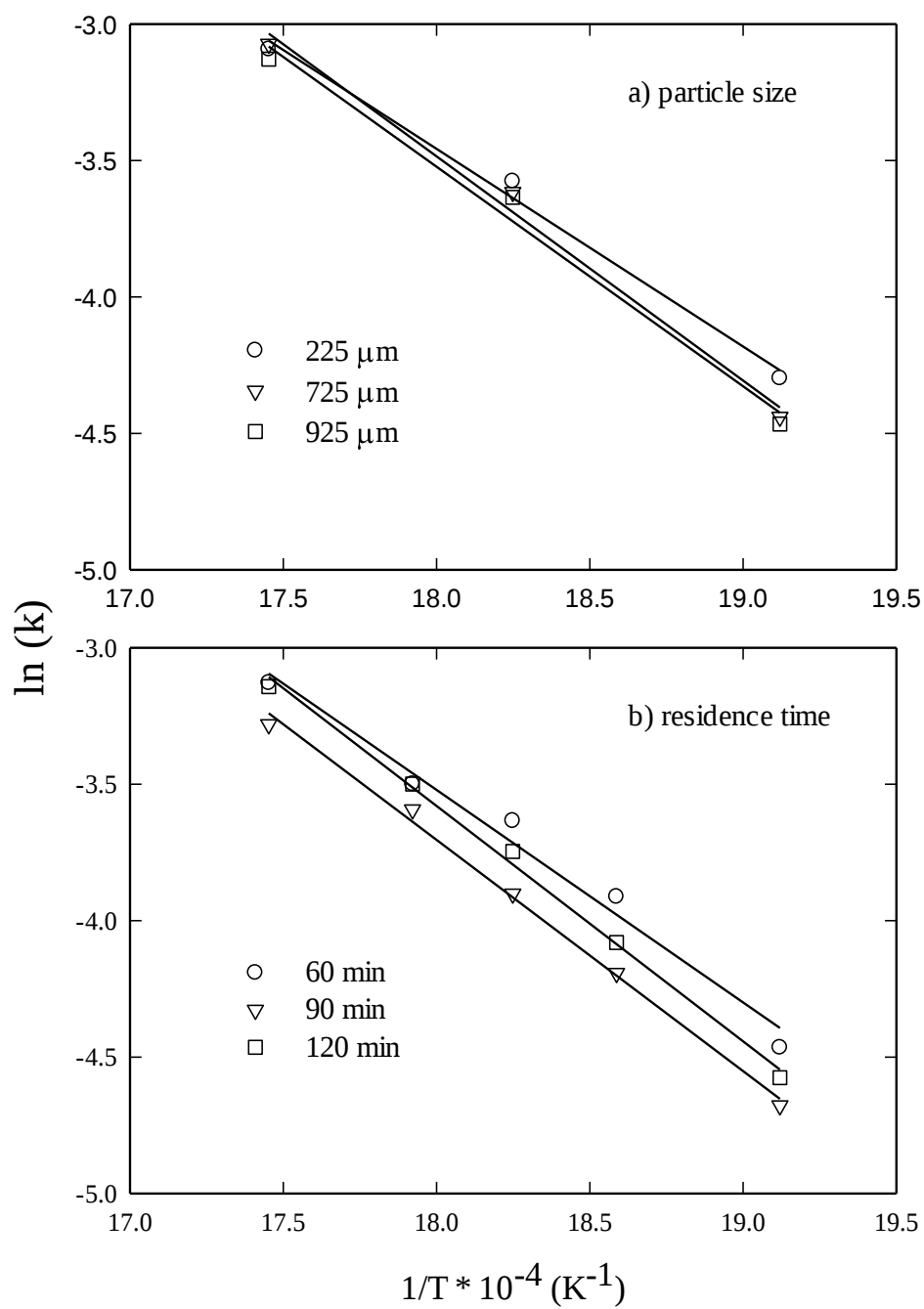


Figure 3.4. Arrhenius plots: (a) different particle size for a residence time of 60 min, and (b) different residence time for a particle size of 925 μm

Chapter Four: Mass transfer studies during CO₂ gasification of torrefied and pyrolysed char

4.1 Introduction

Biomass is an renewable energy. It is considered to be a Carbon neutral energy source as well. The thermo-chemical pre-treatment processes of biomass such as torrefaction and pyrolysis produces a char that is rich in carbon content, low in moisture and volatile content. The gasification of the solid char that is produced using the thermo-chemical pre-treatment methods is endothermic in nature and is a slow process. Gasification of the biomass char can be performed either by using CO₂, H₂O or O₂ (Kannan et al., 1990). The present study is conducted on CO₂ gasification and the advantage of using CO₂ as a gasifying agent is to recycle the CO₂ that is produced during the pre-treatment processes and to convert it into useful form of gas (Mani et al., 2011). Gasification process is one of the simplest ways for the production of synthetic gas (CO and H₂) and the process also helps in the production of mechanical and electrical energy (Khalil et al., 2009).

The gasification of the biomass char is a gas-solid reaction and it is usually limited either rate or by intra-pore diffusion. Also, determination of the gasification rate of the biomass char is one of the most important factors for the design of a gasifier as it provides information about the volume required by the gasifier to carry out the gasification process (Gomez-Barea et al., 2006a). The other physical parameters that influence the gasification rate are the operating temperature, partial pressure of the gasifying agent, particle size of the char, surface area and porosity of the char (Ollero et al., 2002).

The CO₂ gasification kinetics of the biomass char provides valuable information that is useful for the proper design, operation and modeling of a gasifier. The gasification kinetic data are usually determined by a TGA and the findings may deviate from data observed when using commercial equipment (Gomez-Barea et al., 2005a).

When the biomass undergoes rapid heating under inert atmosphere (pyrolysis) the volatiles that are released are intensified. The effect is a change in the biomass structure and an increase in the macro pore surface area of the char produced. This phenomenon in turn increases the reactivity of the resultant char (faster diffusion of reactant and products into and out of the solid char). During the torrefaction process the volatile release is increased under slow heating rate condition. The char produced by the torrefaction process is expected to exhibit a higher reactivity (Fisher et al., 2012). The reactivity of the char is dependent on two factors namely, the nature and internal structure of the carbonaceous material. The internal structure of the pores and the size of each pore determine the available surface area for the movement of the oxidant and products into and out of the surface of the char particle. This process determines the rate of reaction (Standish et al., 1988). Reactivity is also dependent on the chemical structure and the inorganic materials that are present in the biomass. However, the kinetic model does not take these basic components into account because they are very difficult to measure and vary widely with the level of conversion of the char. Thus, the kinetic model is based on global reactivity that takes into account the interaction between the solid (char) and the gas (gasifying agent) (Mani et al., 2011).

The reactivity that is calculated using TGA may differ from that calculated using commercial reactors (Ollero et al., 2002). However, the reactivity calculated using TGA provides valuable information about the diffusion effects that takes place during the char gasification inside a gasifier. In the TGA experiments, a few milligrams of biomass sample are placed in a sample holder and the gasifying agent (gas) flows across the mouth of the crucible at known concentration and temperature. Thus, a stagnant gas region exists between the bulk of the gas, upper surface of the sample that is placed in the sample holder as well as the bed consisting of small particles surrounded by the empty space or macropores. The gasifying agent should diffuse through these pores to reach the external structure of the char particles (Ollero et al., 2002).

The gasification process is carried out at isothermal condition and very small amount of sample is used to carry out the gasification process in a TGA. Thus heat transfer by convection and conduction are negligible. The steps that occur during the TGA gasification experiments are:

- a. External mass and heat transfer: The transfer of gasifying agent and heat from the bulk of gas to the external layer of the char particle that is placed in the sample holder.
- b. Internal mass and heat transfer: Diffusion of the gasifying agent and heat from the external layer into the bed of the char particle.
- c. Pore diffusion: Diffusion of the gasifying agent and heat from the bed of char particles into the interior of the char particle. During this stage effective conduction of heat occurs through the porous char particle.

- d. The final step is the surface chemical reaction. During this final stage adsorption of CO₂ and desorption of product gases from the pores to the external surface of the char particle occurs.

This entire gasification process which is carried out using a TGA, may affect the rate of gasification. This should be taken into account when interpreting the results for determining the kinetic parameters (Gomez-Barea et al., 2005).

Although numerous studies have been conducted on the CO₂ gasification of the biomass char that is produced by the pyrolysis process, very little research has been done on the CO₂ gasification of the torrefied char. Also, lacking are comparative studies of the torrefied char in comparison to the pyrolysed char CO₂ gasification. The present work aims to study the comparison of CO₂ gasification of flax straw char that is produced by torrefaction and pyrolysis processes. The major goal of this work was to study the diffusion and surface reactions that occur in the torrefied and pyrolysed char during the CO₂ gasification, and to determine the effect of temperature and char particle size (torrefied and pyrolysed) on the rate of char gasification.

4.2 Experimentation

4.2.1 Pyrolysis and torrefaction experiments

Flax straw used for this study was obtained from a farm in Saskatchewan, Canada. The flax straw was ground and sieve analysis was performed to obtain average particle sizes of <90 µm, 287, 512, 725 and 925 µm. Torrefaction and pyrolysis processes were carried out in a horizontal split tubular furnace . The reactor used was 25 cm long and had an inner diameter of 3

cm. About 8 gm of flax straw sample was loaded in to the reactor at the beginning of each run. Nitrogen gas was used as a carrier gas, at a flow rate of 50 ml/min.

The torrefaction process was carried out at 300°C. The furnace took about 10 minutes to reach 300°C. When the furnace reached the desired temperature, the sample was held at that temperature for 60 minutes. Similarly, the pyrolysis process was carried out at 500°C and the sample was held at that temperature for 60 minutes. Once both the processes were completed, the reactor was allowed to cool down using Nitrogen gas to room temperature and the char was collected and stored in the desiccators. Similar procedure was followed to produce char using different particle sizes.

4.2.2 Char gasification

TGA was used to perform the gasification experiments. 10 mg char sample was placed in a ceramic crucible and the sample was heated from room temperature to four different gasification temperatures ranging from 750 to 900°C in an inter atmosphere of nitrogen, at a flow rate of 45 ml/minute. The sample was held at the selected temperature for about 5 minutes in order to dry out the sample completely (Gomez-Barea et al., 2006a). The sample was also held at the gasification temperature for further 45 minutes to allow for a complete gasification reaction to take place. For the duration of this 45 minute period, the gas used was switched to CO₂ at a flow rate of 45 ml/minute.

4.3 Results and Discussion

4.3.1 Intrinsic kinetics

In order to perform intrinsic kinetics, very fine powdery torrefied and pyrolysed char particle size of <90 μm was chosen. The rate equation used is as follows

$$r = \frac{dX}{dt} = k * (1 - X)^n \quad (4.1)$$

Solving the above equation, we get

$$\ln r = \ln k + n \ln(1 - X) \quad (4.2)$$

Where X= Conversion (g), k=rate constant (1/s), n=order of reaction and r=rate of the reaction (s^{-1}). From the experimental data, a plot of $\ln r$ vs $\ln(1-X)$ for four different gasification temperatures was plotted, respectively. The slop of the plot is equal to the order of reaction and its intercept is equal to the rate constant k. From the rate constant values at four different gasification temperature, activation energy was calculated using Arrhenius equation. i.e.,

$$k = A * e^{\left(-\frac{E}{RT}\right)} \quad (4.3)$$

Taking logarithm on both sides, we get,

$$\ln k = \ln A - \frac{E}{RT} \quad (4.4)$$

Where, A=pre-exponential factor [s^{-1}], E=activation energy [kJ/mol], R=Ideal gas constant [kJ/mol K] and T=temperature [K]. An Arrhenius plot of $\ln k$ vs $1/T$ for four different gasification temeptratures was plotted and its slope is equal to the activation energy and intercept correspond to the pre-exponential factor. Figures 4.1 and 4.2 shows Arrehenius plot for torrefied

and pyrolysed char. Thus the obtained rate equation for torrefied and pyrolysed char is as follows,

$$r = 95742[1/s]\exp\left(\frac{-150[kj/mol]}{RT}\right)(1 - X)^{1.09} \quad (4.5)$$

$$r = 49290[1/s]\exp\left(\frac{-243[kj/mol]}{RT}\right)(1 - X)^{0.89} \quad (4.6)$$

Since the gasification temperatures range was in the lower range (750 to 900 °C) and the particle size used was <90 µm, the kinetic parameters that were calculated are considered intrinsic (Mani et al., 2011). The order of the reaction was 1.09 for torrefied char and 0.89 for pyrolysed char, and their activation energies were 150 kJ/mol and 243 kJ/mol, respectively. The activation energy obtained for torrefied char was rather low when compared to the activation energy obtained for pyrolysed char. The activation energy obtained for other biomass char such as for spruce 220 kJ/mol and 215 kJ/mol for birch. The resulted kinetic models determined are:

For particle sizes other than <90 µm, the obtained activation energy for both torrefied and pyrolysed char were similar in range.

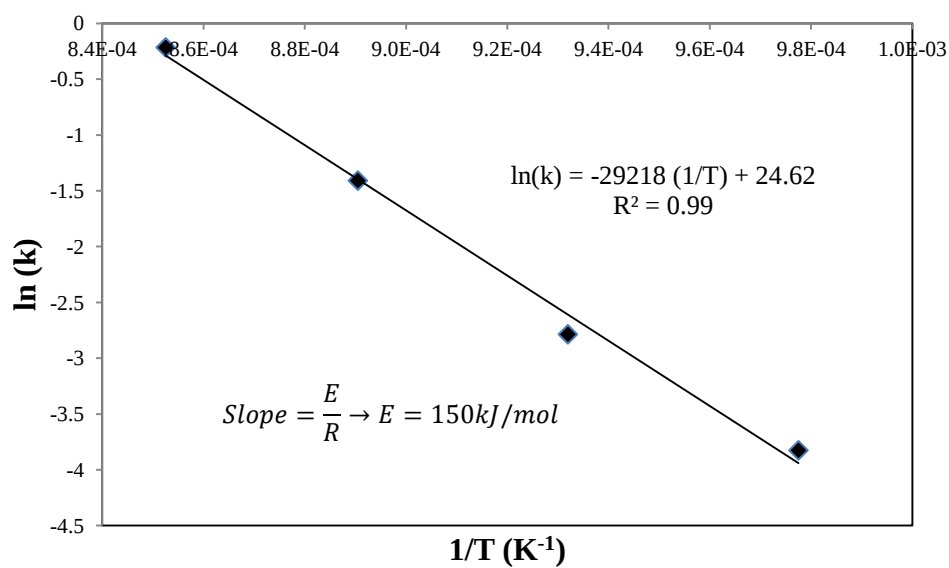


Figure 4.1 Arrhenius plot of torrefied char particle size of <90 μm

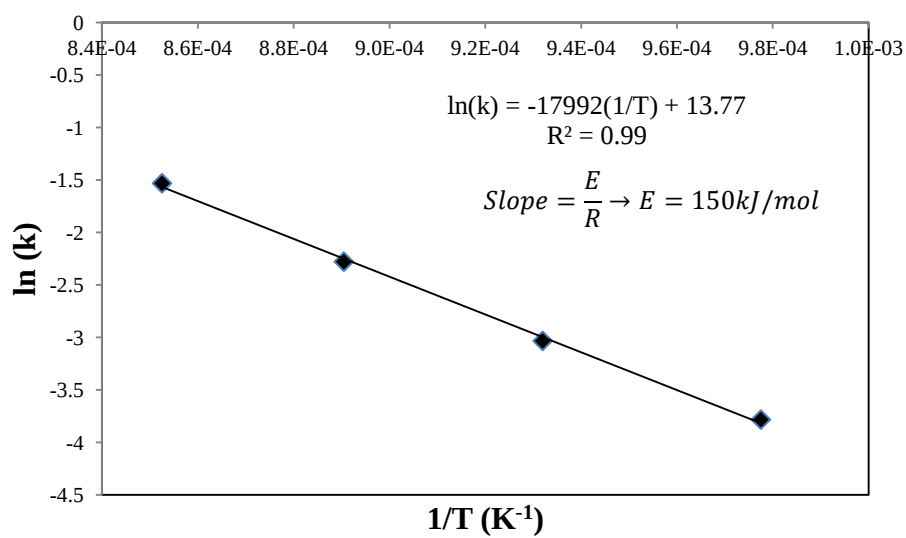


Figure 4.2 Arrhenius plot of pyrolysed char particle size of <90 μm

4.3.2 Effect of gasification temperature on torrefied and pyrolysed char

Figure 4.3 illustrates char conversion vs. time plot for torrefied char for each gasification temperature studied (750, 800, 850 and 900 °C) and for the different particle sizes studied. The conversion is calculated from the experimental data using the equation

$$X = \frac{w_o - w_t}{w_o - w_f} \quad (4.7)$$

where

w_o = initial weight of the sample

w_t = Weight of the sample at time t (minutes) and

w_f = final weight of the sample on ash free base

It is clear from the graph that as the gasification temperature increased the rate of char conversion shifted to a higher degree of conversion. At a lower gasification temperature of about 750 °C the reaction was very slow, and only about 70% of the conversion was achieved for a residence time of 45 minutes. Further, as the gasification temperature was increased to about 900°C the reaction was faster and complete conversion was achieved at the same duration of time of 45 minutes. This trend was observed for all the particle sizes. By taking the experimental reactivity R_{50} (reactivity at 50% conversion) values for all the particles sizes, and for all the gasification temperatures studied, the trend observed is validated. The reactivity is calculated from the experimental data and the equation used to calculate the reactivity is as follows,

$$R = \frac{1}{1-X} \frac{dX}{dt} \text{ [s}^{-1}\text{]} \quad (4.8)$$

Table 4.1 shows the reactivity values for different gasification temperatures and for different particle sizes. It can be observed from Table 4.1, that the reactivity value increases with the increase in the gasification temperature, and decreases with an increase in the particles size.

These results coincide with the results reported by other researchers (Mani et al., 2011; Gomez-Barea et al., 2006a) for pyrolysed char.

Figure 4.4 illustrates char conversion vs time plot for pyrolysed char for different gasification temperatures and for different particle sizes. The pyrolysed char exhibited similar trends related to char conversion of torrefied char. At a lower gasification temperature of about 750°C, the pyrolysed char achieved a conversion rate of 80%, for the residence time of 45 minutes. The complete conversion was achieved at a higher gasification temperature of 900°C. However at the higher gasification temperature, the torrefied char required less time to reach complete conversion than the pyrolysed char. Table 4.2 provides the reactivity values for the pyrolysed char for different gasification temperatures and for different particle sizes. The reactivity values of the pyrolysed char followed a trend similar to the torrefied char. However, the calculated reactivity value was higher for the torrefied char than the pyrolysed char and hence at a higher gasification temperature, the reaction was faster for torrefied char than pyrolysed char.

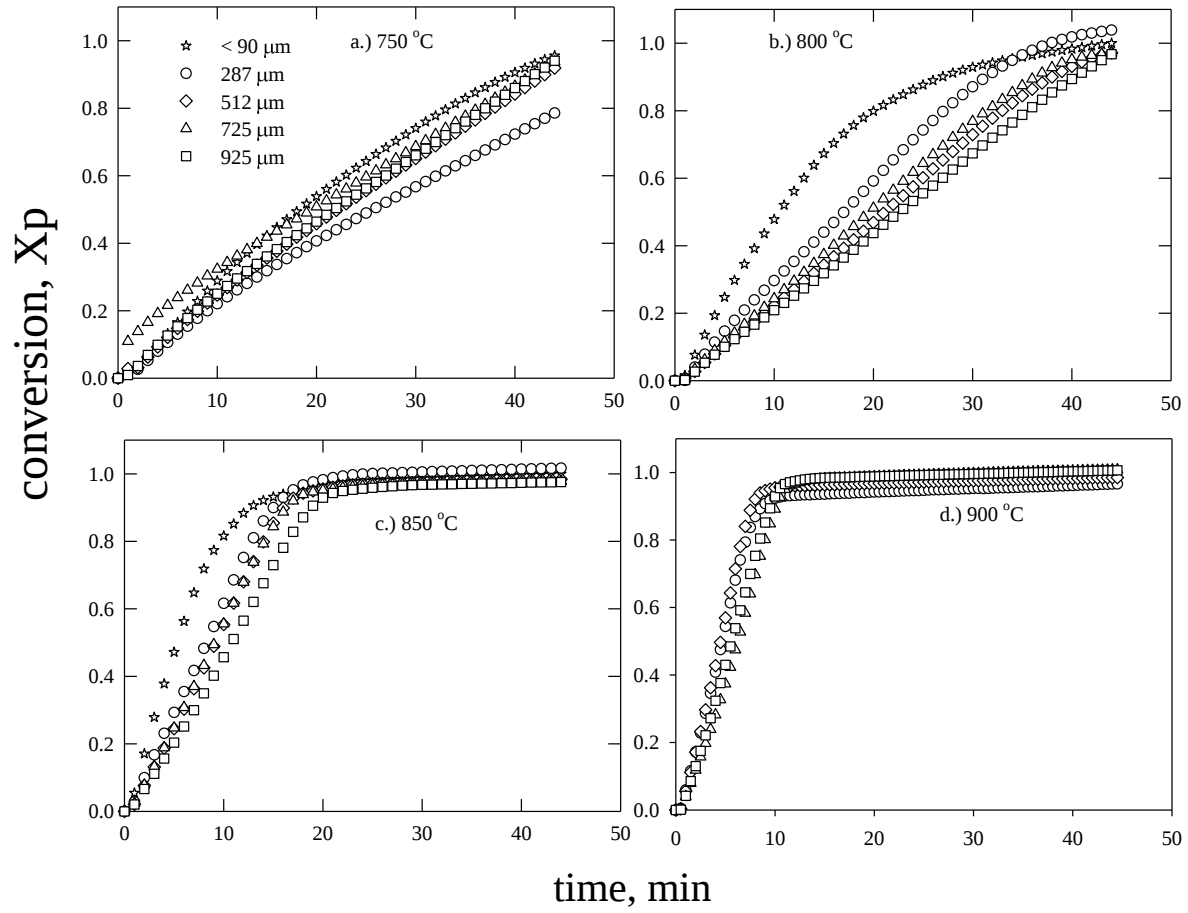


Figure 4.3 Conversion vs time plot for torrefied char at different gasification temperatures and at different particle sizes

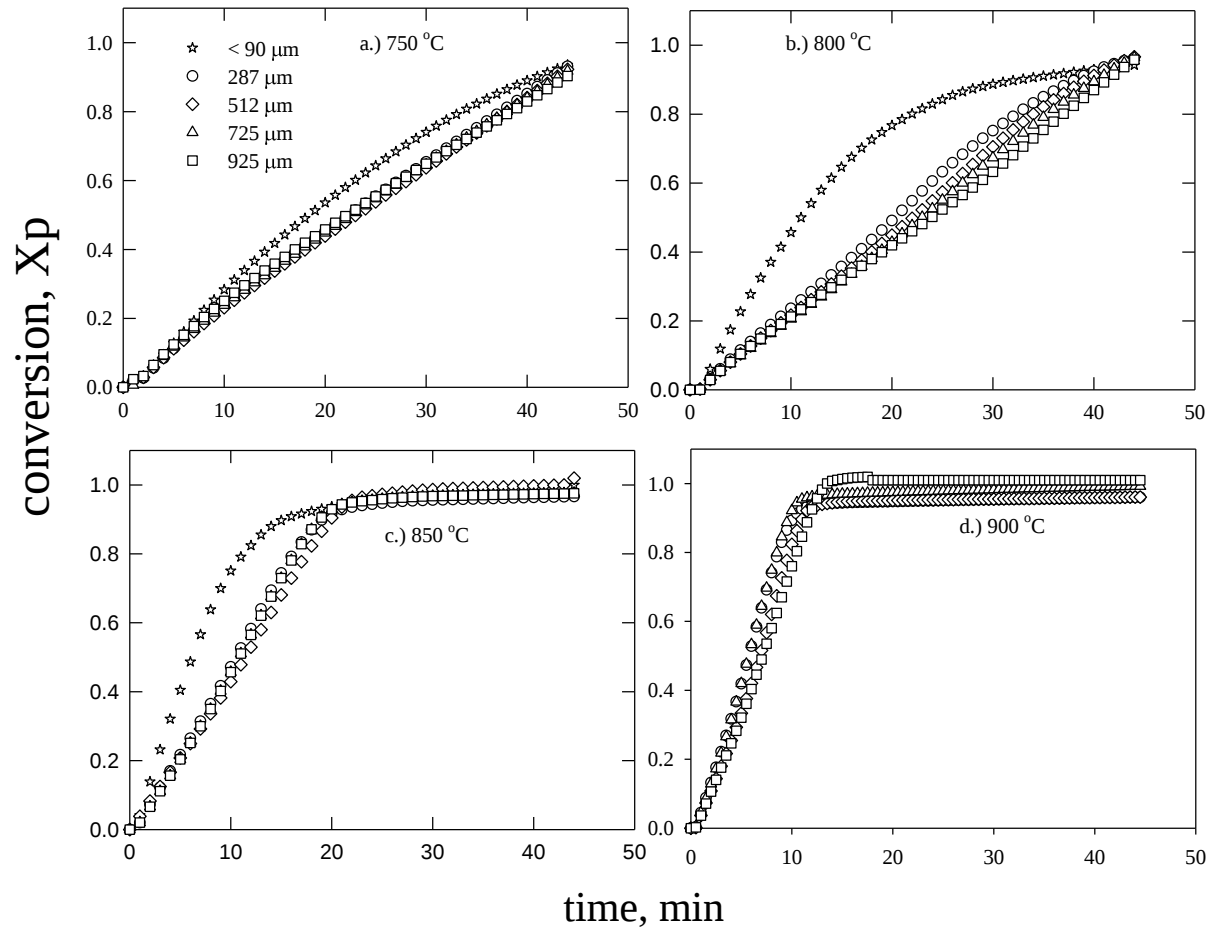


Figure 4.4 Conversion vs time plot for pyrolysed char at different gasification temperatures and at different particle sizes

Table 4.1 Experimental reactivity for torrefied char

	Experimental reactivity, r_{50} (s^{-1})			
	750°C	800°C	850°C	900°C
<90 μm	0.031	0.069	0.147	0.249
287 μm	0.013	0.049	0.093	0.202
512 μm	0.012	0.052	0.123	0.225
725 μm	0.012	0.051	0.121	0.229
925 μm	0.014	0.052	0.120	0.227

Table 4.2 Experimental reactivity for pyrolyzed char

d_p (μm)	Experimental reactivity, r_{50} (s^{-1})			
	750 °C	800 °C	850 °C	900 °C
<90 μm	0.021	0.062	0.13	0.244
287 μm	0.016	0.054	0.110	0.213
512 μm	0.015	0.048	0.107	0.195
725 μm	0.013	0.046	0.109	0.176
925 μm	0.009	0.035	0.067	0.155

4.3.3 Effect of torrefied and pyrolysed char particles size on CO₂ gasification

Figure 4.3 shows char conversion vs time plot for different particle sizes of torrefied char, for different gasification temperatures and for different particle sizes. The particle size of <90 µm achieved the greatest char conversion when compared to the other particle sizes that were studied. At a lower gasification temperature of 750°C, the maximum conversion obtained for fine powder particle was 98%, for all the other particle sizes it was around 70% at a same residence time of 60 minutes. This may be due to the larger total surface area of the fine powder particle collectively. This effect of particle size was verified when reviewing the experimental reactivity data. Table 4.1 shows the reactivity data at different gasification temperatures for all the particles size studied. The reactivity increased with an increase in temperature. There was very little decrease, and constant reactivity values were observed with an increase in the particle sizes and thereby it shows that intra-particle diffusion is limiting the rate of reaction for larger particle sizes.

Char conversion vs time plot for different gasification temperatures, and for different particle sizes of the pyrolysed char are shown in Figure 4.4. Among the various particle sizes studied, the smallest particle size (<90 µm) attained the highest char conversion of 90%, while the largest particle size (925 µm) achieved the lowest conversion of at same gasification temperature of 750°C. For pyrolysed char, a low rate of char conversion was observed for higher particle size of 925 µm at all the gasification temperatures studied. This trend was confirmed when reviewing all the experimental reactivity data. In Table 4.2 the reactivity data, at various gasification temperature, and for all the pyrolysed char particle sizes are summarized.

Figures 4.5 and 4.6 shows a plot of activation energy vs the particle sizes for torrefied and pyrolysed char. It is clear from the graph that the physical effects such as growing alkali concentration and phase change that occur during the gasification process are prominent at higher gasification temperature and for larger particle sizes (Gomez-Barea et al., 2006 _(b)). With an increase in the particle sizes the surface area and rate of reaction decreases dramatically and this phenomenon in turn indicates that for larger particle size, the intraparticle concentration gradient exists and thereby possesses mass-transfer limitations (Shen et al., 1996). Thus, with an increase in the particle sizes, decrease in the activation energy was observed for both the torrefied and pyrolysed char particles. However, the activation energy for the particle sizes of 725 and 925 μm of the torrefied char was in close range, while, a consistence decrease in the activation energy with an increase in the particle was observed for pyrolysed char.

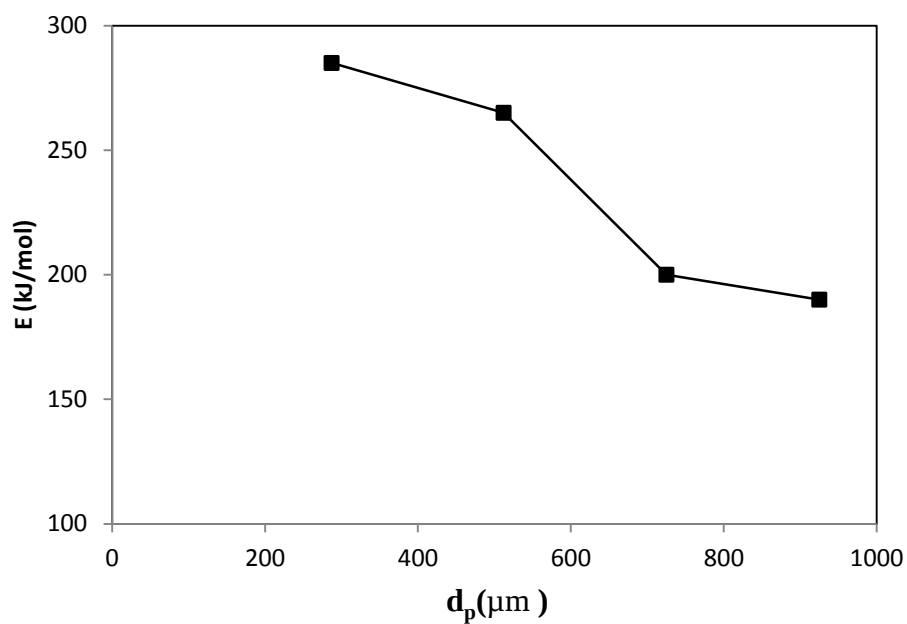


Figure 4.5 Activation energy (E) vs particle sizes (d_p) plot for torrefied char

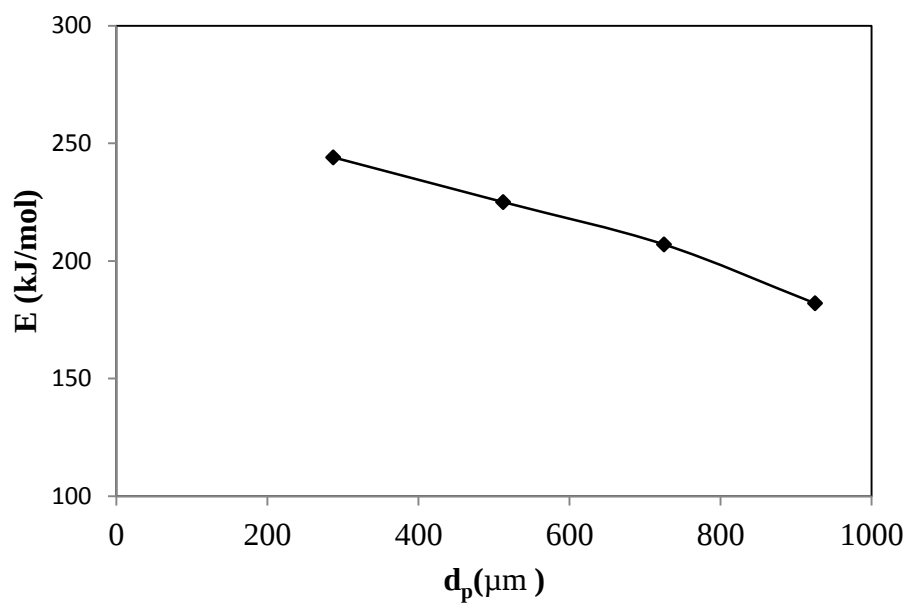


Figure 4.6 Activation energy (E) vs particle sizes (d_p) plot for pyrolysed char

4.3.4 SEM and BET analysis of the char particles

SEM analysis provides information about the structural changes that takes place on the raw biomass char during the torrefaction and pyrolysis processes. Figure 4.7(a) and (b) show the SEM analysis results of raw and pyrolysed char particles respectively. An application of temperature to the raw flax straw biomass causes the chemical bonds to break thermally and this, in turn, breaks the fibrous structure of the raw flax straw biomass and increases the pores in the char particles. However, this effect was most prominent for torrefied char than pyrolysed char. (Dutta et al., 1977).

Tables 4.3 and 4.4 shows BET surface area of torrefied and pyrolysed char. During the BET analysis, torrefied char particles exhibited larger surface area than pyrolysed char particles. This difference in the surface areas was possibly due the difference in the compositions and difference in the distribution of lignicellulosic materials in the char particles. Surface area had significant effect on the reactivity values of both the torrefied and pyrolysed char. As the surface area decreased with an increase in the particle size, the reactivity of both the torrefied and pyrolysed char particles also decreased with an increase in the particle size. However, torrefied char had higher reactivity than pyrolysed char and this was due to the larger surface area of torrefied char (Tushar et al., 2010).

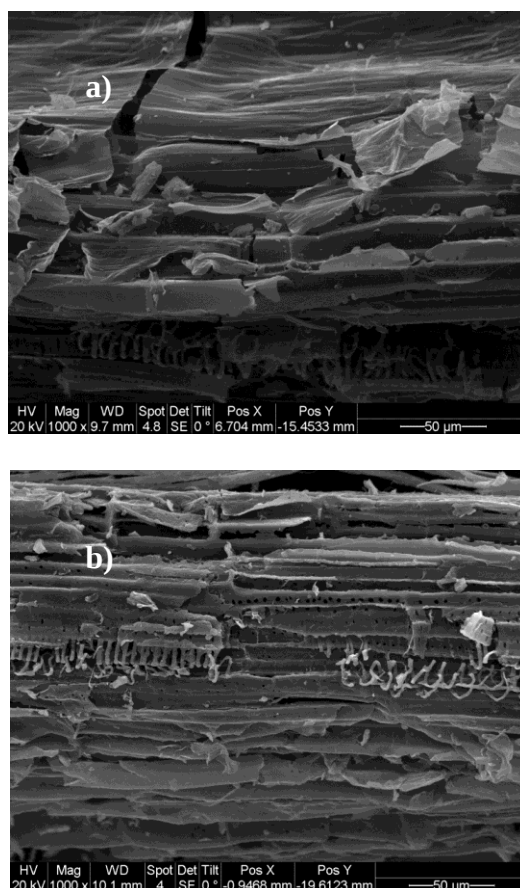


Figure 4.7 SEM images (a) raw flax straw (b) pyrolysed flax straw char

Table 4.3 BET surface area for torrefied char

d_p (μm)	Surface area (m^2/g)
<90 μm	1.48
287 μm	0.90
512 μm	0.71
725 μm	0.61
925 μm	0.59

Table 4.4 BET surface area for pyrolysed char

d_p (μm)	Surface area (m^2/g)
<90 μm	0.59
287 μm	0.31
512 μm	0.17
725 μm	0.09
925 μm	0.08

4.3.5 Effectiveness factor

Effectiveness factor is used to measure how much the rate of reaction is lowered due to the resistance of the pore diffusion (mani et al., 2011). It is also defined as the ratio of the actual conversion (X_p) to the conversion obtained when there is no external, or intra-particle gradient observed ($X_{p,int}$) at any instant of time.

$$\eta_R((t)) = \frac{X_p(t)}{X_{p.int}(t)} \quad (4.9)$$

Where, X_p = Conversion of particles (with diffusion effects) at any time t

$X_{p,int}$ = Conversion of char particle size of $<90\mu\text{m}$

Effectiveness factor is useful for directly predicting the diffusion effects from the experimental conversion vs time data (Gomez-Barea et al., 2006_(b)). The effectiveness factor presented in this chapter is calculated from the experimental conversion vs the time curve (Gomez-Barea et al., 2006_(b)). Figures 4.8 and 4.9 show a plot of the effectiveness factor vs the different particle sizes for the torrefied and pyrolysed biomass char gasification. The effectiveness factor for the particle size of $<90\mu\text{m}$ was 0.98 at all gasification temperatures studied for torrefied char and 1.0 for the pyrolysed char particles. The diffusion path increases with an increase in the particle size and hence, no significant drop in the effectiveness factor was observed for particle sizes other than $<90\mu\text{m}$. This effect was similar for both the torrefied and pyrolysed char types. For effectiveness factor near to unity, the entire volume of the char particles reacts at higher rate, because, the reactant is able to diffuse quickly into the pores of the char particles. Thus, when diffusion rate is faster than the reaction rate and when the effectiveness factor is near to unity, we say that the char particle is reaction limited. However,

for effectiveness factor lower than unity, the char particles react at a lower rate as they cannot penetrate into the interior of the char particles significantly. Thus, when the diffusion rate is lower than the reaction rate, we say that the char particles are diffusion limited (Noble, 2011). Thus, it is clear from figures 4.6 and 4.7 that, the larger particle sizes of both the torrefied and pyrolysed char are diffusion limited and particle size of $<90\mu\text{m}$ is reaction limited. The maximum effectiveness factor observed for the torrefied and pyrolysed char was at 750°C , for all the particle sizes studied. The effectiveness factor obtained at other gasification temperatures for all the particle sizes included in this study was almost equal for torrefied char and a moderate decrease in the effectiveness factor was observed for pyrolysed char. In the present study, the particle size $>90\mu\text{m}$ is governed by intra pore diffusion and hence, the effectiveness factor depends on the structure, volume and shape of each of the pores which varies for each of the particle sizes. This was the reason for the variation in the effectiveness factor for torrefied char and pyrolysed char. Also, torrefied char particle sizes had almost similar reactivity, while, for the pyrolysed char the reactivity decreased considerably (Table 4.1 and 4.2). Similar response was obtained by Gomez-Barea et al (2006_(b)) and Mani et al., (2011) for pyrolysed char.

Table 4.5 and 4.6 are the effective diffusivity values for torrefied and pyrolysed char. They are calculated according to the methods suggested by Gomez-Barea et al., (2006_(b)). Appendix A provides an explanation of the equations used to calculate the effective diffusivity. The effective diffusivity values increased considerably with an increase in the particle size and moderate increase was observed with an increase in the gasification temperature for torrefied char. The effective diffusivity values were observed to show similar trends for the pyrolysed char.

gasification. The diffusivity value obtained for torrefied char was higher when the particle size was 925 μm , and the diffusivity value was 2.0 m^2/min . For pyrolysed char, the maximum diffusivity value observed was also at higher particle size of 925 μm . However, the diffusivity value was around 5 m^2/min . Thus the pyrolysed char has a faster diffusion of CO_2 into the pores of the char than the torrefied char.

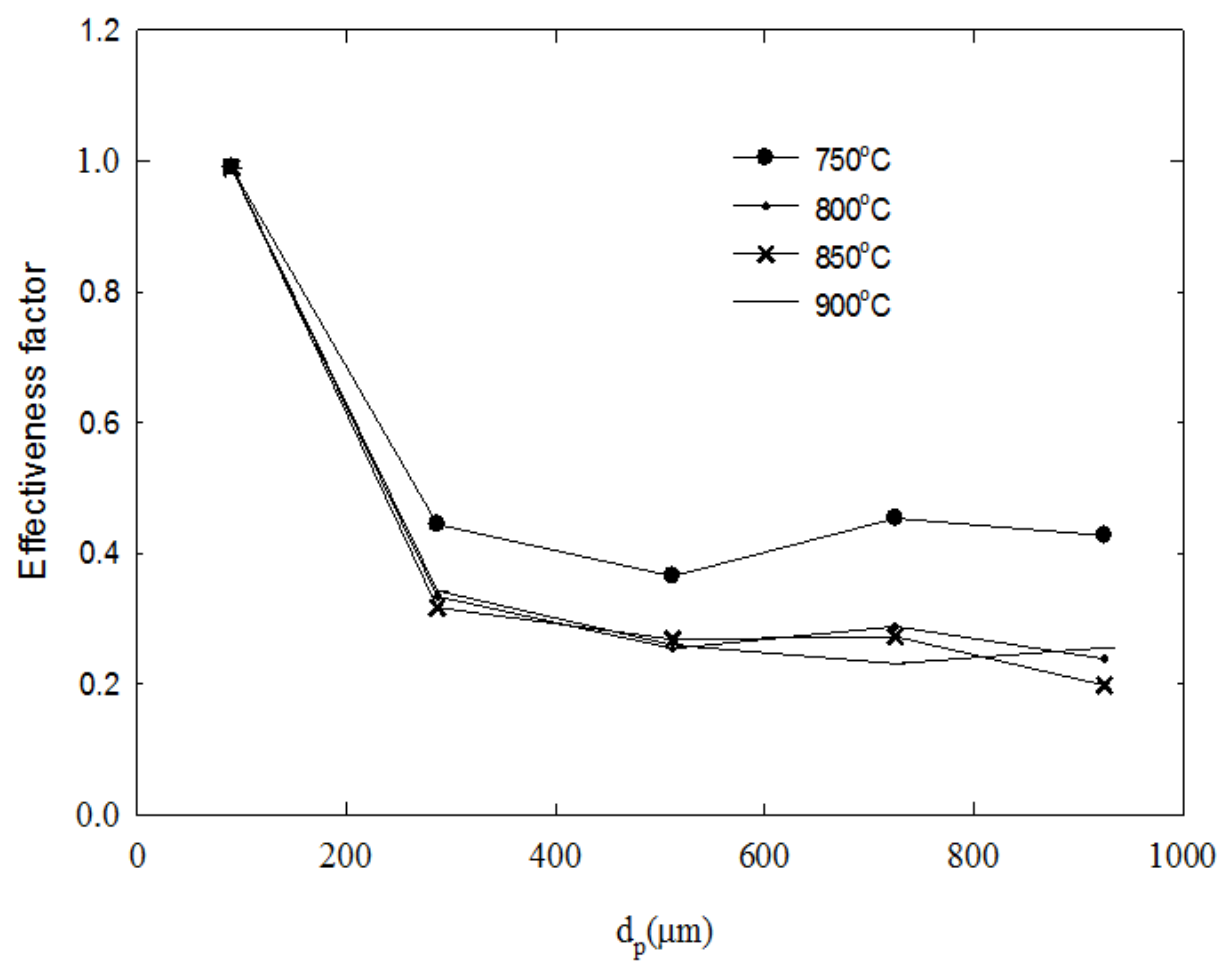


Figure 4.8 Plot of Effectiveness factor vs particle size for torrefied char

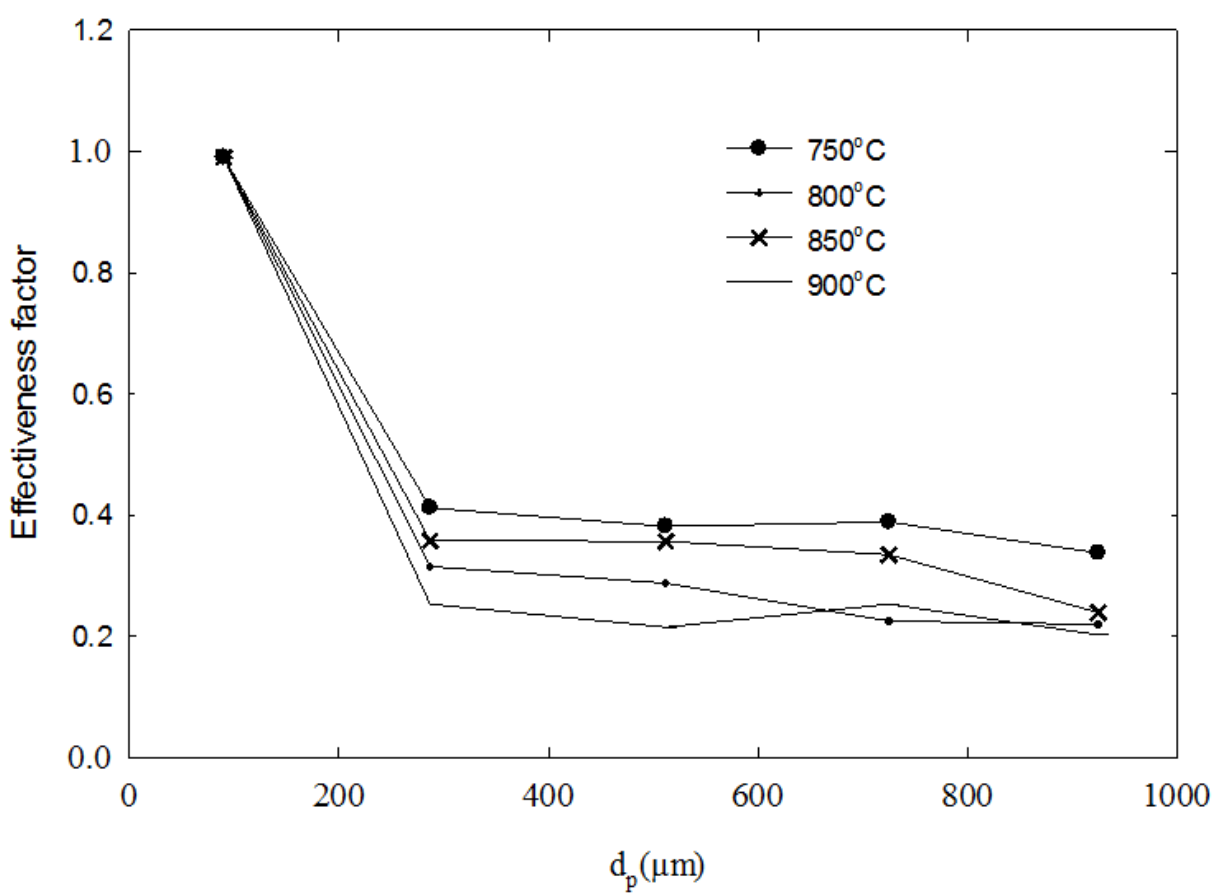


Figure 4.9 Plot of Effectiveness factor vs particle size for pyrolysed char

Table 4.5 Effective diffusivity values for torrefied char

d_p (μm)	Effective diffusivities, D_e (m^2/min) $\times 10^{-4}$			
	750°C	800°C	850°C	900°C
<90 μm	0.0036	0.0037	0.0038	0.0038
287 μm	0.040	0.041	0.042	0.043
512 μm	0.286	0.293	0.300	0.307
725 μm	0.933	0.968	0.981	1.000
925 μm	1.920	1.970	2.020	2.070

Table 4.6 Effective diffusivity values for pyrolysed char

d_p (μm)	Effective diffusivities, D_e (m^2/min) $\times 10^{-4}$			
	750°C	800°C	850°C	900°C
<90 μm	0.056	0.0574	0.0587	0.06
287 μm	0.0806	0.0825	0.0845	0.0863
512 μm	0.576	0.591	0.605	0.619
725 μm	2.26	2.32	2.39	2.46
925 μm	4.85	5.03	5.21	5.38

4.3.6 Diffusion limitation index (DLI)

The convective mass transfer is not as effective however, its effects on the gasification rate must be determined. In order to account for this effect, DLI is calculated for each experiment as follows (Gomez-Barea et al. 2006a),

$$DLI = \frac{\text{observed gasification rate } \left(\frac{1}{s}\right) \text{ at } X=50\%}{\text{maximum molecular diffusion rate } (1/s)} = \frac{r_{obs}}{r_{D,e}} \quad (4.10)$$

While observed gasification rate is calculated using the equation below (Gomez-Barea et al. 2006a),

$$r_{obs} = \frac{R_{50W}}{M_c} \quad (4.11)$$

The external diffusion is estimated by assuming that the movement of the reactant into the sample takes place by Fick molecular diffusion and therefore the length of the diffusion path is equal to half the radius of the hemisphere of the sample tray (Ollero et al., 2003). The molecular diffusion is calculated according to the following equation (Gomez-Barea et al. 2006a),

$$r_{D,e} = c_0 D_m \pi d_t \quad (4.12)$$

The calculated DLI values up to 0.1 are considered as acceptable range for the CO₂ gasification process. The calculated DLI values for the particle size of <90 µm for the torrefied and pyrolysed char are found in Table 4.7. It can be noted from Table 4.7, that the DLI values for the torrefied and pyrolysed char for gasification temperatures of 750 and 800°C are within the range of 0.1. At higher gasification temperatures of 850 and 900°C, the calculated DLI values were greater than 0.1, both for the torrefied and pyrolysed char. This is may be due to the

uncertainty/experimental errors of the R_{50} values. Similar results for the DLI values were obtained by Gomez-Barea et al. (2006a) and Ollero, P et al. (2003)

Table 4.7 Diffusion limitation index for torrefied and pyrolysed char for a particle size of
<90 μm

Temperature ($^{\circ}\text{C}$)	DLI values (Torrefied)	DLI values (Pyrolysed)
750	0.047	0.081
800	0.096	0.132
850	0.187	0.149
900	0.374	0.584

Chapter Five: Conclusion and recommendations

5.1 Conclusion

Torrefaction of the flax straw has been performed with different parameters such as temperature, particle size and the residence time. The weight loss during the torrefaction process increased significantly with an increase in the torrefaction temperature compared to other parameters. Significant increase in the carbon content of ultimate analysis was observed in small particle size range (225 to 725 μm) compared to larger particles. The carbon content values indicate that the torrefied flax straw char resembled the low grade charcoal (lignite). Results from proximate analysis showed that the moisture content was reduced from 5% (raw biomass) to approximately 0.1% (torrefied biomass) at higher temperature of 300 °C. The fixed carbon content increased from its initial value of 16% to about 45% which eventually increased the heating value of the torrefied char from 18,000 kJ kg⁻¹ to 24,000 kJ kg⁻¹. From both the analyses (Ultimate and Proximate), it was observed that the particle size and the residence time have less significant effect on the torrefaction process. The activation energy required for the torrefaction of flax straw was 76.64 kJ mol⁻¹ for the residence time of 60 min and for the particle size of 925 μm . This activation energy was close to the activation energy required for hemicelluloses degradation (Prins et al., 2006a and Branca and Blasi 2003).

The results of torrefied char and pyrolysed char CO₂ gasification experiments with different gasification temperatures and for different particle sizes have been presented. The reaction was a first order rate equation with respect to char conversion for both the torrefied and pyrolysed char. Maximum char conversion were obtained at a gasification temperature of 900°C

for both the torrefied and pyrolysed char, at this temperature of 900°C the reaction was faster for torrefied char than pyrolysed char. There was very little change observed for torrefied char in the reactivity values when particle size increased, other than smallest particle size of <90 μm . From $\ln t_{30}$ vs $\ln d_p$ plot, smaller particle size had very little significant effect on the gasification process. For the pyrolysed char, a decrease in the reactivity values was observed with an increase in the particle size and from $\ln t_{30}$ vs $\ln d_p$ plot it is concluded that the larger particle size of the pyrolysed char had a significant effect on the gasification process. It can be concluded that diffusion is rate limiting for larger particles size for both torrefied and pyrolysed char. The maximum effectiveness factor was observed at the lower gasification temperature of 750°C, for both torrefied and for pyrolysed char. The effectiveness factor at higher gasification temperatures of 800, 850 and 900°C were similar for all particle sizes of torrefied char. The effectiveness factor decreased moderately with an increase in the gasification temperature for pyrolysed char. The greater effective diffusivity was observed at higher particle size of 925 μm for both torrefied and for pyrolysed char. Their values were 2 and 5 m^2/min , respectively. Hence pyrolysed char had a faster diffusion of CO_2 into the pores of the char than the torrefied char.

5.2 Recommendations

Torrefaction process has been recognized as a viable pre- treatment method to reduce the cost of storage, transportation and size reduction of lignocellulosic biomass feed-stock. It has been proposed by Bergman et al., (2005) and Arias et al., (2008) that the torrefaction process should be optimized to obtain maximum brittleness of the biomass feed-stock. Optimizing the torrefaction process for specific end use of the torrefied biomass char may deteriorate the

characteristics of the final products and thus reduces the profit and process economy. Therefore, research has to be conducted on optimization of the torrefaction process that establishes suitable operating conditions to yields a final char product that is suitable for all the downstream processes.

Proximate and ultimate analysis has been continuously applied in research on the torrefied biomass char to assess the chemical changes that occurs in the torrefied char. However, these analysis processes are very slow, time consuming and sometimes they are technically demanding. Hence, rapid methods for the analysis and quality control of the torrefied char must be developed and adapted in research and in large scale productions.

Research has to be conducted on torrefaction reactor design that utilizes biomass feedstock with minimum pre-treatment and thus increasing the economy of the torrefaction process. Experimental researched has to be conducted on the potential utilization of the volatiles released during the torrefaction process. The experimental gasification data of the torrefied and pyrolysed char can be verified by developing different models.

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APPENDIX A. Calculation of effective diffusivity

To calculate effective diffusivity (D_e), two diffusion mechanisms must be taken into account, one inside the porous material (bulk) and second Knudsen diffusion. D_e is calculated according to Bosanquet formula which is as follows:

$$D_e = \frac{1}{1/D_b + 1/D_{Kn}} \quad (\text{A. 1})$$

Where D_b , D_m and D_{Kn} are calculated according to the following equations:

$$D_b = \left(\frac{\epsilon}{\tau_t}\right) D_m \quad (\text{A. 2})$$

$$D_m = 1.4 \times 10^{-5} \left(\frac{T}{273}\right) 1.8 \quad (\text{A. 3})$$

$$D_{Kn} = \frac{2}{3} \sqrt{\frac{8R_g T}{\pi M_g}} r_p \quad (\text{A. 3})$$

Where r_p is the porosity ratio and it is estimated as $r_p = 4\epsilon/S_c$.