Assessment of Pyrolysis techniques of Lignocellulosic Biomass for Biochar production

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ABSTRACT

Biomass pyrolysis at temperatures above 300°C, with the biochar being returned to the soil is a possible strategy for climate change mitigation and reducing fossil fuel consumption. In this study, an attempt has been made to develop a finite element model (FEM) in order to couple thermal heating and heat and mass transfer phenomena during pyrolysis. This numerical modelling and simulation approach helped the visualization of the process and optimized the production of biochar.

In this work, cylindrical sections of birch wood biomass were pyrolysed in a laboratory-scale thermal desorption unit. The influences of final pyrolysis temperature, heating rate, and pyrolysis atmosphere on the product yields were investigated. Results showed that the yield of pyrolysis products was reduced with increasing time and temperature. On the other hand, the char content in the wood increased together with increasing pyrolysis temperature as well as time for both slow and fast pyrolysis. A technique to maximize the amount of char in the product was also identified through this study and optimized along with the yield. The resulting biochar was tested through proximate analysis and differential scanning calorimetry to determine its thermodynamic qualities, which were analysed and compared according to their physical characteristics like porosity and reflectance.

RESUMÉ

La pyrolyse de biomasse à des températures excédant 300°C, suivi d'un retour au sol du produit de carbonisation de matériel biologique, s'avère une stratégie permettant de possiblement atténuer le changement climatique et réduire la consommation de combustibles fossiles. Dans la présente étude, nous tentâmes de créer un modèle d'éléments finis (MEF) permettant de coupler le réchauffement thermique et les phénomènes de transfert de chaleur et de masse opérant durant la pyrolyse. Cette démarche de modélisation et simulation numérique améliora notre habilité à visualiser le procédé et à optimiser la production de biochar.

Des sections cylindriques de biomasse de bois de bouleau furent soumises à une pyrolyse dans un désorbeur thermique de laboratoire. L'influence de la température finale de pyrolyse, la vitesse d'élévation de température, et l'atmosphère de pyrolyse fut investiguée. Les résultants démontrèrent que tandis que le rendement en produits de pyrolyse diminua avec une augmentation de la température et du temps de la pyrolyse, le contenu en charbon du bois augmenta avec une augmentation ces paramètres, tout autant pour une pyrolyse lente qu'une pyrolyse rapide. A travers cette démarche, nous identifiâmes une technique permettant de maximiser la quantité de charbon dans les produits de pyrolyse ainsi que le rendement global du procédé. Le biochar ainsi généré fut testé par analyse immédiate et analyse calorimétrique à compensation de puissance afin de déterminer ses propriétés thermodynamiques, qui furent analysées et comparées selon les caractéristiques physiques des différents biochars, soit leur porosité et leur réflectance.

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DEDICATION

This research is dedicated to all the scientists, researchers and environmentalists who are soldiering to keep the sanctity of our Earth's atmosphere preserved.

Kudos to you!

CONTRIBUTIONS OF THE AUTHORS

The authorship for the three manuscripts making up this thesis is as follows

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This study was performed by the candidate and supervised by Dr. G. S. V. Raghavan. The entire research work was done at the postharvest Technology laboratory of McGill University.

Mr. Y. Gariépy was involved from a technical point of view in the instrumentation and control of all the experiments in this study, giving expert guidance in the usage of equipment and provided a major contribution in reviewing and revising the papers. Mr. S.R.S. Dev was responsible for the simulation and modelling part of the thesis as well as his personal involvement in giving valid suggestions for improvement in every stage of the study. Dr. M. Ngadi, A. Adedeji and Dr. L. Liu provided support and guidance in using the hyperspectral imaging equipment and pycnometer, respectively, as well as for further data analysis.

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General Introduction

1.1 Problem Statement

Combating global climate change and meeting the ever rising energy demands of the world are the twin concerns which have occupied researchers all around the world. The consumption of fossil fuels that started with the Industrial Revolution has released ever increasing amounts of Carbon-dioxide (CO_2) and other greenhouse gases into the environment. In the last 50 years, the amount of atmospheric CO_2 measured at Mauna Loa in Hawaii has risen from a mean of 316.98 ppm in 1959 to 387.8 ppm in 2009 (Tans, 2010) .

The production of biochar has come under a lot of focus in the recent years due to its many advantages in terms of its efficiency as an energy source, its use as a fertilizer when mixed with soil, its ability to stabilize as well as reduce emissions of harmful gases in the atmosphere. Biochar finds use in the release of energy-rich gases which are then used for producing liquid fuels or directly for power and/or heat generation. It is highly useful in the mopping up of excess Green House Gases (GHGs) from fossil fuels. Biochar can potentially play a major role in the long term storage of carbon. This is the main focus of researchers all over the world in recent times. It is used in sequestration of carbon in soil and thereby reducing carbon dioxide levels in the atmosphere through uptake by plants. Biochar increases the fertility, water retention capability of the soil as well as increasing the rate of mineral delivery to roots of the plants.

Biochar can be an important tool to increase food security and cropland diversity in areas with severely depleted soils, scarce organic resources, and inadequate water and chemical fertilizer supplies.

The co-production of biochar and bioenergy can help in combating global climate change by displacing fossil fuel use and by sequestering carbon in stable soil carbon pools. Studies have also shown that it may also reduce emissions of nitrous oxide.

This simplistic yet powerful, approach can be used to store 2.2 gigatons of carbon annually by 2050. It is one of the few technologies that are relatively inexpensive, widely applicable, and quickly scalable (IBI, 2010). Charcoal in wood is estimated to be 40-50% (Renewable Energy UK, 2009). If the conversion of merchantable wood yield to carbon yield by species is carried out, the percentage of carbon in most wood biomass falls under the range of 47-53% (Birdsey 1996, Sampson and Hair 1996). On the other hand, the amount of carbon in charcoal is estimated to be around 75-85% (Hsiang-Ceieng Kung, 1972). This, in turn, would imply that about 43-45% of carbon can be conserved in the biochar.

Biochar is produced from a wide range of feedstock sources such as wood waste, timber, agricultural wastes, manure, leaves, food wastes, straw, paper sludge, green waste, distiller's grain, bagasse and many others (UK BRC, 2009). The three main technologies used for the production of biochar from different biomass sources are pyrolysis, gasification and combustion.

The production of biochar through the process of pyrolysis has become an extremely efficient and popular technology in recent years. The technique of pyrolysis consists of the thermal decomposition of biomass at low or absence of oxygen.

Amongst the various sources of biomass which have been used for pyrolysis, cellulosic and lignocellulosic feedstock make up the major portions. In fast pyrolysis systems, dry biomass is heated very rapidly (up to 1000°C/s) in the absence of oxygen and the products quickly removed and quenched to maximize production of bio-oils. Traditional charcoal-making typically employs slow pyrolysis conditions: slow heating rates (1–208C/min) in the absence of oxygen, and long char residence times (hours to days). The pyrolysis products and their yields depend on the source of the biomass and on the process settings like lignin, protein and ash content, pyrolysis temperature, process pressure, vapour residence time, particle size, heating rate, heat integration (Evans et. al., 1987).

The increase of the biochar yields is based on the minimization of the losses of carbon in the form of gases and liquids. Biochar is a product of both primary (char) and secondary (coke) reactions. There are number of methods employed to improve the yields of biochar with factors like low pyrolysis temperature (<400 ºC), high process pressure, long vapour residence time, extended vapour/solid contact, low heating rate, large biomass particle size, optimised heat integration (Masek, 2009).

The approach of the viability of using a continuous disposition or removal of the secondary gases and liquids produced during the pyrolytic reactions for the production of biochar from lignocellulosic biomass has not been investigated. Moreover, the comparison and characterization of the quality of biochar produced through slow and fast pyrolysis in terms of its physical properties such as porosity and its relation to the reflectance in the NIR/SWIR spectrum has seldom been reported in literature.

1.2 Proposed Solution

Though the different technologies of using pyrolysis for the production of biochar have been present for several millennia, it is only during the past decade that it has gained proper research value. This has come about due to the recent interest in using biochar for climate change mitigation strategies as well as its importance for soil amendment. The aim of this research was to evaluate the efficacy of the continuous disposition of the secondary syngases and liquids as a method employed to improve the yields of biochar produced through lignocellulosic biomass. In this study, the usage of Chinese birch wood samples for production of biochar was investigated. The effects of the pyrolysis conditions such as temperature and heating rate, on the biochar yields and fuel properties of biomass samples were determined by using statistical design techniques and through the results obtained from Differential Scanning Calorimetry. A single number (ratio) which would be able to quantify the efficiency of a particular pyrolysis technique to maximize the amount of char in the product was also identified through this study. A comparative assessment was also conducted to ascertain these structural differences between a slow and a fast pyrolysis biochar. The structure of the chars was characterized using Helium pycnometer as well as sample visualization by hyper spectral imaging to study of the influence of porosity on the reflectance of the biochar samples.

1.3 Objectives

1. Better understanding of the process of pyrolysis of biomass through numerical simulation studies.

2. The quantification of the thermodynamics and yields of the process and comparison between slow and fast pyrolysis.
3. The quantitative analysis of the biochar product through porosity studies and spectral evaluation.

1.3.1 Primary objectives

In this study, the first objective was to develop a finite element model (FEM) in order to couple electromagnetic heating, combustion, and heat and mass transfer phenomena during pyrolysis. The resulting sets of partial differential equations would then be solved simultaneously using the COMSOL Multiphysics software package. This numerical modelling and simulation approach helps the visualization of the process. It can eventually be used to study and optimize the production of biochar from a wide variety of lignocellulosic biomass.

The second objective of the thesis was to carry out quantitative analysis of the thermodynamic aspects of the pyrolysis process. This would include the assessment of the process in terms of the exothermic enthalpy of the biochar formed as the product. It would require the determination of the effects of pyrolytic conditions on the yields of the products and compare the results between different heating rates and the effect of continuous removal of secondary reaction products. This study would focus on the establishment of the relationship between product yield and pyrolysis conditions and would try to develop empirical models to predict product yields. This research would define the product in terms of the solid residence time, the higher and lower heating rates of the process and the amount of char formed by weight during the process.

1.3.2 Secondary objectives

The secondary objective of the thesis entailed carrying out the qualitative analysis of the biochar product through two different pyrolytic heating rates. Porosity measurements and their relation to reflectance in the biochar samples would be used to carry out further evaluation of the products formed in the pyrolysis process in terms of its physical composition.

Chapter 2

General Review of Literature

2.1 Introduction

"*Biochar is a black carbon material produced from the decomposition of plant-derived organic matter (biomass) in a low- or zero-oxygen environment (i.e. pyrolysis or gasification) to release energy-rich gases which are then used for producing liquid fuels or directly for power and/or heat generation."* (UK BRC, 2009)

In general, the thermochemical conversion of biomass leads to the formation of biochar at temperatures above 300°C. The structure of biochar is more or less amorphous but contains some local crystalline structure of highly conjugated aromatic compounds whose dimensions are in nanometers and consists of graphite-like non aligned layers. Biochar is also composed of aromatic-aliphatic organic compounds of complex structure like residual volatiles and mineral compounds such as inorganic ash, ibid. The carbon atoms, in biochar, are strongly bound to one another and this causes them to be resistant to attack and decomposition by microorganisms (UK BRC, 2009). The morphology of the biomass directly reflects on the structure of biochar.

Biochar – a vehicle for carbon sequestration

Biochar is carbon negative, while biofuels are generated in the process. The production of biochar has come under a lot of focus in the recent years due to its many advantages in terms of its efficiency as an energy source, its use as a fertilizer when mixed with soil, its ability to stabilize as well as reduce emissions of harmful gases in the atmosphere. Biochar finds use in the release of energy-rich gases which are then used for producing liquid fuels or directly for power and/or heat generation. It is highly useful in the mopping up of excess Green House Gases (GHGs) from fossil fuels. Biochar can potentially play a major role in the long term storage of carbon. This is the main focus of researchers all over the world in recent times. It is used in sequestration of carbon in soil and thereby reduces carbon dioxide levels in the atmosphere through uptake by plants. Biochar increases the fertility, water retention capability of the soil as well as increasing the rate of mineral delivery to roots of the plants.

Biochar is produced from a wide range of feedstock sources such as wood waste, timber, agricultural wastes, manure, leaves, food wastes, straw, paper sludge, green waste, distiller's grain, bagasse and many others (UK BRC, 2009). The three main technologies used for the production of biochar from different biomass sources are pyrolysis (P), gasification (G) and combustion (C). These three processes are differentiated based on the Equivalence ratio, which are the actual air fuel ratio / the air fuel ratio for complete combustion.

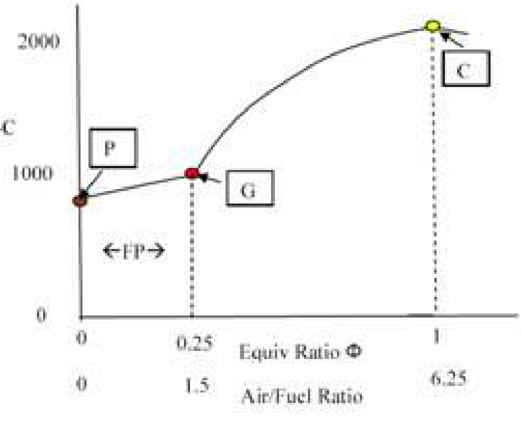


Figure 2.1. Equivalence ratio and air fuel diagram

(Source : Masek, 2009. Biochar- production technologies.)

Fig.2.1 shows the classification of the controlled incineration of biomass in terms of equivalence ratio. Liquefaction in a reducing medium generates solids and gases. Gasification produces hydrogen, carbon monoxide, carbon dioxide, and water by partial combustion. Gasification also produces hydrocarbons, particularly in the lower temperature ranges in fluidized-bed reactors. Pyrolysis converts organic substances to solid, liquid and gas by heating in the absence of atmospheric oxygen. The amounts of solid, liquid, and gaseous fractions formed and the distribution of their products are dependent distinctly on the process variables. The production of biochar through the process of pyrolysis has become an extremely efficient and popular technology in recent years. The thermal decomposition of biomass at low or absence of oxygen shown in the graph as the point P at $\Phi=0$ (T. Reed and R. Desrosiers, 1980). This takes place at temperatures of 300°C and above at which polymeric building blocks undergo cross linking, depolymerisation and fragmentation. The reaction scheme which takes place in the pyrolysis of biomass into biochar consists of smaller molecules being released in the form of gases and vapours – these can react with solid residues forming more condensed structures. The process of pyrolysis produces solids (charcoal), liquids (H_2O and organics), and gases (CO, CO_2, CH_4, H_2). Proportions and composition depend on feedstock and process conditions (e.g., heating rate).

The classification of biomass pyrolysis processes can be done on the basis of the heating rates involved in the process (Fig. 2.2.). It is based on the average heating rate of the reaction, which can be divided as fast, intermediate and slow pyrolysis. The fast pyrolysis would entail a heating rate > 1000 K/min which produces high yields of liquids e.g., bio-oil while the slow pyrolysis of biomass takes place at heating rates <10 K/min with high yields of solids, i.e., biochar. The fast pyrolysis takes place at moderate temperatures with short residence times while the slow pyrolysis process usually takes place at low temperatures with longer residence times.

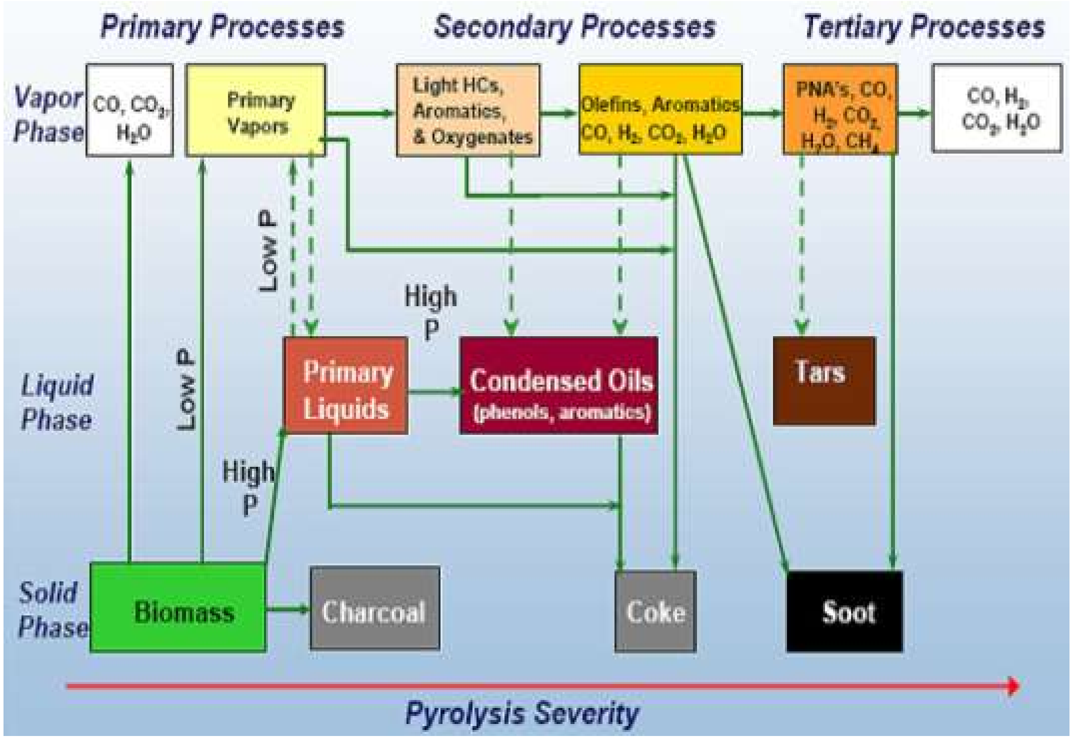


Figure 2.2. Biomass pyrolysis pathways

(Source: Evans, R.J and Milne, T.A., Energy & Fuels 1987, 1, 123-137)

The compositions of char, liquids and gases through fast pyrolysis of a biomass are found to be 12%, 75% and 13% respectively. At the same time, the slow pyrolysis yields 35%, 30% and 35% respectively of the three products. One of the recent technologies developed and least implicit of the thermal degradation processes in this context is fast pyrolysis. The products produced from this technology are complex. Although, overall pyrolysis is an endothermic process, in case of char formation, the process becomes exothermic at a temperature range of 280-350°C.

The heat for the pyrolysis process may be supplied in the following ways:

- directly as the heat of reaction
- directly by flue gases from combustion of by-products and/or feedstock
- indirectly by flue gases through the reactor wall
- indirectly by heat carrier other than flue gases (e.g., sand, metal spheres, etc.)

There are three basic technologies involved in the pyrolysis process which involve the formation of biochar and other products. These can be classified on the basis of the products and by-products of the process. There are technologies dedicated to bio-oil production, where biochar is an undesirable by-product. The second type of technology is dedicated to charcoal (biochar) production, without or with minimum production of useful by-products (gases and liquids) and the third category of technologies relate to the co-production of biochar and useful by-products (liquid fuels, syngas, chemicals, heat, electricity etc.). The pyrolysis products and their yields depend on the composition of the biomass like lignin, protein and ash content and on the process settings like pyrolysis temperature, process pressure, vapour residence time, particle size, heating rate and heat integration (Evans et. al., 1987).

The modifications that occur during the process of pyrolysis are described below

(1) Increase in the temperature inside the fuel due to the heat transfer from a heat source;

(2) At higher temperatures, there is an initiation of primary pyrolysis reactions which releases volatiles and forms char;

(3) Hot volatiles flow towards cooler solids, resulting in heat transfer between hot volatiles and cooler unpyrolyzed fuel;

(4) Tar is produced through the condensation of some of the volatiles in the cooler parts of the fuel, followed by secondary reactions;

(5) Autocatalytic secondary pyrolysis reactions proceed along with the primary pyrolytic reactions occurring simultaneously in competition; and

(6) Further thermal decompositions, reforming, water gas shift reactions, recombination of radicals, and dehydrations can also occur, which are depended on the process's residence time/ temperature/pressure profile.

The increase of the biochar yields is based on the minimization of the losses of carbon in the form of gases and liquids. Biochar is a product of both primary (char) and secondary (coke) reactions. There are number of methods employed to improve the yields of biochar with factors like low pyrolysis temperature (<400 ºC), high process pressure, long vapour residence time, extended vapour/solid contact, low heating rate, large biomass particle size and optimised heat integration (Masek, 2009).

Pyrolysis of Lignocellulosic Biomass

Amongst the various sources of biomass which have been used for pyrolysis, cellulosic and lignocellulosic feedstocks make up the major portions. Several conversion processes, which are currently under development, may result in increased residue utilization in the future.

The thermal degradation of lignocellulosic material is one of the most viable of these processes. It is being studied with great interest as a possible route to alternate energy sources and chemical raw materials. The average elemental composition of the lignocellulosic biomass is $CH_{1.4}O_{0.6}$. The composition of a lignocellulosic biomass is given by Fig. 2.3.

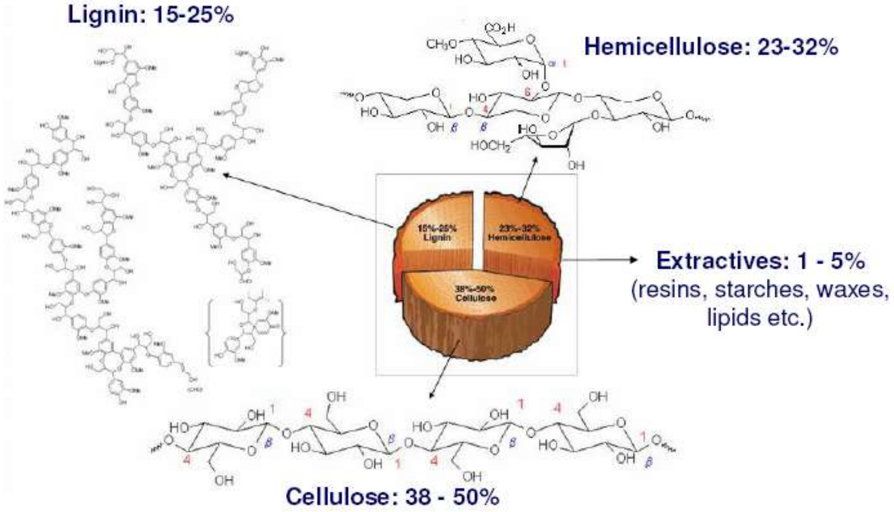


Figure 2.3. Average elemental composition of Lignocellulosic biomass

(Source : Masek, 2009. Biochar- production technologies.)

Structure of Cellulose

Cellulose fibers are responsible for providing wood's strength and comprises of approximately 40-50 % weight of dry wood. Cellulose is a linear polymer of β-(1$\rightarrow$4)-D-glucopyranose units in the $^4C_1$ conformation which leads to it having a high molecular weight (10^6 or more). The basic repeating unit of the cellulose polymer consists of two glucose anhydride units, called a cellobiose unit. Cellulose is insoluble with a crystalline structure, consisting of between 2000 and 14000 residues with each residue oriented 180° to the next within the chain. Individual strands of cellulose have similar hydrological properties like other soluble polysaccharides such as amylase.

However, cellulose’s utilizes its extensive intramolecular and intermolecular hydrogen bonding to form crystals making it completely insoluble in normal aqueous solutions. Ribbon like micro-fibril sheets, which are the basic construction units for a variety of complex fibers, are formed due to twisting of groups of individual cellulose chains in space. This crystalline structure of cellulose helps it to have better resistance against thermal decomposition than hemicelluloses. Thermal degradation of cellulose occurs due to the amorphous regions that contain waters of hydration, and free water is present within the wood. This water, upon being rapidly heated, disrupts the structure of wood by a steam explosion-like process. Anhydrocellulose and levoglucosan are produced due to thermal degradation of cellulose at 240-350 °C.

Upon heating in a nonreactive environment, cellulose decomposes homogeneously to various pyrolysis products following first-order reaction kinetics. These products may be grouped into three classes: chars, tars, and gases depending on their volatility. Chars are the carbon-rich non-volatile residue. Tars are high molecular weight products, which are rich in 1, 6 anhydro compounds that are volatile at pyrolysis temperature but condense near room temperature. Gases consist of lower molecular weight products such as CO and CO_2, and water, whose vapor pressure can be measured at room temperature (Fig. 2.4.) (Masek, 2009).

Structure of Hemicellulose

The second major wood chemical constituent is hemicellulose, which is also known as polyose. The usual percentage of hemicellulose in different woods ranges from 25-40% of the total mass of the dry wood.

Hemicellulose is a mixture of various monosaccharides such as glucose, mannose, galactose, xylose, arabinose, and 4-O-methyl glucuronic acid and galacturonic acid residues. Hemicelluloses have lower molecular weights than cellulose as well as lower number of repeating saccharide monomers approximately 150-200 compared to 4000-12000 in cellulose.

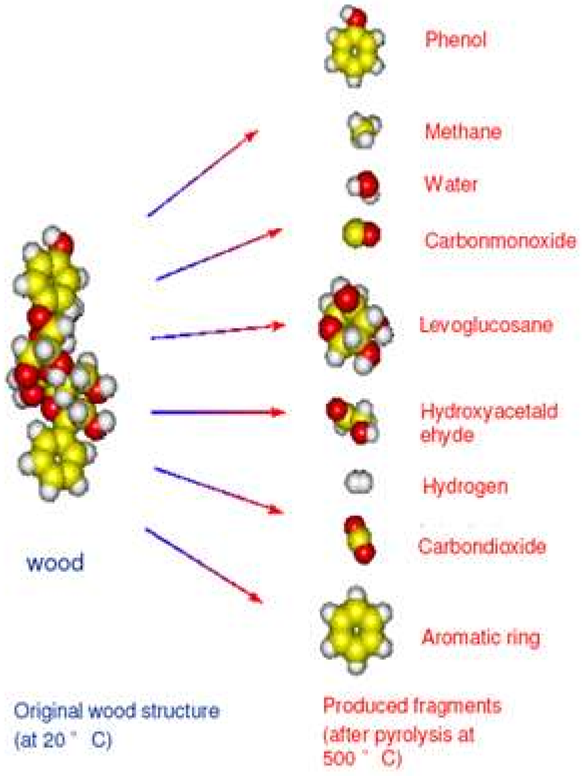


Figure 2.4. Pyrolysis of wood at 600°C

(Source: Masek, 2009. Biochar- production technologies.)

The decomposition of hemicellulose begins at lower temperatures compared to the crystalline structure of cellulose at around 200-260 °C. In slow pyrolysis of wood particularly, the loss of hemicellulose occurs in the temperature range of 130-194 °C, with most of this loss occurring above 180 °C (Mohan et. al, 2006). Hemicelluloses produce more tars and less char and other gases than cellulose on decomposition.

During the pyrolysis process, cellulose and hemicelluloses undergo degradation through cycloreversion and dehydration followed by transglycosylation. The cycloreversion leads to unspecified low molecular weight products. At the same time, dehydration leads to more intact cyclic and bicyclic degradation products such as anhydropyranoses or anhydrofuranoses. Hydroxyacetaldehyde, acetic acid, hydroxypropanone, 3-hydroxypropanol, 5-hydroxy-2,3- dihydro-(4H)-pyran-4-one, 5-hydroxymethyl-2-furaldehyde, 2-hydroxymethyl-5-hydroxy-2,3-dihydro-(4H)- pyran-4-one, 1,5-anhydro-fl-D-xylofuranose, levoglucosan are the compounds formed in the degradation mixture (Agrawal, 1988).

Structure of Lignin

Lignin accounts for 23%-33% of the mass of softwoods and 16%-25% of the mass of hardwoods and hence is the third major component of wood. It has no exact structure. It is an amorphous cross-linked resin. The structure of lignin is that of a three-dimensional, highly branched, polyphenolic substance consisting of an irregular array of variously bonded “hydroxy-” and “methoxy-” substituted phenylpropane units. These three general monomeric phenylpropane units of lignins show the p-coumaryl, coniferyl, and sinapyl structures. Hardwood and softwood lignins are different in their structures. Lignins also consist of carbon to carbon linkages. The presence of covalent linking is also found between lignin and polysaccharides, which strongly enhances the adhesive bond strength between cellulose fibers and its lignin “potting matrix”. The different lignins have variation in their physical and chemical properties and this depends on the extraction technique used to isolate them. The decomposition of lignin occurs at 280-500 °C. The pyrolysis of lignin yields phenols via the cleavage of ether and carbon to carbon linkages. It is more difficult to dehydrate lignins than cellulose or hemicelluloses. The pyrolysis of lignin produces more residual char than does the cellulose pyrolysis. The pyrolysis of lignins produces about 55, 20, 15 and 10% of char, liquids (bio-oil), tars and gaseous products respectively (Davin and Lewis, 2005).

Pyrolysis processes can be divided into three subclasses: conventional pyrolysis, fast pyrolysis and flash pyrolysis, depending on the operating temperature and the properties of the biomass used in the process (Demirbas, 1999). Fast pyrolysis is a process which occurs in a few seconds or less. It involves major changes in chemical reaction kinetics with heat and mass transfer processes. Phase transition phenomena also play an important role. Fast pyrolysis of biomass can be brought about by using small particles, for example in the fluidized bed processes or by transferring heat very fast only to the particle surface that contacts the heat source. This method of pyrolysis makes use of a moderate temperature, short residence time particularly of vapour. Much greater percentages of vapours and aerosols than charcoal are produced through the fast pyrolysis of biomass. Cooling and condensation of these vapours and aerosols result in a dark brown liquid called bio-oil. The heating value of this bio-oil is approximately half that of conventional fuel oil (Bridgwater, 2001).

In slow (or conventional) wood pyrolysis, biomass is heated to 500 °C. The vapor residence time varies from 5 min to 30 min. Vapors do not escape as rapidly as they do in fast pyrolysis. Thus, components in the vapor phase continue to react with each other, as the solid char and any liquid are being formed.

Flash pyrolysis is a technique in which finely divided feedstock is quickly heated to between 350 and 500 C for less than 2 seconds (Bridgewater, 2001).

2.2 Kinetics of Pyrolysis

Optimization of system design and control of the pyrolysis process could be enhanced by furthering knowledge of the kinetics of the process. The complex composite structure of wood complicates kinetic analysis of the pyrolysis process. Hemicellulose, cellulose, lignin, and extractives (which consists of resins, starches, waxes, lipids etc.), each have their own pyrolysis chemistry. Kinetic modelling consists of the following simplifying steps:

"(1) Degradation of the virgin biomass materials into primary products (tar, gas, and semi-char),
(2) Decomposition of primary tar to secondary products, and
(3) Continuous interaction between primary gas and char" (Chen et al., 2003).

The last step is usually disregarded completely by kinetic models in the literature. Furthermore, the kinetic models which have appeared in the literature did not consider either the effects of the wood composite morphology on heat-transfer differences or the actual chemical degradation kinetics of individual wood components (Di Blasi., 2008).

Wood pyrolysis operating parameters in a fluidized-bed reactor which considers factors such as bed temperature, suspension bed temperature, particle size and feed rate, have been modelled by Luo et al., 2004. Not surprisingly, in this model, they found that the reaction temperature has a major important role in wood pyrolysis (Di Blasi., 2008).

In addition to this, the kinetics of the primary product formation is also to a great extent dependent on the heating rates of the process. These primary kinetic mechanisms, based on heating rates may be either in a single step or in multiple parallel steps. The basic knowledge of the different kinetic constants helps in qualitatively determining the correct behaviour of the large particle wood pyrolysis. It has been suggested that as wood is heated slowly, three main zones of devolatization can be seen through the weight loss dynamics. According to this, hemicelluloses decompose at 498-598 K, cellulose at 598-648 K, whereas lignin decomposes gradually over the temperature range 523-773 K. The yields of the different products at each of the reaction stages, is required for evaluation of the formation rates of the three main classes of products. (Di Blasi et. al, 2001)

The evaluation of the kinetic parameters of wood pyrolysis is done by collection of the relevant data and its subsequent analysis to form a mathematical or computational model. There are two main methods of accomplishing this, either by isothermal methods or by non-isothermal ones. In case of the isothermal process of evaluation, the biomass (wood) is heated up to a temperature where reaction starts, and then the reaction is allowed to continue at constant temperature with variation in time. On the other hand, the biomass is allowed to heat up slowly to its reaction temperature and the progress of the reaction is subsequently measured with respect to time and temperature (Willner et. al, 2005).

In case of isothermal methods, a series of evaluations are carried out at different temperatures to determine the reaction rate. Then, Arrhenius equations are used to calculate the activation energies and frequency factors for these reactions. On the other hand, non isothermal methods are dependent on the temperatures at which the reaction rates take place (Willner et. al, 2005).

It has been found that laboratory scale reactors allow only the total final yields to be obtained hence there is no alternative to a one-stage mechanism of primary wood degradation. As a result, the mechanism with three parallel reactions for the formation of the main product classes has come about to be the most feasible for determining kinetics of wood pyrolysis. The advantage of this mechanism lies in the comparable activation energies of reactions which do not allow the selectivity to be displaced toward only one of the products (Di Blasi et. al, 2001).

It has been observed that in wood pyrolysis, both liquid and gas yields continuously increase at the expense of char. The action of different temperatures on pyrolysis product yields is about the same for conventional as well as fast pyrolysis from the qualitative point of view. As the temperature is increased, the liquids go through a maximum, whereas the gases continuously increase, and the char yields decrease. At temperatures above 773K (500°C), the secondary reactions increase for the yields of different products (Di Blasi et. al, 2001).

The quantitative nature of the pyrolysis products is largely dependent on the reactor configuration, the chemical and physical properties of the biomass as well as on the heating rate of the process. For a lignocellulosic biomass, e.g. wood, the yield depends on the wood structure and particle size. In a conventional pyrolysis process, a classical hardwood produces lower char yields with respect to the initial dry mass than classical softwoods. Moreover, as the particle size of the wood block increases, liquid production becomes successively less favoured. Many researchers have attributed differences in heating rates to be an important factor for varying quantitative yields of the lignocellulosic pyrolysis products.

The thermal behaviour of the main components of the biomass and their relative contribution in its chemical composition is very significant in the determination of the primary decomposition rates of the process. The weight loss curves are determined taking into account the loss in the weight of the solid residue. This calculation becomes very important in the mathematical modelling of the pyrolysis reactions. The solid residue consists of mainly charcoal. According to researchers, Van Krevelen et. al., there is a linear relationship between the weight of the raw biomass and the weight of the solid residue (Willner et. al, 2005). The component dynamics lead to the formation of several zones in the weight loss curves of the different pyrolysis reactions for heating rates at low or near moderate temperatures. It has been observed by researchers, according to these curves, that hemicelluloses decompose at 498–598K, cellulose at 598–648K, whereas lignin decomposes gradually over the temperature range of 523–773K. With the increase in heating rates, the different peaks in the degradation rate tend to merge and the characteristic process temperatures tend to become progressively higher provided that the range of the degradation temperatures of components is relatively narrow. Considerable degradation rates are concurrently attained by all the components when the temperatures are sufficiently high. (Di Blasi, 2008)

The residence time of solids is another important parameter. In the case of fast pyrolysis, at low temperatures, it is longer than the residence time of volatiles. Often time’s particles may be forced out before complete conversion. In such cases, char yields are often higher than the other products. (Di Blasi et. al, 2001)

Rates of pyrolysis reactions are determined by taking into account the different paths involved in these reactions. As mentioned earlier in this review, due to the predominant formation of three zones in the weight loss curve, there are many suggestions in the research circle to divide the mechanism of wood pyrolysis into three independent parallel reaction paths (Di Blasi, 2001). The design consists of utilising analytical methods to assign the different reaction paths to either single component, e.g. gas or vapour phases or to groups of products like char, tar and gases. Although the wood pyrolysis process is known to have certain autocatalytic reactions, it has been largely categorized as a first order reaction mechanism. Many investigations have been carried out by researchers which use the three component mechanism showing decomposition reaction kinetics of the major wood components- Cellulose, Hemicellulose and Lignins (Masek, 2009).

Research until now has shown that the degradation rate of the main components of wood through pyrolysis increases in the order- lignin, wood, cellulose and hemicelluloses. But this trend might change with the different kinds of lignins present in the wood.

Pyrolysis mechanism of cellulose

The destructive reaction of cellulose is initiated at temperatures lower than 325 K and is characterized by a decreasing polymerization degree. Thermal degradation of cellulose undergoes two types of reaction: a gradual degradation, decomposition and charring on heating at lower temperatures, and a rapid volatilization accompanied by the formation of levoglucosan on pyrolysis at higher temperatures. The glucose chains in cellulose are broken down to glucose and this leads to the formation of glucosan by the splitting of one molecule of water. Since cellulose and levoglucosan have the same elementary formula, $C_6H_{10}O_5$, a yield of 100% of the latter might be expected. The initial degradation reactions comprises of depolymerization, hydrolysis, oxidation, dehydration, and decarboxylation (Demirbas, 2000).

Researcher Demirbas (1999) investigated the isothermal pyrolysis of cellulose in air and milder conditions, in the temperature range of 623±643 K. At the end of the pyrolysis process, the residue was found to consist of some water soluble materials, in addition to char and undecomposed cellulose. The decreased formation of char at the higher rate of heating was observed to be accompanied by an increased formation of tar. Three distinct stages of pyrolysis were identified through the kinetics of the reaction: in the first stage, a rapid decomposition was seen to take place with a weight loss that increased with rising temperature; in the second stage, decomposition and volatilization occurred; while in the third stage, the biomass was seen to undergo an even more extensive decomposition and volatilization.

Pyrolysis mechanism of Hemicellulose

The reaction in hemicelluloses was seen to take place more readily than cellulose during heating. In the thermal degradation of hemicelluloses, which begins above 373 K during heating for 48 h; hemicelluloses and lignin are depolymerized by steaming at high temperature for a short time. In comparison with lignins, hemicelluloses contain more combined moisture as well as have a low softening point. Moreover, the thermal decomposition of hemicelluloses occurs at a lower temperature than that of lignin as observed through the exothermic peaks of hemicelluloses which appeared at lower temperature (Demirbas, 1999).

Pyrolysis mechanism of Lignins

Guaiacol, one of the pyrolysis products of lignin could be used to exhibit the aromatic nature of lignin. Though lignin has a threefold higher methoxyl content than wood, it has been observed to produce higher yields of charcoal and tar from wood. Derivation of phenolics from lignin is conducted by cracking of the phenyl propane units of the macromolecule lattice. Lignin is broken down by extensive cleavage of b-aryl ether linkages during steaming of wood under 488 K. Lignin decomposition is started at about 550 K with a maximum rate occurring between 625 and 725 K and the completion of the reaction occurs at 725 and 775 K (Demirbas, 1999).

2.3 Pyrolysis and Recent Developments

Though the different technologies of using pyrolysis for the production of biochar have been present for several millennia, it is only during the past decade that it has gained proper research value. This has come about due to the recent interest in using biochar for climate change mitigation strategies as well as its importance for soil amendment.

The origins of the use of biochar can be traced back to the pre- Columbian era, when, terra preta (dark earth, in Portuguese) soil was made by humans in the central Amazon basin. It is believed that this man-made soil is 70 times more concentrated in organic content than the surrounding soils. It is formed by heating feedstock in low or absence of oxygen. This long lasting soil has in the recent years, attracted the attention of many research scientists all over the world due to its ability to trap the carbon for a long time (Kleiner, 2009).

The processes used for the pyrolysis of biomass are usually classified into three categories, such as, Batch, Continuous and Novel processes. Batch processes like earth pits, mounds, bricks, concrete and metal kilns produce a char yield of about 20-30%. The continuous processes on the other hand, have char yields of about 30-35%, while the highest yields of char can be obtained by novel processes like Flash carbonization of more than 40-50% (Masek, 2009).

A lot of work has been done on the analysis of different kinetic models in the pyrolysis of various biomasses. Orfao, Antunes and Figueiredo (1998) mentioned the three independent reaction model involved in the kinetic models in the pyrolysis of lignocellulosic materials. The focus of their study was to determine a method to analyse the model parameters like the activation energies and pre-exponential factors for the pyrolysis of the remaining two pseudo-components and two additional parameters related to the biomass composition. Similar studies have been carried out by various research teams on different biomass sources such as cellulose, starch etc. Babu and Chaurasia (2003) worked on the improvement of the models for simultaneous kinetics and transport of heat, mass and momentum involved in the pyrolysis of biomass.

Researchers Gonza´ lez-Vila et al., (2001), carried out the pyrolysis-gc-ms analysis of the formation and degradation stages of charred residues from lignocellulosic biomass. Similarly, the pyrolysis technology and its kinetic studies have been carried out for a number of biomass materials, ranging from poultry litter, cellulosic or lignocellulosic feedstock, starch, sewage sludge and even casein by a number of scientists throughout the globe (Chan et al., 2008, Chen and Jeyaseelan, 2001, Purevsuren et al., 2003).

Recently, there has been a surge on finding alternate methods of efficient pyrolysis techniques for different biomass sources. One of the methods proven to have measured up to a good efficiency standard is the use of microwave or microwave assisted pyrolysis methods to form biochar and other useful volatiles.

2.4 Microwaves and their Applications in Pyrolysis

The wavelengths from 1 mm to 1 m with corresponding frequencies between 300 MHz and 300 GHz belong to microwaves in the electromagnetic spectrum as in Figure 2.5. Two frequencies, 0.915 and 2.45 GHz, are reserved by the Federal Communications Commission (FCC) for industrial, scientific, and medical (ISM) purposes which could be commonly used for microwave processing (Thostensen et. al, 1999).

Microwave assisted pyrolysis techniques for the production of biochar is becoming extremely popular as more number of scientists realizes the advantages of using microwaves to enhance the yield and quality of the biochar produced in a biomass. Carbonscape, a company in New Zealand, has developed and patented a process for manufacturing charcoal using microwave energy - a vastly more energy efficient process than what is currently used. Its Director, Chris Turney, is majorly backing the approach to utilize industrial-scale microwaves for the production of biochar (Nature Reports Climate Change, 2009).

In 2004, a work carried out by Menéndez et. al., consisted of the use of microwave pyrolysis of sewage sludge to analyse the different gas fractions coming out from the system. Lei et. al., (2009) focused on the effects of reaction temperature and time and particle size of corn stover on microwave pyrolysis. They determined the effects of reaction temperature and time of pyrolytic conditions on the yield of bio-oil, syngas, and biochar. They also checked the mineral analysis which indicated that most minerals stayed with the biochar. The GC/MS analysis indicated that the bio-oil contained a series of important and useful chemical compounds like phenols, aliphatic hydrocarbons, aromatic hydrocarbons, and furan derivatives. These chemical compounds which evolved were related to the pyrolysis conditions.

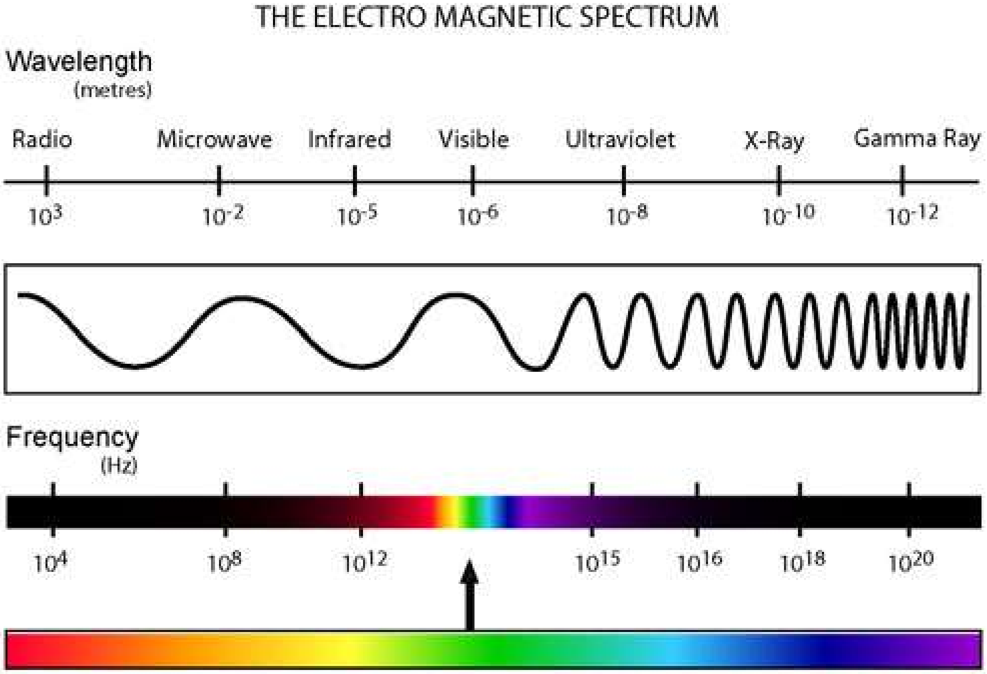


Figure 2.5. Electromagnetic Spectrum

(Source:http://www.atmos.washington.edu/~hakim/301/electromagnetic-spectrum.jpg)

2.5 Modelling and Simulation

There has been an overwhelming interest in the scientific arena regarding the research of modelling and simulation studies involved in the production of biochar as well other by products in the process of pyrolysis. One of the earliest researches done in this area was carried out by Chan et. al., in 1985 to model and verify experimentally the physical and chemical processes involved during the pyrolysis of a large biomass particle. It emphasized the need for more information regarding the char deposition rates and its thermal properties over a wide range of temperatures.

Babu et. al., (2004) carried out modelling, simulation and estimation of optimum parameters in pyrolysis of biomass. They solved modelling equations numerically using the fourth order Runge–Kutta method over a wide range of heating rates (25–360 K/s) and temperatures (773–1773K). The simulated results when compared with those reported in the literature were found to be in good agreement qualitatively in the range of operating conditions covered. They found some interesting trends to the effect of net heating rate and temperature on final pyrolysis time. They saw that the final pyrolysis time first decreases at lower values of net heating rate or temperature and then increases as net heating rate or temperature is further increased, providing an optimum value of net heating rate or temperature at which final pyrolysis time is minimum.

Di Blasi (2008) conducted modelling of the chemical and physical processes of biomass pyrolysis with special focus on wood. He presented different approaches used in the transport models at both levels of a single particle and of the reactor. Moreover, this study highlighted the main achievements of numerical simulations.

2.6 Mass – Energy Economics of Pyrolysis

The pyrolysis process which takes place in a patented industrial oven for the production of biochar converts 40-50% of the wood sent through it into charcoal. Though there is a carbon footprint present in a microwave of its own, the amount of carbon that gets fixed in the biochar, outweighs the carbon released into the atmosphere during the process. Thus, the charcoal in wood is estimated to be 40-50% (Renewable Energy UK, 2009). If the conversion of merchantable wood yield to carbon yield by species is carried out, the percentage of carbon in most wood biomass falls under the range of 47-53% (Source: Birdsey 1996, Sampson and Hair 1996). On the other hand, the amount of carbon in charcoal is estimated to be around 75-85% (Hsiang-Ceieng Kung, 1972). This, in turn, would imply that about 43-45% of carbon can be conserved in the biochar. This can be produced by pyrolysis from any amount of biomass which consists of 47-53% of carbon present in it. Thus, we would get a conversion success of about 50% of carbon from the microwave pyrolysis of any woody biomass, which in turn, would help us to fix the carbon and thus to reduce the concentration of CO_2 in the atmosphere and thereby helping us to fight global warming.

About 60 billion tonnes of carbon is taken up annually by photosynthesis and amongst these; around ten per cent becomes available as agricultural residue such as corn and rice stalks, or forestry residue such as branches and leaf litter, as well as animal waste. If all of this 10% i.e., 6 billion tonnes of carbon were put through the pyrolysis process, approximately 3 billion tonnes of biochar would be produced every year, reducing atmospheric carbon emissions by the same amount (Amonette, J. et al., 2007). This could offset a substantial proportion of the 4.1 billion tonnes of excess carbon dioxide that accumulates annually in the atmosphere. According to Lehmann's calculations, one-third of the biomass could be converted to biofuel (Nature Reports Climate Change, 2009).

For a lignocellulosic biomass, with the above mentioned composition, the average specific heat is 0.42 kJ/kg.K (Hyper physics, 2010). This requires about 180 kJ/kg of energy for reaching a temperature of 450°C from ambient temperatures. Also, the mean Activation energy required for pyrolysis is approximately 1220 kJ/kg based on the mole fractions of the different components of the biomass (Orfao, et al., 1998). Thus, the entire process of pyrolysis of the lignocellulosic biomass consumes about 1400kJ/kg.

2.7 Life Cycle Assessment of Biochar Systems

Biomass pyrolysis with biochar returned to soil is a possible strategy for climate change mitigation and reducing fossil fuel consumption. Pyrolysis with biochar applied to soils results in four coproducts: long-term carbon (C) sequestration from stable C in the biochar, renewable energy generation, biochar as a soil amendment, and biomass waste management. Roberts et al., (2010) used life cycle assessment to estimate the energy and climate change impacts and the economics of biochar systems. Figure 2.6 is an example of such a lifecycle. The feedstocks analyzed represent agricultural residues (corn stover), yard waste, and switchgrass energy crops. Their study shows that the economic viability of the pyrolysis-biochar system is largely dependent on the costs of feedstock production, pyrolysis, and the value of C offsets.

Biomass sources that have a need for waste management such as yard waste have the highest potential for economic profitability. For each feedstock assessed, the net energy of the system was found to be positive, i.e., more energy is generated than consumed. Another detailed analysis from Gaunt and Lehmann (2008) calculated the avoided GHG emissions for biochar production and found it to 10.7 t CO_2 ha^{-1} yr^{-1} for corn stover and 12.6 t CO_2 ha^{-1} yr^{-1} for switchgrass. The transportation distance for feedstock creates a significant hurdle to the economic profitability of biochar-pyrolysis systems. Biochar may at present deliver only climate change mitigation benefits and be financially viable as a distributed system using waste biomass.

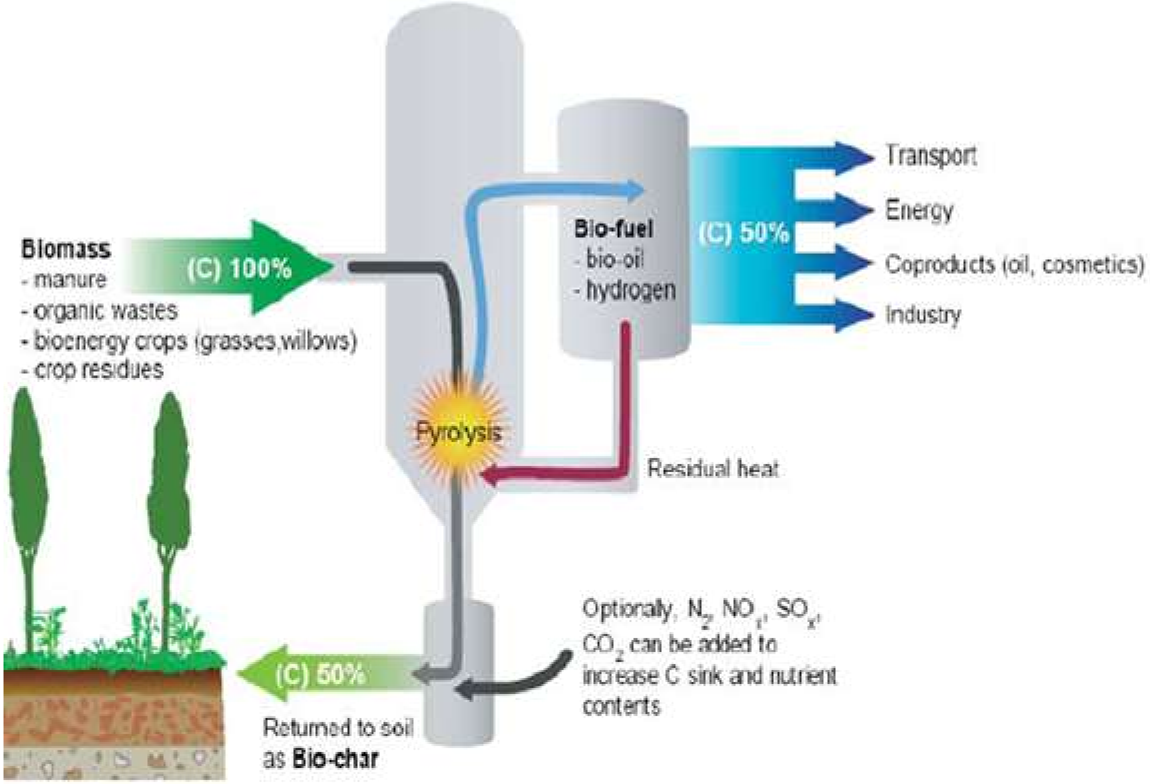


Figure 2.6: Biochar- Bioenergy Lifecycle

Source: Evelyn Krull, CSIRO

2.8 Future Prospects of the Study

The future prospects of this thesis research would be many-fold. The most important one would be the use of the biochar produced in the pyrolysis process for the sequestration of a fraction of the carbon in the soil, which is sent to the atmosphere during plant respiration, it would help mitigate climatic changes caused due to global warming.

A further benefit which could arise through the use of biochar production is its use as a source in soil amendment by mixing it with natural fertilizers, thereby increasing cost effectiveness in agriculture.

The biochar produced during the pyrolysis of lignocellulosic biomass could be used as solid fuel by pelletization. Also, it could be converted to biofuel by the process of gasification. If this biofuel is used in place of fossil fuels, for example in transport, there is a possible promise of the reduction of a significant amount of carbon emissions per year.

The extra heat that is generated during the making of biochar could be used for heating applications as well as for generation of electricity. The economics of biochar will be determined by a combination of its value as a soil additive, as a carbon offset measure and as an energy source.

Connecting text

Pyrolysis is a process by which a biomass feedstock is thermally degraded in the absence of air/oxygen. It is used for the production of solid (charcoal), liquid (tar and other organics) and gaseous products. The actual reaction scheme of pyrolysis of biomass is extremely complex because of the formation of over a hundred intermediate products. Pyrolysis of biomass is, therefore, generally modelled on the basis of apparent kinetics. Ideally, the chemical kinetics model should account for the primary decomposition reactions as well as the secondary reactions. Finite Element Modelling (FEM) can readily model heterogeneous and anisotropic materials as well as arbitrarily shaped geometries. Hence the utilization of FEM can help in the visualization of the process. It can eventually be used to study and optimize the production of biochar from a wide variety of lignocellulosic biomass.

Chapter 3

Finite Element Modelling of Pyrolysis of Lignocellulosic Biomass

3.1 Abstract.

Considerable research has been devoted towards determining the kinetics of the pyrolysis of lignocellulosic biomass such as wood residues and agricultural waste. The end product of this process is usually referred as biochar and it is considered as an efficient method for sequestering carbon to offset atmospheric carbon-dioxide. In this study, an attempt has been made to develop a finite element model (FEM) in order to couple thermal heating, combustion, and heat and mass transfer phenomena during pyrolysis. The resulting sets of partial differential equations were then solved simultaneously using the COMSOL Multiphisics software package. This numerical modelling and simulation approach helped the visualization of the process. It can eventually be used to study and optimize the production of biochar from a wide variety of lignocellulosic biomass.

Keywords. Biochar, Pyrolysis, Reaction kinetics, Lignocellulosic biomass

Numerical modelling.

3.2 Introduction

One of the important thermochemical conversion techniques of biomass is known as pyrolysis. It is the thermal decomposition of biomass at low or absence of oxygen. Pyrolysis converts organics to solid, liquid and gas by heating in the absence of oxygen. The amounts of solid, liquid, and gaseous fractions formed and the distribution of their products are dependent distinctly on the process variables. The process of pyrolysis produces solids (charcoal), liquids (H_2O and organics), and gases (CO, CO_2, CH_4, H_2). Proportions and composition depend on feedstock and process conditions (e.g., heating rate) (Masek, 2009). The production of biochar through the process of pyrolysis has come about to be an extremely efficient and popular technology in recent years.

Biochar finds use in the release of energy-rich gases which are then used for producing liquid fuels or directly for power and/or heat generation. It is highly useful in the mopping up of excess Green House Gases (GHGs) from fossil fuels. It is used in sequestration of carbon in soil and thereby reduces carbon dioxide levels in the atmosphere through uptake by plants.

Recently, there has been a surge on finding alternate methods of efficient pyrolysis techniques for different biomass sources. There is a growing interest in the scientific world regarding the research of modelling and simulation studies involved in the production of biochar as well other by products in the process of pyrolysis. One of the earliest research work done in this area was carried out by Chan et al., in 1985 to model and verify experimentally the physical and chemical processes involved during the pyrolysis of a large biomass particle. It emphasized the need for more information regarding the char deposition rates and its thermal properties over a wide range of temperatures. Numerical and modelling studies have been conducted which focus on estimation of optimum parameters for pyrolysis of biomass (Babu et al., 2004). Different approaches used in the transport models have also been presented at both the single particle and reactor levels, together with the main achievements of numerical simulations (Di Blasi., 2008).

FEM technique competes very favourably with the other numerical methods due to the Partial Differential Equations (PDE’s) discretization and solution procedure applied in the analysis of the model (Baggio et al., 2009). The advantage of FEM is that it allows modelling of complicated boundary shapes with relative ease of flow and heat transfer problems (Prakash & Karunanithi, 2009).

Taking into account all the above mentioned facts, in this study, a Finite Element Model (FEM) of the pyrolysis of lignocellulosic biomass was developed and simulation studies were conducted for biomass subjected to 10, 15 and 20 minutes of heating at 300°C, 350°C and 400°C in order to visualize and investigate the temperature distribution within the biomass. The objective was to maximize the production of biochar.

3.3 Materials and Methods

In this study, the mechanisms involved in production of biochar through pyrolysis were investigated. A Finite Element Model was made in order to simulate the heating of biomass and to predict the optimal conditions for the maximization of biochar using the process. The wood sample was subjected for a maximum of 1.25 hrs (75 mins) of heating at 300°C, 350°C and 400°C for simulation purposes.

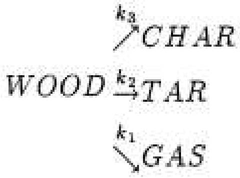
3.3.1 Reaction kinetics model for simulation

For this simulation, isothermal conditions were assumed. In case of isothermal methods, a series of evaluations were carried out at different temperatures to determine the reaction rate. Then, Arrhenius equations were used to calculate the activation energies and frequency factors for these reactions. On the other hand, non isothermal methods were dependent on the temperatures at which the reaction rates took place (Willner et. al, 2005).

The three step mechanism described by author Di Blasi in 1998 was used as the kinetics model for modelling and simulation of the pyrolysis of wood. The advantage of this mechanism lies in the comparable activation energies of reactions which do not allow the selectivity to be displaced toward only one of the products (Di Blasi et. al, 2001).The kinetic constants applied to this model were researched by the author through a literature survey from different experimental sources. This simulation work was conducted on the basis of the Scheme C of the three step mechanism model.

3.3.2 Three-step mechanism:

The Kinetic constants for this scheme were:



A_1=1.30 x108 s^{-1}, E_1= 1.40 kJ mol^{-1}

A_2=2.00 x108 s^{-1}, E_2= 1.33 kJ mol^{-1}

A_3=1.08 x107 s^{-1}, E_3= 1.21 kJ mol^{-1}

This mechanism has been applied to model large particle biomass pyrolysis. This scheme has been adopted for this study because it can predict the qualitative correct behaviour of wood pyrolysis along with the dependence of product yields on temperature when coupled with secondary tar reactions and transport phenomena.

3.3.3 Finite element modelling and simulation

A 3D Finite Element Model was developed using COMSOL Multiphysics version 4.0 (COMSOL Inc., USA) software package to simulate the pyrolysis process for the Chinese birchwood sample. The meshed structure of the quartz tube and wood sample is shown in Figure 3.2.

Figure 3.1: Finite Element Mesh Structure

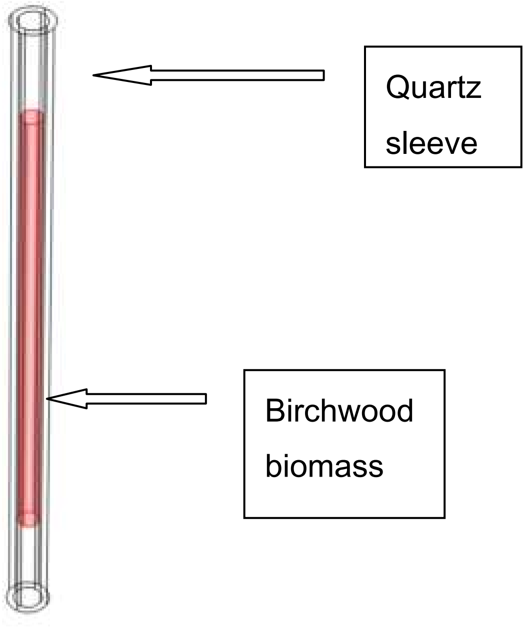


Figure 3.2 Structure of quartz tube (sleeve) with biomass

The dimensions of the cylindrical wood sample were taken as 3 mm ϕ X 70 mm h and the quartz sleeve were taken as 6mm outer ϕ and 4 mm inner ϕ X 100 mm (Figures 3.1 and 3.2) . A custom built computer with two AMD Opteron quadcore 2.4 GHz processors and 32 GB primary memory was used to run the simulations.

3.3.4 Mathematics of the model

The temperature distribution inside the lignocellulosic biomass sample was obtained by solving the conductive heat transfer equations.

3.3.5 Heat transfer

For an incompressible material heated under constant pressure, the thermal energy equation is given by equation 3.1 (Zhou et al., 1995)

$$\rho C_p \frac{\partial T}{\partial t} = \nabla.(K \nabla T) + Q \qquad 3.1$$

Where ρ is the density (kg.m^{-3}), Cp is the specific heat (kJ.kg^{-1}.K^{-1}) and K is the thermal conductivity of the material ((W·K^{-1}·m^{-1}) and T is the absolute temperature in Kelvin (K).

Different mesh element sizes were used for different sub-domains based on the dielectric properties of the sub-domain and the precision required in the sub-domain of interest.

3.3.6 Boundary conditions

Temperature boundary conditions were used for all the boundaries except the circular ends of the cylindrical wood sample. Surface to ambient boundary conditions were applied for the circular ends in order to simulate the heating mechanism inside the quartz sleeve of the Thermal Desorption Unit.

3.3.7 Experimental set up for validation of the simulation

Longitudinal pieces of Birch wood obtained from the local market were cut into pieces of 3mm diameter and 70mm length. In this study, the pyrolysis experiments were conducted in a Thermal Desorption Unit (Supelco, Inc.) (Figure 3.3) with the sample wood pieces insulated inside quartz tubes of 6mm outside diameter and 100mm in length. The objective of this investigation was to determine the effect of the pyrolysis temperature on pyrolysis yields. Thus a quantity of ~0.5 g of the sample was placed in the reactor and the temperature was raised to 20°C/min and a fast pyrolysis rate of 1000°C/min to final test temperatures of 300, 350, and 400°C and held for 10, 15 and 20 min respectively. The volatiles produced during the process constantly displaced with nitrogen gas purged into the system and then condensed in a water- bath. After pyrolysis, the solid char was removed and weighed to analyze the yield of the products.

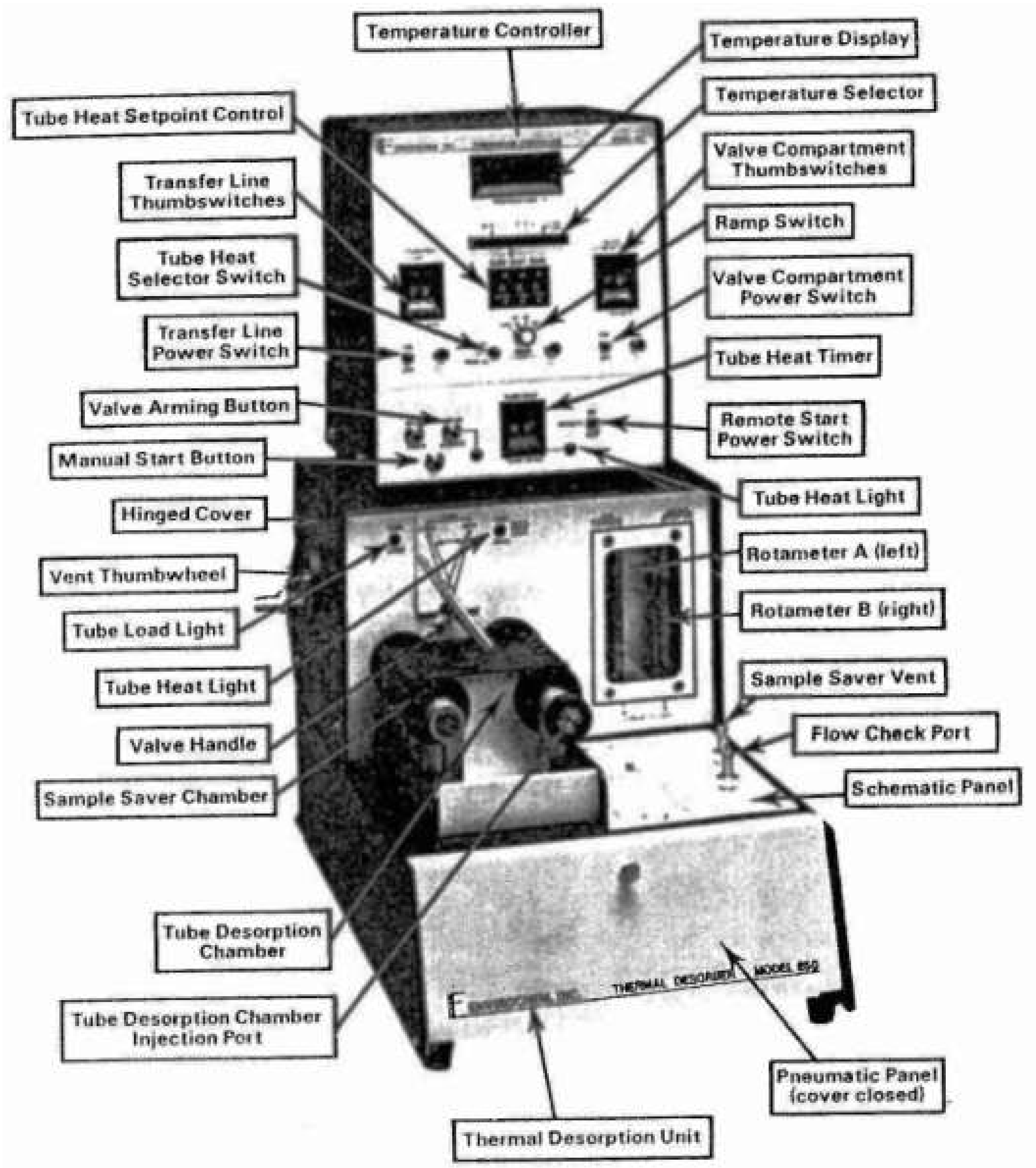


Figure 3.3 Experimental set up for validation: Thermal Desorption Unit (Supelco, Inc.)

3.4 Results and Discussion

3.4.1 Simulation results

The quantitative nature of the pyrolysis products is largely dependent on the reactor configuration, the chemical and physical properties of the biomass as well as on the heating rate of the process. For a lignocellulosic biomass, e.g.

wood, the yield depends on the wood structure and particle size. In a conventional pyrolysis process, a classical hardwood produces lower char yields with respect to the initial dry mass than classical softwoods. Moreover, as the particle size of the wood block increases, liquid production becomes progressively less favoured. Many researchers have attributed differences in heating rates to be an important factor for varying quantitative yields of the lignocellulosic pyrolysis products. (Masek, 2009, Di Blasi et. al, 2001, Wang et al. 2009)

The weight loss curves are determined by taking into account the loss in the weight of the solid residue. It has been observed by researchers, according to these curves, that hemicelluloses decompose at 498–598K, cellulose at 598–648K, whereas lignin decomposes gradually over the temperature range of 523–773K. Considerable degradation rates are concurrently attained by all the components when the temperatures are sufficiently high. (Di Blasi, 2008)

The increase of the biochar yields is based on the minimization of the losses of carbon in the form of gases and liquids. Biochar is a product of both primary (char) and secondary (coke) reactions. There are number of methods employed to improve the yields of biochar with factors like low pyrolysis temperature (<400 ºC), high process pressure, long vapour residence time, extended vapour/solid contact, low heating rate, large biomass particle size, optimised heat integration (Masek, 2009).

Another important parameter is the residence time of solids. In case of fast pyrolysis, at low temperatures, it is longer than the residence time of volatiles; particles may be expelled before complete conversion. In such cases, char yields are often higher than the other products. (Di Blasi et. al, 2001)

This simulation study was carried out at a range of temperatures of 300°C, 350°C and 400°C for 0 to 75 minutes of heating. The initial concentration of the wood or biomass sample was taken to be 3800 mol m^{-3} .

The results of the simulation of the heating of biomass sample with temperature variation profile between 0 to 20 min indicated that at 0 min, the whole birchwood sample was around the temperature of 300 ° C. With the progress of the pyrolyses reactions, due to the conductive nature of the heating, the exteriors of the wood sample reached higher temperatures before the interiors of the biomass. Given the kinetic parameters discussed previously, the resulting numerical model for the pyrolysis of the lignocellulosic biomass, at a temperature of 573K, showed minimal amount of products formed in the reaction as shown in Figures 3.4, 3.5 and 3.6. The wood sample did not show any significant variation from its initial concentration during the pyrolysis process.

Figure 3.4: Simulation of heating of biomass sample with temperature variation profile at: 0 min

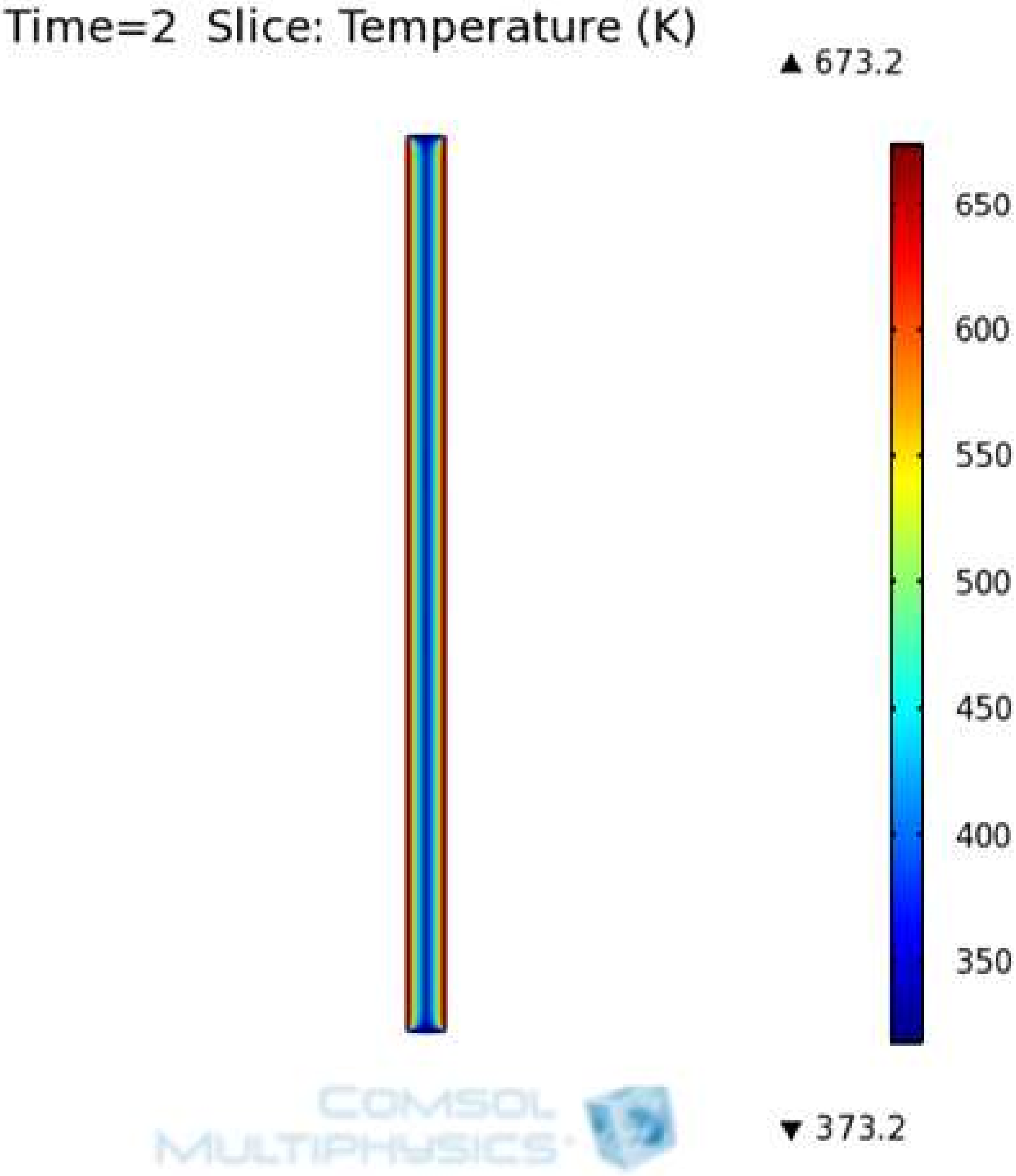
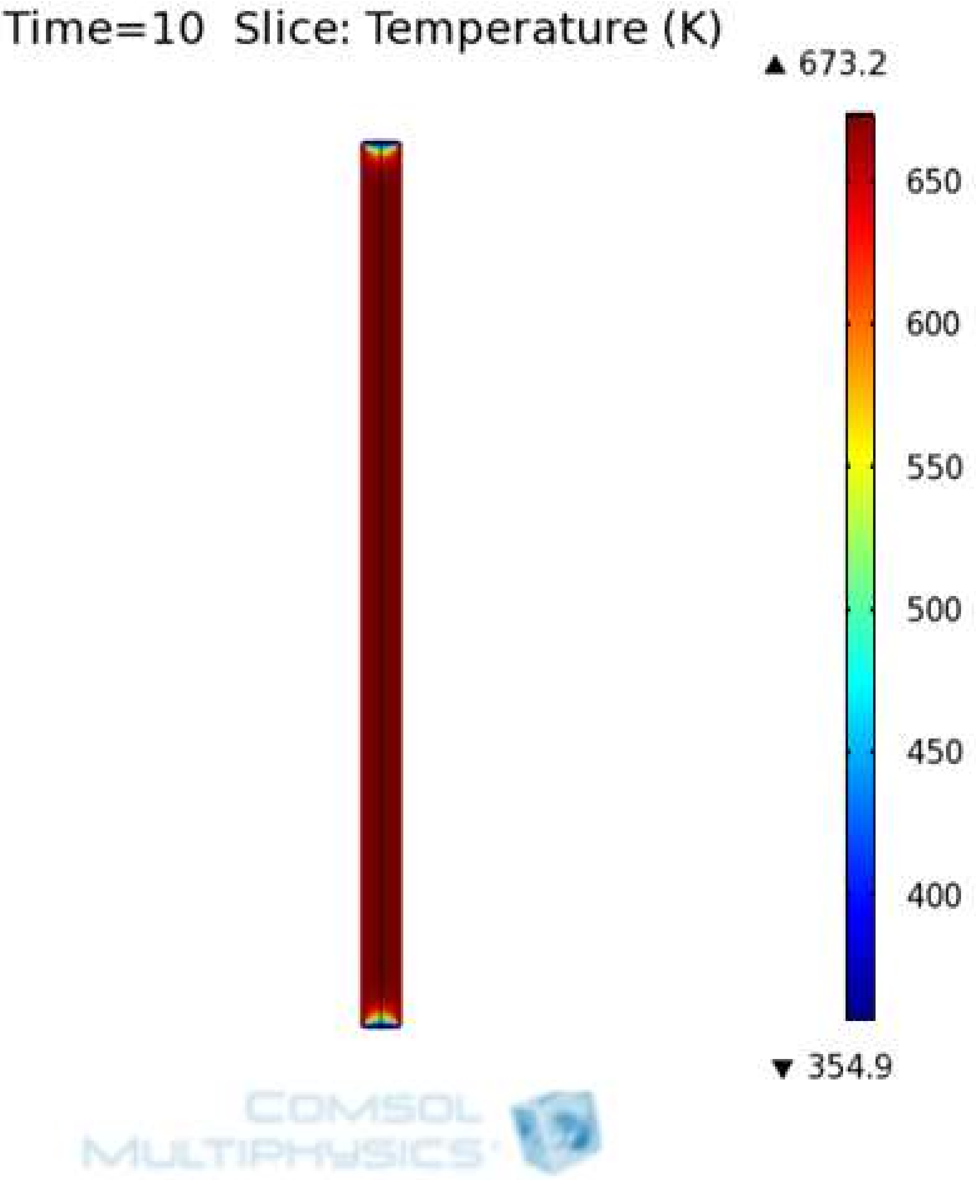


Figure 3.5: Simulation of heating of biomass sample with temperature variation profile at 2 min



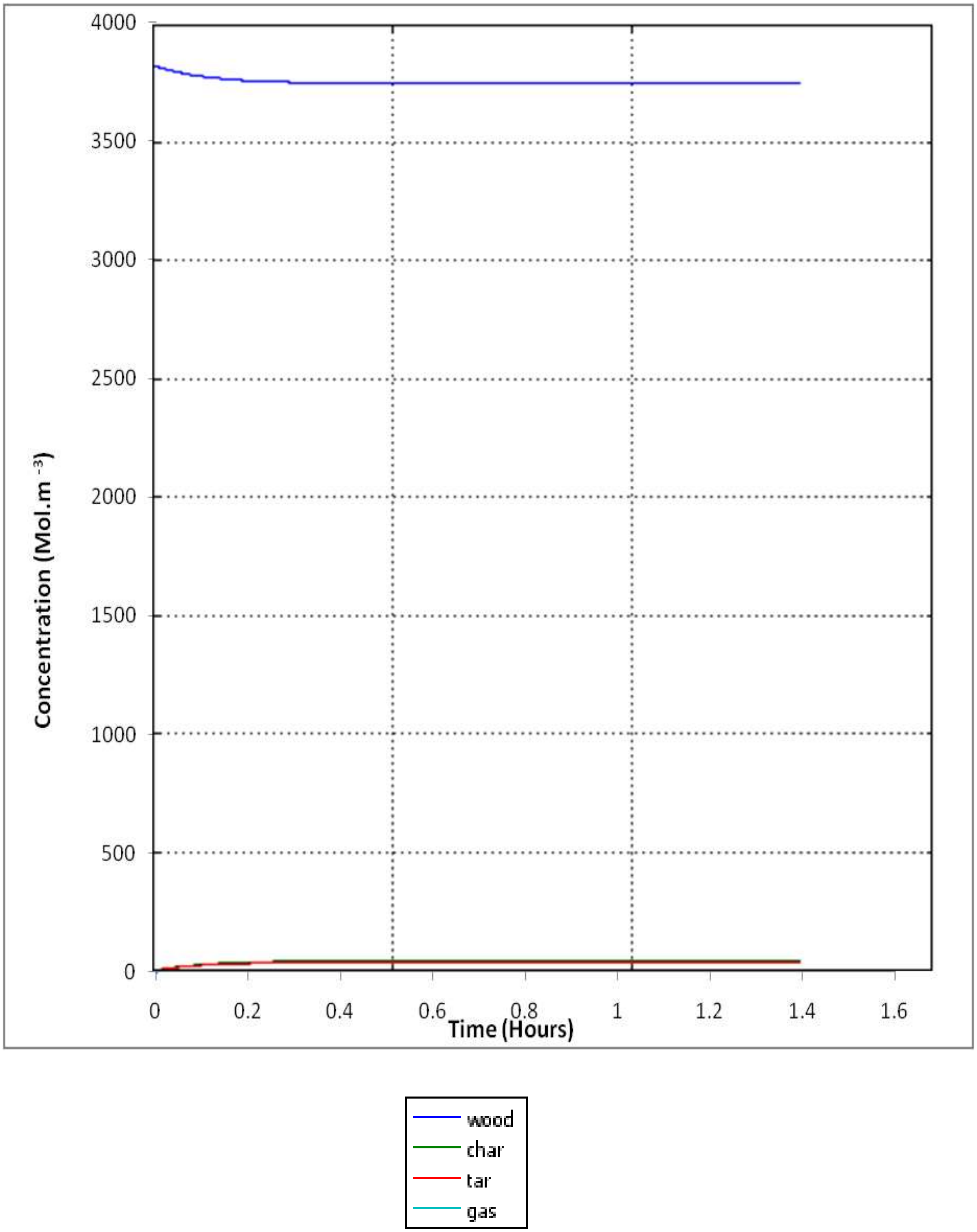
(c)

Figure 3.6: Simulation of heating of biomass sample with temperature variation profile at 10 min

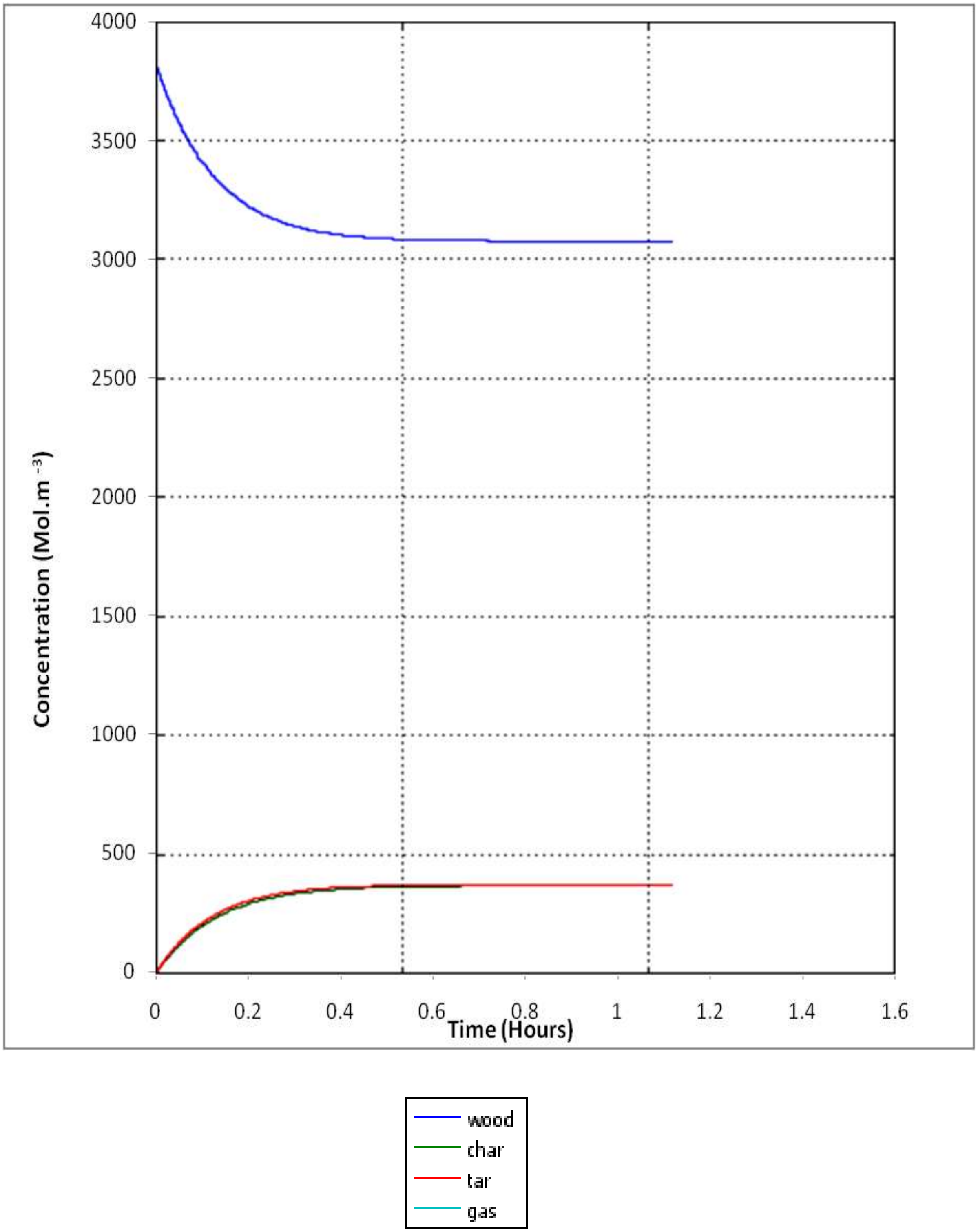
When the temperature was raised to 623K, the model showed a visible change in concentration of the biomass, thereby implying the incidence of the pyrolysis reaction. In figure 3.7(b), it was seen that the wood sample underwent a decrease in concentration until about 0.6 hours (36 min) of the reaction period and then remained constant. Product formation was observed in this model when compared to the one taking place at 573K. All three phases of products were formed at this temperature although char and syngas formation went only until 0.6 hours while concentration of tar increased until the wood sample completely reacted.

At a higher temperature of 673K, the concentration vs. time curve showed an exponential decrease in the concentration of the wood biomass. In turn, the concentrations of tar and char were significant compared to the previous profiles of the model. The concentration of biochar went up to about 1400 mol m^{-3} in a matter of 0.5 mins as seen in Figure 3.7(c) and remained constant with further increase in reaction time. The production of syngases in this reaction remained at bare minimum throughout the pyrolysis of the biomass.

The desired temperature of 673K was equilibrated in 10 min of the reaction and by 20 min; the entire biomass had converted into the pyrolyzed products (Figure 3.6). The change in temperature or ΔT for this time period was observed to be about less than 50K.


4000
3500
3000
2500
2000
1500
1000
500
0
Concentration (Mol.m $^{-3}$)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
Time (Hours)
wood
char
tar
gas

(a)


4000
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1000
500
0
Concentration (Mol.m $^{-3}$)
0
0.2
0.4
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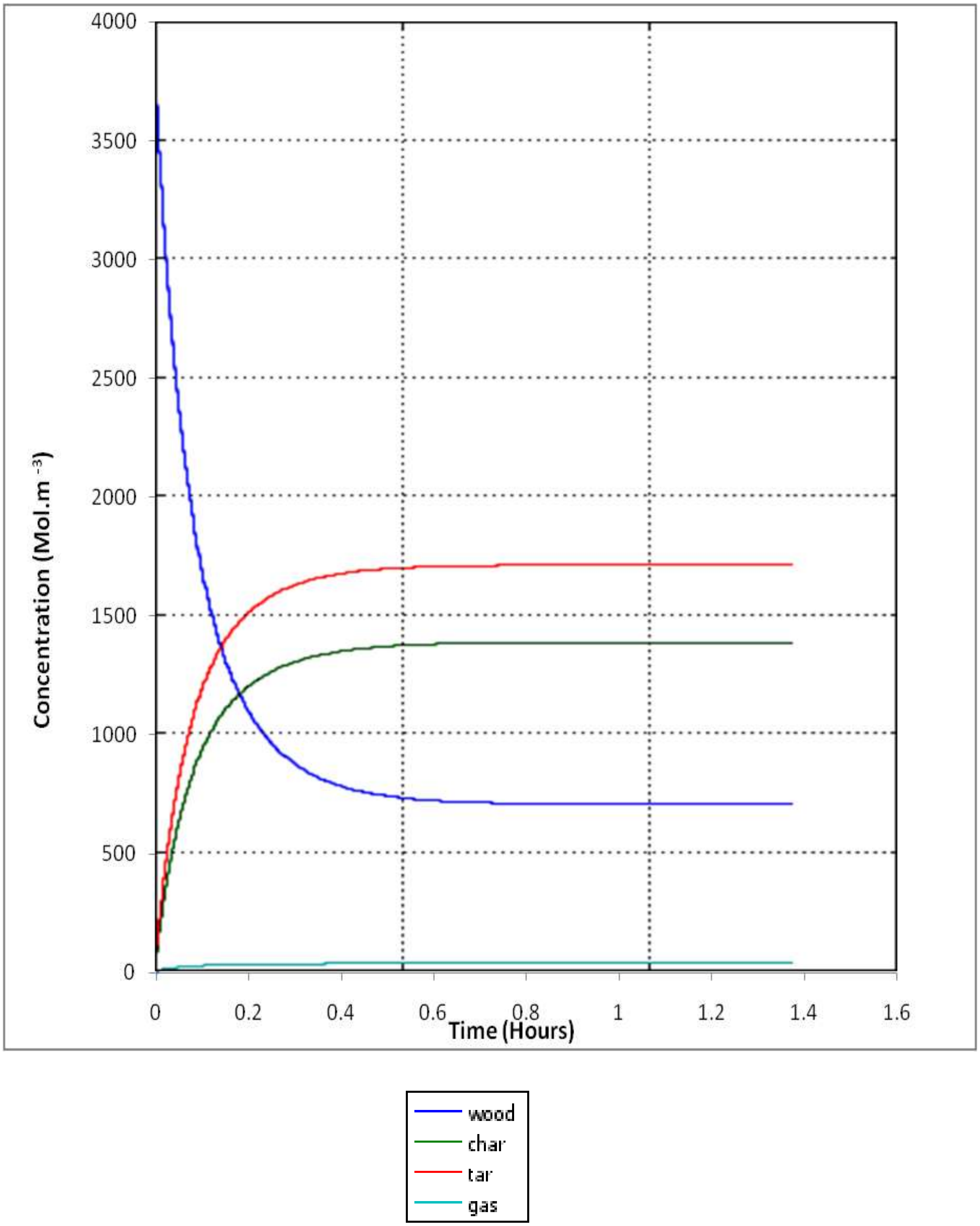
0.8
1
1.2
1.4
1.6
Time (Hours)
wood
char
tar
gas

(b)



(c)

Figure 3.7: Concentration vs. Time profiles of the different simulation models at temperature range of 573K-773K. (a) 573K (b) 623K (c) 673K

3.4.2 Experimental validation

The experimental validation of the simulation results was carried out in the Thermal Desorption Unit (Supelco, Inc.) (Figure 3.3) with the sample wood pieces insulated inside quartz tubes of 6mm outside diameter and 100mm in length. The simulation results indicated that the desired temperature of 673K was equilibrated in 10 min of the reaction and by 20 min, the entire biomass had converted into the pyrolyzed products. The change in temperature or ΔT for this time period was observed to be less than 50K. This led to the configuration of an experimental design for the experiment to be conducted at 10, 15 and 20 min for the heating rate of 1000°C/min. The experimental results were explained through the quantification of the process efficiency using the ratio, coined as, the Efficiency of Charring (EoC), and obtained through the equation 3.2.

$$EoC = 1 - \frac{\frac{C}{W}}{\frac{C}{Y}} \qquad \ldots 3.2$$

where,

C is the mass of the residual carbon in the biochar;

Y is the mass of the yield after pyrolysis; and,

W is the initial mass of the wood taken for pyrolysis;

This parameter would be able to define the potential of a pyrolysis process to produce good quality biochar. Biochar is said to have good quality if the total carbon content in it is nearly 50% or more. The process quality is said to be high if it gives a high yield of good quality char with respect to the total amount of pyrolysed products (McClaughlin et al., 2009). Thus the ratio EoC takes into account both the above mentioned parameters. The right hand side of the equation takes into account the efficiency of the process to remove components other than the char from the products. It would be expected that the higher the value of this parameter, the better is the efficiency of the pyrolysis technique to maximize the content of char in the system. The EoC, varies in the range of 0 to 1, where 1 indicated the best process efficiency and 0 the least. Though, for all practical cases, the EoC can never be 1. The Efficiency of Charring for fast pyrolysis was found to be the highest at 400°C for 15 min at 0.708.

In this work, the mass of the residual carbon was experimentally derived through the standard ASTM procedures for proximate analysis of coal and coke.

3.5 Conclusions

Simulation results from this study indicated 673K to be the optimum temperature at which highest yield of biochar is found by the process of pyrolysis based on the kinetics of the model taken into consideration. It also showed that the amount of char formed would vary based on the retention time.

Though the thermal equilibrium was attained in approximately 10 mins the pyrolysis process continued for a maximum of only 20 mins. Through this simulation and modelling study, the kinetics of the different pyrolysis parameters as well as further attempts of optimizing char yield through variation of time, temperature and power densities of the reaction is highlighted. This numerical simulation model could be used to further look into designing a bioreactor for pyrolysis which aims at higher yields of biochar.

3.6 Acknowledgements

The financial support of NSERC (Natural Sciences and Engineering Research Council), Canada is gratefully acknowledged.

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Connecting text

The results of the Finite Element Modelling (FEM) were instrumental in visualizing the heat transfer mechanism inside the quartz sleeve with birchwood biomass during the pyrolytic reactions. After the simulation, it was important to verify the findings through an appropriate experimental design and testing. The findings of the simulation also makes it crucial to compare these results for different heating rates in order to assess the importance of heating rate as a factor for the heat transfer in the pyrolysis of lignocellulosic materials. Moreover, it is essential to have a better understanding of the thermodynamics of the pyrolysis reactions and of the biochar produced during the process. Hence a study which examines the exothermic energy of the biochar would shed light on the thermodynamic potency of the product.

Chapter 4 **A Comparative Study of the Assessment of Biochar Production through Slow & Fast Pyrolysis**

4.1 Abstract

Considerable research has been carried out to convert wood biomass to liquid fuels and chemicals since the oil crisis in mid-1970s. Biochar has successfully emerged as a solid biofuel to address the concerns of bulky, fibrous, high moisture content and low-energy-density nature, leading to key issues including high transport cost and poor grindability of biomass for the production of liquid fuels. In this work, cylindrical biomass of 70 mm length of birch wood were pyrolysed in a laboratory-scale thermal desorption unit. The influence of final pyrolysis temperature, heating rate, and pyrolysis atmosphere on the product yields was investigated. Pyrolysis runs were performed using reactor temperatures ranging between 300 and 400°C as slow and fast pyrolysis of the wood sample. Results showed that the yield of the pyrolysis products reduced with increasing effects of time and temperature. On the other hand, the char content in the wood increased together with increasing pyrolysis temperature as well as time for both the slow as well as fast pyrolysis. A single ratio, termed as the Efficiency of Charring (EoC), which would be able to quantify the efficiency of a particular pyrolysis technique to maximize the amount of good quality char in the product was also identified through this study and optimized along with the yield. The resulting biochar was tested through proximate analysis, differential scanning calorimetry to determine its thermodynamic potential.

Keywords. Biochar, Biomass, Pyrolysis, Heating rate, Thermodynamics

4.2 Introduction

The contribution of biomass to today's world energy supply is about 12%, while in many developing countries, its contribution ranges from 40 to 50%. The term `Biomass' is a generic term which not only applies to crops, forestry and marine products but also to organic wastes, such as municipal solid waste, sewage and pulp derived black liquor, is widely included. Biomass, as an energy source, has two striking characteristics. Firstly, biomass is not only one of the most abundant resources but is also the only renewable organic resource. Secondly, biomass fixes carbon dioxide in the atmosphere by photosynthesis. Among the various kinds of biomass, woody biomass is the most popular in terms of its application as an energy source, in the form of firewood or charcoal. It is, however, next to impossible to use firewood or charcoal as an alternative fuel for commercial equipment and industrial processes where fossil fuels, in particular oil, are used at present. Thus it becomes necessary to develop a technology which leads to conversion of biomass to a more suitable form, such as liquid or gas (Demirbas, 2000).

Traditionally, the recovery of energy from biomass has been centered on biochemical or thermochemical conversion processes. Wood and wood waste (slabs and blocks of wood, chips, and sawdust), energy crops, agricultural waste, and refuse are the most common feedstocks generally considered for thermochemical conversion. One of the most common and convenient routes for conversion of biomass into energy is through thermochemical conversion. This includes combustion, gasification, liquefaction, and pyrolysis (Sensoz & Can, 2001).

In the majority of these studies, the yields of oil products from thermochemical biomass conversion processes have been investigated

(Xianwen et al., 2000). The process conditions of the pyrolysis technique may be optimised to produce high energy density pyrolytic oils in addition to derived charcoal and gas which makes it very prominent amongst the thermochemical processes. The product, in this case, is an intermediate energy gas that can be used for power generation or as a source of heat for a variety of processes (Demirbas, 2000).

The role of pyrolysis is vital in the reaction kinetics and hence in reactor design. Thus, the determination of parameters such as product distribution, composition, and properties becomes important in all thermochemical conversion processes, (Raveendran et al.,1995; Raveendran et al., 1996). The reaction which takes place in the pyrolysis process is the decomposition of the organic part of the material to lower molecular weight products, liquids or gases, which can be useful as fuel or chemical sources (Torres et al., 2000). It has also been well documented that a pyrolysis step is always present in the initial stages of gasification and of combustion (Cozzani et al., 1997; Yu et al., 1997). The pyrolysis of lignocellulosic materials has been widely studied by a great number of researchers using different techniques: fixed-bed reactor, vacuum pyrolysis reactors, fluidized bed reactors, Differential Thermal Analysis (DTA) and Thermo Gravimetric Analysis (TGA), ablative reactors, wire-mesh reactors etc. Static batch reactors are the simplest configuration to study the pyrolysis of biomass. In these reactors, a weighed sample is introduced into a vessel in which the experimental conditions are fixed. The product yield and type are dependent on the reactor type and the pyrolysis conditions, in particular on the maximum pyrolysis temperature and heating rate for a given lignocellulosic material. Some of the other factors that influence the pyrolysis processes are the size of the initial particles, pressure, and residence time (Sensoz & Can, 2001). Product composition from these processes varies with reaction conditions and includes noncondensable gases (syn or producer gas), condensable vapors/liquids (bio-oil, tar), and solids (char, ash). In fast pyrolysis systems, dry biomass is heated very rapidly (up to 1000°C/s) in the absence of oxygen and the products quickly removed and quenched to maximize production of bio-oils. Traditional charcoal-making typically employs slow pyrolysis conditions: slow heating rates (1–20°C/min) in the absence of oxygen, and long char residence times (hours to days) (Brewer et al., 2009). Reaction parameters can be varied easily to alter the relative quantities and qualities of the resulting products. Pyrolysis processes are classified as conventional or fast pyrolysis, depending on the operating conditions that are used. Conventional pyrolysis may also be termed as slow pyrolysis. The terms “slow pyrolysis” and “fast pyrolysis” are somewhat arbitrary and have no precise definition of the duration or heating rates involved in each (Mohan et al., 2006). A significant part of the new thermochemical conversion methods for wood-based materials is performed under pyrolytic conditions. A good understanding of the pyrolytic properties of wood constituents will be of benefit to the development of these methods (Sensoz & Can, 2001).

In general, the thermochemical conversion of biomass leads to the formation of biochar at temperatures above 300°C in the absence (or under reduction) of oxygen. Biochar is a 2,000 year-old practice that converts agricultural waste into a soil enhancer that can hold carbon, boost food security and discourage deforestation. It is a process which creates a fine-grained, highly porous charcoal that helps soils retain nutrients and water as seen in Figure 4.1. The carbon in biochar has the capability to resist degradation and can hold carbon in soils for hundreds to thousands of years.

Figure 4.1 Chinese birchwood Biochar

Apart from its benefits as a soil enhancer, sustainable biochar practices can produce oil and gas by products that can be used as fuel, providing clean, renewable energy. When the biochar is buried in the ground as a soil enhancer, the system can become "carbon negative." Biochar and bioenergy co-production can help combat global climate change by displacing fossil fuel use and by sequestering carbon in stable soil carbon pools (IBI website, May 6th, 2010).

Differential Scanning Calorimetry (DSC) has become an established technique with regards to the measurement of the energetics of a biochemical process and the thermodynamic mechanisms which are underlying these reactions. The purpose or function of the DSC is to measure the apparent molar heat capacity of a protein or other macromolecule as a function of temperature. This information enables the subsequent manipulation of the molar heat capacity and leads to a complete thermodynamic characterization of a transition taking place during the reactions. The information which can be extracted from the DSC can be categorized into three types:-

1. The absolute partial heat capacity of a molecule;
2. The overall thermodynamic parameters (enthalpy change [∆H], entropy change [∆S], and heat capacity change [∆Cp] associated with a temperature induced transition; and
3. The partition function and concomitantly the population of intermediate states and their thermodynamic parameters (Freire, 1995).

The utilization of the expertise of a DSC study with respect to biochar studies has been in the continuous recording of the energy flux into and out of the sample. This would lead to an indication of whether or not a reaction at a particular temperature is exothermic or endothermic. These results can be coupled with an associated weight loss through a thermo-gravimetric analysis, or TGA.

In addition to the estimation of the proportions of biochar using the observed weight loss, the DSC curves by themselves, can be used to decompose to resolve individual peaks which correspond to different components, and the subsequent quantification of these components from the peak height or peak area measurements. This is an area which needs to be further explored for better biochar identification and characterization (Lehmann and Joseph, 2009).

In this study, the usage of Chinese birch wood samples for production of biochar was investigated. The effects of the pyrolysis conditions such as temperature and heating rate, on the biochar yields and fuel properties of biomass samples were determined by using statistical design techniques and through the results obtained from Differential Scanning Calorimetry. A single number (ratio) which would be able to quantify the efficiency of a particular pyrolysis technique to maximize the amount of char in the product was also identified through this study.

4.3 Material and Methods

Longitudinal pieces of Birch wood obtained from the local market were cut into pieces of 3 mm diameter and 70 mm length. In this study, the pyrolysis experiments were conducted in a Thermal Desorption Unit (Supelco, Inc.) (Figure 4.2) with the sample wood pieces insulated inside quartz tubes of 6 mm outside diameter and 100 mm in length. The objective of this investigation was to determine the effect of the pyrolysis temperature on pyrolysis yields. Thus a quantity of ~0.5 g of the sample was placed in the reactor and the temperature was raised at 20°C/min and also at a fast pyrolysis rate of 1000°C/min to final test temperatures of 300, 350, and 400°C and held for 10, 15 and 20 min respectively. The experimental conditions were established through a two factorial face centered design obtained from MATLAB R2009b with variable test temperatures of 300, 350, and 400°C and held for 10, 15 and 20 min respectively as shown in Table 4.1. Although 16 treatments were identified through the experimental design, the centre point of the cube was replicated for 8 times and the averages of the replicates were considered for the quantitative and qualitative analysis.

The volatiles produced during the process were constantly displaced with nitrogen gas purged into the system and then condensed in a water- bath. After pyrolysis, the solid char was removed and weighed to analyze the yield of the products.

The biochar products were analyzed through proximate analysis of the char (ASTM procedures) in a Barnstead Thermolyne 48000 Furnace. A Response Surface Optimization analysis was carried out to evaluate the optimum conditions for the maximization of biochar yields as well as to find the best quality biochar from the biomass sample.

Table 4.1. Experimental conditions with a two factorial face centered design

Test No	Temperature °C	Time Min
1	300	10
2	300	20
3	400	10
4	400	20
5	300	15
6	400	15
7	350	10
8	350	20
9	350	15
10	350	15
11	350	15
12	350	15
13	350	15
14	350	15
15	350	15
16	350	15

The instrument used to measure the exothermic enthalpy of the biochar samples was a TA Instruments Q100 Differential Scanning Calorimeter (NewCastle, DE, USA) (Figure 4.3) operated with the TA Instruments Q100 DSC 7.0 Build 244 software. The samples were first placed in aluminium pans (10 mg/pan) and then hermetically sealed. The pans were transferred to the instrument pan holder. The pans were then made to equilibrate to 0°C and then heated from 0°C to 550°C at a constant rate of 50°C/min. An empty pan was used as a reference.

Biochar pH was measured in deionized water using a 1 to 3 wt/wt ratio. Samples were thoroughly mixed and the pH was measured with a Hydrion pH paper 6.0-8.0 (Fisher Scientific, USA).

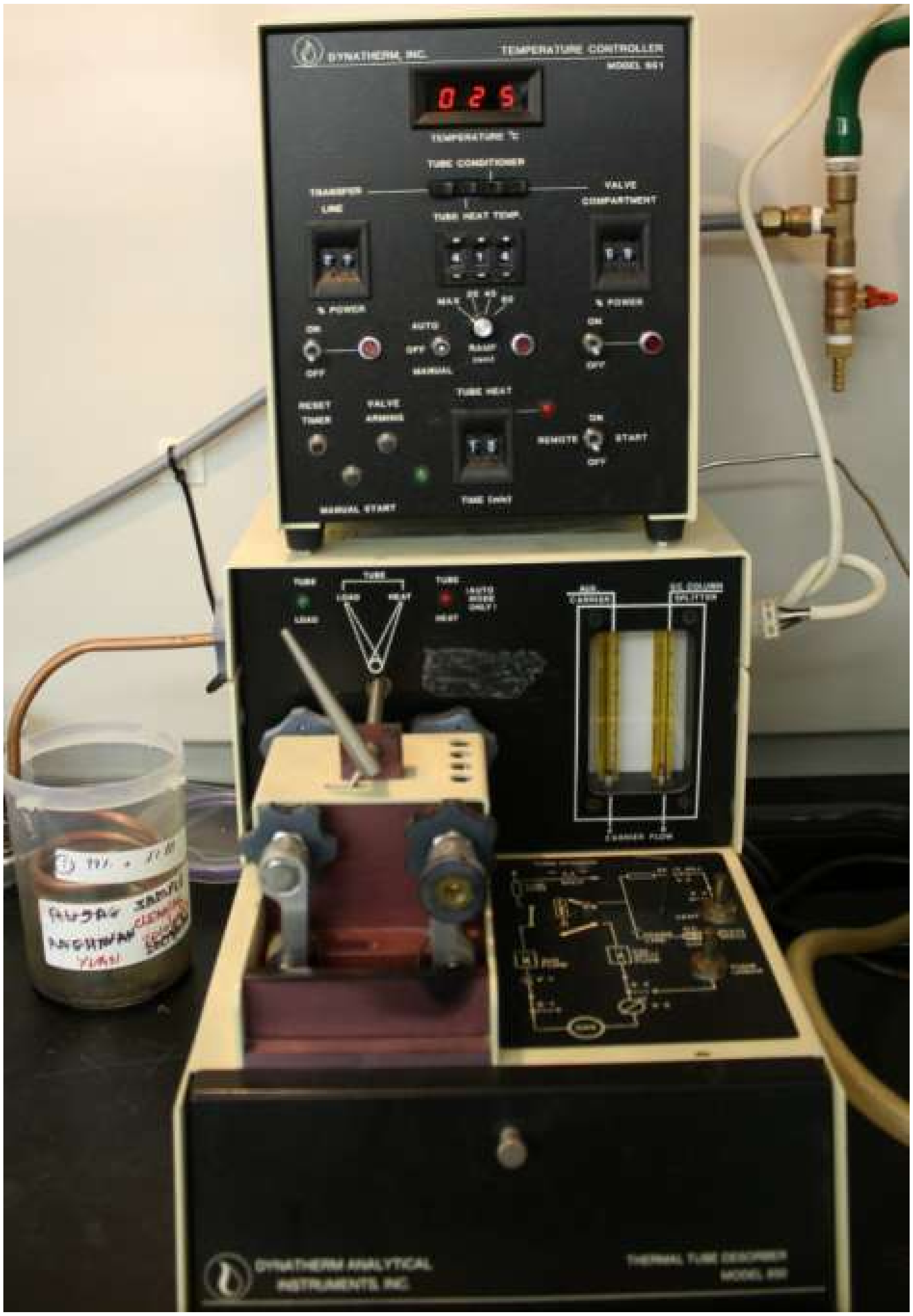


Figure 4.2 Thermal Desorption Unit (Supelco, Inc.)

Figure 4.3 TA Instruments Q100 Differential Scanning Calorimeter

4.4 Results and Discussion

4.4.1 Statistical comparison of biochar yields at slow and fast pyrolysis

The interpretation of the experimental results given in Table 4.2 was achieved by the use of the factorial design technique. In this technique, the influences of the two experimental variables and their interaction effects on the results are investigated. Based on the experimental results, the following biochar yields were obtained from slow and fast pyrolysis of the Chinese birch wood samples as shown in Table 4.2.

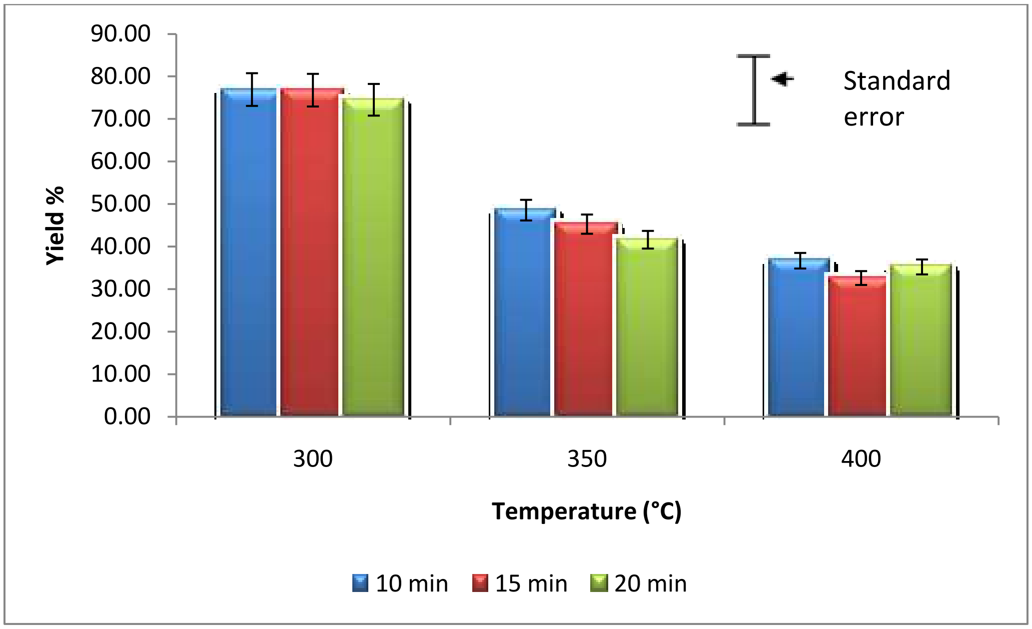
In this investigation, temperature and time were taken as the two factors and a face centered cubic design matrix was formed with eight central levels of the design. The same design was applied with replicates for two different heating rates chosen, 20°C/min as the slow pyrolysis and 1000°C/min as the fast pyrolysis.

The product yields from the pyrolysis of the birch wood samples with heating rates of 20 and 1000°C/min in relation to final pyrolysis temperatures of 300, 350, and 400°C is shown in Figure 4.4. At both the heating rates, together with increasing pyrolysis temperature as well as time, the char yield is decreased. With the increase in temperature of pyrolysis, the total product yield after the process reduced from approximately 75% at 300°C (10 min) to 35% at 400° C (20 min) for slow pyrolysis and a similar trend was observed in the case of fast pyrolysis, from 77% to about 32% for the same periods of time. As reported by many researchers who have attributed this decrease in the char yield with increasing temperature, either to greater primary decomposition of the wood at higher temperatures or to secondary decomposition of the char. This conclusion is consistent with previous studies of cellulose and lignocellulosics (Sensoz and Can, 2002, Valenzuela-Calahorra et al., 1987).

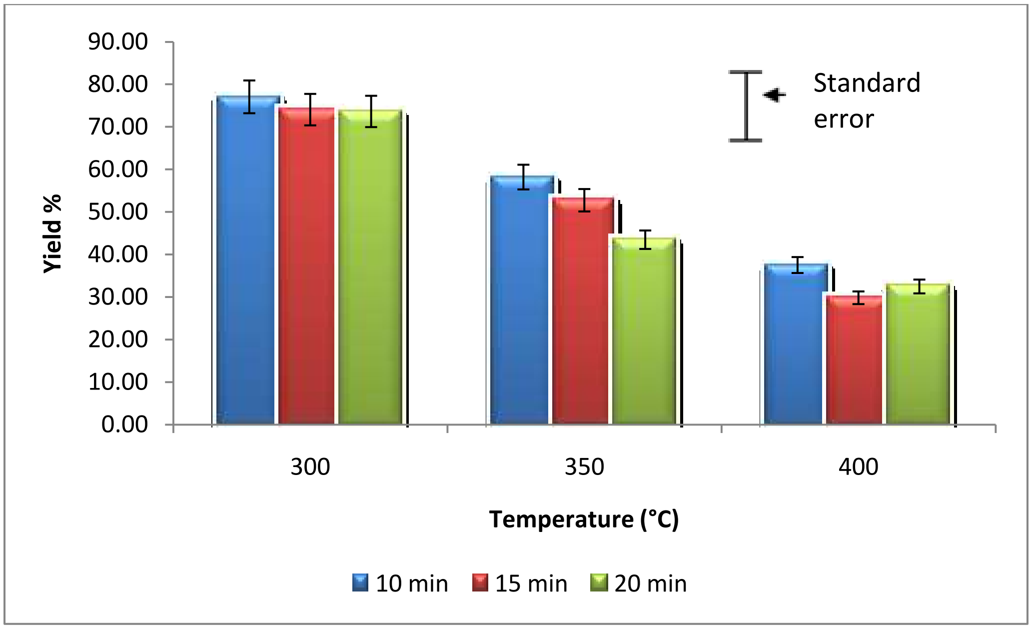
Table 4.2 Biochar yield values of Chinese birch wood at slow & fast pyrolysis heating rates for the experimental design matrix

Test	Yield_Slow%	Yield_Fast%
1	76.90	77.05
2	74.49	73.62
3	36.65	37.50
4	35.19	32.46
5	76.75	74.04
6	42.90	29.81
7	38.30	58.18
8	50.36	43.46
9	53.95	50.16
10	48.21	49.64
11	49.20	59.71
12	49.50	49.35
13	48.36	49.84
14	51.42	49.80
15	55.80	58.68
16	51.48	54.68

A multiple comparison of the results of the yields of the wood samples treated with two different heating rates of 20 and 1000°C/min was conducted through ANOVA and Duncan's test with an $R^2 > 0.90$, to ascertain the effects of the different treatments/processes on the yields of the product. The results in Figure 4.5 indicates that for the temperatures of 300 and 400° C with pyrolysis time of 10 and 20 min, there was no significant difference between the slow and fast heating rates. Furthermore, all the treatments at 350°C for different pyrolysis lengths of time were found to have no significant difference, with respect to the slow pyrolysis treatment. On the other hand, the pyrolysis temperature of 350°C, for the two heating rates of 20 and 1000°C/min was statistically different at all periods of time.



(a)



(b)

Figure 4.4 The comparison of pyrolysis yields on varying pyrolysis temperatures & time at (a) 20°C/min & (b) 1000°C/min

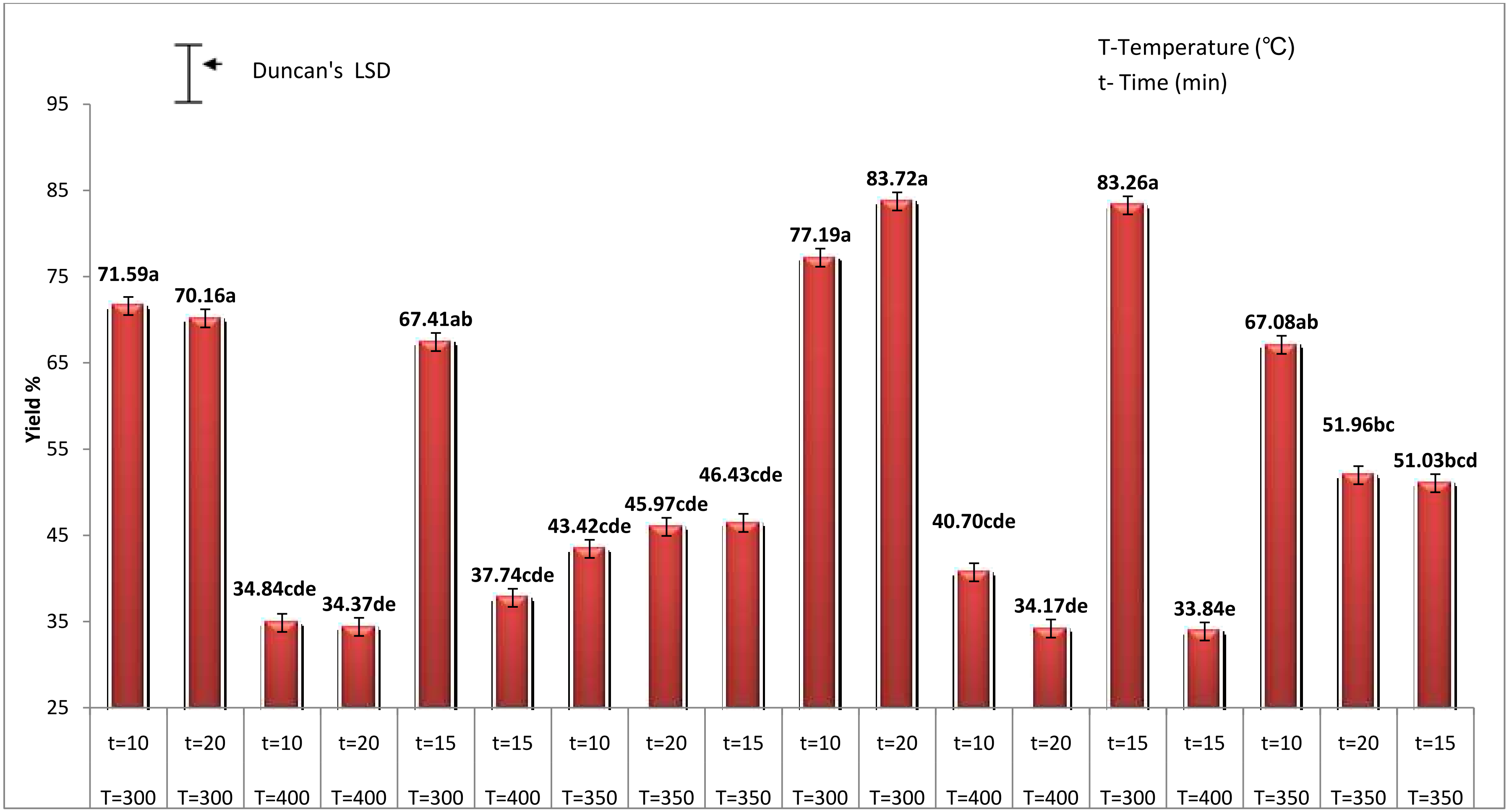


Figure 4.5 Duncan's multiple test comparison analysis of slow (20°C/min) and fast pyrolysis (1000°C/min) yields representing statistical significance among the treatments. The means followed by the same letter are not significant at $P<0.05$ level.

4.4.2 Biochar yield and its properties as a fuel

Proximate analysis of the Chinese birch wood biochar samples were also performed according to ASTM standards (ASTM), and the results are given in Tables 4.3 and 4.4. As can be seen from Table 4.3, Biochar obtained from slow pyrolysis at 400°C for 20 min had the best potential as a carbon-rich fuel and contains 37.84% mobile matter, 4.77% ash and 57.39% residual matter. It is evident from Table 4.3 and 4.4 that the biochar which was obtained from fast pyrolysis had a very low fuel capacity, with respect to the ones obtained from slow pyrolysis. The best properties of a fuel were seen at the fast pyrolysis temperature of 300°C for 20 min with 44.45% mobile matter, 5.51% ash and 50.04% residual matter. A biochar sample can be characterized as a carbon-rich solid fuel with high fixed carbon content but low volatile matter content (Sensoz and Can, 2002, Boetang et al., 2007). The presence of higher ash contents occurs at the expense of the carbon content in the biochar sample. Research dedicated to biomass combustion has shown that feedstocks containing more silica in their ash content have relatively high slagging tendencies compared to the hardwood biomass which have been reported to contain more alkali metals. Furthermore, contamination by sand or soil during biomass collection enhances this tendency. It has been shown by researchers Brewer et al., (2009) that chars from switchgrass and corn stover would inherently have three challenges of high overall ash content, high silica content, and contamination by soil compared to traditional charcoals for use as fuels.

The aim of this investigation was to determine the efficiency of the slow and fast pyrolysis in the production of good quality biochar from the wood samples. In order to achieve this, it was important to account for the amount of carbon conserved during the process with respect to the initial wood sample.

Table 4.3 Proximate analysis of biochar samples at different pyrolysis temperatures and times at 20°C/min

Test	Temp	Time	Mobile matter%	Ash%	Residual matter%	MC%
1	300	10	82.90	5.53	11.57	2.30
2	300	20	74.41	2.48	23.11	2.25
3	400	10	39.18	5.79	55.03	1.98
4	400	20	37.84	4.77	57.39	1.96
5	300	15	83.10	8.25	8.65	2.01
6	400	15	38.23	6.51	55.26	0.00
7	350	10	51.53	4.46	44.01	1.84
8	350	20	50.76	4.91	44.34	1.61
9	350	15	55.07	5.91	39.02	1.67

Table 4.4 Proximate analysis of biochar samples at different pyrolysis temperatures and times at 1000°C/min

Test	Temp	Time	Mobile matter%	Ash%	Residual matter%	MC%
1	300	10	79.03	7.35	13.63	2.73
2	300	20	44.45	5.51	50.04	2.26
3	400	10	63.51	2.94	33.55	1.65
4	400	20	49.90	5.84	44.26	3.13
5	300	15	61.22	8.01	30.77	2.35
6	400	15	86.38	7.43	6.19	1.90
7	350	10	91.93	5.33	2.74	2.40
8	350	20	65.33	4.26	30.41	2.47
9	350	15	70.33	5.04	24.64	2.17

The quantification of the process efficiency can be explained using the ratio, coined as, the Efficiency of Charring (EoC), and obtained through the equation 4.1.

$$EoC = 1 - \frac{\frac{C}{W}}{\frac{C}{Y}}$$

...4.1

where,

C is the mass of the residual carbon in the biochar;

Y is the mass of the yield after pyrolysis; and,

W is the initial mass of the wood taken for pyrolysis;

This quantity would be able to define the potential of a pyrolysis process to produce good quality biochar. This parameter would be able to define the potential of a pyrolysis process to produce a good quality biochar. Biochar is said to have a good quality if the total carbon content in it is nearly 50% or more. The process quality is said to be high if it gives a high yield of good quality char with respect to the total amount of pyrolysed products (McClaughlin et al., 2009). Thus the ratio EoC takes into account both the above mentioned parameters. The ratio, $\frac{\frac{C}{W}}{\frac{C}{Y}}$ quantifies the quality of the char with respect to the process. While taking the totality of the constituents present in the biomass as 1, the complete right hand side of the equation takes into account the efficiency of the process to remove components other than the char from the products. It would be expected that the higher the value of this parameter, the better is the efficiency of the pyrolysis technique to maximize the content of char in the system. The EoC, varies in the range of 0 to 1, where 1 indicated the best process efficiency and 0 the least. Though, for all practical cases, the EoC can never be 1. The Efficiency of Charring for slow pyrolysis was found to be the highest at 400°C for 10 min at 0.681 and for fast pyrolysis, it was found to be at the same temperature but for the pyrolysis time of 15 min with 0.708 as the ratio as indicated in Figure 4.6 (a) and (b). Moreover, it could be clearly observed from Figure 4.6 (a) and (b) that the efficiency of pyrolysis was more linear for slow pyrolysis than for a faster heating rate.

A response surface optimization for the results of the EoC was also carried out for both slow as well as fast pyrolysis. This optimization was carried out with the help of MATLAB R2010a. Figures 4.7 and 4.8 show the response surface plot for slow and fast pyrolysis respectively. The maximum predicted value of EoC for slow pyrolysis was optimized to be at the pyrolysis temperature of 400°C for 11.4 min and for fast pyrolysis the same was optimized to be at 400°C for 20 min. It can be clearly deciphered from Figures 4.6 and 4.7 that as a pyrolysis process, the efficiency of fast pyrolysis to maximize biochar production is higher than that of slow pyrolysis which corroborates with the results discussed in Boetang et al., 2007.

The equations for the optimization of the EoC results for the slow and fast pyrolysis were obtained as Equation 4.2 and 4.3:

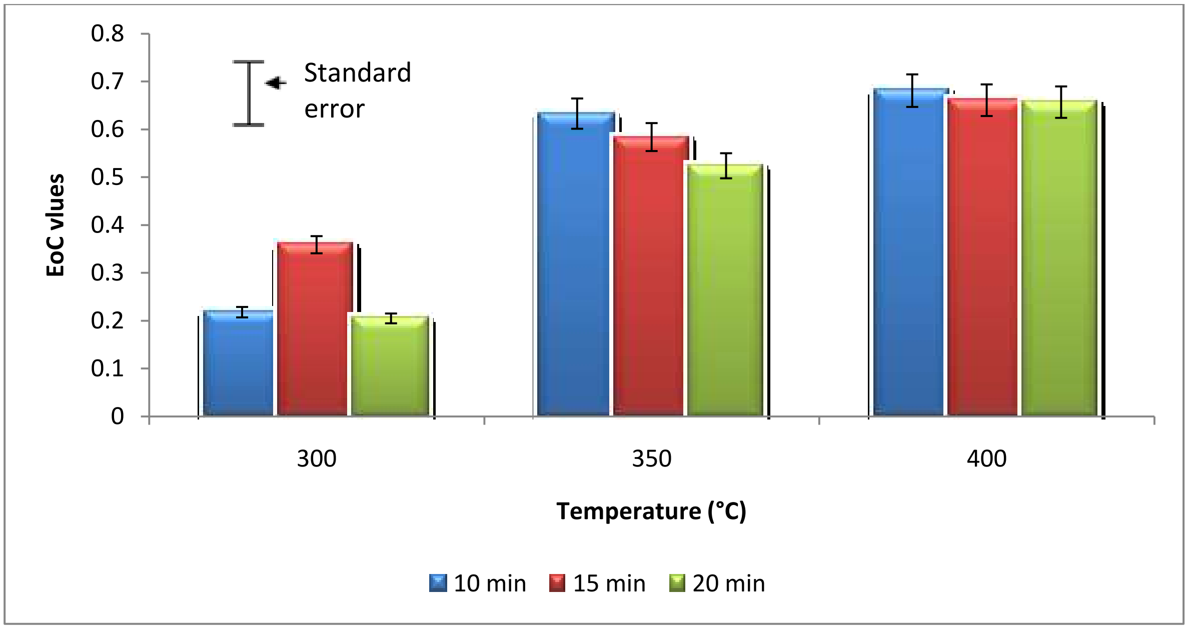
$$-5.29686 + 0.028709 * T + 0.021729 * t - 1.1 * 10^{-5} * T * t - 3.5 * 10^{-5} * T^2 - 0.00076 * t^2 \qquad 4.2$$

$$-1.62677 + 0.00685 * T + 0.031147 * t - 3.7 * 10^{-5} * T * t - 5.65 * 10^{-6} * T^2 + 0.000435 * t^2 \qquad 4.3$$

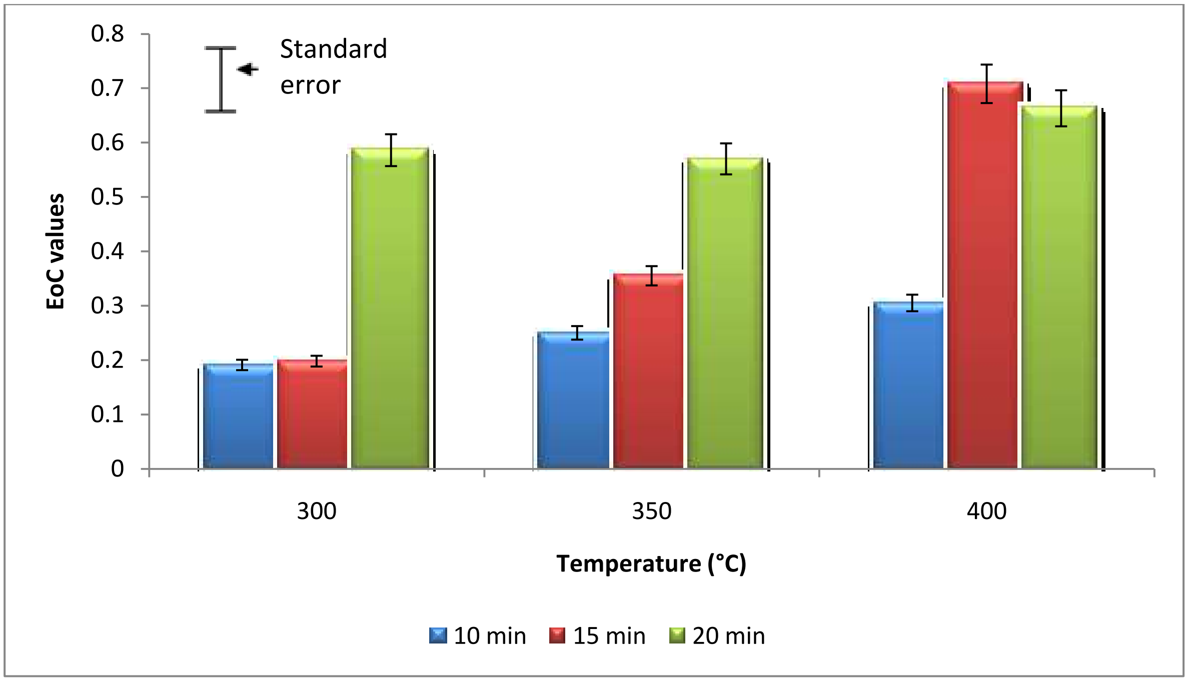
where,
T is the pyrolysis temperature; and
t is pyrolysis time.

It was important to note from the Figures 4.6 and the response surface plots (Figures 4.7 and 4.8) of both the slow and fast pyrolyses, that the treatments with longer holding times had a higher efficiency to produce biochar which confirms the findings of Di Blasi (1996). Also, this effect is more pronounced with the increase in heating rate. The char produced by fast pyrolysis at 400°C, in general, had a significantly lower yield compared to the same at 350°C.

A Differential Scanning Calorimetry (DSC) was also conducted on the Chinese birch wood samples maintaining the same experimental design matrix. The calorimetry study was conducted for a temperature range of 0°C to 550°C as mentioned earlier. The objective of this investigation was to compare the exothermic enthalpy of the biochar samples produced from slow and fast pyrolysis and then to optimize the results through a response surface optimization. The results of the DSC study is shown in Figure 4.9 (a) and (b), which clearly indicates that the fast pyrolysis samples had a higher exothermic enthalpy than the ones produced through the slow pyrolysis technique. Furthermore, it could be observed from Figure 4.9 that for both slow as well as fast pyrolysis, the highest exothermic enthalpy was found to be at the pyrolysis temperature of 350°C for 10 min, with 66.31J/g for slow pyrolysis and 89.46 J/g for fast pyrolysis.



(a)



(b)

Figure 4.6 Efficiency of Charring for different treatments for (a) slow pyrolysis (20°C/min) and (b) fast pyrolysis (1000°C/min)

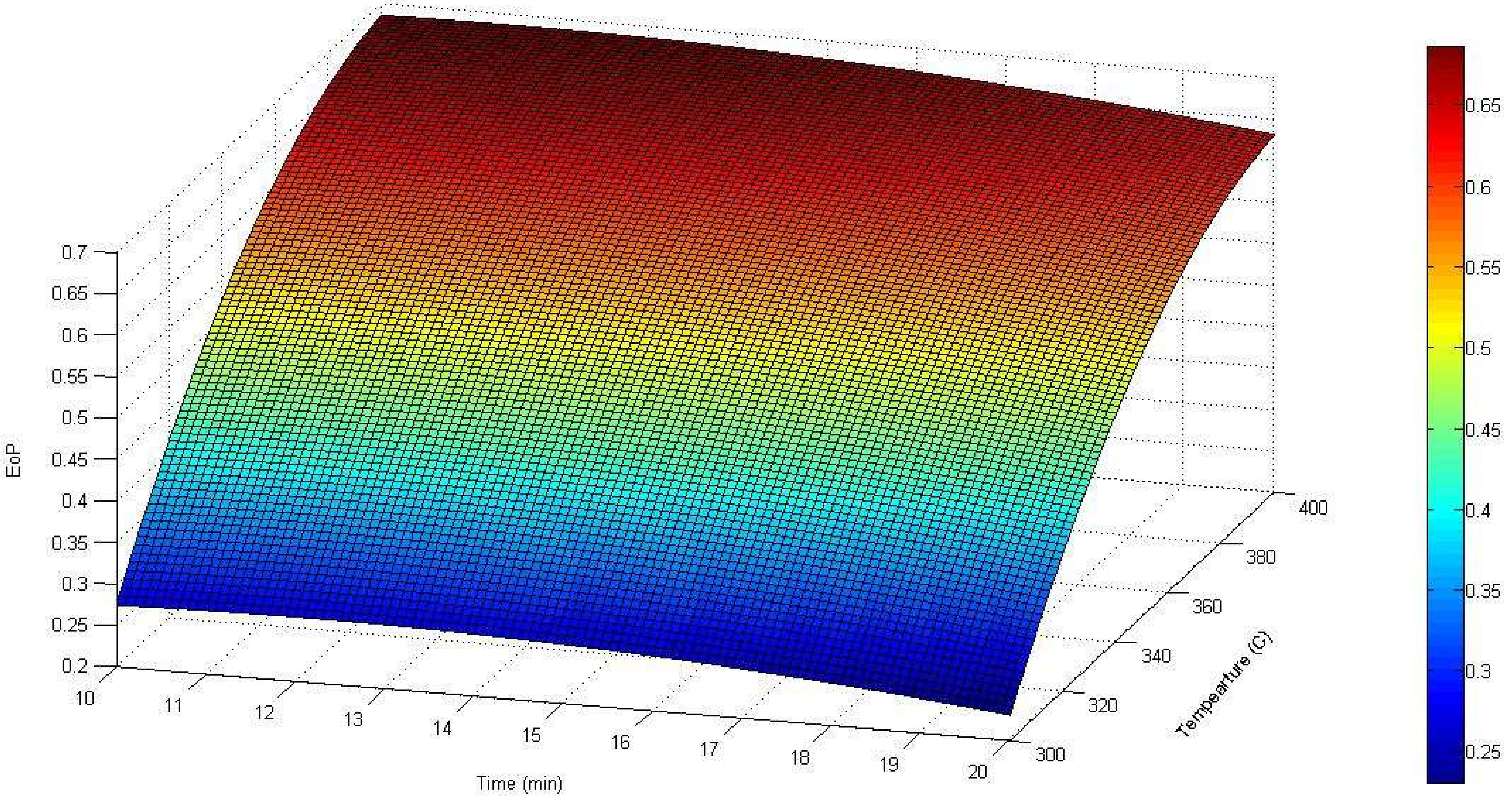


Figure 4.7 Response surface plot for EoC of slow pyrolysis yielding biochar

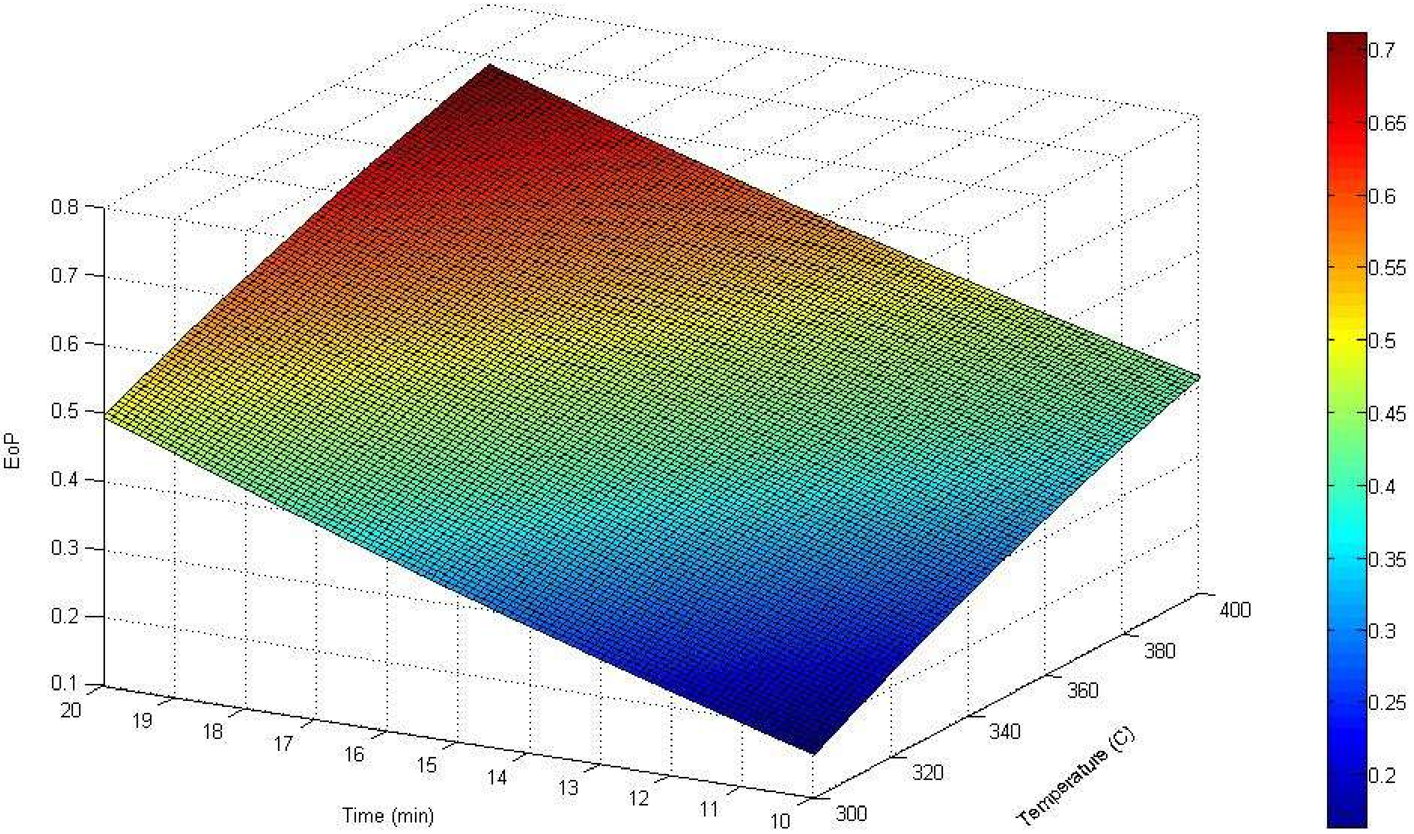


Figure 4.8 Response surface plot for EoC of fast pyrolysis yielding biochar

A response surface optimization for the results of the DSC was also carried out for both slow as well as fast pyrolysis. This optimization was carried out with the help of MATLAB R2010a. Figures 4.10 and 4.11 show the response surface plots for slow and fast pyrolysis respectively. The maximum exothermic enthalpy for slow pyrolysis was optimized to be at the pyrolysis temperature of 357°C for 13.5 min and for fast pyrolysis the same was optimized to be at 367°C for 10 min.

The equations for the optimization of the DSC results for the slow and fast pyrolysis were obtained as Equation 4.4 and 4.5:

$$-582.2427 + 3.4803 * T + 0.3704 * t + 0.028 * T * t - 0.0054 * T^2 - 0.3845 * t^2 \tag{4.4}$$

$$-789.4433 + 4.7333 * T + 2.8362 * t - 0.03157 * T * t - 0.00602 * T^2 + 0.190233 * t^2 \tag{4.5}$$

where, T is the pyrolysis temperature; and t is pyrolysis time.

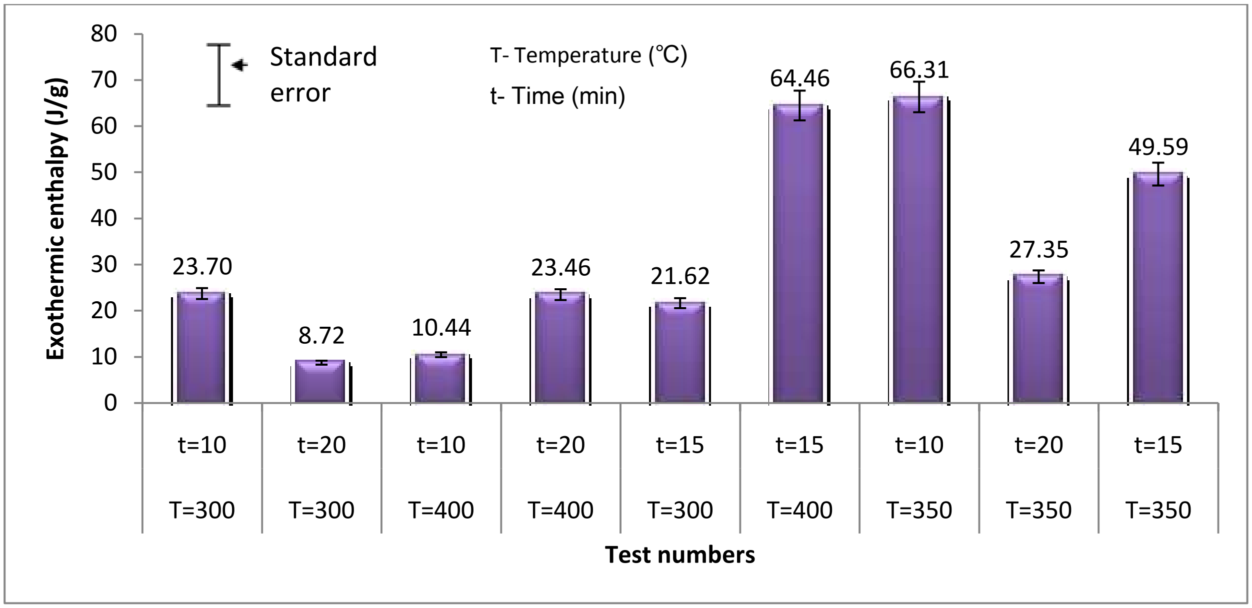
In an oxidizing atmosphere, reactions which involve the combustion of the organic matter present in the biochar samples are exothermic in their thermodynamic nature. It has been observed by Lehmann and Joseph (2009) that in such a study with DSC, oxidation of the sample begins at around the temperature of 200°C and the weight losses complete by 550°C. The present investigation found similar results with DSC showing exothermic curves ending at around 535°C. Further studies which combine the DSC results to weight loss in the determination of the inorganic and organic impurities in the biochar can be investigated.

4.4.3 pH of biochar samples

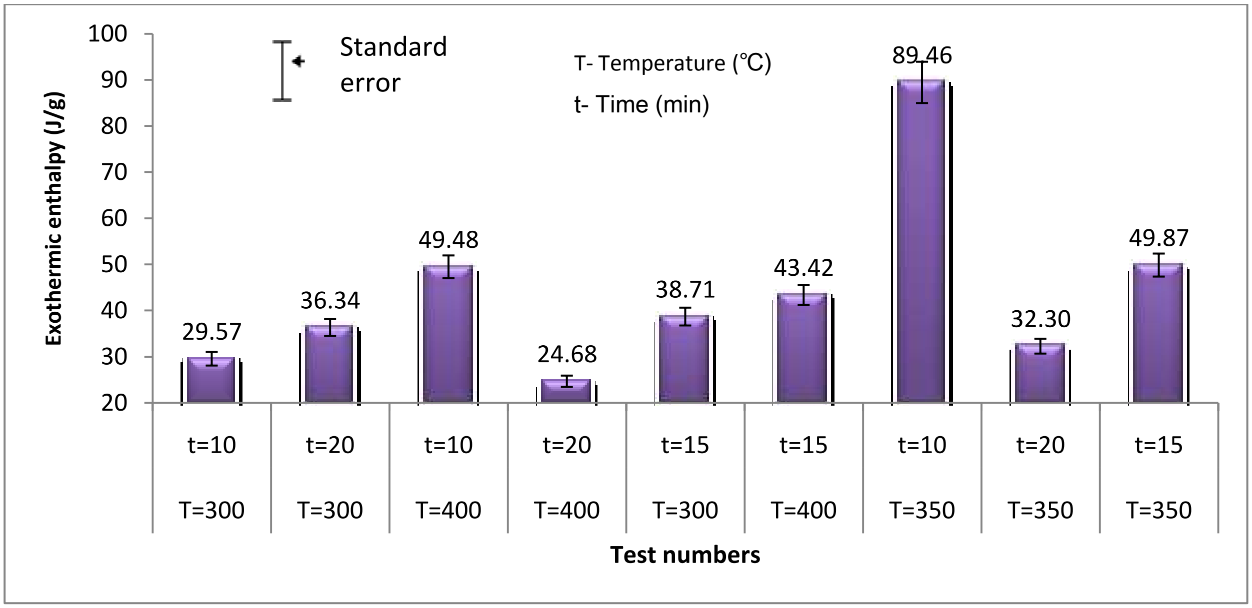
The pH range of the biochar samples produced through slow pyrolysis was found to be 6.0 to 6.5 while those produced from fast pyrolysis was found to be in the range of 6.2 to 6.8. This clearly indicates the less acidic nature of the char produced through a faster heating rate. A higher pH of the biochars has been identified as a key feature in improvement of acidic soils (Lehmann et al., 2003).

4.5 Conclusions

In this study, the possibility of Chinese birch wood samples for production of biochar was investigated. The effects of the pyrolysis conditions such as temperature and heating rate, on the biochar yields and fuel properties of biomass samples were determined by using statistical design techniques. Results showed that the yield of the pyrolysis products reduced with increasing effects of time and temperature. On the other hand, the char content in the wood increased together with increasing pyrolysis temperature as well as time for both the slow as well as fast pyrolysis. Also, a single number (ratio) which would be able to quantify the efficiency of a particular pyrolysis technique to maximize the amount of char in the product was also identified through this study. The maximum predicted value of EoC for slow pyrolysis was optimized to be at the pyrolysis temperature of 400°C for 11.4 min and for fast pyrolysis the same was optimized to be at 400°C for 20 min. Through the results obtained from Differential Scanning Calorimetry, fast pyrolysis was identified to have a higher exothermic energy than slow pyrolysis. The highest exothermic enthalpy was found to be at the pyrolysis temperature of 350°C for 10 min, with 66.31J/g for slow pyrolysis and 89.46 J/g for fast pyrolysis while the optimization results indicated that the maximum exothermic enthalpy for slow pyrolysis was at the pyrolysis temperature of 357°C for 13.5 min and for fast pyrolysis the same was optimized to be at 367°C for 10 min.



(a)



(b)

Figure 4.9 The comparison of exothermic enthalpy on varying pyrolysis temperatures & times at (a) 20°C/min & (b) 1000°C/min

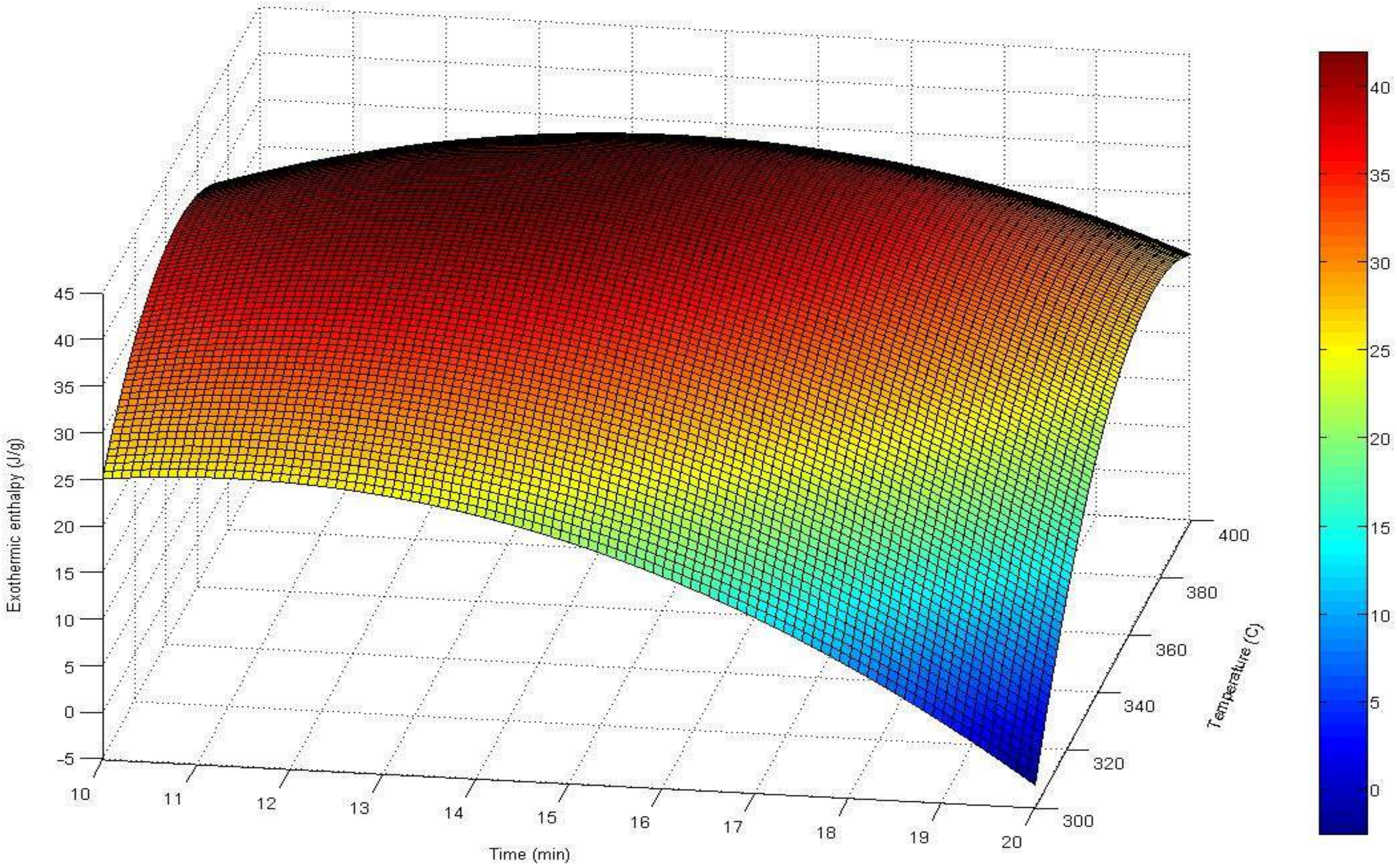


Figure 4.10 Response surface plot for exothermic enthalpy of slow pyrolysis yielding biochar

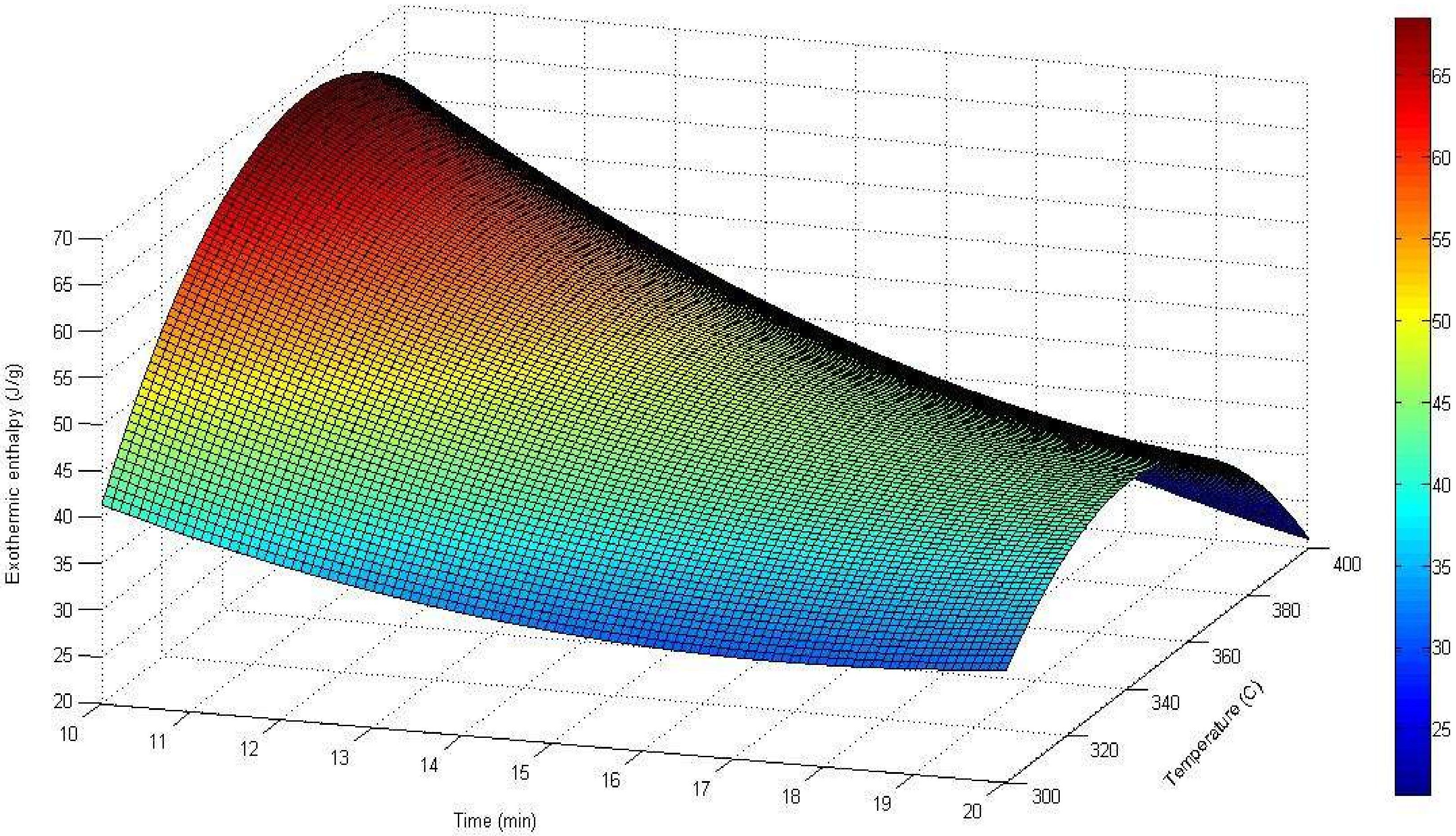


Figure 4.11 Response surface plot for exothermic enthalpy of fast pyrolysis yielding biochar

4.6 Acknowledgements

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Connecting text

The previous section dealt with defining the product of pyrolysis in terms of the solid residence time, the higher and lower heating rates of the process and the amount of char formed by weight during the process.

After the quantification of the pyrolysis reactions for both slow and fast heating rates, it was essential to carry out the qualitative analysis of the biochar product through two different pyrolytic heating rates. Density is a physical property of all matter; it is simply the unit quantity of mass per volume of the same quantity. Porosity measurements and their relation to reflectance in the biochar samples can be used as an index for further evaluation of the products formed in the pyrolysis process in terms of its physical composition.

Chapter 5

Characterization of Birchwood biochar by Pycnometry and Hyper-spectral imaging

5.1 Abstract

The birchwood biochar produced by slow as well as fast pyrolysis were analysed and compared according to their physical characteristics like porosity and reflectance. A relation between char porosity and the reflectance of the biochar structure was found. From the pycnometry data gathered, it was observed that the treatments at 350°C and 400°C with the longest holding times for slow as well as fast pyrolysis had the highest porosity compared to the other biochar samples.

Very high reflectances were observed for certain infra red wavelengths and resulted in poor visibility of the biochar samples. Therefore, the wavelengths providing images with maximum clarity were established for classification through hyper-spectral imaging technique. The wavelengths which were found to be optimum for both slow and fast pyrolysis biochars were 947 nm and 1685 nm which fall in the Near-IR and Short IR wavelength ranges respectively. The results of the hyperspectral imaging support the findings of the porosity evaluations which showed that the biochar sample treated at 350°C for slow pyrolysis and 400°C for fast pyrolysis both for a holding time of 20 min had the highest porosity and in turn showed the least reflectance mean values. Thus, the theory that with increasing porosity of the char structure, its reflectance decreases was substantiated through this qualitative study.

Keywords. Biochar, Pyrolysis, Porosity, Hyperspectral imaging

5.2 Introduction

In general, the thermochemical conversion of biomass leads to the formation of biochar at temperatures above 300°C. The structure of biochar is more or less amorphous but contains some local crystalline structure of highly conjugated aromatic compounds whose dimensions are in nanometers and consists of graphite-like non aligned layers. One of the main technologies used for the production of biochar from different biomass sources is pyrolysis, which involves the decomposition of the biomass at temperatures above 260°C - 300°C in an oxygen free environment (UK BRC, 2009). The product composition from this process varies with reaction conditions and includes noncondensable gases (syn or producer gas), condensable vapors/liquids (bio-oil, tar), and solids (char, ash). Pyrolysis processes are classified as conventional or fast pyrolysis, depending on the operating conditions that are used. Conventional pyrolysis may also be termed slow pyrolysis. The terms “slow pyrolysis” and “fast pyrolysis” are somewhat arbitrary and have no precise definition of the times or heating rates involved in each (Mohan et al., 2006). In fast pyrolysis systems, dry biomass is heated very rapidly (up to 1000°C/s) in the absence of oxygen and the products quickly removed and quenched to maximize production of bio-oils. Traditional charcoal-making typically employs slow pyrolysis conditions: slow heating rates (1–20°C/min) in the absence of oxygen, and long char residence times (hours to days) (Brewer et al., 2009). Reaction parameters can be varied easily to alter the relative quantities and qualities of the resulting products (Avenella et al., 1996).

During the devolatilization of the biomass, as volatile matter is generated, there are significant changes to the physical structure of the char. The chemistry of a char is strongly dependent on the raw biomass properties. The char by itself is highly heterogeneous and complex inside an individual particle and between different particles. Char's structure is strongly influenced by temperature, heating rate and pressure. Understanding the fragmentation of biomass and the formation of char's pore structure during the devolatilization of pulverized biomass is essential to the development of advanced biomass utilization technologies. Many researchers have studied the impacts of pyrolytic reaction conditions on the char reactivity for biomass fuels. But, the relation between the pyrolytic conditions and char reactivity has been recently recognized through the structural evolution and morphological changes of the char generated in the pyrolysis stage. However, only a limited number of studies have dealt with the relation between the pyrolytic conditions and char structure (Hu et al., 2008).

The comparison of the pyrolysis and gasification of eucalyptus under different conditions was undertaken by Pindoria et al. (1998). Their study highlighted the importance of biomass pyrolysis by reporting conversion levels of up to 95% without any reactive gas input. Biagini, et al. (2005) studied biomass char morphology under various devolatilization conditions at atmospheric pressure. They found that the occurrence of particle melting was a result of plastic deformation at high heating rates and its impact on the char structure and reactivity. Koranyi (1989) reported that a good correlation existed between a char's reactivity and its microporosity. Hu et al., (2008) studied the structural evolution during rapid pyrolysis and the influence of such evolution on char reactivity.

The detailed chemical, moisture, and other descriptions of constituent parts of an item can be provided by Vis/NIR spectroscopy with the help of vital spectral response information (Casasent and Chen, 2003). A key role in the success of hyperspectral target detection and classification is played by *Feature*

Extraction, which is the reduction of data dimensionality by extracting features from original spectral space or transformed feature spaces (Cheriyadet and Bruce, 2003). The requisite to establish a proper protocol for classification is the choice of the wavelengths in the analysis. The benefits of wavelength selection are many, such as the stability of the model to the collinearity in multivariate spectra as well as the interpretability of the relationship between the sample composition and the model (Jiang et al., 2002).

The division of optical radiation into the following three bands has been recommended by the International Commission on Illumination (CIE) (Henderson & Roy, 2007):

- IR-A: 700 nm–1400 nm (0,7 µm – 1.4 µm)- Near IR
- IR-B: 1400 nm–3000 nm (1.4 µm – 3 µm)- Short range IR
- IR-C: 3000 nm–1 mm (3 µm – 1000 µm)- Mid and Long range IR

The aim of this study was to investigate the structural development of the biochar and the influence of the pyrolysis temperature and residence time on these changes. A comparative assessment was also conducted to ascertain these structural differences between a slow and a fast pyrolysis of biochar. The structure of the chars was characterized by using Helium pycnometer as well as samples visualization by hyper spectral imaging to study of the influence of porosity on the reflectance of the biochar samples.

5.3 Material and Methods

5.3.1 Production of biochar by slow and fast pyrolysis

The biochar from the Chinese Birchwood biomass samples were produced through slow and fast pyrolysis as described in the section 4.3.1 of Chapter 4 of this thesis.

5.3.2 Measurements of biochar porosity

The char particle density was measured using a helium pycnometer (Model 1305 Multivolume, Micromeritics Instrument Corporation, Norcross, GA) as shown in Figure 5.1. The samples were weighed prior to analysis. The solid volume of the samples excludes pores within the sample material. Using the pycnometry method, the sample was placed in the 5 cm^3 sample chamber. The samples were subjected to purging with helium gas by pressurizing and depressurizing prior to analysis in order to expel all the air and vapors trapped in the pores and crevices. Initially, all valves were closed while the system equilibrated to atmospheric pressure. The detailed methodology and procedure can be referred through the standard protocol (Operator's manual, Micromeritics, Corp.)

5.3.3 Definitions applied in this study

Density is a physical property of all matter; it is simply the unit quantity of mass per volume of the same quantity (kg. m^{-3}). The densities used in this study are defined as follows:

Bulk density: All pores, interparticle spaces, moisture, and air in the material are included in the measure of bulk density of a particle.

Particle density: The apparent density measures consist of the blind and non-interconnected pores of the material and exclude the open, interconnected, and interparticle pore spaces.

Porosity Analysis

Porosity is defined as the air or void volume per total volume of material and is a measure of the volume fraction of void space or air in a material matrix. It is commonly computed based on the measured bulk and apparent density as described above and calculations based on the following relationship:

$$\varepsilon = 1 - \frac{\rho_b}{\rho_p} \qquad 5.1$$

where $\mathcal{E}$ is the open pore porosity, ρ_b is the bulk density, and ρ_p is the particle density of the biochar sample (Kassama & Ngadi, 2005).

Figure 5.1 Helium Pycnometer (Model 1305 Multivolume, Micromeritics Instrument Corporation, Norcross, GA)

5.3.4 Hyper- spectral imaging of biochar

The hyperspectral imaging system used for the study consists of a line-scan spectrograph namely: HyperspecTM (Headwall Photonics Inc. USA) with the spectral range of 900 to 1700 nm (Figure 5.2). The HyperspecTM was connected to an InGaAs camera, mounted above a moving conveyor which was driven by a stepping motor with a user-defined speed (MDIP22314, Intelligent Motion System Inc., USA). A tungsten halogen lamp was used to illuminate the samples as they are moved across the field of view of the cameras.

Data Analysis

Classification of the spectral data was performed by mosaicking the images of the slow pyrolysis images together and conducting a multiple comparison analysis of the same regions of interests in those samples. This was done using the software, ENVI version 4.7 (ITT Visual Information Solutions, CO, USA). The same data analysis was conducted for the fast pyrolysis biochar.

The porosity results obtained through the pycnometer readings were analyzed using a multiple comparison test by ANOVA, and separated by a Duncan's Multiple Range test.

5.4. Results and Discussion

5.4.1 Porosity analysis

The porosity results obtained through the pycnometer readings were analyzed using a multiple comparison test by ANOVA and Duncan's multiple comparison analysis. The slow pyrolysis results (Figure 5.3) showed that the treatment of 350°C with a holding time of 20 min had the highest porosity while the least was seen at 300°C for 15 min. Moreover, there was no significant difference ($P \leq 0.05$) between the treatments at 300°C.

The treatments at 400°C for 10 min, 300 and 350°C both for 15 min holding time, were found to be not significantly different from each other ($P > 0.05$) for fast pyrolysis as seen in Figure 5.4. In this case, the highest porosity was found to be at 400°C for 20 min and the lowest was noted to be at 350°C with the holding time of 10 min.

Furthermore, a Fisher's multiple comparison tests was carried out for the slow as well as the fast pyrolysis treatments together (Figure 5.5). The results of this test showed that the same treatments at slow and fast heating rates were significantly different from each other ($P > 0.05$). It was seen from the results of the multiple comparison that the sample of the highest porosity in slow pyrolysis was 12.1% more porous than the highest of the fast pyrolysis.

The results of the pycnometry indicated that as the development of the reaction of pyrolysis takes place, the surface texture of the biochar become more irregular possibly due to the phenomena of devolatilization. This result in the shrinkage of the globular structures inside the biochar, which in turn, would increase the evaporation of the volatile matter trapped in the structure of biochar. With the increase in temperature and severity of pyrolysis, the surface pores of the char which are created have a rough surface and irregular outlet. This phenomenon becomes more prominent with increase in heating rate. These results were found to be in agreement with the findings of Hu et al., 2005. This could explain the reason for 350°C having higher porosity than 400°C for slow pyrolysis and vice versa in the case of fast pyrolysis.

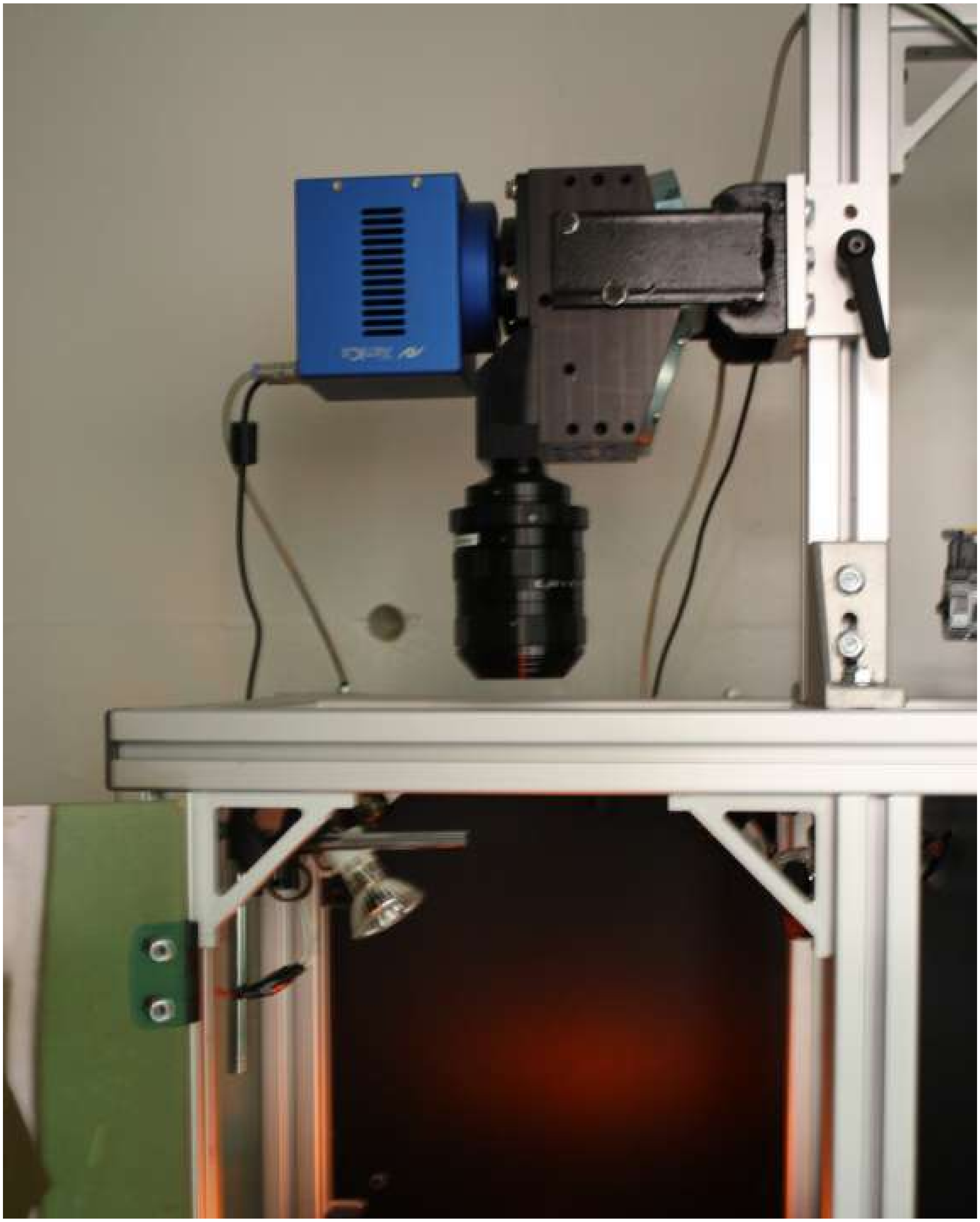

Figure 5.2 Hyperspectral imaging system (HyperspecTM) for the classification of biochar

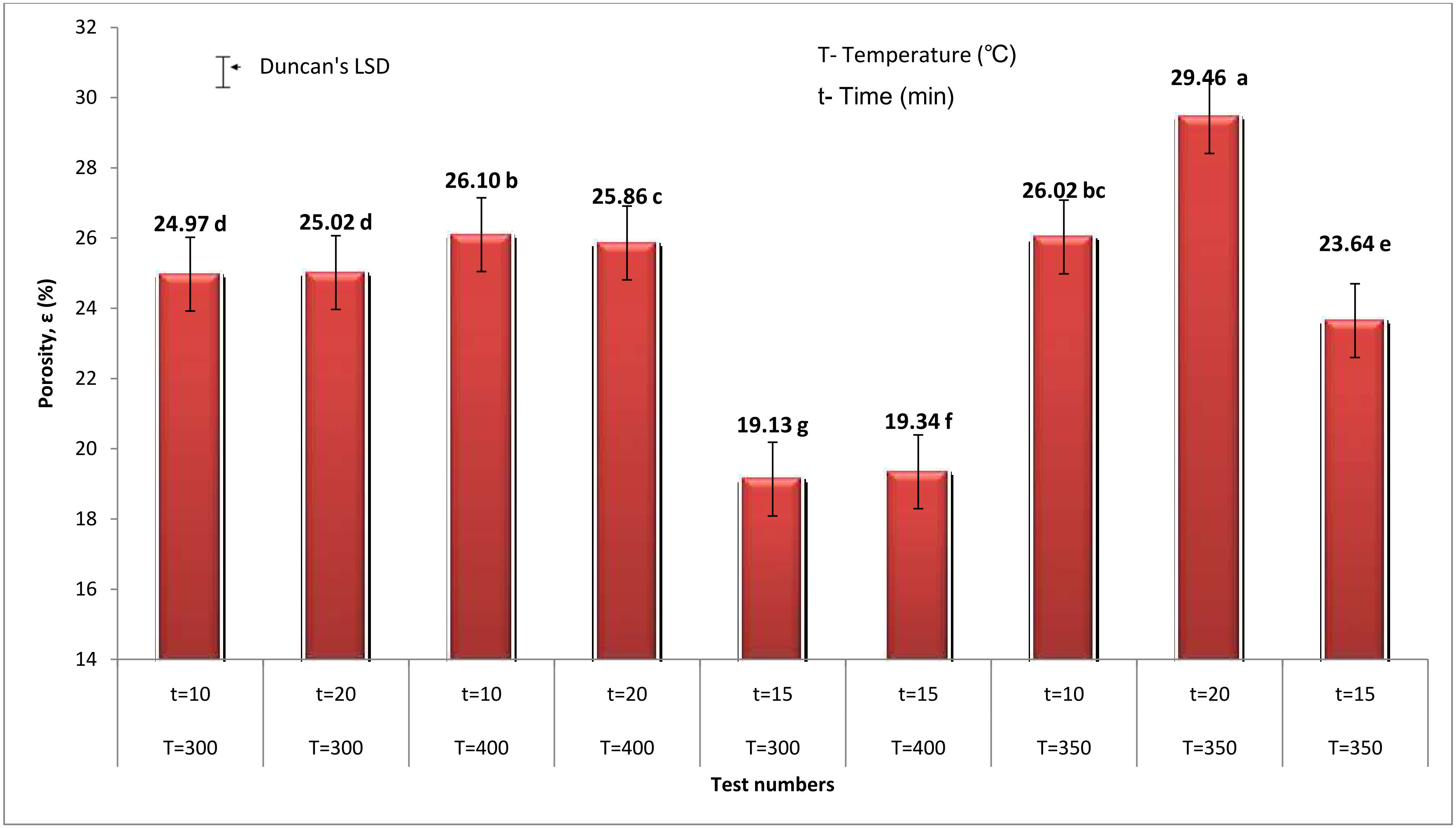

Figure 5.3 Duncan's multiple comparison test results for pycnometry for slow pyrolysis of biochar with statistical significance among the treatments. The means followed by the same letter are not significant at P<0.05 level.

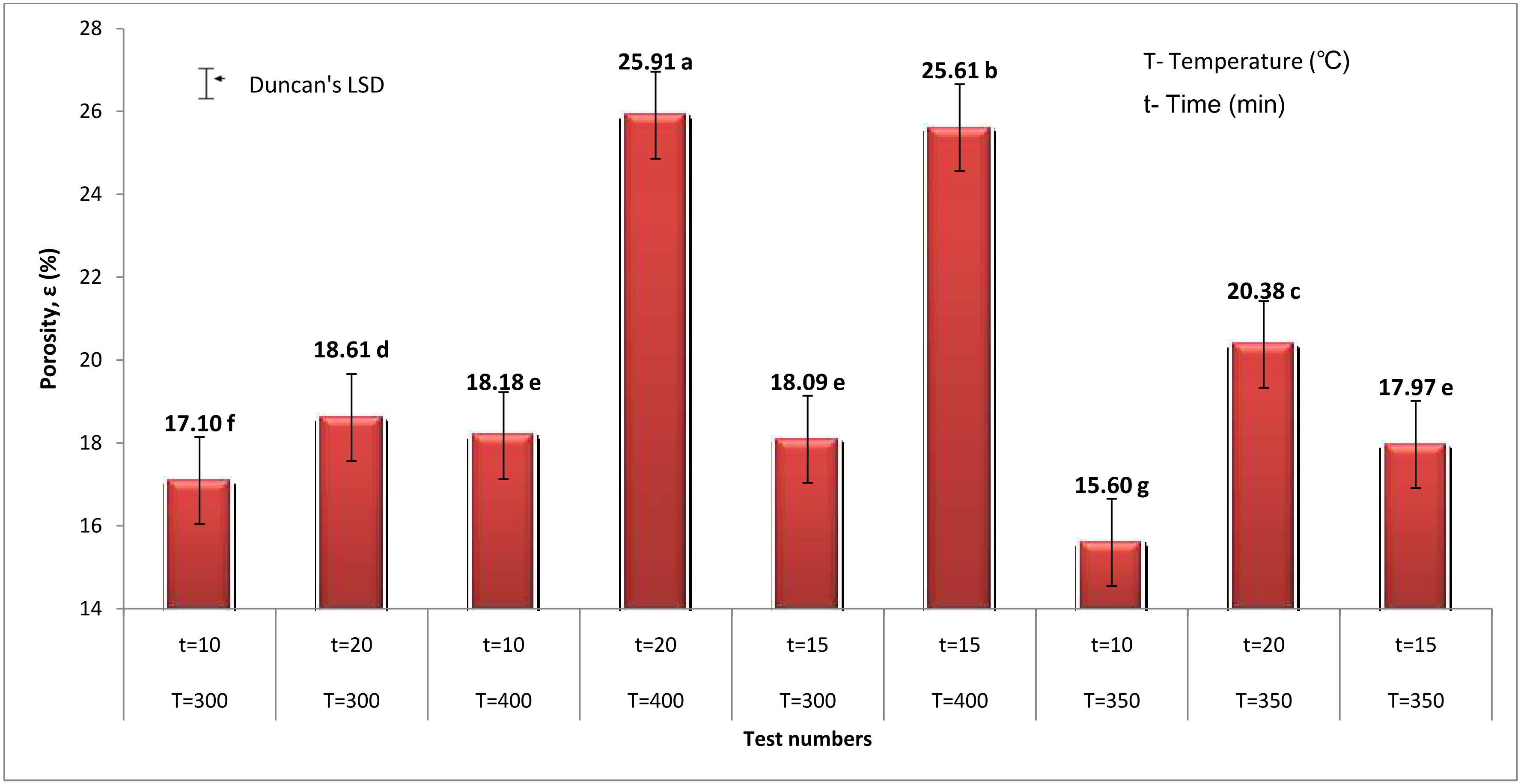

Figure 5.4 Duncan’s multiple comparison test results for pycnometry for fast pyrolysis of biochar with statistical significance among the treatments. The means followed by the same letter are not significant at P<0.05 level.

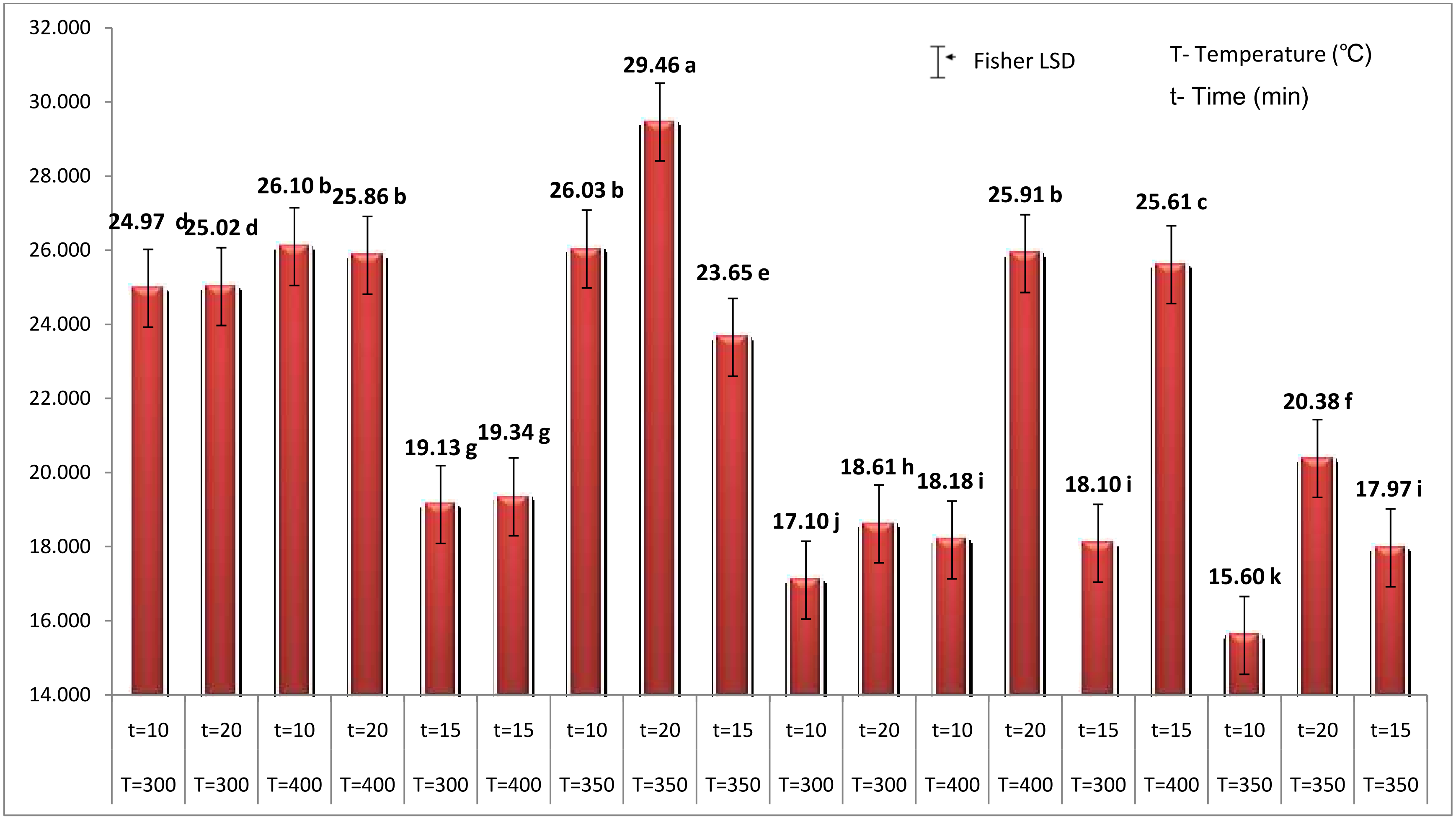

Figure 5.5 Fisher's multiple comparison results of porosity of slow and fast pyrolysis with statistical significance among the treatments. The means followed by the same letter are not significant at $P<0.05$ level.

It was seen in earlier studies that helium density values of the biomass/chars increases gradually in the whole process, especially at the end of the reaction. Villagens et al., (1998) reported this increase of helium density in their study and contributed it to the aromatization process. They also attributed the development of porosity in the chars on the amount of volatile matter removed at each temperature during pyrolysis and on the structural shrinkage of the residual carbon. Both factors were found to act contrarily on the pore structure of the chars with the latter effect being stronger at the initial stage of rapid pyrolysis.

Karaosmanogˇlu et al., (2000), also reported that increase in the heating rate resulted in some variations in the porosity characteristics of the biochar samples. The results of pore characteristics showed that average pore diameters and total pore volumes decreased with increasing heating rate while the specific surfaces increased. They attributed their findings to the removal of only a small fraction of volatile matter led to a considerable development of the char porosity. Hu et al., noted in their investigation on rice husk biochar, that there is an increase in open porosity during pyrolysis. Their study involved the analysis of pore size distribution with open porosity of char particles. Their results indicated that volume of the char particle is smaller than that of rice husk. This in turn indicated that the particle size shrinks remarkably at the beginning stage of the reaction.

5.3.2 Hyper-spectral imaging of biochar

The classification of the spectral data was performed by mosaicking the images of the pyrolysis images together as shown in Figures 5.6, 5.7, 5.8 and 5.9 for slow and fast pyrolysis respectively. A multiple comparison analysis of the same regions of interests in those samples was carried out. The wavelengths were chosen using a visual analysis procedure which was based on optimum reflectance of the samples. The procedure involved examination of the clarity of mosaic images made with all the treated biochar samples. Certain wavelengths had very high reflectance resulting in poor visibility of the biochar samples. Therefore, the wavelengths providing images with maximum clarity were chosen to be optimum for classification. The wavelengths which were found to be optimum for both slow and fast pyrolysis biochars were 947 nm and 1685 nm which fall in the Near-IR and Short IR wavelength ranges respectively as discussed earlier.

The multiple comparison of the biochar produced by slow pyrolysis was conducted through the Duncan's test (Figure 5.10 (a) & (b)) and the results indicated that treatment of 350°C for a holding time of 20 min had the lowest mean value of reflectance while the highest were for the 300°C biochar samples. The samples of the 350°C at 10 min and 15 min treatments were found to be not significantly different from each other.

The same data analysis was conducted for the fast pyrolysis of biochar. A similar trend to slow pyrolysis results was seen even in this case (Figure 5.11 (a) & (b)), where the lowest reflectance mean was observed for 400°C at 20 min holding time in both the chosen wavelengths. The highest mean of reflectance was found to be for the 300°C samples. In both the wavelengths, it was seen that all the three holding times of 10 min, 15 min and 20 min at 350°C did not have any significant difference.

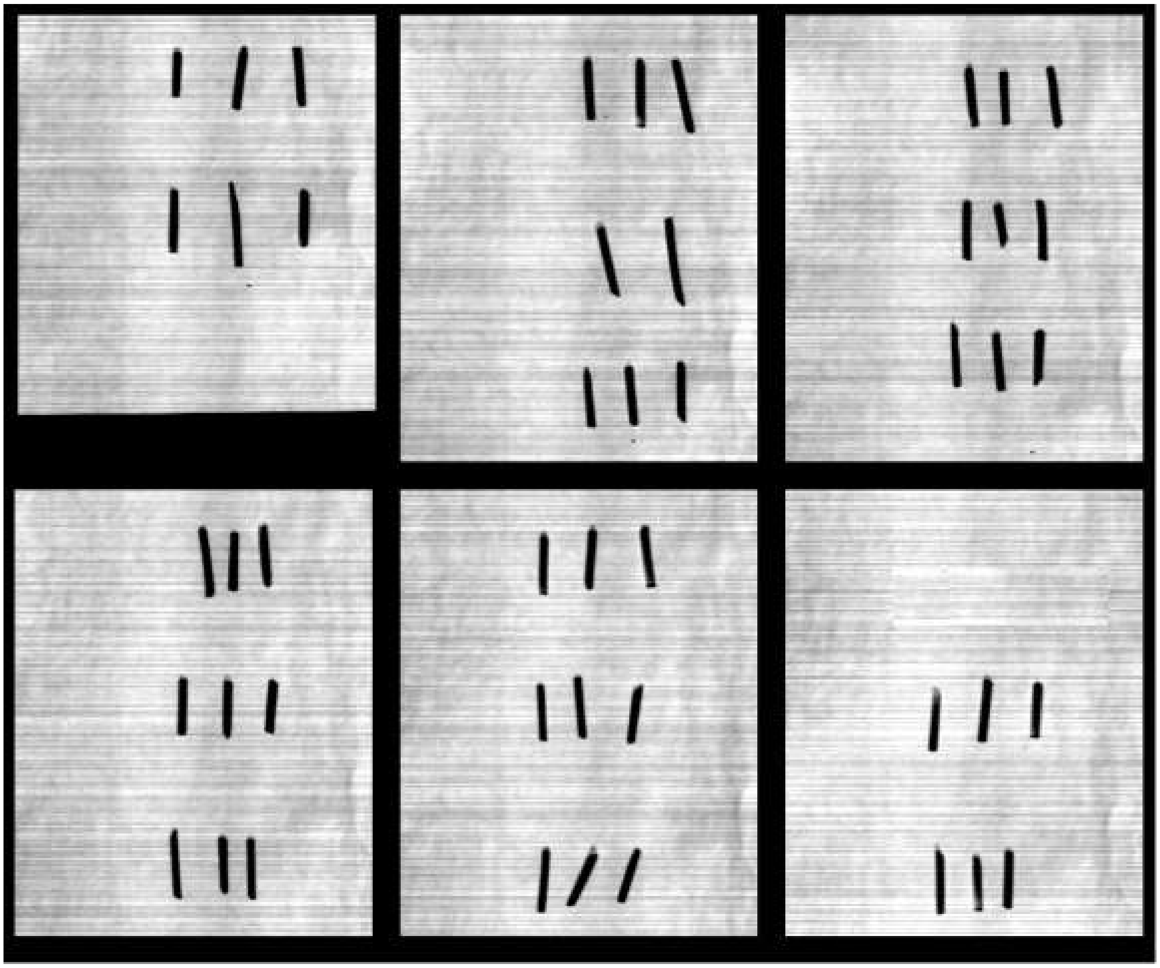

Figure 5.6. Images of slow pyrolysed birch wood samples at wavelength 947 nm

From left to right:

Details of the conditions of pyrolysis w.r.t corresponding position in figure 5.6.

Column 1	Column 2	Column 3
350°C, 15 min	350°C, 15 min	350°C, 15 min
350°C, 15 min	350°C, 15 min	350°C, 15 min
	350°C, 15 min	350°C, 15 min
350°C, 20 min	400°C, 10 min	
350°C, 10 min	400°C, 20 min	300°C, 20 min
400°C, 15 min	300°C, 15 min	300°C, 10 min

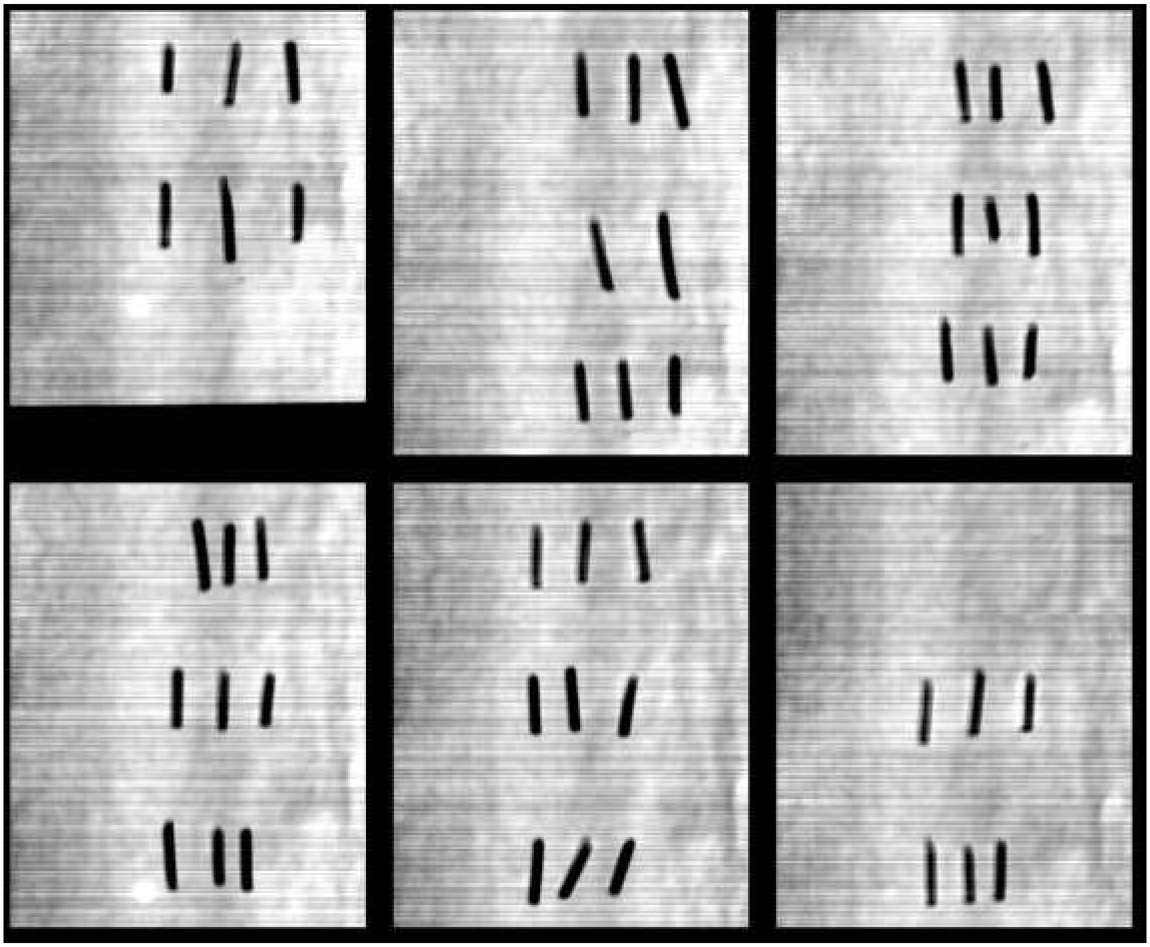

Figure 5.7. Images of fast pyrolysed birch wood samples at wavelength 1685 nm

Details of the conditions of pyrolysis w.r.t corresponding position in figure 5.7.

From left to right:

Column 1	Column 2	Column 3
350°C, 15 min	350°C, 15 min	350°C, 15 min
350°C, 15 min	350°C, 15 min	350°C, 15 min
	350°C, 15 min	350°C, 15 min
350°C, 20 min	400°C, 10 min	
350°C, 10 min	400°C, 20 min	300°C, 20 min
400°C, 15 min	300°C, 15 min	300°C, 10 min

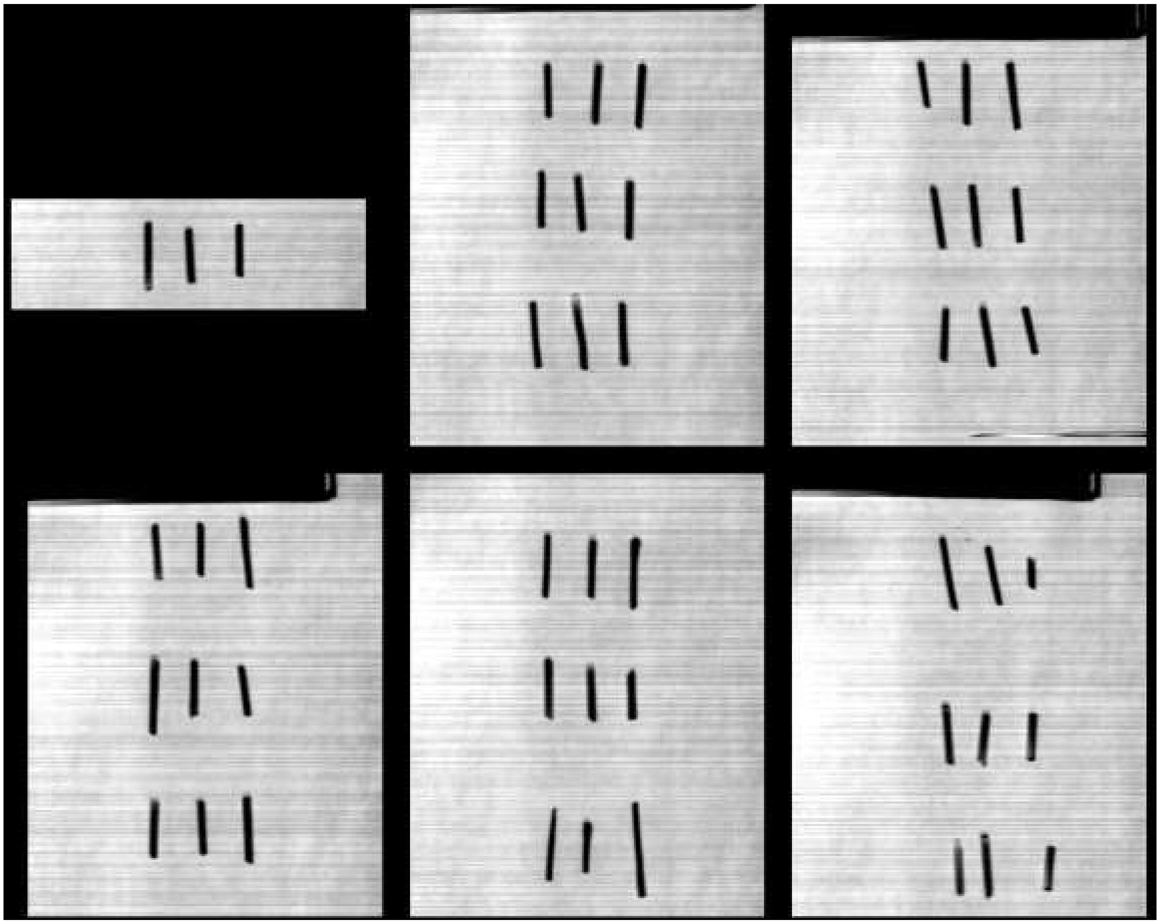

Figure 5.8. Images of fast pyrolysed birch wood samples at wavelength 947 nm

Details of the conditions of pyrolysis w.r.t corresponding position in figure 5.8.

From left to right:

Column 1	Column 2	Column 3
350°C, 15 min	350°C, 15 min	350°C, 15 min
350°C, 15 min	350°C, 15 min	350°C, 15 min
	350°C, 15 min	350°C, 15 min
350°C, 20 min	400°C, 15 min	400°C, 10 min
350°C, 10 min	300°C, 15 min	300°C, 20 min
	400°C, 20 min	300°C, 10 min

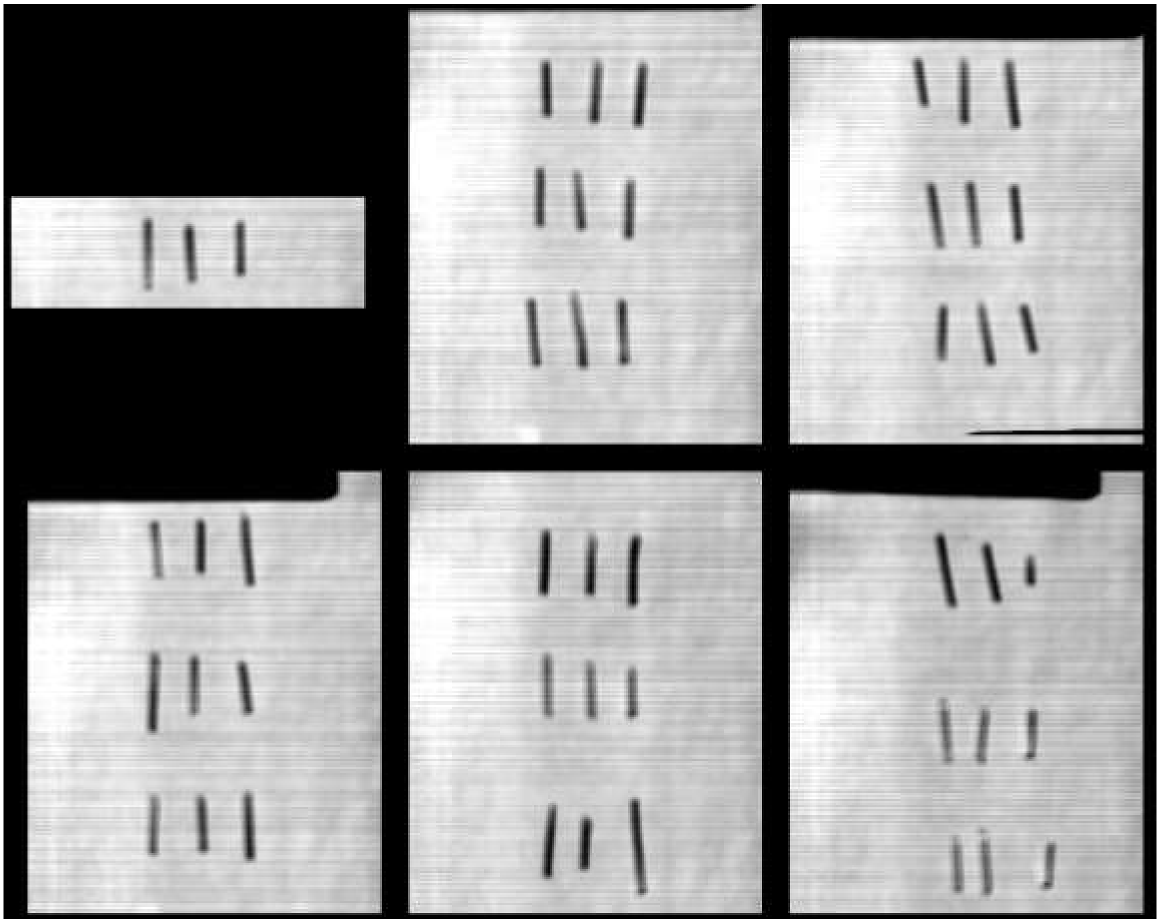

Figure 5.9. Images of fast pyrolysed birch wood samples at wavelength 1685 nm

Details of the conditions of pyrolysis w.r.t corresponding position in figure 5.9.

From left to right:

Column 1	Column 2	Column 3
350°C, 15 min	350°C, 15 min	350°C, 15 min
350°C, 15 min	350°C, 15 min	350°C, 15 min
	350°C, 15 min	350°C, 15 min
350°C, 20 min	400°C, 15 min	400°C, 10 min
350°C, 10 min	300°C, 15 min	300°C, 20 min
	400°C, 20 min	300°C, 10 min

These results were in good agreement with the pycnometry (porosity) data which showed that the biochar samples treated at 350°C for slow pyrolysis and 400°C for fast pyrolysis both for a holding time of 20 min had the highest porosity. It has been suggested by researchers Tang et al., (2005) that with the increase of coal reflectance, the porosity of formed char decreases. Also, a model was developed by researchers Sheng and Azevedo (2000) and Yu et al., (2004) which describe the bubble char evolution in the complex process of pyrolysis. The char structure evolution depends on the particle's volatile content, the bubble expansion rate and the viscosity of metaplast formed during the initial stages of the reaction. Hence it has been summarized that high volatile matter content coal does not necessarily generate highly porous char particles. These could be a few possible explanations of the observations in the reflectance of the biochar produced in this investigation as well.

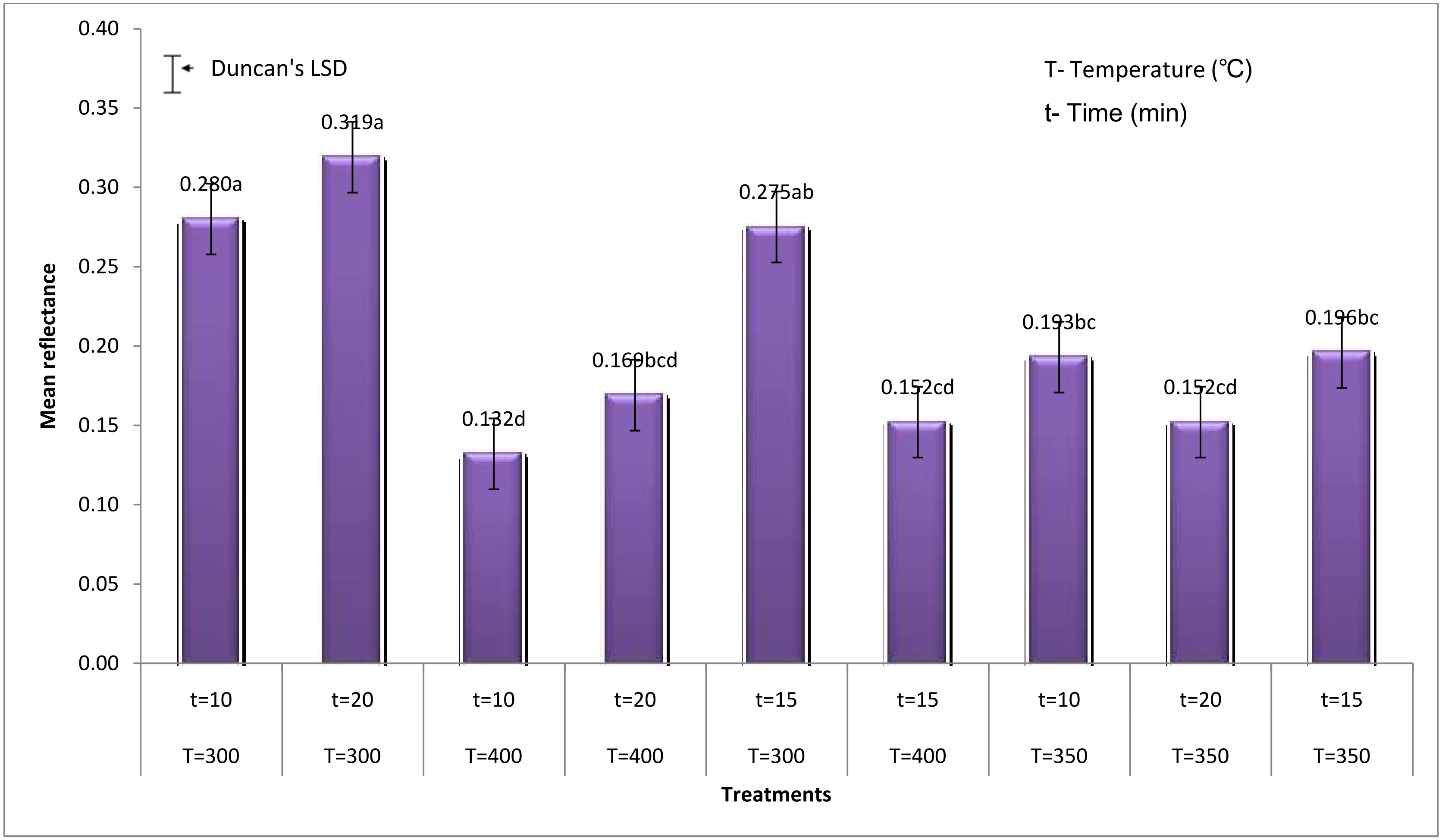

Figure 5.10. a) Multiple comparison test (Duncan's test) of reflectance means of slow pyrolysis samples at 947 nm with statistical significance among the treatments. The means followed by the same letter are not significant at $P<0.05$ level.

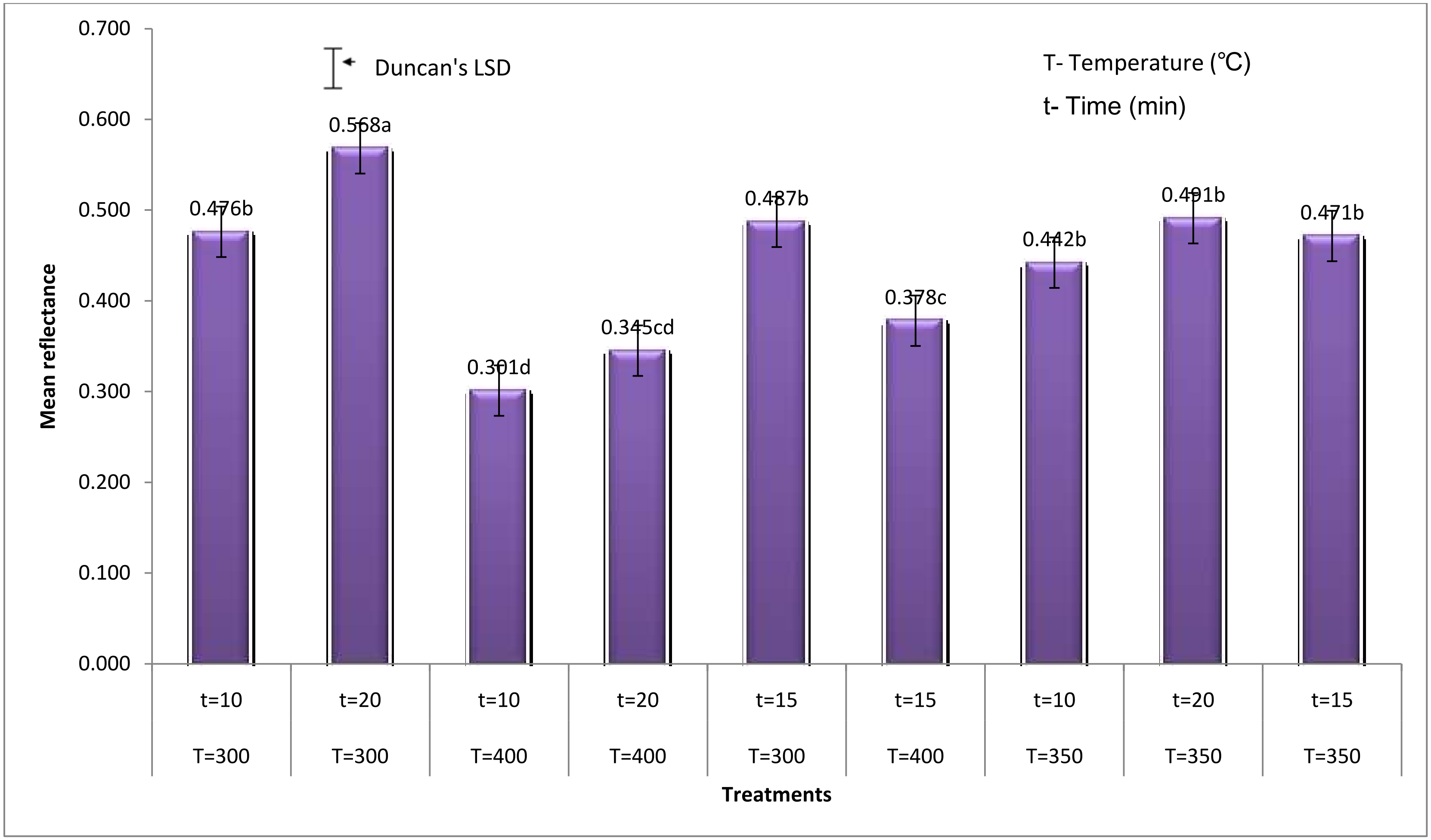

Figure 5.10. b) Multiple comparison test (Duncan's test) of reflectance means of slow pyrolysis samples at 1685 nm with statistical significance among the treatments. The means followed by the same letter are not significant at P<0.05 level.

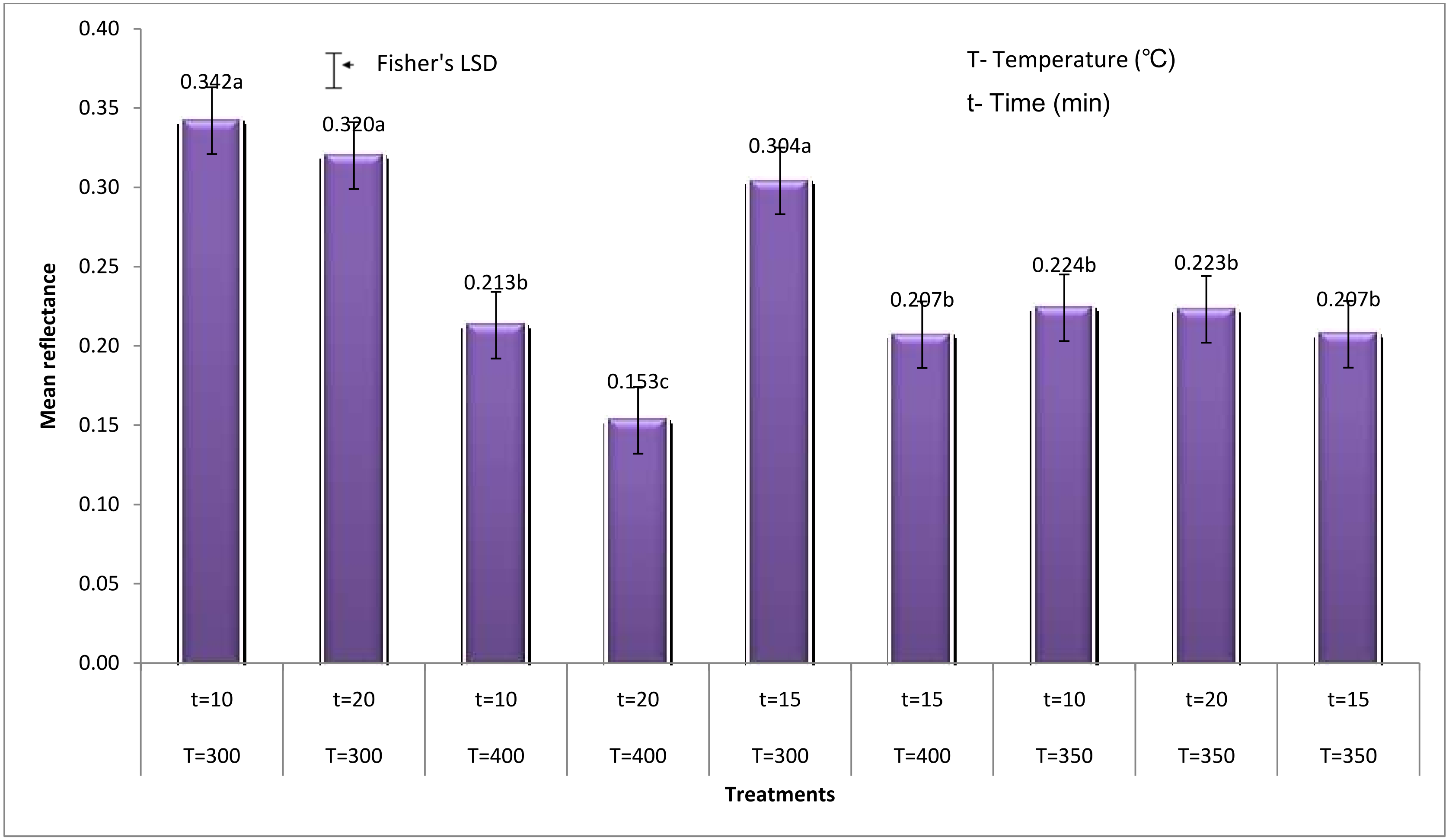

Figure 5.11. a) Multiple comparison test (Fisher's test) of reflectance means of fast pyrolysis samples at 947 nm with statistical significance among the treatments. The means followed by the same letter are not significant at $P<0.05$ level.

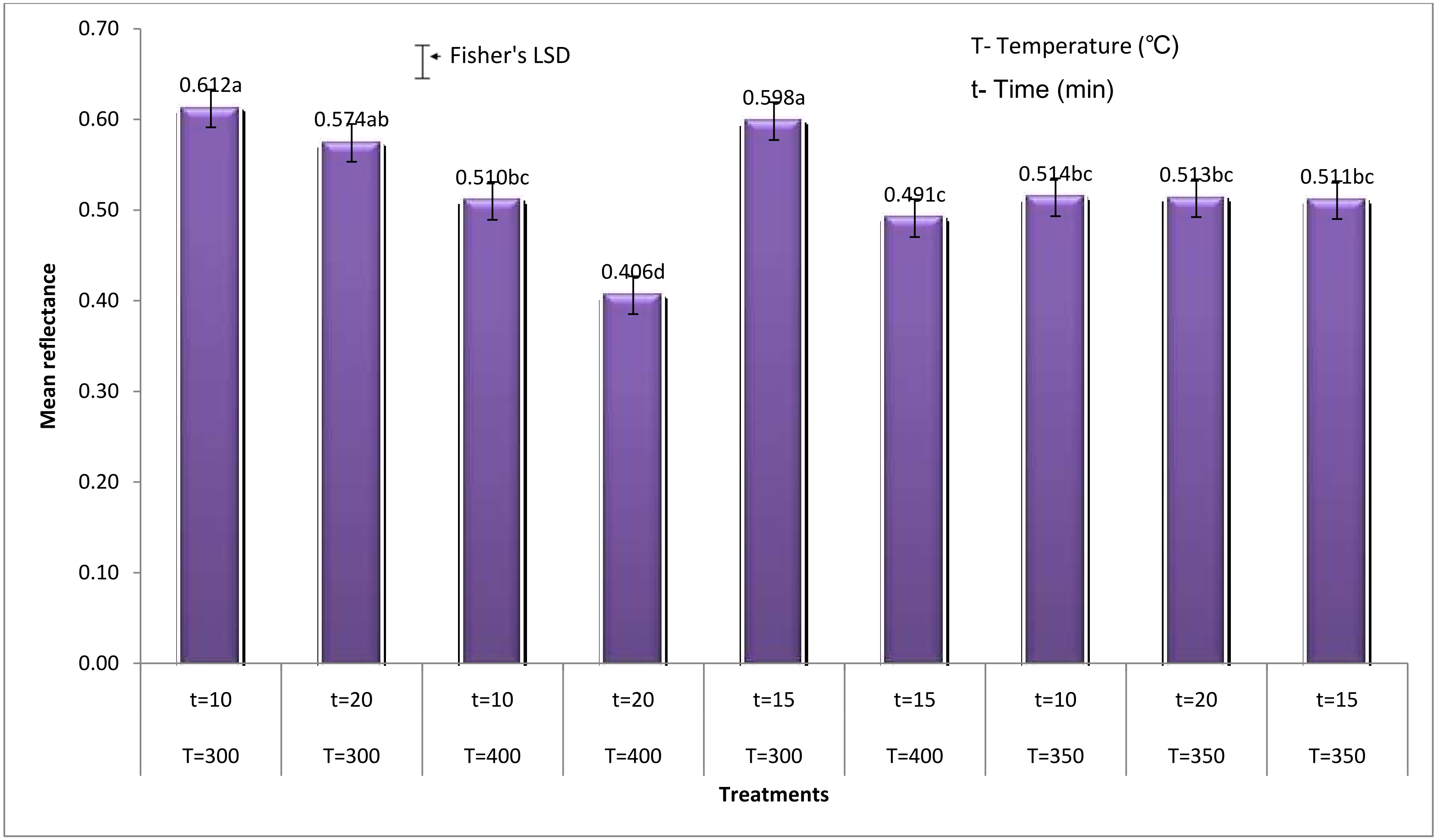

Figure 5.11. b) Multiple comparison test (Fisher's test) of reflectance means of fast pyrolysis samples at 1685 nm with statistical significance among the treatments. The means followed by the same letter are not significant at $P<0.05$ level.

5.5 Conclusions

The aim of this study was to investigate the structural development of the biochar and the influence of the pyrolysis temperature and residence time on these changes. A comparative assessment was also conducted to ascertain these structural differences between a slow and a fast pyrolysis biochar. The structure of the chars was characterized using Helium pycnometer as well as sample visualization by hyper spectral imaging to study of the influence of porosity on the reflectance of the biochar samples.

- From the pycnometry data gathered, it was observed that the treatments at 350°C and 400°C with the longest holding times for slow as well as fast pyrolysis had the highest porosity compared to the other biochar samples. It was also seen from the results of the multiple comparison that the sample of the highest porosity in slow pyrolysis was 12.1% more porous than the highest of the fast pyrolysis. These results support the theory that as the development of the reaction of pyrolysis takes place, the surface texture of the biochar becomes more irregular possibly due to the phenomena of devolatilization and increase in the evaporation of the volatile matter trapped in the structure of biochar. This phenomenon becomes more prominent with increase in heating rate.

- The hyperspectral imaging experiments showed that certain infra-red wavelengths had very high reflectance resulting in poor visibility of the biochar samples. Therefore, the wavelengths providing images with maximum clarity were chosen to be optimum for classification. The wavelengths which were found to be optimum for both slow and fast pyrolysis biochars were 947 nm and 1685 nm which fall in the Near-IR and

Short IR wavelength ranges respectively. Thus, the results of the hyperspectral imaging clearly supported the findings of the porosity evaluations which showed that the biochar sample treated at 350°C for slow pyrolysis and 400°C for fast pyrolysis both for a holding time of 20 min had the highest porosity and in turn showed the least reflectance mean values. These findings corroborate with previous studies which indicate that with the increase of coal reflectance, the porosity of formed char decreases. It has also been found that longer residence or holding times might also be a factor in giving a significantly higher reflectance than the other coke samples.

5.6 Acknowledgements

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Chapter 6

Summary and Conclusions

Biomass pyrolysis with biochar returned to soil is a possible strategy for climate change mitigation and reducing fossil fuel consumption. Pyrolysis with biochar applied to soils results in four coproducts: long-term carbon (C) sequestration from stable C in the biochar, renewable energy generation, biochar as a soil amendment, and biomass waste management.

Pyrolysis is the thermal decomposition of organic material in the absence of oxygen, and is also an initial stage in both combustion and gasification processes. Three coproducts are usually the resultant of both slow and fast pyrolysis of biomass: char, gas, and tarry oils, where the relative amounts and characteristics of each are controlled by the pyrolysis processing conditions such as temperature, residence time, pressure, and feedstock type. Slow pyrolysis is generally carried out at lower temperatures and longer residence times than fast pyrolysis, and the typical product yield is 35% char, 35% gas, and 30% liquid compared to 12%, 75% and 13% for fast pyrolysis.

Through the Finite element simulation and modelling study in this research, the kinetics of the different pyrolysis parameters as well as further attempts of optimizing char yield through variation of time, temperature and power densities of the reaction was investigated and highlighted. This numerical simulation model could be used to further look into designing a bioreactor for pyrolysis which aims at higher yields of biochar.

In this work, cylindrical biomass of 70mm length of birch wood were pyrolysed in a laboratory-scale thermal desorption unit and the influences of final pyrolysis temperature, heating rate, and pyrolysis atmosphere on the product yields were investigated. The wood sample was subjected to 10, 15 and 20 minutes of heating at 300°C, 350°C and 400°C as slow and fast pyrolysis. Results showed that at both the slow as well as fast pyrolysis, together with increasing pyrolysis temperature as well as time, the char yield increased. A single ratio, termed as the Efficiency of Charring (EoC), which would be able to quantify the efficiency of a particular pyrolysis technique to maximize the amount of char in the product was also identified through this study and optimized along with the yield. The resulting biochar was tested through proximate analysis, differential scanning calorimetry, pycnometry and hyper-spectral imaging to determine its quality.

The results obtained from Differential Scanning Calorimetry showed that fast pyrolysis biochar product had a higher exothermic energy than slow pyrolysis. The highest exothermic enthalpy was found to be at the pyrolysis temperature of 350°C for 10 min, with 66.31J/g for slow pyrolysis and 89.46 J/g for fast pyrolysis while the optimization results indicated that the maximum exothermic enthalpy for slow pyrolysis was at the pyrolysis temperature of 357°C for 13.5 min and for fast pyrolysis the same was optimized to be at 367°C for 10 min.

From the pycnometry data gathered, it was observed that the treatments at 350°C and 400°C with the longest holding times for slow as well as fast pyrolysis had the highest porosity compared to the other biochar samples.

Certain infra red wavelengths were observed to have very high reflectance resulting in poor visibility of the biochar samples. Therefore, the wavelengths providing images with maximum clarity were chosen to be optimum for classification. The wavelengths which were found to be optimum for both slow and fast pyrolysis biochars were 947 nm and 1685 nm which fall in the Near-IR and Short IR wavelength ranges respectively. The results of the hyperspectral imaging support the findings of the porosity evaluations which showed that the biochar sample treated at 350°C for slow pyrolysis and 400°C for fast pyrolysis both for a holding time of 20 min had the highest porosity and in turn showed the least reflectance mean values. These findings corroborate with previous studies which indicate that with the increase of coal reflectance, the porosity of formed char decreases. It has also been found that longer residence or holding times might also be a factor in giving a significantly higher reflectance than the other coke samples.

This study was able to confirm the viability of the continuous disposition of secondary products such as gases and liquids in the pyrolytic reaction as an effective means for maximization of biochar yield in both slow and fast pyrolysis systems.

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