STUDIES INTO THE EFFECT OF TORREFACTION ON GASIFICATION OF BIOMASS

by

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I dedicate this dissertation to my parents:

Mrs. Manju Devi and Mr. Ram Ekwal Raut

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ABSTRACT

The utilization of biomass sources can reduce greenhouse gas emission. Presently, biomass is being considered as a potential energy resource to substitute fossil fuel for large-scale power generation through combustion as well as a chemical feedstock. Gasification can turn biomass into convenient product gas that could be used for both energy conversion and chemical production. Biomass gasification is being recognized as an alternative to combustion for the production of clean energy and provision of syn gas for production of chemicals. However, major limitation of the biomass gasification is the tar produced during the process and the high-energy cost associated with its removal from the product gas. Torrefaction is a new pretreatment method for biomass that has positive features such as reduced the storage, transportation cost, increased energy density, easier grinding. The torrefaction process partially removes the low quality volatiles matter thereby making the gas cleaning simpler and increasing energy density of the biomass. Furthermore, it lowers the O/C ratio of biomass fuel making it more favorable for gasification.

To examine the above potential steam-gasification of raw biomass char and torrefied biomass char was investigated and studied their product gas composition and its other attributes. In this study, poplar wood was torrefied at 250°C and 275°C for 1 hour and gasified at different gasification temperatures (700-950°C). Measured and analyzed syngas gas yield, syngas composition and heating value. The kinetics of the process was also studied and it showed that torrefied (250°C with 1 hour residence time) biomass char had activation energy of 92.30 kJ/mol. Furthermore, SEM analysis of the char produced from the torrefied biomass and raw biomass was conducted to observe any difference in the microstructure their structure. The gasification experiments indicated that torrefied biomass produces slightly higher concentration of hydrogen and lower concentration of carbon dioxide than untreated biomass. Furthermore, this study showed that torrefaction has minor reduction in syngas yield, but major reduction in tar production. Overall combination of torrefaction and gasification of biomass is a promising technology for the future energy generation.

LIST OF ABBREVIATIONS AND SYMBOLS USED

ASTM	American Society for Testing and Materials
BFB	Bubbling Fluidized Bed
CFB	Circulating Fluidized Bed
daf	Dry Ash Free
dp	Particle size
db	Dry basis
EDR	Energy Densification Ratio
FC	Fixed Carbon
H/C	Ratio of hydrogen to carbon
HHV	Higher Heating Value
LHV	Lower Heating Value
Nm^3	Normal cubic meter (volume referred to 0^oC and 1 atm pressure)
O/C	Ratio of oxygen to carbon
odt	Oven-dry ton
QWM	Quartz Wool Matrix
RSD	Root Square Deviation
SEM	Scanning Electron Microscope
SLPM	Standard liter per minute
S/B	Steam-biomass ratio
VM	Volatile Matter

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CHAPTER 1: INTRODUCTION

1.1 Background

Global warming is a major concern for fossil fuel based power generation as well as fossil fuel based transportation and chemical production. Coal is the traditional fuel option for power generation, but it is also the main source of global carbon emission.

Biomass, on the other hand, is a carbon dioxide (CO_2) neutral fuel since the CO_2 released when the biomass is burnt was previously absorbed from the atmosphere and fixed by photosynthesis in the growing plants (Kırtay, 2011). It is renewable. Its burning does not make net addition of CO_2 to the atmosphere. In principle biomass is capable of delivering almost everything, whether it is chemical, transportation fuel or power, one gets from fossil fuel. Thus, energy or chemicals from biomass, when produced in a sustainable manner, can drastically minimize greenhouse gas emissions compared to fossil derived energy (Faaij, 2007). Additionally, biomass is the only renewable energy sources that have the potential to directly replace fossil fuels (Kaygusuz, 2009) in all of its current usage. In the near term even partial substitution of fossil fuel with biomass through co-firing in existing coal burning plants could reduces the net amount of CO_2 released to the atmosphere.

Traditional conversion of biomass into energy (heat and electricity) is done through established technology of combustion. Much work has been done on this to transform biomass into coal like solid fuel using the process of torrefaction. But for enhanced use of biomass for production of chemicals and or transport fuels requires gasification of biomass. Such conversion of biomass into fuel gas can also improve its utilization for energy generation because gas is easily storable, and transferable. The fuel gas being clean and can be used in highly efficient energy conversion systems, and allow carbon capture from this for sequestration. For production of chemicals using Fisher-Topsch or other synthesis process, it is necessary to produce Syn gas (mixture of CO and H_2) from the product gasification, which is a mixture of H_2, CO, CH_4, CO_2 and N_2.

Biomass gasification reduces the emission of harmful gas like CO_2, NO_x and more efficiently controlled the combustion of solid biomass. Biomass gasification has also lower thermal efficiency loss and better energy use of the fuel than the combustion. The main purpose of biomass gasification is the production of high quality gas such as high heating value, good composition of fuel with fewer impurities in the gas. Because of these gas impurities, sometimes it gets clogged in to the engine and turbine of the power plant and makes damage to the operation. Therefore, tar and dust free gas is good for the power generation plant. The conversion of biomass to the gaseous fuel through the thermo chemical process like gasification is found to be most convenient for biomass to energy conversion (Rapagna et al., 2000).

The conversion of biomass into gases can be achieved through one of two major routes: biochemical and thermochemical conversion (Basu, 2013). Table 1-1 displays the various biomass conversion technologies. Among all these different methods of conversion, thermal gasification is the most promising technique.

Table 1- 1: Biomass conversion techniques (Basu, 2013)

Technology	**Conversion process**	**Major biomass feedstock**	**Energy/fuel production**
Thermochemical Process	Pyrolysis	Wood, agricultural waste and municipal solid waste	Synthetic fuel oil (bio-crude) and charcoal
	Gasification	**Wood, agricultural waste and municipal solid waste**	**Producer gas**
	Liquefaction	Wood, agricultural waste and municipal solid waste	Bio-oil
	Combustion	Wood, agricultural waste, municipal solid waste and residential fuels	Heat, steam And electricity
Biochemical Process	Digestion (a) Anaerobic (b) Aerobic	Animal manure, agricultural waste, landfills and wastewater	Methane
	Fermentation	Sugar or starch crops,	Ethanol for automotive

1.2 Gasification Process

Gasification is the process in which the biomass or other solid or liquids is converted into a mixture fuel gas by using high temperatures. This gas mixture is called syngas or producer gas. Biomass gasification produces gases like hydrogen (H_2), carbon dioxide (CO_2), carbon monoxide (CO) and methane (CH_4) (DuPont, 2007). The biomass gasification is typically a two-stage process, which includes pyrolysis and conversion of the char. Pyrolysis is a process of rapid thermal decomposition, which occurred in the absence of oxygen (Zanzi, 2001). In this process, biomass converts its lignocellulose contents into condensable volatiles, non-condensable gas mixture and solid residue called char. Now the second process starts in presence of a gasifying agent like air, steam or CO_2 i.e. char conversion. Pindoria et al. (1998) compared the pyrolysis and gasification of eucalyptus at different parameters and found that the conversion level was 95% of biomass pyrolysis without using any kind of gasifying agent.

The gasification process needs gasifying agents, air or steam for conversion. Oxygen is employed as a gasification agent, to reduce the diluting effect of nitrogen from air and producing higher heating value syngas (Gao et al., 2008). Steam is especially beneficial as it produces a gaseous fuel with relatively high H_2 content, and eliminates the need for an expensive oxygen plant.

The inherent properties of biomass, however, such as high moisture content and difficulties in pulverizing, make its use unfavorable for fluidized bed and entrained bed gasification technologies. Typically there are three steps for gasification; drying, pyrolysis and char gasification. The sequence of the steps varies from gasifier to gasifier. Normally this process is different in fluidized bed gasifiers and moving bed gasifiers.

Following section presents an excerpts of gasification reactions retrieved from Rezaiyan and Cheremisinoff (2005); Basu (2010); Chen et al. (2013); Kuo et al., (2014).

1. **Drying:** In this process, the solid fuel gets dried and then vaporizes its moisture. There is no decomposition of the solid fuel because the temperature is low (100-150°C). The rate of drying depends upon the temperature, velocity, and moisture content of the drying gas, as well as the external surface area of the feed material, the internal diffusivity of moisture and the nature of bonding of moisture to that material, and the radioactive heat transfer.

2. **Pyrolysis:** This is the devolatilization process, which occurs before the gasification. This process takes place in the absence of oxygen and above 350°C. The products of pyrolysis are gases, liquid (tars and oil), and char (Equation 1.1). Among all these, one of the major products of pyrolysis is tar formation. This tar comes from the condensation of condensable vapor from the pyrolysis process (Basu, 2013).

$$\begin{aligned}\text{Fuel} &= \text{Char} + \text{Condensable gases} + \text{Non-condensable gases} \\ &= \text{Char} + \text{Gases} + \text{liquids} \qquad (1.1)\end{aligned}$$

The condensable gas could break into non-condensable gas and the overall process may represented by equation (1.2).

$$\text{Biomass fuel} \rightarrow \alpha_1\text{CH}_4 + \alpha_2\text{H}_2 + \alpha_3\text{CO} + \alpha_4\text{CO}_2 + \alpha_5\text{H}_2\text{O} + \alpha_6\text{char} + \alpha_7\text{ash},$$
$$\textstyle\sum_i \alpha_i = 1 \qquad (1.2)$$

The amounts of each of these products vary depending on the zone temperature, rate of heating, structure, and composition and size of catalysts.

3. **Char Gasification:** This process occurs after the devolatilization of the fuel i.e gasification of char which produced during the pyrolysis. This is the most important step

in gasification, because it produces the most energy carrying gases. Additionally, this being the slowest of three steps controls the overall gasification process. Thus the characteristic of a gasifier is determined by how it gasifies the char.

In this process, different reactions occurred between supplied fuel and gasifying medium in the gasifier. Present research uses steam as the gasifying medium and poplar wood as the biomass feedstock. The output of these chemical reactions mainly comprises H_2, CO_2, CO and CH_4. The following are the main chemical reactions occurred during the gasification of woody biomass char and steam.

$$\text{Primary: } \mathrm{C + H_2O \rightarrow CO + H_2} \tag{1.3}$$

$$\text{Secondary: } \mathrm{C + 2H_2O \rightarrow CO_2 + 2H_2} \tag{1.4}$$

Water gas shift reaction: This chemical reaction process occurs in gas phase where carbon monoxide converts to hydrogen. It is an exothermic process where ratio of H_2/CO matters a lot. This gasification reaction converts all of CO present in the syngas to CO_2, yielding the maximum possible amount of hydrogen.

$$\mathrm{CO + H_2O \rightarrow CO_2 + H_2} \tag{1.5}$$

1.3 Biomass as a Feedstock

The rising costs of fossil fuels along with more stringent environmental regulations and incentives for clean, renewable energy are encouraging some power plant owners to consider biomass as a fuel. Senneca (2007) observed that approximately 14% of world final energy consumption comes from the biomass, which is higher than that of coal (12%) and comparable to those of gas (15%) and electricity (14%). Moreover, approximately 1.4% of Canada's total electricity supply comes from the biomass (www.nrcan.gc.ca). Biomass that comes from forest, agricultural and organic processing residues, can be converted to energy via thermochemical processes (Wanga et al., 2008). Since biomass is a carbon neutral source of energy, it can be compared on par with other renewable energy options, and it is one of the least capital intensive and high efficiency renewable energy options. In general, this biomass is considered as more reactive than coal upon pyrolysis, combustion and gasification (Senneca, 2007).

1.3.1 Feedstock Properties

Biomass is a combination of many compounds and its composition influences the combustion and gasification process. The composition is different from biomass to biomass. So, it directly affects the performance of the gasifier, especially due to the following properties:

1. ***Moisture Content:*** Biomass has a large percentage of moisture level, up to 90%. Such high moisture percentage directly affects the gasification process and restricts the gasification temperature attained unaided. This means higher the concentration of moisture in the biomass, the lower the gasification temperature due to the energy required to evaporate the water from the feedstock. Therefore, it reduces the cracking of hydrocarbons in the biomass and the devolatilization process. Due to the lower cracking of hydrocarbons, gasification yields product gas with reduced heating value and higher CH_4.
2. ***Ash Content:*** It is the leftover inorganic substance after gasification. The mass percentage of ash is typically less than 1% in wood to 15% in herbaceous biomass agricultural residues (Daiz, 2006). The biomass ash, though low creates the slagging problems into the gasifier if the ash has a higher alkali oxide.
3. ***Volatiles Matter:*** It is a gaseous product in the form of condensable or non-

condensable that comes out from the feedstock when heated. This volatile matter depends upon the biomass compositions, heating rate and heating temperature (Basu, 2013).

4. ***Particles Size:*** The particle size of the feedstock also affects the gasifier operation. Larger sizes of the biomass can form a bridge in the bunker and prevent the feedstock from moving down whereas smaller sizes of the feedstock could create obstruction for the air passage. Smaller particles also increase the pressure drops that could lead to shutdown of the gasifier.

The substitution of coal with biomass is an upcoming short term economically attractive option for reducing the CO_2 emission from large coal burning plants. However, biomass is characterized by much higher H/C and O/C ratio (van Krevelen diagram, Figure 1-1) than coal has, which makes major difference in combustion characteristics between biomass and coal. Due to this difference in the composition, it is hard to substitute coal with biomass. Additionally, these characteristics of the biomass do not allow to directly combust in the coal fired plant. Additionally, unlike coal biomass cannot be easily stored for longer periods of time, and because of its relatively low energy density requires considerable large amount of space storage for given energy content.

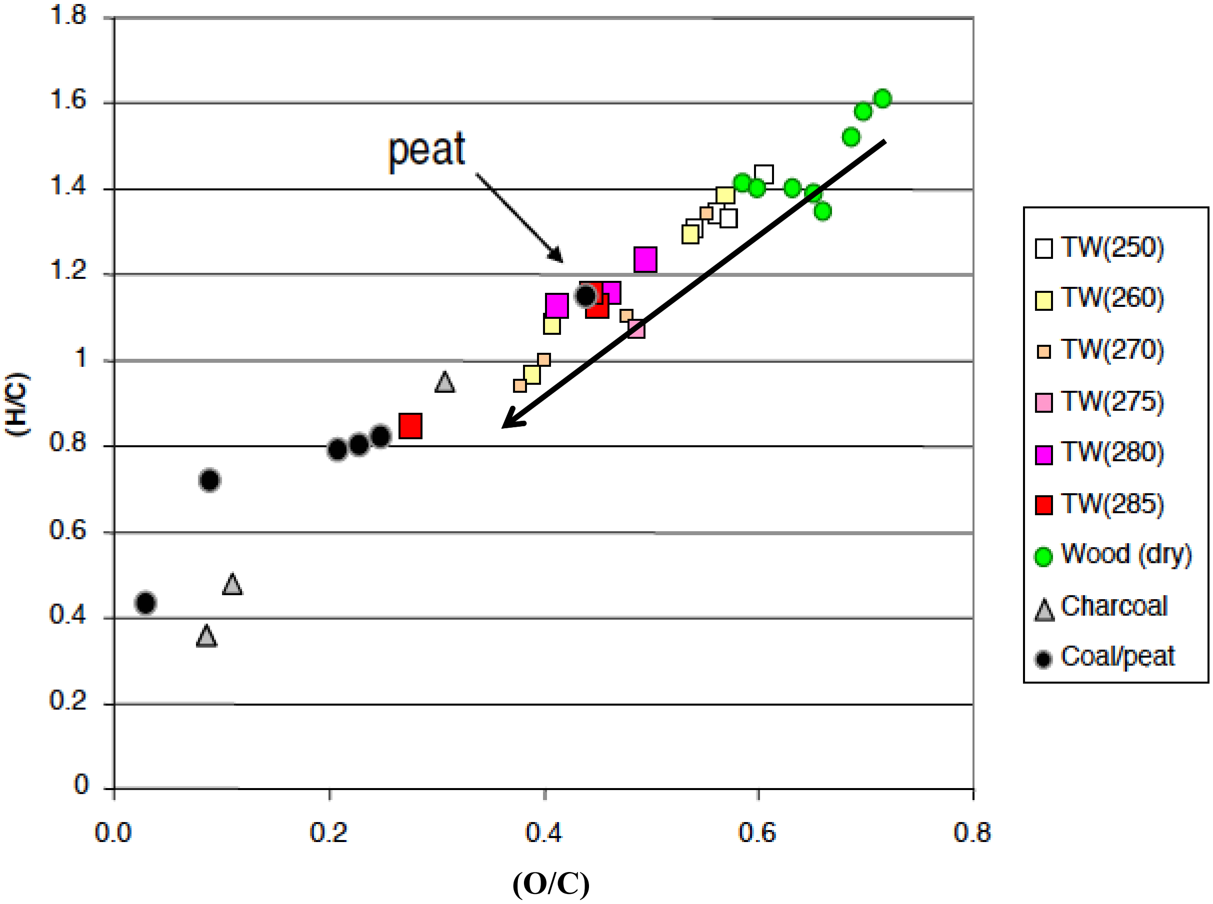


Figure 1- 1: Comaprison of the composition of wood and torrefied wood (obtained at temperature from 250-285°C) on van Krevelen diagram (Boerrigter et al., 2006)

[Symbol: TW stands for torrefied wood]

A relatively new pretreatment process called "Torrefaction" could remove many of the above problems of biomass associated with its use in coal burning plants. Torrefaction reduces the gap between coal and biomass. This pretreatment increase the heating value of biomass, as one can see Figure 1-1, brings the H/C and O/C of biomass comes closer to that of coal and charcoal.

Such compatibility is also applicable for the use of biomass in a coal gasifier. Torrefaction allows the manufactures to avoid extra investment necessary for modification of the gasifier if it has to use biomass instead of coal as the feedstock.

Published literature report extensive information how biomass handling characteristics, thermophysical properties and energy value of the biomass improves by means of torrefaction pretreatment (Tumuluru et al, 2011). But very limited information about how torrefaction pretreatment could improve the gasification of biomass. The present thesis is about this important unanswered question.

1.4 Problem Statement

There has been much speculation and theoretical prediction on how torrefaction pretreatment could improve gasification of biomass, but very few experimental data is available to establish if torrefaction indeed improves gasification as speculated. This important gap in our knowledge may deter full utilization of improved gasification through torrefaction pretreatment.

Moreover, many industries are ready to use the torrefied product for gasification, but this technology is not completely acceptable in these industries because of the lack of in-depth and objective research in the field of utilization of torrefied biomass as a feedstock for gasification. So, more in depth research and knowledge are required for better application and development of this technology. In addition, there are some technical challenges for utilization of torrefied biomass in gasification that has to be addressed for better output. A major challenge in the utilization of biomass for gasification is tar formation. Such tars condense in the reactor plugging the tubes and ducts, which increases the operating cost of the gasifier. This underscores the direct need for systematic research in the general field of gasification of torrefied biomass, which this present research proposes, in part, to do.

1.5 Objectives of the Thesis

The primary objective of this research is to access the effectiveness of torrefaction pretreatment for gasification of the biomass. The specific objectives of this research are:

- To compare composition of product gas obtained from gasification of raw and torrefied biomass;
- To study the kinetics of steam gasification and measure rate parameters for raw and torrefied biomass;
- To study of morphological structure of torrefied biomass;
- To examine the effect of torrefaction pretreatment on tar reduction during gasification;
- To study continuous gasification of torrefied biomass and raw biomass in a bubbling fluidized bed steam gasifier.

1.6 Outline of the Thesis

This thesis is divided into six chapters. Chapter 1 gives an overview of the thesis. It includes: brief introduction of biomass gasification, research objectives and the organization of the thesis. Chapter 2 presents a brief summary of the current state of the torrefaction pretreatment and gasification. It also describes how torrefaction affects the biomass gasification process.

Chapter 3 details the methodology used in this research. It describes the two test units, QWM and BFB used for experiments on different aspects of torrefied biomass gasification. This chapter is broken into two main sub-chapters. The first is batch mode reactor cum gasifier (QWM) gasification and second one is continuous mode gasifier (BFB) gasification. It also discusses techniques employed for analyzing products of torrefaction and gasification.

Chapter 4 discusses results of torrefaction and batch mode gasification in the QWM reactor under different experimental conditions. After discussing the characteristics of torrefied product obtained, this chapter analyses the results obtained on tar formed and product gas produced through gasification of the char from torrefied biomass. It compares results obtained from raw biomass. Additional characterizations of the gasification process through study of kinetics of reaction are included. Studies into morphological changes in the biomass during torrefaction and devolatilization using SEM analysis and gas adsorption measurements are also presented here.

Chapter 5 discusses results of the continuous mode torrefied biomass gasification, which was done to validate results obtained in batch mode gasification in the QWM reactor. It compares quality of produced gas and effectiveness of the torrefaction the findings for different experimental conditions.

Chapter three, four and five were based on a manuscripts that has been submitted for publication in *Energy and Fuels* journal under the title " AN EXPERIMENTAL STUDY OF STEAM GASIFICATION OF TORREFIED BIOMASS" and 9th International Green Energy Conference (IGEC-IX) in China under the title “EFFECT OF TORREFACTION PRETREATMENT ON GASIFICATION OF BIOMASS”.

Finally, the conclusions and recommendations derived from the experience gained in this investigation are presented in Chapter 6. This results and recommendations made from this research can be beneficial for the further improvement in future work of torrefied biomass gasification.

CHAPTER 2: LITERATURE REVIEW

Biomass is a carbon neutral source of energy, it can be compared on par to other renewable energy options, and it is one of the least capital intensive and high efficiency renewable energy options. The most important biomass energy sources include wood and wood waste (64%), municipal solid waste (24%) and agricultural waste (5%) (Chiriac and Rusu, 2011). Biomass is a fast growing resource for the renewable energy and these renewable sources of energy are being steadily introduced in many countries. As per the World Energy Council (2004), the availability of biomass of the world is 220 billion oven-dry ton (odt) per year and the rate of using the biomass shows that it increases to 20% of its overall energy needs from renewable sources by 2020.

Biomass can be converted into solid, gaseous or liquid fuels to generate energy and chemicals through different processes (Svoboda et al., 2009). It could be directly burnt in boilers to produce heat and electricity. One of the thermal processes to convert biomass into the gases is gasification. During the gasification process a number of chemical reactions takes place producing different gases, char and liquid tars. These gases are not readily usable and require some extra equipment processing for purification. The production of clean tar free and quality gas through the gasification is very challenging. Therefore, pretreatment of biomass before its gasification has been suggested Chen et al. (2013) for production of cleaner gas. It is believed that energy gasification of torrefied biomass is a promising technique for producing synthesis gas (syngas) of higher quality than has previously been available.

This chapter presents a short state of the art of the torrefaction process and a critical review of gasification of torrefied biomass based on the research objective focus.

To that end, fundamental aspects of gasification of torrefied biomass are presented towards detailed understanding of its science.

2.1 Torrefaction Process

Torrefaction is gaining a widespread interest in the last few years, as confirmed by the high number of works that can be found in literature (Prando et al., 2014). It is a technique known to improve the biomass fuel property. Torrefaction is a thermal process operated at 200^{o}C to 300^{o}C in absence of oxygen and for a relatively long residence time, typically 1 hour. The properties of the biomass are modified through limited de-volatilization that occurs under these conditions. During the torrefaction process, the biomass loses its volatiles and produces the solid product, called torrefied biomass. These volatiles are the combination of condensable and permanent gases. The yield of the biomass torrefaction depends on the different factors such as torrefaction temperature, residence time, and biomass properties (physical and chemical).

Figure 2-1 shows the overall torrefaction process and torrefied product of raw biomass. In this process, there are three different states observed based on the room temperature. The solid state consists of polymer fractions, which are less reactive during the torrefaction process. These solid products that remain solid are original sugar structures, large modified sugar structures, typical carbon rich char structures and the ash fraction (Bergman et al., 2005). Similarly, the liquid state is the combination of condensable liquids and those are water, organic matters and lipids. The water comes from the thermal decomposition of biomass during the torrefaction. Whenever the biomass is heated up to torrefaction temperature, it starts evaporation and releases the moisture, which produces water. Additionally, during devolatilization and carbonization of biomass in torrefaction process, it produces the organic products such as sugars, polysugars, alcohols, ketones, etc. Prins et al. (2006a) found that hemicelluloses contain acid and alcohol groups and during the thermal degradation of hemicelluloses during the torrefaction process acetic acid and methanol are released.

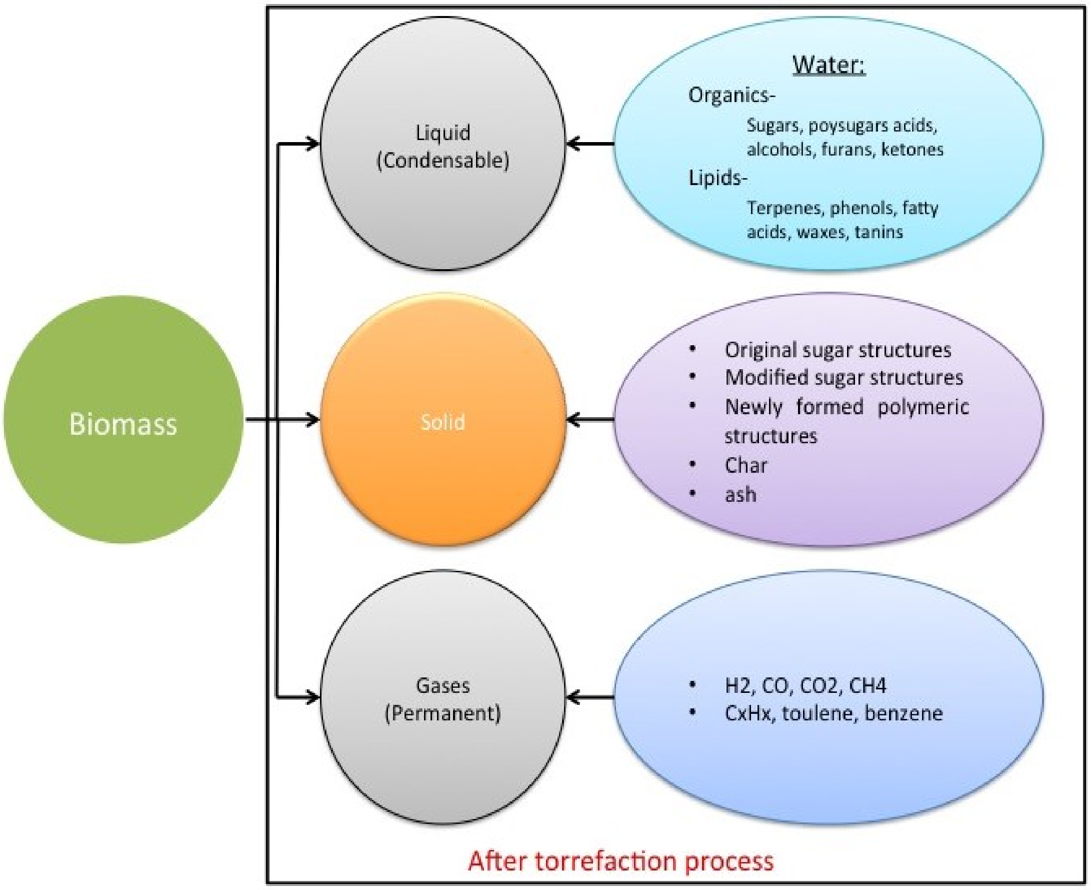


Figure 2- 1: Actual product output during the torrefaction of biomass (Bergman et al., 2005)

Finally, gas state contains some permanent gases like H_2, CO, CO_2, CH_4, benzene etc (Bergman et al., 2005; Pach et al., 2002; Prins et al., 2006a). Among these permanent gases, CO_2 and CO is present in large quantities however other gases are found in only trace amounts.

During torrefaction, the biomass loses more oxygen and hydrogen compared to carbon. As a result the net heating value of the torrefied biomass increases. The moisture content of the torrefied biomass is low because of dehydration reactions (Bergman et al., 2005) during torrefaction. The biomass becomes more porous and more fragile after torrefaction because it loses its mechanical strength. The lower ratio of oxygen/carbon can improve the gasification properties of the torrefied biomass compared to the raw material (Prins et al., 2006). The torrefaction process is a slightly endothermic process requiring approximately 0.6–1 MJ kg^{-1} based on an energetic balance of the overall process and products in higher heating value (HHV) terms (Svoboda et al., 2009).

Figure 2-2 shows that when 1 unit mass of biomass is torrefied it produces 0.7-unit mass of solid product because it loses some moisture and the volatiles of the biomass but it retains 90% of the original energy content. Thus the torrefaction process increases the energy density of the biomass from (1E/1M) to (0.9E/0.7M) which is a 30% increase in energy density on heating value. After the torrefaction of raw biomass, biomass looks like roasted coffee and has a brittle structure, which improves the milling properties compared to the raw biomass.

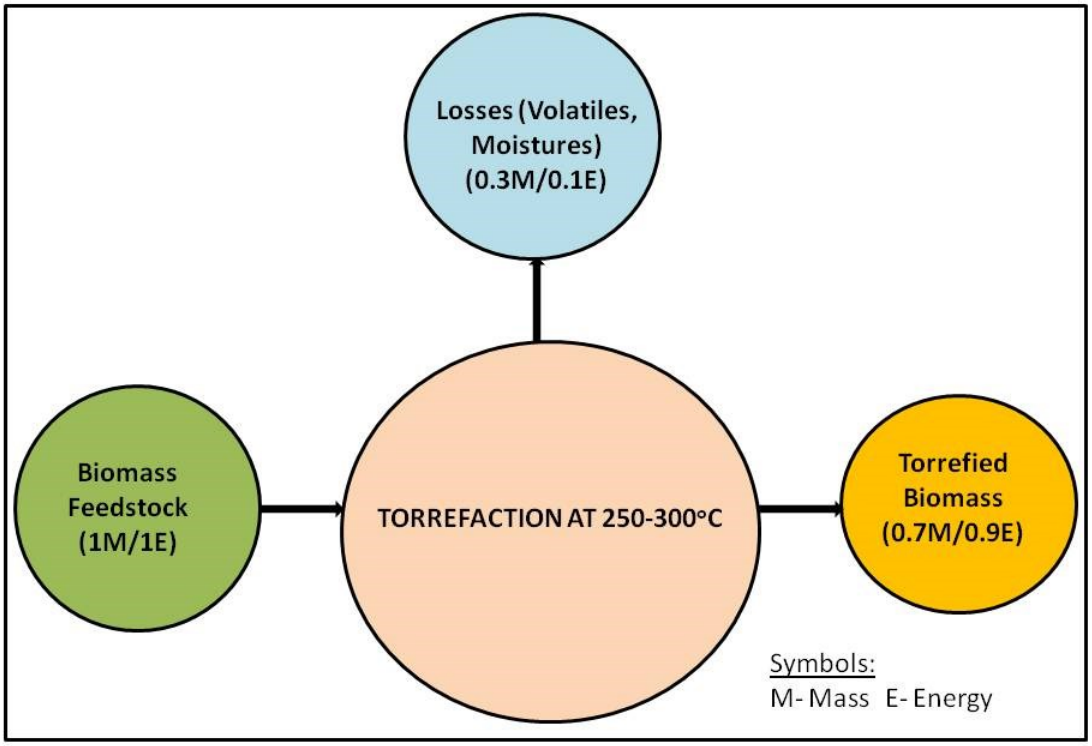


Figure 2- 2: Typical mass and energy balance of torrefaction process (Bergman et al., 2005)

Another important use of the torrefied biomass is as a fuel for the combustion and gasification applications. Prins et al. (2006) found that the thermodynamic losses are reduced if the biomass is torrefied prior to gasification. For the entrained flow gasification process, there is a feeding problem with the raw biomass but the torrefied biomass solves this and smoothly flows in the gasifier. Additionally, the torrefied biomass produced significantly less smokes than raw biomass during combustion and a relatively faster rate of combustion (Pentananunt et al., 1990). Another important characteristic is energy yield, which is lower in carbonization and increased by slow heating at low temperature i.e. torrefaction which gives the high energy yield and moderate energy density. This indicates that torrefied biomass offers efficiency advantage over raw biomass when the biomass is pre-treated before entrained flow gasification (Van der Stelt et al., 2011).

According to Bergman et al. (2004), torrefaction not only reduces the size of the biomass volume, it also minimizes the operational costs. Utilization of torrefied biomass suggests that a simpler and less expensive gasifier can be used for the gasification process, as the biomass is more easily milled into powder due to the more porous structure (Håkansson, 2007). This means the total investment cost will decrease and capacity will be increased. There are number of improvements in biomass by torrefaction, particularly reduction in moisture and hemicellulose content, lowered O/C ratio, a more porous structure with larger specific surface area as well as higher content of alkali metals. This suggests that it would positively affect gasification reactivity and promising technology for gasification (Xue et al., 2014). The torrefied biomass can also be used for pelletization, which can greatly decrease the transportation and handling cost of biomass.

2.2 Torrefied Biomass Gasification

Gasification is a high temperature thermochemical process that is conducted in the presence of a gasifying medium such as steam, air, CO_2 or a combination of steam and air. It is an attractive means of energy conversion especially while taking into account the concern over global warming and green house effects. For biomass one of the best options for energy conversion is gasification. It is a promising technology that provides a competitive means for producing chemicals and energy from renewable energy sources (Zhao et al., 2009). Many earlier researchers (Huber et al., 2006; Bartels et al., 2008; Fryda et al., 2008; Kruse, 2009) of biomass gasification found problems with agglomeration, corrosion, slagging and fouling. This mostly happens due to the higher alkali level and low calorific value in the fuel feedstock. Due to this corrosion and slagging, there would be more breakdowns and a larger startup time. Furthermore, condensation of the tar also creates problems like choking of equipment and pipelines of the plant. Moreover, the fibrous nature of the biomass makes it difficult to grind into desired sizes. All of these drawbacks lead to the high operational and maintenance cost of the plant, which directly affects the consumers. However, many techniques were developed, like physical separation and thermal and catalytic cracking, to overcome these problems. However the implementation of these techniques increases the complexity and requires more investment. Bridgwater (1995) observed that thermal cracking of biomass product gas is difficult and expensive because it requires direct contact with a hot surface.

Furthermore, raw biomass has another challenge regarding storage, handling, feeding, and ash issues during the gasification. Pretreatment of such raw biomass through torrefaction, a low temperature roasting process, is gaining popularity owing to its appeal for gasification. Prins et al. (2006a) concluded that torrefied biomass has favorable properties for its application as a fuel for gasification and co-combustion. This thermochemical pretreatment method will improve the physical as well as chemical properties of the raw biomass. According to Chen et al. (2011), torrefied biomass is beneficial to storage, transportation and subsequent treatments of biomass on a large scale.

Gasification characteristics of biomass are mainly dependent on the biomass type and operating conditions. The physical factors that influence the gasification rates are particle size, char porosity, mineral content of the char, temperature and partial pressure of the gasifying agents (Mani et al., 2011). Among all these, the most affecting factor is gasification temperature. Ciferno and Marano (2002) suggested that operating the gasifier at high temperature would provide the best result. They recommended that the gasification temperature above 1200^{o}C produced less or no amount of methane and higher percentage of H_2 and CO in the product gas. The higher gasification temperature also helps to reduce the tar contents as well as hydrocarbon through thermal cracking, giving a cleaner gas, which is more suitable for gas transportation (Pinto et al., 2002).

Additionally, raw biomass gasified at a lower gasification temperature such as 950^{o}C produces a considerable amount of over-oxidation, which negatively influences the gasification efficiency and it could be improved by torrefaction (Prins et al., 2006). Torrefied wood produces greater regularity in the composition of gases during gasification and produces a very clean and high quality gas (Chen et al., 2013; Chen et al., 2011). Torrefied wood produced in bulk at low cost could be an attractive standardized fuel for small modular downdraft gasifier distributed power systems.

Also, it was found that the gasification of torrefied biomass retains a substantial amount of energy and reduces the milling power consumption by 70-90% for the gasification (Bergman, 2005; Prins et al., 2006). Similarly, Svoboda et al. (2009) suggested that the pretreatment of biomass with torrefaction is the best option for the gasification process over other pretreatment processes like liquefaction and pyrolysis because torrefaction reduces the energy required in preparing biomass for the entrained flow gasification. Due to the brittle nature of torrefied biomass, it is superior to raw biomass for the co-firing and the gasification process. Furthermore, the properties of torrefied biomass should lead to an improved operation in gasifiers for which the stability of the process is important (Pach et al., 2002).

2.2.1 Effect of Temperature on Gasification

According to Rapagna et al. (2000), gasification is a complex thermo chemical process where the supplied feedstock is converted into the different gases and produces some tar and chars. This implies that the gasification temperature plays vital role in the production of syngas and tar formation. Furthermore, biomass is a lignicellulosic structure and the lignin does not completely gasify at lower temperature which forces to increase the temperature about 800-900^{o}C (Basu, 2013). Kalinci et al. (2009) investigated that higher gasification temperature produces higher quantity of H_2, CO and hydrocarbons with smaller quantity of CH_4. Similarly, Mayerhofer et al. (2012) studied the tar concentration in steam gasification at 750^{o}C and 840^{o}C and found that the sum of all tar species is reduced by 17% and 44% respectively.

2.2.2 Torrefied Biomass Feeding

Biomass feeding in an existing coal gasifier is problematic due to the physical and chemical properties of the biomass. To feed the biomass in a conventional coal fired gasifier requires additional equipment and extra investment. Moreover, before feeding into the gasifier, biomass feedstock must be ground into small particles for smooth fluidization, which is Geldart ‘A’ particle sizes (Bergman et al., 2004). Due to very fine particle sizes, electricity consumption is increased by approximately 7% of the energy value of the biomass and is still not fluidized properly because of the fibrous property of biomass feedstock, which plugs the pipe lines (Zwart et al., 2006). However, pretreatment of biomass is the other option for improving the biomass properties, which is similar to the coal and easily fluidized in the gasifier. Torrefaction reduces the fibers of the biomass and after the milling processes its shape is spherical which allows better fluidization.

To increase the syngas production, it is necessary to increase the biomass feed rate but it depends upon the gasifier design. This means higher feeding rate increases the syngas quantity. However, excess feeding rate of biomass decreases the quality of the syngas due to the shorter residence time in the gasifier. The comparison of steam gasification operating conditions is mentioned below in Table 3-1, according to the gasifier size. However, here is a comparison of the biomass-feeding rate with different literatures to ensure the consistency of the biomass-feeding rate. Table 3-1 shows that biomass feeding rate 1.5-4.0 kg of biomass/hr is optimal for steam gasification of approx. 6 inches inner diameter and 60 inches height of gasifier.

Table 2- 1: Biomass feeding rate comparison according to reactor dimensions

Gasifying Agent	Gasifier		Biomass feeding rate (kg of biomass/hr)	Reference
	Inner diameter (inch)	Height (inch)		
Steam	5.90	47.24	1.5-4.0	Herguido et al. (1992)
Steam	6.06	59.05	2.6	Mayerhofer et al. (2012)
Steam	7.87	57.08	6.6-8.7	Ross et al. (2007)

Furthermore, gasifier bed height also affects the gasification operation. The higher the bed height means the longer the gasification time. This longer residence time allows the feedstock for more thermal decomposition and increase the heat transfer rate. This result shows the more producer gas yields because of increased amount of char and tar conversion to the gas. Sadaka et al. (1998) observed that a higher bed height resulted in greater conversion efficiency. However, the higher bed height drops the bed pressure in the dense bed but resulted in no significant changes in the freeboard region.

2.2.3 Steam- Biomass (S/B) Ratio

Steam-biomass ratio is a ratio of moles of steam feed into a gasifier to the moles of biomass feed in a gasifier. This ratio also affects the product gas quality as well as whole process. Moreover, the product gas yield, lower heating value (LHV) and carbon conversion efficiency are also improved by proper selection of S/B ratio. Lv et al. (2004) found that S/B ratio of 0-1.35 decreased the CO and increased CO_2 and CH_4 however LHV, product gas yield and carbon conversion efficiency decreased when the S/B ratio was 1.35-4.04. This is also in agreement with Mayerhofer et al. (2012) who concluded that an increase of the S/B ratio from 0.83 to 1.2 leads to a significant reduction of all tar species due to reforming reactions. In addition to the increasing S/B ratio's effect on the gas composition i.e. higher H_2 and CO_2 content, CO and CH_4 decrease in the product gas. Franco et al. (2003) found that steam-biomass ratio of about 0.6–0.7 was best operating condition for gasification and produced higher energy and carbon conversion. However, Gil et al. (1999) recommended that S/B ratio 0.8-0.9 is suitable for the steam gasification.

2.3 Tar Reduction through Torrefaction

During the devolatilization process at high temperature, the bonding between the molecules of the biomass breaks into smaller molecules, which produces different light gases such as H_2, CO, CH_4 and liquid tars. The tar control and conversion is a key issue for a successful application of biomass-derived producer gas (Li & Suzuki, 2009). Rabou et al. (2009) defined the gasified tar as an organic compound with a molecular weight higher than benzene, which causes fouling and emission problems in equipment using the producer gas. Therefore, if the condensed tar is not removed, it sticks on the wall of down-stream equipment such as heat exchangers, combustion engines, and reactors of fuel cells (Kumar et al., 2009). This tar is a part of the biomass volatile matter, which does not decompose completely into lighter gases.

Thus, the reduction or decomposition of tar in biomass derived fuel gases is one of the biggest obstacles in its utilization for power generation and commercialization of gasification technology (Han & Kim, 2008). To find a solution for these problems related to tar, it is necessary to develop techniques that produce tar free product gas. However, the removal of tar content increases the economic viability of the biomass gasification process. Saw et al. (2012) concluded that the formation of tars during the gasification of biomass is a technical issue hindering the development of bio-solids gasification. Due to the importance of tar reduction on the commercial success of biomass gasification, a number of methods have been proposed and tested to produce low-tar synthesis gas. Weerachanchai et al. (2009) increased the gasification temperature of larch biomass steam gasification from 650 to 750^{o}C, which increased the percentage of LHV by about 23.14–29.05% and decreased total tar by about 5.59–13.04%. Håkansson (2007) experimented in entrained flow gasifiers, which normally operate at temperatures around 1200- 1400°C and are often pressurized. He noted that due to such higher temperatures, the unconverted char in products of incomplete gasification is also reduced and an almost tar free product gas is produced.

Similarly, Lucas et al. (2004) suggested that incremental raising of the feed gas temperature also reduces production of tars, soot and char residue as well as increases heating value of the dry fuel gas produced. It may however be noted that higher gasification temperatures could reduce the cold gas efficiency of the gasification process.

Using catalysts, as a fluidizing agent is another option, which decreases the formation of tar and increases the fuel conversion efficiency (Kumar et al., 2009). However the above tar removal technique is limited to fluidized bed gasifier and is expensive. So finding an alternative technology for tar reduction from the biomass gasification is necessary. Some researchers (Prins et al., 2006a; Kuo et al., 2013; Bergman et al., 2004) speculated that torrefaction of biomass before gasification could be a good option. The torrefaction process reduces the moisture level, and the volatile matter of the biomass. The tar formation depends on the volatile matter, which is reduced during the torrefaction process. So it could naturally reduce tar production during subsequent gasification processes.

Chew & Doshi (2011) compared the performance of raw and torrefied pine during gasification, and they observed a reduction for the synthesis of tar precursors such as acetol and guaicol. Similarly, Sweeney (2012) reported that medium torrefied biomass produced 23% (by weight) less (20.5 g/Nm^3) tar and severe torrefied biomass produced 66% less (9.2 g/Nm^3) tar than the raw biomass (26.7 g/Nm^3). Furthermore, Wannapeera et al. (2011) found that during torrefaction of leucaena, the tar yield decreased significantly with the increase in the holding or residence time. It decreased from 41.9% (by weight) for raw leucaena to only 7.6% for torrefied leucaena at 250^{o}C and 15 hours. It clearly showed that the cross-linking reactions occurred during the pyrolysis of the torrefied leucaena resulting in increase in char yield and decrease in tar yield. A recent study, Phanphanich & Mani, (2011) reported that torrefied char in comparison to raw biomass, may also produce less tar during gasification while its energy content is higher than the raw biomass.

2.4 Torrefied Biomass Porosity Effect on Gasification

Biomass is a fibrous and porous feedstock and contains much moisture. The porosity of the biomass also plays a crucial role in gasification. Biomass losses its initial mass during the torrefaction process in the form of liquids and gases, which cause the biomass to become more porous. The accessibility of pores may depend on different parameters such as the size and shape of the gas molecules, the area of, and the volume enclosed by, the internal surface as determined by gas adsorption (Sing et al., 1985). Deng et al. (2009) reported that the higher porosity feedstock has a greater reactivity during combustion and gasification. When biomass rapidly pyrolyzed, the rapid release of volatiles deforms the biomass structures and typically leads to higher macro pore surface areas and thus to higher reactivity (Fisher et al., 2012).

Ravendraan & Ganesh (1998) reported that pore development depends on the char gasification rate. A slower rate of char gasification results in micro pore development with a larger surface area. However, pore diameter and particle size distribution are useful as indicators in controlling the conversion rate of char to a particular gas under gasification conditions (Roberts et al., 2000). Additionally, Zanzi et al. (2002) found that the porosity of both the raw material and its char is higher for straw in comparison to wood. They concluded that the higher porosity of the particle the faster gas is released from the particles and the longer the particle spends in the reactor. Furthermore, Di Blasi (2009) compared the porosities of wood char and coals. Wood chars have porosities with values from 40% to 50% and pore sizes between 20 and 30nm, whereas coals have porosities ranging from 2% to 18% and pore size around 0.5nm. The pretreatment of biomass before gasification is a better option to break the fibrous properties and make its structure porous. When the biomass is heated at 200-300°C for a reasonable time, its molecular bonds break and release the volatiles. At the time of devolatilization, the biomass molecules try to find a path to escape and that creates new pores. Torrefaction thus creates more complex pore structure. Chen et al. (2011) also concluded that due to the release of gaseous and volatile products from the biomass during the torrefaction, the total pore volumes of torrefied fuels were higher than that of raw sawdust.

Prins et al. (2006a) describes torrefaction as a mild pyrolysis process and its product has a brown/black color, reduced volatile content and increased energy density: 20.7 MJ/kg (after 15 min residence time at 270°C) compared to 17.7 MJ/kg for untreated willow. Furthermore, biomass loses more oxygen and hydrogen than carbon during the torrefaction and this makes its less dense and porous. Couhert et al. (2009) carried out gasification experiments using torrefied beech wood in an entrained flow gasifier. This study confirmed that torrefaction reduces the oxygen to carbon ratio in the feedstock and thus the quality of the synthesis gas produced is improved. Synthesis gas produced from torrefied wood gasification was shown to produce 7% (by volume) more H_2, 20% more CO and approximately the same concentration of CO_2 as produced with the raw wood feedstock. This is also supported by Chen et al. (2011) who conducted an experiment with sawdust and torrefied at 250°C for the gasification process. They concluded that the produced syngas has a better quality and improved cold gas efficiency compared to raw sawdust. Moreover, torrefied sawdust particles had the largest surface area and smallest pore size. This change in the torrefied biomass is due to the release of gases and volatile products during the pretreatment process. The pore diameter, total pore volume and specific area of the torrefied biomass depend on the torrefaction temperature and residence time (Chen et al., 2011). Park et al. (2012) reported that the biomass char, which was pyrolyzed at 850°C, had good combustion reactivity resulting from the high porosity due to the pyrolysis.

The porosity development is dependent on the heating rate of biomass. Fisher et al. (2012) conducted an experiment with raw and torrefied biomass char gasification at low and high heating rate temperatures. Torrefaction avoided the deformation of biomass structure due to the rapid release of volatiles, unlike in a raw biomass. This study confirmed that the high heating rate of chars of both raw and torrefied biomass causes some pores, but no pores were visible on the low heating rate chars. However, Sing et al (1984) categorized all these pores into nanometric pores in terms of internal width. According to their observation, micropores has pores of internal width less than 2 nm, mesopores has pores of internal width 2-50 nm and the last one macropores has greater than 50 nm of pores of internal width. Pastor-Villegas et al. (2006) who observed that wood charcoal has pores in the range of micro to macropores. Mermoud et al. (2006) studied the porosity of charcoals during steam gasification and concluded that the mesopore and macropore surface areas are a better indicator for the reactive surface during gasification, but cannot be precisely correlated to the reactivity of the charcoals.

2.5 Char Analysis of Torrefied Biomass during Gasification

For commercial purposes, the gasification can be conducted with a controlled amount of air, steam, or steam-oxygen mixtures. Most gasification activities and published data in the world are on gasification with air, which produces a gas with a low heating value (4-7 MJ/Nm^3) and 8-14 vol % H_2 content only (Delgado et al., 1997). Gasification with steam (with or without O_2 added) produces a medium heating (10-16 MJ/Nm^3) value gas with

30-60 vol % H_2 content. Biomass can be used alone or combined with coal for the gasification process (Ahmed & Gupta, 2012; Chmielniak & Sciazko, 2003). However, co-gasification of biomass like wood and straw requires some modification because these biomasses have different combustion properties, low moisture in straw and a lower ash-melting point. Furthermore, raw biomass has a lower energy density (15-20 MJ/kg) than coal (25-35MJ/kg) and a higher moisture level. The solid residue of the biomass after the devolatilization process in the presence of inert gas is char and its reactivity is another important parameter for the gasification or combustion process.

Generally, char is made at 800-900^{o}C with a low heating rate in order to have sufficient time to ignore the effect of volatiles. Min et al. (2011) gasified the char from agricultural wastes with CO_2 at 850^{o}C and concluded that the global char gasification reactivity decreased with the pyrolysis temperature increase. Ahmed & Gupta (2009) found that char gasification is more sensitive to the reactor temperature than pyrolysis because pyrolysis can start at low temperatures of 400^{o}C. However char gasification starts at 700^{o}C. To fill the gap between the biomass and coal in terms of energy density and other fuel combustion properties, pre-treatment is required and torrefaction is the most suitable process for it to bring about the property uniformity.

A mixture of lignin or torrefied wood could enhance the gasification properties of the feed (Prins et al., 2007). Torrefied biomass has properties similar to coal, which enables the use of commercially available coal gasification processing equipment (Clausen et al., 2010). Currently, there is increasing interest in utilization of torrefied biomass for the gasification, as the torrefaction modified its properties, so it makes more attractive for subsequent use. Torrefied biomass has many potential applications where coal is currently being used such as in the heating sector, power generation (co-firing), gasification, and steel production (as reducing agents). Biomass may be treated as a coal-like feed when it is torrefied at 250-300^{o}C. This makes the biomass brittle, and easy to pulverize (Zhang, 2010). The torrefied biomass is better than the raw biomass for the entrained flow gasification process because torrefaction made the particle biomass more spherically shaped during grinding or milling which gives the better flow in the gasifier (Bridgeman et al., 2008). Moreover, torrefaction reduces the oxygen/carbon ratio and this makes a biomass better suited for gasification (Batidzirai, 2013) as it avoids over oxidization. In the present scenario, very little research has been done with torrefied biomass char in the gasification process. Char reactivity is affected by the morphological structure, which, for a given fuel, is especially influenced by the release rate of volatiles, that is, the pyrolysis conditions, the amount, composition of inorganic matter and porosity (De Blasi, 2009; Mani et al., 2011). Char gasification reactions have relatively high activation energy compared to pyrolysis reactions (Ahmed & Gupta, 2009). This difference in activation energies reveals higher sensitivity of gasification to the reactor temperature than that for pyrolysis. Matsumoto et al. (2009) in their experiments with H_2O and CO_2 gasification of biomass found that the activation energy depends on multiple factors, including the pore structure, the carbon structure of the biomass, and the obstruction of gasification by generated H_2 or CO in the micro pores due to the high gasification rate. They concluded that the activation energy for H_2O gasification tend to be higher than for CO_2 gasification at high temperature where reaction rate is high.

De Blasi (2009) found that product char properties completely depend on pyrolysis conditions and especially on the heating rate during pyrolysis. Van der Stelt et al. (2011) studied the combustion properties of raw and torrefied biomass by differential thermal analysis which showed that both volatile and char combustion of the torrefied biomass become more exothermic compared to the raw biomass. This indicates that torrefied biomass starts char combustion faster than the raw biomass, although char combustion is slower for the torrefied biomass. Furthermore, torrefied biomass has higher fixed carbon content and less moisture percentage compared to raw biomass, which produced greater combustion, heat during char burnout and takes less time for ignition (Rousset et al., 2011; Bridgeman et al., 2008). Deng et al. (2009) co-gasified torrefied agricultural residues with coal in entrained flow gasifiers, and observed that if the location of the torrefaction plant is near the gasifier (a common milling of torrefied biomass and coal in the mill) then it is possible to use the torrefaction gas as an energy source in the pyrolysis reactor. They also suggested mixing of torrefaction liquids with coal slurry to improve gasification of moist biomass.

Couhert et al. (2009) carried out steam gasification of Beech wood in a high temperature entrained flow reactor, and it was confirmed that chars from torrefied woods are less reactive than the char from raw wood at a lower temperature (1200^{o}C). This is also in agreement with Fisher et al. (2012) who compared the steam gasification of chars from raw and torrefied willow chips. This study has found lower combustion and gasification reactivity for chars produced from torrefied biomass fuels, in comparison to those produced from the same raw biomass fuels, under high heating rate charring conditions. However, Tumuluru et al. (2011) suggested that torrefied wood is highly reactive, similar to coal; therefore it is to be stored in an inert environment to avoid accidents due to spontaneous combustion. Furthermore, torrefied wood will increase cold gas efficiency (Chen et al., 2011) and higher torrefaction temperature has higher gasification reactivity (Deng et al., 2011).

CHAPTER 3: METHODOLOGY

The experimental research has been conducted at Dalhousie University, in particular the Circulating Fluidized Bed (CFB) Laboratory. The Lab is well known internationally for its pioneering work on circulating fluidized bed combustion of coal, but in the recent past it has moved more towards Biomass energy conversion leaving its traditional research on coal combustion. The name of the lab, however, not been changed. The lab is well equipped with experimental facilities and analytical equipment for wide range of energy conversion experimental research. This chapter discusses the experimental methods used and gives a description of the equipment used in those experiments to achieve the objectives of this research. Figure 3-1 presents a flow diagram of the over all process that has been investigated experimentally in this thesis.

The production of gas from biomass is a two stage process. The first one is torrefaction and the other is gasification.

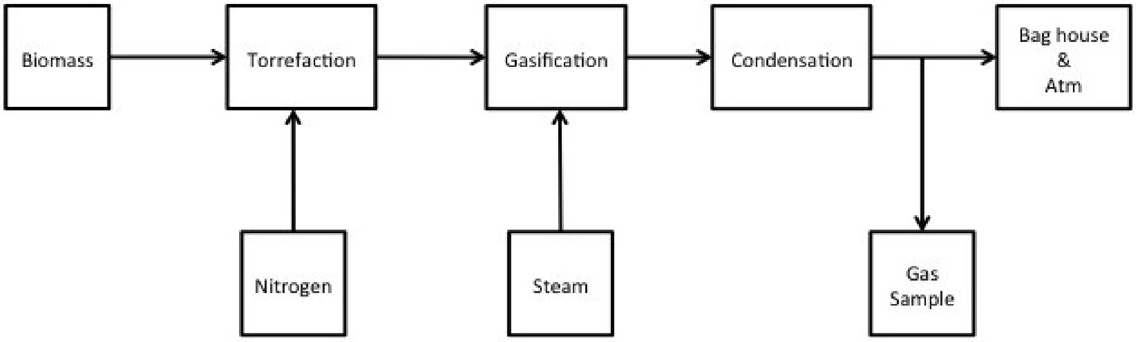


Figure 3- 1: Flow diagram of gasification

The torrefaction process was conducted under the nitrogen atmosphere and gasification of biomass was performed using steam as a gasifying agent.. The product gas was condensed into water. The whole experimental methodology is described in the following sections.

1. Description of reactors
2. Feedstock selection for experiment
3. Torrefaction process for raw and torrefied wood
4. Char preparation from raw and torrefied wood
5. Gasification process for pretreated wood and raw wood
6. Analysis of Gas and Tar Samples
7. Description of analytical methods used

3.1 Description of Reactors

In this experimental research, there were two different kinds of reactors used to achieve the objectives of the research work. These two different reactors were used for analyzing the process as well as the assessing the effectiveness of the process. The batch reactor works with a small batch of sample held in a holder the ambience around which is controlled at will. Such flexibility for controlling the process parameter is vital for in depth analysis of both torrefaction and gasification process. So, in the batch mode gasification, quartz wool matrix (QWM) reactor was used. In this reactor only one small size of solid particle was used for torrefaction and subsequently it was gasified under controlled environment.

In commercial units gasification is conducted in continuous mode, where a large quantity of biomass is continuously fed into the reactor whose environment is determined by complex interaction of all process and design variables. It is very difficult to control the gasification environment, and even if that is possible measurement on one individual biomass particle is very difficult. For this reason continuous reactor was not used for reactivity and other studied. However, to check the product gas quality from steam gasification of torrefied biomass a continuous mode, bubbling fluidized bed (BFB) reactor was used. It gasified both the raw and torrefied biomass at different temperatures, which provided a better understanding of commercial gasifier, and checked if the data from batch reactor qualitatively agree with these.

The details of the methods and description of the experimental setup are discussed below. By using these two reactors, all the experiments were done separately to compare the final results.

3.3.1 Quartz Wool Matrix (QWM) Reactor

The QWM reactor is a fixed bed reactor and is used for batch mode gasification purpose. The setup of this reactor is shown in Figure 3-2. The cross section of the reactor is given in Figure B-1 (Appendix B). The QWM reactor is used for producing torrefied wood samples as well as for gasifying both torrefied and raw biomass. The QWM unit consists of a reactor enclosed by electric heaters. A weight measurement balance sits at the top of the reactor to continuously measure the change in weight of the sample. The gaseous medium enters the reactor at the bottom and leaves from the top. In order to measure gas yield, tar yield and gas composition, the reactor is modified. The top of the reactor is closed and a separate line is connected to the top of the reactor for drawing gas samples. The line takes the gas sample to a condenser first and then into a *Tedlar* gasbag. The condensable part of the product is condensed in the condenser.

Figure 3- 2: Quartz Wool Matrix (QWM) reactor

3.3.2 Bubbling Fluidized Bed (BFB) Reactor

Bubbling fluidized bed reactors are especially suited for gasification of biomass (Basu, 2013, pp-259). In the reactor, inert bed particles were transformed into a fluid state (fluidized) through contact with steam. The bed materials of hot sand are fluidized by steam wherein solid particles, behave like fluid. Due to this phenomenon, a biomass particle fed into it is vigorously mixed together, which allow the fresh feed biomass to reach the gasification temperature quickly. Therefore, the reactor has a high heat transfer coefficient and a uniform temperature distribution over the entire bed. This helps for continuous production and uniformity in gas quality.

The second set of experimental research was carried out using this “BFB gasifier”. Figure 3-3 shows the experimental setup. The details of the reactor and methodology are described in the section below and were utilized to complete the objectives of this research. The important parameters such as temperatures, steam flow rates, and gas composition, which affect the operating conditions throughout the system, were monitored and continuously recorded throughout an experimental campaign.

Figure 3- 3: Bubbling Fluidized Bed (BFB) reactor

3.2 Feedstock Selection for Experiment

In this research, the poplar wood is used as a feedstock. The standard size of poplar dowel diameter of 1-1.5 inch and 3 feet long (obtained from Canadian Tire, Halifax, NS, Canada) is used for sample preparation. These dowels were cut into small pieces as per requirement, and the details of the sample sizes are given in corresponding sections.

3.3 Torrefaction of Raw Wood

Torrefaction is a roasting process in the absence of oxygen. Torrefied samples of raw biomass were prepared in two different reactors: QWM and BFB reactor for subsequent use in the gasification experiments. In QWM reactor only one sample was placed inside the reactor tube while in BFB reactor large number of sample was placed.

3.3.1 Torrefaction in QWM Reactor

A cylindrical shaped (dowel) of Poplar wood of 25mm diameter and 75mm length is chosen for the torrefaction process. A fine hole was drilled at the centre of the wood cylinder halfway down its length. A thermocouple wire was pushed inside the hole. The biomass sample is held in the reactor by means of the thermocouple wire whose other end is connected to the weighing scale (shown in Figure 3-4).

Torrefied samples of biomass are produced at three torrefaction temperatures: 250^{o}C, 275^{o}C and 300^{o}C in the presence of nitrogen for a fixed residence time of 60 min. Before torrefying the biomass, the reactor is first heated to the desired temperature. Once the temperature of the reactor is stable, the weighted raw biomass sample is inserted into the reactor by means of a thermocouple wire (shown in Figure 3-4).

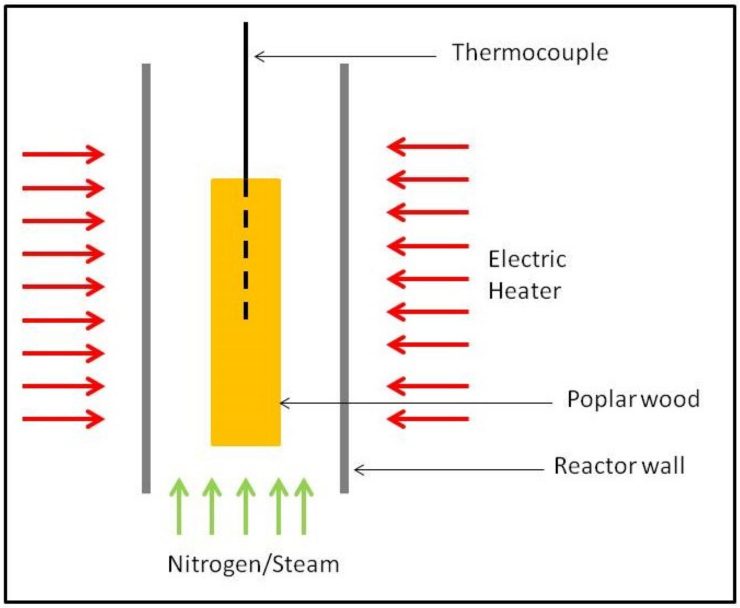


Figure 3- 4: Schematic diagram of mass hanging inside the QWM reactor with thermocouple for torrefaction

By doing so, both mass loss and the temperature of the suspended biomass are continuously measured and data are collected at regular intervals of 1 second. The torrefied samples are measured for mass loss and analyzed for proximate (ASTM D1762-84, 2007) and high heating value. Solid samples were dried in an oven at 105°C for 24 hr prior to analysis. Ultimate analysis of both biomass; raw and torrefied biomass was performed with an EA 1110 (Thermo Quest) elemental analyzer for full determination of carbon, hydrogen, nitrogen, sulphur and the oxygen content.

3.3.2 Torrefaction in BFB Reactor

The poplar wood dowel (38mm × 915mm) was collected and cut into small pieces (38mm × 10mm) for torrefaction as shown in Figure 3-5 (A) and (B).

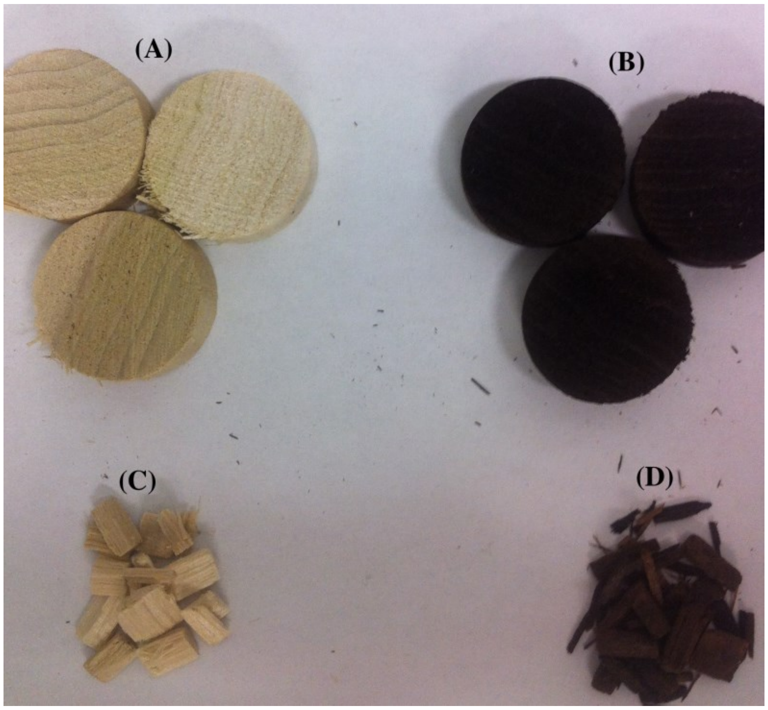


Figure 3- 5: Biomass used for gasification (A) raw biomass (B) torrefied biomass at 250°C (C) raw biomass grinded for gasification (D) torrefied biomass grinded for gasification

Since continuous mode of gasification required large number of torrefied samples, it was decided to use another bubbling fluidized bed reactor for the torrefaction. This unit is shown in Figure 3-6. Ultra high purity nitrogen was flushed inside the reactor (Figure 3-6 (b)) continuously at the rate of 1.5 SLPM to avoid cold zone and also to maintain the pyrolysis conditions during the torrefaction process. During torrefaction the reactor was heated to the desired temperatures at a heating rate of 10°C min^{-1} and thereafter maintained at this temperature. After achieving the reaction temperature, the sample of poplar wood was fed into the cylindrical reactor (Figure 3-6b) and the whole reactor was placed into the bubbling fluidized bed (Figure 3-6a). The thermocouple inserted inside the reactor continuously monitored the biomass before and after it started reacting. During this process the flow rate of nitrogen was kept constant. The sample was kept for 60 minutes for reaction and after this the sample was taken out, quenched in cold N_2 and placed in desiccators till its properties were measured.

Figure 3- 6: Set up for biomass torrefaction in BFB (a) bubbling fluidized bed reactor (b) reactor tube

3.4 Char Preparation from Raw and Torrefied Wood

It has been explained later that for comparison of gasification of two sample of wood (torrefied and raw) both were devolatilized at the same temperature under identical conditions. The resulting char was used for gasification in the batch (QWM) reactor.

Samples of raw and torrefied biomass were ground to small sizes of particles and then passed through a sieve of 300-450 microns. Sieved samples were collected in zipper bags until needed. The collected samples, raw and torrefied biomass were used for char production. Char was produced in the QWM reactor by devolatilizing the samples in nitrogen at specified char production temperatures.

When the electrically heated QWM reactor reached the set char production temperature i.e. 800°C, 1.5 SLPM of nitrogen is passed through the reactor. The sieved raw and torrefied biomass samples were placed in the QWM reactor with the help of special type of bucket which was made with stainless steel mesh. This bucket allowed the samples to contact the reacting agent freely. The samples were kept for 60 minute inside the reactor to complete the reaction in the presence of nitrogen.

Table 3-1 summaries the relevant parameters of the charring or devolatilization process. The reactor was turned off and the sample was cooled to 50-80°C and removed. Finally, the char was kept in a desiccator until it was used for further steam gasification.

Table 3- 1: Summary of raw and torrefied biomass charring parameter

Sample	Torrefaction temp (°C), Residence time: 60min	Heating rate (°C/min)	Charring agent	Charring temp (°C), Residence time: 60min
Raw biomass		6	N_2	800
Torrefied biomass	250	6	N_2	800
Torrefied biomass	275	6	N_2	800
Torrefied biomass	300	6	N_2	800

3.5 Gasification Process for Raw Wood and Torrefied Wood

Gasification was done in the presence of steam alone in both batch and continuous flow reactor. In batch reactor, char from raw and torrefied biomass was used as the fuel while in continuous reactor raw and torrefied biomass was used for gasification.

3.5.1 Gasification in QWM Reactor

Chars produced from both raw and torrefied biomass is used in the gasification process. The schematic diagram of the QWM reactor for gasification is given below in Figure 3-7.

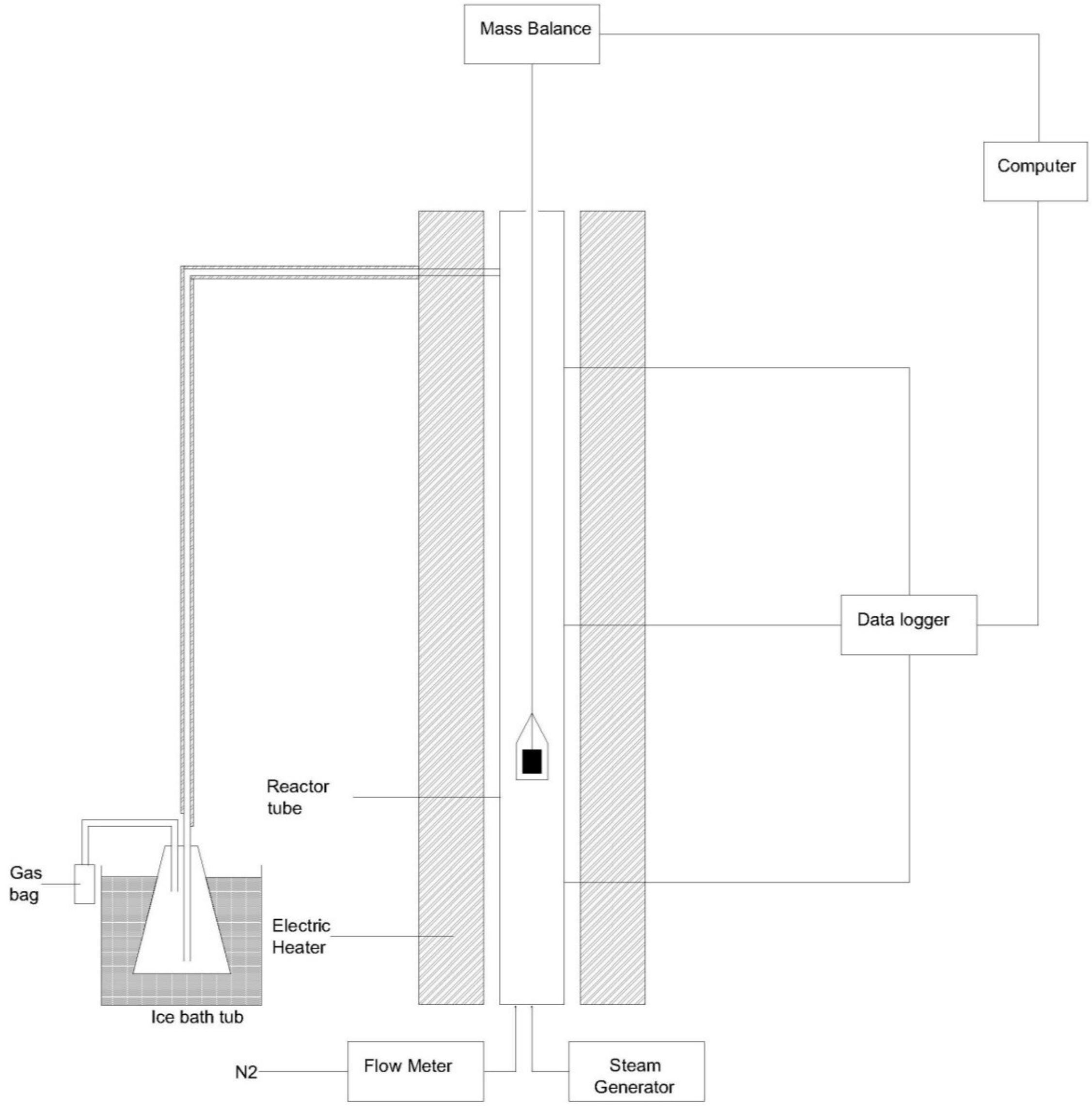


Figure 3- 7: Schematic diagram of QWM reactor

Gasification of both raw and torrefied biomass was studied in presence of steam alone and it was done at five different gasification temperatures: 750^{o}C, 800^{o}C, 850^{o}C, 900^{o}C, and 950^{o}C. Similar to the torrefaction process, the reactor was heated at first to the desired temperature and once the temperature of the reactor became stable, the sample was inserted inside. At the start of the experiment, the reactor was flushed with nitrogen instead of the gasifying agent to prevent any char gasification reaction. About 50-100mg samples of raw and torrefied biomass char were placed in the stainless steel mesh bucket and hung inside the reactor from electronic balance. The end of devolatilization process was marked by the time when the known weight of sample as measured by the electronic balance did not change anymore.

This process allows comparison of gasification of raw and torrefied biomass on a common basis, which is a comparison of gasification of char produced through devolatilization at gasification temperature with that of biomass pretreated by torrefaction at specific torrefaction temperatures. After this time, the nitrogen is replaced with the gasifying agent, steam. Same gasification temperatures were maintained for both raw biomass and torrefied biomass. Thus we had isothermal gasification of biomass char and torrefied biomass in steam at atmospheric pressure. This procedure is similar to that of Fisher et al. (2012) except that they put ground samples in a crucible, which could inhibit perfect contact of steam with all sample particles. In this study, the sample was freely suspended and had good access to steam and therefore the external mass transfer resistance was negligible.

3.5.2 Gasification in BFB Reactor

This continuous gasification test was conducted to validate the results obtained by mode ideal condition of batch reactor (QWM).

Raw and torrefied poplar samples were chipped (average size: 10mm × 10mm × 4mm; shown in Figure 3-5 (C) and (D)) for the gasification. A lab scale bubbling fluidized bed gasifier used in the experiment and schematic diagram is shown in Figure 3-8. The gasifier was circular in cross-section with an inside diameter of 150 mm and a height of 1500 mm. The bottom part of the gasifier was placed inside an electric heater to heat the gasifier for the reaction. Silica sand of average diameter of 250-300 micron was poured inside the gasifier for use as the bed material. The overall property of the silica sand is given in Table 3-2. The bed depth to radius ratio of reactor was 1:1.

Both the raw and torrefied samples were used for the gasification tests. The torrefied samples were prepared at 250°C and 275°C and for 60 minutes. For gasification a different range of temperatures was used. The chosen gasification temperature was 700°C, 750°C, 800°C, 850°C. The samples were fed one at a time into the reactor and the heating rate was same as torrefaction i.e. 10°C/min. After achieving the reaction temperature, biomass particles were fed at a very constant mass flow rate of 3 kg/hr through screw feeder and gravitational flow.

Table 3- 2: Properties of bed material

Properties	Units
Sand size distribution	250-300 micron
Density of sand (ρ)	2500 kg/m^3
Specific heat of sand (C_p)	830 J/kg °C
Partical Size (d_p)	300 micron

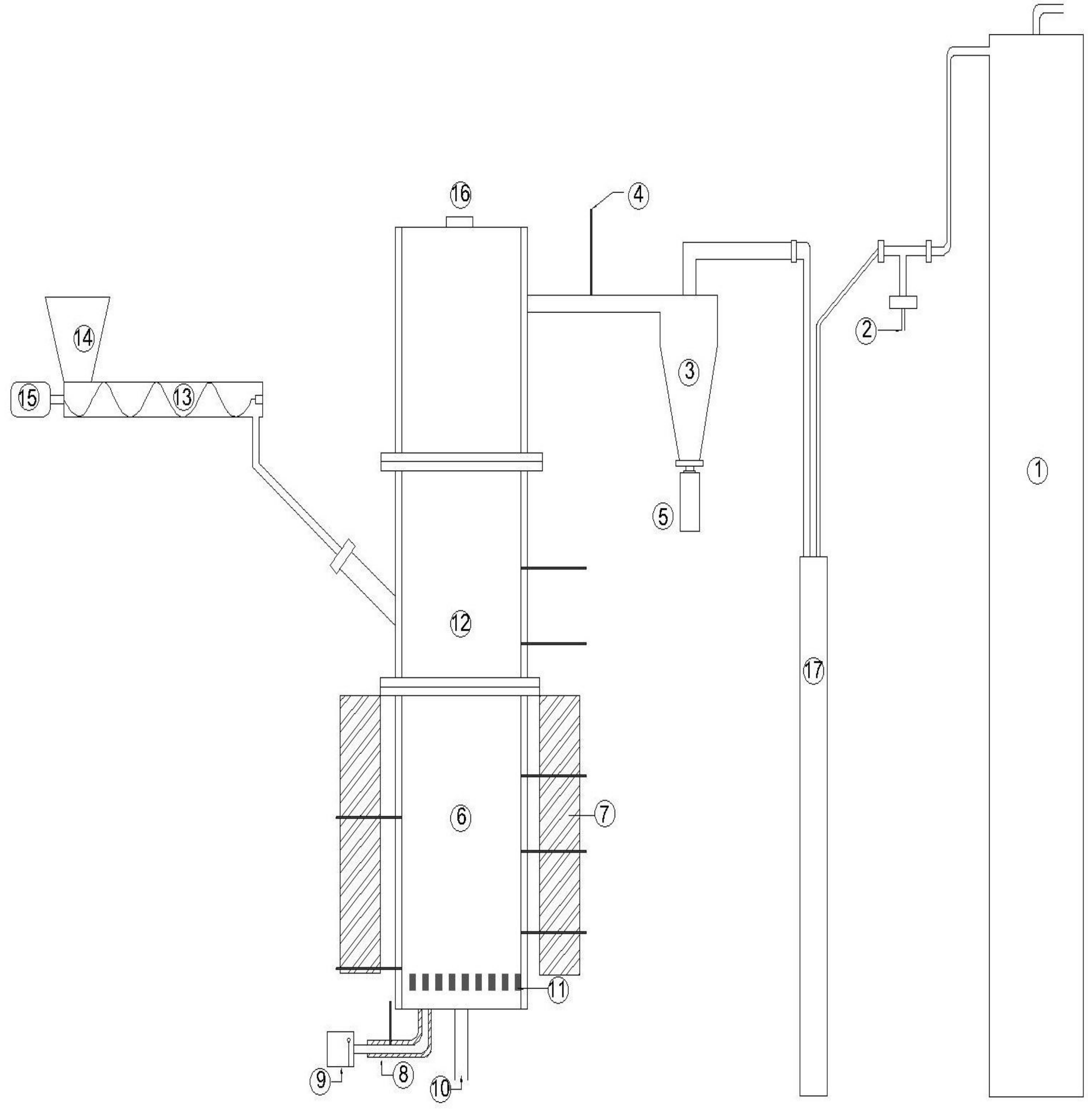


Figure 3- 8: A schematic diagram of laboratory scale bubbling fluidized bed gasifier

Symbols: 1: bag house, 2: gas sampling point, 3: cyclone, 4: thermocouple, 5: ash collector, 6: fluidized bed, 7: heater, 8: tape heater, 9: steam generator, 10: drain, 11: distributor plate, 12: freeboard, 13: screw feeder, 14: biomass hopper, 15: motor, 16: view point, 17: cooling tank

The reactor took about 40-60 minutes to stabilize the bed temperature. Thermocouples of K-type were installed at different points in the gasifier to measure the gasifier and product gas temperature (Figure 3-9).

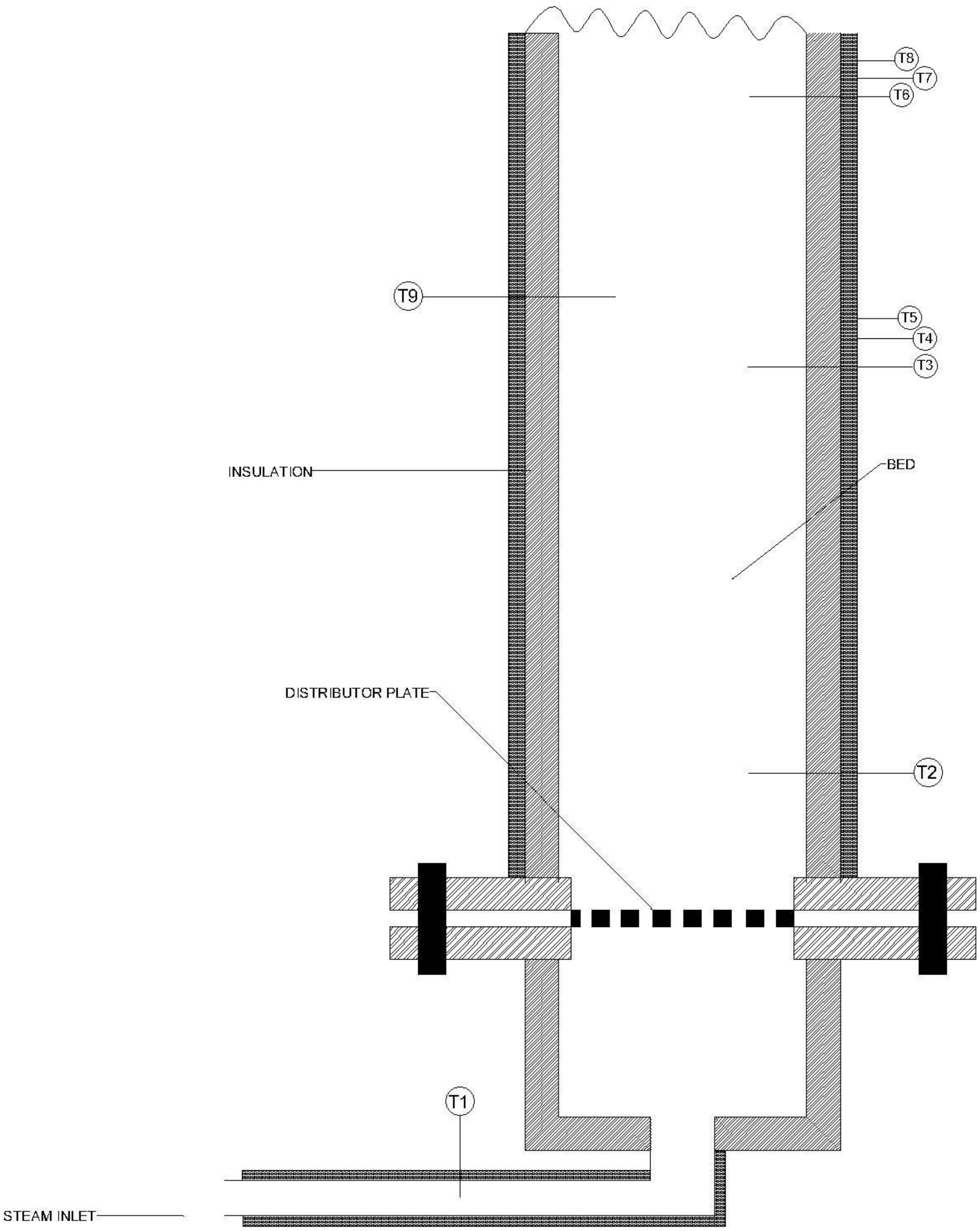


Figure 3- 9: A locations of thermocouples in BFB gasifier

The positions of different thermocouples were as follows:

- The thermocouple T1 was placed at the steam inlet to monitor the steam temperature feeding into the gasifier.

- Thermocouples T2, T3, T6 and T9 were placed at different heights 40 mm, 90 mm, 95 mm, and 157 mm above the distributor plate to measure the gasifier inner temperature.

-Thermocouples, T4 and T7 were placed at heights of 91 mm, 3.58 and 149 mm above the distributor plate to measure gasifier bed wall temperature.

- Thermocouples T5 and T8 were placed on the outer surface of the insulation material to measure this temperatures at heights of 92 mm and 150 mm above the distributor plate.

The gasifier was fluidized by the gasifying agent; steam at 200-250^{o}C. Steam at atmospheric pressure but superheated was introduced from the bottom through a distributor for the gasification process. In this experiment, the steam-biomass (S/B) ratio was kept constant, at 0.6 and the steam flow rate supplied as a fluidizing medium was kept constant at 1.8 kg/hr, which gave a fluidizing velocity 0.18 m/s, which is well above the minimum fluidization velocity. During the whole process, the flow rate of steam was kept constant and the steam temperature was maintained to prevent the condensation by providing an extra heater throughout the supply line.

The gas produced was discharged from the top of the rector and passed through the cyclone, which was used to separate the fine particulates from the gas. The cyclone was insulated to prevent condensation of tar. The cleaned product gas was condensed into a cylindrical vessel, which was surrounded by cold water. Then the dry and clean gas was collected in one liter Tedlar gasbag to analyze them in a gas chromatograph for H_2, CO, CO_2 and CH_4. This was done every 5-minute time intervals until 30 minutes. The dry and clean gas was analyzed on a SRI 8610C Gas Chromatograph (Figure B-3) with helium as carrier gas. The rest of the gases were burnt and passed through a bag house to the atmosphere.

3.6 Analysis of Gas and Tar Samples

The product gas of gasification was collected in the Tedlar gas bag, and was analyzed by SRI 8610C Gas Chromatograph with helium as a carrier. This analysis helped determination of the gas yield and product gas composition. The condensate as collected in the condenser was analyzed for the amount of gravimetric tar produced during gasification. For measurement of tar quantity gravimetric method was chosen as many researchers for have successfully used it over a decade (Li and Suzuki, 2009). The collected condensate liquid was kept inside the oven at $105^{o}C$ for few hours to evaporate all the moistures. After evaporation, the collected samples were weighed on weighing scale. This gave the actual amount of tar.

3.7 Description of Analytical Methods Used

In this section, different techniques of analyzing the properties of chemical reactions are discussed. These properties are interrelated with each other and allow fulfilling the objectives of the research. There are many techniques but some of these are very useful for this research. These techniques are as follows and discussed below:

1. Proximate and Ultimate Analysis of Samples
2. Higher Heating Value Measurement

3. Lower Heating Value Measurement
4. SEM Analysis of Samples
5. Kinetic Model Development for QWM Reactor

3.7.1 Proximate and Ultimate Analysis of Samples

Proximate analysis is for the determination of biomass composition in terms of moisture, volatile matter, ash and fixed carbon. This analysis of biomass was performed by using Benchtop Muffle Furnace (Omega Lux, LMF-3550) and Analytical Balance (Intell-Lab, PXC-200) and followed by ASTM D1762-84 (2007) for the present research. The actual set up for the proximate analysis is shown in Figure B-4. All the dried raw and torrefied sample was grounded before analysis with the help of portable coffee grinder. The porcelain crucibles was placed inside the heated at 750°C furnace for 10 min and took it out for cool down. For cooling process, the hot crucibles were placed into a desiccator for 1 hr. After that, about 1 g of grounded samples were put into a crucible and placed in the oven at 105°C for 2 hr. Then the samples were placed in the desiccator for cool down and measured the weight loss. The weight loss in this process gives the moisture content of raw and torrefied sample.

$$Moisture\ (wb)\% = \frac{Mass\ of\ wet\ biomass - Mass\ of\ dry\ biomass}{Mass\ of\ wet\ biomass} \times 100 \tag{3.1}$$

$$Moisture\ (db)\% = \frac{Mass\ of\ wet\ biomass}{1 - Mass\ of\ wet\ biomass} \times 100 \tag{3.2}$$

Again the furnace was heated up to 950°C and preheated samples which were used for moisture determination was placed inside the oven with lids for 6 min. After that samples were kept into the desiccator for cool down and measured. The weight loss at this process corresponds to the volatiles loss of the raw and torrefied samples. Further, the samples was placed in the furnace at 750°C for 6 hr and cooled down and measured the weight loss. This weight loss during the process gives the ash content of the raw and torrefied sample.

$$Fixed\ Carbon\ \ (db)\% = 100 - Volatile\ matter\ (db) - Ash\ (db) \tag{3.3}$$

The completion of the entire proximate analysis process took about 11 hr.

Ultimate analysis of raw and torrefied samples was performed by using an Elemental Analyzer (Thermo Quest, EA 1110) (shown in Figure B-5) to analyze the hydrogen, carbon, nitrogen, sulfur and oxygen content. The analyzer is equipped with a gas chromatographic Porapak PQS column and auto sampler. The sample was ground to the desired size, dried overnight, placed into a thin capsule and put into the auto sampler. The auto sampler transferred the samples to the combustion column of analyzer, which was heated to 1050°C. Samples sizes introduced to the analyzer are 0.2 - 0.4g.

3.7.2 Mass and Energy Yield Analysis

The quality of torrefied biomass depends on the mass and energy yield. During the torrefaction, biomass released volatiles and losses some energy. So it is more important to calculate how much of mass and energy losses after to torrefaction. Therefore mass and energy yield is defined by using following formula:

$$\text{Mass (daf) Yield} = \frac{\text{Mass (daf) of torrefied biomass}}{\text{Mass (daf) of raw biomass}} \tag{3.4}$$

$$\text{Energy Yield} = \frac{\text{Mass (daf) of torrefied biomass} \times \text{Higher Heating Value of torrefied biomass}}{\text{Mass (daf) of raw biomass} \times \text{Higher Heating Value of raw biomass}} \tag{3.5}$$

3.7.3 Energy Densification Ratio (EDR) Analysis

It is also an important parameter of torrefaction process and its product. Basu (2013) defined the EDR as a quantity of energy released when unit mass of the torrefied product burnt and its product is cooled. EDR is defined by ratio of HHV of product to HHV of raw biomass i.e.

$$\text{EDR} = \frac{\text{Higher Heating Value of torrefied biomass}}{\text{Higher Heating Value of raw biomass}} \tag{3.6}$$

3.7.4 Higher Heating Value Measurement

The higher heating values of the raw and torrefied poplar wood were obtained by using Parr 6100 calorimeter (Figure B-2). The sample (1.0-1.2g) was dried at 105°C in the oven for 24 hr prior to analysis and placed inside the cylindrical shaped bomb and tightened with airtight lid. The oxygen was filled inside the bomb and placed into the water-jacketed bucket for analysis. This took about 15 min to complete analysis.

3.7.5 Lower Heating Value Measurement

When the biomass was gasified at high temperatures, there were mainly three phenomenon that happened; first was devolatilization, second was volatile products release and finally, chars gasification. The product gas from the biomass gasification was the combination of a number of reactions, which were given, in Chapter 1. Considering the importance of the product gas, only four components of the product gas H_2, CO, CO_2 and CH_4 were measured. After measurement of the product gas composition, it was easy to calculate the LHV of product gas, which is given by (Lv et al., 2004):

$$\text{LHV} = (30 \times \text{CO} + 25.7 \times \text{H}_2 + 85.4 \times \text{CH}_4 + 151.3 \times \text{C}_\text{n}\text{H}_\text{m}) \times 4.2 \qquad [\frac{\text{kJ}}{\text{m}^3}] \tag{3.7}$$

where C_nH_m is assumed to be zero and H_2, CO and CH_4 are the gas concentrations of the product gas in fraction.

3.7.6 Surface Area and Porosity Analysis of Samples

All prepared samples from raw poplar wood, torrefied poplar wood and char from both raw and torrefied wood were used to analyze the morphological changes during the torrefaction and charring process. Three different methods: SEM, BET and gas adsorption are employed for the measurement and detail discussions are given below.

3.7.6.1 Scanning Electron Microscope (SEM) Analysis of Samples

SEM was used for analysis of structural changes in the biomass. All samples were cut into small cubic pieces approximately 6 mm x 6 mm x 6mm for the amalysis. After that the sample pieces were attached to the top of the holders and coated with gold palladium to enhance the electrical conductivity of the wood samples. The coated samples were placed inside the SEM and micrographs were taken for both raw and torrefied biomass as well as char from raw and torrefied biomass. This analysis provides information about the structural changes obtained after torrefaction of biomass. Similarly this also allowed comparing the changes between char obtained from raw and torrefied biomass.

3.7.6.2 Brunauer-Emmett-Teller (BET) Analysis of Samples

The single-point BET surface area of raw poplar wood, torrefied poplar wood and their char powders was measured with a Micromeritics Flowsorb II 2300 surface area analyzer (Figure B-6, Appendix B) equipped with a thermal conductivity detector. A gas mixture with a molar ratio of 0.3: 0.7 of N_2: He was used for the measurements. The samples were degassed at 150-250°C for a minimum of 2 hours before the surface area was measured. Multiple measurements were performed on each sample to ensure that a stable surface area value was obtained.

3.7.6.3 Gas Adsorption Analysis of Samples

The pore surface area (BET), pore volumes and average pore diameter measurements were carried out using a Micromeritics ASAP-2000 automated surface area analyzer (Figure B-7, Appendix B) with nitrogen gas as the adsorbate. Samples were degassed at 150-250°C overnight under vacuum to a final pressure of 0.25 Pa. After degassing at under vacuum, the sample tube was transferred to the analysis station and then allowed to equilibrate with sequential 5 cm^3/g doses of N_2 (UHP - Liquid Air). Equilibration was deemed to have occurred when the rate of change of gas pressure was less than 0.01 %, averaged over 10-20 second intervals. The gas adsorption data is presented as volume adsorbed as a function of relative pressure, P/P_o, where P is low-temperature adsorption equilibrium pressure and P_o is the saturation pressure of the gas (101 kPa for N_2 at 77K).

3.7.7 Kinetic Model for QWM Reactor

Mass of the sample was measured at regular intervals of 1 sec. From these measurements mass loss was determined and the degree of conversion was calculated by using the following equation (Slopiecka et al, 2012):

$$\text{Degree of mass conversion,} \, X = \frac{m_i - m_t}{m_i - m_f} \qquad (3.8)$$

Where, m_i is an initial mass of sample before gasification, m_t is the mass of sample at time t during the gasification and m_f is the final mass of sample after completion of gasification. The kinetics of gas-solid reactions is described by the following equation (Slopiecka et al., 2012):

$$\text{Rate of conversion,} \, \frac{dx}{dt} = A\,(1-x)^n e^{\frac{-E_A}{RT}} \qquad (3.9)$$

Assuming zero order (n=0) reaction, solving the above equation (3.9), we get

,

$$\frac{dx}{dt} = A\, e^{\frac{-E_A}{RT}} \tag{3.10}$$

According to Arrhenius equation, the temperature dependence of the reaction rate constant, $k(T)$ (Slopiecka et al., 2012):

$$k(T) = A\, e^{\frac{-E_A}{RT}} \tag{3.11}$$

From the rate constant values at five different gasification temperature, activation energy was calculated using Arrhenius equation. Activation energy, E_A (kJ/mol) is the minimum energy needed for the reaction to occur, A (sec^{-1}) is frequency factor, T is the absolute temperature (K) and Universal gas constant, $R = 8.3144 \times 10^{-3}$ kJ/mol K.

Taking logarithm on both sides of equation (3.11),

$$\ln k(T) = \ln A - \frac{E_A}{RT} \tag{3.12}$$

An Arrhenius plot of $\ln k$ vs $1/T$ for five different steam gasification temperatures was plotted and its slope is equal to the activation energy and intercept correspond to the pre-exponential factor.

CHAPTER 4: QUARTZ WOOL MATRIX REACTOR

4.1 Analysis of Torrefied Biomass

4.1.1 Proximate and Ultimate Analysis of Raw and Torrefied Biomass

The proximate, ultimate analysis and heating value of raw biomass are shown in Table 4-1 along with those for the torrefied biomass at different temperatures. Table 4-1 show that raw biomass has 85.25% of volatile, and this amount decreases to 71.48% after torrefaction at 300^{o}C. From the same table one notes, torrefied biomass has higher percentage of ash and fixed carbon. The fixed carbon content of raw biomass is 9.23%, which increased to 20.22% after torrefaction at 300^{o}C. This increment is due to the devolatilization and carbonization of hemicellulose, which decreases the moisture and volatile matter during torrefaction (Sadaka and Negi, 2009). Furthermore, a significant increase in the carbon content and a decrease in the hydrogen and oxygen of the torrefied biomass were observed with an increase in the torrefaction temperature. However, there was only trace of other gas nitrogen and sulfur found. This indicates that the volatile released during torrefaction is mostly combination of hydrogen and oxygen. Therefore torrefaction directly affects the volatiles and helps to increase the carbon content in the torrefied biomass. Additionally one notes that the moisture level of torrefied samples decreased with increased torrefaction temperature.

Table 4- 1: Comparison of raw and torrefied biomass compositions

<table>
<tr><th></th><th>Raw Poplar Wood</th><th>Torrefied Poplar (250°C, 1hr)</th><th>Torrefied Poplar (275°C, 1hr)</th><th>Torrefied Poplar (300°C, 1hr)</th></tr>
<tr><td colspan="5">Proximate Analysis:</td></tr>
<tr><td>Moisture (dry basis) %</td><td>4.86</td><td>2.49</td><td>1.93</td><td>1.72</td></tr>
<tr><td>Volatile (dry basis) %</td><td>85.25</td><td>81.35</td><td>76.51</td><td>71.48</td></tr>
<tr><td>Ash (dry basis) %</td><td>5.52</td><td>6.52</td><td>7.64</td><td>8.3</td></tr>
<tr><td>Fixed Carbon (dry basis) %</td><td>9.23</td><td>12.13</td><td>15.85</td><td>20.22</td></tr>
<tr><td>Heating Value (MJ/kg)</td><td>18.34</td><td>20.33</td><td>21.53</td><td>26.44</td></tr>
<tr><td colspan="5">Ultimate Analysis (daf mass %):</td></tr>
<tr><td></td><td colspan="2">Raw Poplar Wood</td><td colspan="2">Torrefied Poplar (250°C, 1hr)</td></tr>
<tr><td>Carbon</td><td colspan="2">47.47</td><td colspan="2">51.73</td></tr>
<tr><td>Hydrogen</td><td colspan="2">7.18</td><td colspan="2">6.33</td></tr>
<tr><td>Nitrogen</td><td colspan="2">0.55</td><td colspan="2">0.55</td></tr>
<tr><td>Oxygen</td><td colspan="2">44.79</td><td colspan="2">41.38</td></tr>
<tr><td>Sulfur</td><td colspan="2">0.00</td><td colspan="2">0.00</td></tr>
</table>

4.1.2 Mass Loss during Torrefaction

Figure 4-1 shows a typical mass loss variation with time during torrefaction of the sample biomass at 250°C for one hour. The torrefaction test was conducted many times to observe the nature of the curve and was found to be consistent every times.

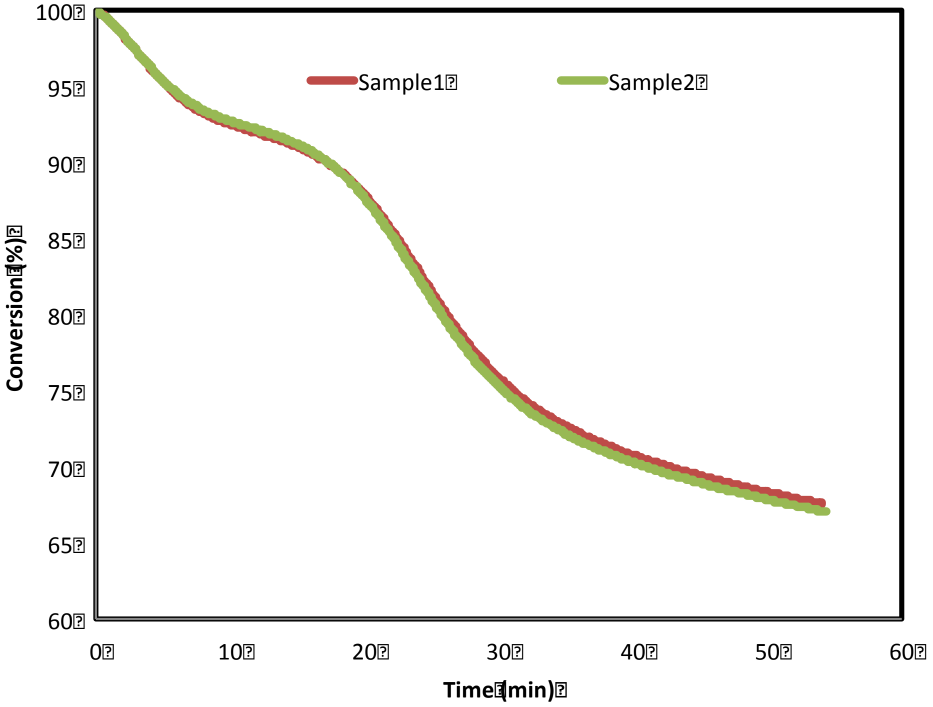


Figure 4- 1: Mass conversion during torrefaction of biomass at 250°C, 1 hour residence time

4.1.3 Analysis of Mass and Energy Yield of Torrefied Wood

Figure 4-2 compares the mass and energy yield of the torrefied biomass at different torrefaction temperatures and residence time. As the torrefaction temperature and residence time, increase the moisture and hemicelluloses content of torrefied biomass decreases, which in turn increases in the energy and mass yield of the product. When the torrefaction temperature was increased from 250°C to 325°C for a given residence time of 60 min, the mass yield of torrefaction decreases from 77.46% to 32.20% and energy yield from 86.08% to 51.41%.

It further shows that when residence time was increased 1 hr to 3 hr at 250 C the mass and energy yield decreased, but this decrease was much less than that is observed when for 1 hr residence time the torrefaction temperature was increased progressively from 260 to 325 C. This data trend is an agreement with those of many investigators including Basu (2013) and Bergman et al (2005).

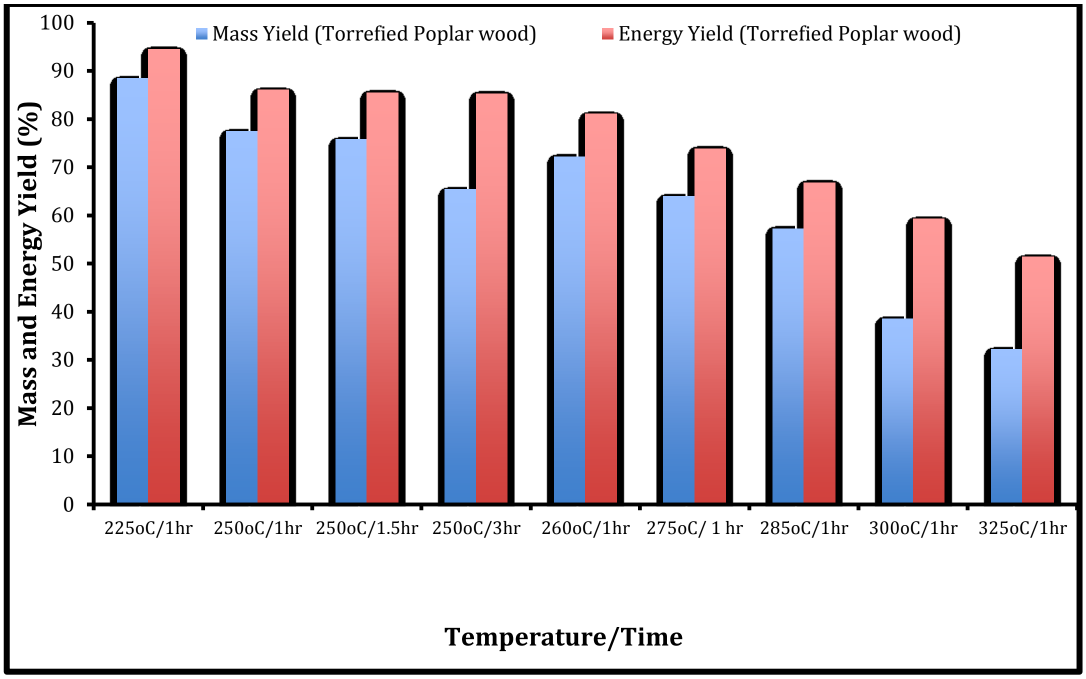


Figure 4- 2: Mass and Energy Yield vs temperature

4.1.4 Analysis of Energy Densification Ratio (EDR) of Torrefied Wood

Equation 3.6 defined energy densification ratio as the fractional increase in energy density in biomass through the torrefaction process. Figure 4-3 shows that EDR increases with increase in both torrefaction temperature and residence time. The residence time has significant impact on energy densification ratio. At 250°C, the EDR of poplar is 1.11 for 60 min residence time which increases to 1.30 with increase in residence time to 180 min. The increase due residence time is however, less than that observed for temperature especially on percentage change basis. For example EDR increased from 1.06 to 1.59

when temperature increased from 225°C to 325°C for 60 min residence time. It is interesting to note that increase in EDR is relatively modest for temperature rise from 225°C to 285°C, but there is a major increase in EDR when temperature rises to 300°C. This is because of decomposition of cellulose at that higher temperature.

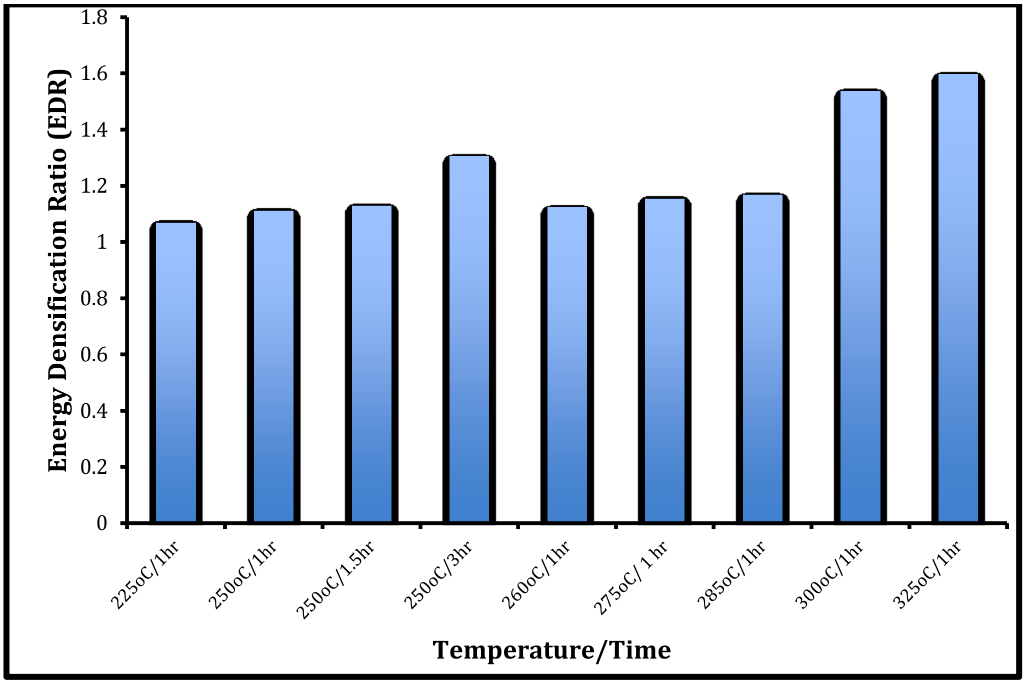


Figure 4- 3: Comparison of energy densification ratio with respect to temperature torrefied poplar wood

4.2 Production of Char from Raw and Torrefied Wood

4.2.1 Mass Loss during Charring

It was explained earlier that the torrefied wood as produced in the previous section is not devolatilized at 800 °C to produce char. It was also produced by direct devolatilization of raw wood at the same temperature. Table 4-2 shows the mass loss details of the char production from raw and torrefied wood. This result shows that mass loss during charring (char production process) increases with the increase in the torrefaction temperature, and this mass loss is due to the breakdown of lignocelluloses materials, moisture loss and volatile losses during the torrefaction process.

Table 4- 2: Mass loss during char preparation
(devolatilization temperature: 800^{o}C, residence time: 60min)

	Raw Biomass	Torrefied Biomass		
Torrefaction temperature (^{o}C)		250	275	300
Torrefaction time (min)		60	60	60
Mass loss (%)	91.36	81.24	75.87	69.89

4.2.2 Higher Heating Value of Char

The higher heating value (HHV) of the char produced from raw and torrefied (250^{o}C) biomass as measured in the bomb calorimeter was 31.78 MJ/kg and 31.41 MJ/kg respectively. The HHV of biomass char torrefied at 275^{o}C, and 285^{o}C was 31.03, and 31.52 MJ/kg respectively (Figure 4-4). It shows very little difference in HHV of char produced from raw and biomass torrefied at different temperatures.

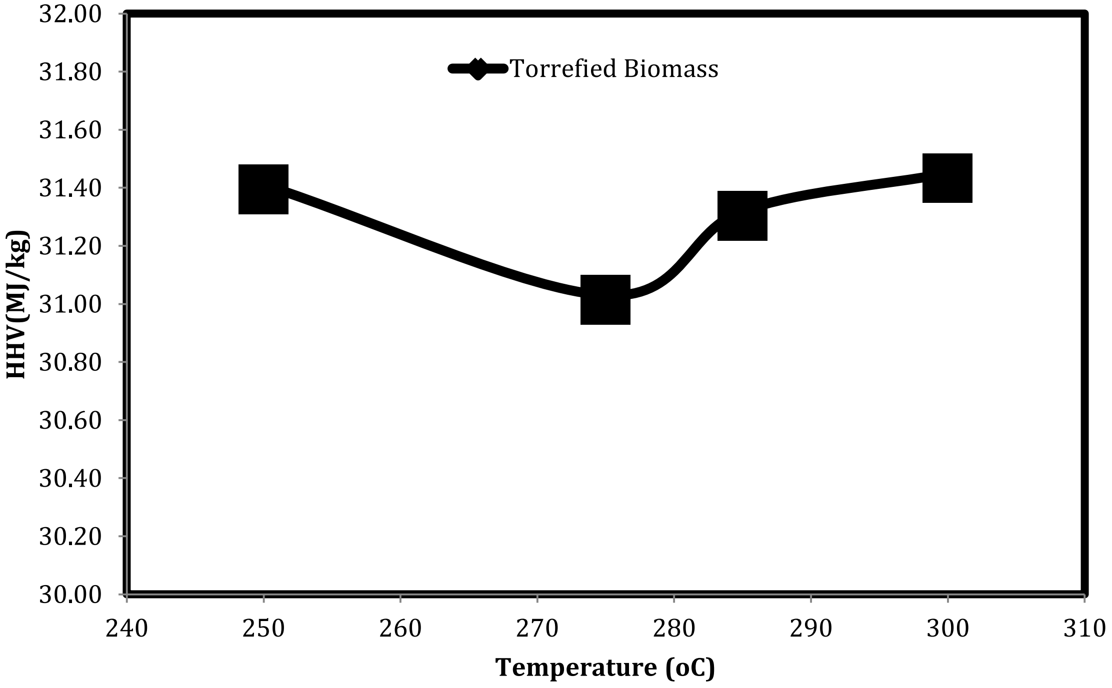


Figure 4- 4: Higher heating value of devolatilized char produced from biomass torrefied at different temperatures

One data point showed decrease when the torrefaction temperature increased as shown in Figure 4-4. This is inconsistent with measurements for torrefied biomass, which is different from the devolatilized torrefied biomass of the present case (Pimchua et al., 2010). Even then there is no reason for this drop, which therefore may be attributed to experimental error.

4.3 Analysis of Gasification Performance

4.3.1 Kinetic Studies of Char during Gasification

The Arrhenius plot for the gasification reaction of char produced from raw and torrefied biomass in presence of steam is shown in Figure 4-5. The average reactivity of the raw and torrefied biomass is calculated for the degree of conversion between 20% and 90%. The range of conversion for computation of reactivity was chosen based on the different literatures (Fisher et al., 2012, Cetin et al., 2004, Dupont et al., 2011). Table 4-3 shows the activation energy, frequency factor and reactivity rate determined for raw and torrefied biomass char. The activation energy of the torrefied biomass char is higher compared to the raw biomass char. The activation energy for raw biomass char is 81.32kJ/mol however after torrefaction pretreatment it increased in range from 92.30-116.35 kJ/mol. This shows that as torrefaction temperature is increased from 250°C to 300°C, the activation energy also increased. Moreover, when compared the reactivity rate of raw and torrefied biomass char, it shows that raw biomass char has higher rate of reaction than the torrefied biomass char. This is an agreement with Fisher et al. (2012) who found that char from torrefied biomass are less reactive than char from raw biomass. A table 4-3 shows that the kinetic rate of raw poplar wood char is 3.43×10^{-4} sec^{-1} however torrefied poplar wood char (250°C) is 1.88×10^{-4} sec^{-1}.

Table 4- 3: The kinetic results of raw and torrefied wood char gasification

	Raw Poplar Wood	Torrefied Poplar Wood (250°C, 60min)	Torrefied Poplar Wood (275°C, 60min)	Torrefied Poplar Wood (300°C, 60min)
E_A (kJ/mol)	81.32	92.30	109.64	116.35
A (sec^{-1})	3.12	5.88	43.14	95.67
k(sec^{-1}) (800°C)	3.43×10^{-4}	1.88×10^{-4}	1.97×10^{-4}	2.06×10^{-4}

Figure 4-5 also shows that the kinetic rate of gasification of torrefied biomass char is lower than that of raw biomass. The difference in reactivity could be because of the changes happened during torrefaction, as the other processes are similar for both raw and torrefied biomass.

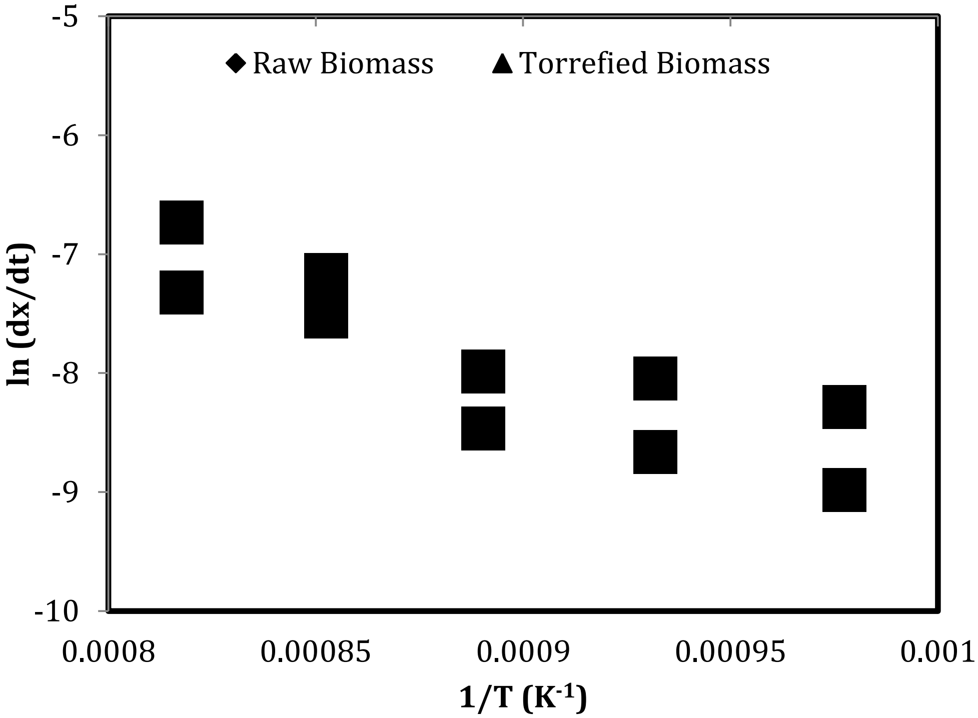


Figure 4- 5: Arrhenius plot for gasification reaction of torrefied (250°C, 60min) char from biomass and raw or untorrefied biomass (time in sec)

During torrefaction, which is characterized by slow heating rate, the volatiles find sufficient time to undergo condensation on pore walls of char forming secondary char. This is more prominent in larger size biomass similar to that considered in this study (Dhungana, 2011). For this reason the char yield from torrefied biomass after devolatilization is around 13% higher than that from the raw biomass, which confirms the formation of secondary char. Fisher et al. (2012) found secondary char formed during torrefaction has lower reactivity. So, gasification of torrefied biomass involves less reactive secondary char and generally more reactive primary char. Therefore, the overall reactivity of torrefied biomass during gasification is lower than the raw biomass. Furthermore, the smaller size of torrefied biomass heats up faster with longer residence time at peak temperature compared to raw biomass which forces the torrefied biomass to lower reactivity (Fisher et al., 2012).

Figure 4-6 and Figure 4-7 shows the mass conversion rate and influence of torrefaction temperature and residence time on gasification process. Figure 4-6 shows the conversion during the low gasification temperature (700-850°C) and there is some deviation in mass loss however at the higher temperature (900-950°C), the nature of the conversion is almost the same and is shown in Figure 4-7. These two figures show that the mass loss of raw is higher than the torrefied poplar wood, however the nature of the curve for all the biomass is same. This is in agreement with Fisher et al. (2012) that the global gasification mechanism was not affected by the torrefaction of biomass.

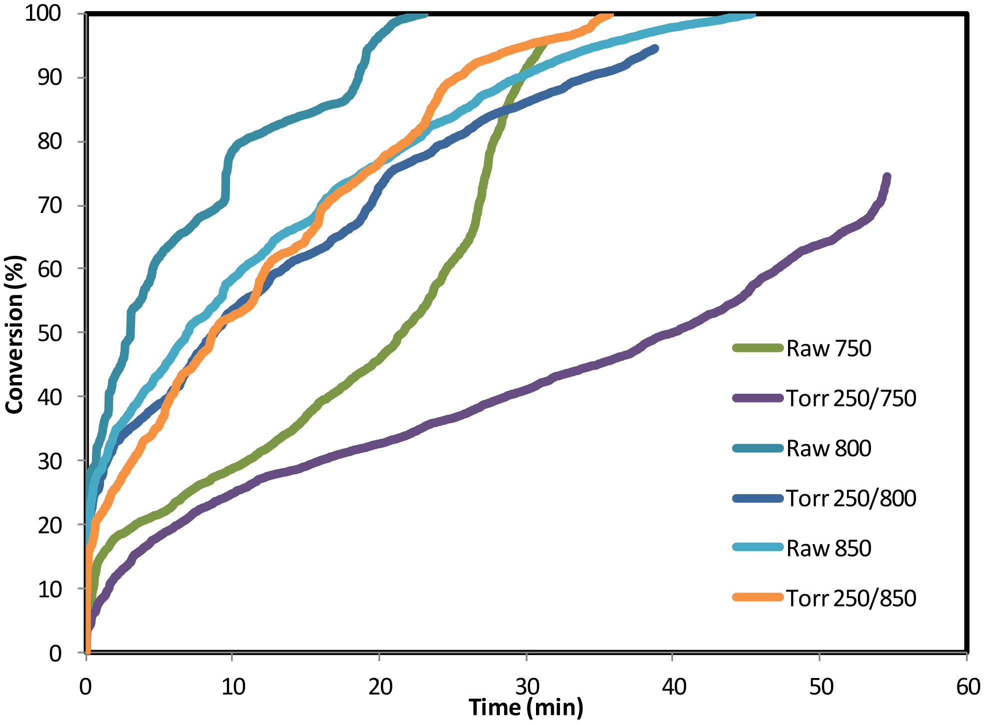


Figure 4- 6: Mass conversion vs time during gasification of raw and torrefied (250°C, 60min) biomass char

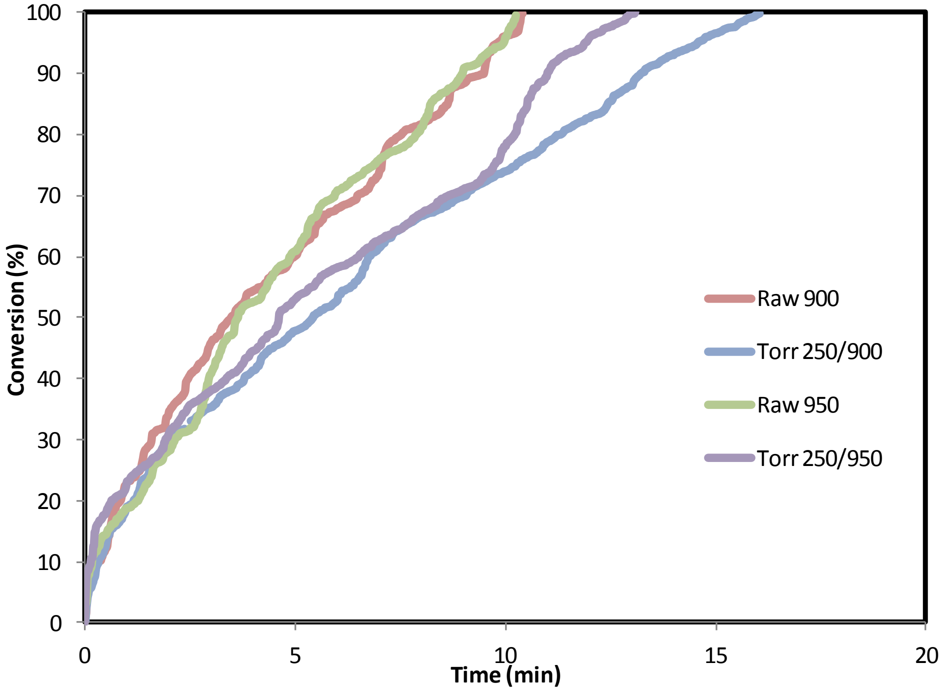


Figure 4- 7: Mass conversion vs time during gasification of raw and torrefied (250^{o}C, 60min) biomass char

Furthermore, each raw and torrefied biomass char sample is found to have its own conversion rate curve and this different rate of conversion are due to the difference in their pore characteristics.

4.3.2 Scanning Electron Microscope Analysis

This section discusses the structural change that take place during torrefaction and devolatilization of the wood. Present work was done with Poplar which is a hardwood. Figure 4-8 shows the artist's sketch of fibers of a typical hardwood. A major characteristic of hardwood is large open pores or vessels with diameters of 20 to 30 micron size (Reed, 2002, pp-51) as we see that in the sketch on Figure 4-8. Now when we compare it with the scanning electron microscope (SEM) micrograph of raw Poplar wood (Figure 4-9) we do not see this easily. The micrograph has ×3000 magnification. Images were taken at various magnifications ranging from ×200 to ×10,000. Images were taken from both axial and longitudinal direction of the poplar sample. Micrograph of raw biomass along the axis of the sample shows great many fibers but no holes. No cellular structure as in the sketch could be detected from the more than 10 SEM micrographs taken at various points and magnification of the raw Poplar wood.

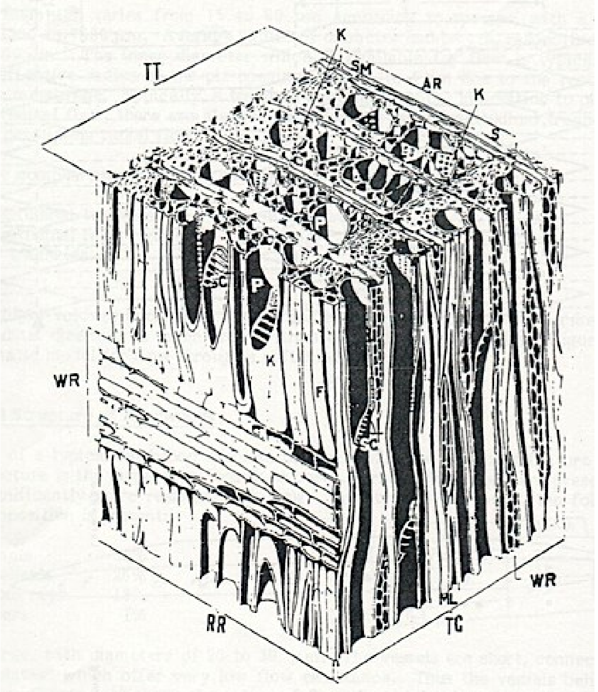
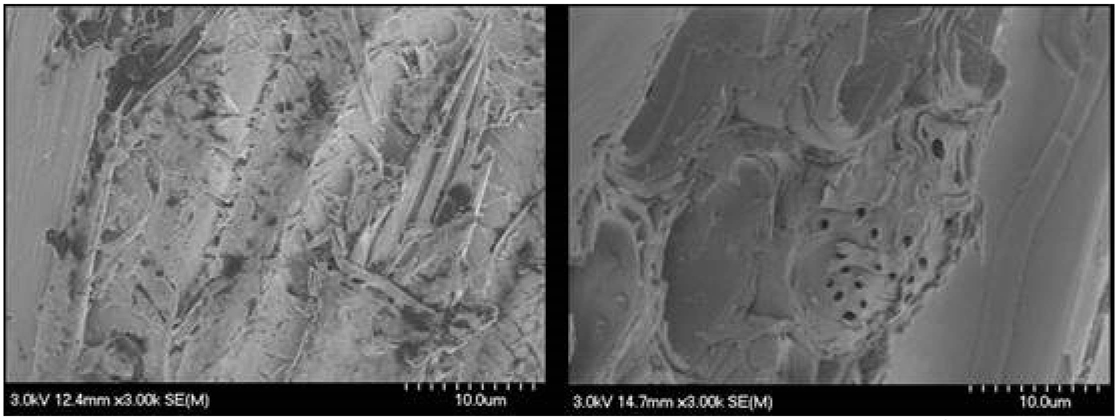


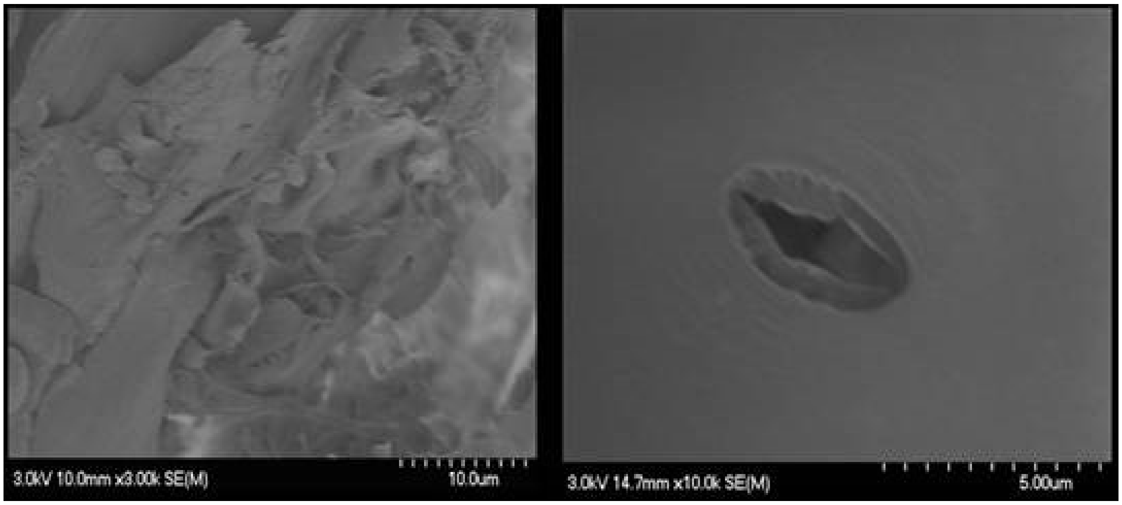
Figure 4- 8: Artist's rendering of structure of a typical hardwood (Adapted from Reed, 2002, pp-II-53)

Figure 4-9 compares the scanning electron microscope (SEM) micrographs of raw poplar with that of torrefied samples of the same poplar wood sample. SEM of the same sample after torrefaction showed many holes, some very large and some small. SEM micrograph taken at different points of the torrefied wood sample showed the same structure with holes. A closer inspection shows some layers forming around the inner walls of the pores. These are probably the deposition of char during the process of torrefaction.



[Raw Biomass] [Torrefied Biomass: 250°C, 1hr]

Figure 4- 9: SEM micrographs of raw and torrefied biomass taken parallel to the axis



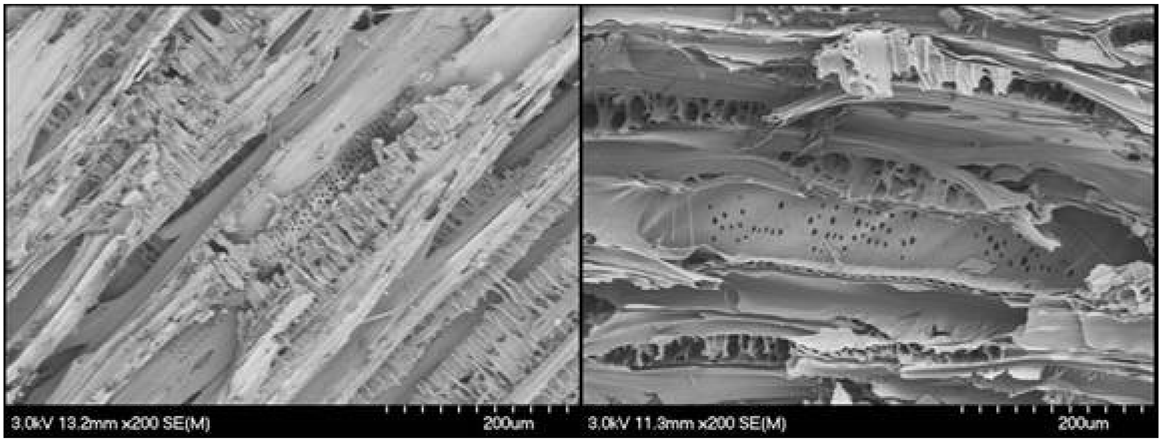
(a) Images of torrefied sample taken normal to axis (b) Closer images of one of the holes in torrefied sample

Figure 4- 10: Additional SEM micrographs of torrefied poplar

Here, it can be seen that the raw biomass is more fibrous in nature. But as it is torrefied, we note distinct change in the structure of the same wood (Figure 4-9). The fibrous structure is broken down into a structure with increased pores. These pores are created by the volatiles as they escape from the biomass interior during torrefaction. Such increased pore area could speed up the process of gasification after devolatilization. Chen et al. (2011) suggested that the volume of pores with diameter 20-100nm increased after torrefaction of the biomass, which in turn resulted in improved syngas quality and cold gas efficiency over those for raw biomass during gasification. Luo (2011) also found that the number of opening on the surface of the biomass has increased after the torrefaction. These additional pore walls serve as site for the char reaction. Thus one expects higher reaction surface areas for a given mass of char. Therefore, a torrefied wood should have higher gasification rate.

Several micrographs including Figure 4-10 (b) shows that the inner wall of the pore appear to be lined with a coating. This could be char deposited on the pore wall due to secondary char reaction. Some of the pores are very large and some as fairly small.

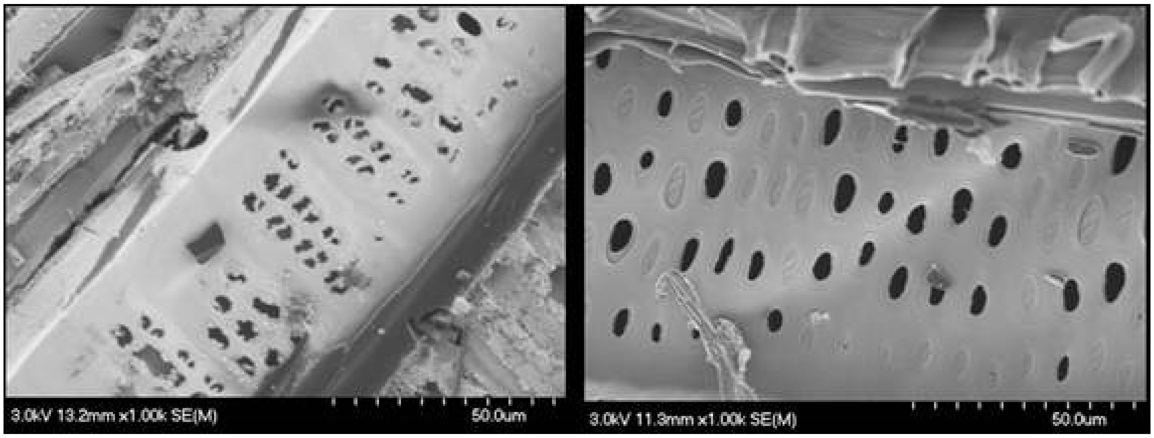
From the micrograph of raw biomass, it is confirmed that the characteristics of raw biomass is amorphous and heterogeneous however the surface morphology and porosity is changes after devolatilization (Zhu et al., 2008). Char produced from devolatilization of raw biomass was analyzed through SEM micrograph at different magnification starting from 200 to 10,000. Following figures shows SEM micrographs of the sample looking axially into the sample. This is a cross-section across the fibers. At 200 magnifications we see some visible pores and fibers (Figure 4-11). At higher magnification (Figure 4-12), it is visible that the pores sizes to consistently increases in photographing size without revealing any additional fine pores around it.



[Raw Biomass Char] [Torrefied Biomass Char: 250°C, 1hr]

Figure 4- 11: SEM (×200) micrographs of raw and torrefied poplar wood char at 800°C

During the devolatilization of biomass, the chemical bonds of the biomass break which allow breaking the fibrous structure and create the pores. Both SEM in Figure 4-11 shows vessels or large pores with pits or small pores on walls of the vessels. Images taken at higher magnification (Figure 4-12) including one at 30,000 magnification do not reveal any more details than what is seen with 200 magnification (Figure 4-11). Analysis of char from raw and torrefied (250°C) biomass showed both have similar pores (Figure 4-12).



[Raw Biomass Char] [Torrefied Biomass Char: 250°C, 1hr]

Figure 4- 12: SEM micrographs (×1000) of pore developments in raw and torrefied poplar wood char at 800°C

Therefore, the pore characteristics and reactivity of char depends on the temperature, pressure, heating rate during devolatization process (Dutta et al., 1977). From these two SEM micrographs, it is apparent after devolatilization that raw biomass still retains their fibrous nature and retains their original shape whereas torrefied biomass breaks into smaller particles (Figure 4-13). This happened due to complete dissolution of hemicelluloses during torrefaction.

Figure 4- 13: Images of char produced at 800^{o}C from raw (left) and torrefied (250^{o}C, 1hr) (right) biomass

The measurement of pore diameter of char is difficult because of micro and macro sizes. Smaller size of pores could make more reaction surface available initially. Thus one would expect faster conversion of char into gases during the initial stage of gasification. It can be seen from the mass loss history measured in QWM reactor. So, the difference in pore size is not significant. This observation is different from those of Luo (2011). The slight increase in pore size could be responsible for very small difference in product gas composition. Thus one cannot account for the difference in reactivity based on difference in pore sizes.

The observed difference in reactivity must be related to the formation of secondary char, which is less reactive. Moreover, torrefied biomass requires longer time to burnout compared to the raw biomass (Fisher et al., 2012) though torrefied biomass char has larger pores. Present experiment also showed lower reactivity for torrefied biomass char. So, answer to the observation that reactivity of raw biomass char is higher than that of torrefied biomass char is not tenable from pore size difference. So, it is necessary to find the answer somewhere else. Fisher et al. (2012) through their detailed study showed that the secondary char produced during the torrefaction has reactivity lower than that of primary char produced during devolatilization. This reduced reactivity of secondary char contributes to reduce the overall reactivity of torrefied biomass when gasified with steam. Lin et al., (2010) speculates that char reactivity is also affected by the morphological structure, which is especially influenced by the composition of inorganic matter and the pyrolysis conditions.

4.3.3 Surface Area and Porosity Measurement

The surface area of biomass is very important, since the physical and chemical characteristics which strongly affects its reactivity and conversion properties. The surface areas of raw and torrefied biomass with char from its biomass as measured for Poplar wood samples are presented in Table 4-4.

Table 4- 4: Single point BET surface area of biomass determined by physical adsorption of nitrogen

	Surface Area (m^2/g)			
Sample No.	Raw biomass	Torrefied biomass	Raw char	Torrefied char
1.	0.0098	0.42	616.7	747.0
2.	0.0098	0.36	611.3	773.9
3.	0.0098	0.36	613.3	767.2

The surface area of raw biomass is almost zero compared to those of char because the raw biomass is more fibrous and it is also seen from the SEM micrographs (Figure 4-9). Similarly the biomass is torrefied at 250^{o}C, its fibrous characters are broken and surface area increased by about 50 times. During the pretreatment process, the biomass losses its volatile matters and increases its pores structure which was seen in the SEM micrographs.

The chars formed by devolatilization at 800°C for raw biomass increased the BET surface area by as much as 1500 times to 616.74 m^2/g. This area increase was a little higher (747.02 m^2/g) for char formed at 800°C from torrefied biomass (250°C). This small surface area was possibly due to the difference in the distribution of lignocellulose materials in the char particles. To verify these surface areas, the same analysis is carried out on automated surface area analyzer and the results are presented below in Table 4-5.

Table 4- 5: BET surface area measured from automated surface area analyzer by gas adsorption method

	Surface Area (m^2/g)	
Sample No.	Raw biomass char	Torrefied biomass char
1.	700	820
2.	570	672

These surface areas are found similar as measured by single point surface area analyzer gas adsorption method. This automated area analyzer measured 700 m^2/g and 820 m^2/g for char made from raw and torrefied biomass respectively. The details lab reports of torrefied biomass char is given in Appendix E. This is an agreement with Dong et al. (2007) who found that surface area of char from sawdust and corn straw are 854.8 and 680.9 m^2/g respectively. The difference in the surface areas of sample 1 and 2 in Table 4-5 is due to the samples is not stable. All these samples were degassed 1-2 days before analyzed and sometimes it took more than that time. Moreover, different literatures (Sharma et al., 2001, Dong et al., 2007) found that the lowered surface area of chars supported to lower char reactivity however in this experiment it's adverse. However, the reactivity of char does not always correlate well with the total surface area of a char (Roberts, 2000). The char from torrefied biomass has higher surface area but kinetics of the reactivity shows it has lower reactivity.

4.3.4 Mass Balance of Raw and Torrefied Wood

Both torrefaction and gasification reactions involve change in solid mass. There transformation of mass from one form to another. Figure 4-14 shows this change through a process block diagram. This diagram also checks the accuracy of the experiment as it carries out a mass balance across the process. Here we note that 1.0 mass unit of raw biomass produces 0.1072 units of solid char, 0.019 mass unit of liquid tar and 0.8815 units of volatiles. When 0.1072 units of char are gasified it produced 0.0831 unit of gas, 0.0012-unit liquid tar and 0.0228 unit of unconverted solid char. It is the product distribution (in mass units) obtained after both devolatilization and subsequent gasification of raw biomass.

Figure 4-15 shows the same distribution for torrefied biomass, but adds the step for torrefaction. As anticipated, the volatile from the torrefied biomass gasification was less than that from raw biomass because the torrefied biomass had already lost some amount during the torrefaction process. Thus, char yield for torrefied biomass after devolatilization is higher than that obtained from raw biomass. This higher amount of solid char produced from the torrefied biomass confirms that during torrefaction some part of the volatiles undergoes charring action increasing the char yield compared to that obtained for direct devolatilization of raw biomass.

As indicated earlier the higher char yield in torrefied biomass is due to the secondary char reaction that occurred during torrefaction process where some of the volatiles and tar condenses to form char. Di Blasi (2009) noted that the secondary char reactivity is lower than primary char reactivity. Since the secondary char gasifies slower than primary char does in a given time, torrefied biomass produces less gas than produced by raw biomass. Because of that reason, gas yield during gasification for the raw biomass is higher compared to that from torrefied biomass (Figure 4-14 and Figure 4-15).

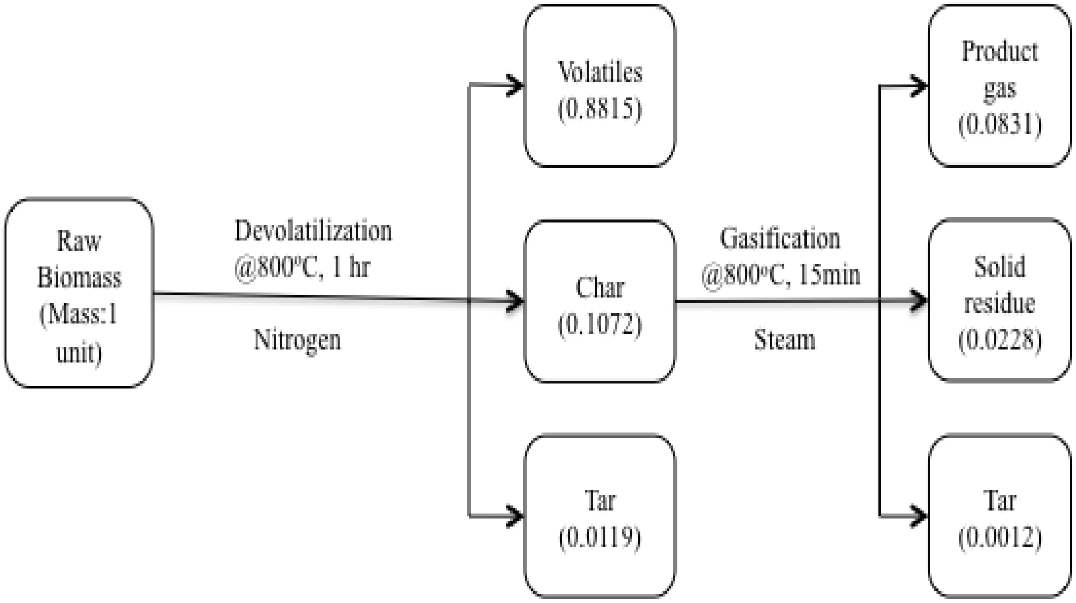


Figure 4- 14: Product distribution for raw biomass

It was noted earlier that torrefaction lowered the volatile matter of the char produced (Figure 4-14 and Figure 4-15). This being the precursor of tar, one note that tar production during gasification of this char is consequently decreased. One could therefore expect from torrefied biomass a superior quality gas, which is clean and less tar with slightly higher H_2 and CO concentration though the amount of gas per unit parent biomass may be lower.

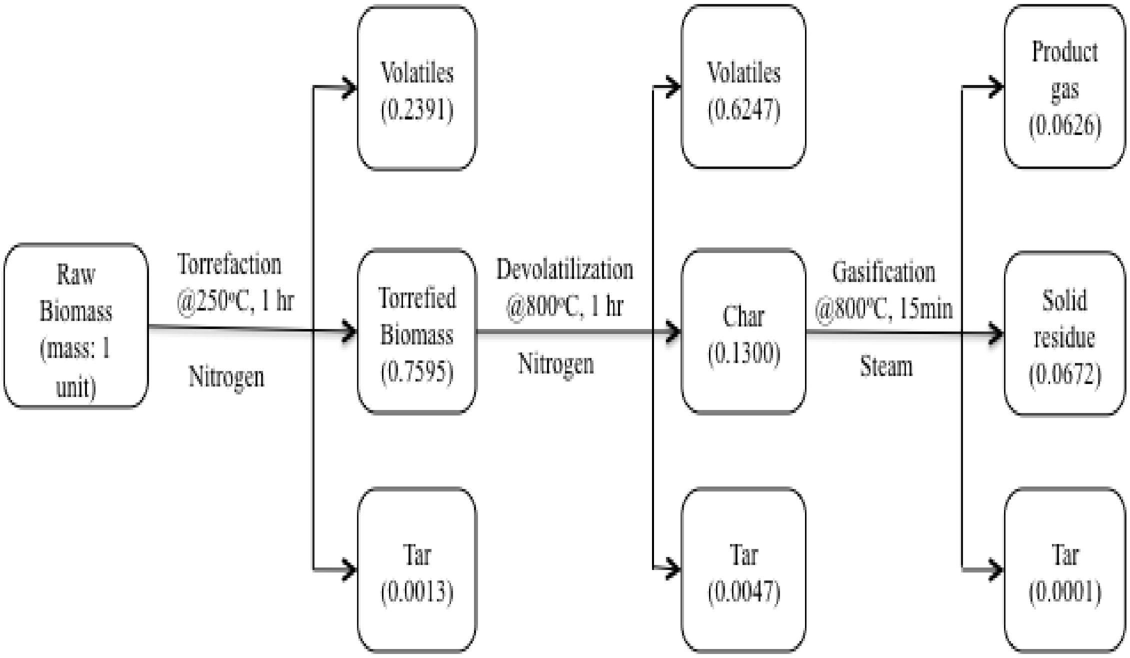


Figure 4- 15: Product distribution for torrefied biomass

The total tar yield from raw biomass during devolatilization followed by gasification is 1.31% (1.19% + 0.12%) while that from the same biomass with an intermediate torrefaction pretreatment step is only 0.61% (0.13% + 0.47% + 0.01%).

4.3.5 Product Yield during Gasification

Results of steam gasification of torrefied and raw biomass char are shown in Figure 4-16 to 4-19. It shows the composition of gas obtained over 5-minute time intervals at different periods during gasification of the raw and torrefied biomass char. In Figure 4-18, the gas yield is shown for raw and torrefied biomass, for raw biomass, the gas yield is 0.95 Nm^3/kg of biomass during the initial 5 minutes, and it dropped to 0.65 over the next 5 minutes and to 0.39 Nm^3/kg over the last 5 minutes interval. From the product gas composition obtained from the gasification of raw biomass (Figure 4-16), the hydrogen concentration at the beginning of the experiment was 43.31%, which increased to 48.51% at the end of the experiment time of 15 minutes.

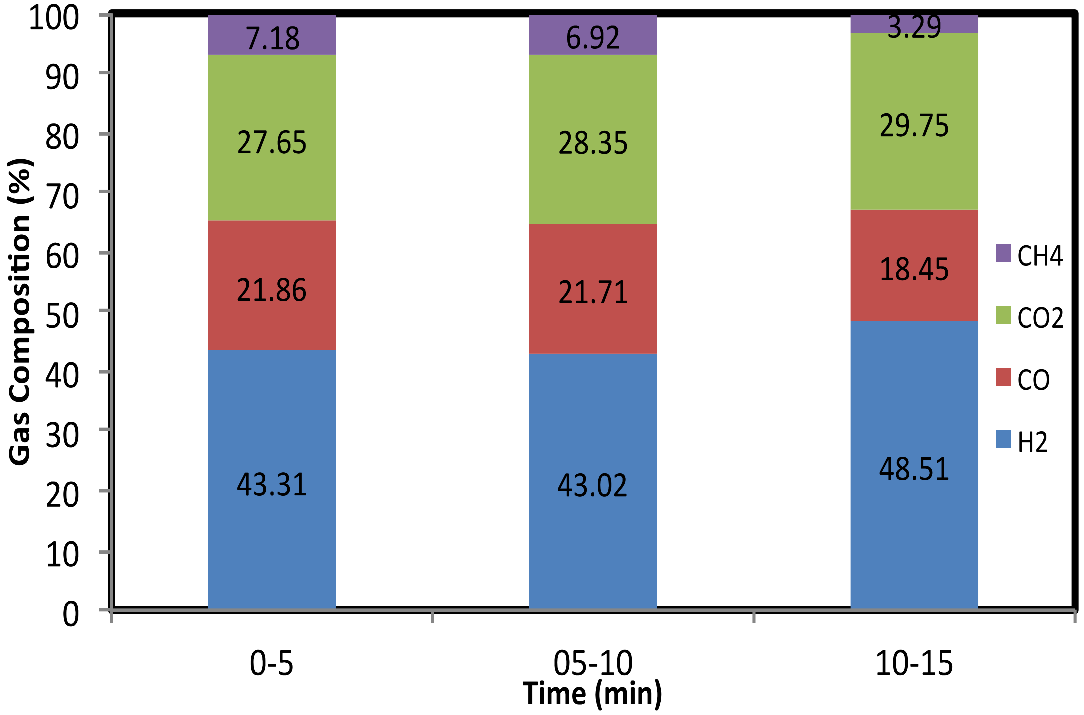


Figure 4- 16: Product gas composition of raw biomass char measured at different time intervals as the gasification progressed at the fixed temperature of 800°C.

Similarly, carbon monoxide is higher at the beginning but later on decreased during time of experiment. In case of carbon dioxide, it increased with time. The methane concentration however decreased progressively with time for the raw biomass gasification.

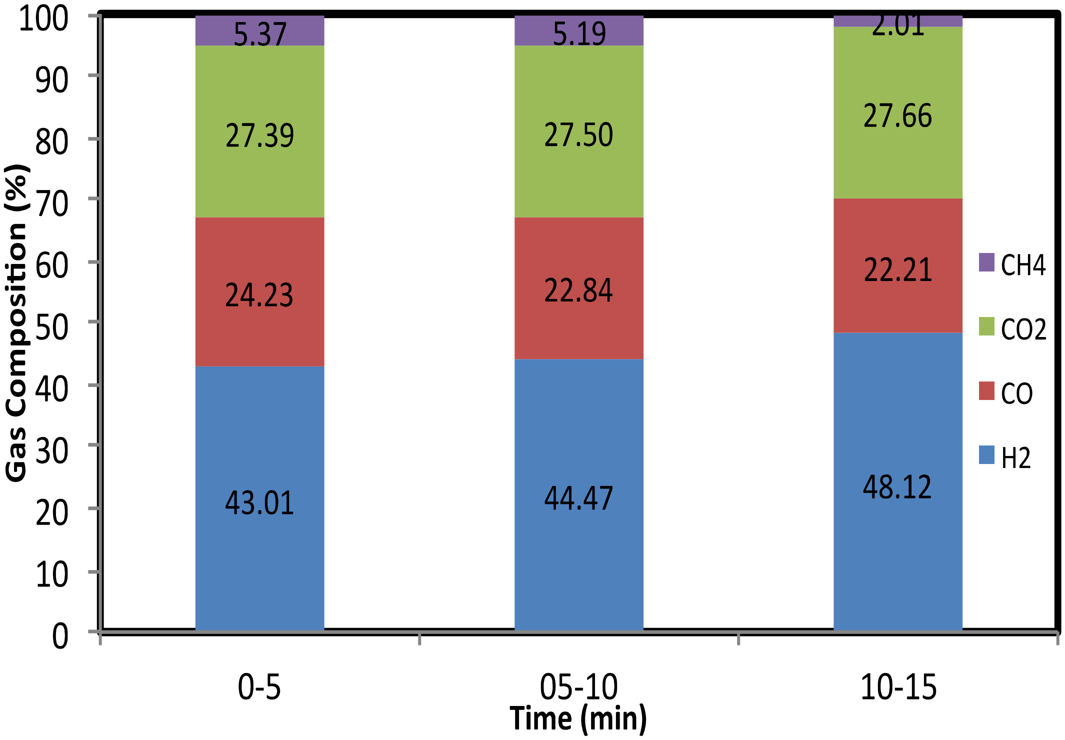


Figure 4- 17: Product gas composition of torrefied biomass char measured at different time intervals as the gasification progressed at the fixed temperature of 800°C.

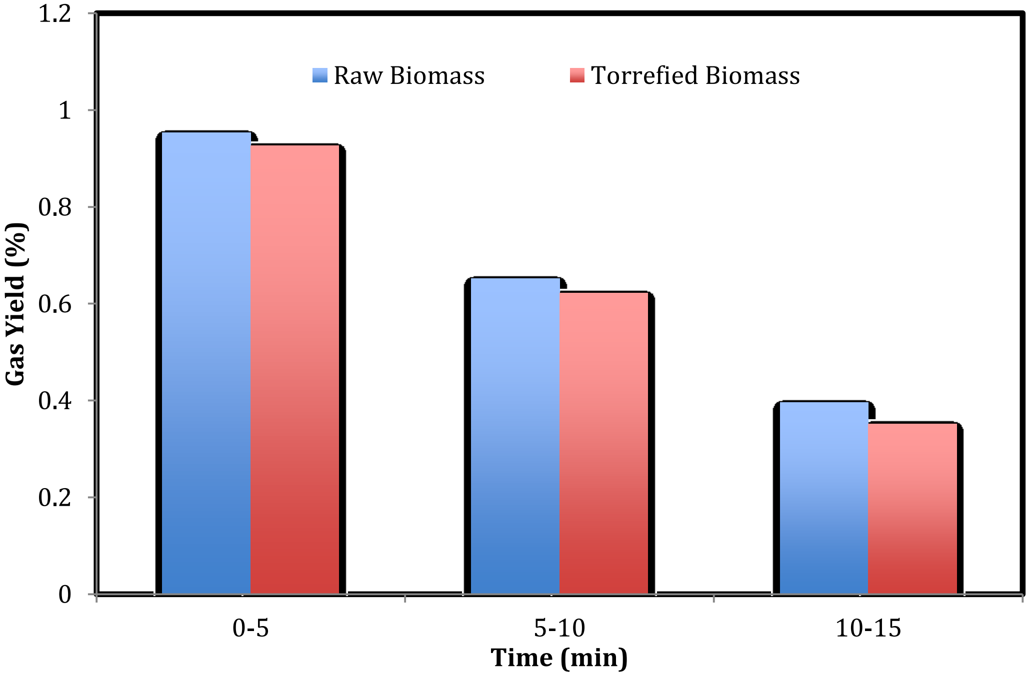


Figure 4- 18: Comparison of time resolved gas yield of raw and torrefied biomass char during gasification at 800°C

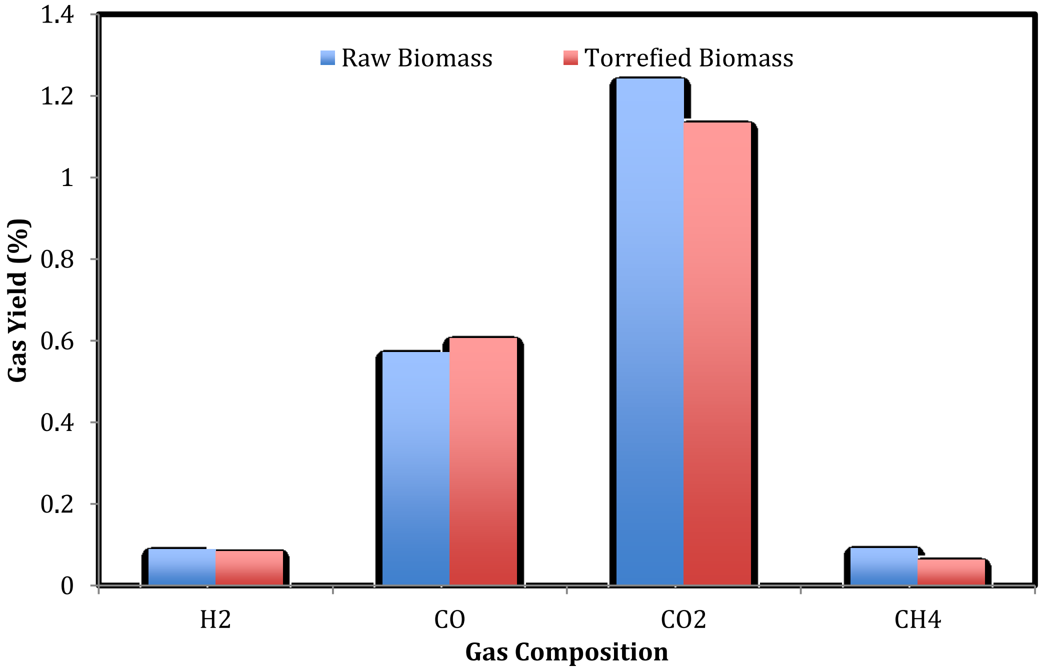


Figure 4- 19: Comparison of relative concentration of gas in gasification products of raw and torrefied biomass char at 800^{o}C

The gas yield totaled over 15 minutes is 2.00 Nm^3/kg of raw biomass char whereas it is only 5% lower at 1.89 Nm^3/kg for torrefied biomass char. The total hydrogen yield over the 15-minute period is slightly (0.5%) higher for torrefied biomass char but the CO yield of torrefied biomass char is 19 % higher than that for raw biomass char. Couhert et al. (2009) also did not see much difference in hydrogen yield, but CO from gasification of torrefied biomass was higher than that for raw biomass char. Torrefaction pretreatment reduces the moisture and oxygen level of a biomass, which lowered the oxygen-carbon ratio from 0.94 to 0.79. Reduced oxygen increases the CO concentration in the syngas as noted above that for the raw biomass char. The yield of CO_2 is also lower for torrefied biomass char compared to that for raw biomass char for reduced oxygen in the feed stock. Couhert et al. (2009) noted only very small change in CO_2 yield between raw and torrefied biomass.

4.3.5.1 Discussion of Gasification Reactions

Following section briefly describes the potential reaction occurring during gasification of char produced from raw biomass and torrefied biomass. For convenience reactions mentioned in Chapter 1 are reproduced here without changing the equation numbers.

$$\text{Fuel} = \text{Char} + \text{Gases} + \text{liquids} \tag{1.1}$$

$$\mathrm{Char} \rightarrow \alpha_1\mathrm{CH_4} + \alpha_2\mathrm{H_2} + \alpha_3\mathrm{CO} + \alpha_4\mathrm{CO_2} + \alpha_5\mathrm{H_2O} + \alpha_6\mathrm{char} + \alpha_7\mathrm{ash},$$
$$\textstyle\sum_i \alpha_i = 1 \tag{1.2}$$

where $\alpha_6$char is the unconverted char

$$\mathrm{C} + \mathrm{H_2O} \rightarrow \mathrm{CO} + \mathrm{H_2} \quad \text{Water gas primary reaction} \tag{1.3}$$

$$\mathrm{C} + 2\mathrm{H_2O} \rightarrow \mathrm{CO_2} + 2\mathrm{H_2} \quad \text{Water gas secondary reaction} \tag{1.4}$$

$$\mathrm{CO} + \mathrm{H_2O} \rightarrow \mathrm{CO_2} + \mathrm{H_2} \quad \text{Shift reaction} \tag{1.5}$$

The initial stage (when the sample temperature is around 400^{o}C-600^{o}C) of the 800^{o}C gasification process (0-5 minute), mostly involves pyrolysis where volatiles are released according to reaction (1.1). The volatile gases consist of condensable gases that produce tar and non-condensable gases. The non-condensable gases are mostly carbon dioxide, but due to the presence of steam some of the hydrocarbon may undergo reformation to hydrogen and carbon monoxide. In the later stage of gasification, mostly the char gasification reaction (1.3) and the shift reaction (1.5) occur. Among these reactions, char gasification reaction (1.3) being slow, controls the conversion process.

In case of raw biomass as the carbon monoxide is produced through reaction (1.3). The reaction (1.5) converts some part of carbon monoxide into hydrogen and carbon dioxide. This increases the concentration of hydrogen and correspondingly decreases the concentration of carbon monoxide. Midway through gasification, the carbon dioxide production is highest because of the reaction (1.3) and (1.5). However in case of torrefied biomass, the carbon monoxide concentration remains higher than that for the raw biomass but the corresponding hydrogen concentration is slightly higher in raw biomass. During torrefaction O/C ratio decreases, so at the reduced oxygen concentration, partial oxidation of carbon will result in more CO along with the CO produced from the reaction (1.3) (Chen et al., 2011).

Table 4-4 shows the composition of the product gas averaged over the entire time of the experiment. It shows higher H_2 and CO for torrefied biomass with lower carbon dioxide concentration. The concentration of methane is lower (4.19%) in the product gas for torrefied biomass, which implies that most of the carbon in biomass is converted into CO and CO_2. This confirms that chemical reaction kinetics in gas phase is almost same (Couhert et al., 2009). The heating value of product gas is marginally lower for torrefied biomass as compared to raw biomass as feedstock owing to lower amount of CH_4.

Table 4- 6: Average gas composition in the product gas from the gasification

	H_2 (%)	CO (%)	CO_2 (%)	CH_4 (%)	Gas Yield (Nm^3/kg of biomass)	LHV (MJ/Nm^3)
Raw Biomass	44.95	20.67	28.58	5.80	2.00	10.65
Torrefied Biomass	45.20	23.09	27.52	4.19	1.89	10.35

4.3.6 Heating Value of Product Gas

Figure 4-20 shows the change in the heating value of the product gas over three time periods during the gasification of raw and torrefied biomass char. The heating value of the product gas lies between 11.14 and 9.74 MJ/Nm^3. From Figure 4-20, it can be seen that the heating value of the gas obtained from gasification of both raw biomass and torrefied biomas decreases with time and reach nearly the same value at the end of 15 minutes. During the first two periods heating value of products gas from gasification of char from raw biomass is higher than that from torrefied biomass. As most of the volatiles with lower energy value are selectively released during the torrefaction process, the product of its gasification has lower heating value compared to that from raw biomass.

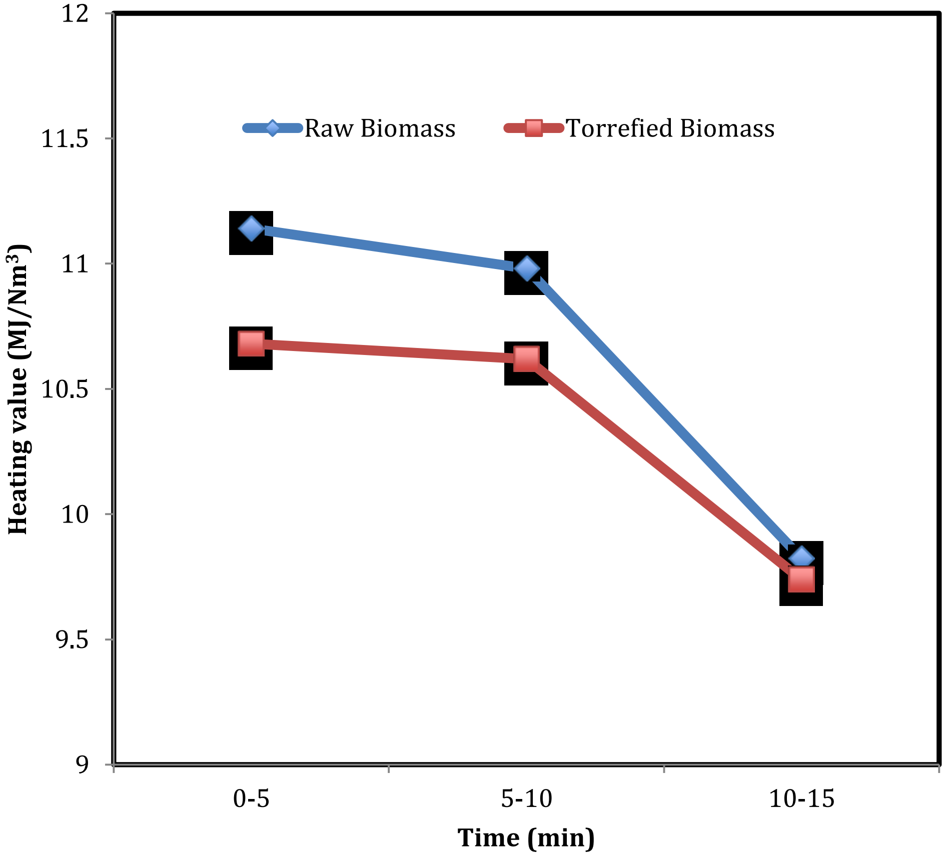


Figure 4- 20: Variation in lower heating value of product gas obtained from raw and torrefied biomass gasification

Subsequently, the gasification process involves gasification of the char. For this reason heating values of product gas generated during the later part of the gasification process is similar between raw biomass and torrefied biomass. This is the reason that the two curves, raw and torrefied biomass (Figure 4-20) have similar shape and meet at a point. Moreover, Table 4-4 confirms that the raw biomass has higher gas yield than torrefied biomass for gasification. However, this observation is inconsistent with the results of Kuo et al. (2013) who found that torrefied bamboo produces more syngas but the energy content of the product gas per unit volume changes only slightly.

4.3.7 Tar Analysis of Raw and Torrefied Wood

Lignocellulosic biomass's structure is made up of cellulose, hemi-cellulose and lignin. During gasification these constituents produces tar. Phanphanich and Mani (2011) found that due to high moisture and high hemi-cellulose and lignin in the biomass produce more tar in syngas than that produced by cellulose alone. This confirms that lignin has a higher tar yield and produces more stable components in tar due to its molecular structure (Yu et al., 2014). The present work measured tar from gasification of chars from both raw biomass and torrefied biomass to examine if torrefaction pretreatment has any positive or negative impact on tar release during gasification. Table 4-5 shows the measured amount of gravimetric tar obtained from gasification of this feedstock. It also shows the effect of torrefaction temperature on the tar production during gasification of the char.

Table 4- 7: Amount of tar obtained while gasifying raw and torrefied biomass

	Raw Biomass	Torrefied Biomass		
		250^{o}C/60min	275^{o}C/60min	300^{o}C/60min
Tar (mg/g of raw biomass)	10.12	6.39	4.27	3.08

It can be seen that tar from torrefied biomass char is clearly lower than that from raw biomass char and torrefaction temperature influences the tar yield. Sweeney (2012) also found 66% reduction in tar yield of gasification for dark roasted torrefied biomass as compared to raw biomass when gasified in a bubbling fluidized bed gasifier. Higher the torrefaction temperature, lower is the tar yield during gasification.

Figure 4-21 plots the tar yield (measured by Yue et al, 2014) of three pure polymeric constituents of biomass (lignin, cellulose and xylan (representing hemicellulose) as a function of gasification temperature. It shows that at all gasification temperature lignin has the highest tar yield. On the same graph is a cross-plotted tar yields from torrefied biomass (measured by the present work) as a function of torrefaction temperature. We note that the effect of gasification temperature and torrefaction temperature are similar.

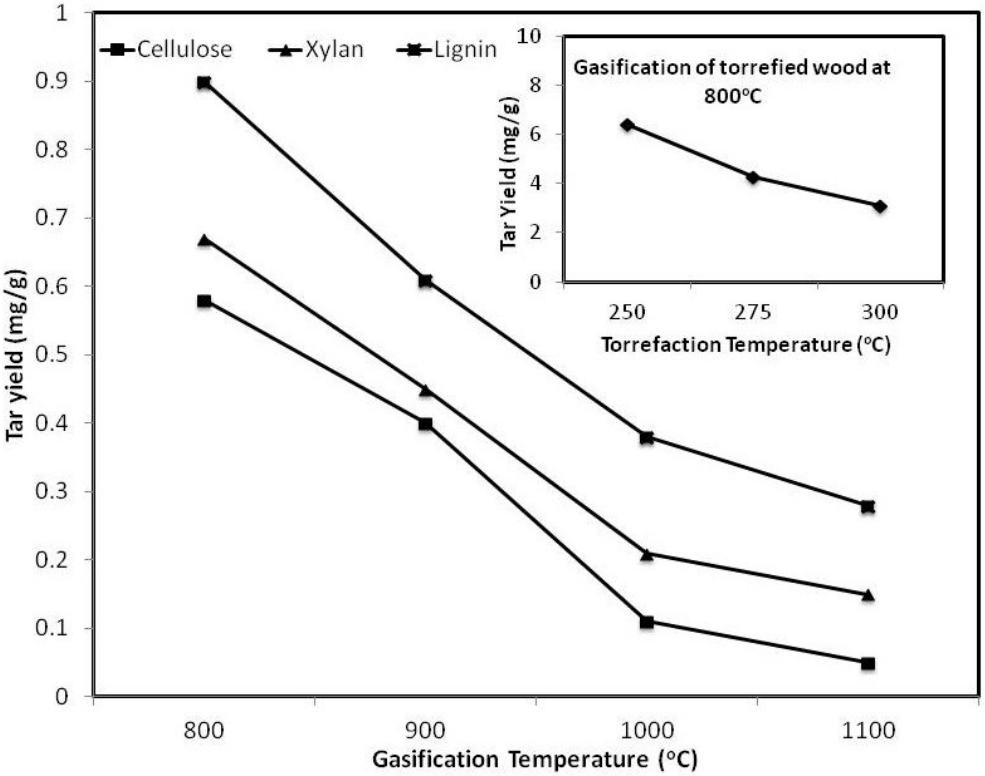


Figure 4- 21: Tar yield comparison made between present data and those of Yu et al. (2014)

It shows that the tar yield decreases with increase in both torrefaction and gasification temperature. Most of the condensable gases in biomass are released during torrefaction. As a result after torrefaction less amount of tar precursor is available in biomass. Higher the torrefaction temperature greater is the condensable vapor released from biomass (Tumuluru et al., 2011) leaving lower amounts of the same in the biomass. So, lower is the tar yield during gasification. At higher gasification temperatures tar constituents break down into smaller molecular weight gas molecules and thereby reducing the tar yield.

The torrefaction process modifies the lignocellulose structures of raw biomass and thereby minimizes the tar content. Furthermore, Prins et al. (2006) suggested that the controlled or proper temperature of torrefaction would minimize pyrolysis of cellulose and avoid tar formation. The tar content also depends on the moisture level of biomass, which would reduce during the torrefaction. Total tar in case of raw biomass was 10.1 mg/g, which dropped to 6.4 mg/g for torrefied biomass. Torrefied biomass, as seen from the above results (Table 4-5) is more suitable fuel for gasification applications from the tar yield standpoint. Lower tar content in the biomass gasification is the merits of torrefied biomass over raw biomass along with additional advantages in handling.

CHAPTER 5: BUBBLING FLUIDIZED BED REACTOR

The foregoing discussion of data from batch gasification in QWM reactor gives a micro view of the process. Data presented in this chapter from continuous gasification in a bubbling fluidized bed (BFB) gives a macro view of the process.

For good understanding of the overall process of gasification with torrefaction pretreatment, it is important to understand properties of biomass after torrefaction. So this chapter first discusses results of torrefaction pretreatment of raw work and then the results of gasification of the same in BFB gasifier.

5.1 Analysis of Torrefied Biomass

The torrefaction process is mostly influenced by temperature and residence time. It also depends on the composition of the biomass fuels used for the torrefaction. Table 5-1 shows the mass loss during the torrefaction of poplar wood samples at 250^{o}C, 275^{o}C and 300^{o}C. This shows that with the increment of temperature, the mass losses increase. This trend is in agreement with both theory of torrefaction and experimental results of other researchers (Acharya et al., 2012)

5.1.1 Mass loss and Composition of product

The torrefied samples were measured for mass loss and analyzed for proximate analysis and higher heating values. The raw wood, torrefied at 250^{o}C and torrefied at 275^{o}C woods contained 4.64%, 2.43% and 1.9% moisture respectively and are reported in proximate analysis, in Figure 5-1.

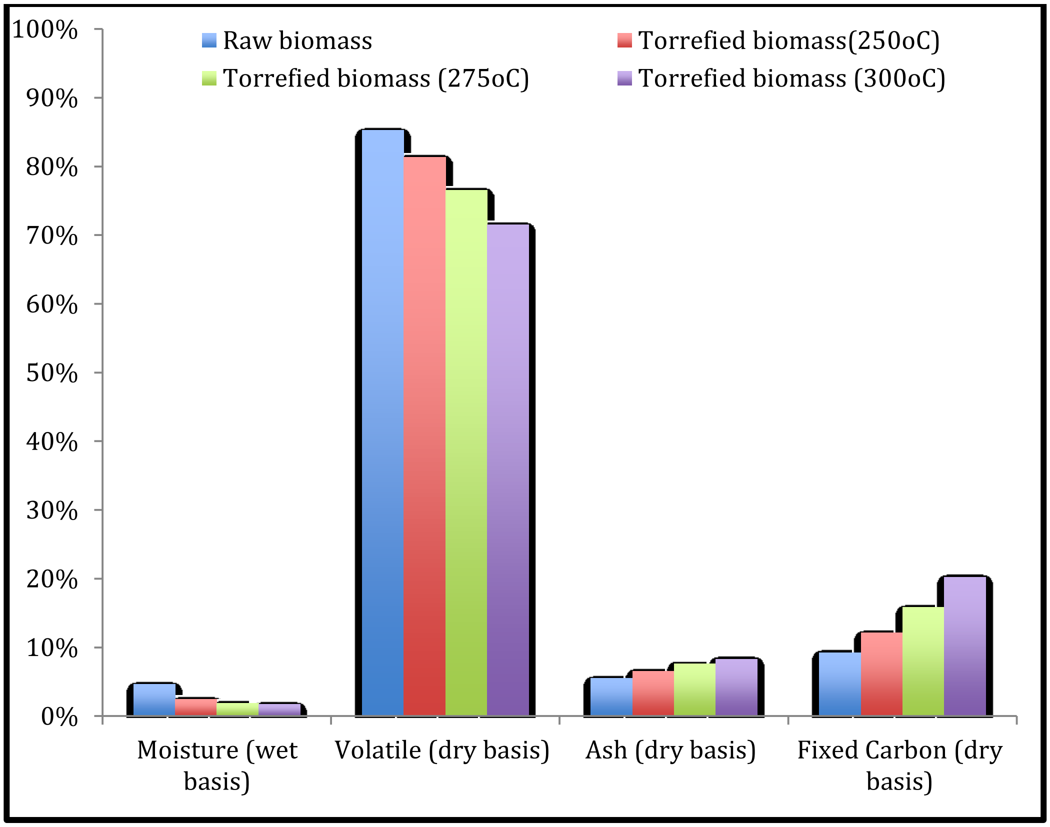


Figure 5- 1: Proximate Analysis of Fuels

The volatile matter content decreased from raw to torrefied woods from 85.25% raw to 81.35%, 76.51% and 71.48% for the torrefied wood at different torrefaction temperatures. According to Bridgeman et al. (2007), the torrefaction process increased the fixed carbon and ash contains significantly, which support the results of Figure 5-1. The biomass loses its fibrous properties after the torrefaction because of decomposition to alkanes, ketones, carboxylic acids, alcohols and other macromolecules (Chen et al., 2011). Finally, the torrefied biomass is easy to handle, minimizes the storage area and transportation cost compared to untreated biomass. Furthermore, torrefaction improves the fluidization behavior of the biomass, which is beneficial for the fluidized bed reactor (Rousset et al., 2012).

5.1.2 Heating Value of Torrefied Product

Figure 5-2 shows that the heating value increased from 18.34-20.33 MJ/kg from raw to torrefied (250°C) poplar wood. When the torrefaction temperature is raised to 300 ^{0}C, the heating value of the product increased further to 28.26 MJ/kg (Figure 5-2). This confirms that the energy density of the biomass increased by torrefaction (Prins et al., 2006a). This increment in the heating value of torrefied biomass is due to the increase in the carbon content and decrease in the volatile matter of the torrefied biomass (Figure 5-1).

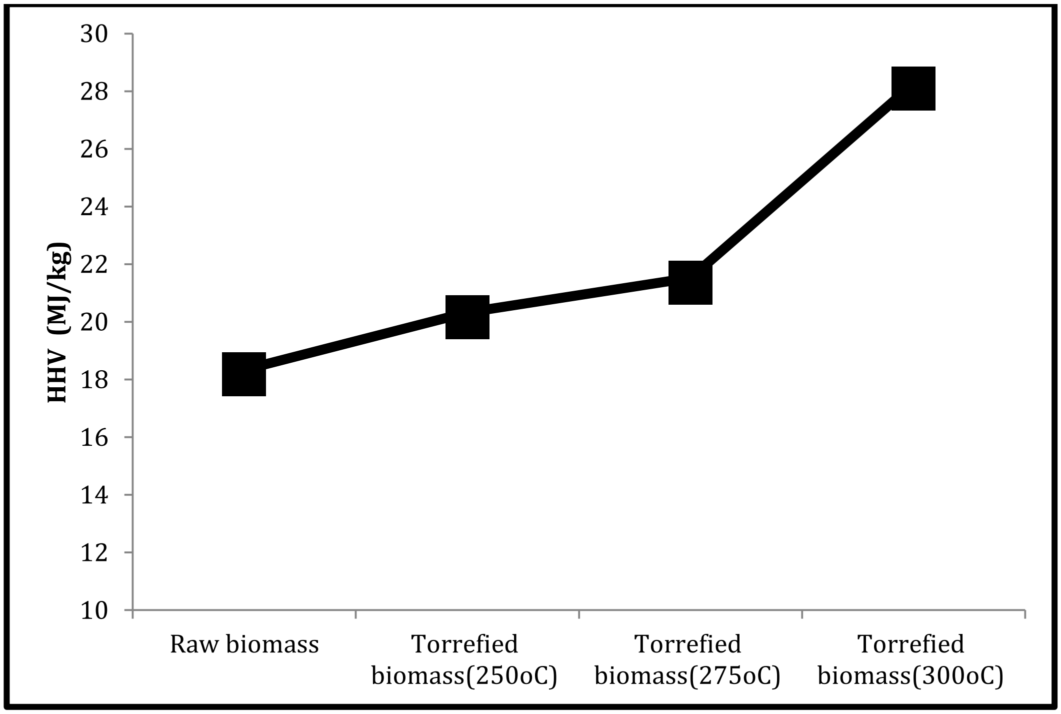


Figure 5- 2: Higher heating value of biomass

Similar effects on heating value was found by Chen et al. (2010) during the torrefaction of biomass materials, including bamboo, willow, coconut shell and wood. The torrefied biomass was uniformly darker than raw biomass when collected after torrefaction. The proximate analysis results also confirms that torrefied biomass were uniformly.

5.1.3 Mass Conversion

Table 5-1 shows the mass loss for different biomass for the residence time of one hour at torrefaction temperatures of 250°C, 275°C and 300°C. This mass loss during torrefaction shows that the loss is greatly dependent on the torrefaction temperature. This confirms that the mass loss during the torrefaction of biomass increases with the increases in torrefaction temperature. This increment in mass loss is due to the moisture and volatile matter loss in the biomass during torrefaction process. This is in agreement with Bergman et al. (2004) who found that the biomass partly devolatilizes which leads to a decrease in mass, but the initial energy content of the biomass is mainly preserved in the solid feedstock during the torrefaction process.

Changes in biomass structure also plays vital role for these losses and is directly related to the combination of three main components, hemicellulose, cellulose and lignin. According to Yang et al. (2007), the weight loss of hemicellulose mainly happens at 220–315°C and that of cellulose at 315–400°C. However, lignin is more difficult to decompose, as its weight loss happens in a wide temperature range (from 160 to 900°C). Thus hemicellulose undergoes the greatest degradation amongst all the components within the torrefaction temperature; however lignin and cellulose decomposes generally at higher torrefaction temperatures. In addition, together with hemicellulose decomposition, cellulose depolymerisation is believed to be responsible for the changes in biomass leading to a decrease of its tenacity and fibrous structure, in respective order (Bergman et al., 2004).

Table 5- 1: Mass loss during torrefaction process

	Torrefied Poplar Wood		
Torrefaction temperature (^oC)	250	275	300
Torrefaction time (min)	60	60	60
Mass Loss (%)	21.41	32.81	61.44

5.2 Gasification Analysis

The carbon content of the torrefied biomass was significantly higher than that of raw biomass shown (Figure 5-1), which affects the char production during the gasification. Due to the higher amount of carbon in the torrefied biomass, it produces a higher amount of char than raw biomass.

In the BFB gasifier, when raw biomass enters into the gasifier, it slowly starts heating and drying. After that the devolatilization process continued and volatiles came out through the gas pipelines and all the chars stayed in the bed. These chars reacted with the dry steam and produced the product gas. The same process repeated when it was fed by torrefied biomass except that less volatiles was released.

In this experiment, it was hard to take out all the char for measurement because all the char was mixed with bed material, sand and there was no easy option of removing char during the process. The product gas of gasification was, however, collected, and its properties are discussed below.

5.2.1 Product Gas Analysis

The gasification of biomass was conducted at different temperatures: 700°C, 750°C, 800°C and 850°C to study the effect of temperature on the product gas properties of treated and untreated biomass. Over this temperature range, H_2, CH_4, CO and CO_2 concentrations in the produced gas were only observed and the balance of the product gas was made up of higher hydrocarbons including ethane, ethylene and propylene were neglected. The Figures 5-3 to 5-6 show the composition of the product gas that resulted from the steam gasification of raw and torrefied biomass.

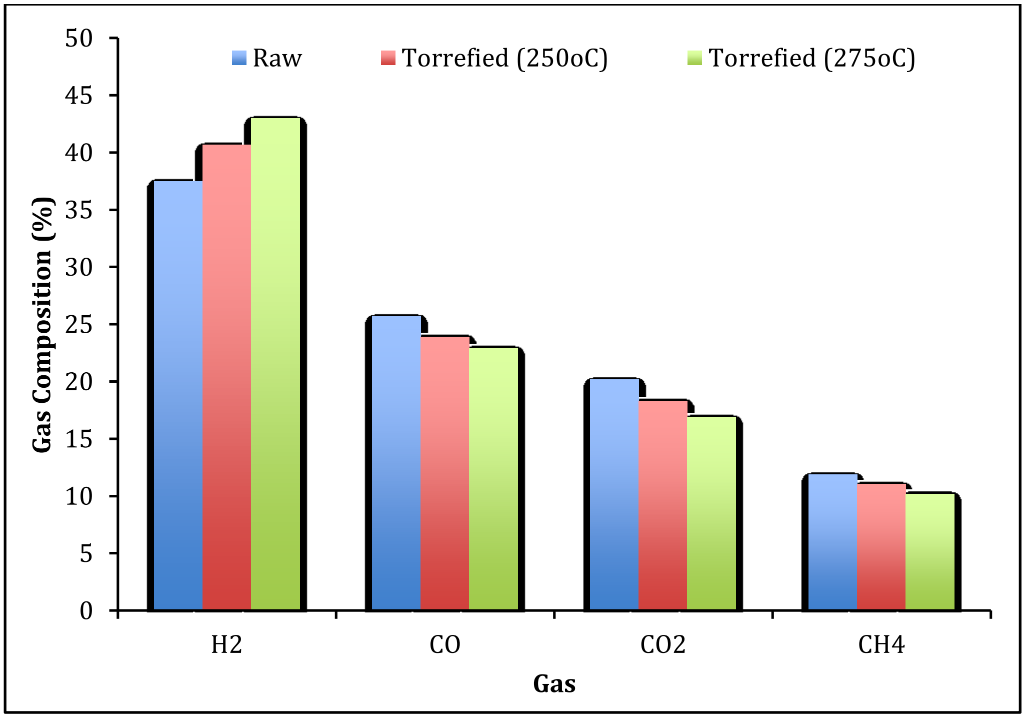


Figure 5- 3: Effect of temperature on the product gas composition from the steam gasification of raw, torrefied (250°C) and torrefied (275°C) woods at 700°C

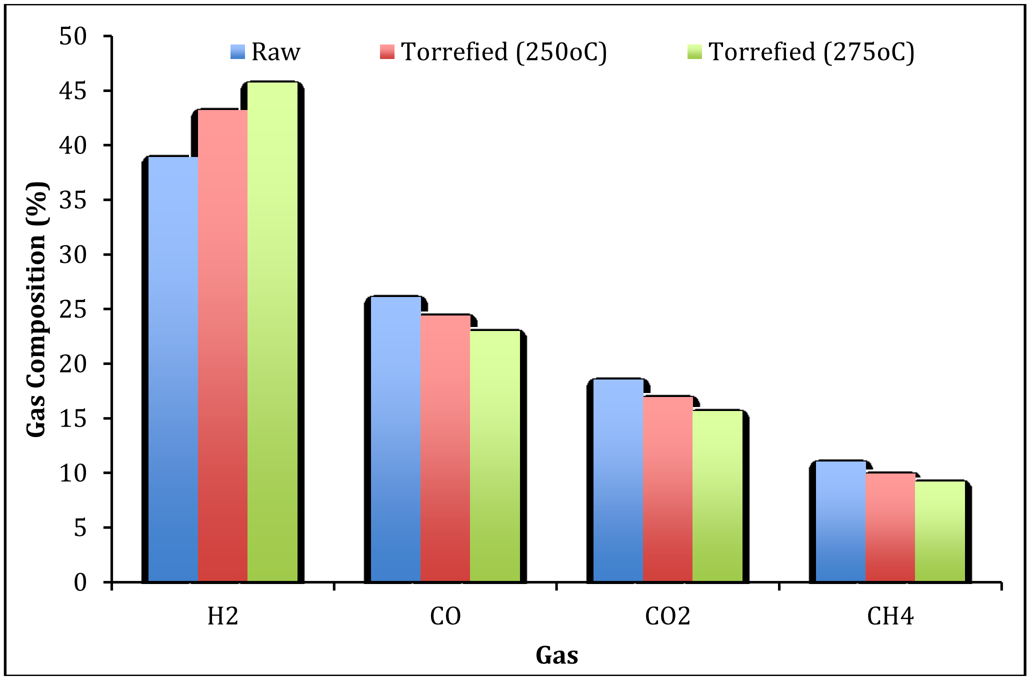


Figure 5- 4: Effect of temperature on the product gas composition from the steam gasification of raw, torrefied (250°C) and torrefied (275°C) woods at 750°C

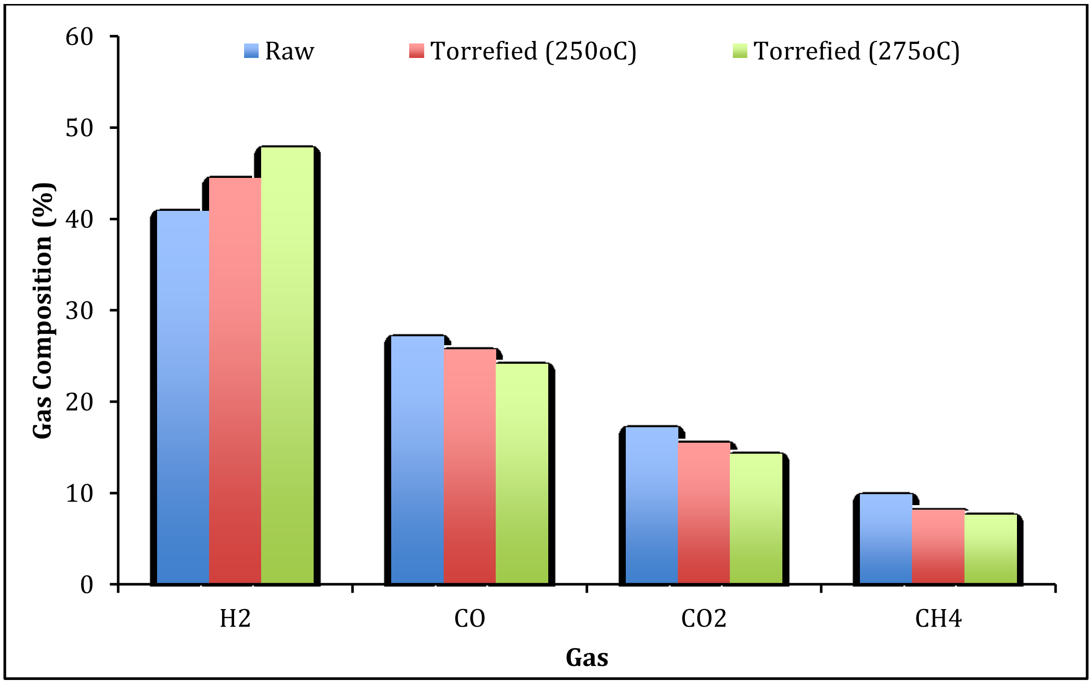


Figure 5- 5: Effect of temperature on the product gas composition from the steam gasification of raw, torrefied (250°C) and torrefied (275°C) woods at 800°C

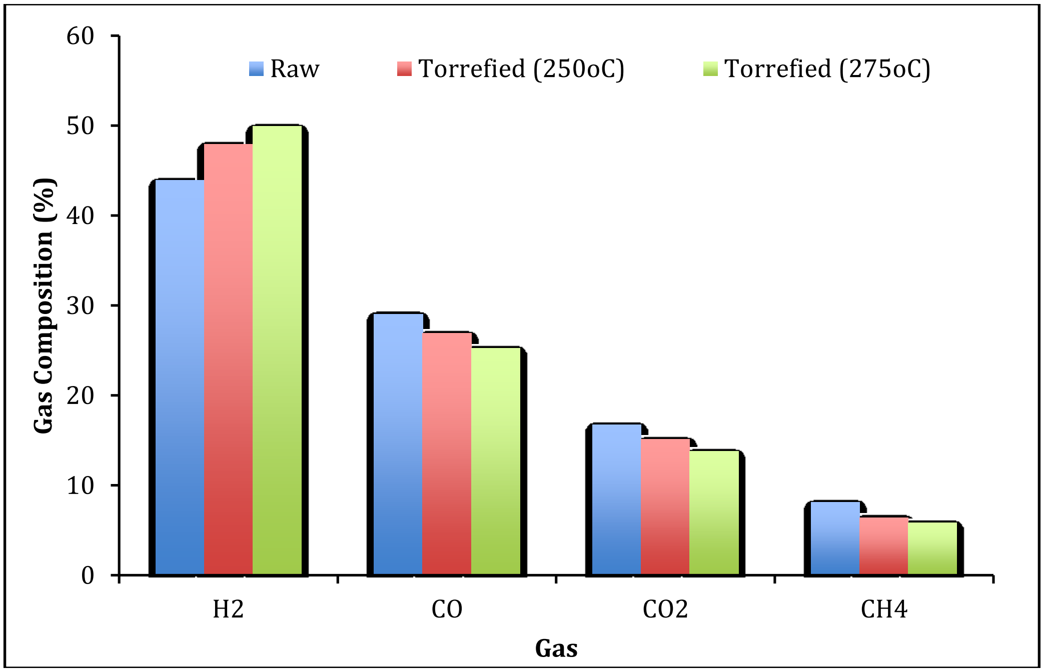


Figure 5- 6: Effect of temperature on the product gas composition from the steam gasification of raw, torrefied (250°C) and torrefied (275°C) woods at 850°C

Figure 5-3 to 5-6, show that the concentrations of H_2 from the gasification of torrefied biomass is slightly higher than that from the raw biomass. When the torrefied biomass is gasified with steam, the formation of H_2 is intensified markedly compared to that of the raw biomass, whereas the CO concentration decreases slightly. Figure 5-3 shows the raw biomass has 37.47% of H_2 whereas torrefied biomass has 40.67% at 250°C and 42.96% at 275°C, at 700°C gasification temperature. Similarly, torrefied biomass has 23.87% and 22.89% of CO which is lower than raw biomass 25.67% of CO during gasification at 700°C. However, the percentages of these gases increases accordingly for both raw and torrefied biomass and rises with temperatures. It is clearly seen in Figure 5-5 and 5-6 that H_2 and CO concentration has increased with increasing temperature. Due to the endothermic nature of the reaction (1.3), the higher gasification temperature increases the production of H_2. The above results show that the H_2 concentration increases from 37.47-43.90% for raw biomass whereas the increase is 40.67-47.91% for torrefied (250°C) biomass from 700-850°C gasification temperatures. At the same temperature, the amount of CH_4 decreased from 11.85% to 8.12% in raw biomass gasification. As the steam gasification depends on a series of complex reactions, which were presented in Chapter 1, the results of gas composition vary with the operating conditions. The decrease in methane confirms that the methane steam reforming reaction favors a higher gasification temperature and this is in agreement with Schuster et al (2001) that if the gasification temperature is more than 800°C then there is no methane production. The experimental result shows that methane content is up to 10% which is disagreement with Aznar et al. (1993) who found 1.30-1.94 vol% at 740-762°C. However, this is an indication that at lower temperature gasification, the chemical reaction is not completed. This increment in the gas is due to cracking and reformation of CH_4 by steam during the gasification.

5.2.2 Heating Value of Product Gas of Gasification

Table 5-2 compares the heating value of product gas obtained from raw biomass and torrefied biomass gasification at different gasification temperature. The heating value of product gas from raw biomass gasification is higher than that for the torrefied biomass. This is due to the fact that LHV of H_2, CO and CH_4 are 10.78 MJ/Nm^3, 12.63 MJ/Nm^3 and 35.88 MJ/Nm^3 respectively. Lower H_2, higher CO and higher CH_4 in raw biomass product gas are responsible for the higher heating value. This difference is even more significant at higher gasification temperature. The energy loss during torrefaction process resulted in lower heating value of the product gas obtained from gasification of torrefied biomass. Also as discussed in tar section, more tar is released from raw biomass char gasification as compared to torrefied biomass. Some of this tar component undergoes reformation adding more energy value to the product gas. As the tar reformation is significant at higher temperature, so the heating value of product gas is higher for raw biomass at higher temperature compared to torrefied biomass. A clear observation is found that decrease of LHV with temperature increase. The product gas LHV shows a minimum value, 11.31 MJ/Nm^3 and 10.86 MJ/Nm^3 for raw and torrefied (250^{o}C) biomass at a temperature of 850^{o}C respectively. Furthermore, it is observed that if lower heating value decreases then the hydrogen concentration will also decrease.

Table 5- 2: LHV (MJ/Nm^3) of produced gas from gasification

Biomass	Low Heating value (MJ/Nm^3)			
	700^{o}C	750^{o}C	800^{o}C	850^{o}C
Raw poplar	11.53	11.42	11.36	11.31
Torrefied poplar (250^{o}C)	11.36	11.28	10.96	10.86
Torrefied poplar (275^{o}C)	11.17	11.12	10.93	10.65

Moreover, when considering the HHV, it is increased with increasing temperature and this improvement of syngas is associated with steam-reforming reactions and char-steam reaction. Due to this higher temperature there was thermal cracking of tar and steam reforming which led to the generation of more incondensable, gaseous hydrogen and carbon monoxide (Nipattummakul et al., 2011). Whenever comparing the HHV of three different fuels; raw biomass, torrefied biomass and coal it is found that raw biomass is the lowest of the three. The HHV of raw biomass is 18.31 MJ/kg, which is lower than torrefied (250^{o}C) at 20.33 MJ/kg and coal 26.22 MJ/kg (Figure 5-2; Chen et al., 2013). This shows that the torrefaction of biomass can improve the energy density and reduces the gap between the raw biomass and coal.

From the above gas analysis, it was observed that the torrefied biomass produced superior quality gas than raw biomass during the steam gasification. In addition, Chen et al. (2011) has suggested that gasification of torrefied biomass at 250^{o}C torrefaction temperature gave the best result and improved the syngas quality as well as cold gas efficiency over raw biomass. Moreover, there is negligible amount of tar observed which was neglected in this analysis. Andrés et al. (2011) found that steam is a more qualitative gasifying agent that improves the composition of the gas from a higher hydrogen production point of view and lower tar content.

5.2.3 H_2/CO and CO/CO_2 Ratio

In the gasification, the quality of the product gas is most important and H_2 and CO are two of the most influential components in the product gas. The ratio of these two gases determines the quality of the product gas and how superior it is compared to other gaseous product. From experimental results in the above Figures (5-3 to 5-6), a comparison of the content of H_2/CO ratio between raw biomass and torrefied biomass was conducted and is shown in Figure 5-7. The H_2 /CO ratio is found to increase with temperature, mainly due to the higher hydrogen release. However, this increase in H_2 /CO ratio at 700^{o}C is lower than that observed in comparison with temperature 850^{o}C, because the rise in H_2 concentration is less at lower temperatures. Herguido et al. (1992) was also observed that increasing temperature from 650-780^{o}C, the H_2 /CO ratio also increased from 1.10-2.37 and this happened due to increase in H_2 concentration in product gas. Figure 5-3 and 5-6 clearly shows that, the concentration of H_2 are 37.38 %, 40.67% and 42.96% at 700^{o}C, which are less than 43.90%, 47.91% and 49.93% at 850^{o}C for raw, torrefied (250^{o}C) and torrefied (275^{o}C) respectively.

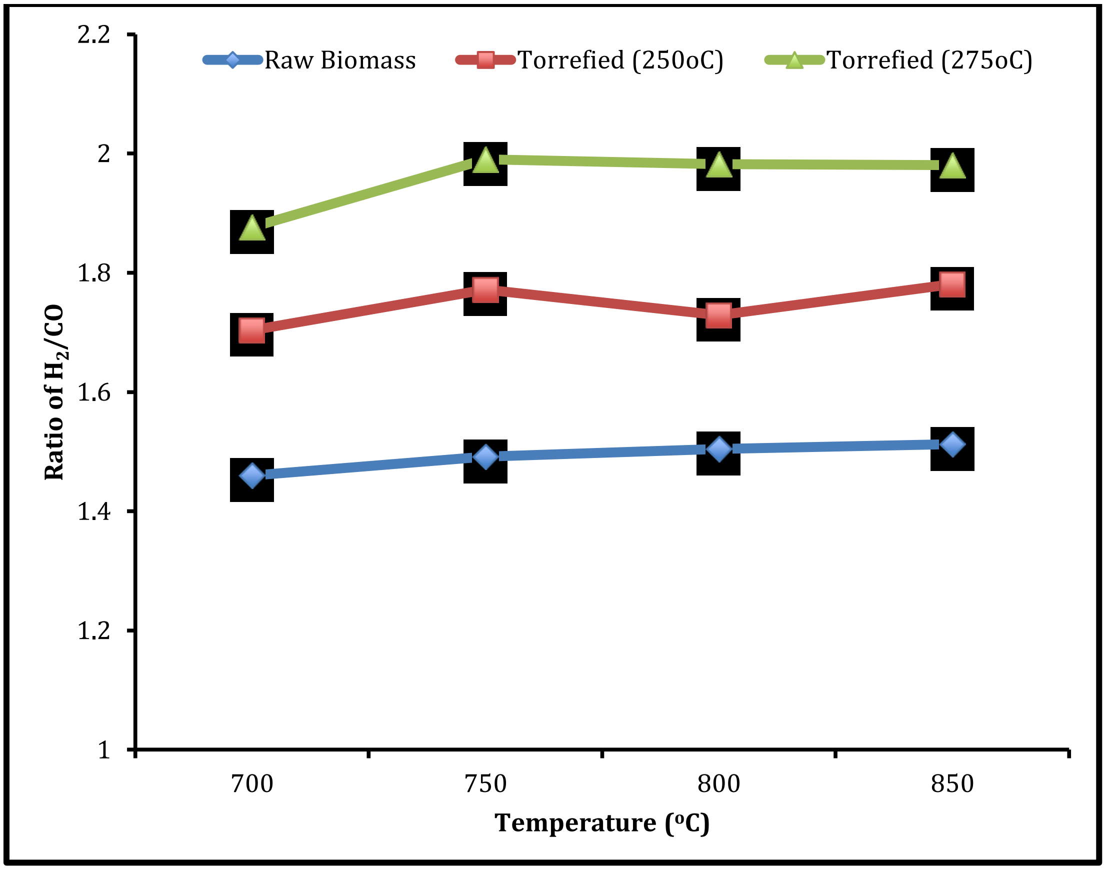


Figure 5- 7: A comparison of H_2/CO ratio between untreated and treated biomass steam gasification

Furthermore, this ratio of H_2 /CO for raw biomass is lower than that of torrefied biomass during the steam gasification. For raw biomass, that value is 1.45-1.51, while for the torrefied (250°C) is 1.71-1.78 and torrefied (275°C) is 1.87-1.98. From this analysis, it is concluded that all the gasification reactions from (1.1 to 1.5) have taken part in this process, however water- gas shift (1.5) reaction have played vital role for this increment in H_2/CO ratio. This can be explained by the fact that gas-solid reaction (1.3) are more likely to happen than gas-gas reactions (1.5) in the reactor for gasification. This also confirms that reaction (1.3) is strengthened under the condition of torrefied biomass gasification and this makes a larger yield of CO.

Similarly, Figure 5-8 shows the ratio of CO/CO_2 in the product gas. This CO/CO_2 ratio increased when the gasification temperature increased. This increment in CO/CO_2 ratio is due to the char reactions with steam. For the torrefied biomass this ratio is higher than the raw biomass. The higher ratio of CO/CO_2 strongly influences the calorific value of the product gas of the biomass steam gasification.

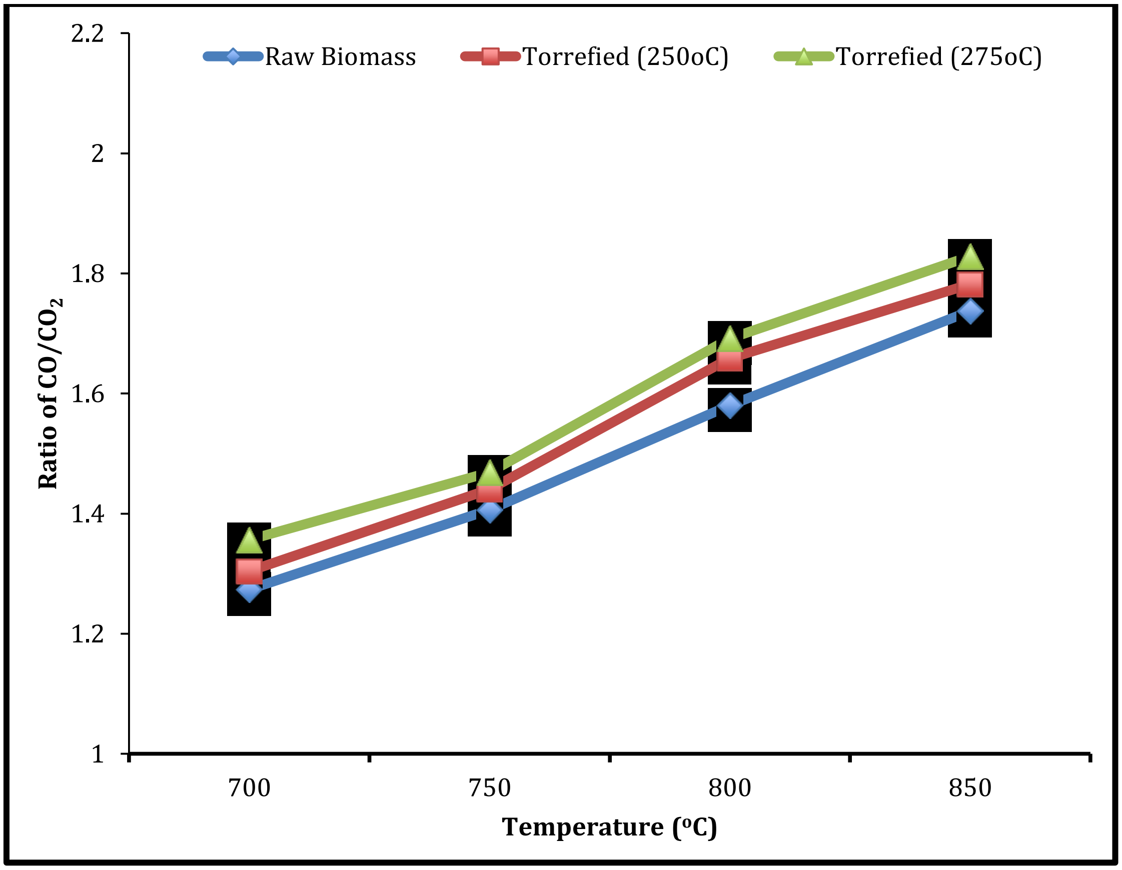


Figure 5- 8: A comparison of CO/CO_2 ratio between untreated and treated biomass steam gasification

This experimental research showed that this CO/CO_2 ratio varies between 1.27-1.73 for raw biomass and 1.30-1.78 for torrefied at 250°C and 1.35-1.82 for torrefied at 275°C biomass. This ratio also has an effect on the product gas's heating value, which is in decreasing order as the temperature increases (as showed in Table 5-2).

5.2.4 Product Gas Yield

The syngas quantity was measured during the gasification of raw and torrefied biomass steam gasification in the bubbling fluidized bed gasifier. It was measured at the different gasification temperatures from 700-850°C. Only three types of biomass were used for the gasification i.e. raw biomass and two different torrefied biomass at 250°C and 275°C torrefaction temperature. The below Figure 5-9 shows the syngas yield observed during the gasification which were measured by summing the mass flow of all the product gases.

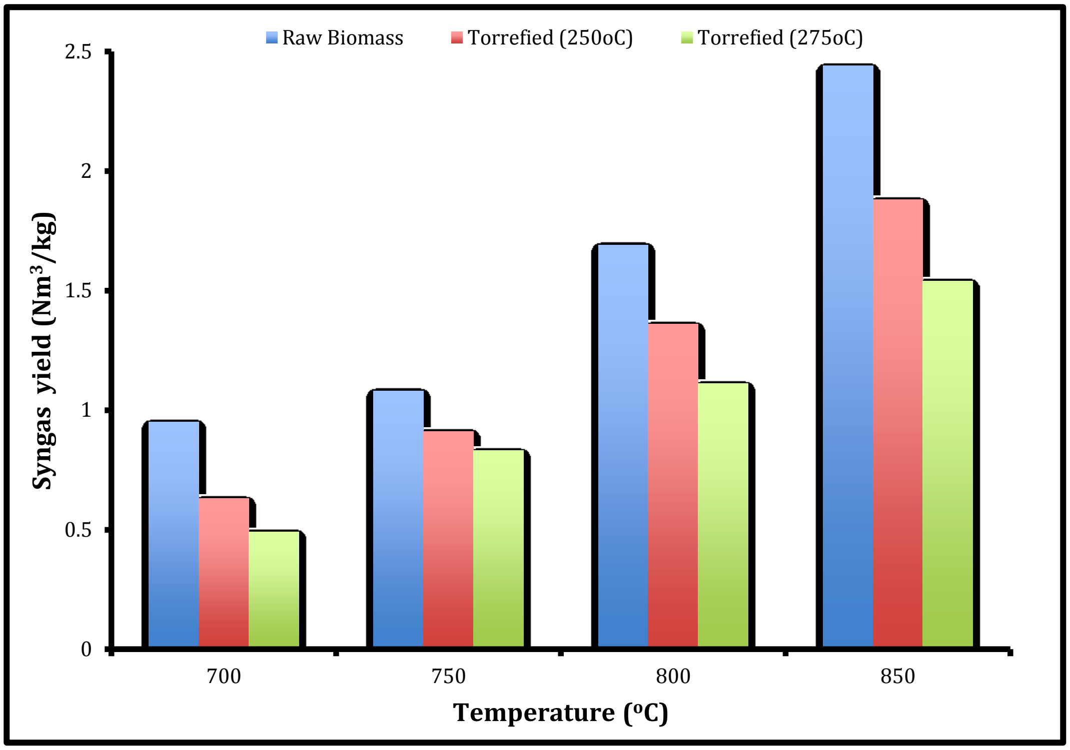


Figure 5- 9: Syngas yield comparison of raw and torrefied biomass at different gasification temperature

From this syngas yield analysis, it shows that the gas yield increased with increasing gasification temperature. This happened due to the biomass devolatilization, which is higher and faster at high gasification temperatures. At lower gasification temperature (700°C), the syngas yield is 0.95 Nm^3/kg whereas the yield is 2.44 Nm^3/kg for higher temperature (850^{o}C) for raw biomass. This increment in the gas yield shows that the higher gasification temperature improves the overall fuel conversion and it is in agreement with Gao et al. (2008).

Furthermore, notable changes are found in comparing raw and torrefied biomass gasification. The torrefaction not only affects the gas composition, it also affects the product gas yield. As seen from the above Figure 5-9, the torrefied biomass has lower gas yield than raw biomass. The product gas yield of raw biomass is 0.95-2.44 Nm^3/kg where as torrefied (250^{o}C) biomass is 0.63-1.88 Nm^3/kg and 0.49-1.54 Nm^3/kg for torrefied (275^{o}C) biomass. This reduction of product gas yield is due to the torrefaction, which was held before the gasification process. Moreover, raw biomass has higher volatiles and less fixed carbon content compared to the torrefied biomass (shown in Table 3-9), which results in higher yields of hydrocarbons and reformed hydrocarbon products, and lower yields of solid residues such as char and ash. Similarly, when considering the gasification temperature and compared these gas yields together, it was seen that higher gasification temperatures increased the product gas yield and torrefied biomass has higher gas yield at 850^{o}C than lower temperature at 700^{o}C.

However, it was found that the torrefaction temperature also affected the product gas yield. Higher torrefaction temperature lowered the product gas yield because of less volatiles and higher carbon content. When comparing torrefied biomass at 250^{o}C and 275^{o}C, the product gas yield decreased from 0.63 to 0.49 Nm^3/kg at 700^{o}C and 1.88-1.54 Nm^3/kg at 850^{o}C. From all the above discussion, it is concluded that

$$Raw\ biomass\ gas\ yield > Torrefied\ (250^oC)\ biomass\ gas\ yield\ > Torrefied\ (275^oC)\ biomass\ gas\ yield$$

CHAPTER 6: CONCLUSION AND RECOMMENDATION

6.1 Conclusions

Experimental investigation of gasification of torrefied biomass shows that torrefied biomass is a better feedstock for gasification than raw biomass. Generally, torrefied biomass is preferred over raw biomass because of improvements in storage, handling and transportation, which makes combustion compatible with that of coal, but at the time of writing it was not certain if torrefaction pretreatment is indeed a better solution for gasification. If torrefaction pretreatment enhances gasification through improved product gas quality as well as cold gas efficiency, the usages of torrefaction can expand. The study on gasification of torrefied biomass showed both positive and negative aspects of the process. The positive side is the lower tar production during gasification. This can reduce the cost and effort for downstream gas cleaning. Higher H_2/CO ratio is another positive aspect of torrefied biomass gasification. Higher H_2/CO ratio product gas with small tar content makes it very suitable for application such as biofuel production.

On the other side, the lower char conversion, which leads to lower gasification efficiency, could be a limiting factor for torrefied biomass. Kinetic studies showed that torrefied biomass has slightly reduced the gasification reactivity due to the formation of secondary char during the process. However, superior handling properties, hygroscopic and non-biodegradable nature, and an enhanced energy density could well compensate some of its limitation, and make it more suitable fuel for gasification. From the study, the following specific conclusions can be made:

1. The composition of product gas batch gasification of torrefied biomass as measured in a QWM reactor is showed slightly higher H_2 and CO but reduced CO_2 and CH_4 for that obtained from raw biomass.
2. The results from the SEM analysis shows that char from torrefied biomass have increased porosity and higher loss of fibrous nature compared to that in char from raw biomass. Gas adsorption and BET measurement confirms that pore surface areas in torrefied char is a little higher than that from raw wood char.
3. Torrefied biomass has lower tar yield during gasification compared to that from raw biomass and tar yields decreases with increases in torrefaction temperature.
4. Torrefaction reduces the moisture level, which affects the tar formation during gasification of the torrefied mass.
5. During steam gasification torrefied biomass gives lower gas yield compared to that by raw biomass. However torrefaction improves the gas quality by increasing the hydrogen than raw biomass.
6. The continuous steam gasification in a bubbling fluidized bed gasifier shows significant difference in the product gas from gasification of torrefaction treated and untreated biomass. The gasification of these raw and torrefied biomass indicated that the torrefied woods produce approximately 9% higher H_2, 7% and 9% lower CO and CO_2 than raw biomass at 850^{o}C respectively. The gasification temperature is also an influencing factor for steam gasification. With increases in gasification temperature, the heating value of the product gas is decreased. Results are similar to that noted for both gasification in QWM and BFB reactor.

7. Product gas yield of raw biomass is 22% and 36% higher than torrefied biomass at 850°C gasification temperature in the BFB gasifier. It is also found that torrefied biomass at 250°C has higher gas yield than torrefied at 275°C during steam gasification in BFB gasifier.

Overall conclusion is that torrefaction pretreatment has marginal positive improvement in product gas composition but reduced gas yield. Most important finding of the work is much reduced tar production for gasification after torrefaction pretreatment.

6.2 Recommendations for Future Research

This experimental research has only provided a basic level understanding of the effects of torrefaction on the gasification. In this research, only poplar wood was used as a feedstock and evaluated all the parameters on the basis of the same feedstock. Therefore, further study is needed on the effects of different classes of biomass. Moreover, these reactors are able to handle different kinds of solid feedstock including agricultural residue and other waste materials, which will give valuable output for torrefaction and gasification. It is also suggested to conduct BFB gasification with char from raw and torrefied biomass and compere with QWM.

Furthermore, there is a possibility to perform further experiment on large scale with different reactors. Therefore, verifying the feed and steam flow rate in the BFB reactor will be the broad area for another research. In addition, more torrefied products at different temperatures and gasification at higher temperatures will be the next steps for the consistent results for the commercialization.

During the torrefied biomass gasification in BFB reactor, tar and its composition was not measured due to the gasifier design limitations. So, it could be measured in future experiments and is possible by adding some modification in the gas lines. This will help to explore more in the field of gasification of torrefied biomass. This is the foundation work in the direction of torrefied biomass gasification and it could be further explored by developing different reactor models for torrefaction and gasification.

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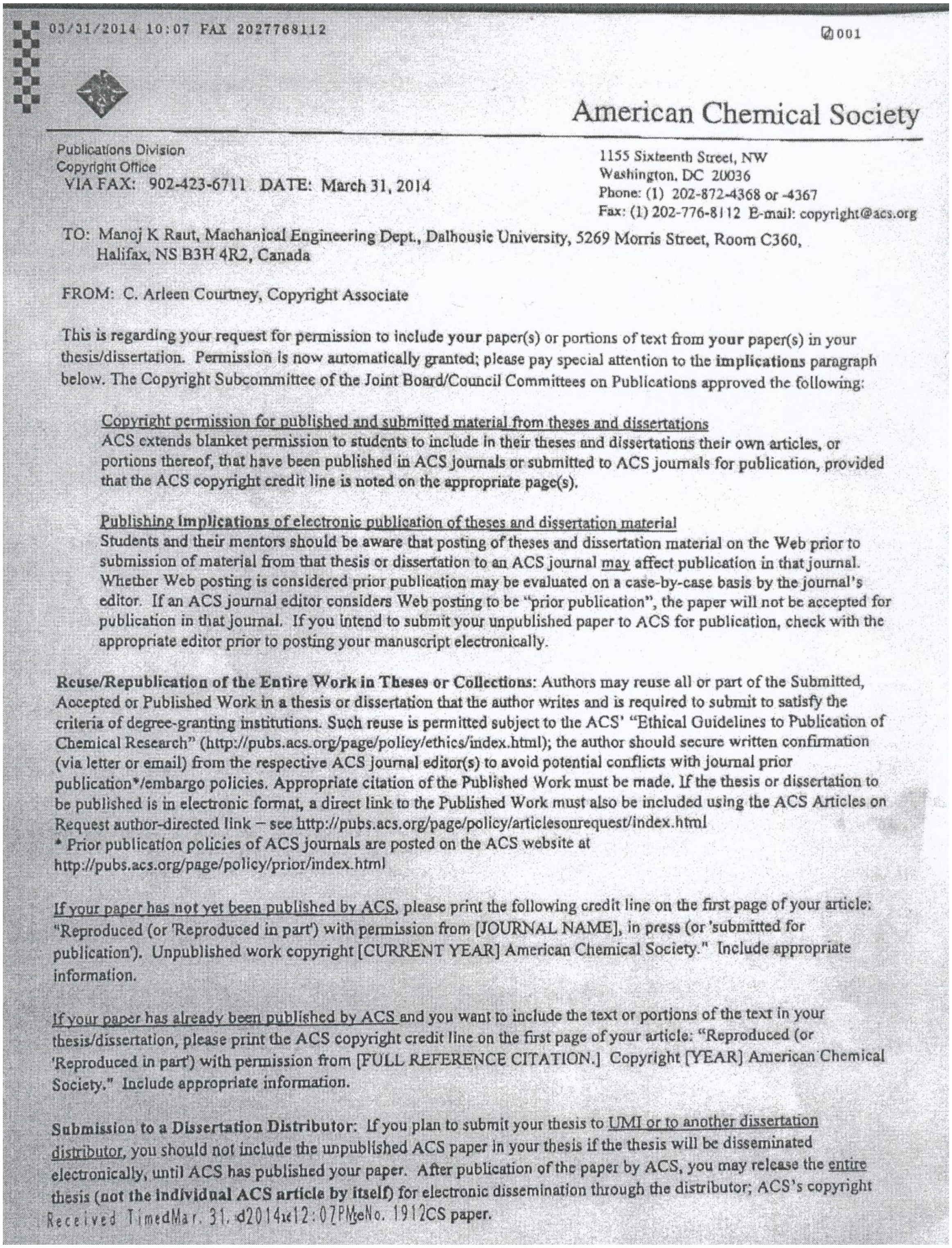

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APPENDIX B: FIGURES

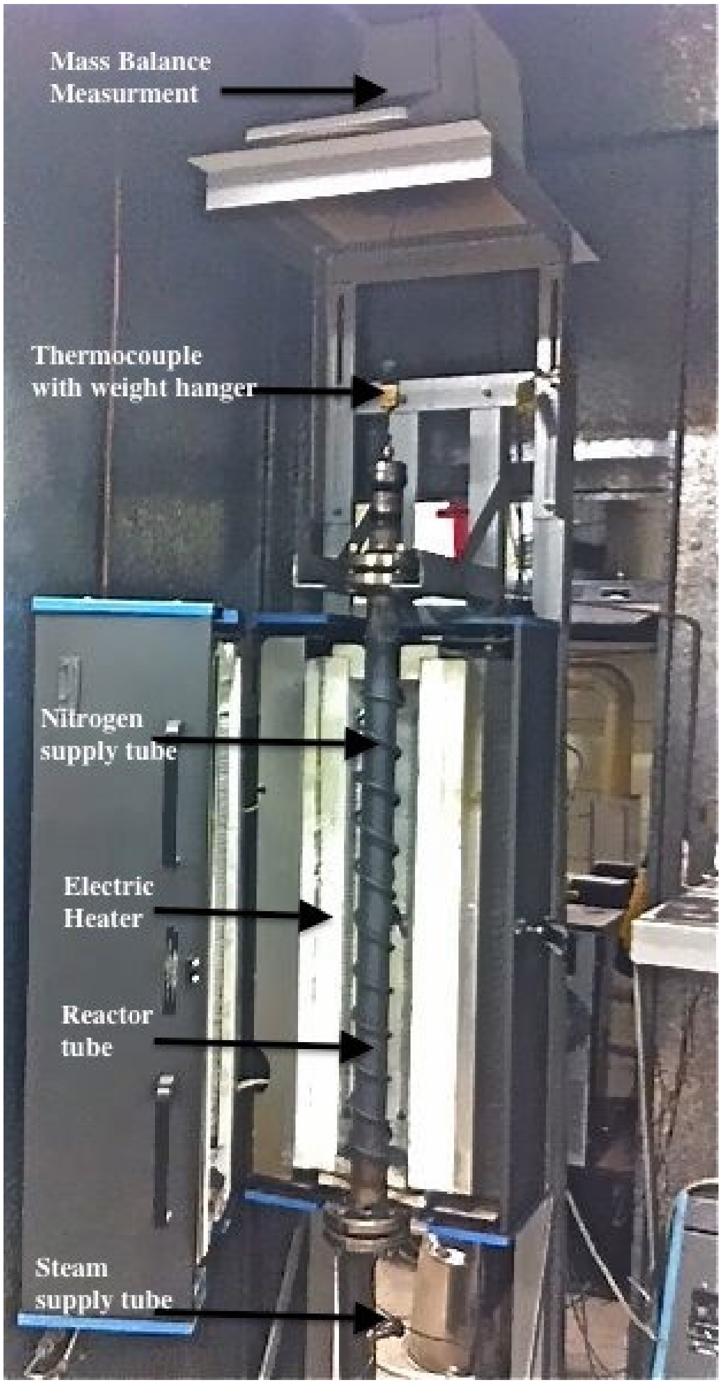


Figure B- 1: QWM Reactor

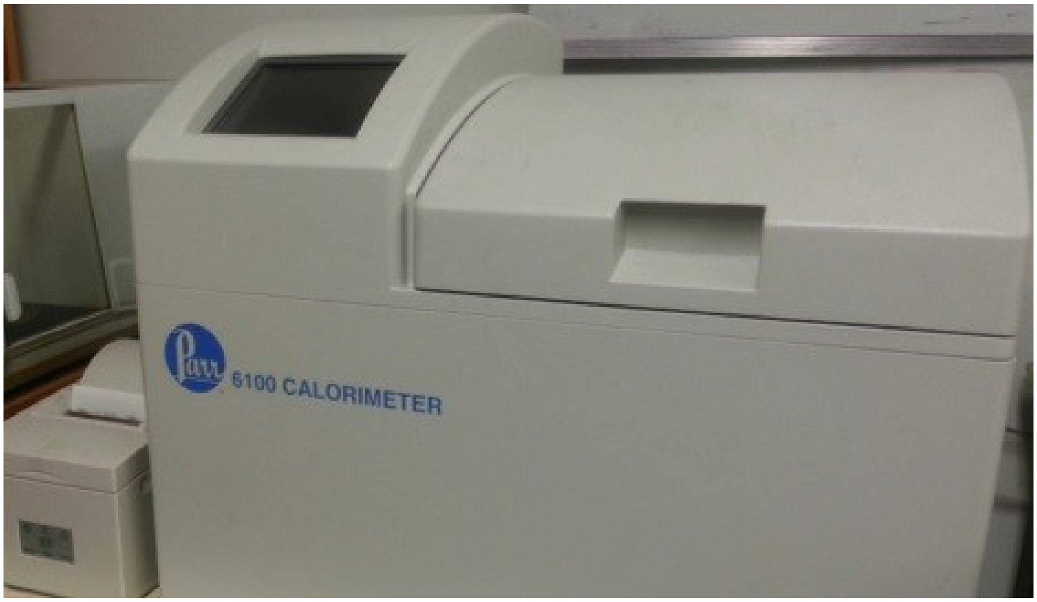


Figure B- 2: Parr 6100 Calorimeter

Figure B- 3: SRI 8610C Gas Chromatograph

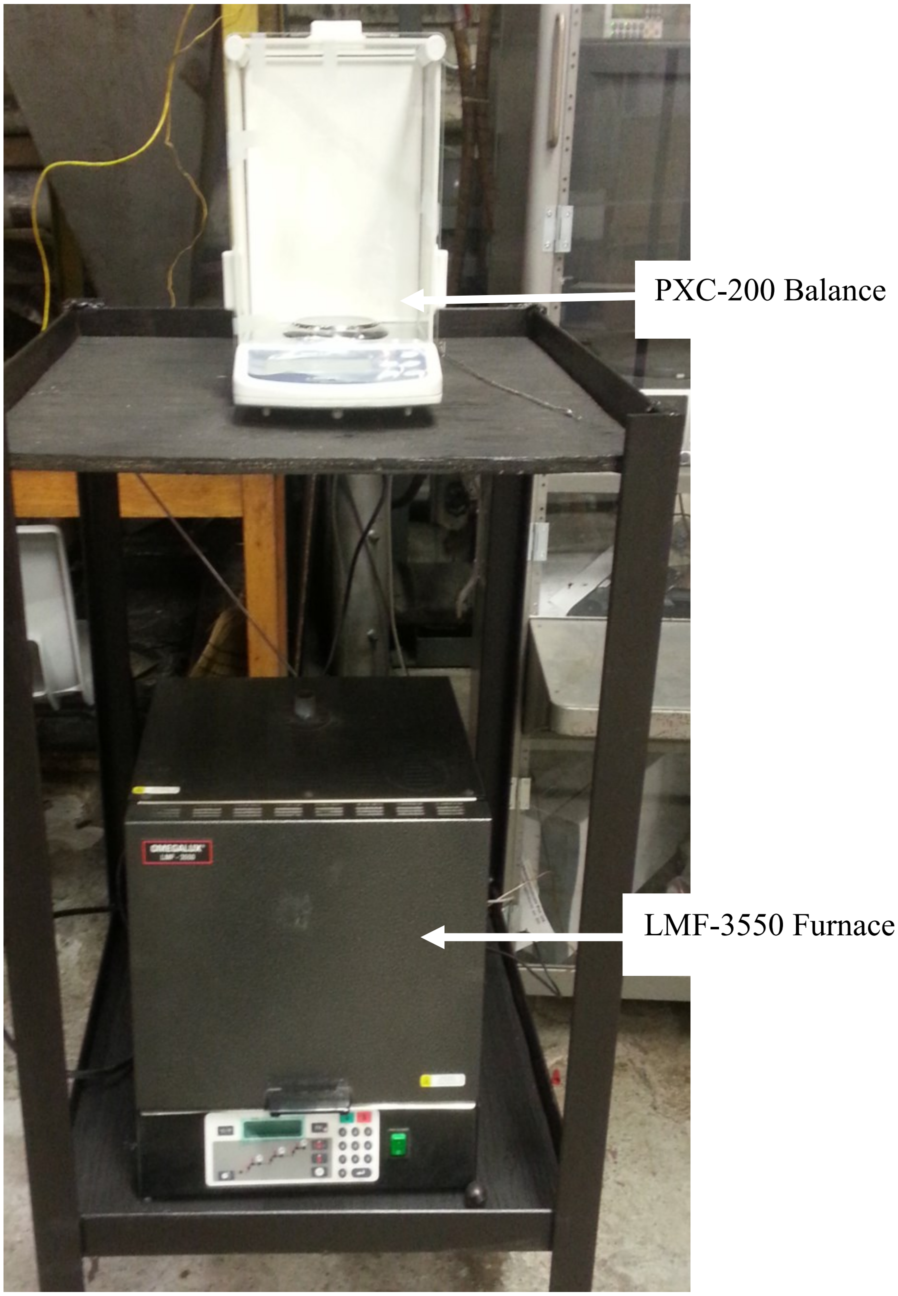


Figure B- 4: Proximate Analyzer Setup

Figure B- 5: EA 1110 Elemental Analyzer

Figure B- 6: Micromeritics Flowsorb II 2300 single point surface area analyzer

Figure B- 7: Micromeritics ASAP-2000 automated surface area analyzer

APPENDIX C: ERROR ANALYSIS

Repeatability Test

All the experiments were done 3-4 times for the accuracy however there is still some experimental and instrumental error. Some of the repeated analysis results are provided in this section.

C-1 Proximate Analysis

The proximate analysis of raw and torrefied biomass had done many times for the accuracy and the accuracy level was within 5%. This accuracy test was done with same sample, which confirmed that the composition and all the pretreatment parameter were on the same basis. This error was due to the man and machine handling and sometimes due to the environmental factor. The repeatability test results are given below in Table C-1 for the reference.

Table C- 1: Biomass proximate analysis repeatability and error test

	Raw Poplar Wood			Torrefied Poplar Wood (Torrefaction temp: 250°C, residence time: 1hr)		
Parameter	Sample No			Sample No		
	1	2	Error (%)	1	2	Error (%)
Moisture (%) (Wet basis)	4.48	4.60	2.60	2.51	2.56	1.95
Volatiles Matter (%) (Dry basis)	85.32	84.53	0.92	79.31	78.99	0.40
Ash (%) (Dry basis)	5.08	5.01	1.37	6.32	6.40	1.25
Fixed Carbon (%) (Dry basis)	9.60	10.46	8.22	14.37	14.61	1.64
	Torrefied Poplar Wood (Torrefaction temp: 275°C, residence time: 1hr)			Torrefied Poplar Wood (Torrefaction temp: 300°C, residence time: 1hr)		
Moisture (%) (Wet basis)	1.90	1.83	3.68	1.7	1.64	3.52
Volatiles Matter (%) (Dry basis)	76.28	77.01	0.94	70.69	71.57	1.22
Ash (%) (Dry basis)	7.30	7.19	1.50	8.30	8.39	1.07
Fixed Carbon (%) (Dry basis)	16.42	15.80	3.77	21.01	20.04	4.61

C-2 Biomass Ultimate Analysis

Biomass ultimate analysis was carried out on EA 1110 (Thermo Quest) elemental analyzer and results are given in Table C-2. Prior to the analysis, all the samples were grounded and dried in the oven for moisture free samples. All the samples were torrefied in the presence of N_2 up to 1-hour residence time.

Table C- 2: Ultimate analysis of biomass with different torrefaction temperature

Biomass	Temperature (^{o}C)	C (%)	H (%)	N (%)	O (%)	S (%)
Raw Biomass		47.47	7.18	0.55	44.79	0.009
Torrefied Biomass	250	51.73	6.33	0.552	41.38	0.008
Torrefied Biomass	275	52.07	6.13	0.55	41.25	0.000
Torrefied Biomass	300	54.30	5.93	0.56	39.21	0.000

C-3 Higher Heating Value

Parr 6100 Calorimeter has used to measure the higher heating value of the raw and torrefied biomass at different torrefaction temperature and the results was very satisfactory. The test was done number of times for the accuracy of the results. This results shows the minimal percentage error i.e. 0- 0.71%. Some of the results have given in the below Table C-3:

Table C- 3: Higher Heating Value repeatability and error calculation

Biomass	Sample No. HHV (MJ/kg)		Error (%)
	1	2	
Raw Poplar Wood	18.34	18.20	0.76
Torrefied Poplar (Torrefaction temp: 250°C, residence time: 1 hr)	20.33	20.33	0.00
Torrefied Poplar (Torrefaction temp: 275°C, residence time: 1 hr)	21.25	21.17	0.39
Torrefied Poplar (Torrefaction temp: 300°C, residence time: 1 hr)	26.44	26.37	0.26

C-4 Measurement Equipment Error Limit

In this research, there were many analog/digital instruments used to measure and verify the data, which had some limitations. All of these have some sort of the manufacturing error, which have provided by the manufacturer. The list of the equipment and their respective error level are given below in the Table C-4.

Table C- 4: Manufacturer Error of Equipment

Equipment Name	Parameter	Value
Parr 6100 Calorimeter	%RSD	0.05
SRI 8610C Gas Chromatograph	%RSD	0.05
Flow Meter FMA-A2321 (Omega)	Accuracy	±1%
K-type Thermocouple (Omega)	Special limit of error (SLE)	± 1^{o}C
Digital Balance (Cole-Parmer)	Least count (Δm)	0.0001g
Water volumetric flask	Error (Δv)	1ml
Analog pressure gauge	Accuracy	±2%

APPENDIX D: KINETICS ANALYSIS OF BIOMASS

Table D- 1: Details of activation energy calculations

Raw Biomass			
T (^{o}C)	dx/dt	ln(dx/dt)	1/T (K^{-1})
750	0.0002	-8.2442	0.00097752
800	0.0003	-8.0061	0.00093197
850	0.0003	-7.9468	0.00089047
900	0.0007	-7.1347	0.00085251
950	0.0012	-6.6965	0.00081766
Torrefied Biomass (250^{o}C, 1hr)			
750	0.0001	-8.9454	0.00097752
800	0.0001	-8.6261	0.00093197
850	0.0002	-8.4246	0.00089047
900	0.0005	-7.4856	0.00085251
950	0.0006	-7.2817	0.00081766
Torrefied Biomass (275^{o}C, 1hr)			
750	0.0003	-7.9212	0.00097752
800	0.0001	-8.5626	0.00093197
850	0.0004	-7.6487	0.00089047
900	0.0010	-6.9072	0.00085251
950	0.0020	-6.1704	0.00081766
Torrefied Biomass (300^{o}C, 1hr)			
750	0.0001	-8.6803	0.00097752
800	0.0001	-8.9386	0.00093197
850	0.0002	-8.1801	0.00089047
900	0.0006	-7.2998	0.00085251
950	0.0012	-6.6543	0.00081766

D-1 Calculations for raw biomass char

Temperature (*T*): 800°C (1073K)

Universal gas constant(*R*): 8.3144 x 10^{-3} kJ/mol K

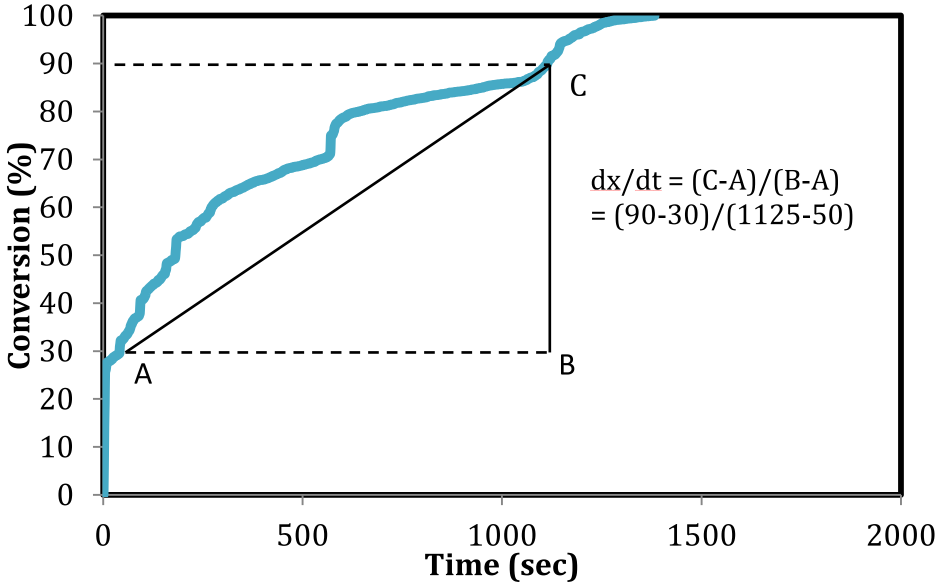


Figure D- 1: Mass conversion vs time during gasification of raw biomass char

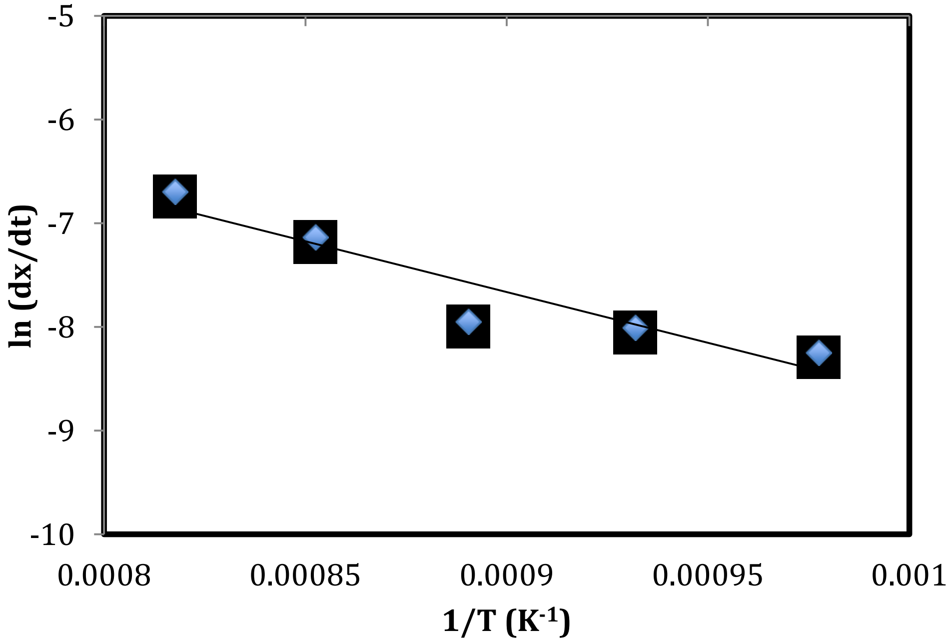


Figure D- 2: Arrhenius plot for gasification reaction of char from raw biomass (time in sec)

The kinetics of gas-solid reactions

$$\frac{dx}{dt} = A\,(1-x)^n e^{\frac{-E_A}{RT}} \tag{D1.1}$$

Assuming zero order (n=0) reaction, we get

$$\frac{dx}{dt} = A\,e^{\frac{-E_A}{RT}} \tag{D1.2}$$

A plot of $\ln\left(\frac{dx}{dt}\right)$ against $1/T$ gives equation

$$y = -9781.4x + 1.139 \tag{D.13}$$

Comparing equations (D1.1) and (D1.2), we get

$\ln A$ =1.1392 and E_A/R = 9781.4

Activation energy (E_A) =9781.4×8.314x10^{-3} = 81.32 kJ/mol

Frequency factor (A): 3.12 sec^{-1}

Applying Arrhenius equation,

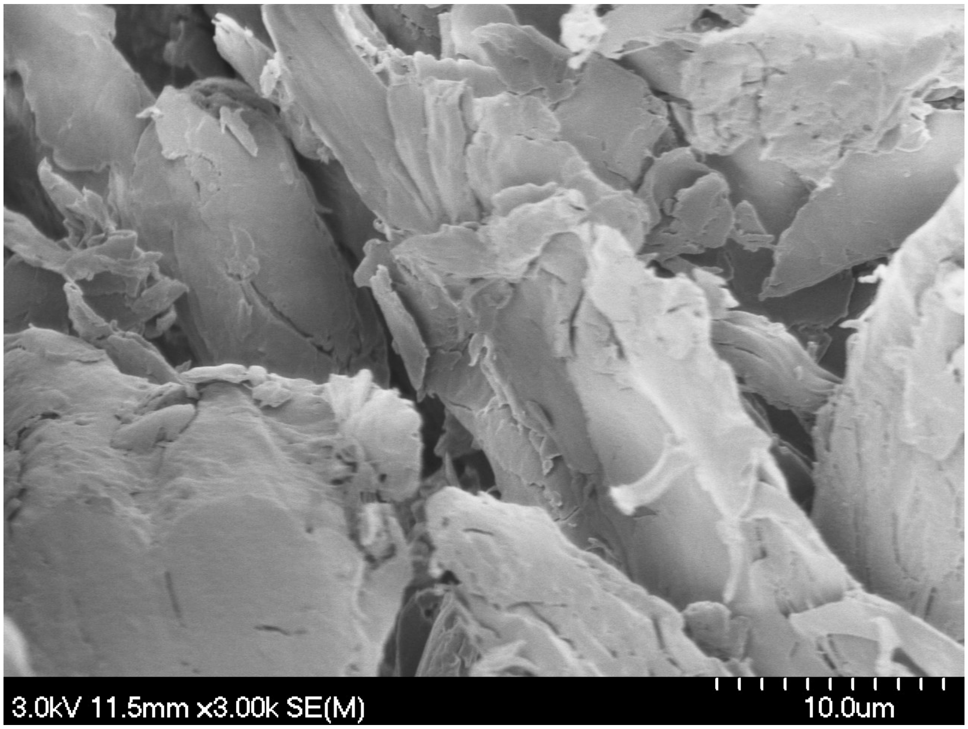
$$k(T) = A\,e^{\frac{-E_A}{RT}}$$

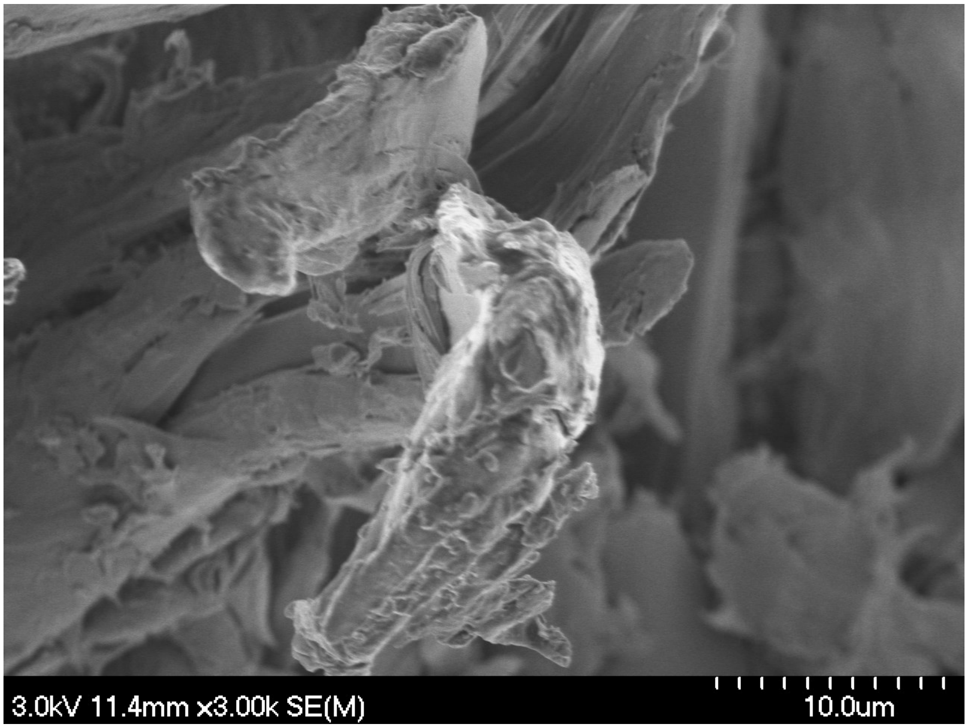
$$k(T) = 3.12e^{\left(\frac{-81.32}{8.3144\times10^{-3}\times1073}\right)}$$

$$k(T) = 3.43\times10^{-4}\ sec^{-1}$$

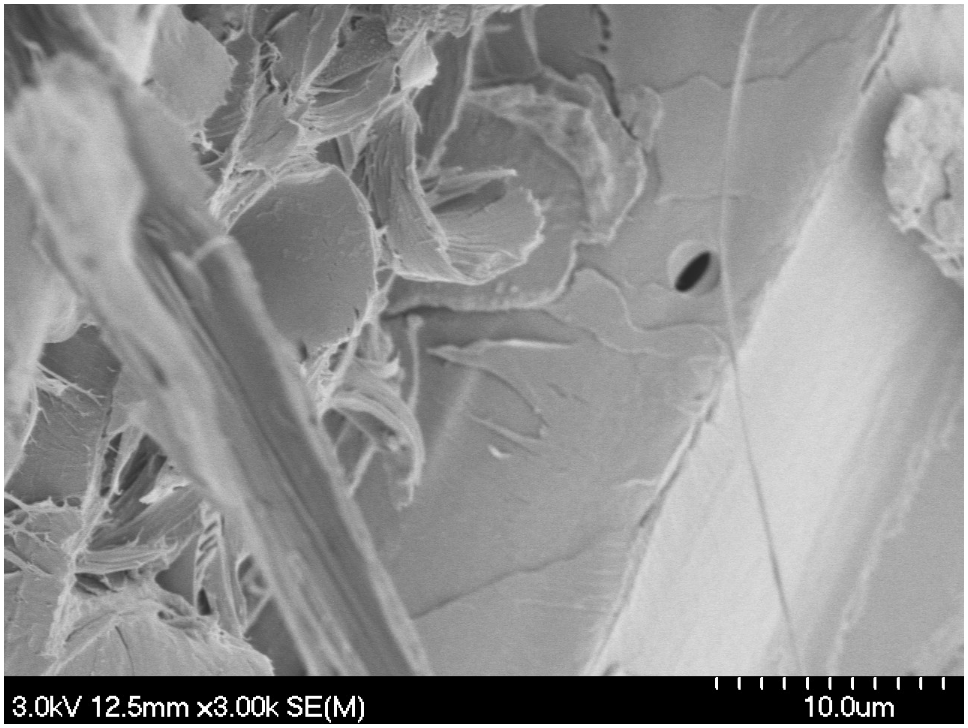
APPENDIX E: SEM MICROGRAPHS

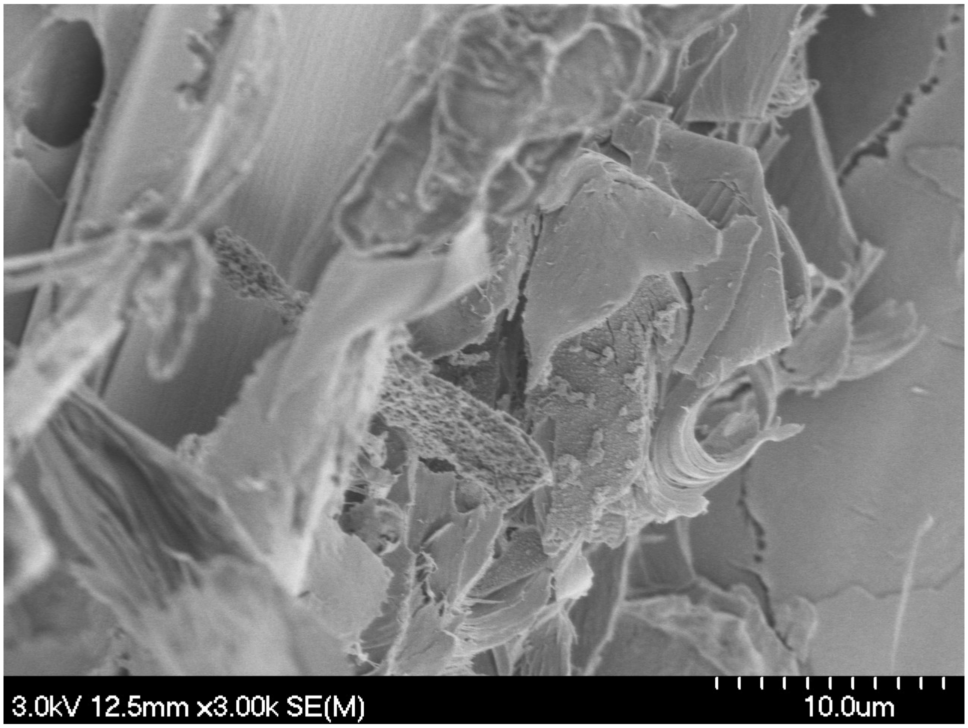
E-1 Raw Biomass (Horizontal face)

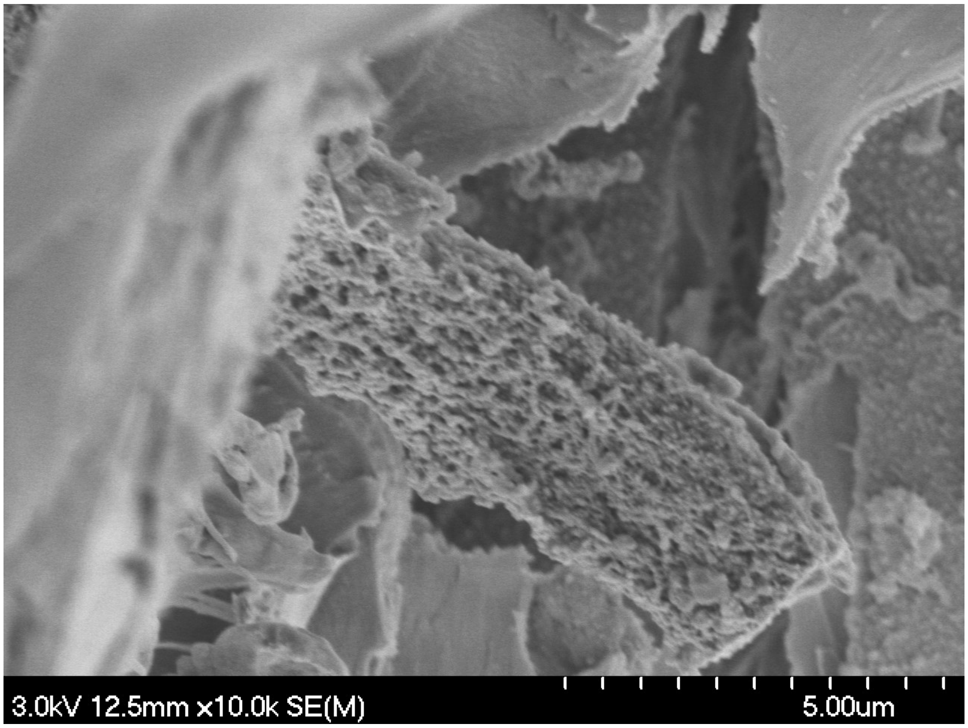


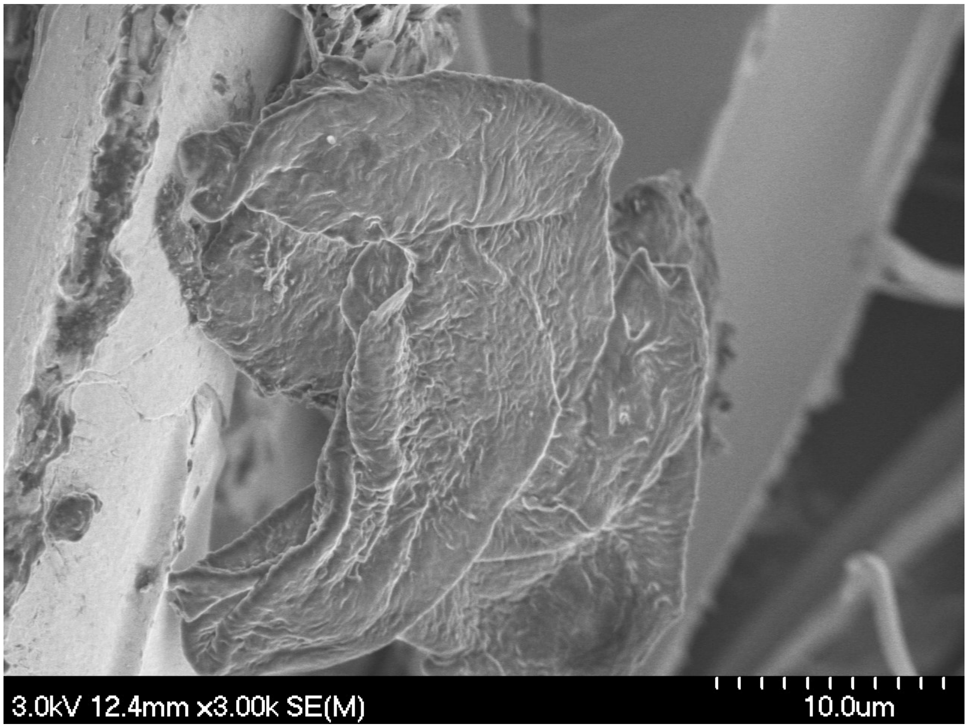


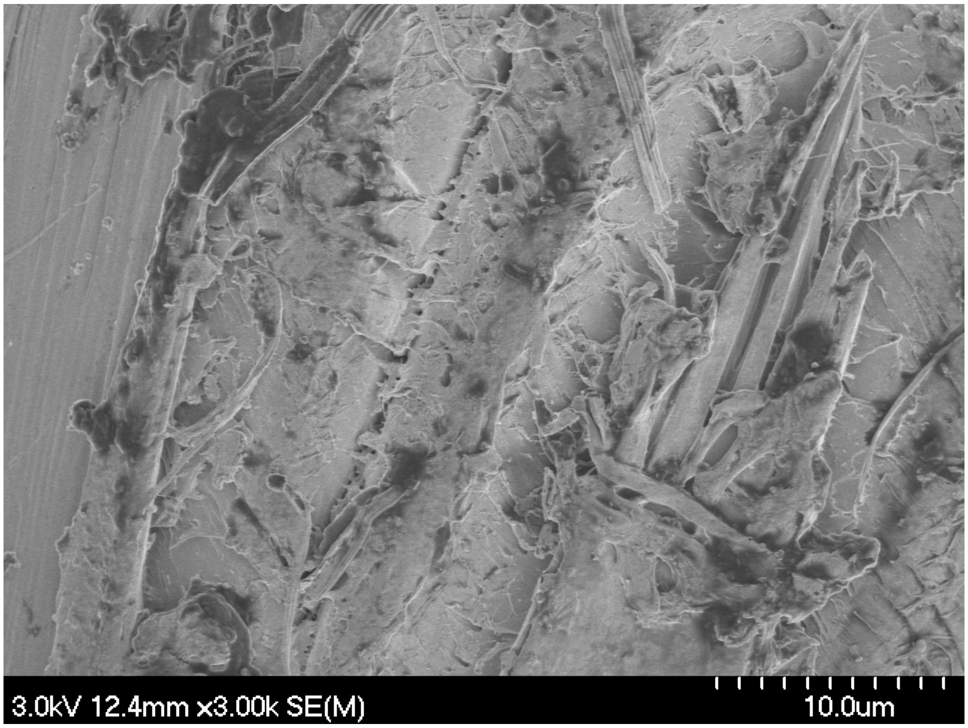
E-2 Raw Biomass (Vertical face)

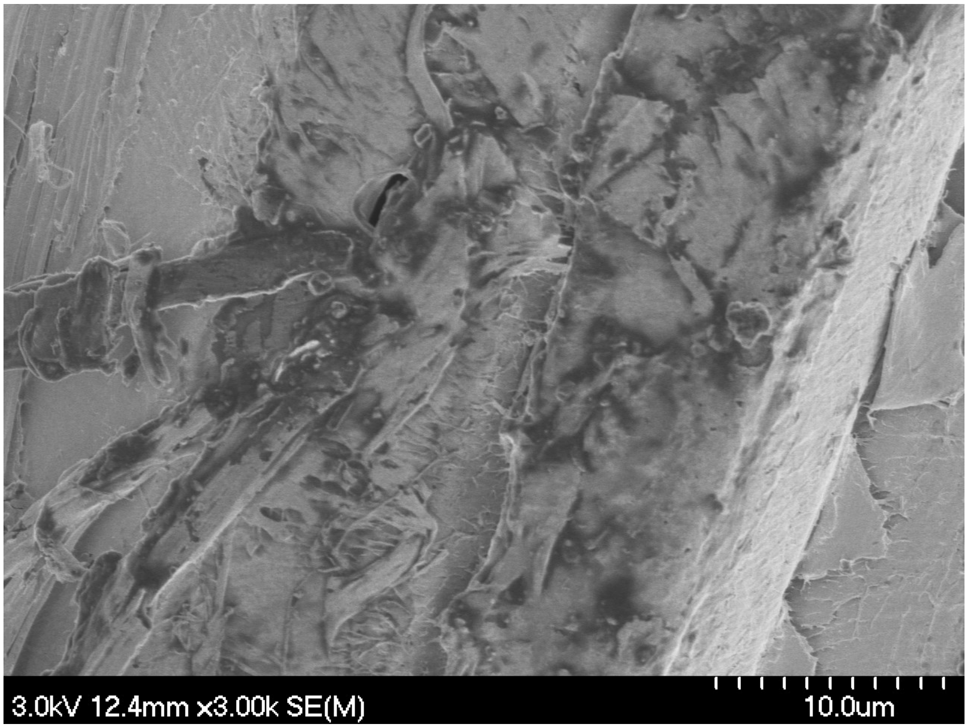




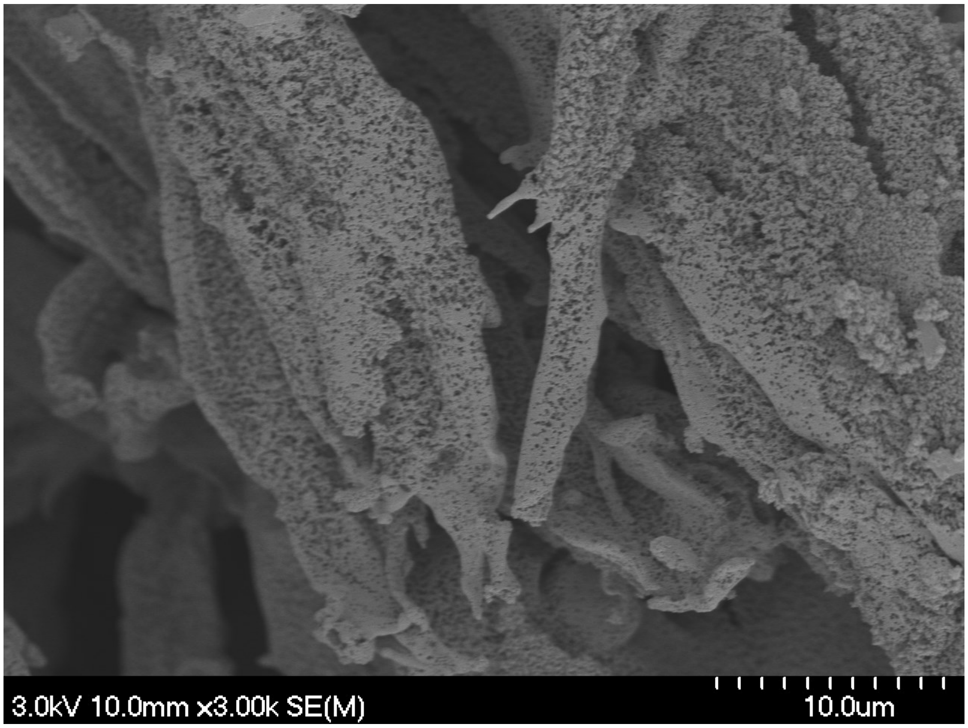

3.0kV 12.5mm x10.0k SE(M)
5.00um

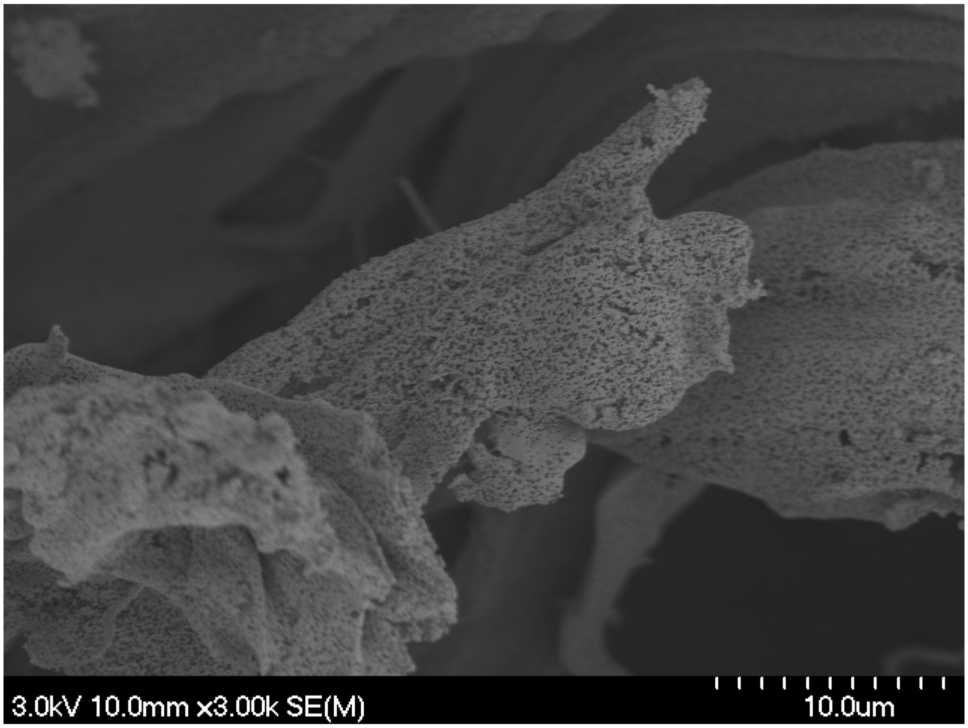

3.0kV 12.4mm x3.00k SE(M)
10.0um

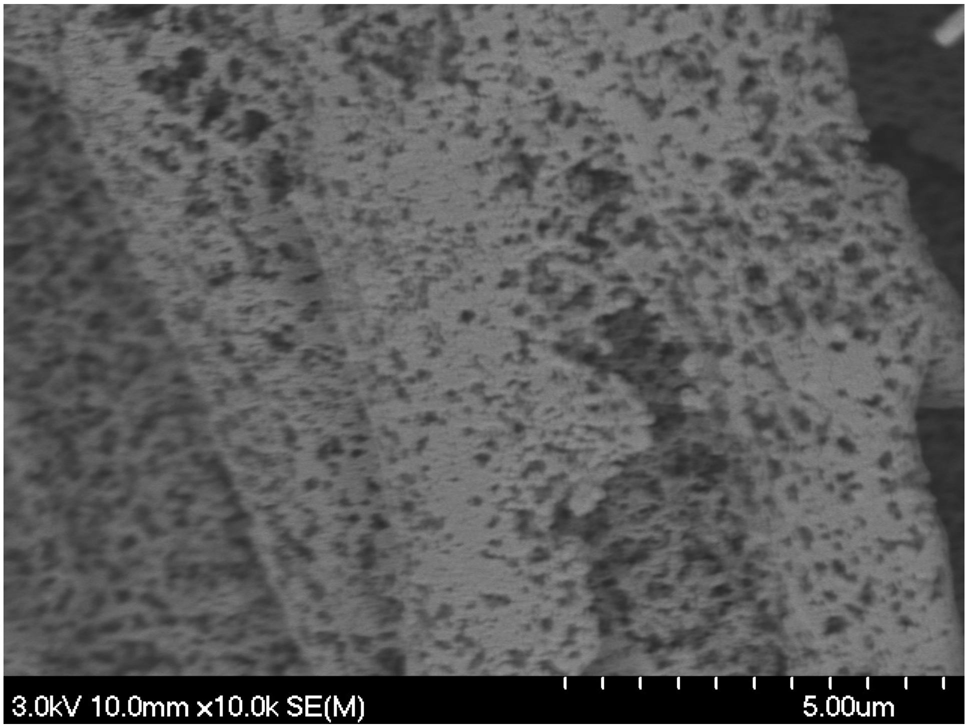

3.0kV 12.4mm x3.00k SE(M)
10.0um

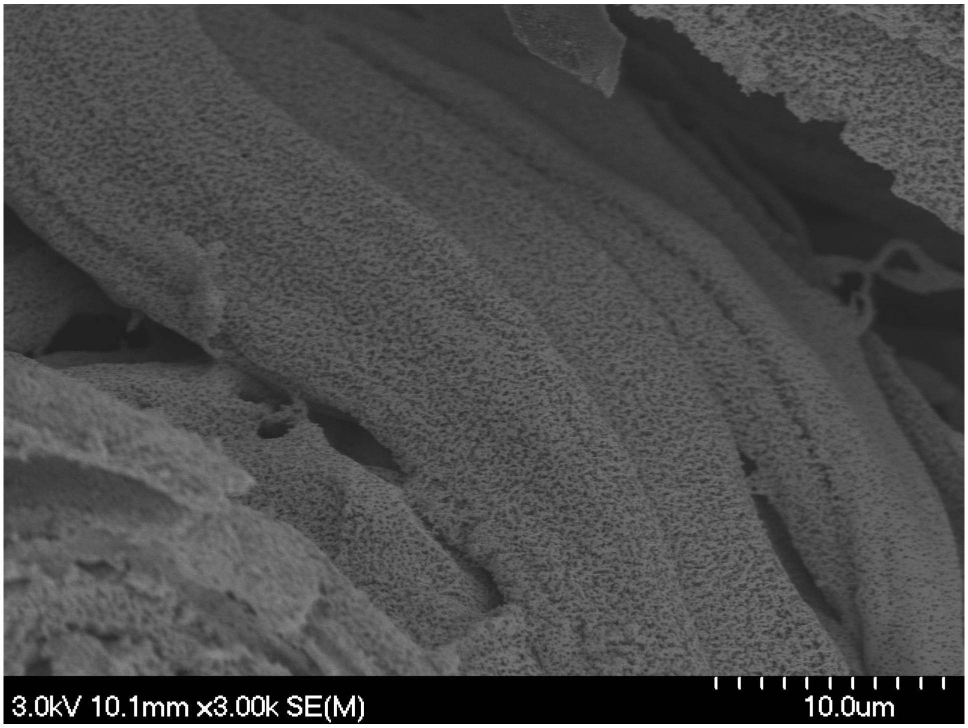

3.0kV 12.4mm x3.00k SE(M)
10.0um

E-3 Raw Biomass Char (Horizontal face)






3.0kV 10.0mm x10.0k SE(M)
5.00um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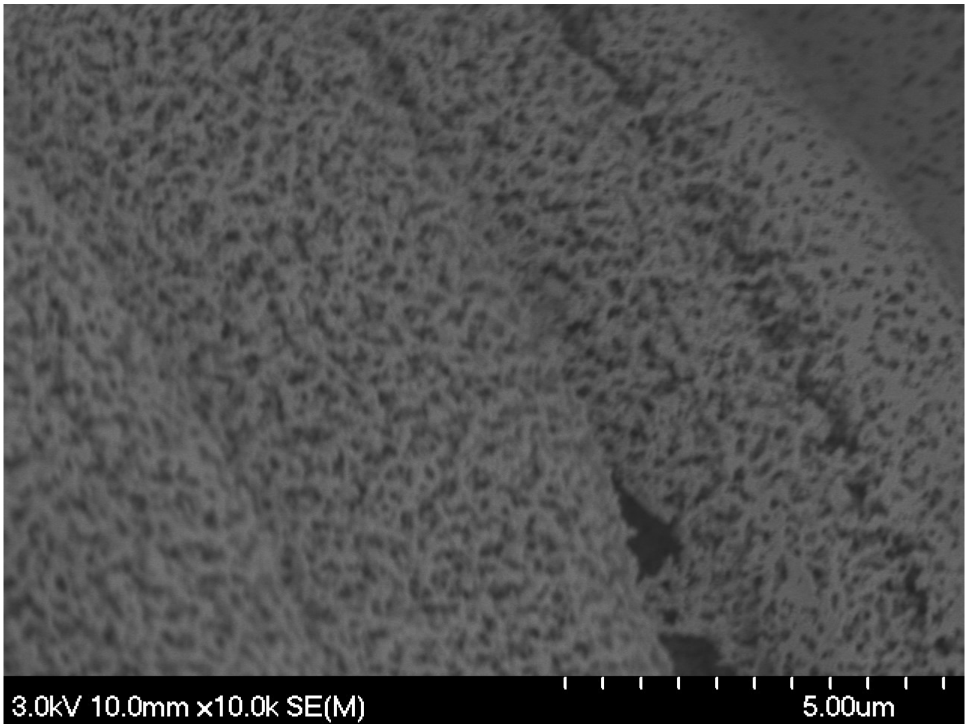
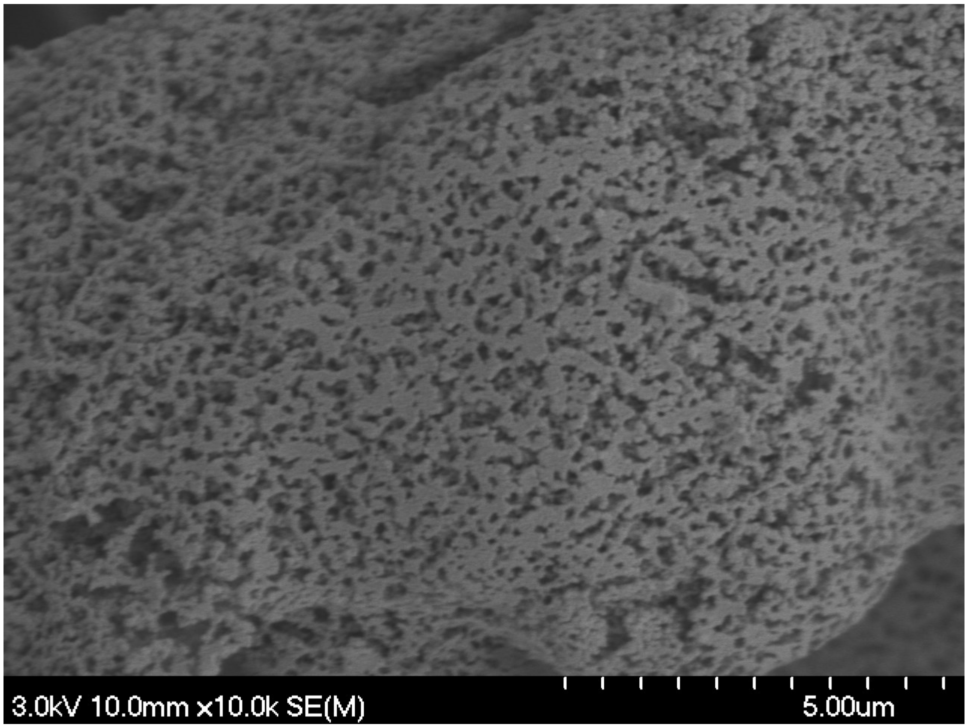
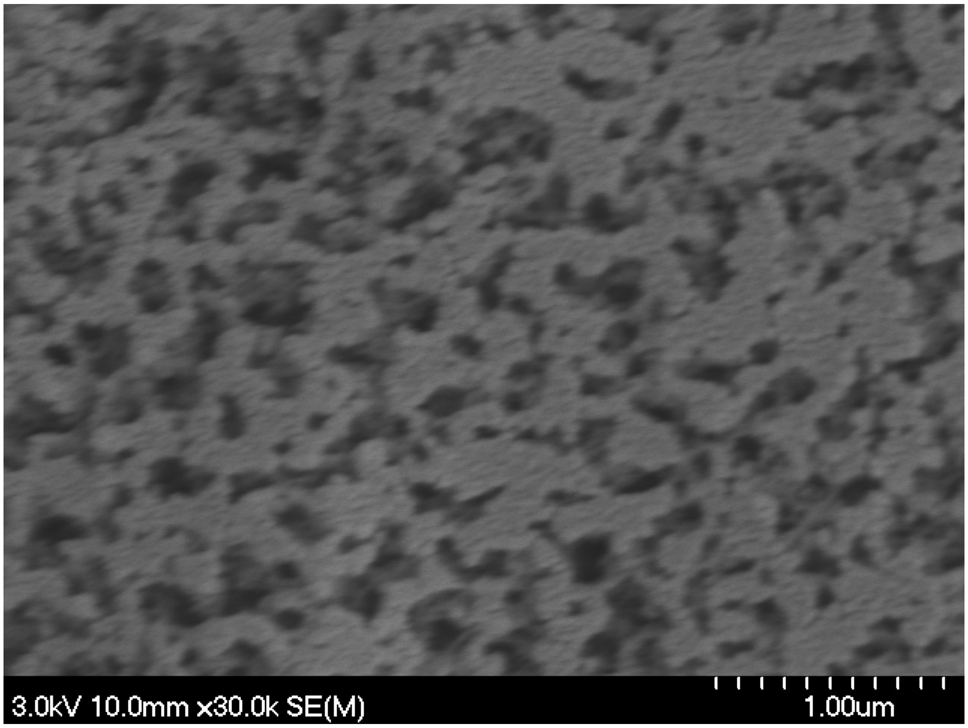
10.0um


3.0kV 10.0mm x10.0k SE(M)
5.00um


3.0kV 10.0mm x3.00k SE(M)
10.0um

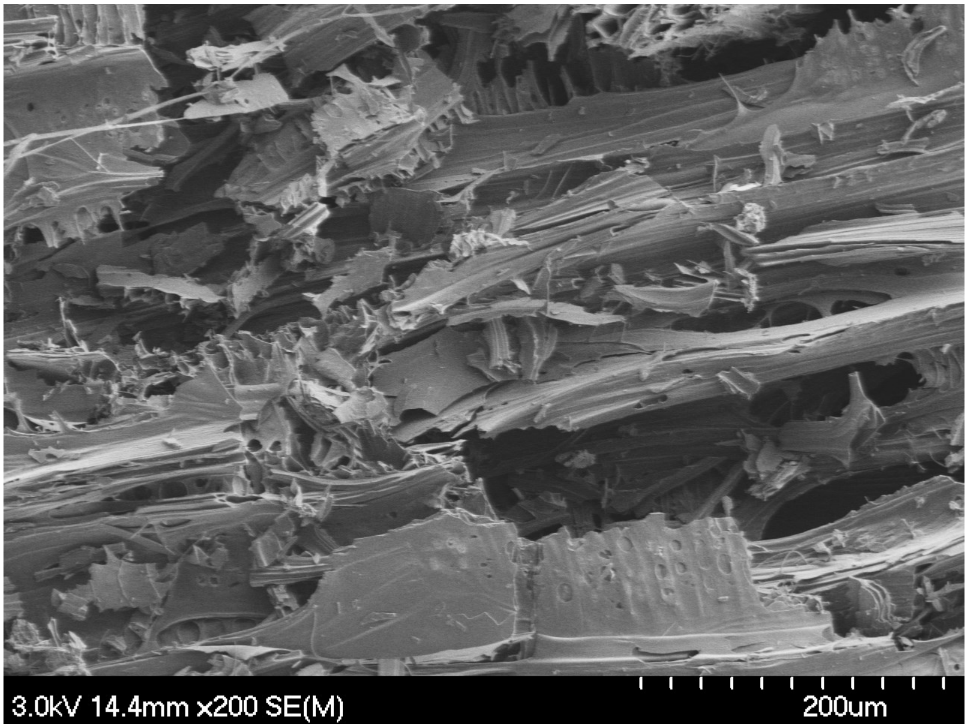


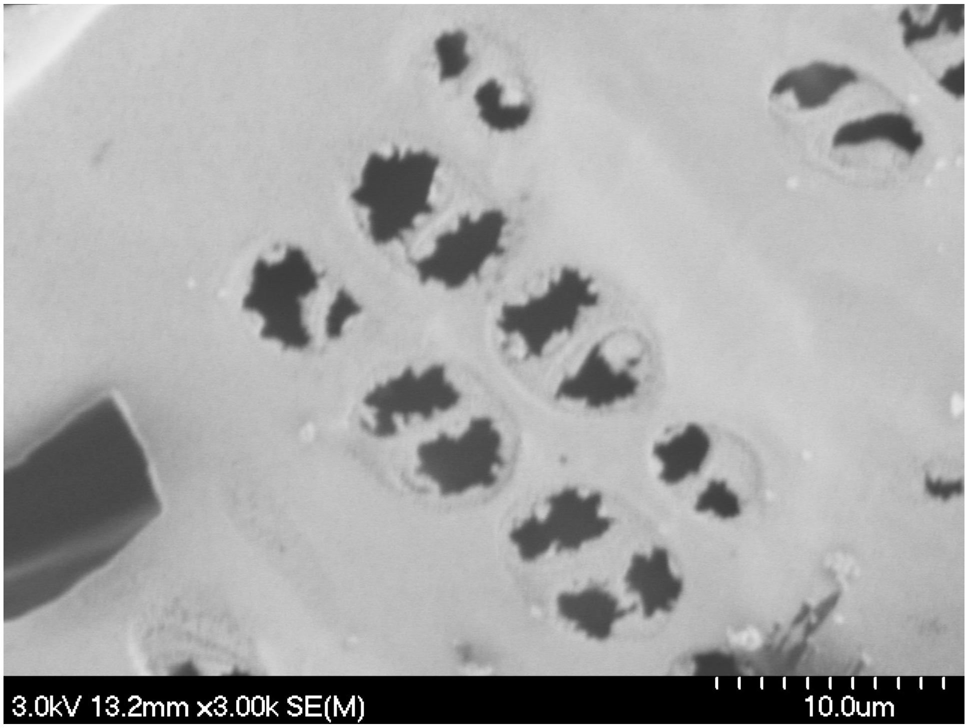
3.0kV 10.0mm x10.0k SE(M)
5.00um

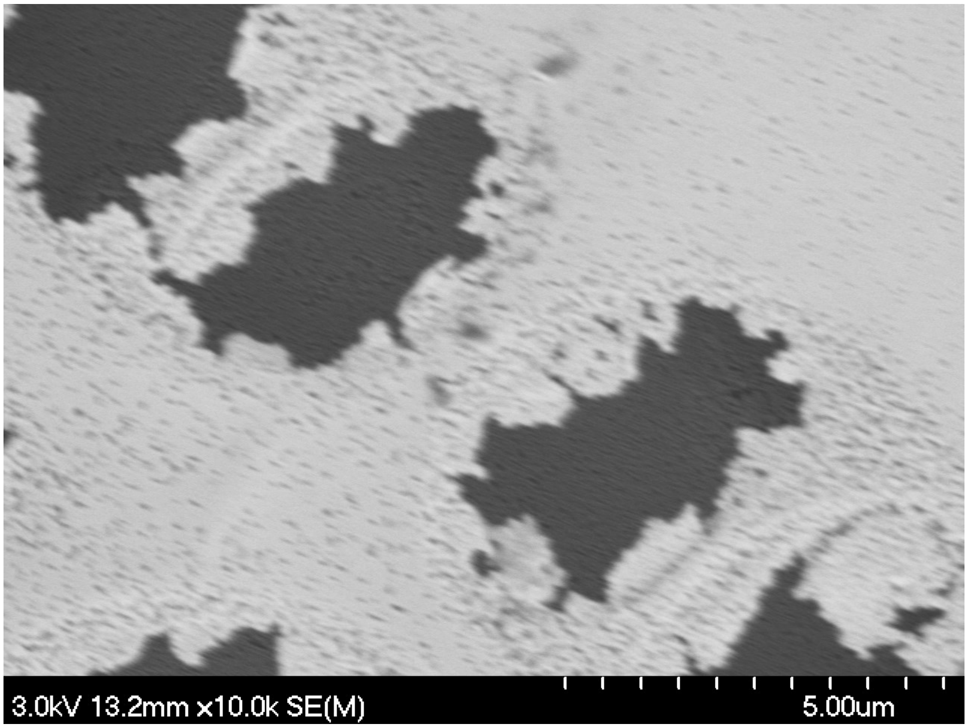


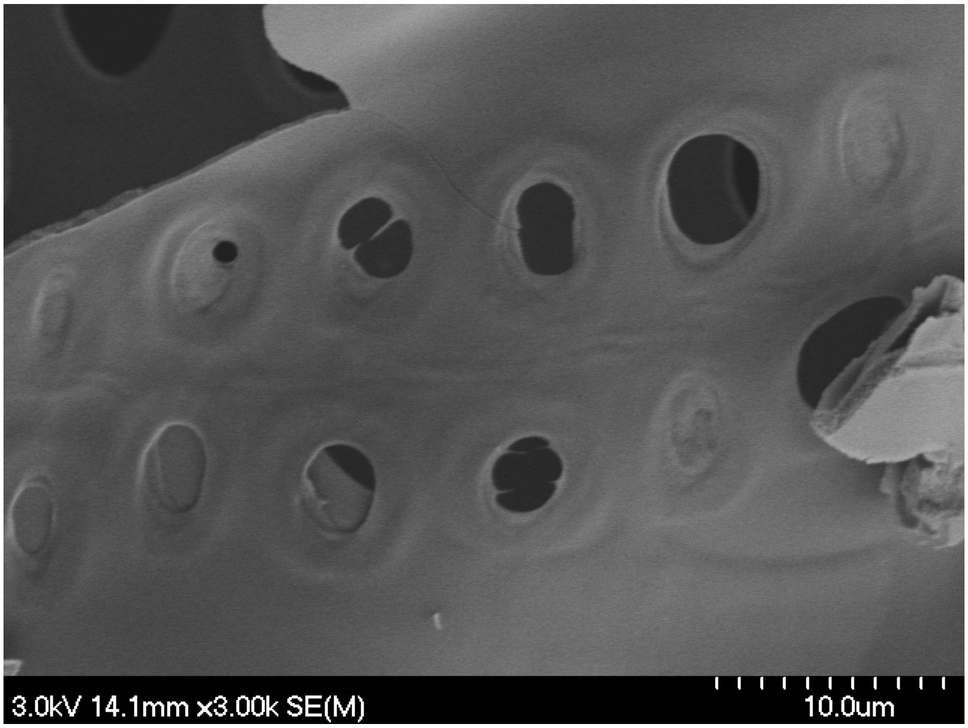
3.0kV 10.0mm x30.0k SE(M)
1.00um

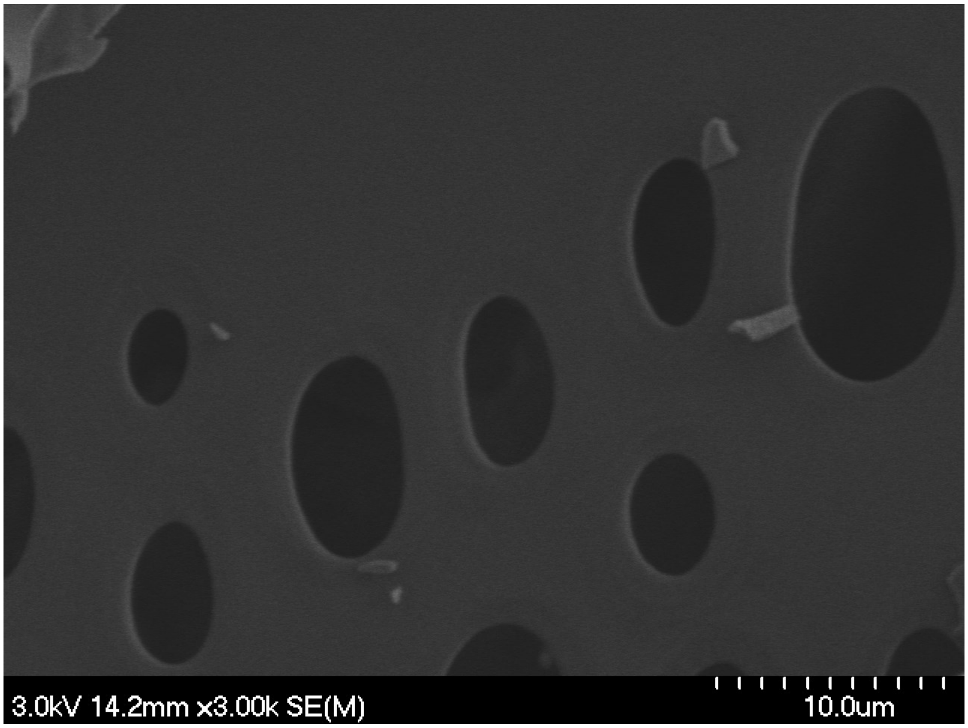
E-4 Raw Biomass Char (Vertical face)






3.0kV 13.2mm x10.0k SE(M)
5.00um


3.0kV 14.1mm x3.00k SE(M)
10.0um


3.0kV 14.2mm x3.00k SE(M)
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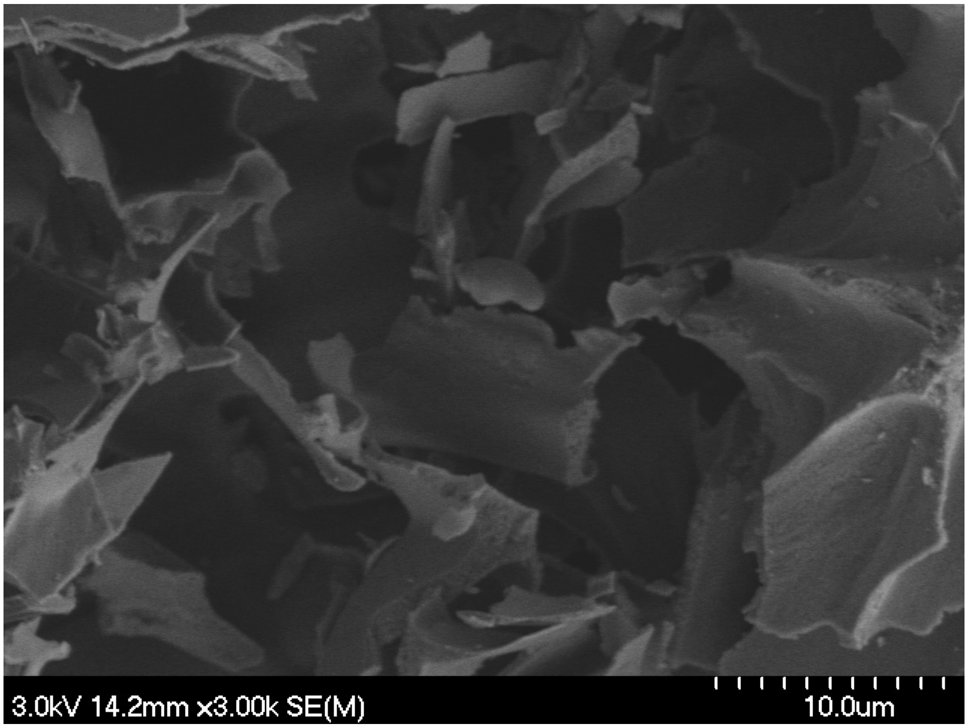
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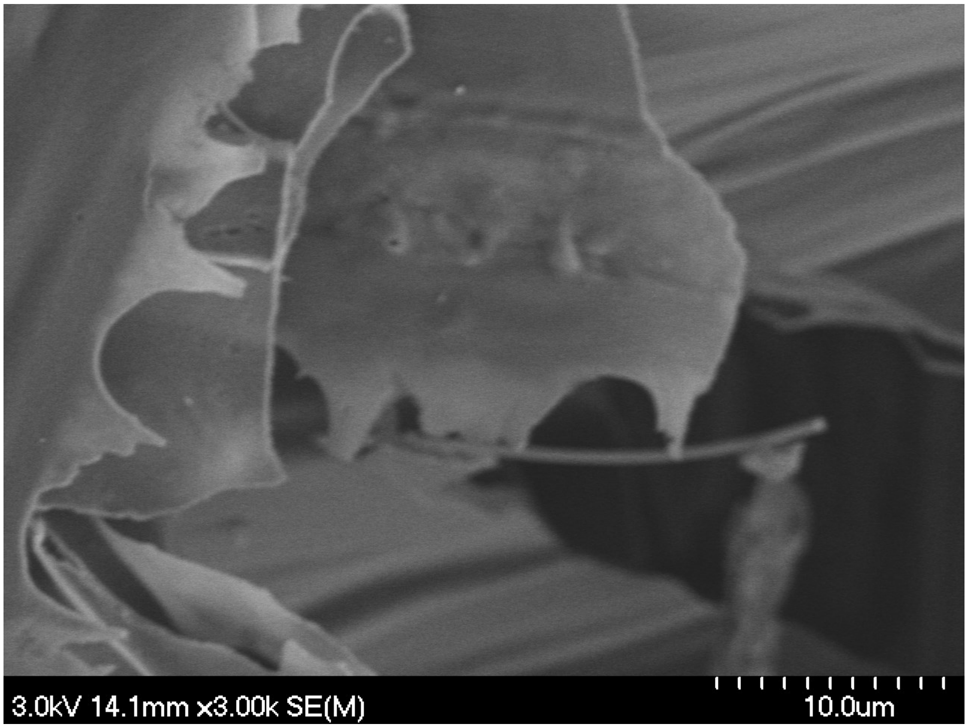
10.0um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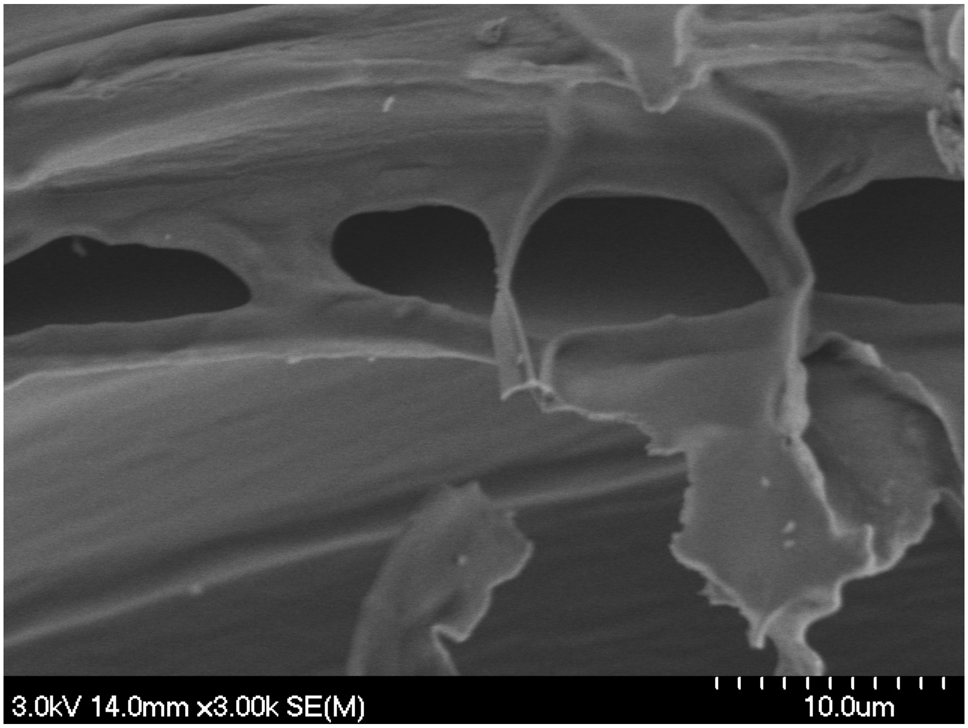
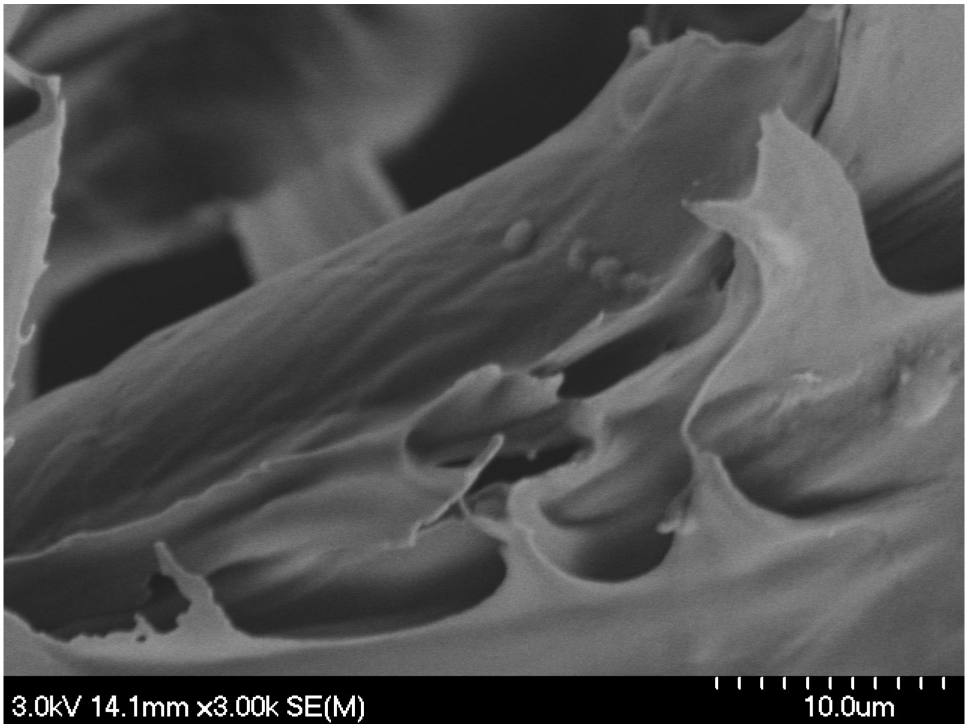
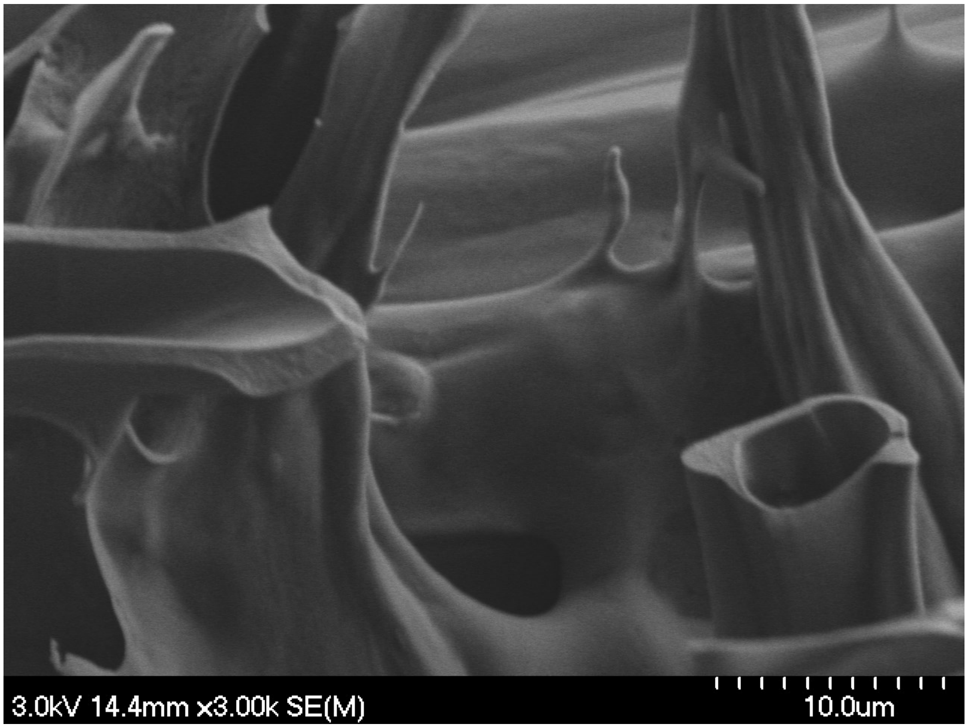
10.0um


3.0kV 14.0mm x3.00k SE(M)
10.0um


3.0kV 14.1mm x3.00k SE(M)
10.0um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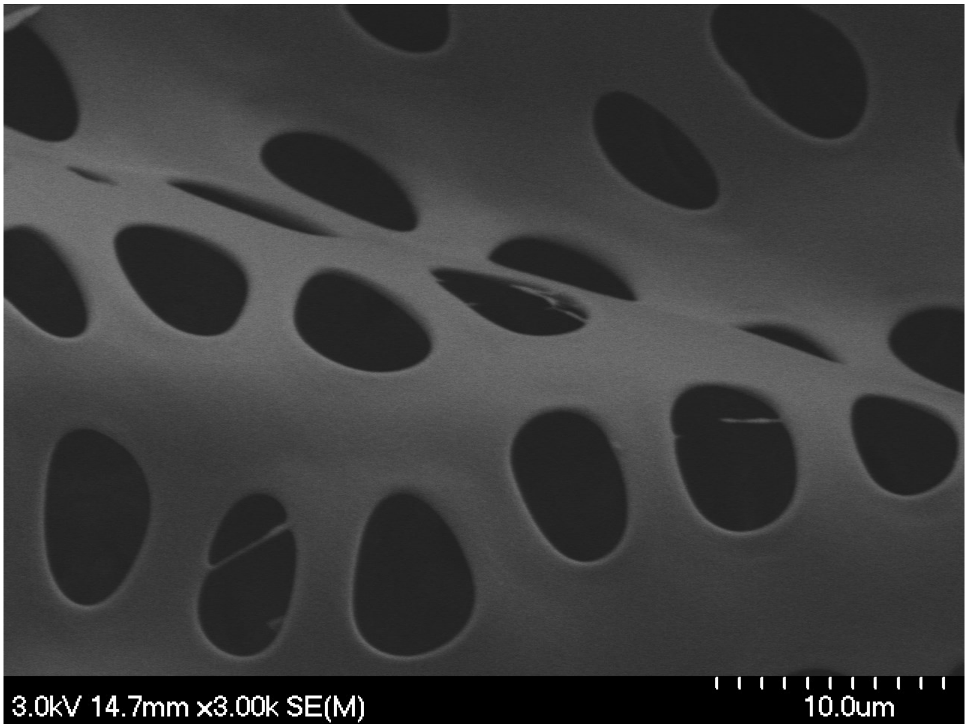
10.0um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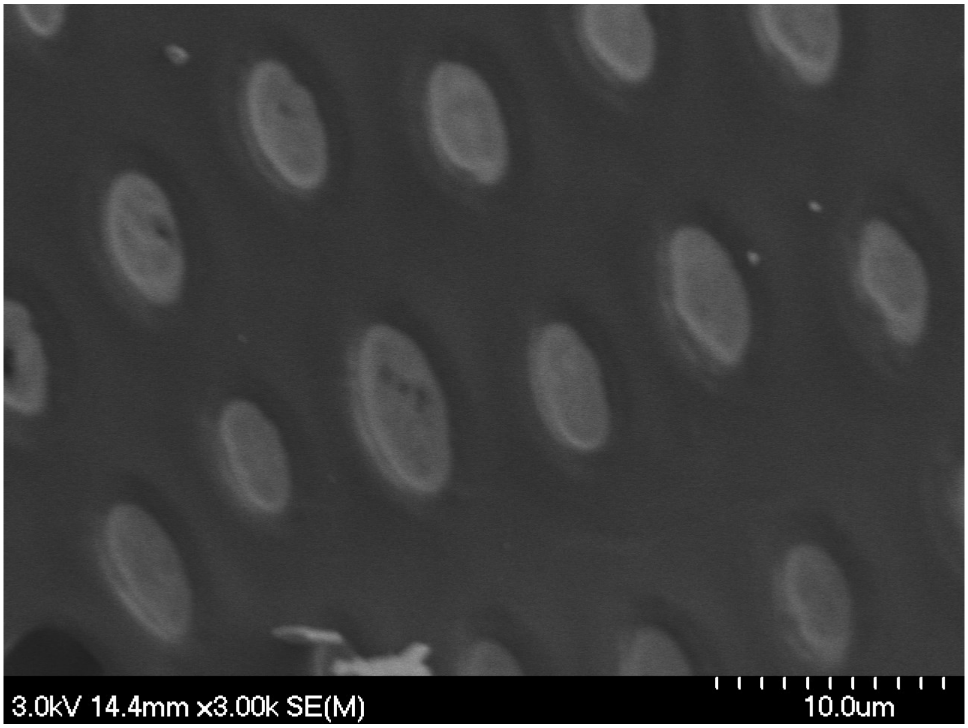
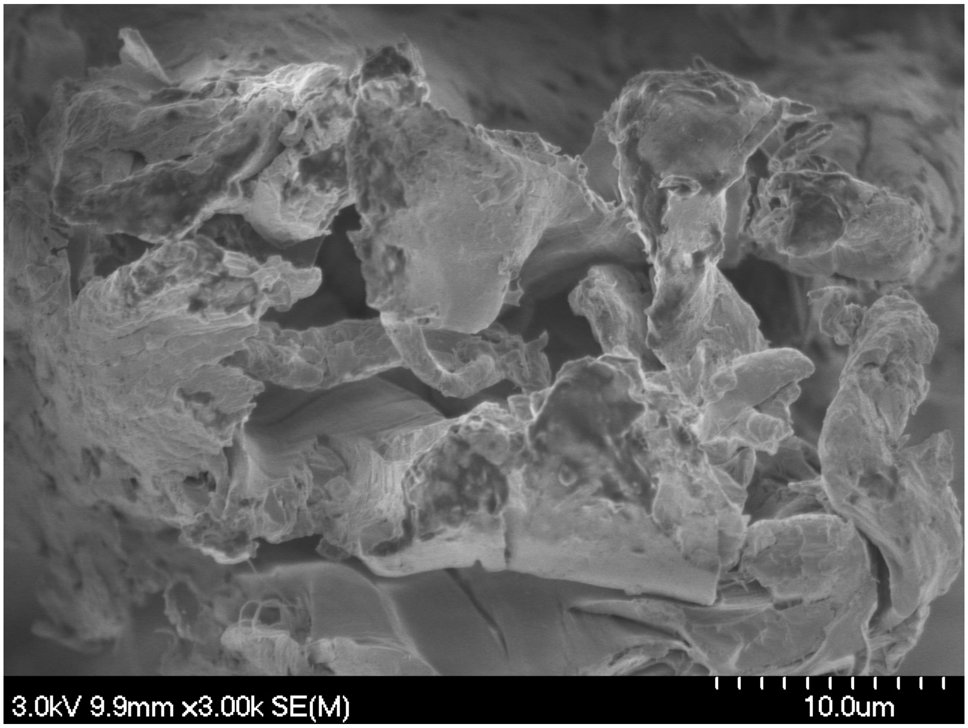
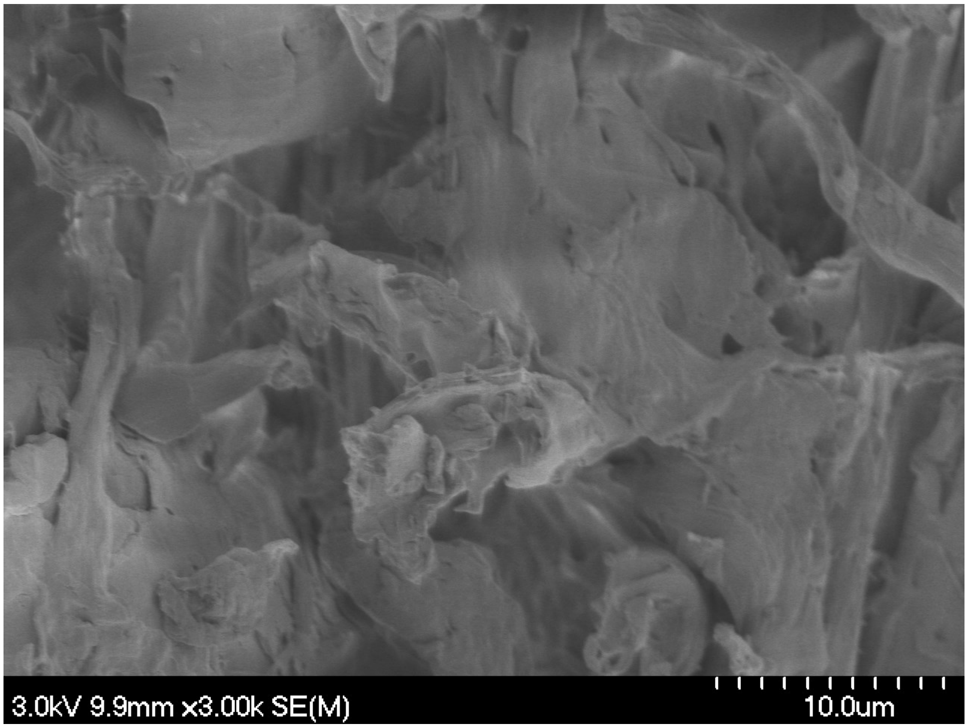
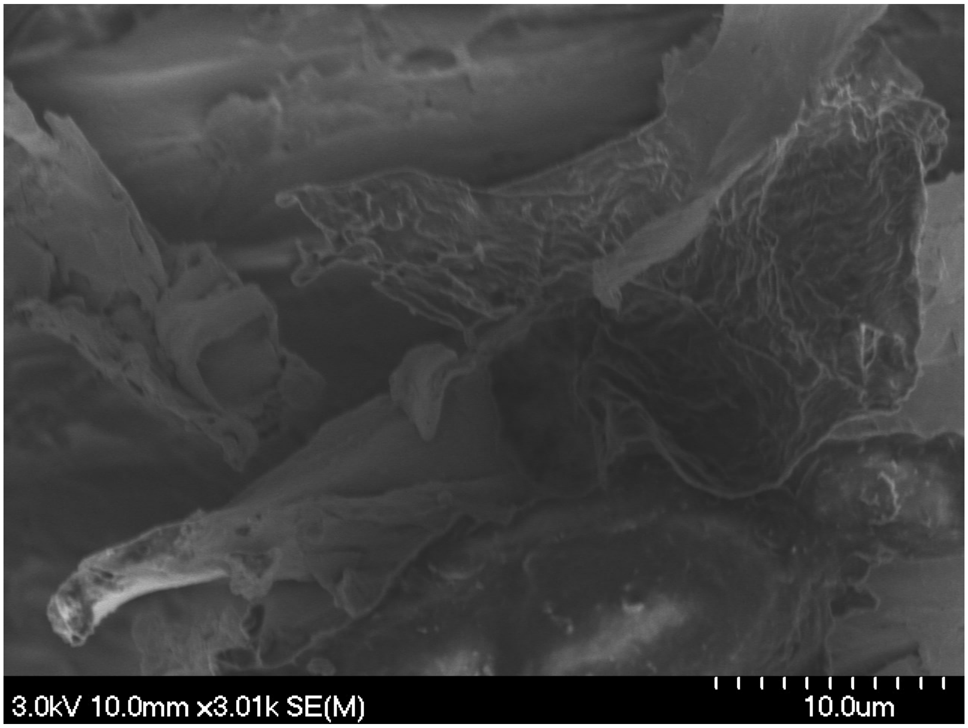
10.0um


3.0kV 14.4mm x3.00k SE(M)
10.0um

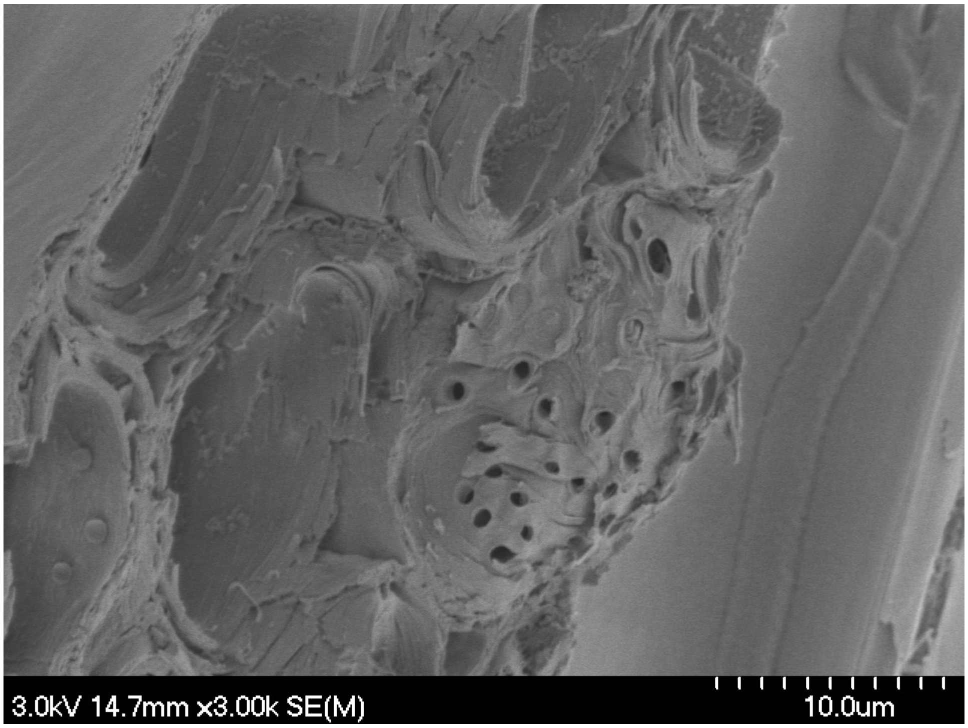
E-5 Torrefied Biomass (Horizontal face)

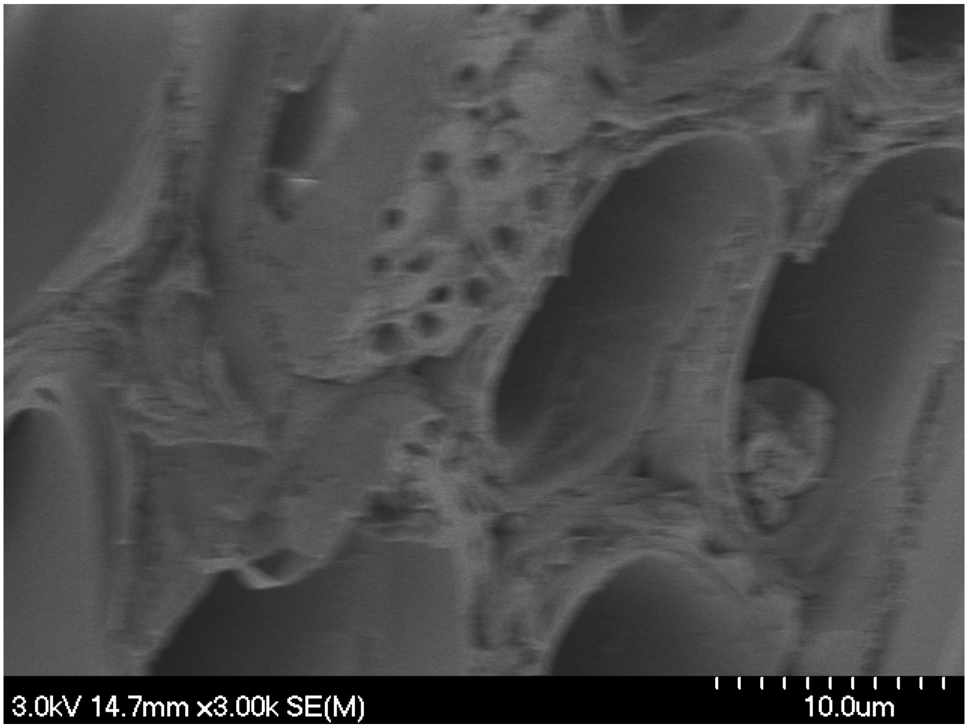


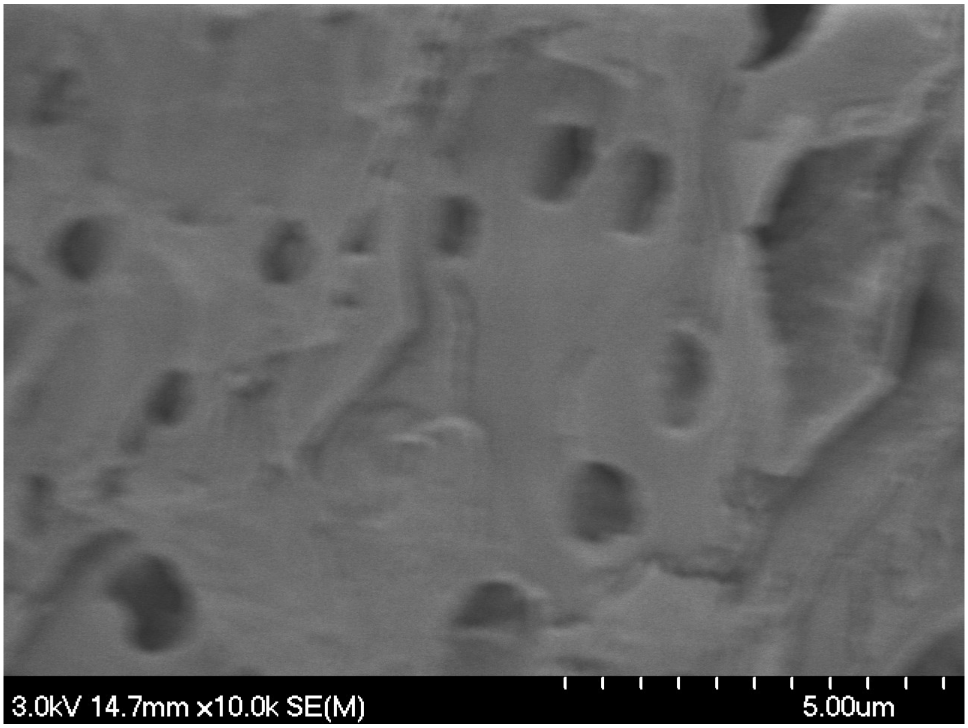

3.0kV 9.9mm x3.00k SE(M)
10.0um

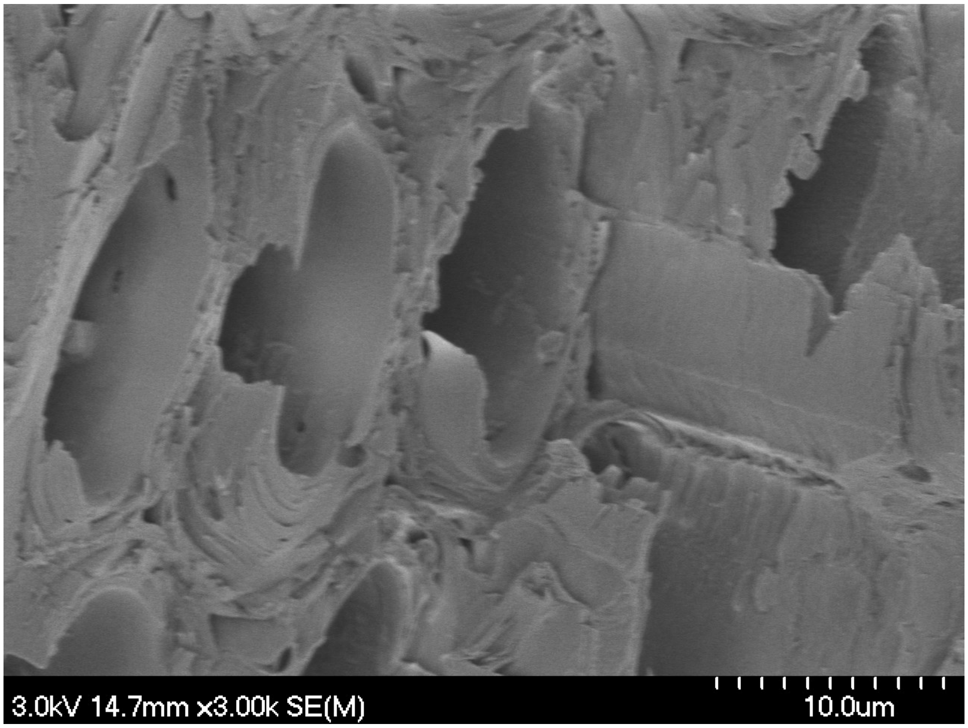

3.0kV 10.0mm x3.01k SE(M)
10.0um

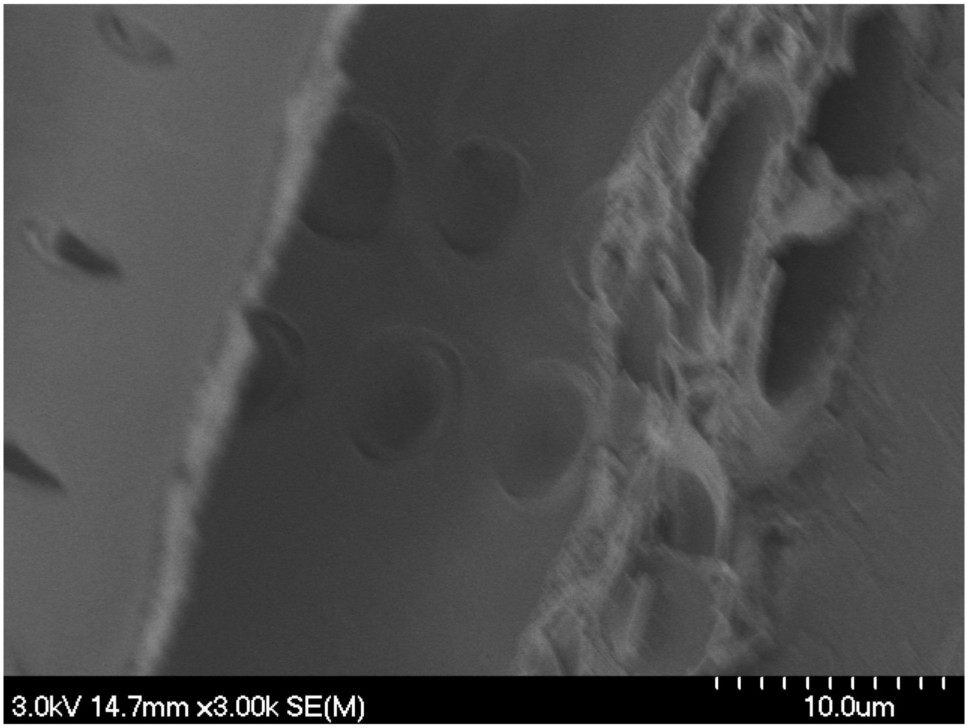
E-6 Torrefied biomass (Vertical face)






3.0kV 14.7mm x10.0k SE(M)
5.00um


3.0kV 14.7mm x3.00k SE(M)
10.0um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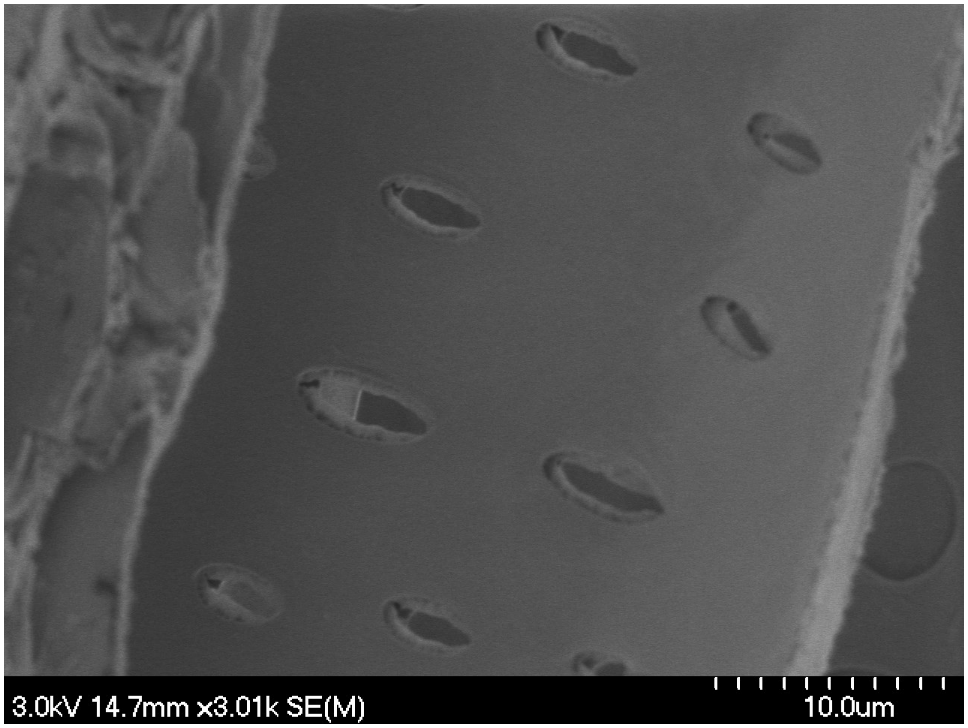
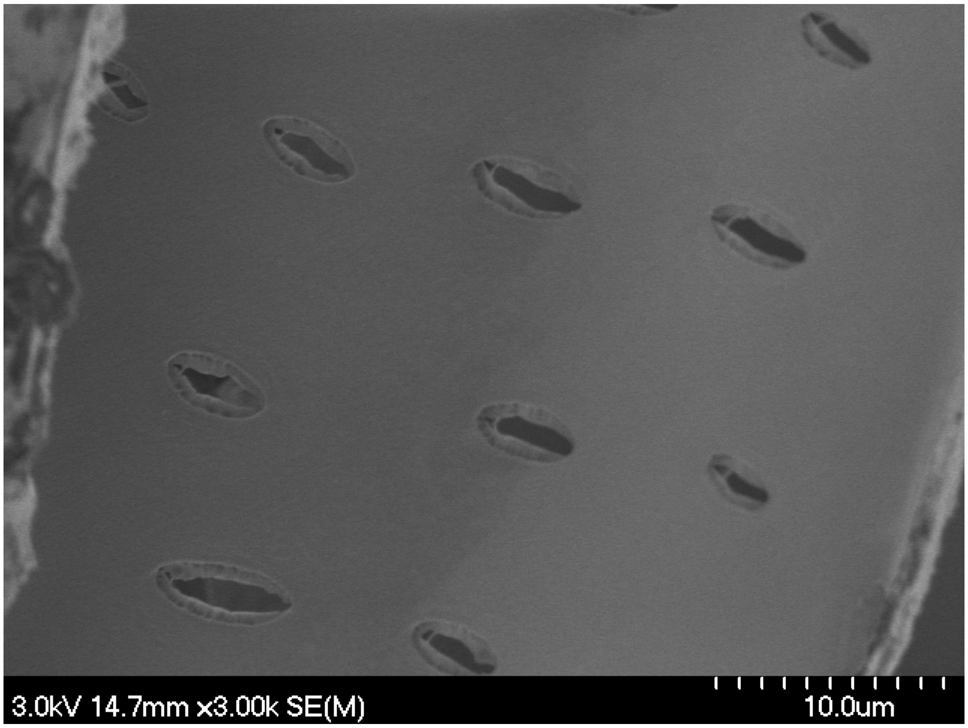
10.0um


3.0kV 14.7mm x3.01k SE(M)
10.0um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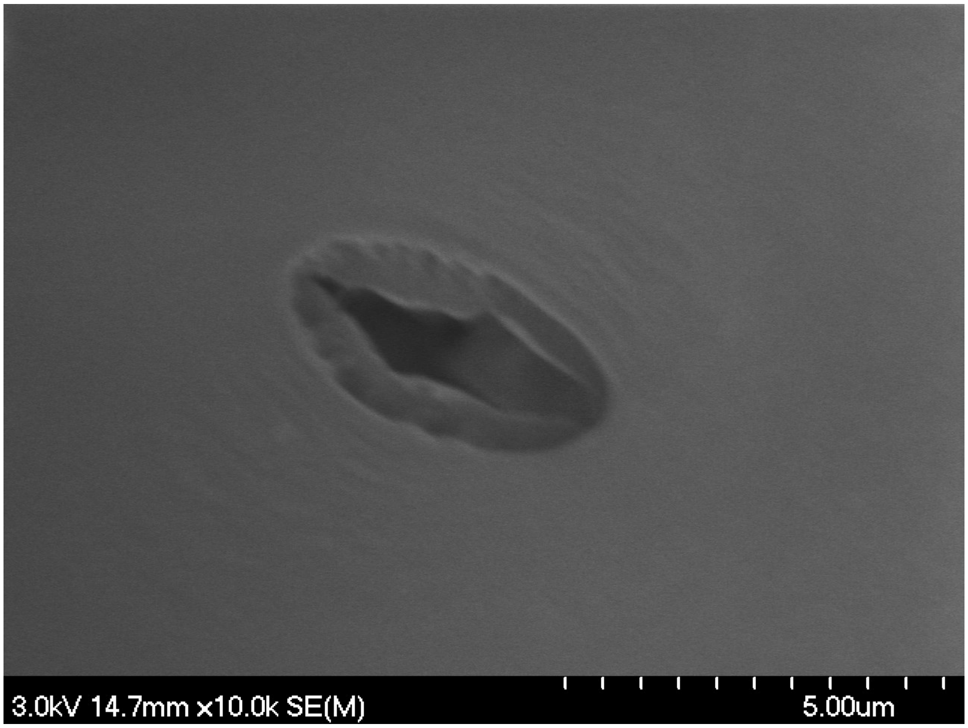
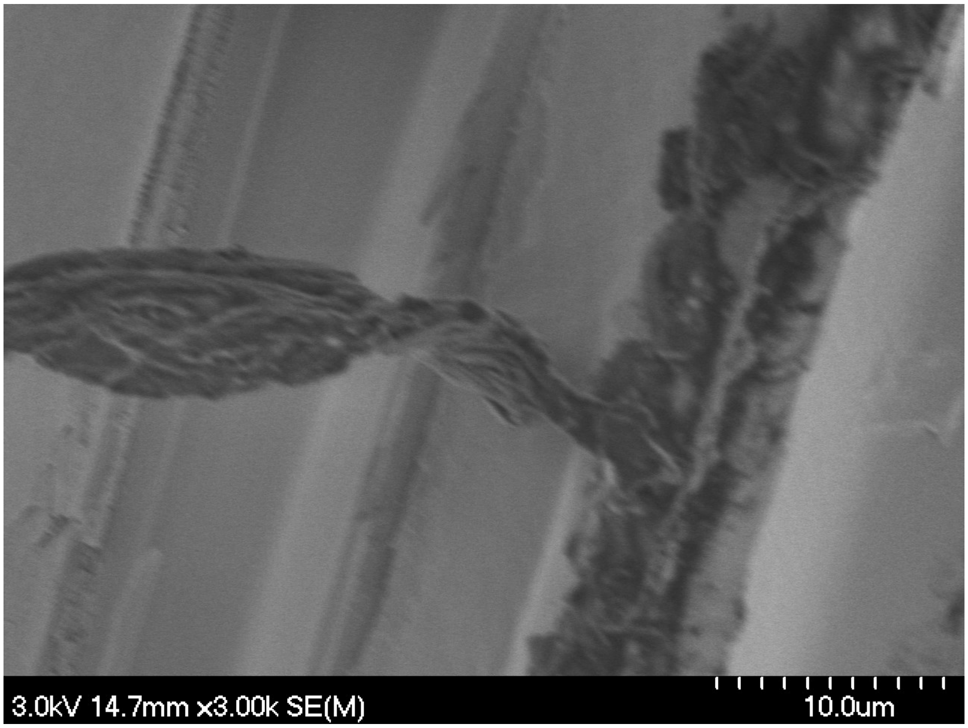
10.0um


3.0kV 14.7mm x10.0k SE(M)
5.00um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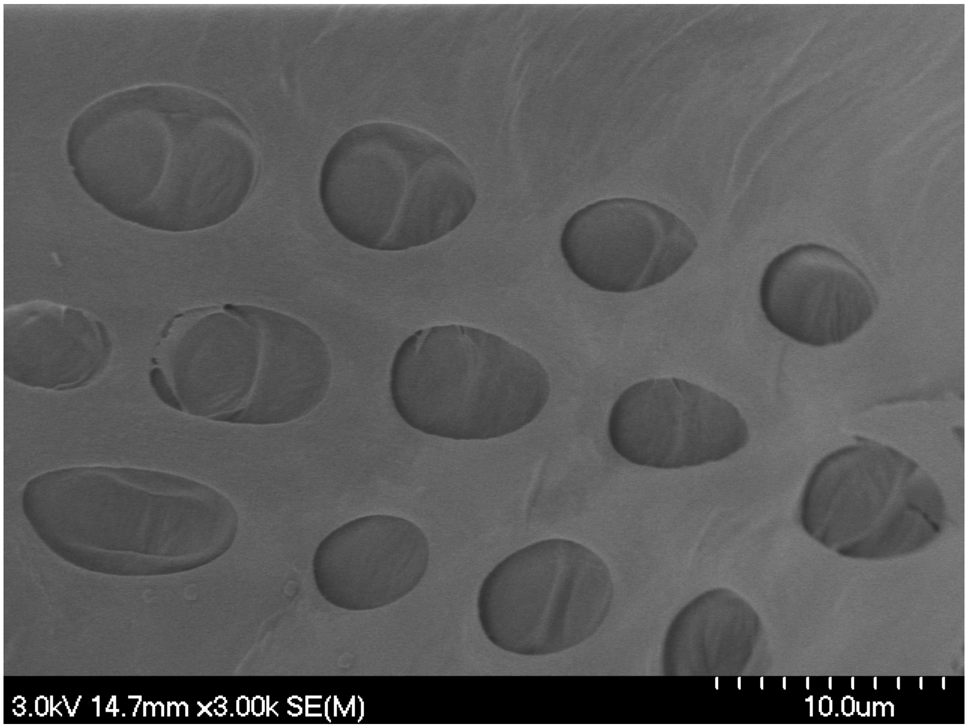
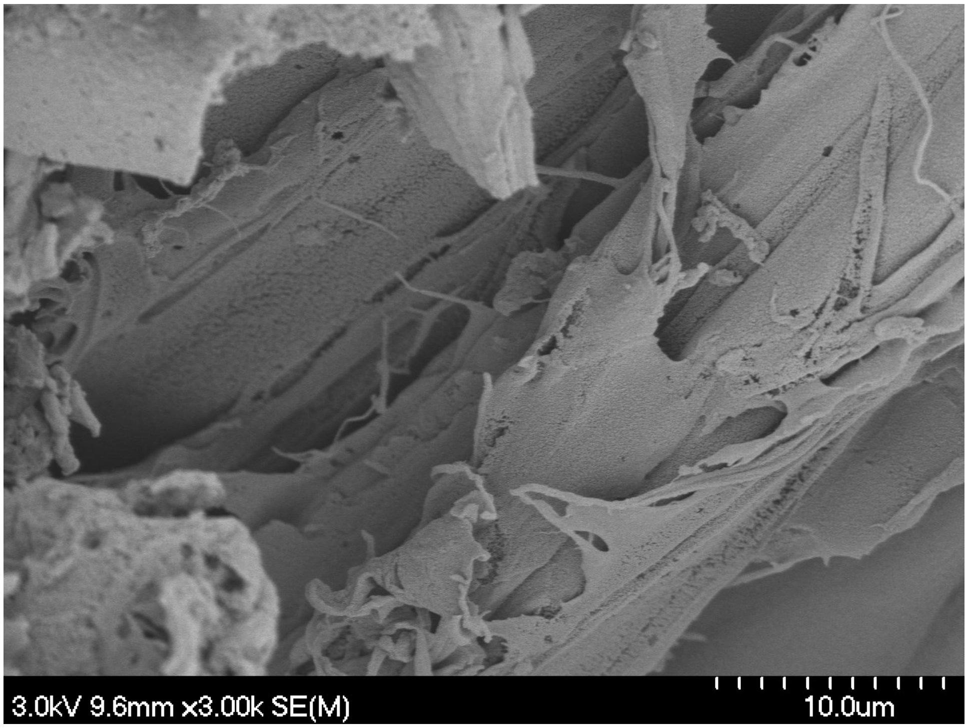
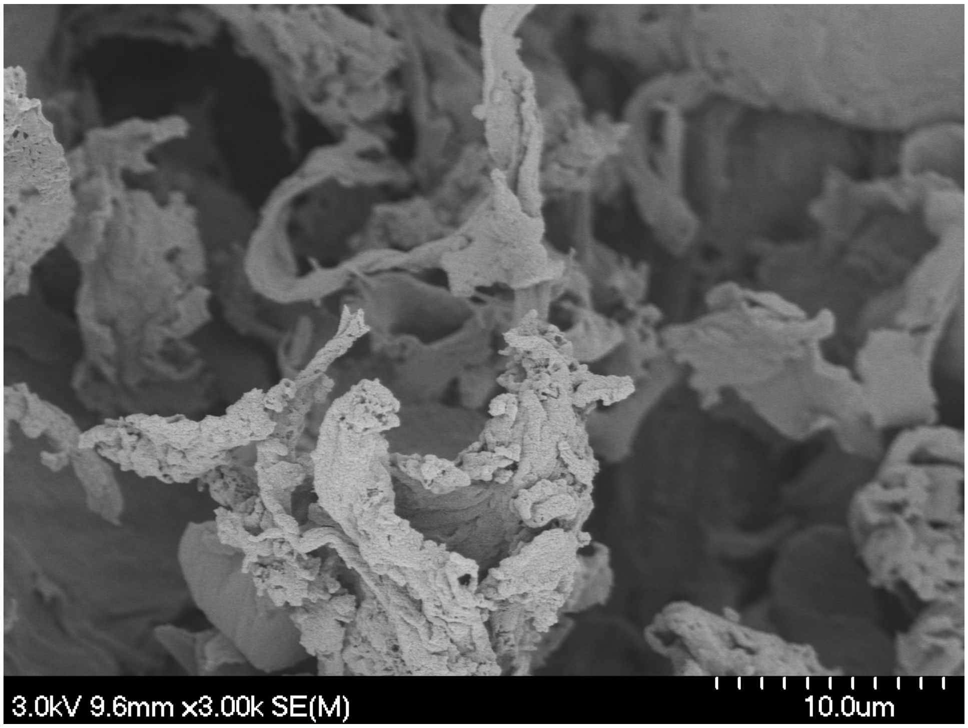
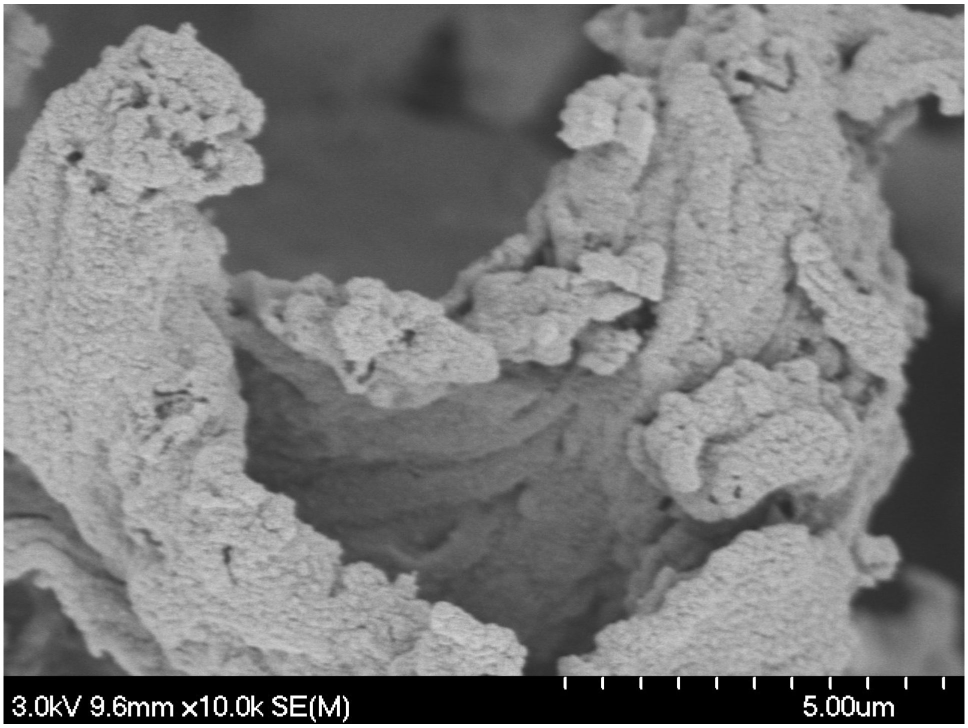
10.0um


3.0kV 14.7mm x3.00k SE(M)
10.0um

E-7 Torrefied biomass char (Horizontal face)



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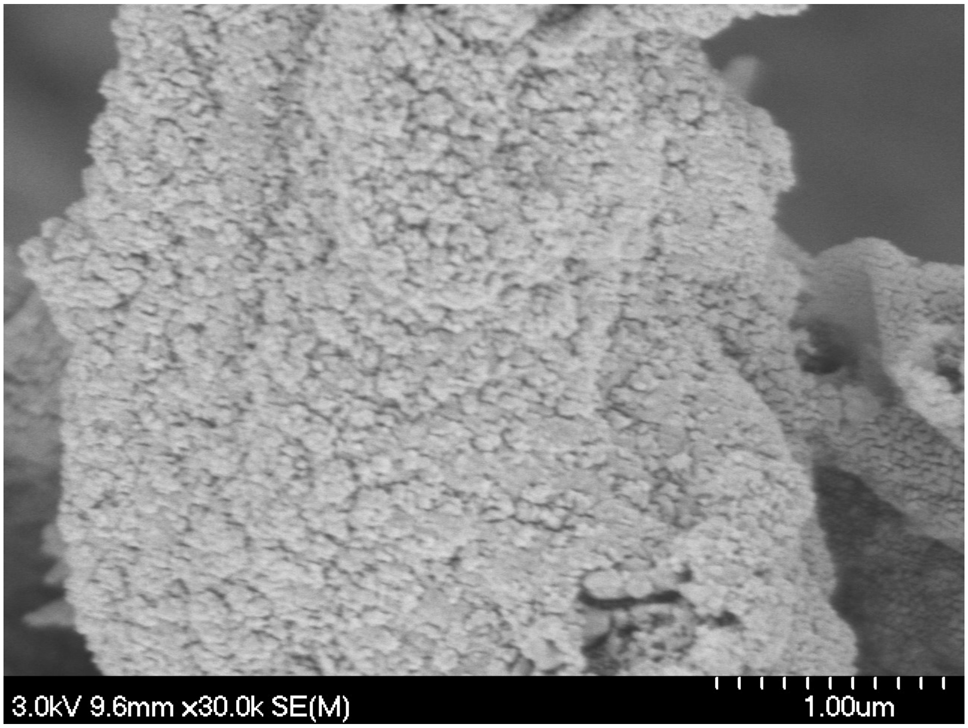
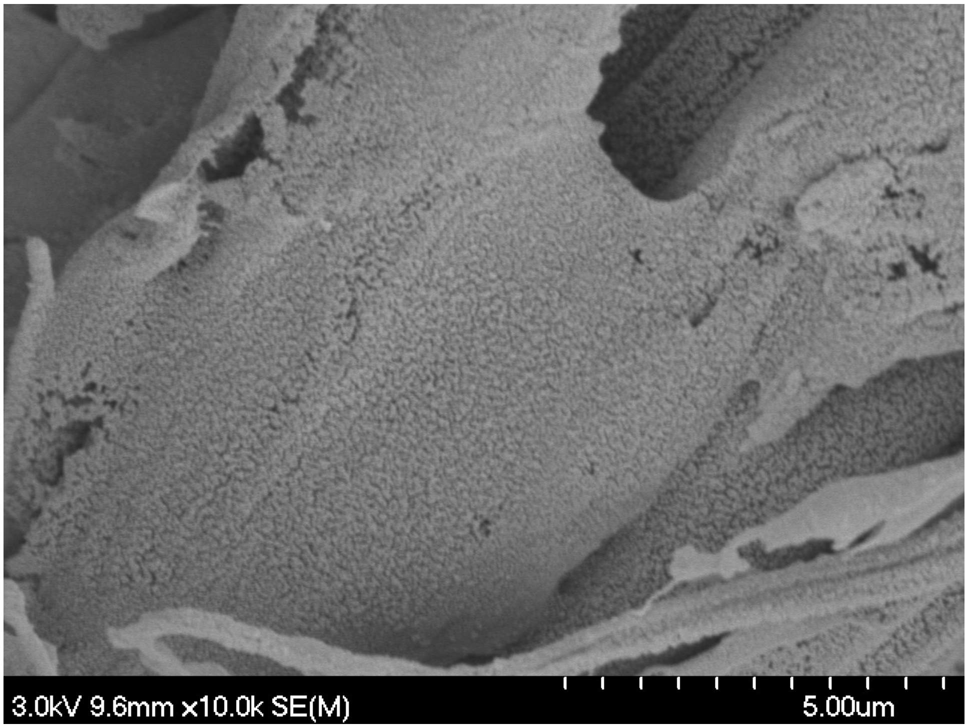
5.00um


3.0kV 9.6mm x30.0k SE(M)
1.00um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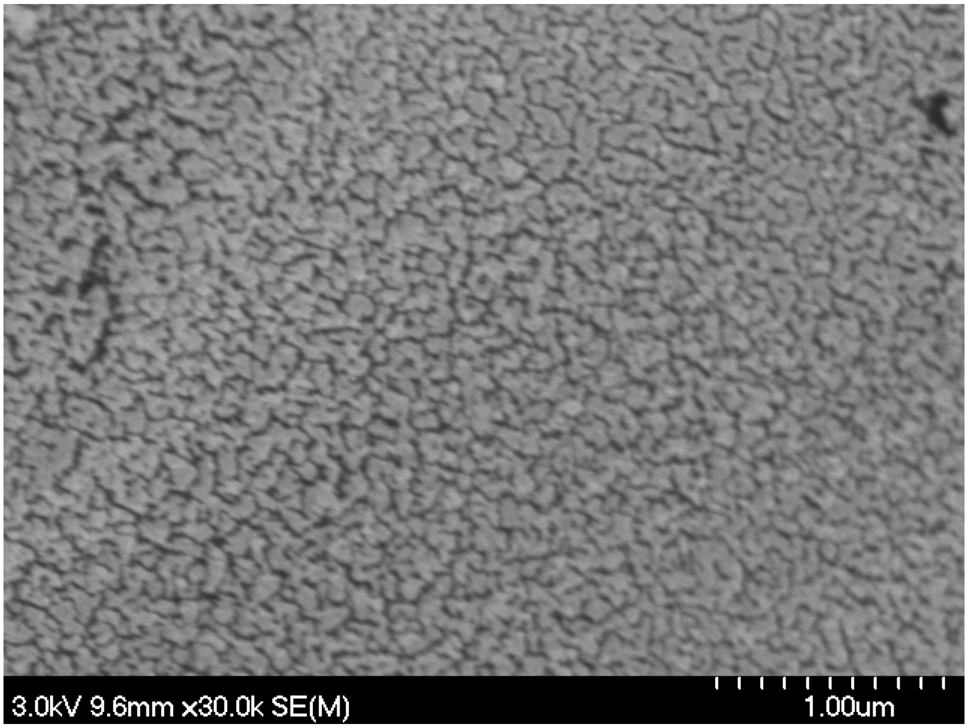
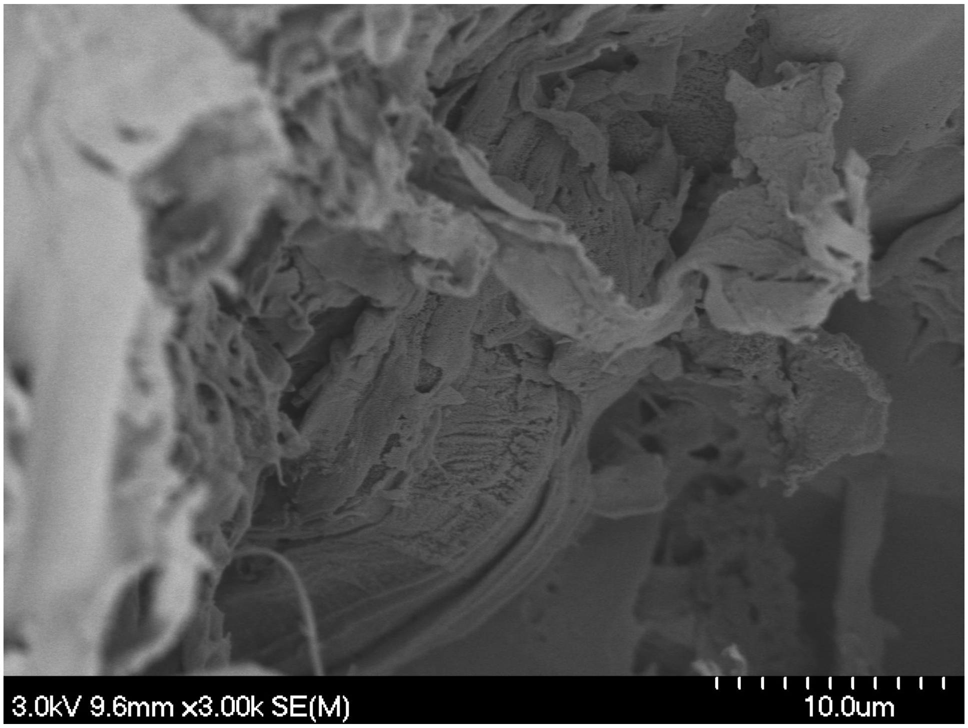
5.00um


3.0kV 9.6mm x30.0k SE(M)
1.00um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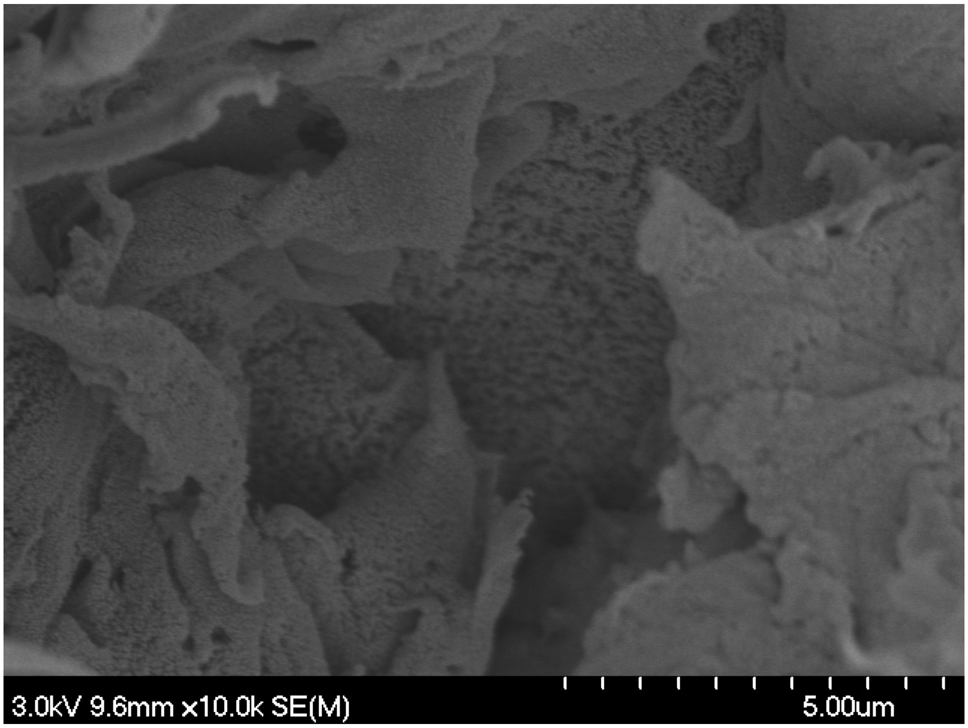
10.0um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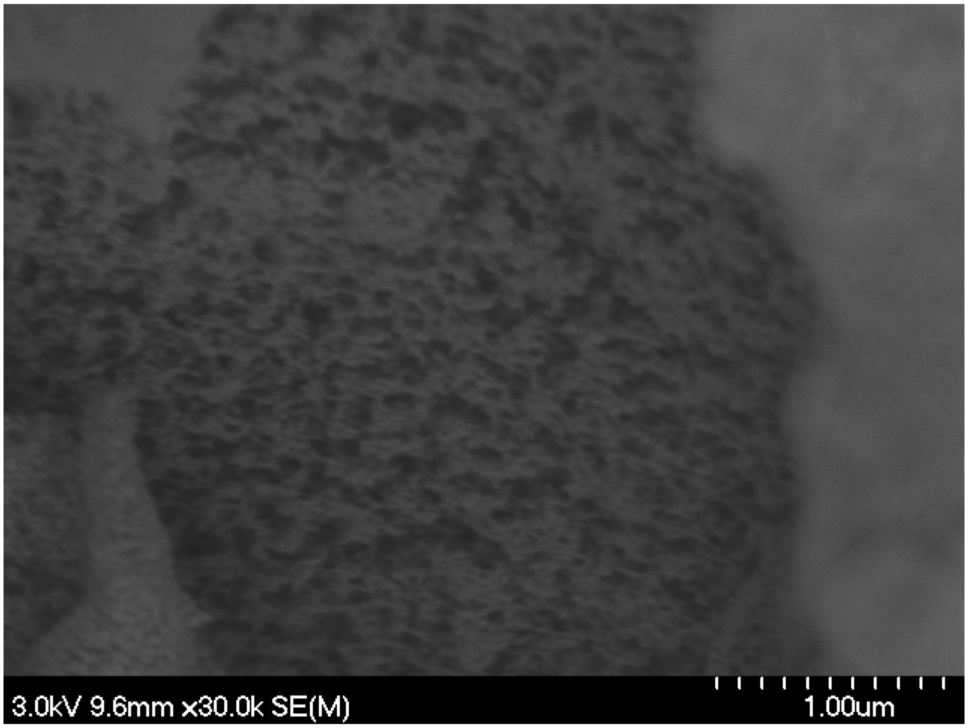
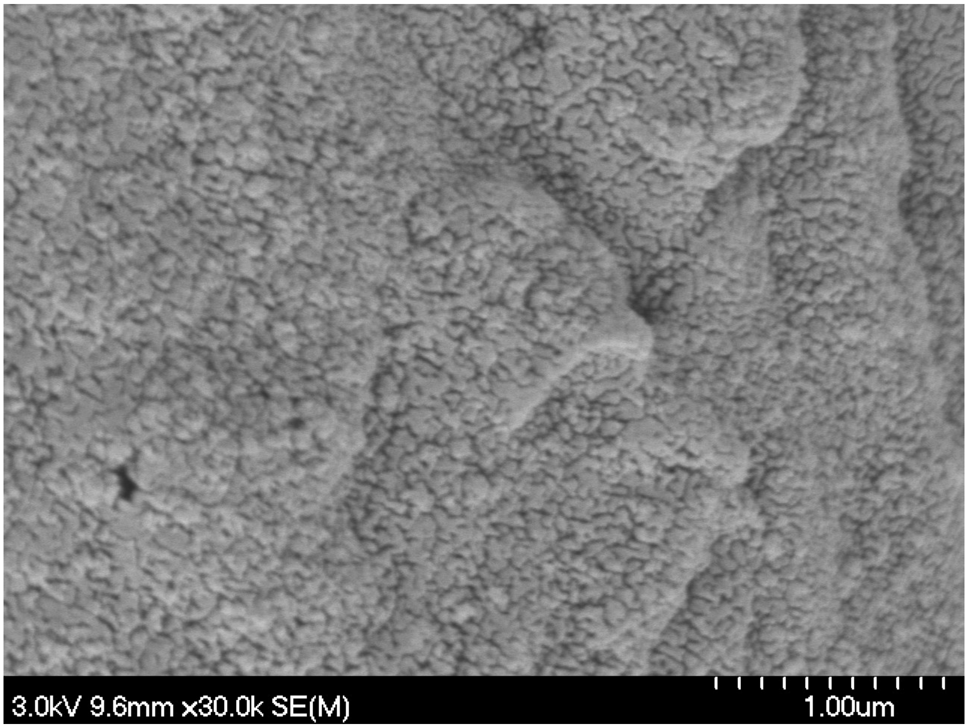
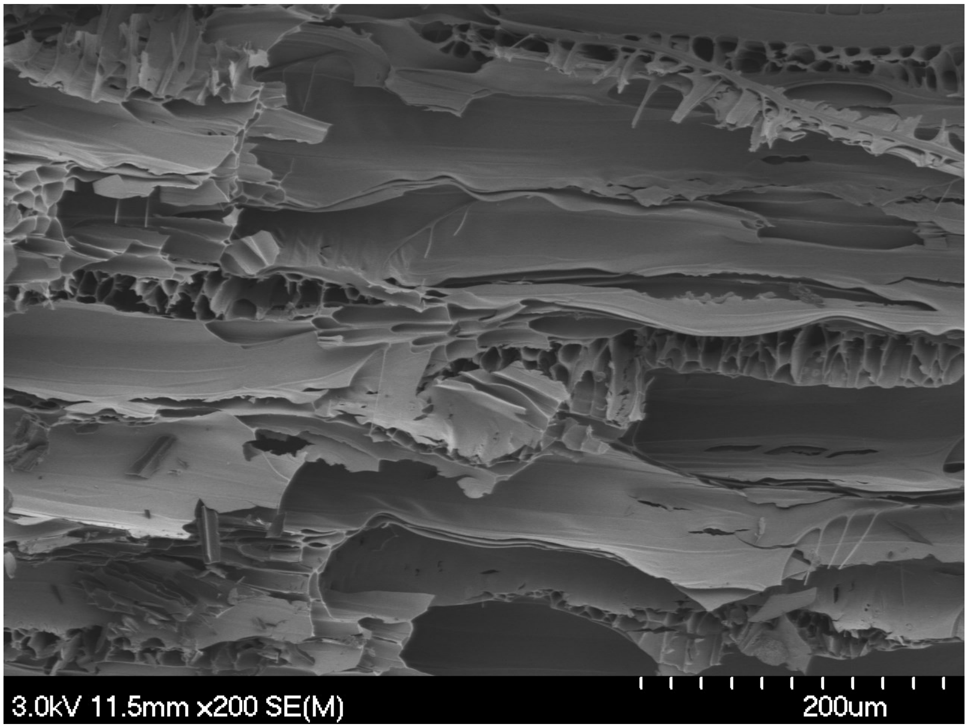
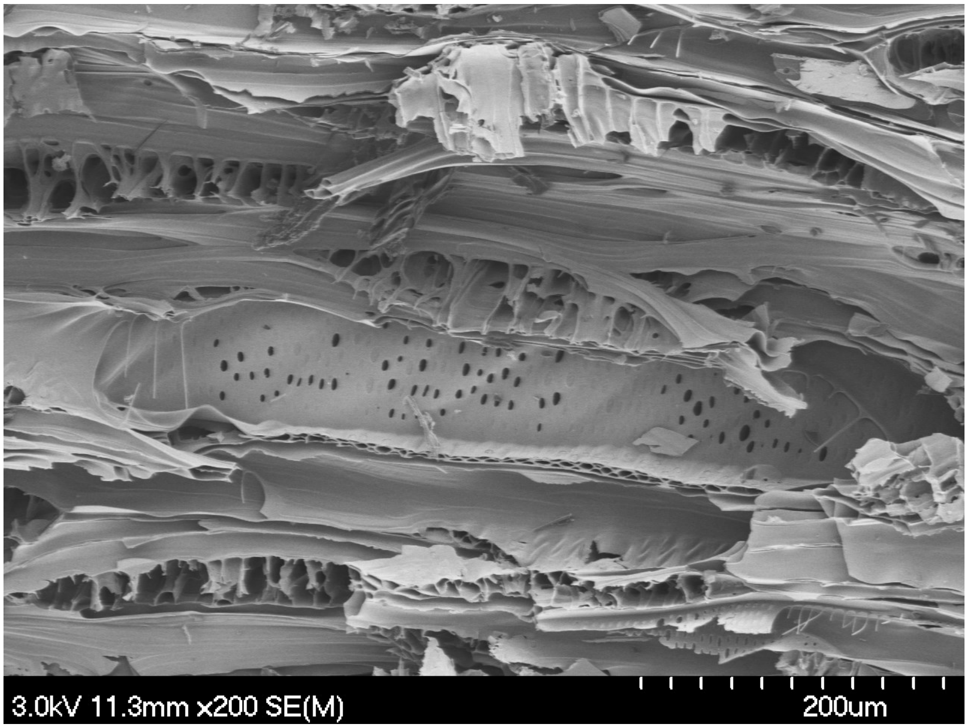
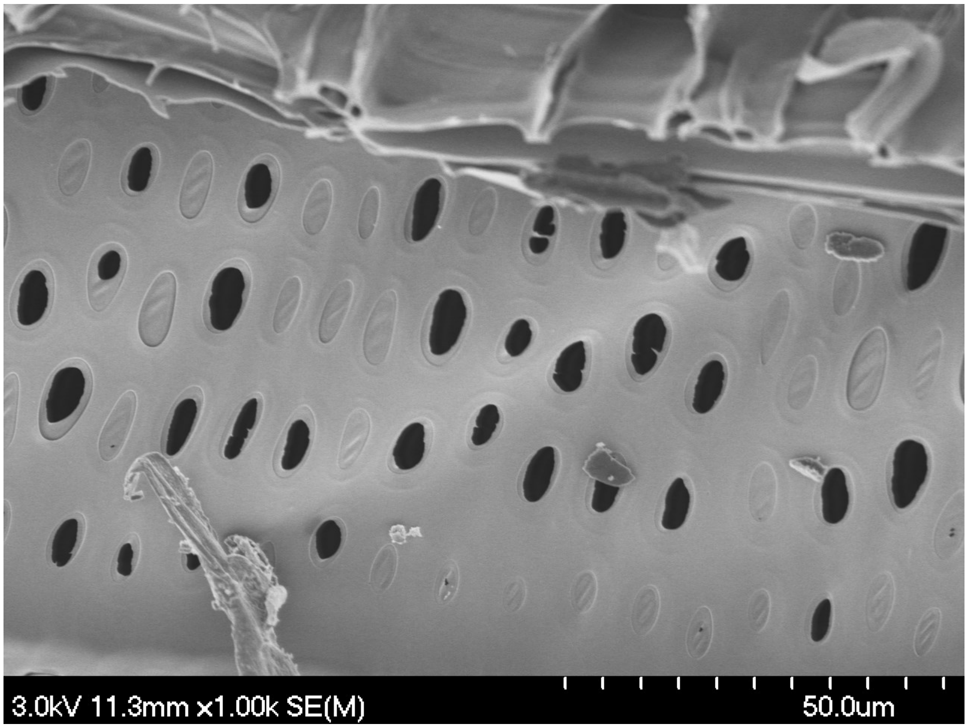

3.0kV 9.6mm x30.0k SE(M)
1.00um

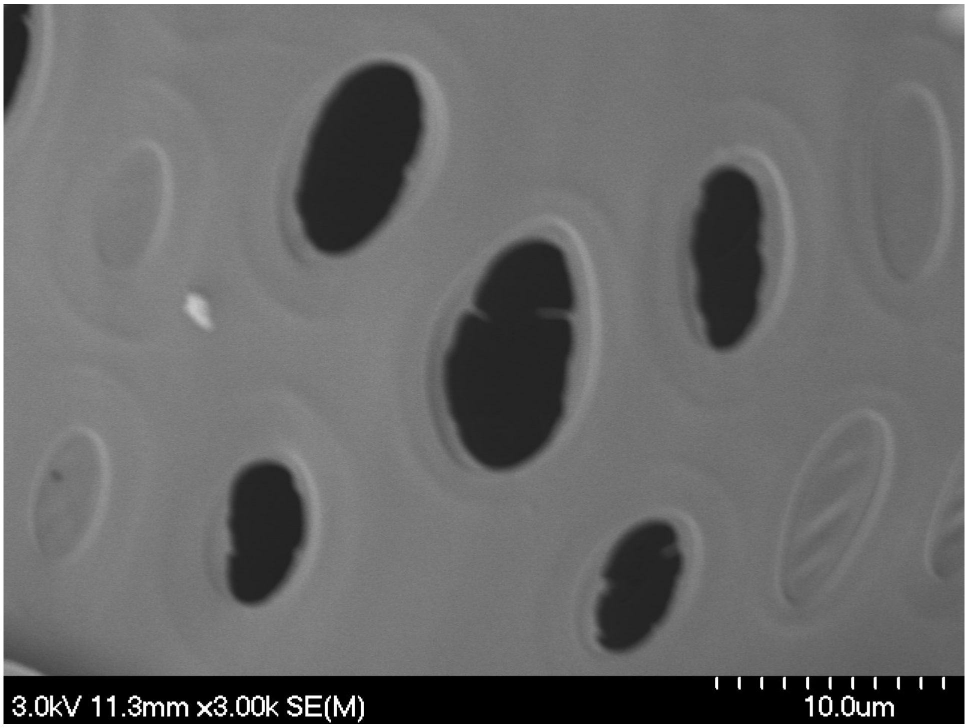

3.0kV 9.6mm x30.0k SE(M)
1.00um

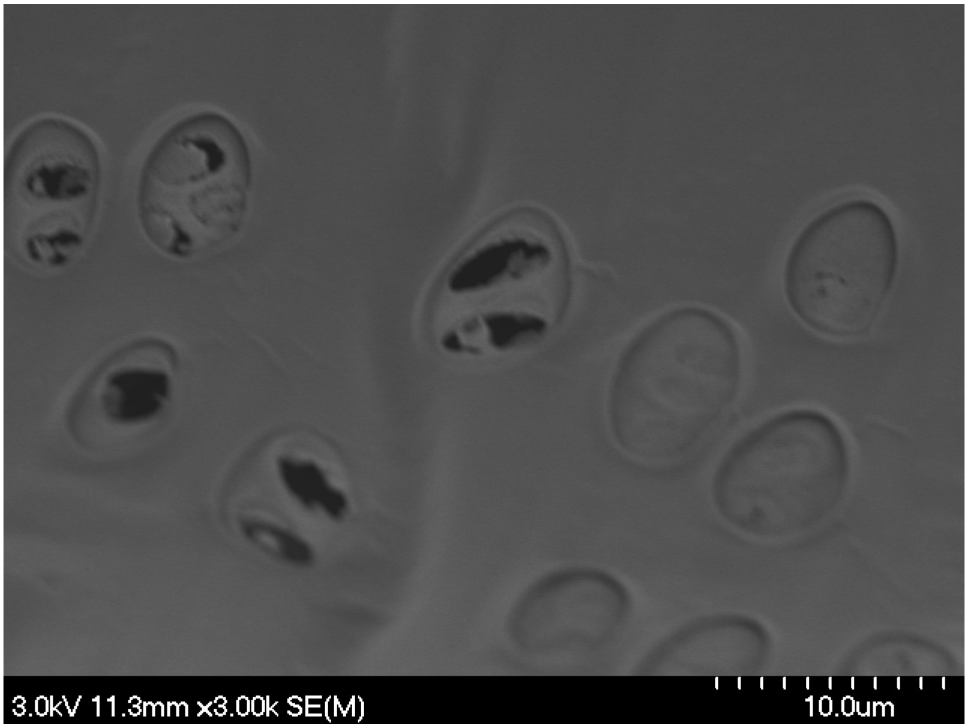
E-8 Torrefied Biomass Char (Vertical face)

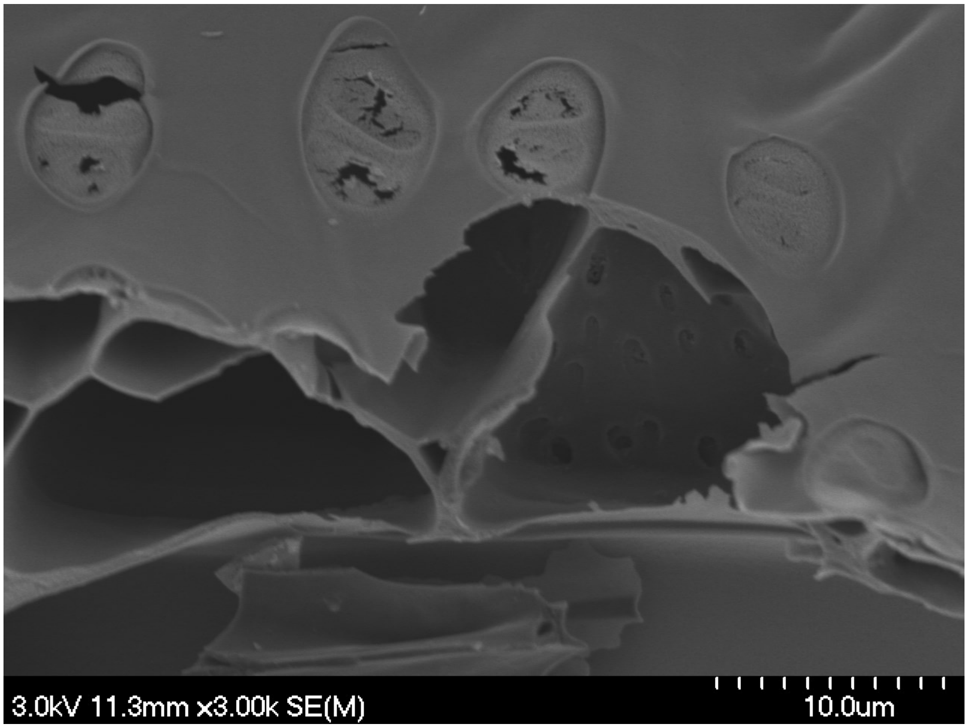


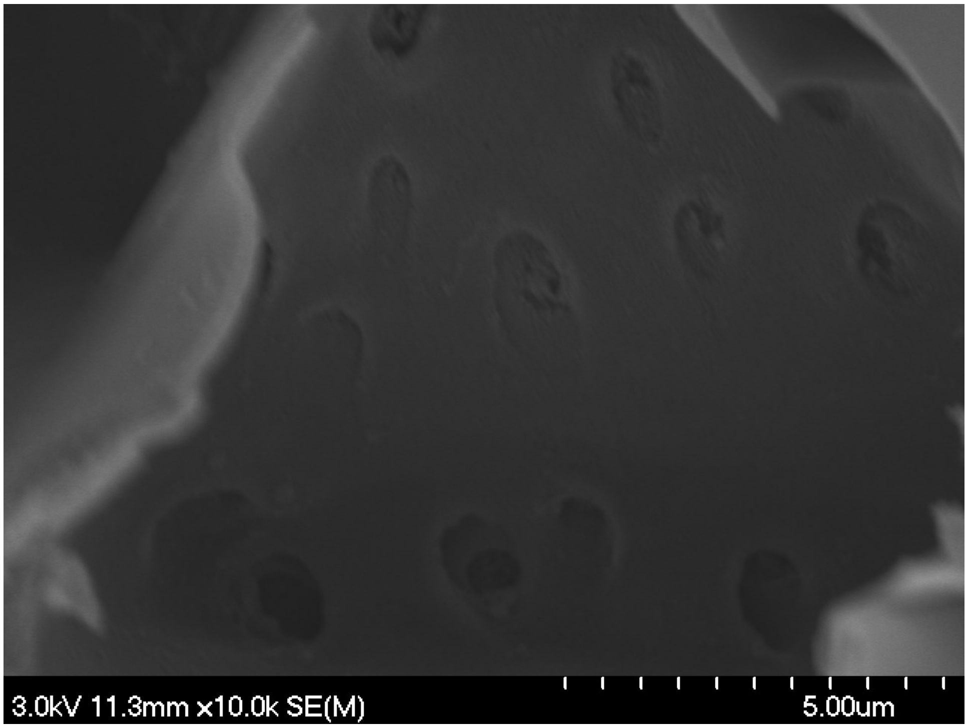


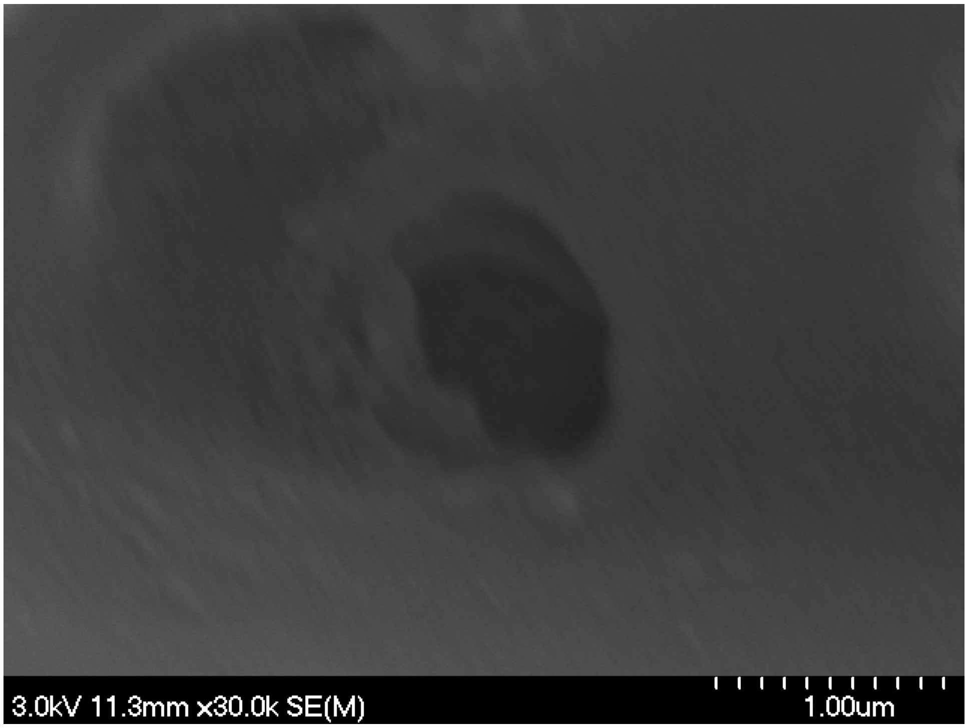

3.0kV 11.3mm x1.00k SE(M)
50.0um


3.0kV 11.3mm x3.00k SE(M)
10.0um


3.0kV 11.3mm x3.00k SE(M)
10.0um


3.0kV 11.3mm x3.00k SE(M)
10.0um


3.0kV 11.3mm x10.0k SE(M)
5.00um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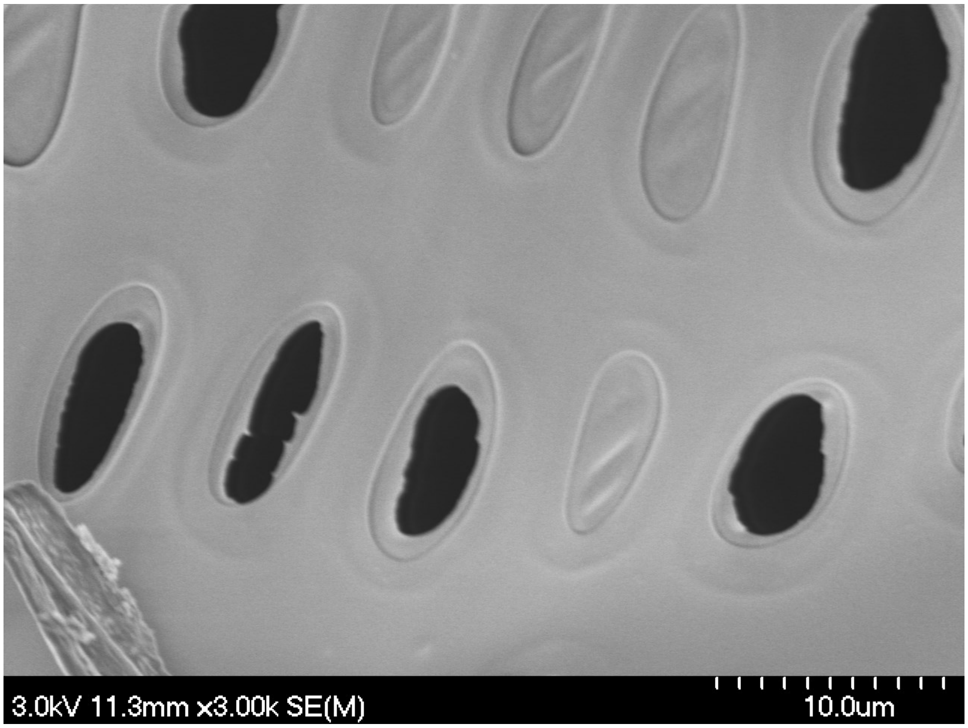
1.00um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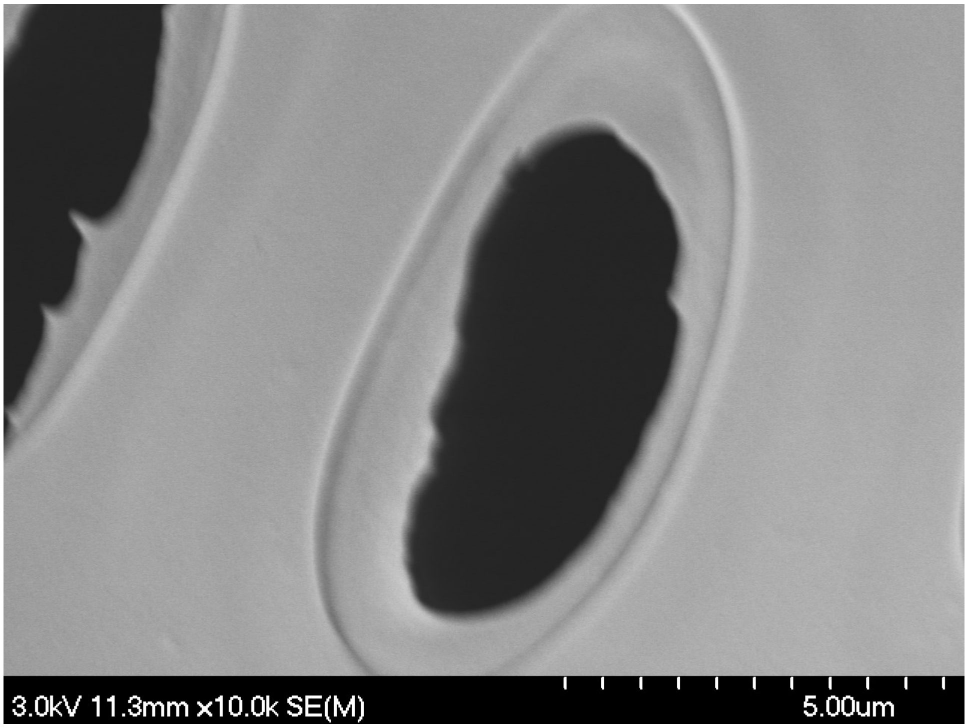
10.0um


3.0kV 11.3mm x10.0k SE(M)
5.00um

APPENDIX F: GLOSSARY

Higher heating value (HHV) - The amount of heat released by a specified quantity at 25°C when the fuel is combusted and the products has returned to a temperature of 25°C.

Lower heating value (LHV) – The amount of heat released by fully combusting a specified quantity of fuels less that the latent heat of vaporization of the water vapor formed by the combustion in the fuel.

Normal cubic meter (Nm^3) – A unit of volume at 0^oC temperature and 1.013 bar atmospheric pressure.

Producer gas - A mixture of gas; hydrogen, nitrogen and carbon dioxide produced from the burning of fuel in presence of air or steam.

Pyrolysis – A thermal decomposition process at $300\text{-}650^oC$ in the absence of oxygen.

SLPM – A measuring unit of volumetric flow rate of gas at standard temperature 15^oC temperature and 1.01325 bar atmospheric pressure.

Standard cubic meter (Sm^3) – A unit of volume at 15^oC temperature and 1.01325 bar atmospheric pressure.

Syngas – A combination of hydrogen and carbon monoxide gas.

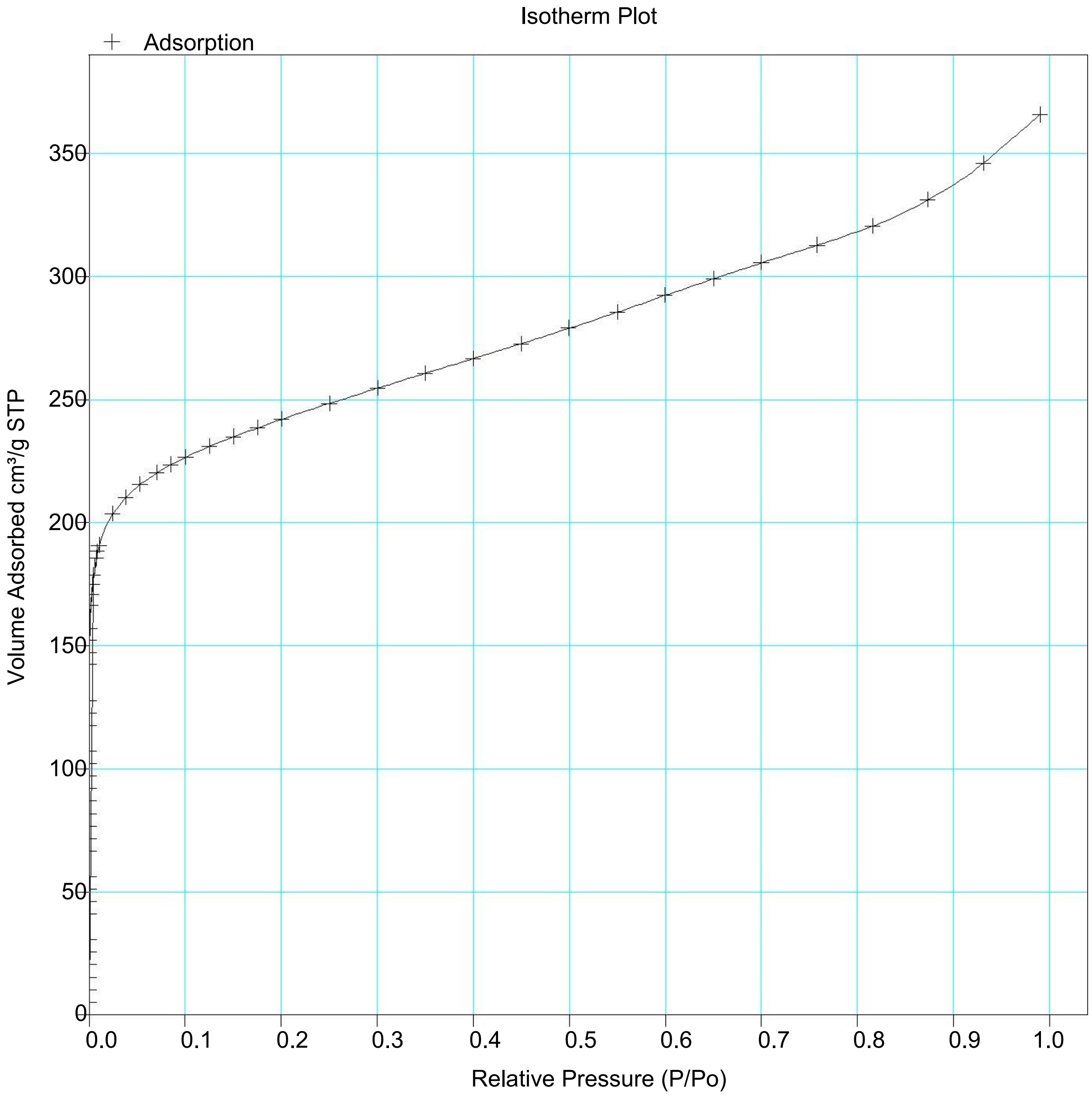
APPENDIX G: GAS ADSORPTION REPORT

```
ASAP 2010 V5.03  C              Unit 1          Serial #                  Page  1
                                                96-2045650

             Sample: TORREFIED CHAR
           Operator: jcb
          Submitter: jcb
          File Name: C:\ASAP2010\DATA\TORREFIED CHAR.SMP

            Started: 4/8/2014 9:26:45AM    Analysis Adsorptive: N2
          Completed: 4/9/2014 3:55:15AM          Analysis Bath: 77.35 K
        Report Time: 4/17/2014 9:53:36AM   Thermal Correction: No
      Sample Weight: 0.0470 g              Smoothed Pressures: No
     Warm Freespace: 17.1075 cm³  ENTERED      Cold Freespace: 53.4727 cm³
    Equil. Interval: 40 secs               Low Pressure Dose: 5.00 cm³/g STP


                                  Analysis Log

     Relative          Pressure       Vol Adsorbed     Elapsed Time       Saturation
     Pressure           (mmHg)        (cm³/g STP)        (HR:MN)        Press.(mmHg)

                                                          00:37           779.18994
    0.000000115         0.00009          5.1139          01:27
    0.000000006         0.00000         10.2294          01:51
    0.000000321         0.00025         15.3428          02:03
    0.000000821         0.00064         20.4577          02:15
    0.000001283         0.00100         25.5738          02:27
    0.000001667         0.00130         30.6868          02:41
    0.000002058         0.00160         35.8012          02:56
    0.000002494         0.00194         40.9170          03:14
    0.000001692         0.00132         46.0343          03:54
    0.000001371         0.00107         51.1508          04:30
    0.000001473         0.00115         56.2649          05:12
    0.000002306         0.00180         61.3784          05:31
    0.000002952         0.00230         66.4918          06:07
    0.000004610         0.00360         71.6025          06:20
    0.000006979         0.00545         76.7133          06:32
    0.000010045         0.00784         81.8216          06:46
    0.000014097         0.01101         86.9301          07:00
    0.000019441         0.01519         92.0360          07:14
    0.000026627         0.02080         97.1388          07:28
    0.000035841         0.02800        102.2362          07:42
    0.000047219         0.03690        107.3282          08:31
    0.000063917         0.04996        112.4137          08:52
    0.000086527         0.06763        117.4865          09:14
    0.000117475         0.09183        122.5450          09:30
    0.000164878         0.12890        127.5735          09:40
    0.000221907         0.17350        132.5844          09:55
    0.000305014         0.23850        137.5477          10:10
    0.000420062         0.32849        142.4524          10:25
    0.000577845         0.45191        147.2802          10:39
    0.000802786         0.62790        152.2127          10:56
    0.001111645         0.86956        157.0607          11:12
    0.001537202         1.20256        161.7857          11:28
```

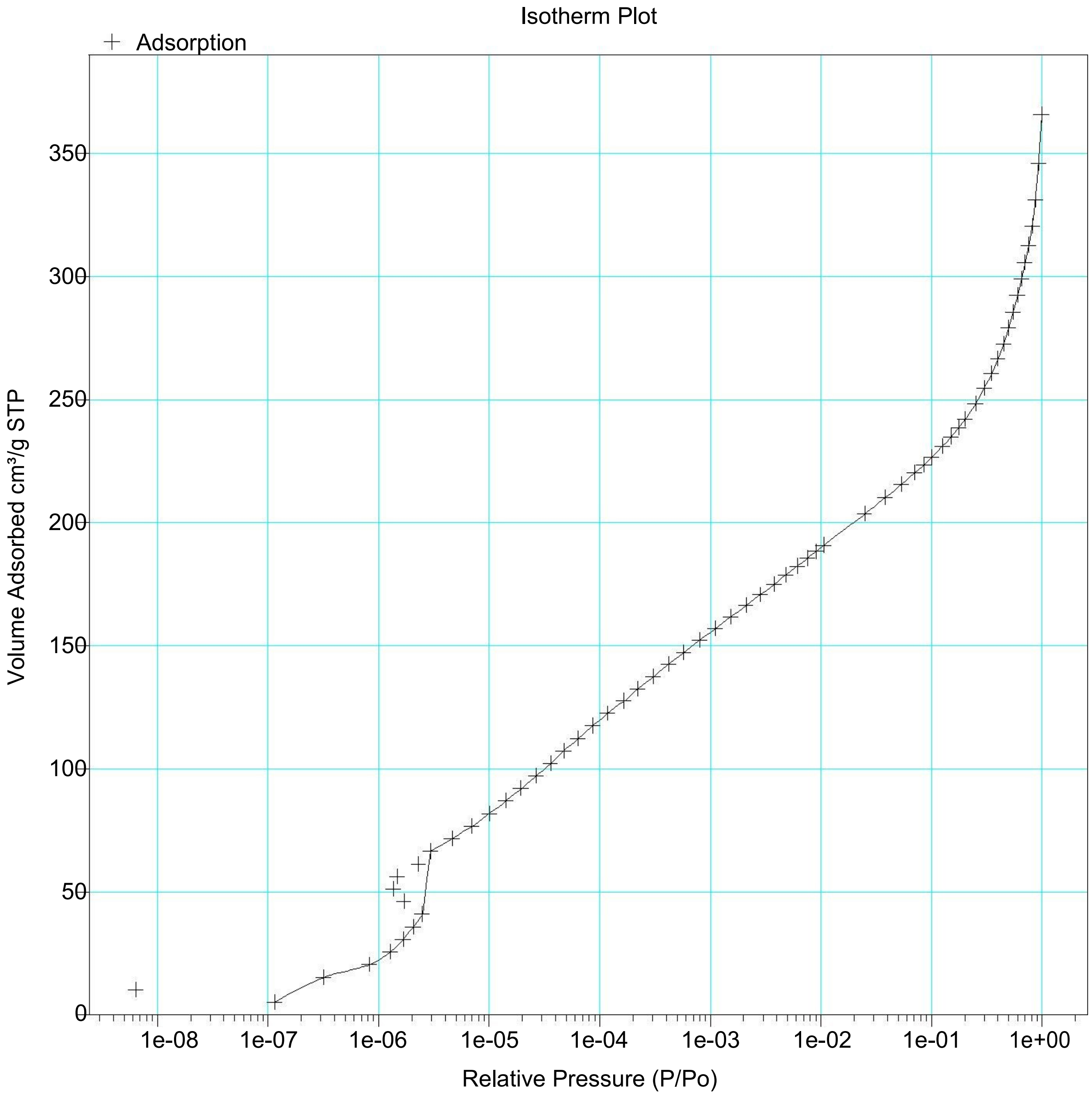
0.002098159	1.64156	166.3586	11:44	
0.002827067	2.21206	170.7383	12:00	
0.003775061	2.95406	174.8213	12:13	
0.004796379	3.75356	178.7223	12:26	
0.006138168	4.80406	182.3271	12:41	
			12:46	782.67780
0.007561778	5.91850	185.5618	12:59	
0.009015325	7.05623	188.2697	13:10	
0.010600966	8.29739	190.8158	13:24	

```
           Sample: TORREFIED CHAR
         Operator: jcb
        Submitter: jcb
        File Name: C:\ASAP2010\DATA\TORREFIED CHAR.SMP

          Started: 4/8/2014 9:26:45AM    Analysis Adsorptive: N2
        Completed: 4/9/2014 3:55:15AM          Analysis Bath: 77.35 K
      Report Time: 4/17/2014 9:53:36AM   Thermal Correction: No
    Sample Weight: 0.0470 g              Smoothed Pressures: No
   Warm Freespace: 17.1075 cm³  ENTERED      Cold Freespace: 53.4727 cm³
  Equil. Interval: 40 secs               Low Pressure Dose: 5.00 cm³/g STP


                                Analysis Log

     Relative         Pressure      Vol Adsorbed     Elapsed Time       Saturation
     Pressure          (mmHg)       (cm³/g STP)        (HR:MN)        Press.(mmHg)

    0.024872356       19.46782        203.5105          13:38
    0.038152380       29.86255        210.1769          13:52
    0.053480362       41.86042        215.5775          14:04
    0.070790225       55.40976        220.2199          14:15
    0.085721354       67.09734        223.6400          14:25
    0.100982523       79.04351        226.7001          14:36
    0.125823423       98.48835        231.0212          14:46
    0.150994161      118.19176        234.8988          14:57
    0.176032333      137.79175        238.5780          15:08
    0.200739911      157.13316        242.0474          15:18
    0.250485799      196.07457        248.4296          15:30
    0.300626900      235.32625        254.6427          15:43
    0.350172714      274.11252        260.7110          15:55
    0.400179991      313.26074        266.7006          16:07
    0.450053988      352.30563        272.7148          16:20
    0.499927212      391.35040        279.0389          16:32
    0.550129473      430.65381        285.5502          16:45
    0.599934377      469.64694        292.3858          16:58
                                                        17:02           782.83295
    0.650271267      509.05377        299.0843          17:14
    0.700147553      548.09857        305.5414          17:26
    0.758255207      593.58716        312.7218          17:39
    0.815820991      638.65155        320.3886          17:51
    0.873029997      683.43665        331.0498          18:06
    0.931289610      729.04419        346.0978          18:21
    0.990156897      775.12744        365.7039          18:31
```

```
           Sample: TORREFIED CHAR
         Operator: jcb
        Submitter: jcb
        File Name: C:\ASAP2010\DATA\TORREFIED CHAR.SMP

          Started: 4/8/2014 9:26:45AM    Analysis Adsorptive: N2
        Completed: 4/9/2014 3:55:15AM          Analysis Bath: 77.35 K
      Report Time: 4/17/2014 9:53:36AM    Thermal Correction: No
    Sample Weight: 0.0470 g               Smoothed Pressures: No
   Warm Freespace: 17.1075 cm³  ENTERED       Cold Freespace: 53.4727 cm³
  Equil. Interval: 40 secs               Low Pressure Dose: 5.00 cm³/g STP
```

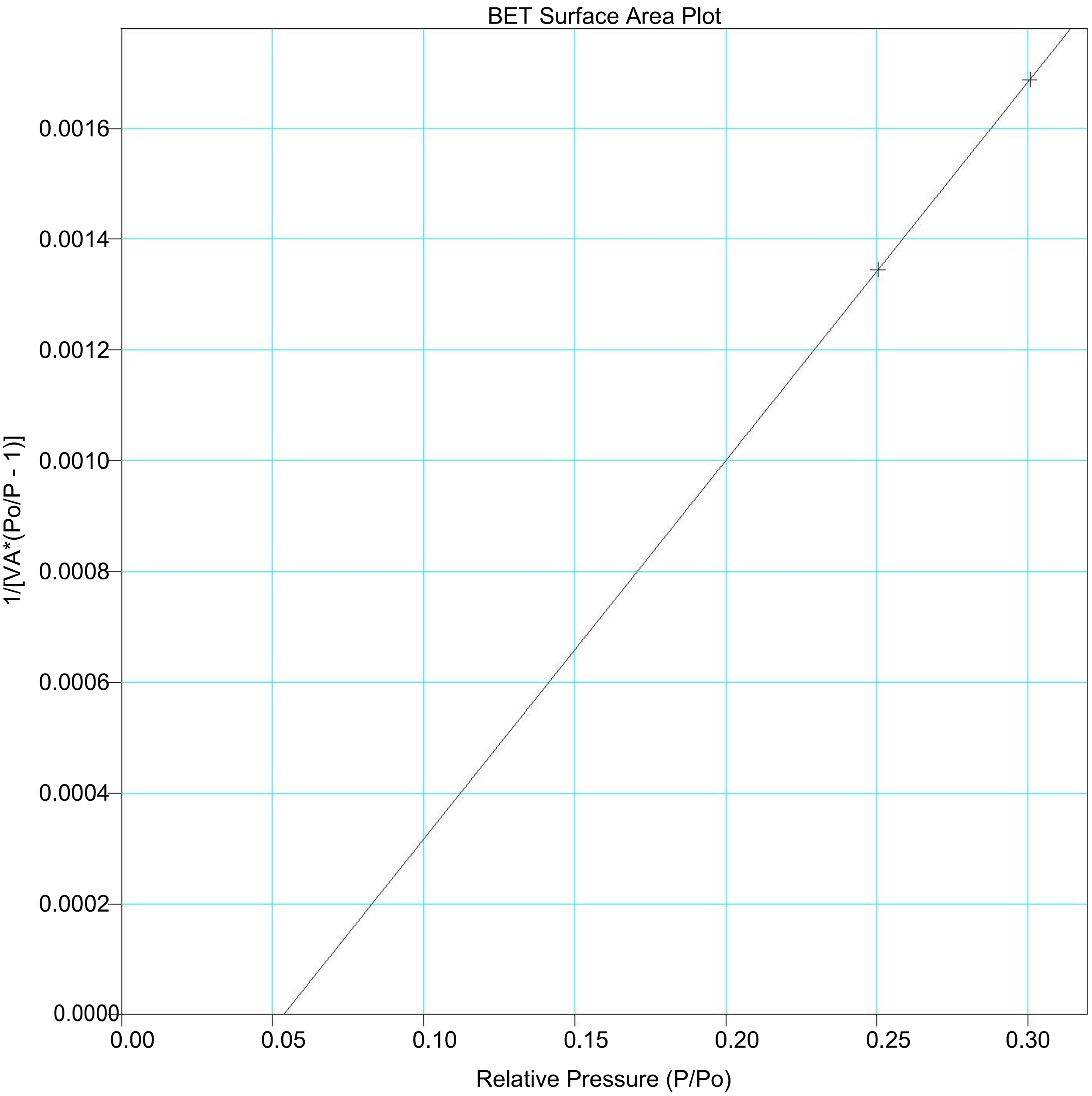


```
         Sample: TORREFIED CHAR
       Operator: jcb
      Submitter: jcb
      File Name: C:\ASAP2010\DATA\TORREFIED CHAR.SMP

        Started: 4/8/2014 9:26:45AM   Analysis Adsorptive: N2
      Completed: 4/9/2014 3:55:15AM         Analysis Bath: 77.35 K
    Report Time: 4/17/2014 9:53:36AM   Thermal Correction: No
  Sample Weight: 0.0470 g              Smoothed Pressures: No
 Warm Freespace: 17.1075 cm³  ENTERED     Cold Freespace: 53.4727 cm³
Equil. Interval: 40 secs               Low Pressure Dose: 5.00 cm³/g STP
```



```
           Sample: TORREFIED CHAR
         Operator: jcb
        Submitter: jcb
        File Name: C:\ASAP2010\DATA\TORREFIED CHAR.SMP

          Started: 4/8/2014 9:26:45AM   Analysis Adsorptive: N2
        Completed: 4/9/2014 3:55:15AM         Analysis Bath: 77.35 K
      Report Time: 4/17/2014 9:53:36AM   Thermal Correction: No
    Sample Weight: 0.0470 g              Smoothed Pressures: No
   Warm Freespace: 17.1075 cm³  ENTERED      Cold Freespace: 53.4727 cm³
  Equil. Interval: 40 secs                Low Pressure Dose: 5.00 cm³/g STP
                    ____________________________________________________

                              BET Surface Area Report

             BET Surface Area:          672.8567    ±   0.0000 m²/g
             Slope:                       0.006837 ±    0.000000
             Y-Intercept:                -0.000367 ±    0.000000
             C:                         -17.611882
             VM:                        154.566046    cm³/g STP
             Correlation Coefficient:     1.000000e+00

             Molecular Cross-section:     0.1620      nm²

          Relative                         Vol                          1/
          Pressure                       Adsorbed               [VA*(Po/P - 1)]
                                       (cm³/g STP)

         0.250485799                      248.4296                     0.001345
         0.300626900                      254.6427                     0.001688
```

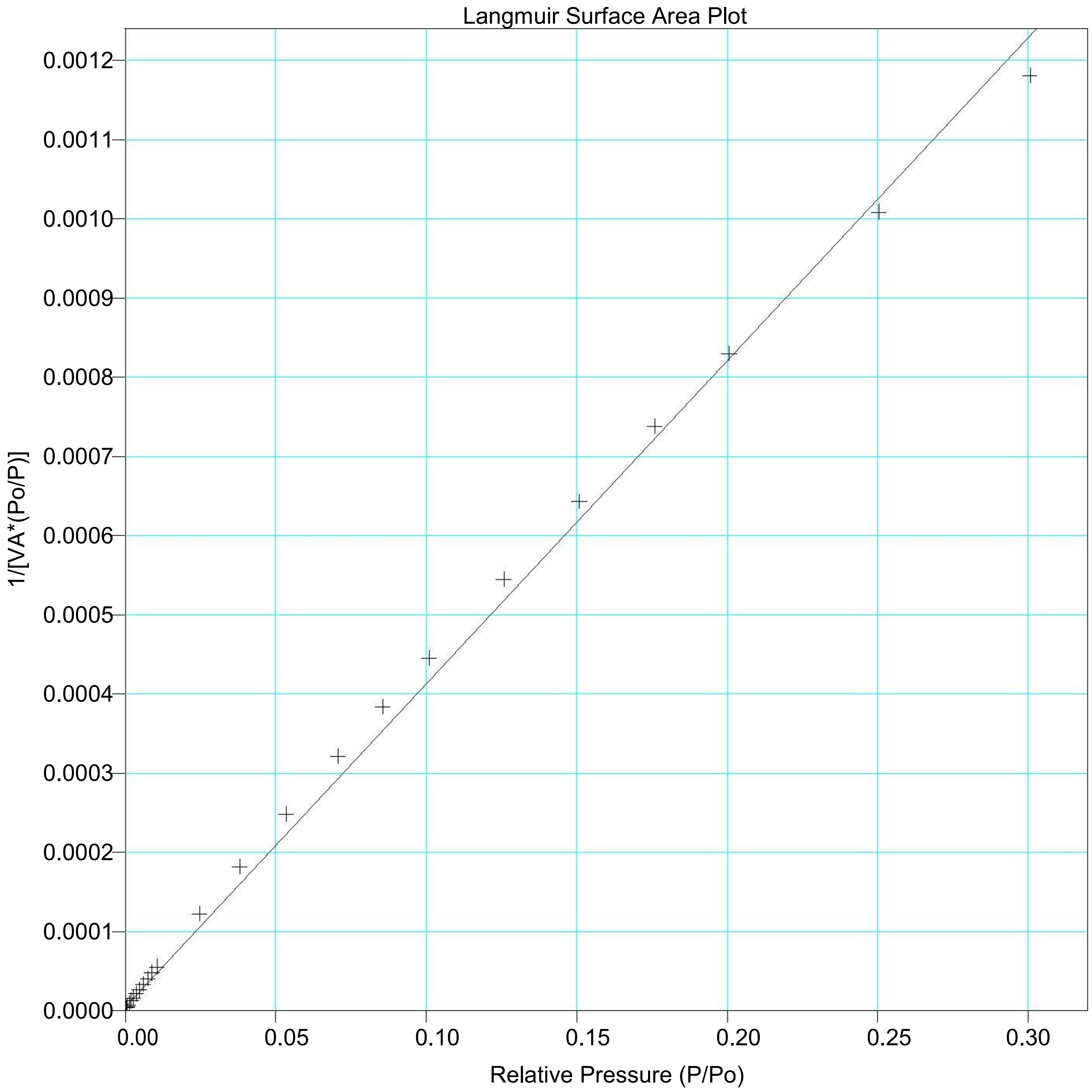
```
           Sample: TORREFIED CHAR
         Operator: jcb
        Submitter: jcb
        File Name: C:\ASAP2010\DATA\TORREFIED CHAR.SMP

          Started: 4/8/2014 9:26:45AM   Analysis Adsorptive: N2
        Completed: 4/9/2014 3:55:15AM         Analysis Bath: 77.35 K
      Report Time: 4/17/2014 9:53:36AM   Thermal Correction: No
    Sample Weight: 0.0470 g              Smoothed Pressures: No
  Warm Freespace: 17.1075 cm³  ENTERED      Cold Freespace: 53.4727 cm³
 Equil. Interval: 40 secs               Low Pressure Dose: 5.00 cm³/g STP
           ____________________________________________________
```



```
           Sample: TORREFIED CHAR
         Operator: jcb
        Submitter: jcb
        File Name: C:\ASAP2010\DATA\TORREFIED CHAR.SMP

          Started: 4/8/2014 9:26:45AM    Analysis Adsorptive: N2
        Completed: 4/9/2014 3:55:15AM          Analysis Bath: 77.35 K
      Report Time: 4/17/2014 9:53:36AM    Thermal Correction: No
    Sample Weight: 0.0470 g               Smoothed Pressures: No
   Warm Freespace: 17.1075 cm³  ENTERED      Cold Freespace: 53.4727 cm³
  Equil. Interval: 40 secs               Low Pressure Dose: 5.00 cm³/g STP


                        Langmuir Surface Area Report

          Langmuir Surface Area:    1067.5711   ±   7.1095 m²/g
          Slope:                      0.004078 ±    0.000027
          Y-Intercept:                0.000006 ±    0.000002
          b:                          0.001359
          VM:                       245.238310     cm³/g STP
          Correlation Coefficient:    9.988931e-01

          Molecular Cross-section:     0.1620      nm²

        Relative                     Vol                         1/
        Pressure                   Adsorbed                 [VA*(Po/P)]
                                 (cm³/g STP)

       0.000000115                  5.1139                    0.000000
       0.000000006                 10.2294                    0.000000
       0.000000321                 15.3428                    0.000000
       0.000000821                 20.4577                    0.000000
       0.000001283                 25.5738                    0.000000
       0.000001667                 30.6868                    0.000000
       0.000002058                 35.8012                    0.000000
       0.000002494                 40.9170                    0.000000
       0.000001692                 46.0343                    0.000000
       0.000001371                 51.1508                    0.000000
       0.000001473                 56.2649                    0.000000
       0.000002306                 61.3784                    0.000000
       0.000002952                 66.4918                    0.000000
       0.000004610                 71.6025                    0.000000
       0.000006979                 76.7133                    0.000000
       0.000010045                 81.8216                    0.000000
       0.000014097                 86.9301                    0.000000
       0.000019441                 92.0360                    0.000000
       0.000026627                 97.1388                    0.000000
       0.000035841                102.2362                    0.000000
       0.000047219                107.3282                    0.000000
       0.000063917                112.4137                    0.000001
       0.000086527                117.4865                    0.000001
       0.000117475                122.5450                    0.000001
       0.000164878                127.5735                    0.000001
       0.000221907                132.5844                    0.000002
       0.000305014                137.5477                    0.000002
       0.000420062                142.4524                    0.000003
       0.000577845                147.2802                    0.000004
       0.000802786                152.2127                    0.000005
       0.001111645                157.0607                    0.000007
       0.001537202                161.7857                    0.000010
```

```
           Sample: TORREFIED CHAR
         Operator: jcb
        Submitter: jcb
        File Name: C:\ASAP2010\DATA\TORREFIED CHAR.SMP

          Started: 4/8/2014 9:26:45AM   Analysis Adsorptive: N2
        Completed: 4/9/2014 3:55:15AM         Analysis Bath: 77.35 K
      Report Time: 4/17/2014 9:53:36AM   Thermal Correction: No
    Sample Weight: 0.0470 g              Smoothed Pressures: No
   Warm Freespace: 17.1075 cm³  ENTERED      Cold Freespace: 53.4727 cm³
  Equil. Interval: 40 secs             Low Pressure Dose: 5.00 cm³/g STP


                         Langmuir Surface Area Report

       Relative                    Vol                          1/
       Pressure                  Adsorbed                  [VA*(Po/P)]
                               (cm³/g STP)

      0.002098159                166.3586                    0.000013
      0.002827067                170.7383                    0.000017
      0.003775061                174.8213                    0.000022
      0.004796379                178.7223                    0.000027
      0.006138168                182.3271                    0.000034
      0.007561778                185.5618                    0.000041
      0.009015325                188.2697                    0.000048
      0.010600966                190.8158                    0.000056
      0.024872356                203.5105                    0.000122
      0.038152380                210.1769                    0.000182
      0.053480362                215.5775                    0.000248
      0.070790225                220.2199                    0.000321
      0.085721354                223.6400                    0.000383
      0.100982523                226.7001                    0.000445
      0.125823423                231.0212                    0.000545
      0.150994161                234.8988                    0.000643
      0.176032333                238.5780                    0.000738
      0.200739911                242.0474                    0.000829
      0.250485799                248.4296                    0.001008
      0.300626900                254.6427                    0.001181
```

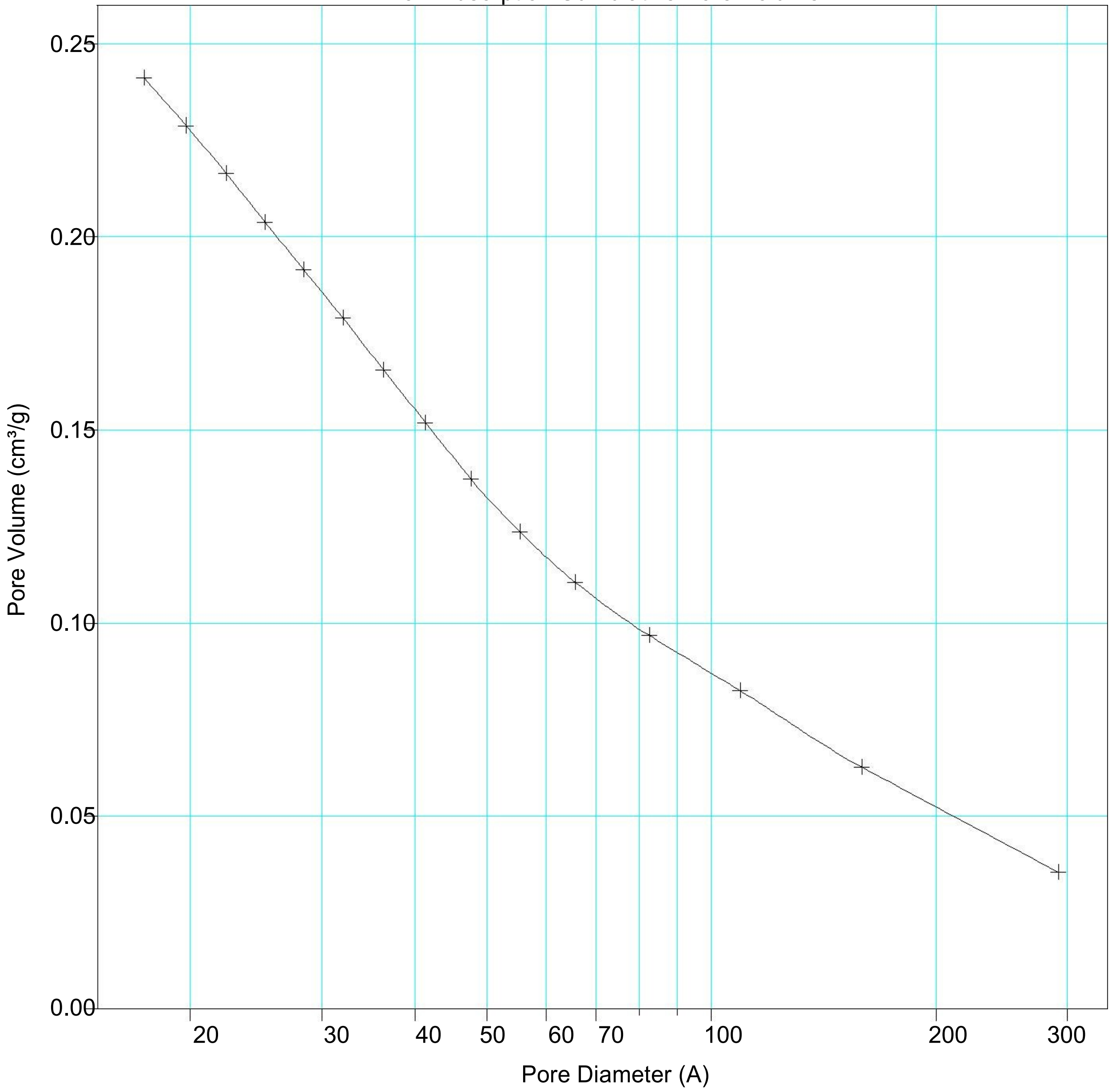
```
          Sample: TORREFIED CHAR
        Operator: jcb
       Submitter: jcb
       File Name: C:\ASAP2010\DATA\TORREFIED CHAR.SMP

         Started: 4/8/2014 9:26:45AM   Analysis Adsorptive: N2
       Completed: 4/9/2014 3:55:15AM         Analysis Bath: 77.35 K
     Report Time: 4/17/2014 9:53:36AM   Thermal Correction: No
   Sample Weight: 0.0470 g               Smoothed Pressures: No
  Warm Freespace: 17.1075 cm³  ENTERED      Cold Freespace: 53.4727 cm³
 Equil. Interval: 40 secs                Low Pressure Dose: 5.00 cm³/g STP
                ____________________________________________________
```



```
           Sample: TORREFIED CHAR
         Operator: jcb
        Submitter: jcb
        File Name: C:\ASAP2010\DATA\TORREFIED CHAR.SMP

          Started: 4/8/2014 9:26:45AM   Analysis Adsorptive: N2
        Completed: 4/9/2014 3:55:15AM         Analysis Bath: 77.35 K
      Report Time: 4/17/2014 9:53:36AM   Thermal Correction: No
    Sample Weight: 0.0470 g              Smoothed Pressures: No
   Warm Freespace: 17.1075 cm³  ENTERED      Cold Freespace: 53.4727 cm³
  Equil. Interval: 40 secs             Low Pressure Dose: 5.00 cm³/g STP
                  ____________________________________________________

                     BJH Adsorption Pore Distribution Report

                     t = 3.5400 x [-5.0000 / ln(P/Po)]0.3330

                         Diameter Range: 17.0000 to 1978.0000 A
                         Adsorbate Property Factor: 9.530000 A
                         Density Conversion Factor: 0.001547
                         Fraction of Pores Open at Both Ends: 0.000

      Pore         Average     Incremental    Cumulative   Incremental   Cumulative
    Diameter       Diameter    Pore Volume    Pore Volume   Pore Area     Pore Area
   Range  (A)        (A)         (cm³/g)        (cm³/g)       (m²/g)        (m²/g)

  1978.2-  292.1      324.6       0.035433       0.035433        4.367          4.367
   292.1-  159.0      187.9       0.027271       0.062704        5.805         10.171
   159.0-  109.3      124.7       0.019750       0.082454        6.335         16.506
   109.3-   82.6       92.0       0.014283       0.096737        6.210         22.716
    82.6-   65.7       72.0       0.013850       0.110587        7.689         30.405
    65.7-   55.4       59.6       0.012973       0.123560        8.705         39.110
    55.4-   47.6       50.8       0.013841       0.137401       10.889         49.999
    47.6-   41.4       44.0       0.014450       0.151851       13.135         63.134
    41.4-   36.3       38.5       0.013746       0.165597       14.293         77.427
    36.3-   32.0       33.9       0.013370       0.178967       15.787         93.214
    32.0-   28.4       30.0       0.012534       0.191501       16.724        109.937
    28.4-   25.2       26.6       0.012388       0.203888       18.636        128.573
    25.2-   22.4       23.6       0.012475       0.216363       21.146        149.719
    22.4-   19.8       20.9       0.012447       0.228810       23.841        173.559
    19.8-   17.3       18.4       0.012331       0.241141       26.849        200.408
```

```
           Sample: TORREFIED CHAR
         Operator: jcb
        Submitter: jcb
        File Name: C:\ASAP2010\DATA\TORREFIED CHAR.SMP

          Started: 4/8/2014 9:26:45AM    Analysis Adsorptive: N2
        Completed: 4/9/2014 3:55:15AM          Analysis Bath: 77.35 K
      Report Time: 4/17/2014 9:53:36AM    Thermal Correction: No
    Sample Weight: 0.0470 g               Smoothed Pressures: No
   Warm Freespace: 17.1075 cm³  ENTERED      Cold Freespace: 53.4727 cm³
  Equil. Interval: 40 secs                 Low Pressure Dose: 5.00 cm³/g STP
```

BJH Adsorption Cumulative Pore Volume



```
          Sample: TORREFIED CHAR
        Operator: jcb
       Submitter: jcb
       File Name: C:\ASAP2010\DATA\TORREFIED CHAR.SMP

         Started: 4/8/2014 9:26:45AM    Analysis Adsorptive: N2
       Completed: 4/9/2014 3:55:15AM          Analysis Bath: 77.35 K
     Report Time: 4/17/2014 9:53:36AM    Thermal Correction: No
   Sample Weight: 0.0470 g               Smoothed Pressures: No
  Warm Freespace: 17.1075 cm³  ENTERED       Cold Freespace: 53.4727 cm³
 Equil. Interval: 40 secs                 Low Pressure Dose: 5.00 cm³/g STP
          ____________________________________________________
```