Development and Optimization of Pyrolysis Biochar Production Systems towards Advanced Carbon Management

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ABSTRACT

About 10% of the 60 Petagram (Pg)-Carbon fixed annually through worldwide photosynthetic activity ends up in agricultural residues. Through a heat-induced chemical conversion process such residues can be converted to biochar, a form of carbon that can be employed as a soil amendment, thereby providing long-term storage of carbon in soil. In this application, it has the ability to both reduce GHG emissions and enhance soil structure, moisture and nutrient retention, thereby also addressing global food security issues by improving soil fertility and crop yields.

Dealing with several aspects of carbon management and resulting mitigation of GHG emissions, the current project sought to maximize biochar yield from microwave-assisted pyrolysis of maple (*Acer* L.) wood biomass. Microwave-assisted heating processes are known to be faster and more energy-efficient, yielding higher quality products than conventional methods. Volumetric, spectral and thermodynamic analysis of biochar developed through microwave-assisted pyrolysis showed it to exhibit greater porosity, lower reflectance and greater exothermic energy, and therefore greater overall quality than conventionally-produced biochar. This study also showed this microwave-assisted process to be capable of both producing high quality char and synthesize value-added carbon products. A three-dimensional finite element numerical model developed to optimize the primary parameters was instrumental in optimizing microwave pyrolytic process parameters so as to maximize biochar yields. The influence of selective heating phenomena on pyrolysis conditions was an important factor maximizing biochar yields arising from microwave-assisted pyrolysis of biomass. The application of a doping agent (*i.e.*, microwave receptor) such as char enhanced the severity of the pyrolysis process by better temperature distribution within the biomass

Based on numerical models and simulation data, the design of a microwave-assisted pyrolysis reactor affording optimal performance in terms of biochar yields was experimentally validated in a custom-built lab-scale unit. Biochar yield decreased with increasing pyrolysis temperature and time while

doping ratio had no significant effect on biochar yields. The maximum predicted yield occurred for a microwave-assisted pyrolysis process optimized at the pyrolysis temperature of 250°C, reaction time of 1 min and doping ratio of 16%.

The biochar resulting from microwave-assisted pyrolysis was characterized through various physical and chemical analyses: hyper-spectral imaging, pycnometry, proximate analyses, Scanning Electron Microscopy, Fourier Transform Infrared Radiation and Differential Scanning Calorimetry. The biochar's structural development was directly influenced by the pyrolysis conditions of temperature, residence time and doping ratio.

In light of GHG emission balances and the economic feasibility of biochar production, a life cycle analysis was important in estimating the benefits of biochar systems over a wide range of biomass, process and application scenarios. The life cycle analysis determined the sustainability — in terms of reducing the undesired effects of pyrolysis biochar systems — of the proposed process for different types of agricultural residues in Quebec, Canada. This would help farmers to assess the economic *vs.* environmental benefits of employing this technology to put the agricultural waste they generate to optimal use. The economic viability of the pyrolysis-biochar system was found to be largely dependent on the costs of feedstock production, pyrolysis, and the value of carbon offsets. Therefore, the conclusions drawn from such a life cycle analysis would represent a useful tool in assessing the potential of biochar systems worldwide.

RÉSUMÉ

Des 60 Petagram (Pg)-C par an fixés à l'échelle mondiale par l'activité photosynthétique, environ 10% demeurent dans les résidus agricoles. Un processus de transformation thermochimique permet de transformer ces résidus en biochar, une forme de carbone (C) dont l'utilisation comme amendement du sol, permet un entreposage du C à long terme, une réduction correspondante des émissions de gaz à effet de serre, ainsi qu'une amélioration de la structure, teneur en eau et rétention d'éléments nutritifs du sol. En améliorant la fertilité des sols et le rendement des cultures, ce procédé s'adresse donc aux enjeux de la sécurité alimentaire mondiale

Le présent projet chercha à maximiser le rendement en biochar advenant d'une pyrolyse de biomasse de bois d'érable (*Acer* L.). Offrant des produits d'une qualité supérieur à celle des procédés conventionnels, le chauffage assisté par micro-ondes est parmi les procédés les plus rapides et écoénergétiques. Les analyses volumétriques, spectrales et thermodynamiques du biochar provenant d'une pyrolyse assistée par micro-ondes (PAM) démontrèrent sa plus grande porosité, son coefficient de réflexion moins élevé et sa plus grande énergie exothermique, et donc sa plus grande qualité globale par rapport au biochar d'origine conventionnelle. La PAM a produit un biochar de haute qualité tout en synthétisant des composés de carbone à valeur ajoutée. Une modélisation tridimensionnelle par éléments finis visant à optimiser les paramètres du procédé de PAM s'avéra clé à l'optimisation du rendement en biochar. L'influence de phénomènes d'échauffement sélectif sur les conditions de pyrolyse s'avéra un facteur important dans l'optimisation du rendement en biochar produit par PAM de biomasse. L'ajout d'un agent dopant (*i.e.*, matériel récepteur des micro-ondes) tel que du biochar, a réduit la sévérité du procédé de PAM en permettant une meilleure distribution de la température à travers la biomasse.

Grâce à des modélisations numériques et des données de simulation, la conception d'un réacteur pyrolytique assisté par micro-ondes, permettant d'obtenir une performance optimale quant au rendement de biochar, fut validée expérimentalement dans un appareil bâti sur mesure à l'échelle du laboratoire.

Face à une augmentation de la température de pyrolyse, le rendement en biochar diminua, mais la fraction d'agent de dopage n'eut aucun effet significatif sur celui-ci. Le rendement maximum prévu pour le procédé de PAM fut obtenu avec une température de pyrolyse de 250°C, un temps de réaction de 1 min, et une fraction d'agent de dopage de 16%.

Diverses analyses physiques et chimiques de biochar provenant d'une PAM servirent à sa caractérisation: imagerie hyperspectrale, pycnométrie, analyses immédiates, microscopie à balayage électronique, spectrométrie infrarouge à transformée de Fourier, analyse calorimétrique différentielle. La structure du biochar fut influencée par les conditions de pyrolyse (e.g., température, temps de séjour, coefficient de dopage).

Une analyse du cycle de vie s'avéra importante à l'évaluation des avantages des systèmes de biochar pour une variété de biomasses, procédés de pyrolyse et taux d'amendement. Cette analyse évalua, pour différents résidus agricoles du Québec, le caractère durable du procédé proposé, particulièrement vis-à-vis la réduction des effets néfastes de la production de biochar par pyrolyse. Cette analyse permettra aux agriculteurs d'évaluer les avantages économiques *vs.* environnementaux de cette technologie pour la mise en valeur optimale des résidus agricoles. La viabilité économique du système de production de biochar par PAM se trouva principalement liée aux coûts de production des matières premières, de pyrolyse, et de la valeur des crédits d'émission de carbone. Les conclusions d'une telle analyse représentent donc un outil d'une grande valeur dans l'évaluation du potentiel du biochar à l'échelle mondiale.

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NOMENCLATURE

A	Cross sectional area of the waveguide (m^2)
AC	Alternating current
ANOVA	Analysis of variance
ASTM	American Society for Testing and Materials
Ax	Arrhenius constant (s^{-1})
CEC	Cation exchange capacity
CO_2e	Carbon dioxide equivalent
Cp	Specific heat capacity of the material (kJ kg^{-1} °K^{-1})
D	Doping ratio (%)
DC	Direct current
E	Total Electric field intensity (V m^{-1})
Ea	Activation energy of reaction (kJ mol^{-1})
Ex	Electric field intensity x component (V m^{-1})
Ey	Electric field intensity y component (V m^{-1})
Ez	Electric field intensity z component (V m^{-1})
FEM	Finite element method
FTIR	Fourier transform infrared spectroscopy
Gg	10^9 gram (g)
GHG	Greenhouse gas/es
H	Total Magnetic Field Intensity (A m^{-1})
HU	Haugh Unit
Hx	Magnetic field intensity x component (A m^{-1})
Hy	Magnetic field intensity y component (A m^{-1})
Hz	Magnetic field intensity x component (A m^{-1})
k	Kinetic reaction constant (s^{-1})
K	Thermal conductivity (W m^{-1} °K^{-1})
LC	Inductive capacitive circuits
LCA	Life cycle analysis

MA	Microwave assisted
MAP	Microwave assisted pyrolysis
MAXR	Maximum R^2
MLR	Multiple Linear Regressions
MM	Mobile matter (%)
MW	Microwave
P	Pressure (Pa)
p	Probability of obtaining a test statistic
Pav	Time average power dissipated (W)
PCA	Principle component analysis
Pg	10^{15} gram (g)
PLS	Partial Least Squares
Q	Power Source Term (W m^{-3})
R^2	Coefficient of determination
RF	Radio frequency
RM	Residual matter (%)
ROI	Region of interest
SEM	Scanning electron microscopy
T	Temperature (°C)
t	Time (min)
Tg	10^{12} gram (g)
V	Volume (m^3)
Vc	Volume of the empty sample chamber
Vis/NIR	Visible/ Near Infrared
Vr	Volume of the reference
Vs	Sample volume
ΔT	Change in temperature (°C)
ε	Open pore porosity
ε'	Dielectric constant

ε''	Dielectric loss factor
ε_0	Permittivity of free space
ε_{eff}''	Effective loss factor
ε_r	Relative permittivity
λ	Wavelength (m)
μ_r	Relative permeability
ρ	Density of the material (kg m^{-3})
ρ	Bulk density (kg m^{-3})
ρ	Particle density (kg m^{-3})
ω	Phase angle (rad/s)

CONTRIBUTION OF AUTHORS

The thesis was completed by principal author Baishali Dutta under the supervision of Dr. G.S. Vijaya Raghavan and all the experimental work was conducted in the Department of Bioresource Engineering, McGill University, Ste-Anne-de-Bellevue, Québec, Canada.

The first manuscript in the thesis, titled “Finite Element Modelling of Microwave Pyrolysis of Biomass” has three authors, Baishali Dutta, Satyanarayan Dev and Vijaya Raghavan and the paper is published in the *Proceedings of the 7th International Conference on Heat Transfer, Fluid Mechanics and Thermodynamics (HEFAT)*, 2010.

The authors of second manuscript titled “Finite Element Modeling of Selective Heating in Microwave Pyrolysis of Lignocellulosic Biomass” are Baishali Dutta, Satyanarayan Dev, Yvan Gariepy and Vijaya Raghavan and the paper has been published in *Progress in Electromagnetic Research (PIER B)*, 2013.

The third manuscript titled “A Study of Effects of Process Parameters and Selective Heating on Microwave Pyrolysis of Lignocellulosic Biomass” is authored by Baishali Dutta, Yvan Gariepy and Vijaya Raghavan.

The contributors of the fourth manuscript titled “Surface Characterization and Classification of Microwave pyrolysed Maplewood Biochar” are Baishali Dutta, Vijaya Raghavan, Michael Ngadi, and Valerie Orsat.

The authors of the fifth manuscript titled “Life Cycle Assessment of Environmental and Economic Balance of Biochar Systems in Quebec” are Baishali Dutta and Vijaya Raghavan. It is accepted for publication in *International Journal of Energy and Environmental Engineering*, 2014.

The supporting manuscript presented in Appendix 2 titled “Socio-economic Assessment of Implementation of Policy Options for Biochar Systems as a Mitigation Strategy for Greenhouse Gas Emissions- India as a Case Study” is authored by Baishali Dutta and G. S. Vijaya Raghavan. It was presented at the Fourth International Conference on Climate Change: Impacts and Responses and consequently published in The International Journal of Climate Change: Impacts and Responses, 4(1):101-114, 2012.

Dr. Vijaya Raghavan is the thesis supervisor and provided scientific advice, technical supervision and guidance. He was also directly associated with editing and reviewing of the manuscripts.

Dr. Satyanarayan Dev contributed with technical information and assistance pertaining to the finite element modeling and simulation studies.

Mr. Yvan Gariepy provided technical advice related to the design and fabrication of the microwave assisted pyrolysis reactor and for dielectric properties measurement studies.

Dr. Michael Ngadi provided laboratory equipment and technical advice on pycnometry and hyper spectral imaging studies and Dr. Valerie Orsat contributed with technical information and assistance related to Fourier Transform Infrared Radiation studies.

Chapter 1

Introduction

1.1. General introduction

Combating global climate change and meeting the ever rising energy demands of the world are the twin concerns which have occupied researchers worldwide. In 2010, speaking at the Technology, Entertainment, Design (TED) conference, Mr. Bill Gates, the chairman of Microsoft Corporation, USA, mentioned that the annual carbon dioxide emissions every year has reached over 26 billion tons. “For each American it's about 20 tons; for people in poor countries it's less than one ton. It's an average of about 5 tons for everyone on the planet” (Gates, 2010). Adding to this dilemma is the ever increasing population which has created enormous stress on our fragile planet.

“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).

Globally about 60 billion tonnes of carbon dioxide (CO_2) is taken up annually by photosynthesis and amongst these; around 10% becomes available as agricultural residue. 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 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. It is predicted that this simplistic, yet powerful, approach can be used to store up to 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).

Canada’s total GHG emissions for 2008 were estimated at 734 Mt of CO_2 (Environment Canada, 2009). Out of this, the contribution of the agricultural sector was nearly 10%. Also this leads to generation of about 300 Mt of agricultural waste (AAFC, 2010; StatCan, 2009). Assuming 50% recovery of carbon from this biomass, we can sequester nearly 150 Mt of carbon dioxide from the atmosphere, in the form of biochar, which is about 20% of Canada’s Green House Gas emissions.

The production of biochar has come under a lot of focus in recent years due to its many advantages in terms of its use as an energy source (Wu and Abdullah, 2009), as a fertilizer when mixed with soil (Lehmann, 2003), as a means for reducing greenhouse gases in the atmosphere by the sequestration of carbon in soil (Joseph et al., 2009). As an alternative, biochar can increase food security by reducing the amount of food crops used for biofuel production (Kleiner, 2009).

One of the important thermochemical conversion techniques of biomass is known as pyrolysis. It is the thermal decomposition of biomass in reduced concentrations 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 on the process variables. The process of pyrolysis produces solids (charcoal), liquids (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 (IBI, 2011).

The quantitative nature of the three main 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 like wood, the yield depends on the wood structure and particle size. In a conventional pyrolysis process, a classical hardwood (such as Aspen, Birch etc.) 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 (Sellaperumal, 2012, Masek, 2009; Di Blasi et al., 2001; Wang et al., 2009).

Pyrolysis processes are classified as conventional or fast pyrolysis, depending on the operating conditions used. Conventional pyrolysis may also be termed slow pyrolysis. The terms “slow pyrolysis” and “fast pyrolysis” are arbitrarily used with no particular definition with reference tied to the holding period or the rate of heating (Mohan et al., 2006). In fast pyrolysis systems, dry biomass is heated very rapidly (up to 1000°C/min) in the absence of oxygen and the products quickly removed and quenched to maximize production of bio-oils (Brewer et al., 2009). 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). There are number of methods employed to improve the yields of biochar with factors like low pyrolysis temperature, high process pressure, long vapour residence time, extended vapour/solid contact, low heating rate, large biomass particle size, optimized heat integration (Masek, 2009).

Conventional methods of supplying thermal energy in the case of lignocellulosic biomass result in poor heating characteristics in the core of the biomass. The temperature profile depends on the volume and bulk density of the biomass processed per batch (Willner et al, 2005). One of the methods proven to have measured up in reaching good efficiency standards is the use of microwave (MW) or microwave assisted pyrolysis (MAP) methods to form biochar, bio- oil and fuel gases. The advantage of microwave pyrolysis over conventional process is the nature of fast internal spatially uniform heating by microwave radiation. Biomass fast pyrolysis has been achieved using microwave radiation (Lei, et al., 2009). Another advantage of microwave pyrolysis for lignocellulosic biomass is that a larger sized biomass can be used for production of biochar in a shorter period of time and thus it is possible to reduce processing costs for pretreatment steps, such as pulverization.

1.2 Problem Statement

Plants store enormous atmospheric CO_2 by photosynthesis. The heating of plant-derived material in the absence of oxygen known as biomass pyrolysis produces a charred by-product in order to capture greenhouse gases. This has been termed as "Biochar". Biochar is a highly stable form of carbon and as such has the potential to form an effective carbon sink, therefore sequestering atmospheric CO_2 (Sohi et al., 2009, CSIRO).

There are many perceived advantages of microwave heating for pyrolysis processes, including energy efficiency, rapid and controlled heating, and the ability to operate from an electrical source. There are two main fundamental features of microwave heating which puts this technology at a substantial advantage over conventional heating: (1) Volumetric heating, in which, each individual molecule is heated directly and instantaneously through interactions with the electric field, and (2) Selective heating, in which, different substances in a heterogeneous material can be heated to variable extents depending on their dielectric properties (Miura et al., 2006).

Despite this, very little research has been carried out on the microwave pyrolysis of biomass/wood. Most research with microwave irradiation for pyrolysis have used commercial multimode cavities and doping agents to improve the microwave absorption. But there is little understanding of the fundamental mechanisms and little indication of why microwave heating offers advantages over conventional heating (Robinson et al., 2010, Miura et al., 2006). Also, there have been very few studies centered on the most important parameters of physicochemical characteristics of the biomass, which determine the progress of the pyrolysis process in a microwave environment (Budarin et al., 2009, Ciacci et al., 2010, and Miura et al., 2006).

In addition to this, the combination of electromagnetic heating, combustion, and heat and mass transfer phenomena during microwave pyrolysis is very difficult to comprehend. Hence the determination of the kinetics of the pyrolysis of a biomass inside a microwave cavity becomes a very difficult goal to achieve which requires extensive modelling and predictive tools (Miura et al., 2006).

1.3 Hypothesis

The advantage of microwave pyrolysis over conventional process is the nature of fast internal heating by microwave radiation. Spatially uniform heating can be brought about by microwave energy deposition in the dielectric loss mode of heating. The volumetric heating nature of microwave pyrolysis not only overcomes the disadvantages of conventional pyrolysis methods of long heating periods, but also improves the quality of final pyrolysed products. It is also advantageous by saving processing time and energy significantly. In this respect, the efficiency of microwave pyrolysis depends to a great extent on the nature of the biomass. With the additional limiting conditions of dissimilar dielectric behaviour of materials, not all materials are similarly heated by microwaves (Fernandez et al., 2011). Also, microwave technology has been mainly applied to fast or flash pyrolysis, which is more suitable for producing higher gas yield with more syngas content (Domínguez et al., 2007).

Particle size and the original characteristics of feedstock are some of the primary factors affecting the product formation and components other than reaction temperature, reaction time, and microwave power in MW pyrolysis processes (Fernández et al., 2011). Due to the inherent property of “selective heating” in microwaves, the microwaves are absorbed by the component that has high dielectric loss while passing through the low loss material with little drop in energy. In some processes and products, this results into the heating of a specific component whilst leaving the surrounding material relatively unaffected; thereby creating hot spots within the material (Fernández et al., 2011).

Although in the recent past, several microwave pyrolysis investigations have been carried out, the data on the particle size effect and pyrolysis process optimization has not been reported. Research undertaken by Lei et al., (2009) is one of the few studies which focussed on the effects of particle size on the efficacy of the microwave pyrolysis. The objective of this study was to investigate microwave pyrolysis of corn stover with variable particle sizes and determine the effects of pyrolytic conditions on the yields of bio-oil, syngas, and biochar. Although their study showed that the effect of particle size was insignificant on the pyrolysis of corn stover, it is essential to investigate further into the effects of the same for other lignocellulosic biomass as well.

Hence it becomes essential for the advancement of the technology of microwave pyrolysis processes to understand the influence of the geometry and particle density on the chemical kinetics and heat transfer during microwave assisted pyrolysis. An important aspect of this is to also evaluate the full potential of GHG abatement using biochar in different scenarios. A life cycle assessment methodology could be employed to gain a comprehensive understanding of the potential of such systems.

1.4. Objectives

1.4.1 Primary Objectives

1. To identify optimal biomass characteristics such as density, geometry and particle size as well as process parameters such as power density, reaction time and temperature at 2.45 GHz through predictive models.

2. To design and develop a MW pyrolysis reactor with the optimized parameters for the maximization of biochar from high density biomass such as lignocellulosics and other agricultural residues.

3. To carry out comparative analyses of biochar characteristics produced through microwave and conventional pyrolysis for the quality, functionality and structural integrity of the char.

4. To develop a life cycle analysis (LCA) to estimate the energy and climate change impacts and the economics of biochar systems. This LCA would determine the sustainability for different types of agricultural residues to reduce the costs associated with the conversion of biomass into biochar systems. This would help farmers to assess the economic versus the environmental benefits of employing this technology for optimal use of the agricultural waste generated.

1.4.2 Short term Objectives

1. To predict and visualize the influence of biomass chemical and physical characteristics on the microwave assisted pyrolysis technique. This would be conducted through the development of appropriate mathematical models and simulation.

2. To evaluate the effects of physical characteristics such as particle bulk density and geometry of the biomass on the progress of microwave pyrolysis.

3. To optimize pyrolysis parameters such as holding time, temperature and power density of the microwave assisted pyrolysis for the maximization of biochar production.

4. To validate the models developed in the previous steps and carry out Microwave Pyrolysis for the maximization of biochar yields from high density biomass such as lignocellulosics.

5. To assess, characterize and compare the biochar produced using microwave pyrolysis and conventional pyrolysis through various physical and chemical investigations such as Hyper-spectral imaging, Pycnometry, Proximate analyses, Scanning Electron Microscopy, Fourier Transform Infrared Radiation spectroscopy and Differential Scanning Calorimetry.

6. To highlight the importance of the methodology of a life cycle analysis to estimate the full life-cycle energy, GHG emissions balance, and economic feasibility of biochar. The purpose of conducting a life cycle analysis is to evaluate the potential of feedstock which could provide insight into the use of biomass “waste” resources rather than bioenergy crops and the resulting energy and climate change impacts and economic costs of each scenario.

Chapter 2

Review of Literature

The past century has seen an average surface temperature increase of 1.3 degrees Fahrenheit on the Earth. However, it has been projected that this temperature increase would be raised by an additional 3.2 to 7.2 degrees over the 21st century by the Intergovernmental Panel on Climate Change (IPCC, 2007). These seemingly slight changes in temperature could have profound implications for farmers. This temperature increase has been attributed to a rise in carbon dioxide and other greenhouse gases released from the burning of fossil fuels, deforestation, agriculture and other industrial processes (Schahczenski and Hill, 2009).

2.1 The Greenhouse Effect

Scientists refer to this phenomenon as the enhanced greenhouse effect. An increase in average temperature on the surface of the Earth could have significant impacts on agriculture such as lengthening the growing season in regions with relatively cool spring and fall seasons; adversely affecting crops in regions where summer heat already limits production. The consequences of this rise in temperatures could increase soil evaporation rates; and increase the chances of severe droughts. These are attributed to the changes in hydrological cycle and its effect in different locations.

Carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) are the primary greenhouse gases associated with agriculture. Nitrous oxide and methane have been known to have longer durations in the atmosphere and absorb more long-wave radiation and thus they can have significant effects on climate change, although carbon dioxide is the most prevalent greenhouse gas in the atmosphere. Figure 2.1 describes the contribution of the three gases as well as of different sectors towards greenhouse gas emissions.

Innovative farming practices such as conservation tillage, organic production, improved cropping systems, land restoration, land use change and irrigation and water management, are ways that farmers can address climate change. Good management practices have multiple benefits that may also enhance profitability, improve farm energy efficiency and boost air and soil quality.

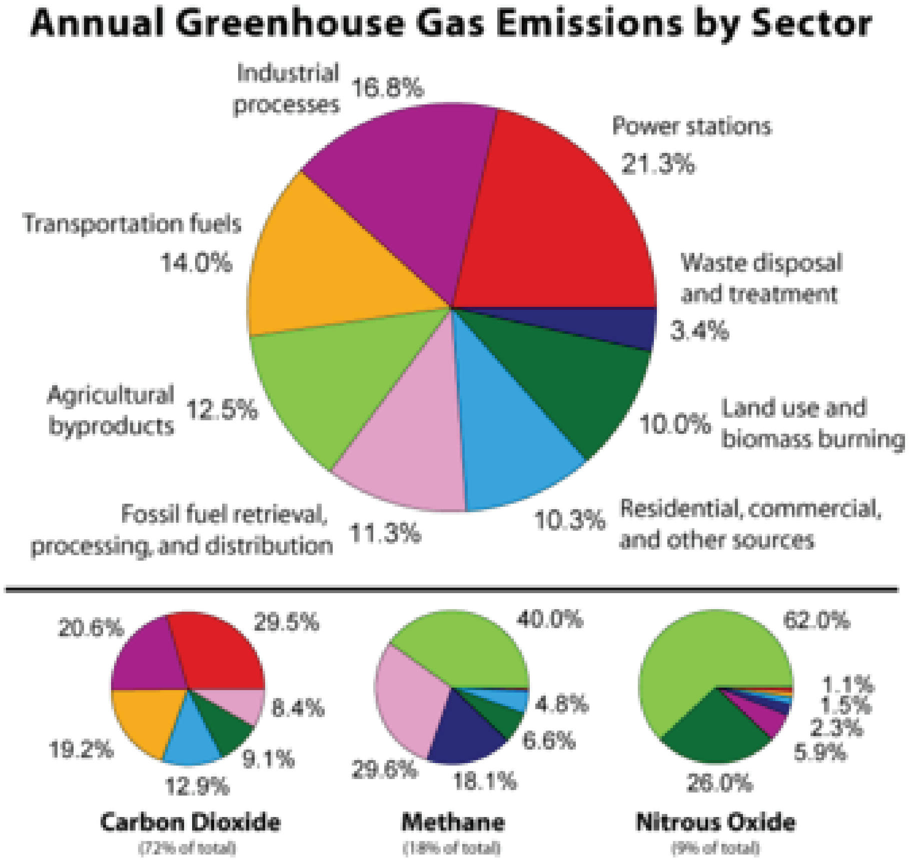


Figure 2.1: Global Annual Greenhouse Gas Emissions

(Source: Rhode, 2000)

2.1.1. Influence of climate change on agriculture

It is largely known that climate change would only produce negative effects but it may also have some beneficial consequences for agriculture. Some research indicates that warmer temperatures lengthen growing seasons and increased carbon dioxide in the air results in higher yields from some crops. However, any benefits to agriculture might be offset by an increased likelihood of heat waves, drought, severe thunderstorms and tornadoes. This sudden climatic variability makes adaptation difficult for farmers (Backlund et al., 2008).

It is expected that with any increase in carbon dioxide and higher temperatures, the life cycle of grain and oilseed crops will likely progress more rapidly. The marketable yield of many horticultural crops, such as tomatoes, onions and fruits, is very likely to be more sensitive to climate change than grain and oilseed crops. Many weeds respond more positively to increasing carbon dioxide than most cash crops; climate change would also result in a northern migration of weeds. With havoc in climatic conditions such as earlier springs and warmer winters, disease pressure on crops and domestic animals would most likely increase. Projected increases in temperature and a lengthening of the growing season will likely extend forage production into late fall and early spring. Climate change-induced shifts in plant species are already under way in rangelands. The establishment of perennial herbaceous species is reducing soil water availability early in the growing season. Higher temperatures will very likely reduce livestock production during the summer season, but these losses will be partially offset by warmer temperatures during the winter season (Backlund et al., 2008).

2.1.2. Agriculture's contribution to greenhouse gas emissions

Agriculture activities serve as both sources and sinks for greenhouse gases. Agriculture sinks of greenhouse gases such as biomass are nothing but reservoirs of carbon that have been removed from the atmosphere through the process of biological carbon sequestration over millions of years. The primary sources of greenhouse gases in agriculture are the production of nitrogen based fertilizers; the combustion of fossil fuels such as coal, gasoline, diesel fuel and natural gas; and waste management. At the same time, methane emissions occur through the fermentation that takes place in the digestive systems of ruminant animals, also called as livestock enteric fermentation (Backlund et al., 2008). Carbon dioxide is removed from the atmosphere and converted to organic carbon through the process of photosynthesis. As organic carbon decomposes, it is converted back to carbon dioxide through the process of respiration (Dutta, 2010). Conservation tillage, organic production, cover cropping and crop rotations can drastically increase the amount of carbon stored in soils. Figure 2.2 depicts the different sources of agricultural greenhouse gas emissions wherein agricultural soil management is the primary contributor.

2.2. Carbon sequestration and biochar

The capacity of lands and forests to remove carbon dioxide from the atmosphere is known as carbon sequestration. Carbon dioxide is absorbed by trees, plants and crops through photosynthesis and stored as carbon in biomass in tree trunks, branches, foliage and roots and soils (EPA, 2008). These forests and stable grasslands play a major role as carbon sinks because they can store large amounts of carbon in their vegetation and root systems for long periods of time. In turn, soils become the largest terrestrial sink for carbon on the planet. The ability of agriculture lands to store or sequester carbon depends on several factors, including climate, soil type, type of crop or vegetation cover and management practices.

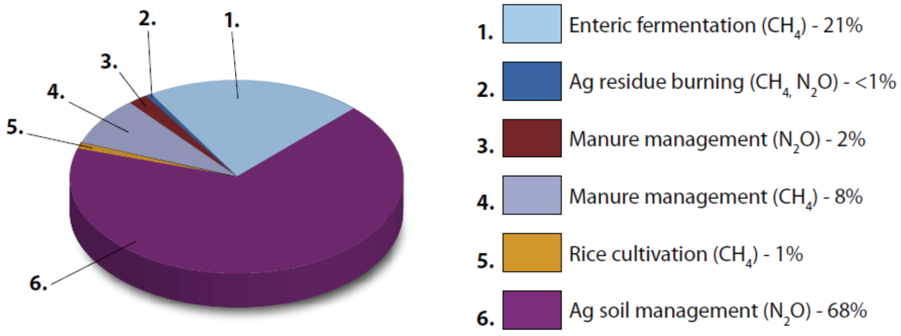
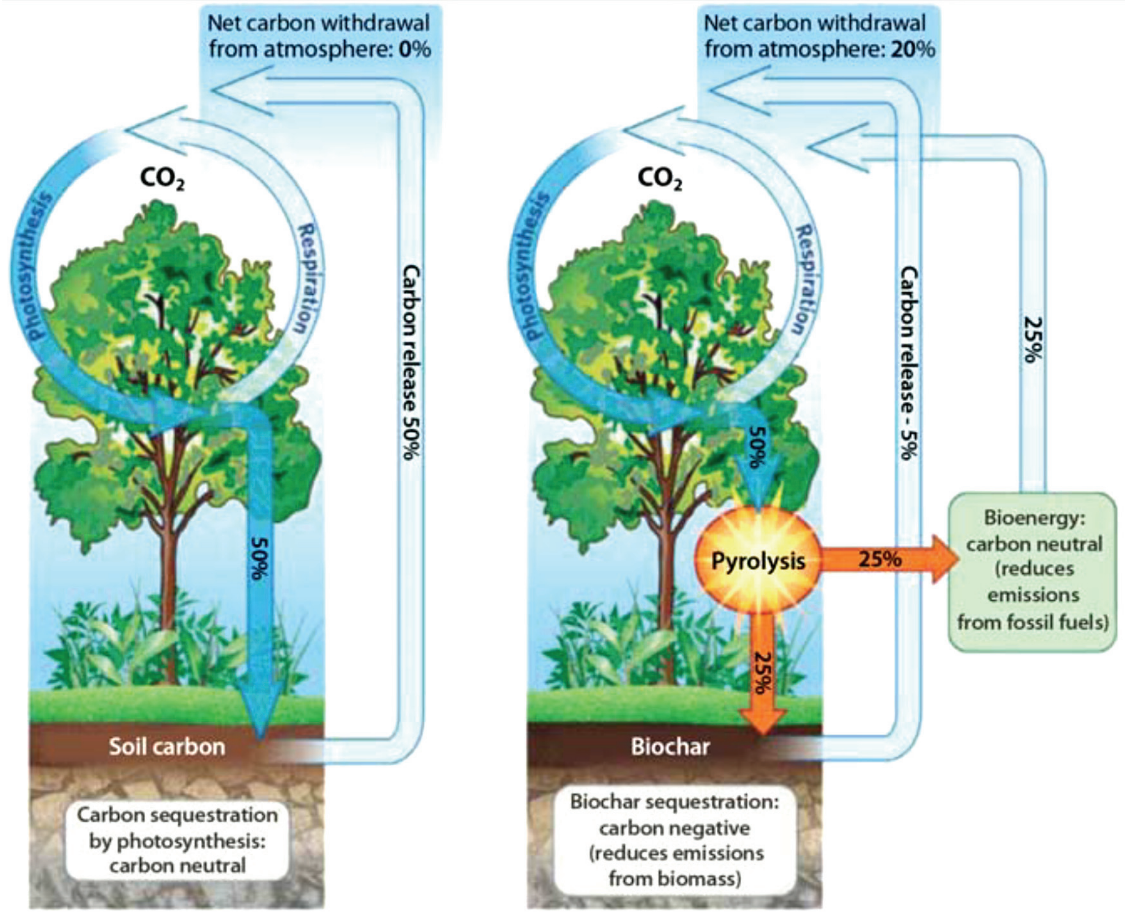


Figure 2.2: Sources of agricultural greenhouse gas emissions
(Source: EPA, 2008)

Biochars refer to the high carbon materials produced from the pyrolysis (heating in the absence of oxygen) of biomass. 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 (Dutta, 2010).

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 on stabilized soil carbon pools. Studies have also shown that it may also reduce emissions of nitrous oxide (IBI, 2011).

The role of biochar as a vehicle for carbon sequestration through a carbon negative process could be well understood through a hypothetical scenario as seen in Figure 2.3. In the case of biochar in Figure 2.3 (a), the natural process consists of capturing of the atmospheric carbon dioxide through photosynthesis but due to respiration and decay, this carbon is returned in completion to the atmosphere. But in the context of biochar technology (Figure 2.3 (b)), this natural process is interrupted by capturing part of the biomass before it reaches the soil directly and using part (25 percent in the example above) for the production of bioenergy and part for the production of biochar by pyrolysis.



(a) (b)

Figure 2.3: Biochar as carbon negative source

(Source: IBI, 2011)

The illustration shows that the biomass that is converted to energy (potentially in the forms of heat, gas or liquid fuels) releases part of the carbon in the form of CO_2 back into the atmosphere in an assumed carbon-neutral process. The other part of the biomass is converted into biochar and because of its stability sequesters all but 5 percent of the carbon (in this illustration) in the soil and hence has the ability to provide a carbon-negative source of energy (Schahczenski and Hill, 2009).

Although agricultural practices such as conservation tillage have been adopted as a means to mitigate climate change, the soil carbon is released much faster into the atmosphere compared to the biochar practices which could provide a means to a permanent sequestration. It also offers safer and likely less expensive carbon sequestration than methods related to the storage of carbon dioxide in underground geologic formations known as carbon capture and sequestration technologies (Schahczenski and Hill, 2009). While considering the benefits, the carbon-negative potential of biochar would either be enhanced or limited by the efficiency of energy production and the ability of the overall production process to limit carbon dioxide and other greenhouse gas emissions.

2.2.1. Biochar – a vehicle for carbon sequestration

In general, the thermochemical conversion of biomass leads to the formation of biochar at temperatures above 300°C. 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 can then be used for producing liquid fuels or directly for power and/or heat generation. The structure of biochar is predominantly 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. 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).

Biochar is a carbon negative product, thereby removing carbon dioxide from the atmosphere, while generating useful biofuels in the process. 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 carbon 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).

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, distillers' grain, bagasse and many others (UK BRC, 2009).

2.3. Stability of biochar in soil

The stability of biochar is of fundamental importance in the framework of biochar use for environmental management. Stability determines how long carbon (C) applied to soil as biochar will remain sequestered in soil and how long it may influence emissions of greenhouse gas from the pedosphere and contribute to the mitigation of climate change. In addition, the knowledge of stability will help determine how long biochar can provide benefits to soil and water quality.

The benefits of biochar would be affected in extent and duration if it decomposes in soil faster. Hence the stability of biochar must be of greater significance than other organic matter in the soil in order to extend the duration of these benefits.

2.3.1. Extent of biochar decay:

Biochar as residues from forest fires is frequently found to be more than 10,000 years old in various soil ecosystems (Preston and Schmidt, 2006). The original biochar found in high proportions in the 'Terra Preta' soils of the Amazon region (Glaser et al., 2001; Liang et al., 2008) have been radiocarbon dated and found to originate from 500 to 7000 years BP (Before Present) (Neves et al., 2003). This provides a compelling proof for the longevity of biochar in the environment. Several regional or global carbon budgeting of biochar, also referred to as biomass derived black C, suggests that biochar has a much greater average stability than plant litter. The global biochar production has been accounted to be only of 0.05Gt C/yr to 0.3Gt C/yr (Forbes et al., 2006). This consists of less than 0.5 per cent of the estimated global net primary productivity of 60Gt C/yr (Sabine et al., 2004). However, biochar concentrations are often above 10 per cent of total organic C in soils (Skjemstad et al., 1996, 2002). These data suggest a difference in decomposition rates of at least one order of magnitude. The form of biochar in the soil is not of much importance from a C accounting viewpoint as related to C sequestration and trading as long as it is not mineralized to CO_2.

2.3.2. Stabilization of biochar in soil:

There are three factors which play a significant role in the Stabilization of biochar in soil. The first of which is “Recalcitrance”; which is increased by the conversion of organic matter to biochar by pyrolysis significantly in the biomass. These changes in the composition of organic bonds by pyrolysis have a significant effect on the stability of biochar. The information related to the relevance of the crystal structure of biochar for its recalcitrance is still scanty in literature. The spatial separation or its particulate nature may also lend stability to biochar, where the outer regions of a biochar particle protect the inner regions from access by microorganisms and their enzymes. This is the second very important property considered responsible for much of the recalcitrance of biochar. The third factor affecting the stability of biochar in soils is its ability to form interactions with mineral surfaces. A significant portion of biochar was found in the organo-mineral fraction of soil (Brodowski et al., 2006; Laird et al., 2008; Liang et al., 2008), suggesting that biochar forms interactions with minerals. Rapid association of biochar surfaces with Al and Si and, to a lesser extent, with Fe was found during the first decade after addition of biochar to soil, which increased more slowly within biochar structures (Nguyen et al, 2008).

2.3.3. Biochar stability framework

The mean residence time of biochar in the environment has been estimated to be about several hundred to a few thousand years, given the available information and a few trials conducted as seen from Figure 2.4. The quantification of the proportion of stable C in biochar can be established through an assessment of the short-term decay and, specifically, the proportion of the relatively labile fraction. It is imperative to consider the following aspects to determine a logistically successful stable biochar framework (Joseph et al., 2009).

- Establish relationships between biochar properties or rapid stability tests and the proportion of the labile fraction of biochar that will decompose in annual to decadal timescales. This may be achieved by incubation experiments over a few years.
- Establish the decomposition rate of the stable fraction of biochar by a combination of long-term incubation experiments with fresh and aged biochar under elevated

temperature, and field experiments that either exclude physical losses or allow their quantification.

- Develop a mechanistic understanding of long-term biochar decay as a function of biochar properties and environmental conditions such as climate and soil.
- Apply the modelling framework recognizing stable and labile fractions of biochar, including decomposition products of biochar, and validate these with long-term field experiments.

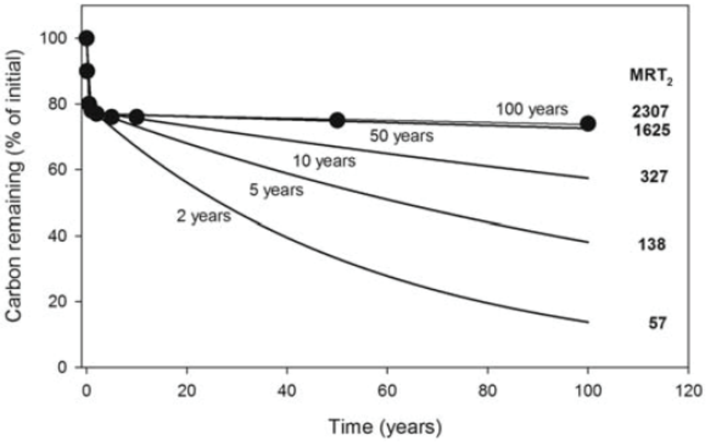


Figure 2.4: Double-exponential model fitted to hypothetical data of biochar decay after 0.1-100 years

(Source: Joseph et al., 2009)

2.4. Technology of Pyrolysis

Pyrolysis is the process of thermochemical decomposition of organic material at high temperatures, starting at 200–300°C without the participation of oxygen. It is a special case of thermolysis which has been adapted for numerous applications such as the chemical industry, cooking, producing carbon fibers, biofuels and also in the production of biochar. The amounts of solid, liquid, and gaseous fractions formed and the distribution of their products are dependent distinctly on the process variables. There are three basic technologies involved in the pyrolysis process which consist of the formation of biochar and other products (Figure 2.5). 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, 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.).

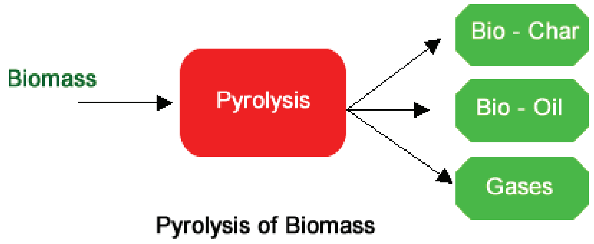


Figure 2.5: Biomass pyrolysis products

Pyrolysis processes can be divided into three subclasses: conventional (slow) pyrolysis, fast pyrolysis and flash pyrolysis, depending on the heating rates and the properties of the biomass used in the process (Demirbas, 1999) (Figure 2.6). Fast pyrolysis systems are targeted towards the production of bio-oils, wherein the biomass is heated very rapidly (up to 1000°C/min) in the absence of oxygen while slow pyrolysis involves slower heating rates (1–20°C/min) in the absence of oxygen, and long char residence times (hours to days) (Brewer et al., 2009).

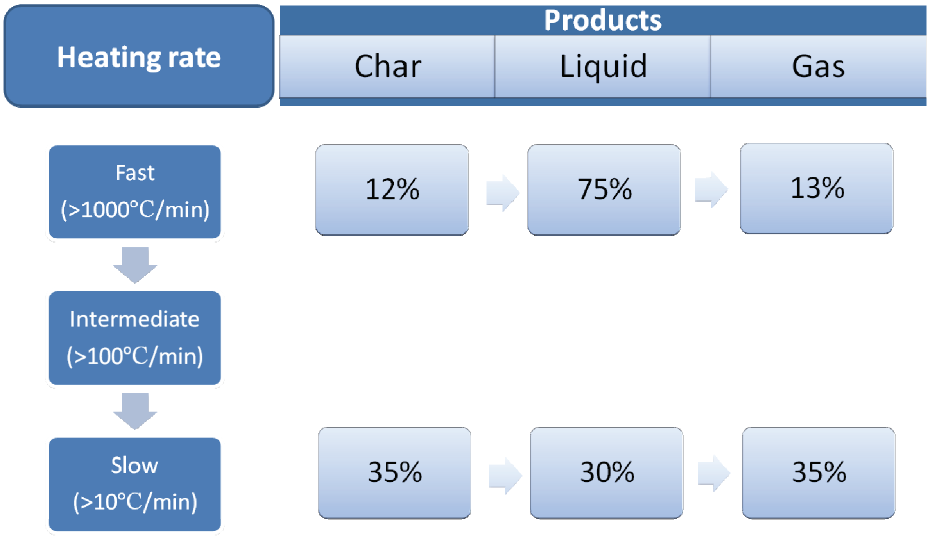


Figure 2.6: Role of heating rate on pyrolysis products

(Source: Masek, 2009)

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. Fast pyrolysis of biomass can be brought about by using small particles, for example in the fluidised 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 and short residence time of vapour in the pyrolysis reactor. Much greater percentage of vapours and aerosols than charcoal is produced through the fast pyrolysis of biomass. Cooling and condensation of these vapours and aerosols results in a dark brown liquid called Bio-oil. The heating value of this bio-oil is approximately half that of conventional fuel oil. Flash pyrolysis is a technique in which finely divided feedstock is quickly heated in the range of 350 and 500°C in less than 2 seconds (Bridgwater, 2001).

The pyrolysis products and their yields depend on the composition of the biomass like cellulose and hemicelluloses, lignin, protein and ash contents 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 to the biomass that occur during the process of pyrolysis are described below:

(1) Increase in the temperature inside the biomass due to the heat transfer from a heat source; this usually translates to the transfer of heat from the surface towards the center of the material by convection, conduction and radiation in the case of conventional pyrolysis while in the case of MAP, these radiation penetrate materials and deposit energy, heat can be generated throughout the volume of the material, rather than from an external source (Orsat et al., 2007, Fernández et al., 2011).

(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 biomass; although the conversions of heterogeneous reactions in MW are always higher than those observed in conventional heating at any temperature.

(4) Tar is produced through the condensation of some of the volatiles in the cooler parts of the fuel, followed by secondary reactions; in this case too, MAP affects and contributes to variable volatile profiles than those in conventional heating. As the volatiles travel from the internal hot regions to external cold regions of the sample, it reduces the activity of the secondary phase reactions in the case of MAP (Fernández et al., 2011).

(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 dependent on the process's residence time/ temperature/pressure profile. But microwaves have been seen to be more potent in carrying out heterogeneous reactions compared to conventional heating (Fernández et al., 2011).

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, high process pressure, long vapour residence time, extended vapour/solid contact, low heating rate, large biomass particle size and optimized heat integration (Masek, 2009).

2.4.1. Pyrolysis of Lignocellulosic Biomass

Amongst the various sources of biomass which have been used for pyrolysis, cellulosic and lignocellulosic feedstock make up the major portions. Several conversion processes, which are currently under development, may result in increased residue utilization in the future. Cellulose is the major component in lignocellulosic biomass, and accounts for approximately 50% by weight. But it is not feasible to obtain cellulose from the biomass in a pure state through general isolation methods for obtaining cellulose from in a pure state, thus the purification process becomes tedious (Shen et al., 2011). Hence 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.

2.4.2. Kinetics of Pyrolysis

Furthering investigations of the kinetics of the process could enhance the optimization of system design and control of the pyrolysis process. The complex composite structure of wood complicates kinetic analysis of the pyrolysis process. Hemicellulose, cellulose, lignin, and extractives each have their own pyrolysis chemistry. Kinetic modeling consists of the following simplified 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 (Masek, 2009).

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). In addition, the kinetics of the primary product formation is dependent to a great extent 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 (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 or by non-isothermal methods. In the case of 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, in the case of the non isothermal process, 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 the 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 are dependent on the temperatures at which the reaction rates take place.

It has been found that laboratory scale reactors allow only the total final yields to be obtained hence a one-stage mechanism of primary wood degradation becomes a preferred method. As a result, a mechanism with three parallel reactions for the formation of the main product classes has been deemed 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 favorability toward only one of the products during the pyrolysis process (Di Blasi et al., 2001).

The final product distribution in a pyrolysis process is also significantly altered by the reactor configuration (Bridgewater, 2003). For a lignocellulosic biomass, e.g. wood, the yield depends on the wood structure and particle size.

The effectiveness of pyrolysis also depends on the particle size and geometry of the biomass. The presence of large sized particles has been known to ultimately have a negative effect on the efficiency of production of biochar (Lei et al., 2009).

Various studies have been conducted which were focussed on the fundamentals of chemical kinetics and heat transfer during pyrolysis influenced by the geometry of the biomass. Babu and Chaurasia (2004) studied the effects of the most important physical and thermal properties of the feedstock on the pyrolysis for different geometries such as slab, cylinder and sphere of the biomass. They found that these properties are important mainly for large particles.

Simmons et al., (1986), analyzed a heat transfer model in order to determine an upper bound for biomass particle size in conducting experimental pyrolysis kinetics. Their study showed that the steady state temperature profile can be used to estimate the maximum particle size for various values of the dimensionless parameters.

The design consists of utilizing analytical methods to assign the different reaction paths to either single component 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. These have shown the decomposition reaction kinetics of the major wood components- Cellulose, Hemicellulose and Lignins. Research till now has shown that the degradation rate of the main components of wood through pyrolysis increases in the order- lignin, wood, cellulose and hemicelluloses.

2.5. Microwave- assisted Pyrolysis (MAP)

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.

Recently, there has been a surge in finding alternate methods for efficient pyrolysis of different biomass sources. Recent interest in microwave-assisted pyrolysis (MAP) has highlighted its unique advantages not attained with conventional heating to form biochar and other useful products (Fernández et al., 2011).

2.5.1. Microwaves and their Applications in Pyrolysis

Electromagnetic waves having wavelengths ranging from 1 mm to 1 m with corresponding frequencies between 300 MHz and 300 GHz belong to microwaves in the electromagnetic spectrum (Figure 2.7). 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 (Thostensen and Chow, 1999).

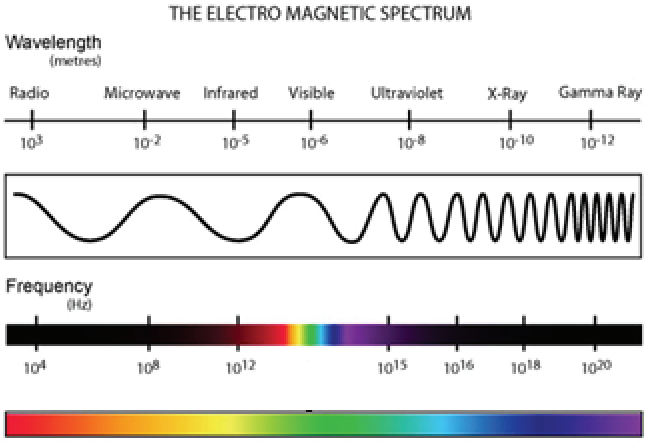


Figure 2.7: Electromagnetic Spectrum
(Source: Hakim, 2013)

As in any electromagnetic radiation, an alternating electric field and an alternating magnetic field perpendicular to each other are created by microwaves. This property has been exploited for the thermal applications of microwaves. Microwaves follow all the basic laws of physics like reflection, refraction, interference, diffraction and polarization as they are electromagnetic radiation similar to visible light. Microwaves are generated in a microwave oven by a high voltage system (Dev et al., 2007). The electromagnetic radiation is generated by the microwave source and the transmission lines would deliver this electromagnetic energy from the source to the applicator. The energy is either absorbed or reflected by the material in the applicator. The theoretical analysis of each of these microwave components is governed by the Maxwell equations (Equations (2.1) and (2.2)) and the corresponding boundary conditions respectively (Equations (2.3) and (2.4)):

$$\nabla X E = \frac{\partial B}{\partial t} \qquad (2.1)$$

$$\nabla X H = \frac{\partial D}{\partial t} + I \qquad (2.2)$$

$$\nabla . B = 0 \qquad (2.3)$$

$$\nabla . D = \rho \qquad (2.4)$$

Where E is the electric field vector,

H, the magnetic field vector,

D, the electric flux density vector,

B, the magnetic flux density vector, and

I, the current density vector.

The physical laws that describe electromagnetic fields that vary with time are described by the Maxwell equations. The knowledge and an understanding of electromagnetic theory is essential for the design of microwave sources, transmission lines, applicators, and the ability to combine these elements into an efficient system to process materials (Thostensen and Chow, 1999).

2.5.1.1. Structure of Microwave Generator

The nucleus of the microwave oven is the high voltage system, the main function of which is to generate required amount of microwave energy. The components of this system generates ample amount of high AC voltage and then converts it into higher DC voltage. This DC power is utilized to produce RF energy to perform operations. The centre of the high-voltage system is the magnetron tube which is a diode-type electron tube. The components of this system include the anode, the filament/cathode, the antenna, and the magnets. The high magnetic field generated by the two powerful permanent magnets, is imposed on the space between the anode, which is a conducting plate and the cathode, which acts as a grid. There is an antenna, connected to the anode and acts as a probe or loop that is coupled to the waveguide, a hollow metal enclosure, into which the antenna transmits the RF and MW energy. The magnetic field is placed inside the cavity of a waveguide such that it is parallel with the axis of the cathode (Gallawa, 1989).

2.5.1.2. Magnetron Operation

The motion of electrons under the combined influence of electric and magnetic fields is the theory behind magnetron operation. Electrons flow from the cathode to the anode for the proper functioning of the tube. The two fundamental laws that govern the trajectory of these electrons are: The force exerted by an electric field on an electron is proportional to the strength of the field. Electrons tend to move from a point of negative potential toward a positive potential as shown in Figure 2.8. The force exerted on an electron in a magnetic field is at right angles to both the field itself, and to the path of the electron. In such a case, the electron proceeds to the anode in a curve instead of a direct path (Gallawa, 1989).

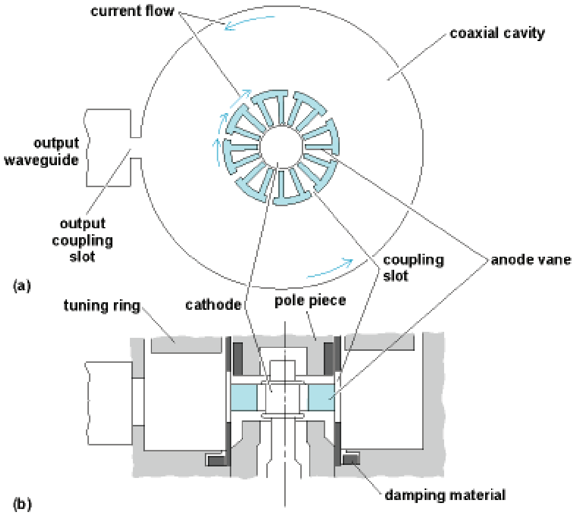


Figure 2.8: Electron motion in a Magnetron tube

Coaxial cavity magnetron. (a) Top view. (b) Cross-sectional view.

(Source: Van Nostrand, 1965)

The high negative potential at the cathode, in turn, puts a high positive potential at the anode, leading to the flow of electrons from the cathode accelerating towards the anode. These electrons then encounter the powerful permanent magnets which are parallel to the cathode. The effect of the magnetic fields leads to the deflection of the speeding electrons away from the anode. They curve to a path at almost right angles to their previous direction, resulting in an expanding circular orbit around the cathode, eventually reaching the anode.

An alternating electromagnetic flow in the resonant cavities of the anode is produced through the interaction of this rotating space-charge with the configuration of the surface of the anode. As a result, the physical structure of the anode forms the equivalent of a series of high-Q resonant inductive-capacitive (LC) circuits. The strapping of alternate segments results in the connection of the LC circuits in parallel (Gallawa, 1989), generating microwaves. The microwaves are then transmitted into the cavity with a series of wave guides (Dev et al., 2007).

The different applicators have great importance as they are responsible for the transfer of microwave energy to materials. Some common microwave applicators include waveguides, traveling wave applicators, single mode cavities, and multi-mode cavities. The type of applicator used in a microwave processing system is dependent on the materials to be processed (Thostenson and Chow, 1999).

2.5.1.3. Applications of microwaves

Microwaves are good for transmitting information from one place to another as microwave energy can penetrate haze, light rain and snow, clouds, and smoke. Microwaves finds use in various fields, such as, Communication, Remote Sensing, Navigation, Power, Spectroscopy and Medical Applications. Thermal application is another important application of microwaves (Dev et. al, 2007). There is potential for microwaves to be introduced and applied to many other heating processes, which offer unique advantages not attained with conventional heating (Fernandez et al., 2011).

Microwave assisted pyrolysis techniques for the production of biochar is becoming extremely popular as more number of scientists realizes the advantage 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, has been at the forefront of advocating for the utilization of industrial-scale microwaves for the production of biochar (Kleiner, 2009). Although microwave assisted pyrolysis has been recognized as an advantageous technique, its applications at the industrial scale are limited to higher yield of bio-oil. It is well known that microwave assisted processes are more energy efficient, rapid and produces high quality products compared to conventional methods. This current research targeted the optimization of this technology in order to maximize biochar of high quality. This could lead to production of nanoscale products, by value addition of the biochar produced, for innovative industrial and medical applications, using novel techniques. Potential uses of these technologies include medical applications such as tissue scaffolds and other industrial applications like fuel cells, electro-filtration, biosensors, effluent treatment etc.

The key point in microwave pyrolysis is to prevent undesired secondary reactions of the volatiles leading to increase in the yields of the biochar produced. The added benefit would be that the chars produced would have large specific surface areas. A slow heating process favours increasing the char yield as found in previous results (Dutta, 2010). It also leads to decreasing the yield of volatiles. Another important feature is to produce chars that have large specific surface areas. These are some of the conflicting features in wood pyrolysis (Sjöström, 1993). It has been proposed that microwave pyrolysis has the potential to satisfy both of these requirements.

2.5.2. Principles governing microwave pyrolysis

2.5.2.1. Dielectric properties

One of the driving principles of microwave heating is based on 'molecular friction' (or dielectric loss) (Venkatesh and Raghavan, 2005). Molecular rotation occurs in materials containing polar molecules having an electrical dipole moment, which will align them in an electromagnetic field. If the field is oscillating, as in an electromagnetic wave, these molecules rotate to continuously align with it. This is called dipole rotation. As the field alternates, the molecules reverse direction. Rotating molecules push, pull, and collide with other molecules (through electrical forces), distributing the energy to adjacent molecules and atoms in the material. This results in heat generation (Metaxas, 1996). Therefore, the energy transfer is not by conduction or convection as in conventional heating.

The principles of dielectric heating as opposed to that of conventional heating can be best summarized through Figure 2.9 below. Dielectric heating of a material causes thermal effects which may cause a different temperature regime within the material (Zhang et al., 2001). The biomass is heated by conduction from the surface to its core in the conventional method and by convective heat transfer from high-temperature gas. The temperature at the surface of the biomass is known to be higher than that at the core because of the poor thermal conductivity of lignocellulosic biomass.

However, in the dielectric heating method, first the core of the lignocellulosic biomass attains a higher temperature as seen in Figure 2.9. It has been found that during microwave or dielectric heating, the temperature at the core of the biomass is higher than that for the surface. In this case, carbonization develops from the centre to the surface layer of the biomass. This demonstrates that early primary volatiles will transfer from the centre to the surface layer. Therefore, it is possible to reduce undesired secondary reactions of the volatiles because the volatiles produced in the core of the biomass will diffuse towards the lower temperature region. This has been explained in detail by the dielectric heating studies conducted through experiments and conforms to results from various researchers (Miura et al., 2004).

The mobility of the dipoles within the structure of a material directly influences the dielectric properties and therefore the dielectric properties are functions of temperature, frequency, and, for reacting systems, degree of reaction. This causes changes in the ability of the material to absorb energy changes during processing (Thostenson and Chow, 1999).

2.5.2.2. Volumetric heating

The implementation of microwave heating technology suffers from difficulties associated with the scaling up of laboratory units to industrial capacities propelled by a lack of fundamental data on material dielectric properties. This in turn implies that commercialisation of microwave heating processes for environmental engineering applications have been limited and requires additional process-specific advantages over conventional methods of heating.

The main advantages of microwave heating in mineral processes are amongst others the concept of volumetric heating (Haque, 1999). During microwave processing, electromagnetic energy at 915 and 2450 MHz can be absorbed by water contained inside the materials or other “lossy” substances, such as carbon and some organics, and converted to heat. These waves can penetrate directly into the material causing a volumetric heating (from the inside out) and provides fast and uniform heating throughout the entire product (Maskan, 2000).

2.5.2.3. Selective heating

Another advantage of microwave processing over conventional heating is that during microwave radiation of a material, the product selectivity is also changed. This has been attributed to the faster, selective dielectric heating provided by microwaves. It was concluded that selective heating is possible with microwave fields of high frequency heating. This selective heating was found to have a strong dependence on catalyst particle size and on microwave frequency (Zhang et al., 2001). Microwave energy is extremely efficient in the selective heating of materials as no energy is wasted in 'bulk heating' of the sample. This is a clear advantage that microwave heating has over conventional methods such as in bulk heating in furnaces (Jones et al., 2002).

It has been seen that different chemical species absorb microwave energy to a different extent which implies that the thermal energy so-produced and imparted to the surrounding environment will also vary with the chemical species. Hence, for systems that possess inherent non-homogeneous structural characteristics, such as lignocellulosic biomass, or that contain different chemical species with different dielectric properties dispersed into a homogeneous environment, such as the use of a doping agent, it is possible to affect a selective heating of some areas, or components of the systems (Paré and Bélanger, 1997).

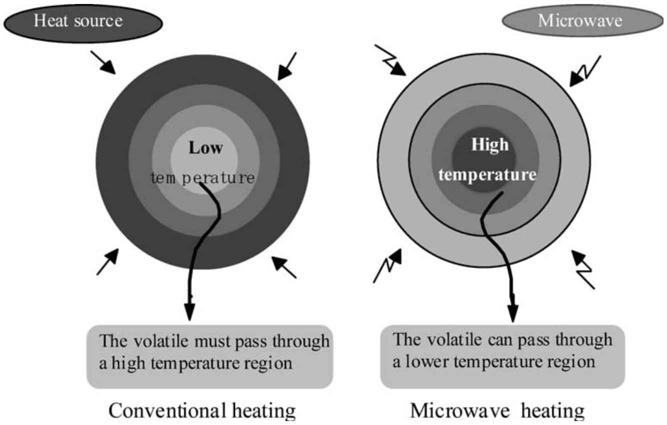


Figure 2.9: Schematic diagram of temperature distribution, heat transfer and mass transfer in the conventional and microwave heating of wood

(Source: Miura et al., 2004)

Lei et al. (2009) focused on the effects of reaction temperature, time and particle size of corn stover on microwave pyrolysis. They determined the effects of reaction temperature and time of pyrolytic conditions on the yields of bio-oil, syngas, and biochar.

Miura et al. (2004) used microwave heating for the rapid pyrolysis of a wood block. They demonstrated that temperature distribution, heat transfer and mass transfer involved in microwave pyrolysis were quite different from a conventional pyrolysis. The char prepared by the microwave heating had a large specific surface area (≈ 450 m^2 g^{-1}). Surface evaluations of the char including scanning electron microscopy showed few pyrolysis carbon-particles in the micropores of the char. In this study, the char yields from cylindrical wood blocks with different diameters were correlated by an equation, in which the electric power consumption per weight was found to be inversely proportional to the square of the wood block diameter. This in turn means that a larger wood block can be pyrolyzed with less electric power consumption per unit weight than a smaller wood block.

Another study was conducted to assess the mechanisms involved in microwave pyrolysis of wood pellets. The pyrolysis of wood pellets was investigated using a single-mode microwave cavity, and the dielectric properties of the wood were measured at 2.45 GHz using a cavity perturbation apparatus capable of measurements at temperatures up to 800°C. This study showed that microwave pyrolysis can take place without the use of carbon-rich dopants, which act as microwave receptors and that the heating of water within the biomass alone can be used to induce pyrolysis of wood. This research also found that the yield of bio-oil and biogas is a function of the heating rate and power density (Robinson et al., 2010).

Recently, different biomass has also been subjected to microwave pyrolysis in order to support the advantages of microwaves in this field. Microwave pyrolysis of distillers dried grain with solubles (DDGS) was investigated to determine the effects of pyrolytic conditions on the yields of bio-oil, syngas, and biochar. Pyrolysis process variables included reaction temperature, time, and power input (Lei et al., 2010).

2.5.3. Potential of Microwave assisted (MA) biochar production as a carbon sequestration tool

The proposed approach of combining pyrolysis for energy production with bio-char additions to soil takes advantage of biochar's proven longevity and ability to retain cations, actively draw CO_2 from the atmosphere, regenerate degraded lands, and reduce environmental pollution (Lehmann, 2007).

The estimates for global carbon dioxide removal from the atmosphere are based on studies related to conventional techniques of biochar production. It has been stated that globally about 60 billion tonnes of carbon is taken up annually by photosynthesis and amongst these; around 10% becomes available as agricultural residue. 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 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. It is predicted that this simplistic, yet powerful, approach can be used to store up to 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).

These data are evaluated on the basis of a conversion rate of 50% from the agricultural residues to biochar during the thermochemical conversion pathways. The sequestration of all this biochar produced, leads to an estimated reduction of approximately 7% of atmospheric carbon emissions. Results obtained through several investigations and largely the technology patented by the prototype microwave oven invented by the New Zealand Company, Carbonscape have established microwave assisted pyrolysis to be a technology which could enhance biochar production. Each patented industrial-scale oven will convert 40-50% of the wood sent though it into charcoal. Using its patented continuous-flow microwave technology (Figure 2.10), Carbonscape is able to produce high-grade and highly-valuable activated carbon in a single processing step (Gaunt, 2012).

Based on these studies, the hypothesis could be made that an improved technology of biochar production through microwave assisted techniques could lead to a higher yield of the char. It is expected that improvements related to the process parameters and better understanding of the microwave heating process would bring about this progress.

Figure 2.10: Carbonscape's demonstration microwave pyrolysis unit (Carbonscape, 2012)

The concept of using microwave radiation to carry out pyrolysis of biomass for the production of biochar is still in its nascent stages. The inherent nature of dielectric heating could be taken advantage of in this process which would lead to higher yields of pyrolytic products. Microwave heating benefits from the fact that it is very efficient at only heating the material which is targeted, microwave chamber walls and exterior surfaces are not directly heated (Gaunt, 2012). Moreover, the microwave process has very short residence times compared with conventional non-microwave processes, improving efficiency and also reducing the process time from hours to minutes.

If we divert all biochar production through the process of microwave assisted pyrolysis (MAP) from agricultural wastes as biomass sources and considering the efficiency rates of 40-50% from these microwave pyrolysis units to produce biochar, we could still obtain sequestration levels of approximately 6-7% of all anthropogenic greenhouse gas emissions.

Thus much of the investigations are now concentrated upon the improvement of these efficiencies. In microwave pyrolysis, the efficiency with which the targeted material actually absorbs the microwave radiation depends significantly on the moisture content of the material: If there is too few polar molecules (typical moisture from water) little to no heating will occur; whereas if there is a significant amount of excess polar molecules, an excessive amount of time and energy is required to heat the material. Efficiency is also significantly determined by the extent to which microwave radiation can pass through the material (Gaunt, 2012). The penetration depth of the feedstock thus selected plays a major role, for example if the material is too large or impenetrable by radiation differential heating is likely to occur.

Important research questions, therefore, for microwave pyrolysis are optimizing the ideal moisture content and size of various feedstock materials in order to maximize heating efficiency. In addition, the manipulation and optimization of the process parameters could also be useful in increasing efficiencies so as to maximize biochar production through microwave assisted technology.

Thus in order to determine the extent of the success of this technology, we must consider the availability of biomass and land for storage as well as the stability of the biochar when placed in soil. Of all the pathways to offset carbon described above, we considered only the ones with the greatest impact: direct sequestration, displacement of fossil energy, increase in Net Primary Production (NPP), and nitrous oxide reduction (Amonette et al., 2007).

Recently, International Biochar Initiative (IBI) had developed a simple model to predict the carbon removing power of sustainable biochar systems. This model consisted of four different scenarios to evaluate the potential of biochar systems to sequester atmospheric carbon dioxide. The "Conservative" scenario assumed that only biomass from cropping and forestry residues that otherwise had no use (about 27% of the total residues) was available. The "Moderate" and "Optimistic" scenarios considered that 50% and 80%, respectively, of all the cropping and forestry residues was available to make biochar. For the "Optimistic Plus" scenario, generous feedbacks related to potential increases in Net Primary Production (25%) and potential decreases in N_2O emissions (50%) stemming from biochar amendments to soil were also added to enhance the outcome of the scenario (Figure 2.11). The N_2O emissions scenario relied on the data and assumptions of Crutzen et al. (2007) and Galloway et al. (2004) (Amonette et al., 2007).

For each base scenario, the estimation was that the amount of biochar produced, as well as the amounts of fossil fuel carbon emissions replaced by the energy generated during biochar production. The additional amount of carbon that could be sequestered if CO_2 emissions generated during biochar production were captured and sequestered in the same manner as proposed for coal combustion facilities. Although, all scenarios in this model assumed that slow pyrolysis was the method used to produce the biochar, which has a carbonization efficiency of about 40% (Amonette et al., 2007), this would hold true for microwave assisted pyrolysis as well.

The results of the scenarios show that most conservatively, the carbon in biochar alone can account for about 1/4 of a wedge (0.25 Gt/year) by 2030. The Optimistic Plus scenario reaches one full wedge around 2040 (Figure 2.11). The most intriguing is the positive feedback shown in the Optimistic Plus scenario, where the impact of biochar is shown to continue to increase after the other scenarios have leveled out. The cumulative impact of the four biochar scenarios showed that as much as 60 gigatons of carbon could be sequestered or offset in just the 40 years to 2050 with the Optimistic Plus scenario (Amonette et al., 2007). Although these calculations highlight the potential of biochar, realistic projections will require rigorous economic and environmental analyses.

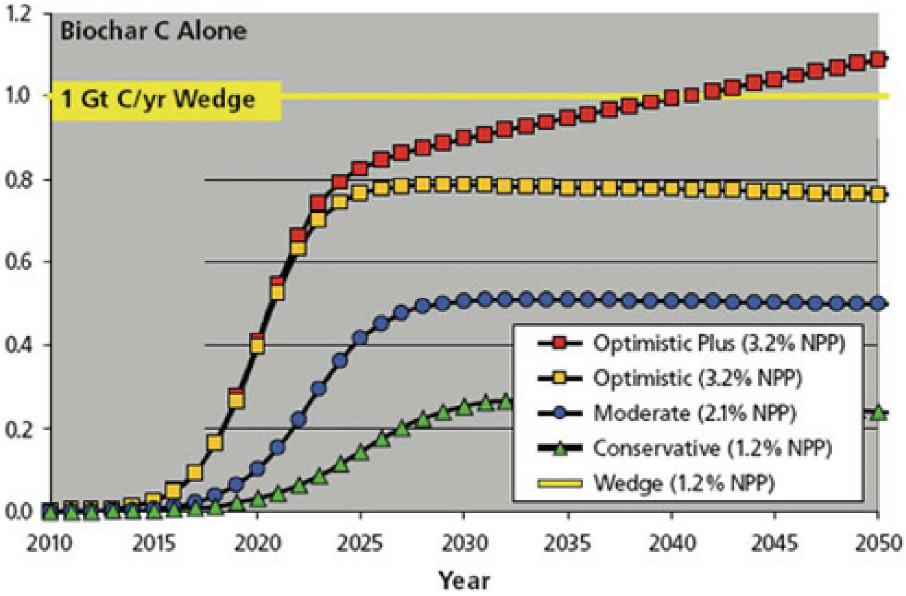


Figure 2.11: Four scenarios for potential biochar offsets
(IBI, 2012)

2.5.4. Microwave Pyrolysis Reactor Design Principles

Although microwave assisted technology for pyrolysis has many advantages over conventional methods, there are still a number of complications which affect the heat, mass transportation mechanism and chemical reactions which act as a barrier towards the widespread acceptance of this technology. 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. In a conventional pyrolysis process, a classical hardwood produces lower char yields with respect to the initial dry mass (Menéndez et al., 2004).

A sound kinetic model is inherent to reactor design. There are many suggestions in the research circle to divide the mechanism of wood pyrolysis into three independent parallel reaction paths. 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 (Di Blasi et al, 2001). 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.

Microwave assisted pyrolysis techniques for the production of biochar is becoming extremely popular as more number of scientists realize the advantage of using microwaves to enhance the yield and quality of the biochar produced in a biomass (Kleiner, 2009). The key points in microwave pyrolysis are to prevent undesired secondary reactions of the volatiles and to increase the yields of the biochar produced. Miura et al. (2004) used microwave heating for the rapid pyrolysis of a wood block. They demonstrated that temperature distribution, heat transfer and mass transfer involved in microwave pyrolysis were quite different from a conventional heating method. Hence, it becomes extremely crucial to understand the influence of microwaves in terms of dipolar heating on the kinetics of the process in order to design a pyrolysis reactor for optimized biochar production in the microwave environment.

2.5.5. Modeling and Simulation of MAP

There has been an overwhelming interest in the scientific arena regarding the research of modeling and simulation studies involved in the production of biochar as well other by products in the process of pyrolysis. One of the earliest studies done in this area was carried out by Chan et al., (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 and Chaurasia (2004) carried out the modelling, simulation and estimation of optimum parameters in pyrolysis of biomass. They solved the model equations numerically using the fourth order Runge–Kutta method over a wide range of heating rates (25–360°C/s) and temperatures (500–1500°C). 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 (Babu and Chaurasia, 2004).

Di Blasi conducted the modelling of the chemical and physical processes involved in biomass pyrolysis with special focus on wood. The different approaches used in the transport models are presented at both the level of single particle and in the reactor, together with the main achievements of numerical simulations (Di Blasi, 2008).

Numerical simulation of the electromagnetic field and the heat and mass transfer processes during microwave-induced pyrolysis of a wood block has also been carried out (Ciacci et al., 2010). The researchers have detailed a two-dimensional mathematical model based on a close combination of the propagation and absorption of electromagnetic waves into the lignocellulosic material and heat/mass transfer with chemical reactions. The model predicted a conversion process controlled by volumetric heating with a reaction zone that traverses from the most internal region towards the external surface.

Although there have been several experimental investigation about biomass pyrolysis induced by microwave heating, very little progress has been made in terms of understanding the chemical kinetics of the microwave pyrolysis technique through numerical simulations (Ciacci et al., 2010). There is poor understanding of the mechanisms involved in application of electromagnetic energy for the pyrolysis of biomass and the actual energy distribution inside the biomass when subjecting them to electromagnetic field. The electromagnetic field distribution inside the microwave oven can be traced out by solving the Maxwell's equations (Dev et al., 2008). Finite Element Method (FEM) is commonly used for solving Maxwell's equations to get the energy distribution in a complex object or within a multimode cavity and it is capable of simulating power density distribution in 3-D space (Fu and Metaxas, 1994; Zhou et al., 1995).

Dutta et al., (2010) developed a finite element model (FEM) in order to simulate the coupled heat and mass transfer phenomena during pyrolysis. The resulting sets of partial differential equations were then solved simultaneously using the COMSOL Multiphisics software package. The influences of final pyrolysis temperature, and pyrolysis holding time on the biochar yields were investigated. Simulation results from this study indicated 400°C to be the optimum temperature at which highest yield of biochar is based on the three step kinetics model taken into consideration under the specified temperature range of 300 to 400°C. It also showed that the amount of char formed would vary based on the pyrolysis holding time.

2.5.6. Thermodynamics 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 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). 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.

For a lignocellulosic biomass, with the above mentioned composition, the average specific heat is 0.42 kJ/kg K (Hyper-physics, 2010). This requires approximately 180 kJ/kg of energy to reach temperatures of 450°C from ambient temperatures. Also, the mean Activation energy required for pyrolysis is approximately 1220kJ/kg based on the mole fractions of the different components of the biomass (ÂrfaÄo et al., 1998). Thus, the entire process of pyrolysis of the lignocellulosic biomass of a very low moisture content of 2-5% consumes about 1400kJ/kg.

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. 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 [ΔH], entropy change [ΔS], and heat capacity change [ΔCp] 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 (Joseph et al., 2009).

In a previous study, Chinese birch wood samples were used for production of biochar wherein 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. 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 (Dutta et al., 2011).

2.5.7. Issues and Concerns related to potential of MAP as a sequestration tool

Microwave assisted pyrolysis techniques are expected to contribute greatly towards the enhancement of biochar production and the subsequent sequestration of carbon in the stable form. This would help in mopping up of the excess carbon dioxide emissions causing drastic climate change. However, as with the implementation of any technology, there are crucial pitfalls and impediments to successful adoption of MAP to bring about large scale mitigation of greenhouse gas emissions.

The following are few of the important issues and concerns related to potential of MAP as a sequestration tool:

2.5.7.1. Economic viability of sources of biomass

Pyrolysis plants that use biochar to offset fossil- fuel consumption are financially viable only when inexpensive feedstock is continuously available in sufficient quantities. Moreover for MAP for biochar production, the selection of biomass is extremely critical as the moisture content in these feedstocks drive the extent of microwave heating. This could lead to further economic implications.

Moreover, for the required higher efficiencies of carbon sequestration, it might also become necessary to include industrial wastes as potential substrate for the MAP system. Some of these could be plastics, tires, etc., which leads to further complications of the purity of carbon in the biochar.

2.5.7.2. Economic viability of microwave utilization

There have been objections raised regarding the economic viability of microwave utilization for the production of biochar caused due to the inherent energy costs of converting electricity into microwave radiation. If we were to completely divert all biochar production through MAP, it would become essential to account for the excess energy to generate microwave. It would be important to look towards a more renewable energy solution for microwave generation to offset the GHG emissions in the process. However, microwave heating benefits from the fact that it is very efficient only at heating the material which is targeted, microwave chamber walls and exterior surfaces are not directly heated (Gaunt, 2010).

2.5.7.3. Biochar performance

Currently, the predictive capacity for biochar 'performance' does not exist. Moreover best way to optimise the multiple useful characteristics of biochar as a function of feedstock has not been assessed. This is currently inhibiting the realisation and application of this technology (Sohi et al., 2009).

2.5.7.4. MAP biochar and soil interactions

The biochar produced through microwave assisted techniques could have properties very different from that produced through conventional methods. A few of these critera are described which need to be assessed with respect to the biochar soil interactions before fully comprehending the potential of a microwave system (Lehmann, 2007).

2.5.7.4.1. Interaction of biochar with soil microbial communities and plants

The physical, biological and chemical processes that biochar may exert on microbial communities and possibly enhanced nutrient use efficiency, are not yet understood for even biochar produced through conventional methods. The application of biochar to soils has shown higher bacterial growth rates. This was explained as better attachment of the microbial biota and, possibly, physical protection of microorganisms within the pore structure. Similar explanations were put forward for greater levels of infection by mycorrhizal fungi. A greater surface area could result in greater water-holding capacity, but has not yet been investigated (Lehmann, 2007). Thus, the relation between the high stability of biochar, soil organic matter accumulation and apparent enhancement of soil microbial activity needs further research work.

2.5.7.4.2. Cation exchange capacity (CEC)

CEC is an extremely important criterion to understand the interactions of biochar with soil. This value differs with the nature of the biochar. The CEC of freshly produced biochar is relatively low. Only aged biochar have shown high cation retention, as in Amazonian Dark

Earths. At high temperatures (30–70°C), cation retention occurs within a few months. The production method that would attain high CEC in soil in cold climates is not currently known (Lehmann et al., 2007; Sohi et al., 2009). Thus, the process parameters that are instrumental in developing CEC over time as well as the effects that lead to an increase in CEC by addition of fresh (low CEC) biochar require detailed understanding.

2.5.7.4.3. Water holding capacity and aggregate stability

While some studies report positive effects of biochar application on water-holding capacity, the specific mechanism that biochar exerts on water retention, macro-aggregation and soil stability are poorly understood. But these conditions are of critical importance in climate change adaptation, where mitigating drought, nutrient loss and erosion are critical (Sohi et al., 2009). Thus these criteria also become critical to consider in relation to the implementation of large scale microwave technology to produce biochar through pyrolysis.

2.5.7.4.4. Erosion, transport and fate

The loss of biochar through vertical or lateral flow is not quantified, and only recently have studies been initiated to examine movement through soil profiles and into waterways. These processes complicate the task of confining the range of current estimates (from hundreds of years to millennia) of the mean residence time of biochar in soil. Long-term monitoring research stations (analogous to the Waite permanent rotation trial in Australia or the Rothamsted long-term experiments in the UK) are required to adequately assess the long-term stability and dynamics of biochar in soil.

2.6. Agronomic value of biochar

The quantification of the agronomic values of biochar as a product in terms of crop response and soil health benefits is extremely important in the future development of agricultural markets for biochars.

The improvements in soil physical conditions of the soil, namely reduction in tensile strength and higher field capacity water content play a significant role in determining the success of these biochar systems. A pot trial was carried out as a collaborative study in Australia to investigate the effect of biochar produced from greenwaste by pyrolysis on the yield of radish and the soil quality of an Alfisol. Three rates of biochar (10, 50 and 100 t/ha) with and without additional nitrogen application (100 kg N/ha) were investigated. The study showed an improvement in the physical soil environment of this hardsetting soil (Mullins et al. 1990). As a result, a more favourable root growth environment was created and therefore increasing the ability of the plants to utilise the applied N, with the resulting increases in dry matter. The biochar application also increased pH and improved the chemical environment of the biochar-amended soils for the radish plants. Furthermore, the increased dry matter of radish at higher biochar rates could partly be attributed to the increased supply of P and K in the biochar-amended soils when N was no longer limiting (i.e. in the presence of N fertiliser). The biochar used in the investigation was high in both of these nutrients (Chan et al., 2007).

The stability of the carbon in the biochar in soil environment and hence the long-term soil carbon sequestration value is of great interest to scientists. Field experiments are also needed to allow hypotheses to be tested that cannot be addressed under pot trial conditions. These include effects of biochar on soil biology, nutrient leaching/retention, and long-term soil structural changes. Some of the changes to biochar when applied to soils could have long-term significance to biogeochemical processes in soils, e.g. increases in cation exchange capacity in relation to nutrient cycling (Liang et al. 2006; Chan et al., 2007).

For such purposes, various studies have been conducted to ascertain the performance of these biochars in crop development. A commercial scale biochar field trial was established on a farm in Québec, Canada, in May 2008 (Husk and Major, 2011). This trial was carried out to evaluate biochar handling and application methods using standard farm equipment, followed by preliminary agronomic performance comparisons over several years. It was further intended as an initial evaluation of the agronomic value of biochar in northerly climates on relatively high quality agricultural soils. This three year commercial scale biochar trial showed increased plant biomass production from biochar-amended soils. The fact that biochar application also favourably influences the nutritional quality of forage plants was illustrated through plant nutritional analysis methods in addition to its positive effects on biomass production.

The improved plant nutritional values in particular could be critical to positively influencing the economics of biochar use on a wider scale in commercial agriculture. Based on these results it is anticipated that, under similar conditions, dairy farm producers could expect both greater biomass production, as well as greater milk production, from the use of biochar as a soil amendment. These new findings also illustrate the importance of studying the effects of biochar on plants over a period of years.

Environmental problems related to the inefficient use of agricultural nutrients could also be alleviated by the use of biochar as a soil amendment due to higher plant nutrient uptake. Amongst these could be lower nitrous oxide greenhouse gas emissions, as well as reduced run-off and leaching of nitrogen and phosphorus to water (Husk and Major, 2011).

The implementation of biochar systems in commercial agriculture affects its future acceptance and use on a large scale. The quantification of the economic advantages which biochar may offer is required for such adaptation of biochar by commercial farm operators. The preliminary findings in this study point to the possibility of substantial economic advantages for the agricultural use of biochar, in dairy farming in particular (Husk and Major, 2011). It has been recommended further that more detailed investigation be undertaken in determining the effects of biochar on such agricultural economic factors as plant nutrient values, animal production and animal health.

2.7. Commercial role of biochar for agricultural sustainability

Issues such as the population of the planet (approaching 9 to 10 billion people), climate change, soil degradation, resource depletion and C-constrained economies are achieving overwhelming worldwide attention. The emergence of biochar as a product, a service and a concept at this time is of great value to the society. The benefits of biochar need to be cogently and credibly presented which would provide a favourable contextual backdrop for the investment community.

The emerging role of biochar in the bio-based economy would be one of the strongest marketing angles for its commercial success (Bevan and Franssen, 2006). Hence it becomes essential to insure that the investment community really understands the profound importance and implications of a bio-based economy. Therefore, the outline of the extraordinary commercial potential of biochar systems need to be comprehensively presented, while emphasizing the importance of sustainable bio-business. It also needs to be made clear that, as with the first-generation biofuels, the product is defined as sustainable by the raw material sourcing and subsequent production pathway.

The ability of the biochar industries to generate sustainable products and outcomes will derive from fully understanding the issues and complexities. The challenge seems to be that the prevailing economic systems have yet to fully appreciate that biomass is a complex and highly differentiated resource (Ragauskas et al, 2006). If we are to avoid ‘food for fuel’ problems or ‘forest to biochar’ business models, a working understanding of biomass is essential.

2.8. Life cycle analysis of biochar systems

The efficiency of energy production and the ability of the overall production process eventually determine whether the carbon-negative potential of biochar is enhanced or limited and would be used to measure the potential of biochar to limit carbon dioxide and other greenhouse gas emissions. Nonetheless, to properly understand these potentials for biochar, a life-cycle analysis of biochar needs to be examined to fully account for energy efficiency and greenhouse gas (GHG) emissions.

A life-cycle analysis (LCA) is a technique to assess environmental impacts associated with all the stages of a product's life using a “cradle-to-grave” approach. In particular, LCAs are highly useful to avoid unwanted outcomes due to the utilization of a product/technology as well as to facilitate appropriate decision making (Dutta, 2011). Only a few researchers have undertaken this type of analysis, but to date their work supports the conclusion that biochar results in a net reduction in greenhouse gas emissions (carbon-negative) and is an energetically efficient use of biomass (Guant and Lehmann, 2008; Lehmann and Joseph, 2009; and Roberts et al., 2010). One of these studies estimated that the production of biochar was 2 to 5 times more likely to reduce greenhouse gas emissions than if the biomass was used just for the production of energy alone (Gaunt and Lehman, 2008). By carrying out an LCA of the process, it also would help scientists to understand the energy intensity of the process. As a result, the quantification of this energy analysis could be plausible by measuring the energy produced per unit of energy input (known as the energy ratio). This was estimated to be in the range of from 2 to 7, which means that output energy of biochar production is between 2 and 7 times greater than the energy input for its production. This estimated energy ratio for biochar is potentially more energetically efficient than energy production for other biofuels like corn ethanol or even new technologies such as cellulosic ethanol. Figure 2.12 provides an example of the details of the life-cycle analysis of biochar, which was conducted at Cornell University (Roberts et al., 2010).

However to fully authenticate the potential of these biochar systems to provide carbon-negative renewable energy, the LCAs need further verification and more careful study. First, the life-cycle analyses to date are based on research that has yet to clearly demonstrate that biochar applied to all soils can both reduce nitrous oxide (N_2O) emissions from soil and enhance fertility. Research shows that the majority of emission reductions come from the stable carbon in the biochar and that the reduced nitrous oxide emissions and synthetic fertilizer reductions contribute only a small amount to the life-cycle greenhouse emissions reductions (Roberts et al., 2010).

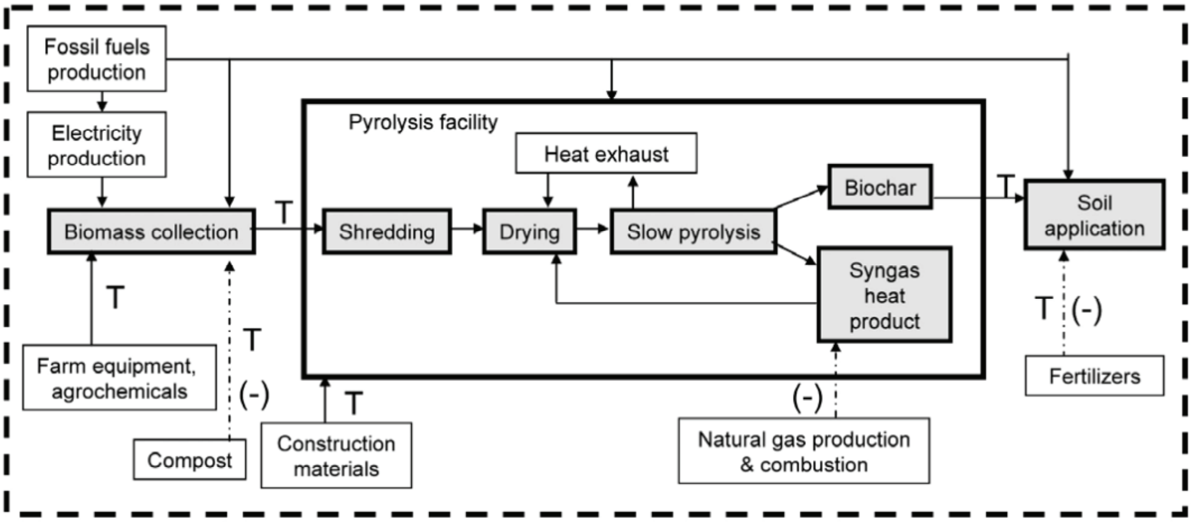


Figure 2.12: Life cycle analysis of a biochar system
(Source: Roberts et al., 2010)

However, other studies that point to both the fertility effect and reduction of other greenhouse gas emissions from the use of biochar as a soil amendment are still limited in number and will require greater research effort to further substantiates results. Second, the energetic analyses of cropping systems, which determine how much energy goes into the production of biomass energy crops, are also limited. Thus, it is difficult to know which biomass cropping systems can reduce fossil fuel use (Schahczenski, 2010). Thus the need of the hour is to resolve these issues during future life-cycle studies so as to be able to measure the full extent of biochar for its carbon-negative fuel capabilities.

2.9. Economic analysis

An economic analysis is of utmost importance to ascertain the potential of biochar systems to provide real-world improvements for greenhouse gas emissions. The value assigned to the biochar is based on three components: (i) the P and K content of the biochar, (ii) the improved fertilizer use efficiency, and (iii) the GHG emission reduction. For valuing the GHG offsets, there are two approaches one can use: either to value only the stable C in the biochar, or to value the total life-cycle GHG emission reduction in the entire biochar system (Roberts et al., 2010).

An analysis of this kind, carried out as a collaborative research by universities in United States and Australia, demonstrated that sustainable biochar production (with addition to soils) has the technical potential to make a substantial contribution to mitigating climate change (Woolf et al., 2010). This in-depth study demonstrated that 1.8 Gt (Giga tonne) CO_2e (carbon dioxide equivalent) annually, and of 130 Gt CO_2e of emissions could be mitigated over the course of a century at current levels of feedstock availability, while preserving biodiversity, ecosystem stability and food security. The model predicts that maximum avoided emissions of 1.0 – 1.8 Gt CO_2e per year are approached by mid-century and that, after a century, the cumulative avoided emissions are 66 – 130 Gt CO_2e. The net carbon sequestered as biochar has been predicted to contribute to half of the avoided emissions while 30 % is attributed to replacement of fossil-fuel energy by pyrolysis energy and 20 % to avoided emissions of CH_4 and N_2O (Woolf et al., 2010).

Feedstock collection and pyrolysis have been cited as the primary costs of biochar production while the feedstock transport, biochar transport, and biochar application have small contributions to the total costs. Another economic analysis carried out by Roberts et al., (2010) used the life-cycle carbon emission reduction to calculate the GHG offset for feedstocks of corn stover, switchgrass and yard waste. The LCA methodology was chosen as it was expected that it would add more value to the biochar because it incorporates the emission offsets from avoided fossil fuels, fertilizers, reduced soil N_2O emissions, etc. Two revenue scenarios (low and high) were considered, where values of \$20 and \$80/tonne CO_2e were used, based on the IPCC recommendations. The economic analysis indicated that the uncertainty in the value of sequestered CO_2e creates a large variability in the net profitability.

The results of this study indicated corn stover to be of moderate economic potential due to its high revenue at +\$35/tonne. The switchgrass scenarios were found to be non profitable in the low revenue scenario while it had marginal potential for profitability (+\$8/tonne) in the high revenue scenario. Despite the revenues from the biochar and energy products for all feedstocks, the overall profitability is hindered by the cost of feedstock collection and pyrolysis, even when carbon is valued at \$80/tonne CO_2e, the higher revenue scenario. A breakeven analysis reveals that the minimum CO_2e price would need to be \$40 /tonne CO_2e for late stover, \$62/tonne CO_2e for switchgrass and only \$2/tonne CO_2e for yard waste (Roberts et al., 2010).

Therefore the overall economic results highlight that the waste stream feedstocks such as yard waste provides the maximum potential revenue of net +\$69 and +\$16/tonne for the high and low scenarios respectively. Other biomass waste resources that may be promising for biochar production are livestock manures such as poultry, horse, and cattle (Roberts et al., 2010). However, the challenge is to decide upon a feedstock with minimum moisture content. The primary barriers to the economic viability of pyrolysis-biochar systems are the pyrolysis process and the feedstock production costs. A diversified farm system with mixed feedstocks for biochar production may bring sustainability benefits that exceed those of a single feedstock alone which should be evaluated in future analyses.

Connecting text

Considerable research has been devoted towards determining the kinetics of the pyrolysis of lignocellulosic biomass such as wood residues and agricultural waste with the goals of increasing the efficiency and yield of the end product of biochar. Among the different methods available, microwave assisted pyrolysis has proven to be very efficient in terms of energy utilization. In the following study, an attempt has been made to develop a finite element model (FEM) in order to couple electromagnetic heating, combustion, and heat and mass transfer phenomena during microwave pyrolysis. 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.

Chapter 3

Finite Element Modelling of Microwave Pyrolysis of Biomass

Abstract

In this study, a finite element model (FEM) has been developed in order to couple electromagnetic heating, combustion, and heat and mass transfer phenomena during microwave pyrolysis. The resulting sets of partial differential equations were then solved simultaneously using the COMSOL Multiphisics software package. The simulation results showed that parameters such as temperature, time and power densities play a major role in the extent of pyrolysis and the products formed. The process was optimized through the simulation with an optimum temperature of 425°C and 7.5W/g power density and duration of 6 min for complete pyrolysis. The experimental validation indicated that process parameters such as pyrolysis temperature and time play a major role in the formation of biochar. However, temperature control was extremely difficult during the MAP trials and there was uneven heat distribution found within the biomass sample. This numerical modelling and simulation approach helped in the visualization of the process. It can eventually be used to study and optimize the production of biochar as well as design of a microwave pyrolysis reactor for the maximization of biochar yields.

Keywords: Biochar, Pyrolysis, Numerical modeling, Process optimization

3. 1. 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 leads to 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. One of the methods proven to have measured up to good efficiency standards is the use of microwave or microwave assisted pyrolysis methods to form biochar and other useful volatiles. There is a growing interest in the scientific world regarding the research of modeling and simulation studies involved in the production of biochar as well other by products in the process of pyrolysis. Numerical and modeling studies have been conducted which focus on estimation of optimum parameters in 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).

There is poor understanding of the mechanisms involved in the application of electromagnetic energy for the pyrolysis of biomass and the actual energy distribution inside the biomass when subjecting them to electromagnetic field. The electromagnetic field distribution inside the microwave oven can be traced out by solving the Maxwell's equations (Dev et al., 2008c). Finite Element Method (FEM) is commonly used for solving Maxwell's equations to get the energy distribution in a complex object or within a multimode cavity and it is capable of simulating power density distribution in 3-D space (Fu and Metaxas, 1994; Zhou et al., 1995).

FEM technique competes very favourably with the other numerical methods, as it is based on reducing the Maxwell's equations to a system of simultaneous algebraic linear equations (Delisle et al., 1991). FEM can readily model heterogeneous and anisotropic materials as well as arbitrarily shaped geometries. It can also provide both time and frequency domain analyses which are important to microwave heating problems like field distribution, scattering parameters and dissipated power distribution for various materials and geometries (Dai, 2006).

Taking into account all the above mentioned facts, in this study, a Finite Element Model (FEM) of the microwave pyrolysis of lignocellulosic biomass was developed and simulation studies were conducted for biomass subjected to 3 to 15 minutes (with increments of 3 minutes) of heating under 2450 MHz and power densities of 5 W/g, 7.5 W/g and 10 W/g in order to visualize and investigate the energy distribution within the biomass. The objective was to maximize the production of biochar.

3.2. Materials and methods

In this study, the mechanisms involved in production of biochar by microwave heating were investigated. A Finite Element Model was built in order to simulate the microwave heating of biomass and to predict the optimal conditions for the maximization of biochar using the process.

3.2.1. Microwave Pyrolysis Set-up for simulation

The pyrolysis bioreactor system made of quartz used for the simulation (to be custom built at a later stage) is shown in Figure 3.1. It consisted of three parts: an upper cylinder, a lower cylinder and a sample stand. The upper cylinder has 40 mm inner diameter and a length of 90 mm length. This was connected to the lower cylinder with an inner diameter of 50 mm and 42 mm height by a taper ground joint. The sample stand had a diameter of 35 mm and 25 mm height. A wood sample of 30 mm diameter and 75 mm length was mounted on the sample stand. The air inside the reactor is purged with nitrogen with a flow rate of 0.003 l/s to create an oxygen free inert atmosphere using two quartz tubings 6.3 mm diameter and 25.4 mm length. The wood sample was subjected to microwave heating at 2.45 GHz frequency with power densities of 5 W/g, 7.5 W/g and 10 W/g at time intervals of 3 mins starting from 3 to 15 min for simulation purposes.

3.2.2. 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 are dependent on the temperatures at which the reaction rates take place (Willner et al, 2005).

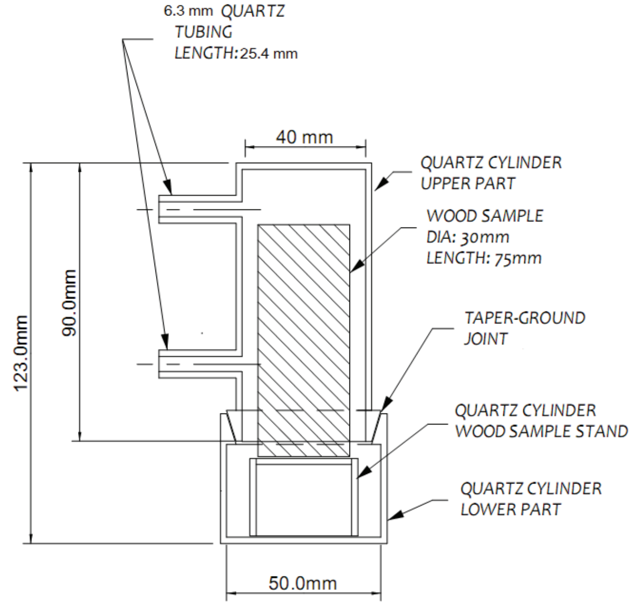


Figure 3.1: Microwave Pyrolysis Bioreactor Setup

The three step mechanism described by Di Blasi (1998) was used as the kinetics model for modelling and simulation of the microwave 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 consisting of the three step mechanism model described by Di Blasi (1998) based on Arrhenius equations wherein A1, A2 and A3 represent the activation constants and E1, E2 and E3 represent the activation energies of gas, tar and char respectively.

Three-step mechanism:

$$\begin{tikzcd} & CHAR \\ WOOD \arrow[ur, "k_3"] \arrow[r, "k_2"] \arrow[dr, "k_1"] & TAR \\ & GAS \end{tikzcd}$$

The Kinetic constants for this scheme are:

$A1=1.30 \text{ x}10^{8} \text{ s}^{-1}$, $E1= 1.40 \text{ kJ mol}^{-1}$

$A2=2.00 \text{ x}10^{8} \text{ s}^{-1}$, $E2= 1.33 \text{ kJ mol}^{-1}$

$A3=1.08 \text{ x}10^{7} \text{ s}^{-1}$, $E3= 1.21 \text{ kJ mol}^{-1}$

This mechanism has been applied to model large particle biomass pyrolysis. This scheme is taken into account in 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.

3.2.3. Finite element modeling and simulation

A 3D Finite Element Model was developed using COMSOL Multiphysics version 3.5a (COMSOL Inc., USA) software package to simulate the Microwave pyrolysis process for a regular domestic multimode microwave oven configuration. The meshed structure of the microwave cavity along with the bioreactor and wood sample is shown in Figure 3.2. The cavity dimensions were taken as 267 mm × 270 mm × 188 mm. A custom built computer with two AMD Opteron quadcore 2.4 GHz processors and 32 GB primary memory was used to run the simulations.

3.2.4. Mathematics of the Model

3.2.4.1. Electromagnetics

The Maxwell's equations that govern the electromagnetic phenomena evolving in a given configuration resolved in 3D space were solved for the Electric field intensity (E) (Vm^{-1}) and H Magnetic Field Intensity (Am^{-1}) (Dai, 2006). The dynamically changing dielectric constant ε' and loss factor ε" were calculated using equations derived from the measurement of dielectric properties.

The time average power dissipated (P_{av}) in each element in a dielectric material was obtained by integrating the poynting vector (P_c) over the closed surface S for each tetrahedral element (Equation 3.1- 3.2) (Jia and Jolly, 1992).

$$P_{av} = -\frac{1}{2}\int_S P_c.dS \qquad (3.1)$$

Where

$$P_c = E \times H \qquad (3.2)$$

Volumetric heat generation, Q can be expressed in terms of power intensity in three orthogonal directions as shown in Equation (3.3) (Lin et al., 1989).

$$Q = \frac{\partial P_{av(x)}}{\partial V} + \frac{\partial P_{av(y)}}{\partial V} + \frac{\partial P_{av(z)}}{\partial V} \tag{3.3}$$

Where are the suffixes x, y and z which indicate time average power dissipated in the corresponding directions and V is the volume in which the heat is generated.

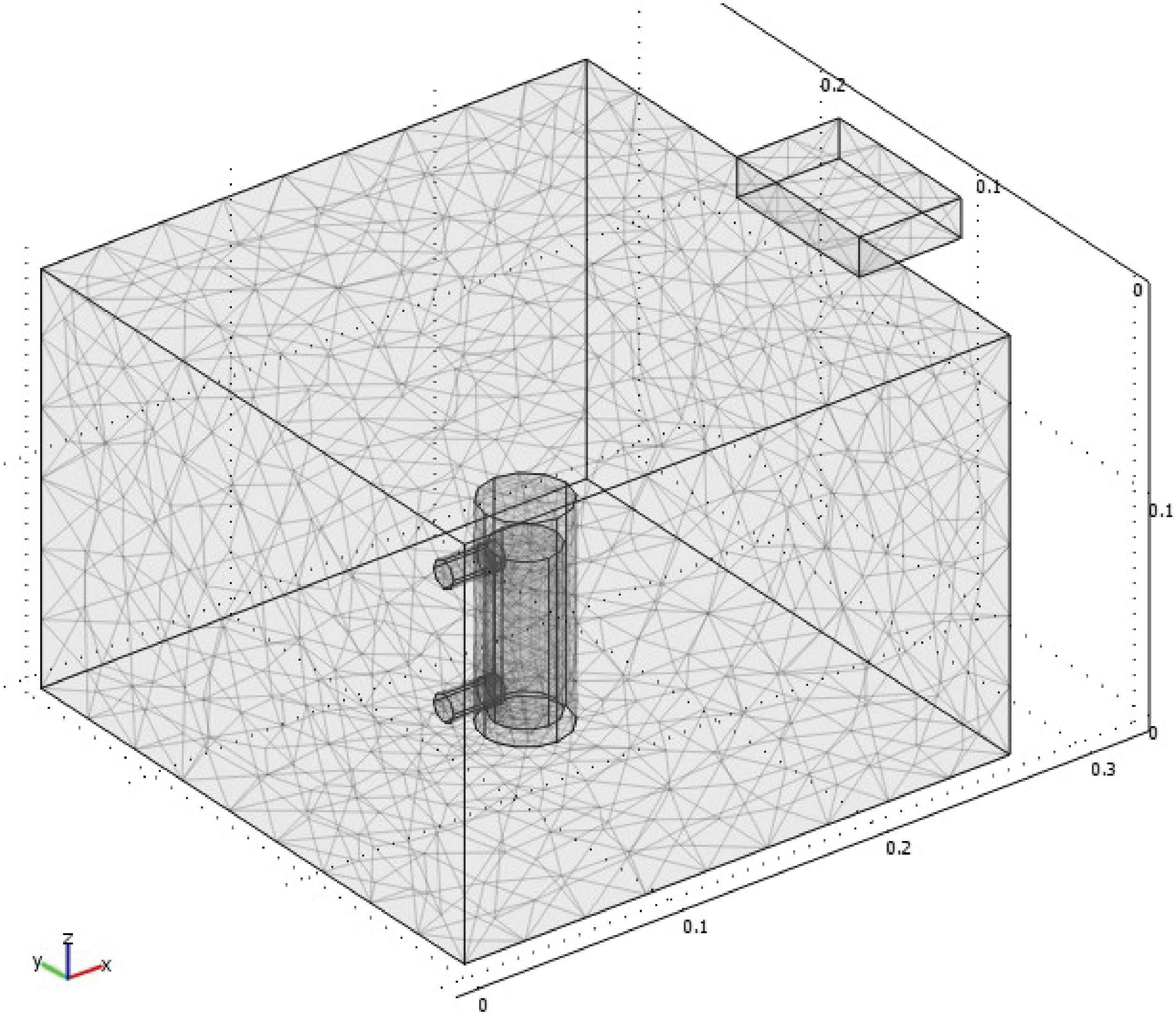


Figure 3.2: Finite Element Mesh Structure

3.2.4.2. Boundary conditions

Perfect Electrical Conductor (PEC) boundary condition ($n \times E = 0$) was used for the walls of the cavity and Perfect Magnetic Conductor (PMC) boundary condition ($n \times H = 0$) was used for the symmetry boundaries (Fu et al. 2004).

Boundary conditions at the port were taken as in Equations 3.4 to 3.6:

$Hy = A \cos(\Pi x/\alpha) \cos(\omega t + \beta y)$ (3.4)

$Ez = (\omega\, \mu 0\, \alpha/ \Pi)\, A \sin(\Pi x/\alpha) \sin(\omega t + \beta y)$ (3.5)

$Hx = (\beta\, \alpha/ \Pi)\, A \sin(\Pi x/\alpha) \sin(\omega t + \beta y)$ (3.6)

Where the x,y and z indicate the corresponding axes and A is the cross sectional area of the waveguide, ω is the phase angle and α & β are arbitrary constants.

3.2.4.3. Heat transfer

For an incompressible food material heated under constant pressure, the thermal energy equation is given by equation (3.7) (Zhou et al., 1995)

$$\rho C_p \frac{\partial T}{\partial t} = \nabla.(K \nabla T) + Q \qquad (3.7)$$

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 and T is the absolute temperature in Kelvin. 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.

3.2.5. Experimental validation

The experimental validation of the simulation results was carried out in a custom-built microwave pyrolysis unit within a regular domestic multimode microwave oven operating at 2.45 GHz, with cavity dimensions of 205 mm × 335 mm × 180 mm located in the laboratories of the Department of Bioresource Engineering, McGill University. The quartz pyrolysis reactor used in the simulation (Figure 3.1) consisted of three parts: an upper cylinder (40 mm inner diameter, 90 mm height), a lower cylinder (50 mm inner diameter, 42 mm height) and a sample stand (35 mm diameter, 25 mm height). Through two quartz tubes, one inlet, one outlet (each 6.3 mm diameter, 25.4 mm length) air inside the reactor was purged with nitrogen at a flow rate of 0.003 L s^{-1} to create an oxygen-free inert atmosphere.

The reactor was placed in the center of the microwave chamber and the two quartz tubes connected to the nitrogen purge line. A K-type thermocouple was inserted into the reactor through the gaseous product release tube and embedded in the biomass to monitor the sample temperature continuously throughout the experiment. The gaseous product release tube was connected to a condensation unit cooled continuously with water at ⩽10°C. After each run, the reactor was cooled to ambient temperature under a nitrogen atmosphere. The biochar remaining in the reactor was weighed to compare yields. The biomass used for the simulation was maple wood (30 mm diameter, 75 mm length) with a moisture content of ≃ 7%. The wood sample was then subjected to microwave heating at a 2.45 GHz frequency at the prescribed power densities.

In order to validate the simulation model, a central composite response surface design was used (Table 3.1) with pyrolysis temperature and holding time as the two factors. Due to the difficulty in the measurement technique, pyrolysis temperature was measured within an approximate range of $\Delta T \approx 50°C$.

Table 3.1: Central composite response surface design for validation of simulation model

Runs	Pattern	Time (min)	Temp
1	A0	350	3
2	a0	250	3
3	0	300	3
4	+−	350	1
5	0A	300	5
6	−+	250	5
7	0	300	3
8	0a	300	1
9	−−	250	1
10	++	350	5

3.3. Results and Discussion

3.3.1. Simulation results

This simulation study was carried out at 2.45 GHz microwave frequency for a range of temperatures 300ºC to 500ºC with power densities of 5 W/g, 7.5 W/g and 10 W/g at time intervals of 3 min starting from 3 to 15 min. The initial concentration of the wood or biomass sample was taken to be 4000 mol/m^3. The results of the simulation indicating the temperature distribution inside the biomass at the end of 15 min of microwave irradiation duration is shown in Figure 3.3.

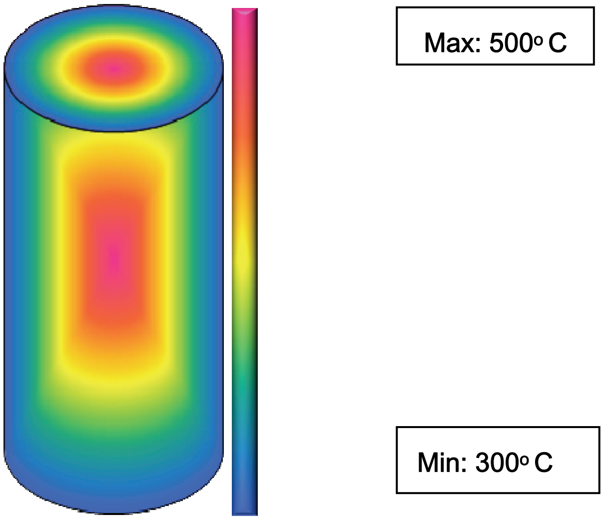


Figure 3.3: Simulation of Microwave heating of biomass sample with variation in temperature

Given the kinetic parameters discussed previously, the resulting numerical model for the pyrolysis of the lignocellulosic biomass, at a temperature of 300ºC, showed minimal amount of products formed in the reaction as shown in Figure 3.4. The wood sample did not show any significant variation from its initial concentration during the pyrolysis process. When the temperature was raised to 350ºC, the model showed a visible change in concentration of the biomass, thereby implying the initiation of the pyrolysis reaction. In Figure 3.5, it was seen that the wood sample underwent a decrease in concentration till about 0.6 min of the reaction period and thereafter remained constant. Product formation was observed at this stage of the model when compared to the one taking place at 300ºC. All three phases of products were formed at this temperature although char and syngas formation went only till 0.6 min while concentration of tar increased till the wood sample completely reacted.

At a higher temperature of 400ºC, 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/mg in 0.5 min as seen in Figure 3.6 and remained constant with further increase in reaction time. The production of syngases in this reaction remained quite low throughout the pyrolysis of the biomass. At the temperature of 425ºC, it was as indicated in Figure 3.7 that the wood sample got converted to its products in less than 0.5 min and the highest amount of tar and char formation was observed at this temperature. The yield of biochar was a little more than 1500 mol/mg in the reaction showing about 40% conversion of the biomass, which is a significant degree of conversion of the biomass into char.

An interesting trend was noticed at the temperature of 450ºC in Figure 3.8, though the tar formation continued to increase with respect to time, the concentration of char was reduced from that at 425ºC. In addition to this phenomenon, the complete pyrolysis of the biomass occurred faster (less than 0.2 min) than at the previous temperatures observed in this model. Finally at the temperature of 500ºC, the complete conversion of the biomass through pyrolysis occurred instantaneously. The char yield at this temperature was less than at 425 ºC while approximately 60% of the biomass was seen to get converted into the liquid product called tar (Figure 3.9).

This model also considered the effect of different power densities on the process of pyrolysis of the biomass at different ranges of time. At power density of 5W/g, no reaction was observed for 3 min of pyrolysis. The desired temperature of 425 ºC was reached in 6 min of the reaction and at 9 min; the entire biomass had converted into the pyrolyzed products. The change in temperature or ΔT for this time period was observed to be about <50 ºC. According to the observations made through this model, the temperature of 425 ºC was achieved in 4 min into the reaction for the power density of 7.5W/g. The entire wood sample was pyrolyzed in 6 min in this case and ΔT for this reaction to take place was around 80 ºC. At the power density of 10W/g, it took the biomass only about 2 min to reach its desired temperature of 425 ºC and in a further 1 min period, the whole biomass was pyrolyzed to the different products. This rate of reaction was much faster, occurring at a ΔT of 120 ºC. Moreover, hot spots were created within the biomass caused through uneven heating.

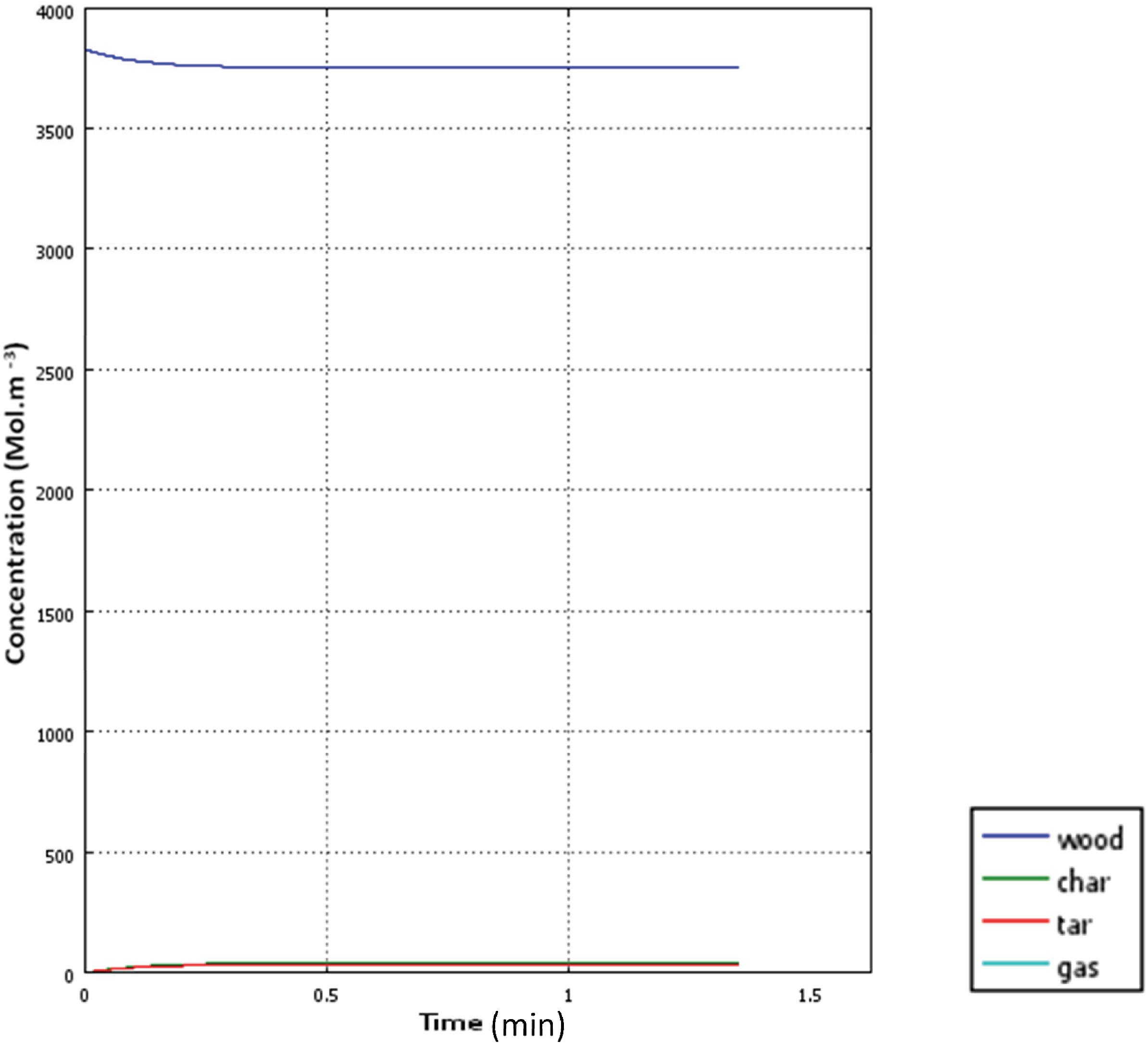


Figure 3.4: Concentration (mol/m^3) vs. Time (min) profiles of the microwave pyrolysis at the temperature of 300ºC

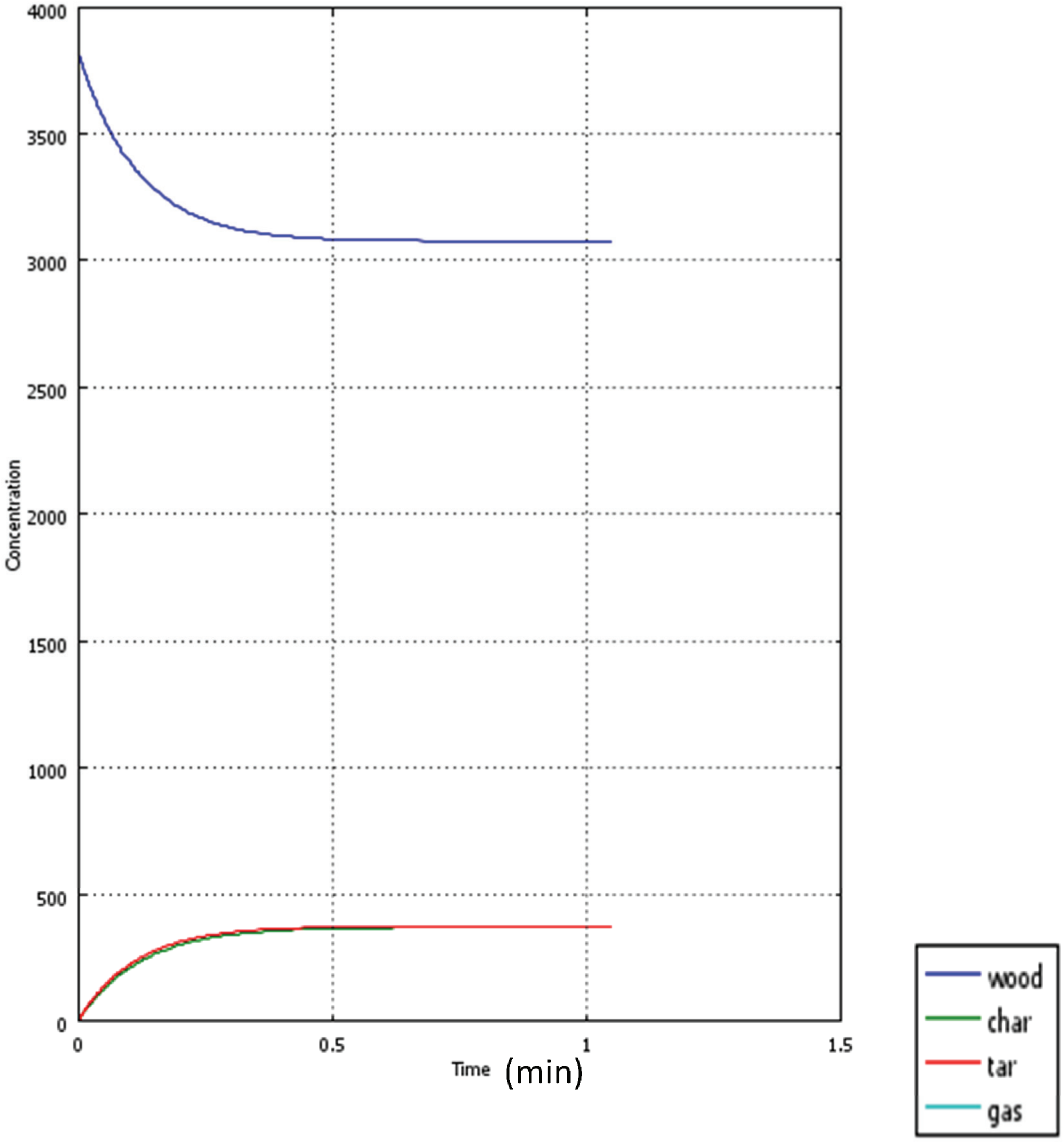


Figure 3.5: Concentration (mol/m^3) vs. Time (min) profiles of the microwave pyrolysis at the temperature of 350ºC

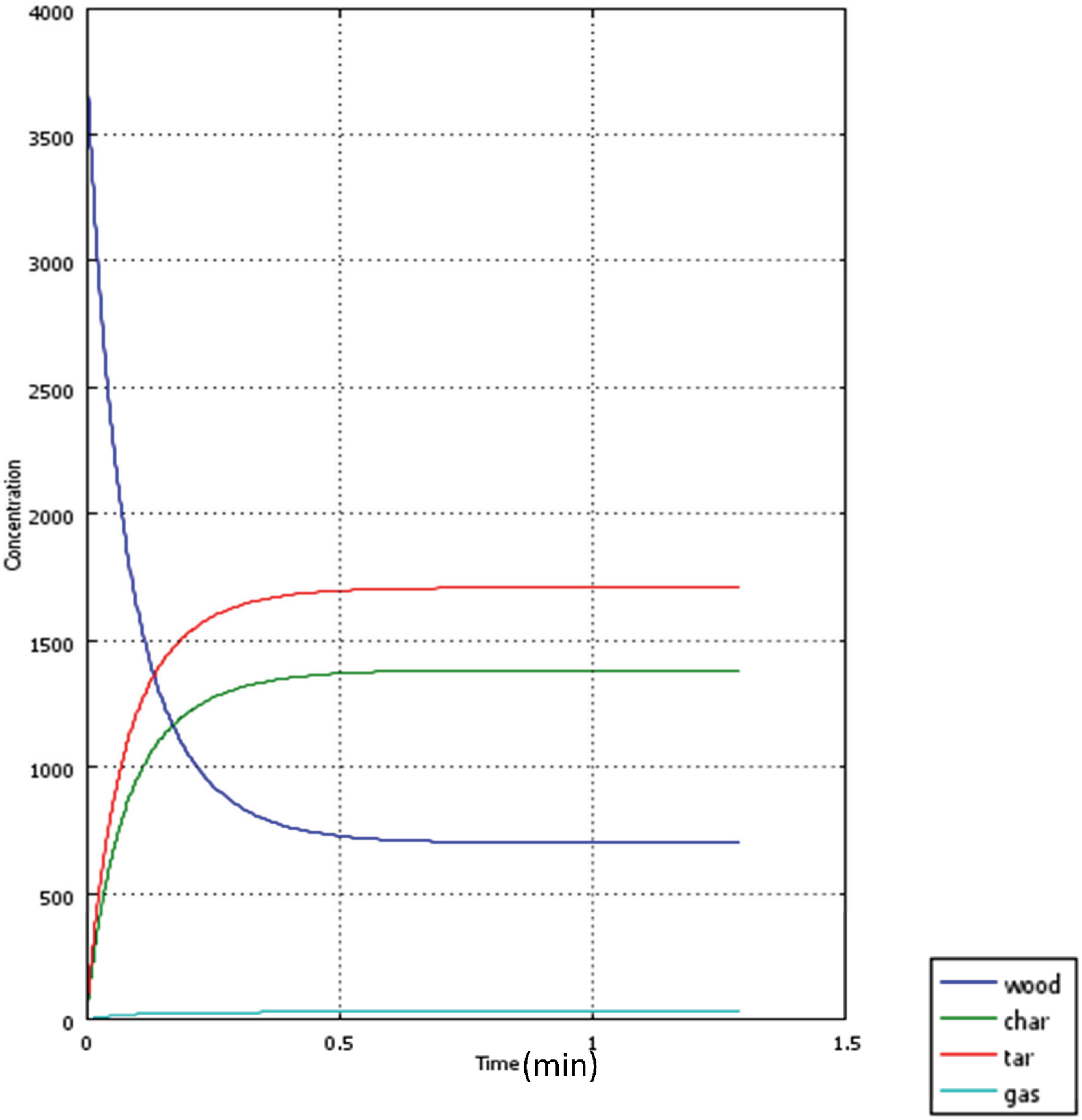


Figure 3.6: Concentration (mol/m^3) vs. Time (min) profiles of the microwave pyrolysis at the temperature of 400ºC

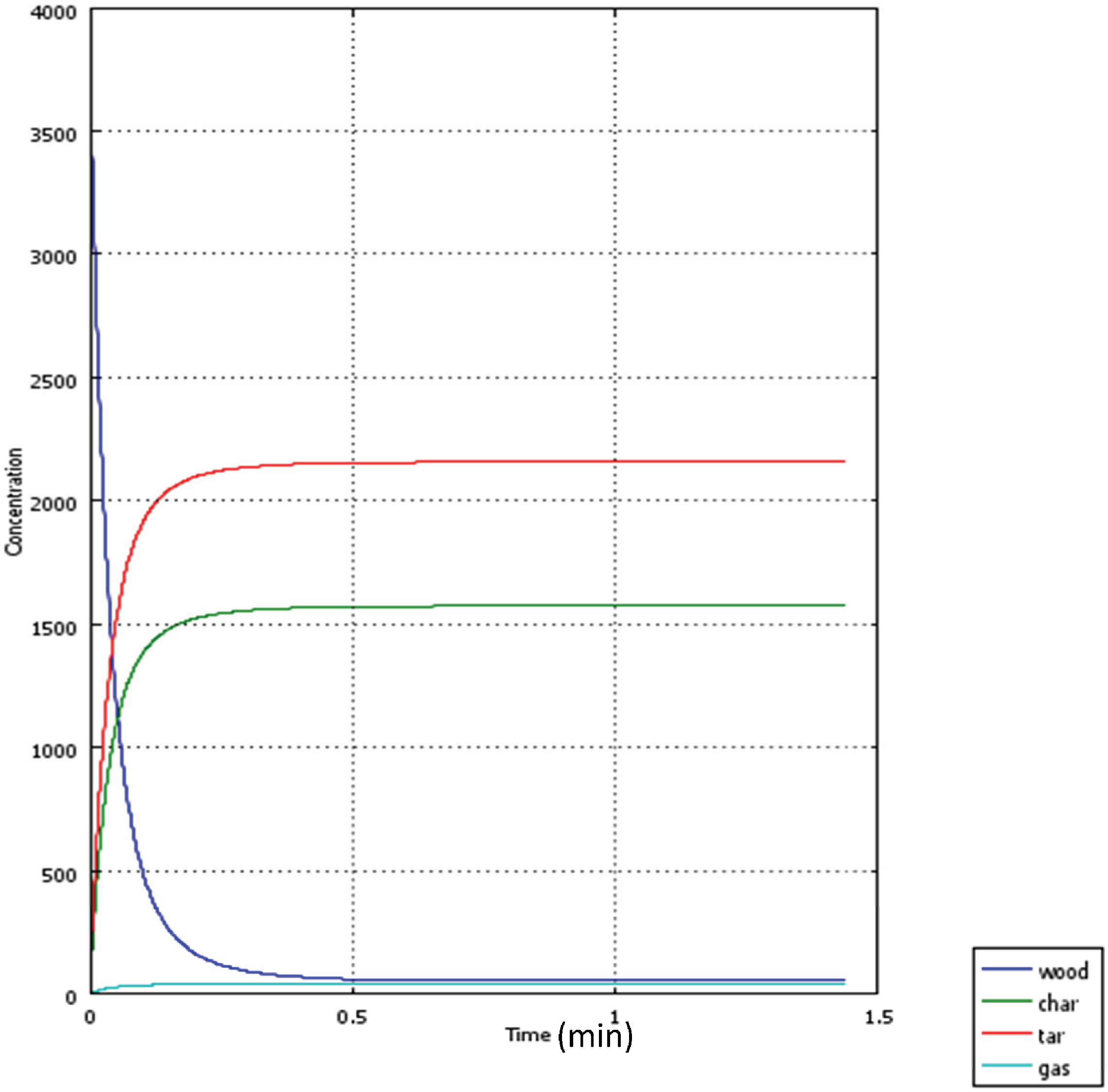


Figure 3.7: Concentration (mol/m^3) vs. Time (min) profiles of the microwave pyrolysis at the temperature of 425ºC

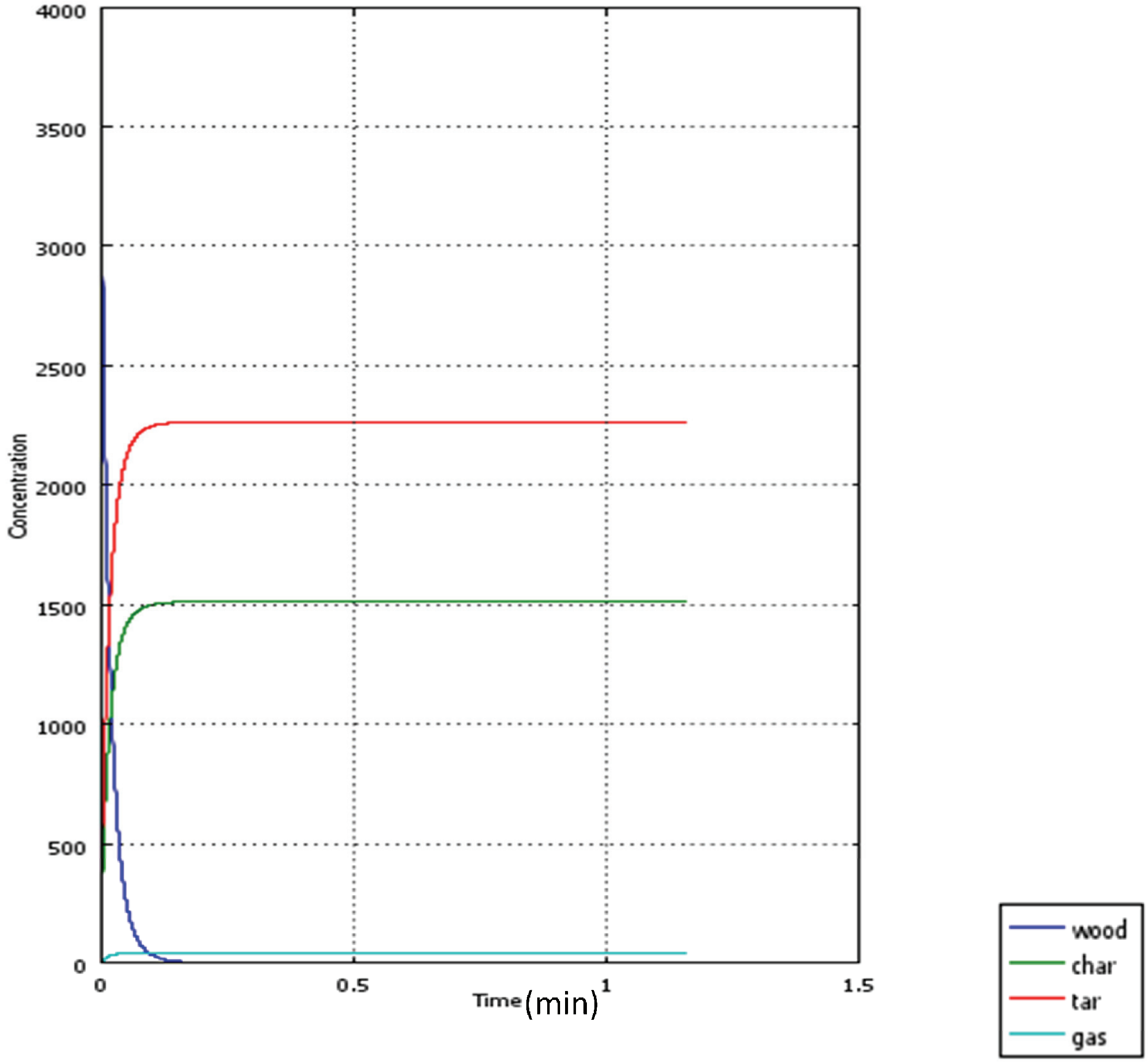


Figure 3.8: Concentration (mol/m^3) vs. Time (min) profiles of the microwave pyrolysis at the temperature of 450ºC

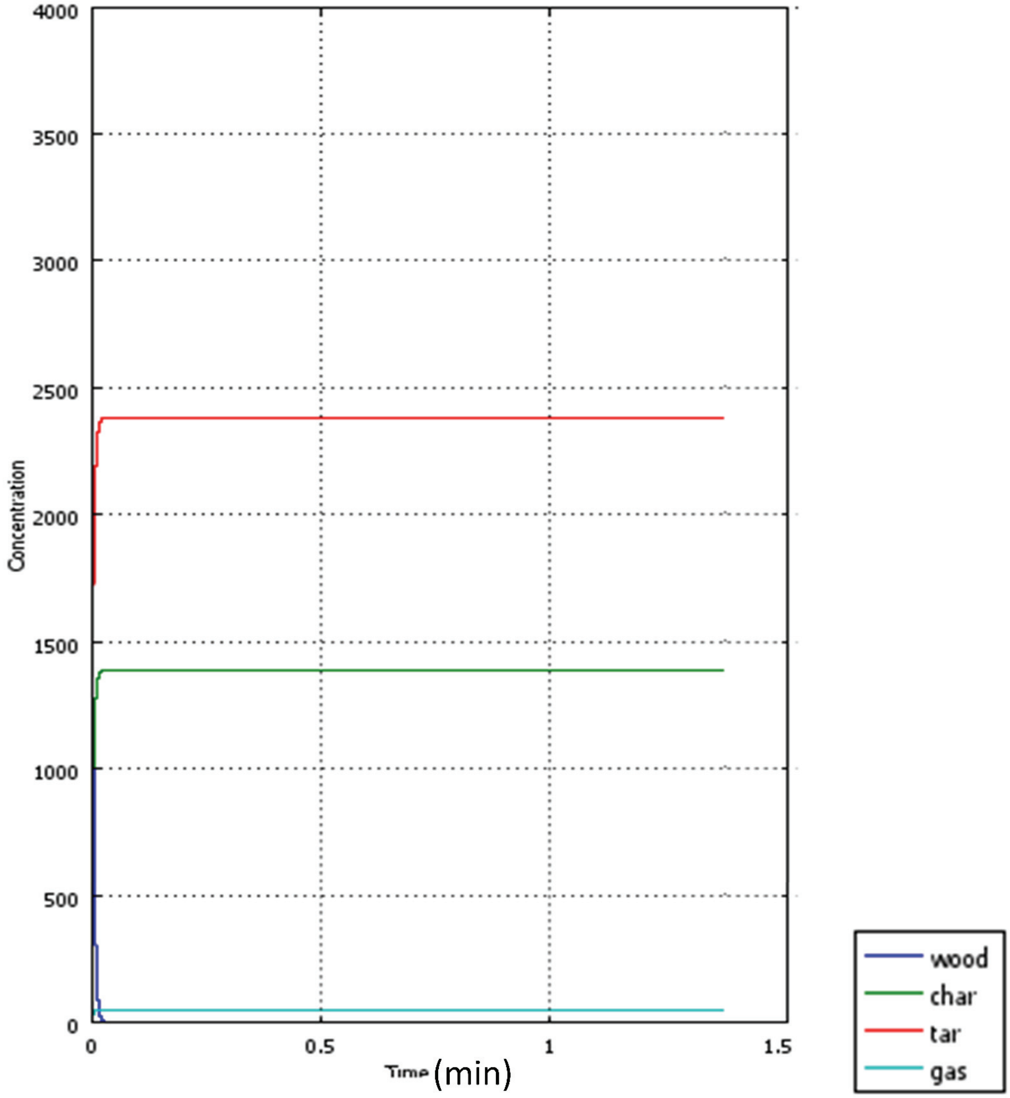


Figure 3.9: Concentration (mol/m^3) vs. Time (min) profiles of the microwave pyrolysis at the temperature of 500ºC

3.3.2. Results of the experimental validation

The major challenge faced during the validation of the simulation of microwave pyrolysis was non uniform heating. This resulted in the creation of hot spots in the biomass during the process. During the validation trials, the pyrolysis was hard to control due to the non uniformity of heating and the generation of sparks in the cavity. This led to severe instabilities in the temperature control of the process as shown in Figure 3.10. The measurement of temperature interfered significantly with the distribution of the electromagnetic field within the cavity and resulted in uneven heat generation inside the biomass sample (Appendix 1). Moreover, microwave energy leaked out of the cavity and was measured to be in excess of ±0.8mW/cm^2 in front of the experimental test bench. This was considered to be a major safety concern. Moreover, the generation of sparks in the cavity did not make it feasible to measure temperatures above 350°C.

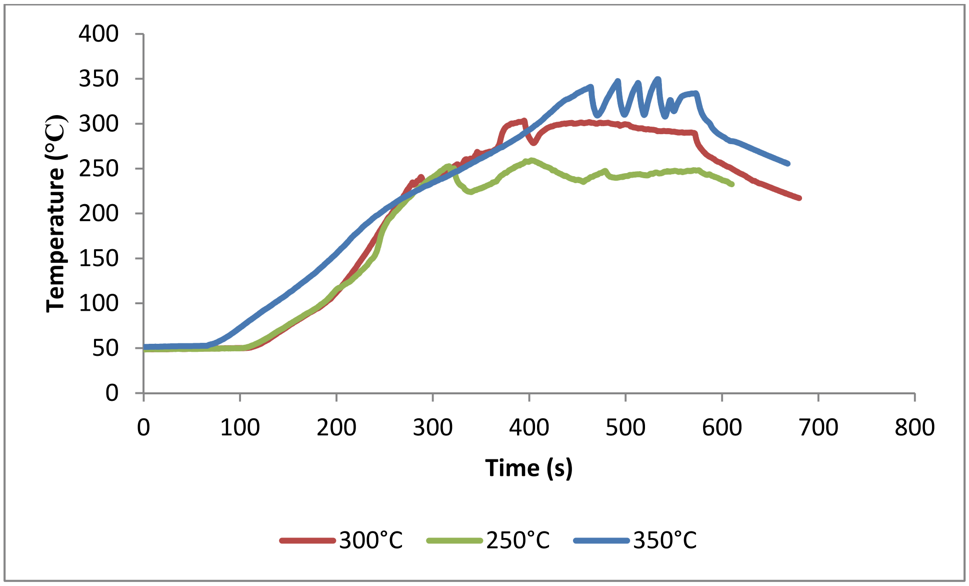


Figure 3.10: Variation of process temperature during pyrolysis of the wood samples during experimental validation of simulation model

According to the simulation results, at the optimal power density of 7.5 W/g, the biochar yields of the maple wood biomass were found to increase with increase in duration of the pyrolysis and decreased with increasing temperature for maximization of biochar. The highest biochar yield of 65.24% was found at the pyrolysis temperature and time of 250°C and 5 min respectively. The regression analysis for the biochar yields obtained through this validation indicated that the observed values were in good agreement with the predicted yields for $R^2= 0.98$ ($P\leq 0.01$) as shown in Figure 3.11. The analysis of variance (ANOVA) for the regression analysis is provided in Table 3.2. An F test was carried out to determine the effect of the two process parameters and their interactions. This indicated that pyrolysis time had a greater effect on the biochar yield than pyrolysis temperature as shown in Table 3.3. The model presented in Equation 3.8 can be used to predict biochar yield% values as functions of temperature (T) in °C and time (t) in min.

$$\mathrm{Yield\%} = 20.91 - 40.77 * \mathrm{T} + 11.81 * \mathrm{t} \tag{3.8}$$

A response surface optimization analysis was carried out to evaluate the optimum conditions for the maximization of biochar yields as shown in Figure 3.12.

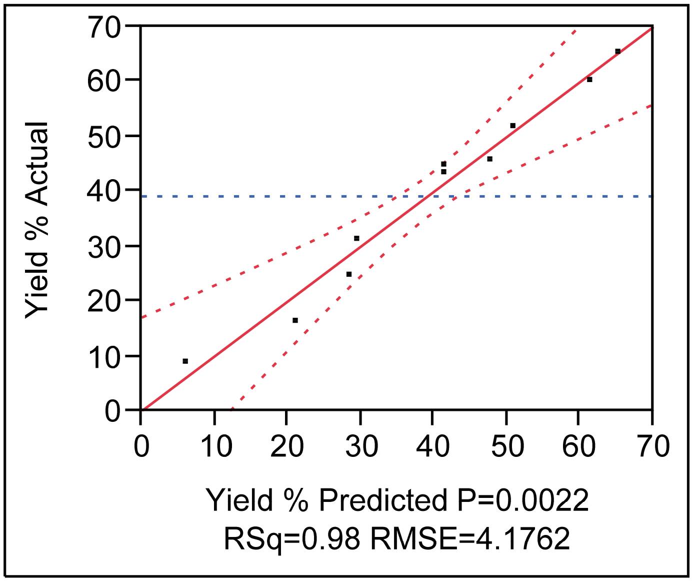


Figure 3.11: Regression model of experimental yield% vs. predicted yield % for microwave pyrolysis of maple wood biomass

Table 3.2: Results from the Analysis of variance (ANOVA) performed on the biochar yield obtained through microwave pyrolysis of biomass

Source	DF	Sum of squares	Mean square	F ratio	Prob > F
Model	5	3021.975	604.395	34.6537	0.0022
Error	4	69.764	17.441		
C. Total	9	3091.739			

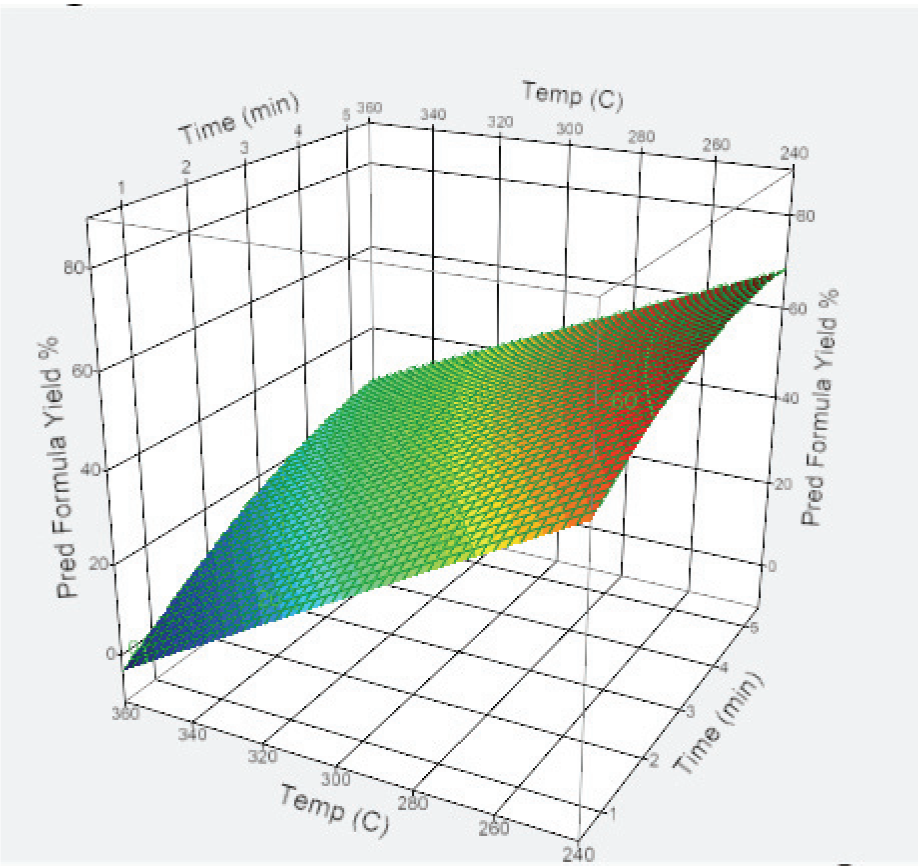


Figure 3.12: Response surface plot of biochar yield for microwave pyrolysis as a function of process temperature (Temp (C)) and duration (Time (min)) for validation of simulation results

A better understanding of the temperature distribution within the biomass during microwave pyrolysis was achieved by cutting the biomass and obtaining a cross section of the sample after 1 min of microwave treatment. Figure 3.13 clearly indicated the presence of volumetric heating leading to higher temperatures at the core of the biomass than at the surface. However, as seen from Figure 3.13, hot spots were found due to uneven heating and the temperature reached within the sample was much lower than the simulation results shown in Figure 3.3. These indicate the effect of the inaccuracy in the temperature measurement. These observations were taken into account in the further development of the design of a more accurate temperature measurement technique for MAP (Appendix 1).

Table 3.3: Analysis of variance (ANOVA) ($P \leq 0.05$) of effects of process parameters on biochar yields obtained through microwave pyrolysis of biomass sample (Probability value with an asterix (*) implies significance of parameter)

Source	Nparm	DF	Sum of squares	F ratio	Prob > F
Temp (C)(250,350)	1	1	220.87557	12.6642	0.0236*
Time (min)(1,5)	1	1	334.84727	19.1989	0.0119*
Temp (C)*Time (min)	1	1	20.28414	1.163	0.3415
Temp (C)*Temp (C)	1	1	0.04188	0.0024	0.9633
Time (min)*Time (min)	1	1	24.61067	1.4111	0.3006

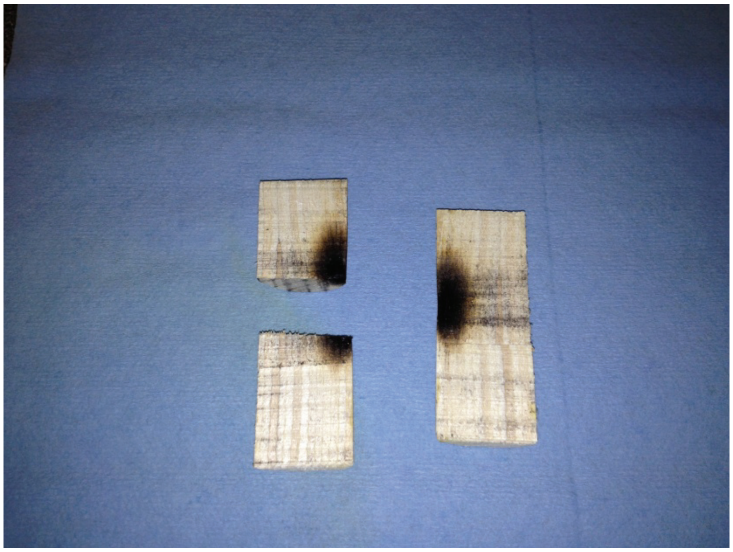


Figure 3.13: Cross-sectional view of biomass sample after 1 minute of microwave assisted pyrolysis

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 (Masek, 2009, Di Blasi et al., 2001, Wang et al., 2009).

The mass loss curves were determined by taking into account the loss in the mass of the solid residue. It has been observed by researchers, hemicelluloses decompose at 225–325 ºC, cellulose at 325–375 ºC, whereas lignin decomposes gradually over the temperature range of 250–500 ºC. 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. At low temperatures, residence time of solids is longer than of volatiles. In such cases, char yields are often higher than the other products (Di Blasi et al., 2001).

3.4. Conclusion

Simulation results from this study showed highest yield of biochar at an optimum temperature of 425 ºC during the process of pyrolysis. These results were based on the kinetics of the model taken into consideration. It also showed that the rate of reaction would vary at this temperature for different power densities applied to the microwave set up. At a power density of 5W/g, negligible reactions were observed in 3 min of the pyrolysis process. The desired temperature was reached in 6 min of the reaction time. The pyrolysis of the entire biomass sample took place in 9 min after reaching the set temperature. A similar trend was observed for 7.5W/g, wherein, the optimum temperature of 425 ºC was reached in 4 min of the reaction, and the sample was pyrolysed in 6 min completely. The optimum temperature was attained in less than 2 min for power density of 10W/g. However it was a very unstable reaction with temperature variation of 120 ºC to reach the final products and produced hot spots. This research illustrated the potential for using microwave assisted technology for the higher yield of biochar through pyrolysis of a given biomass. The experimental validation of the simulation model indicated the trend of increase in yields of biochar with increasing pyrolysis holding time and decrease in temperature. The process temperature was difficult to control inside the microwave environment. This led to inaccuracies in temperature measurements. Through this simulation and modelling study, the kinetics of the different pyrolysis parameters as well as further attempts of optimizing char yield through modulation of time, temperature and power densities of the reaction is highlighted. The proposed numerical simulation model and its validation was used to carry out further investigations into the effect of microwave pyrolysis and process parameters on biochar yield. These types of studies are helpful to further look into designing a microwave assisted bioreactor which aims at higher yields of biochar as well as for better understanding of the process involved.

Connecting text

The results of the Finite Element Modelling (FEM) were instrumental in visualizing the heat transfer mechanism inside the Maplewood biomass during the microwave pyrolytic reactions. However evidence of non uniform heating resulting in the creation of hot spots in the biomass was also observed during the microwave pyrolysis process. Hence the next objective of this thesis was to minimize the non uniformity of the heat transfer as well as better control of the process in the microwave pyrolysis reactor. Literature review in this direction has indicated that the property of selective heating in the form of microwave receptor has a bearing on the yield and the quality of the pyrolysis products, which could determine the process efficiency and the formation of desired compounds. Hence the application of microwave receptors could be a solution to the impediments observed in the previous study. However, information on the effects of microwave receptors as doping agents within the biomass on pyrolysis processing conditions is very scanty. Thus in the following study, an investigation into the relationship between the characteristics of the doping agents and pyrolysis process control to maximize the yield of bio-fuels was undertaken through numerical modeling and experimental trials.

Chapter 4

Finite Element Modeling of Selective Heating in Microwave Pyrolysis of Lignocellulosic Biomass

Abstract

Microwave pyrolysis overcomes the disadvantages of conventional pyrolysis methods by efficiently improving the quality of final pyrolysis products. Biochar, one of the end products of this process is considered an efficient vector for sequestering carbon to offset atmospheric carbon dioxide. The dielectric properties of the doping agents (i.e., char and graphite) were assessed over the range of 25°-400°C and used to develop a finite element model (FEM). This model served to couple electromagnetic heating, combustion, and heat and mass transfer phenomena and evaluated the advantages of selective heating of woody biomass during microwave pyrolysis. The dielectric properties of the doping agents were a function of temperature and decreased up to 100°C and thereafter remained constant. Regression analysis indicated that char would be a better doping substance than graphite. The simulation study found that doping helped to provide a more efficient heat transfer within the biomass compared to non-doped samples. Char doping yielded better heat transfer compared to graphite doping, as it resulted in optimal temperatures for maximization of biochar production. The model was then validated through experimental trials in a custom-built microwave pyrolysis unit which confirmed that char doping would be better suited for maximization of biochar.

Keywords: Microwaves, Pyrolysis, Biochar, Numerical modeling

4. 1. Introduction

Combating global climate change and meeting the world's ever-rising energy demands are twin concerns which challenge researchers all around the world. Evidence strongly supports the occurrence of climate change, based on a wide range of indicators including increases in global average air and ocean temperatures, widespread melting of snow and ice, and rising global sea levels. Carbon dioxide tends to accumulate in the atmosphere for a long time and with continued anthropogenic emissions, CO_2 levels will only continue to build-up in the atmosphere. The Fourth Assessment Report of the Intergovernmental Panel on Climate Change (IPCC) suggests that even with significant reductions in anthropogenic CO_2 emissions, atmospheric CO_2 levels would only decline very gradually as natural processes slowly removed CO_2 from the atmosphere (IPCC, 2007). Therefore past anthropogenic CO_2 emissions will continue to have a destabilizing impact on earth's climate system for a very long time. Climate change has irreversible effects on our economy, infrastructure, and health, the landscapes around us, and the wildlife that inhabit them.

Although climate change has been attributed to both natural processes and human activities, a recent heightening of public awareness regarding greenhouse gases' role in global warming has led to a greater scrutiny of such contributory activities as CO_2 emissions from carbon-based fossil fuel combustion, rising population and irresponsible acts of deforestation and land use. In Canada, over 80 % of total national greenhouse gas emissions are associated with the production or consumption of fossil fuels for energy purposes (Government of Canada, 2013).

Canada's total GHG emissions for 2011 were estimated at 702 Mt of CO_2 equivalents (CO_2e), of which nearly 8% was contributed by the agricultural sector (Environment Canada, 2013). This sector generates roughly 300 Mt of agricultural waste (AAFC, 2010; StatCan, 2009). Assuming 50% recovery of carbon from this biomass, one could sequester nearly 150 Mt of carbon dioxide from the atmosphere, in the form of biochar, or about 20% of Canada's GHG emissions.

An increased need for technologies with long-term sustainability implications for the bioenergy sector has been widely acknowledged. Biochar's uses as an energy source (Wu and Abdullah, 2009), as a fertilizer when mixed with soil (Lehmann, 2007), and as a means of reducing greenhouse gas emissions through the soil-sequestration of carbon (Joseph et al., 2009), have led to its gaining significant attention in recent years. Moreover, biochar can increase food security by reducing the amount of food crops used for biofuel production (Kleiner, 2009).

One of the most important thermochemical biomass-conversion technologies, pyrolysis is a process of thermal decomposition of biomass under conditions ranging from low oxygen (<1% O_2 v/v) to no oxygen. It converts organics to solid (charcoal), liquid (organics) and gaseous (CO, CO_2, CH_4, H_2) products. Their range and relative amounts depend on process variables such as the nature of the feedstock and the heating rate (Brownsort, 2009; Dutta *et al.*, 2011). Biochar production through pyrolysis has become an extremely efficient and popular technology in recent years (IBI, 2011).

Conventional pyrolysis techniques have a few inherent disadvantages such as poor heating characteristics in the core of the biomass as well as being time consuming. One of the methods proven to have measured up to good efficiency and potentially negate the disadvantages of conventional methods is the use of microwave or microwave-assisted pyrolysis methods to generate biochar. The application of microwaves to produce biochar has been proven to enhance biochar yield and quality, and, to a large extent, negate undesirable secondary reactions among volatile compounds. In addition, it is a rapid and energy-efficient technology compared to conventional methods (Dutta *et al*., 2011). One of the driving principles of microwave heating is based on 'molecular friction' (or dielectric loss) (Venkatesh and Raghavan, 2005). Dielectric heating of a material causes thermal effects which may cause a different temperature regime within the material (Metaxas, 1996). The biomass is heated by conduction from the surface to its core in the conventional method and by convective heat transfer from high-temperature gas. The temperature at the surface of the biomass is known to be higher than that at the core because of the poor thermal conductivity of lignocellulosic biomass. Hence as the dielectric properties govern the ability of materials to heat in microwave fields, the measurement of these properties as a function of other relevant parameters such as frequency, temperature, moisture content, etc. is important (Thostenson and Chow, 1999).

There is a growing interest in modeling and simulation studies regarding the production of biochar as well as other pyrolysis by-products. Numerical and modeling studies have been conducted which focus on estimation of optimum parameters in pyrolysis of biomass (Babu and Chaurasia, 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).

There is poor understanding of the mechanisms involved in application of electromagnetic energy for the pyrolysis of biomass and the actual energy distribution inside the biomass when subjected to electromagnetic fields (Dutta et al., 2010). The electromagnetic field distribution inside a microwave oven can be represented by solving Maxwell's equations (Equations 4.1 to 4.6). Finite Element Method (FEM) is commonly used for solving Maxwell's equations to obtain the energy distribution in a complex object or within a multimode cavity. It is capable of simulating power density distribution in a 3-D space (Dev et al., 2009).

$$\frac{\partial \widetilde{D}_x}{\partial t} = \frac{1}{\sqrt{\varepsilon_0 \mu_0}} \left(\frac{\partial H_z}{\partial y} - \frac{\partial H_y}{\partial x} \right) \tag{4.1}$$

$$\frac{\partial \widetilde{D}_y}{\partial t} = \frac{1}{\sqrt{\varepsilon_0 \mu_0}} \left(\frac{\partial H_x}{\partial z} - \frac{\partial H_z}{\partial x} \right) \tag{4.2}$$

$$\frac{\partial \widetilde{D}_z}{\partial t} = \frac{1}{\sqrt{\varepsilon_0 \mu_0}} \left(\frac{\partial H_y}{\partial x} - \frac{\partial H_x}{\partial y} \right) \tag{4.3}$$

$$\frac{\partial H_x}{\partial t} = \frac{1}{\sqrt{\varepsilon_0 \mu_0}} \left(\frac{\partial \tilde{E}_y}{\partial z} - \frac{\partial \tilde{E}_z}{\partial y} \right) \tag{4.4}$$

$$\frac{\partial H_y}{\partial t} = \frac{1}{\sqrt{\varepsilon_0 \mu_0}} \left(\frac{\partial \tilde{E}_z}{\partial x} - \frac{\partial \tilde{E}_x}{\partial z} \right) \tag{4.5}$$

$$\frac{\partial H_z}{\partial t} = \frac{1}{\sqrt{\varepsilon_0 \mu_0}} \left(\frac{\partial \tilde{E}_x}{\partial y} - \frac{\partial \tilde{E}_y}{\partial x} \right) \tag{4.6}$$

FEM technique competes very favorably with the other numerical methods, as it is based on reducing the Maxwell's equations to a system of simultaneous algebraic linear equations (Delisle et al., 1991). FEM can readily model heterogeneous and anisotropic materials as well as arbitrarily-shaped geometries. It can also provide both time and frequency domain analyses which are important to microwave heating problems like field distribution, scattering parameters and dissipated power distribution for various materials and geometries (Dev et al., 2010).

The addition of microwave receptors has been found to improve heat distribution in biological materials during microwave processing. Sanga et al. (2000) investigated microwave and hot air drying characteristics of special cases of biological material (carrots) and compared their drying rates, surface color, re-hydration capacity and shrinkage. The samples were inserted with Teflon at core center of carrots and dried by microwave and hot air drying. It was found that microwave drying of the special case biological material (carrot embedded with Teflon) had higher drying rates and less shrinkage. Re-hydration capacity of biological material dried as a special case was also found to be higher than those dried as stand-alone under the same drying conditions.

Many researchers have concluded that the optimum pyrolysis conditions for by product maximization cannot be attained without adding a microwave-susceptible doping agent which has been found to have significant impact on the pyrolysis conditions and the products formed (Robinson et al., 2010, Al-Sayegh et al., 2010). The goals of using a doping agent are to absorb maximum microwave radiation in the initial phase and then to help sustain the pyrolysis process and final temperatures (Domínguez et al., 2007). The dielectric properties of a microwave-susceptible doping agent are an important factor in its selection for microwave assisted pyrolysis as it determines the extent to which the doping agent will influence the heating mechanism.

4. 1.1. Previous simulation results

Dutta et al., (2010) showed that the highest yield of biochar was found to be at 425°C at a power density of 7.5 W/g and was found to be optimum for pyrolysis of lignocellulosic biomass for maximization of biochar. An evidence of non uniform heating resulting in the creation of hot spots in the biomass was observed through the experimental validation of the simulation of the microwave pyrolysis. Although the biochar yield was found to be in agreement with the simulation results, the pyrolysis process was hard to control due to the non uniformity of heating and the generation of sparks in the cavity.

Taking these facts into account, the dielectric properties of char and graphite were determined in order to select the doping agent best suited to maximize biochar yield through microwave pyrolysis. A Finite Element Model (FEM) of the microwave pyrolysis of lignocellulosic biomass was developed. Simulation studies were conducted for biomass doped with char and graphite and subjected to microwave pyrolysis at a frequency of 2.45 GHz and slow heating conditions as illustrated in Dutta et al. (2010) in order to visualize and investigate energy distribution within the biomass. The simulation results of the microwave heating mechanism and profile obtained for the doped biomass was compared to that of the dope-free sample.

4. 2. Materials and Methods

4.2.1. Dielectric properties measurement

The dielectric properties for char of lignocellulosic origins (willow wood) and graphite obtained from a local store (DeSerres, Montreal, Canada) were evaluated. The dielectric constant (ε') and dielectric loss factor (ε'') were measured using an Agilent 8722 ES s-parameter Network Analyzer equipped with a high temperature probe (model 85070B) and controlled with the Agilent 85070D Dielectric Probe Kit Software (Version E01.02) operating at 2.45 GHz.

Using a furnace, samples of char and graphite were heated to temperatures in the range of 50-400°C prior to measurements being taken. Measurement of the frequency shift and change in quality factor was made at selected resonant frequencies. The dielectric properties of the sample were measured at each temperature through the network analyzer.

According to the manufacturer, the equipment has an accuracy of ±5% for the dielectric constant (ε') and ±0.005% for the loss factor (ε") (HP 1992). A diagram of the experimental setup used for the measurement of dielectric properties is shown in Figure 4.1.

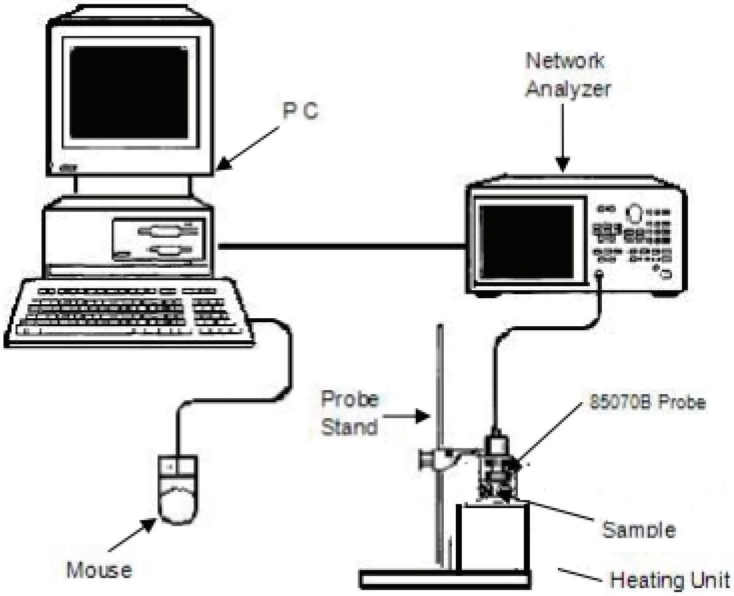


Figure 4.1: Dielectric properties measurement unit

4.2.2. Microwave pyrolysis set-up for experimental validation

The experimental validation of the simulation results was carried out in a custom-built microwave pyrolysis unit within a regular domestic multimode microwave oven operating at 2.45 GHz, with cavity dimensions of 205 mm × 335 mm × 180 mm located in the laboratories of the Department of Bioresource Engineering, McGill University.

The quartz pyrolysis bioreactor system used for the simulation (Figure 4.2) consisted of three parts: an upper cylinder (40 mm inner diameter, 90 mm height), a lower cylinder (50 mm inner diameter, 42 mm height) and a sample stand (35 mm diameter, 25 mm height). Through two quartz tubes, one inlet, one outlet (each 6.3 mm diameter, 25.4 mm length) air inside the reactor was purged with nitrogen at a flow rate of 0.003 L s^{-1} to create an oxygen-free inert atmosphere.

The reactor was placed in the center of the microwave chamber and the two quartz tubes were connected for the nitrogen gas supply and gaseous product release. A K-type thermocouple was inserted into the reactor through the gaseous product release tube to monitor the biomass temperature continuously throughout the experiment. The gaseous product release pipe was connected to a condensation unit continuously rotated in cooling water at $\leqslant$10°C as shown in Figure 4.3. In order to validate the simulation model, an experimental design with temperature as the single factor and triplicate samples was chosen. Three temperatures for each of the experimental set up were selected as follows (Table 4.1):

Table 4.1: Experimental conditions for experimental validation

Experimental set up	Temperature
Doping type (Non doped, Graphite, Char)	250
	290
	330

Each pyrolysis run ended 15 min after the start of microwave radiation. After each run, the reactor was cooled to ambient temperature under a nitrogen atmosphere. The biochar remaining in the reactor was weighed to compare yields.

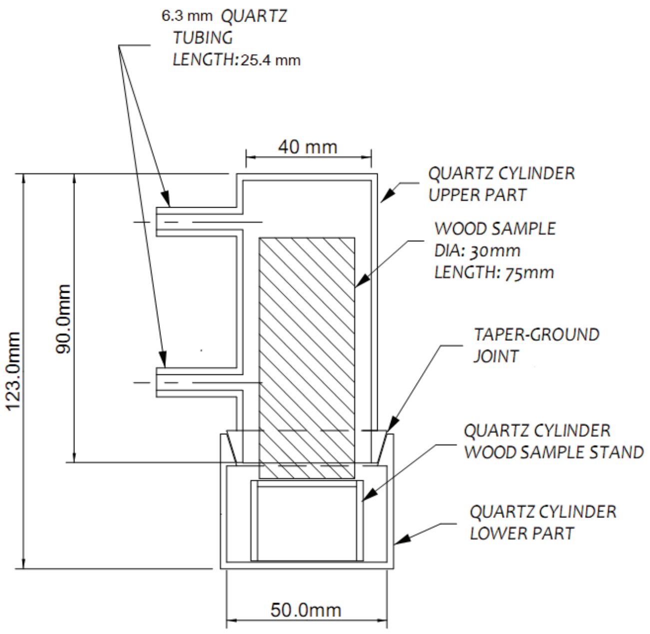
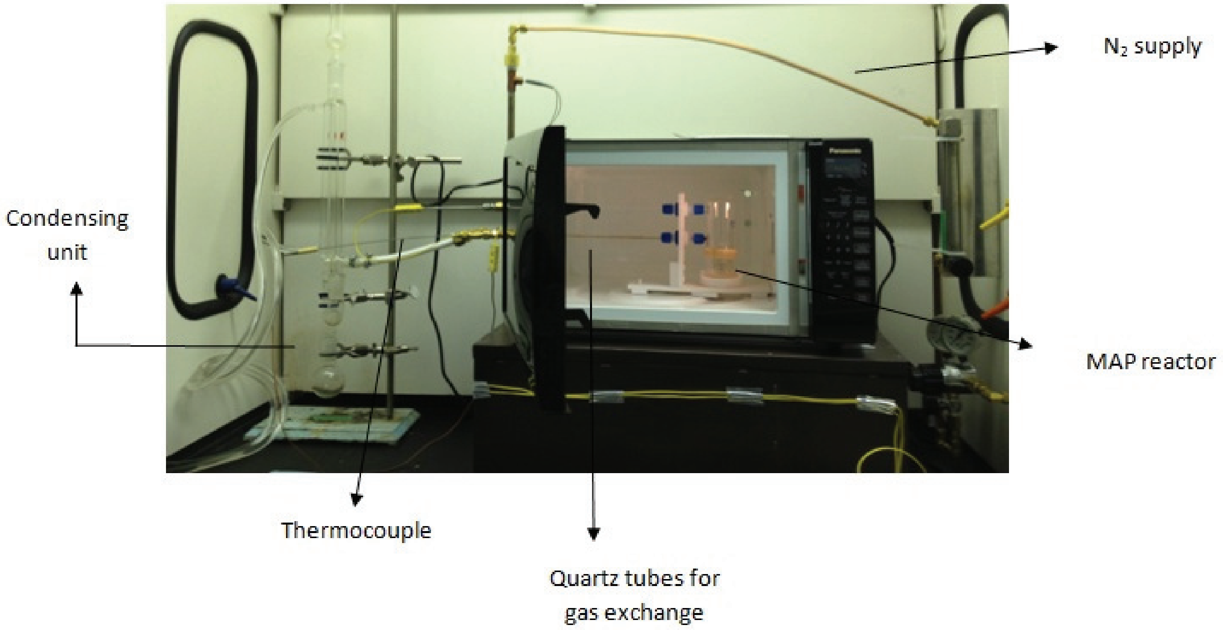
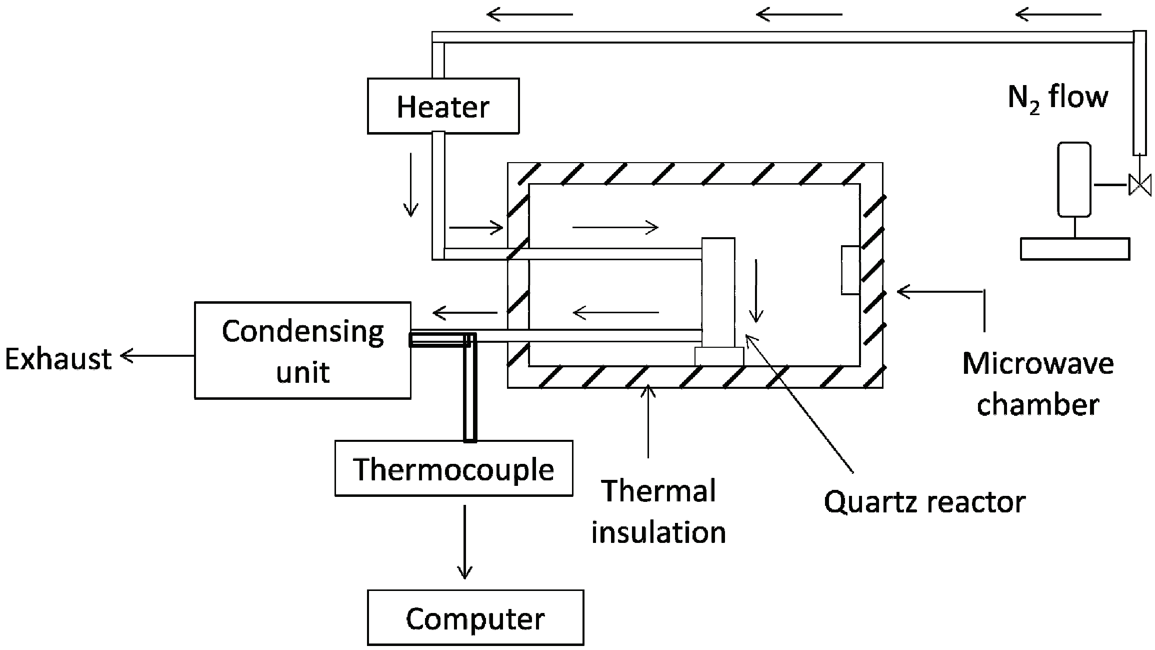


Figure 4.2: Microwave Pyrolysis Bioreactor Setup



(a)



(b)

Figure 4.3: Microwave Pyrolysis Setup (a) Lab scale; (b) Schematic

4.2.3. Sample preparation

The biomass taken into consideration for simulation was maple wood (30 mm diameter, 75 mm length) with a moisture content of ≃ 7%. This was mounted on the sample stand. It was theoretically assumed that the biomass sample was doped with char or graphite of 30 mm diameter and 75 mm length having the dielectric properties determined in separate simulations in a prior experiment. The wood sample was then subjected to microwave heating at a 2.45 GHz frequency and power density of 7.5 W/g for simulation purposes. The thermal properties of the maple wood, char and graphite used for the simulation are shown in Table 4.2.

4.2.4. Development of the mathematics and governing equations for microwave assisted pyrolysis

4.2.4.1. Formulation of the equations for the electromagnetic field (Dutta et al., 2010)

4.2.4.1.1. Electromagnetics

The Maxwell's equations that govern the electromagnetic phenomena evolving in a given configuration resolved in 3D space were solved for the electric field intensity, E (V m^{-1}), and magnetic field intensity, H (A m^{-1}). At the macroscopic level, electromagnetic phenomena were defined using Maxwell Equations (4.1-4.6).

Table 4.2: Thermal properties of sample materials used for simulation purpose

Properties	Wood	Char	Graphite
Thermal conductivity (W/mK)	0.8	150	
Density (kg/m^3)	640	280	1950
Specific heat capacity (constant pressure) (kJ/kg K)	1.63	1	0.71
Relative permittivity (ε_r)	1	1	10 – j
Relative permeability (μ_r)	1		

For the simulation of the biomass pyrolysis in the microwave environment, the Maxwell equations, which govern the electric (E) and magnetic (H) fields decouple polarization state of transverse electric mode (TE) (Ayappa et al., 1992). The electromagnetic field distribution inside the microwave oven was traced out by solving the following Maxwell's equations (Zheng et al., 2000).

The time averaged power dissipation (P_{av}) in each element in a dielectric material was obtained by integrating the Poynting vector (P_c) over the closed surface S for each tetrahedral element (Equation 4.7- 4.8) (Dutta et al., 2010):

$$P_{av} = -\frac{1}{2}\int_S P_c \cdot dS \tag{4.7}$$

where $P_c = E \times H$ (4.8)

Volumetric heat generation (Q) can be expressed in terms of power intensity in three orthogonal directions (Equation 4.9) (Thostenson and Chow, 1999):

$$Q = \frac{\partial P_{av(x)}}{\partial V} + \frac{\partial P_{av(y)}}{\partial V} + \frac{\partial P_{av(z)}}{\partial V} \tag{4.9}$$

where the suffixes x, y and z indicate time average power dissipated in the corresponding directions and where V is the volume in which the heat is generated.

The dynamically changing dielectric constant ε' and loss factor ε" were calculated using equations derived from the measurement of dielectric properties (Equation 4.10 and 4.11):

$$\varepsilon = \varepsilon' - j\varepsilon" \tag{4.10}$$

And the loss tangent is:

$$tan\delta = \frac{-\varepsilon"}{\varepsilon'} \tag{4.11}$$

4.2.4.1.2. Boundary conditions

Perfect Electrical Conductor (PEC) boundary condition ($n \times E = 0$) was used for the walls of the cavity and Perfect Magnetic Conductor (PMC) boundary condition ($n \times H = 0$) was used for the symmetry boundaries.

Boundary conditions at the port were taken as follows (Equation 4.12- 4.14):

$$H_y = A\cos\left(\frac{\Pi x}{\alpha}\right)\cos\left(\omega t + \beta t\right) \tag{4.12}$$

$$E_z = \frac{\omega\mu_0\alpha}{\Pi}A\sin\left(\frac{\Pi x}{\alpha}\right)\sin\left(\omega t + \beta t\right) \tag{4.13}$$

$$H_x = \frac{\beta\alpha}{\Pi}A\sin\left(\frac{\Pi x}{\alpha}\right)\sin\left(\omega t + \beta t\right) \tag{4.14}$$

Where the x, y and z coordinates indicate the corresponding axes, and A is the cross sectional area of the waveguide, ω is the phase angle and α and β are arbitrary constants.

Thermal boundary conditions: The surface of the cylindrical wood sample was used as the thermal boundary conditions for the simulation. Surface to ambient boundary conditions were applied for the circumference of the sample in order to simulate the heating mechanism inside the quartz reactor.

4.2.4.1.3. Heat transfer (Dutta et al., 2010)

The thermal energy is given as Equations 4.15 and 4.16 (Zheng et al., 2000):

$$\rho C_p\frac{\partial T}{\partial t} = \nabla \cdot (K\nabla T) + Q \tag{4.15}$$

$$\nabla \times \mu_r^{-1}(\nabla \times E) = k_0^2\left(\varepsilon_r - j\frac{\sigma}{\omega\varepsilon_0}\right)E \tag{4.16}$$

where, ρ is the density (kg m^{-3}), C_p is the specific heat (kJ kg^{-1} °K^{-1}), K is the thermal conductivity of the material (W m^{-1} °K^{-1}), and T is the absolute temperature (°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. Taking all the above into consideration, a Finite Element Model (FEM) of the microwave pyrolysis of lignocellulosic biomass is an optimum numerical approximation technique for MAP (Di Blasi, 2008). The resulting sets of partial differential equations were then simultaneously solved using the COMSOL Multiphysics software package (ver. 4.1a, COMSOL Inc., USA) (COMSOL Multiphysics, 2012). With this software, a 3D Finite Element Model was developed to simulate the microwave pyrolysis process for a regular domestic multimode microwave oven configuration. The meshed structure of the microwave cavity along with the bioreactor and wood sample are shown in Figure 4.4. A custom-built computer with two AMD Opteron quadcore 2.4 GHz processors and 32 GB primary memory was used to run the simulations.

4.3. Results and Discussion

4.3.1. Dielectric properties

The dielectric properties of char and graphite were found to be consistently uniform at temperatures above 200°C (Figure 4.5). The dielectric constant (ε') of biochar and graphite decreased linearly up to 100°C and remained constant thereafter. The dielectric loss factors of both graphite and char were negligible and remained constant across the entire range of temperature.

A linear regression model was applied to the dielectric properties of both char and graphite to analyze their relationship to temperature. The dielectric loss (ε'') values of both the biochar and graphite did not change significantly with respect to temperature ($P > 0.05$). Changes in ε'' values remained relatively negligible with increases in temperature and hence did not fit a linear model.

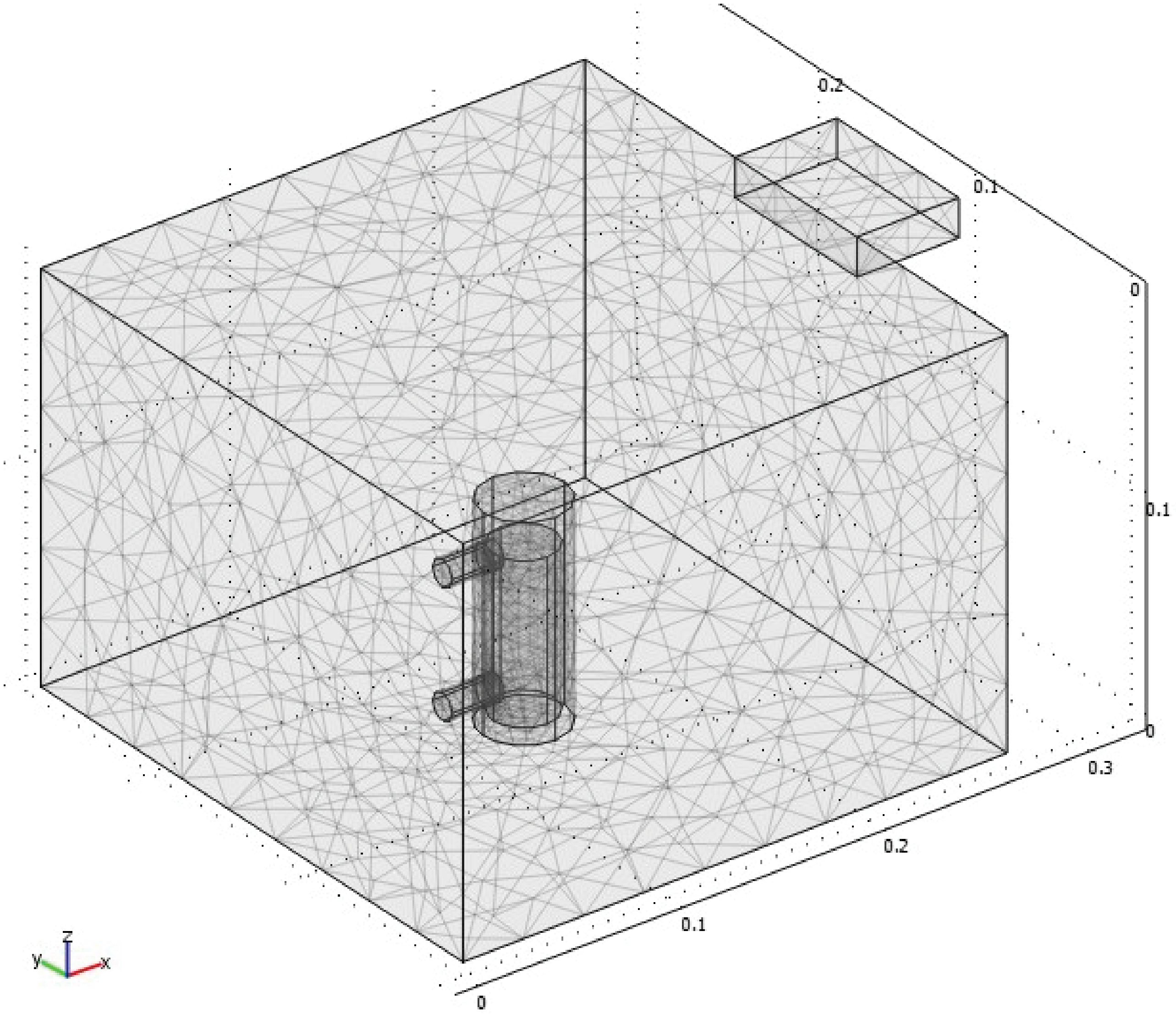


Figure 4.4: Finite element mesh structure of the microwave pyrolysis unit for simulation

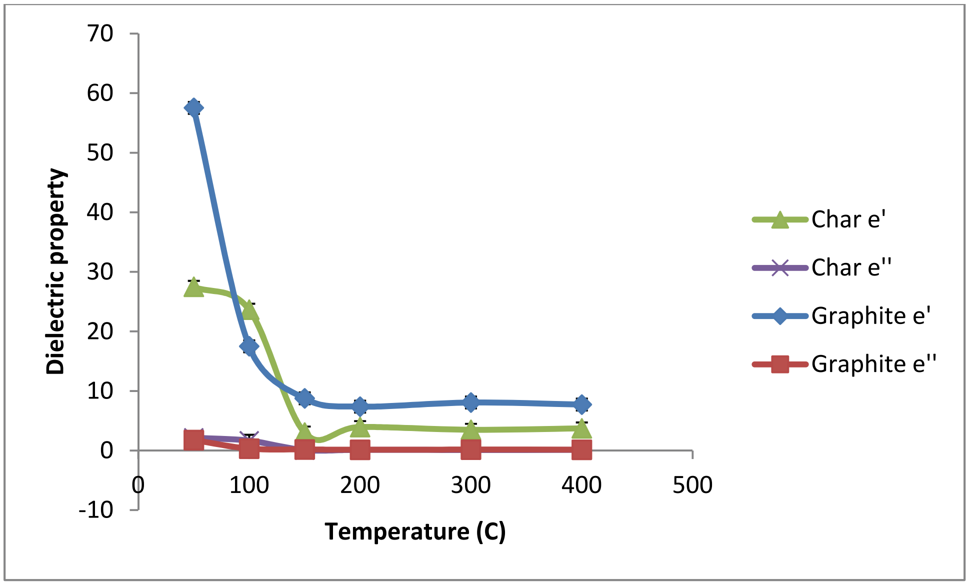


Figure 4.5: Change in dielectric properties of char and graphite with varying temperatures at 2.45 GHz

The ε’ for both char and graphite decreased with increasing temperature. A linear additive model was used to relate ε’ to temperature with a general form of (Equation 4.17):

$$\varepsilon' = a \pm bT \tag{4.17}$$

where, T is the temperature in °C, and a and b are model coefficients,

The regression analysis performed on the collected data yielded the following relationships for char and graphite respectively (Equations 4.18 – 4.19):

$$\varepsilon'_{\mathrm{char}} = 37.35\text{-}0.182T \tag{4.18}$$

$$\varepsilon'_{\mathrm{graphite}} = 62.62\text{-}0.32T \tag{4.19}$$

The coefficient of determination (R^2) value of the dielectric constant values for char and graphite were 0.77 and 0.73 respectively ($P \leqslant 0.05$; Figure 4.6, Figure 4.7). These models are useful in determining the dielectric properties of char or graphite at any given temperature within the range studied.

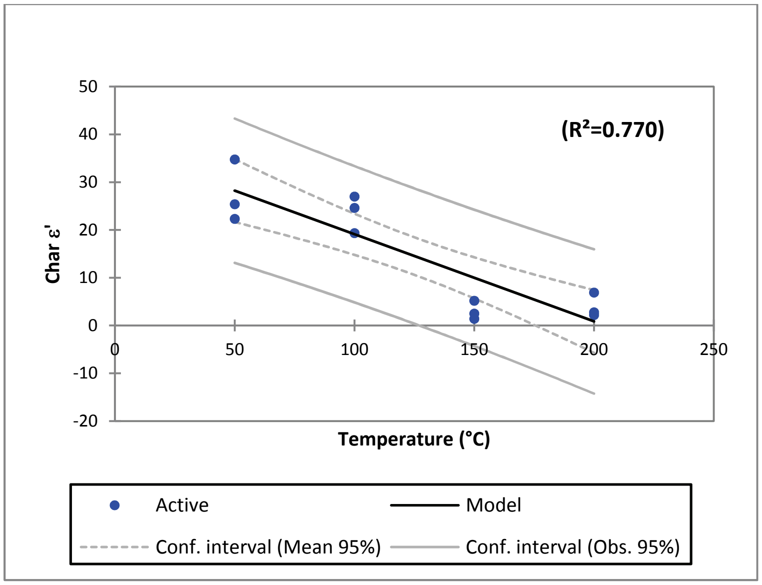


Figure 4.6: Regression analysis for dielectric constant (ε') values for char

The results of the present investigation of the dielectric properties of char produced from wood and graphite concur with the findings of Robinson et al. (2010) who compared the dielectric loss for <1 mm wood pellets, dried at 105°C and with 6.3% water content over a temperature range of 25° to 800°C. Their study also showed a decrease in ε' above 100°C which were attributed to the loss of bound water or capillary water within the structure of the wood. Al Sayegh et al. (2010) also reported similar results, which indicate that dielectric properties are frequency and temperature dependent; they showed a decrease in the dielectric constant of wood beyond 150°C up to 400°C, followed by a slow increase.

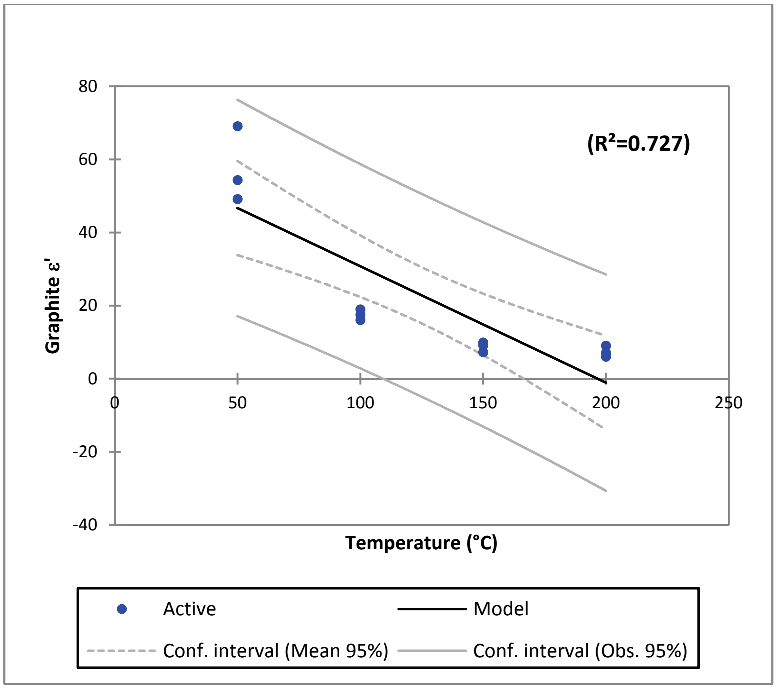


Figure 4.7: Regression analysis for dielectric constant (ε') values for graphite

It has been previously shown that microwave heating is enhanced by the presence of a doping agent such as graphitic carbon, a very good microwave absorber. When the free water is lost upon heating, a wood sample without any doping becomes essentially microwave transparent (Robinson et al., 2010, Zuo et al., 2011, Fernández et al., 2011). The findings of the present study further support this theory. The dielectric properties result indicates that char would be a better doping substance than graphite. In order to investigate this further, numerical modeling and a simulation study of the microwave pyrolysis process were carried out by using the char and graphite dielectric properties models.

4.3.2. Numerical modeling and simulation

4.3.2.1. Meshing

In order to model the effects of a doping material on MAP within the woody biomass, a symmetrical geometry of the entire system as shown in Figure 4.8 was considered. The mesh structures of the non-doped and doped systems are presented in Figure 4.9 and Figure 4.10. Different mesh element sizes were used based on the dielectric properties of the sub-domain and the precision required in the sub-domain of interest.

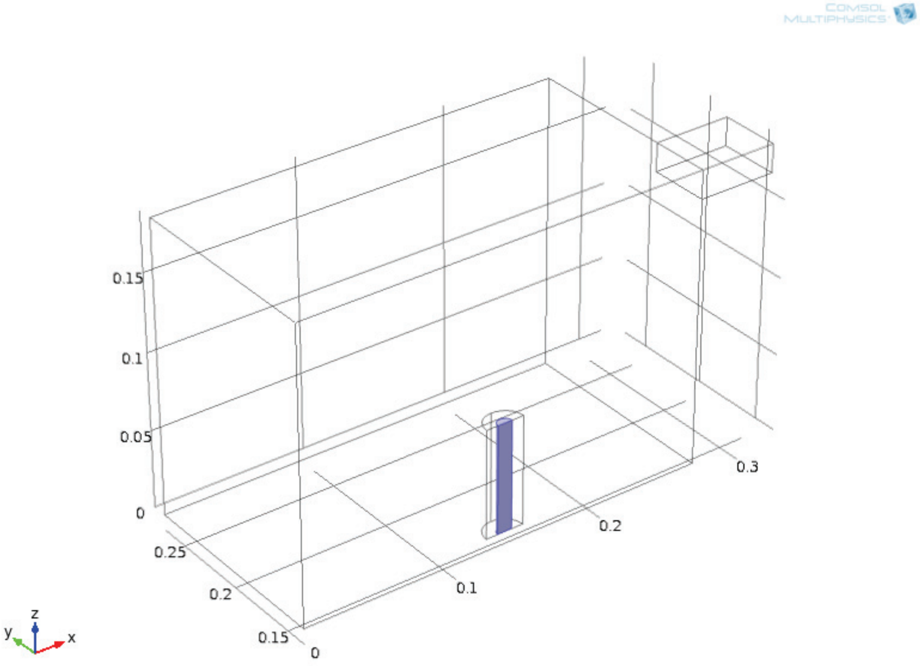


Figure 4.8: Half sectional view of the reactor configuration with a doped region

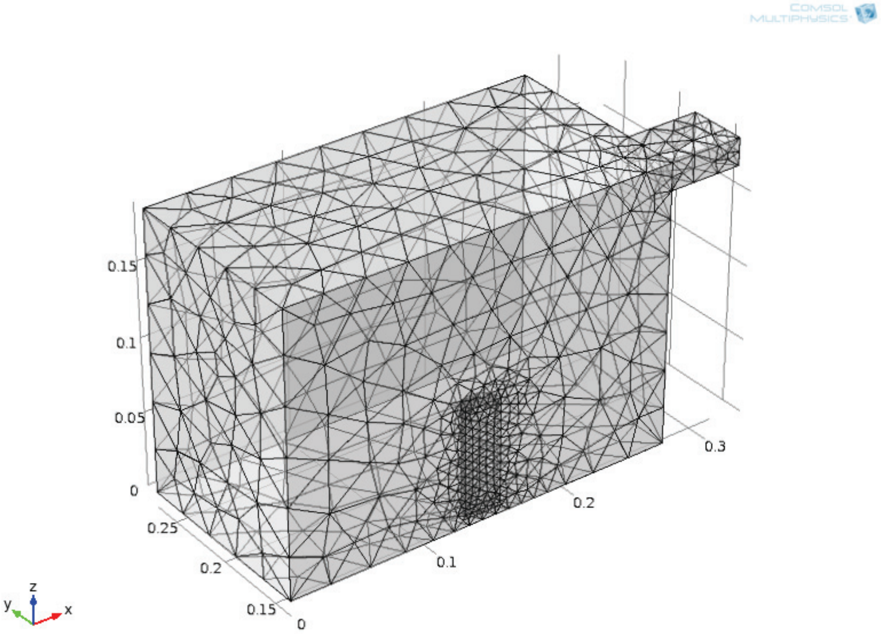


Figure 4.9: Finite element mesh structure for non-doped biomass (Half sectional view)

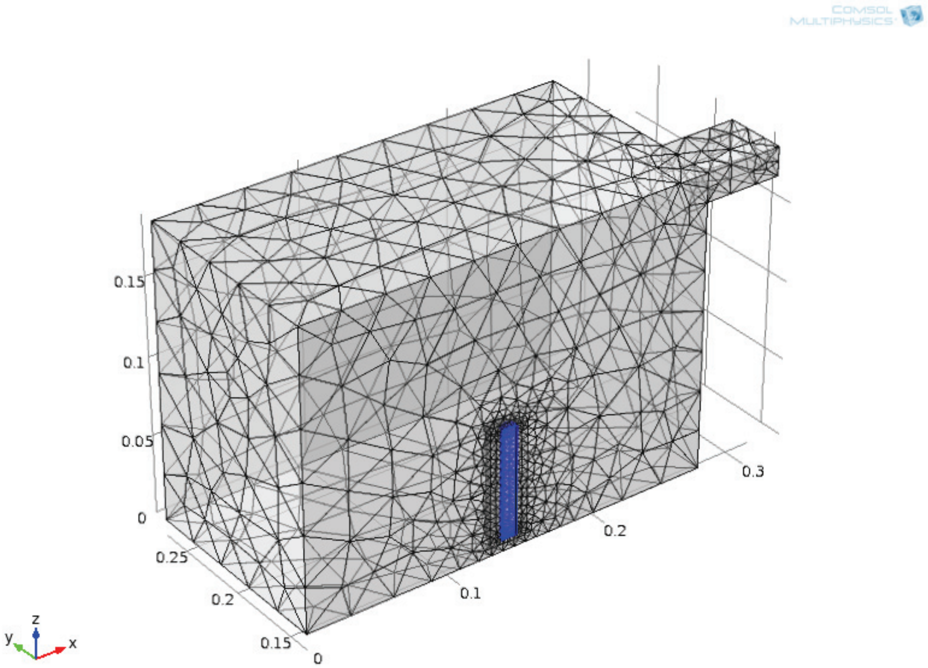


Figure 4.10: Finite element mesh structure for doped biomass (Half sectional view)

Previous simulation work carried out by the authors has shown that a pyrolysis temperature of 425°C is ideal in obtaining the optimum yield of biochar under microwave-assisted conditions for the given range of temperature (Dutta et al., 2010). The present objective was to investigate if doping of the wood sample would assist in it reaching the desired temperatures in a more efficient manner than non-doped samples. The governing physics for electromagnetic radiation and heat transfer were applied for a time range of 15 min (900 s) for each system to determine the temperature distribution within the wood samples.

As seen in Figure 4.11, the highest temperatures attained for the non-doped wood sample remained below 300°C over the 15 min and showed a heat distribution of ΔT°≤1°C within the system. A vertical increase in temperature was observed within the sample with the highest temperature of 296°C occurring at the upper end of the wood and the lowest (295°C) at the bottom.

The ability of a material to absorb microwave energy is related to its dielectric properties and the average power absorbed by a given volume of material when heated dielectrically is given by Equation 4.20 (Oloyede and Groombridge, 2000):

$$P_{av} = \omega\varepsilon_0\varepsilon_{eff}{}''EV \tag{4.20}$$

where P_{av} is the average power absorbed (W); ω is the angular frequency of the generator (rad/s); ε_0 is the permittivity of free space; ε_{eff}” is the effective loss factor; E is the electric field strength (V/m); and V is the volume (m^3). Thus the energy absorbed is proportional to the electric field distribution. The energy within the non – doped biomass sample as governed by the electric field distribution is shown in Figure 4.12.

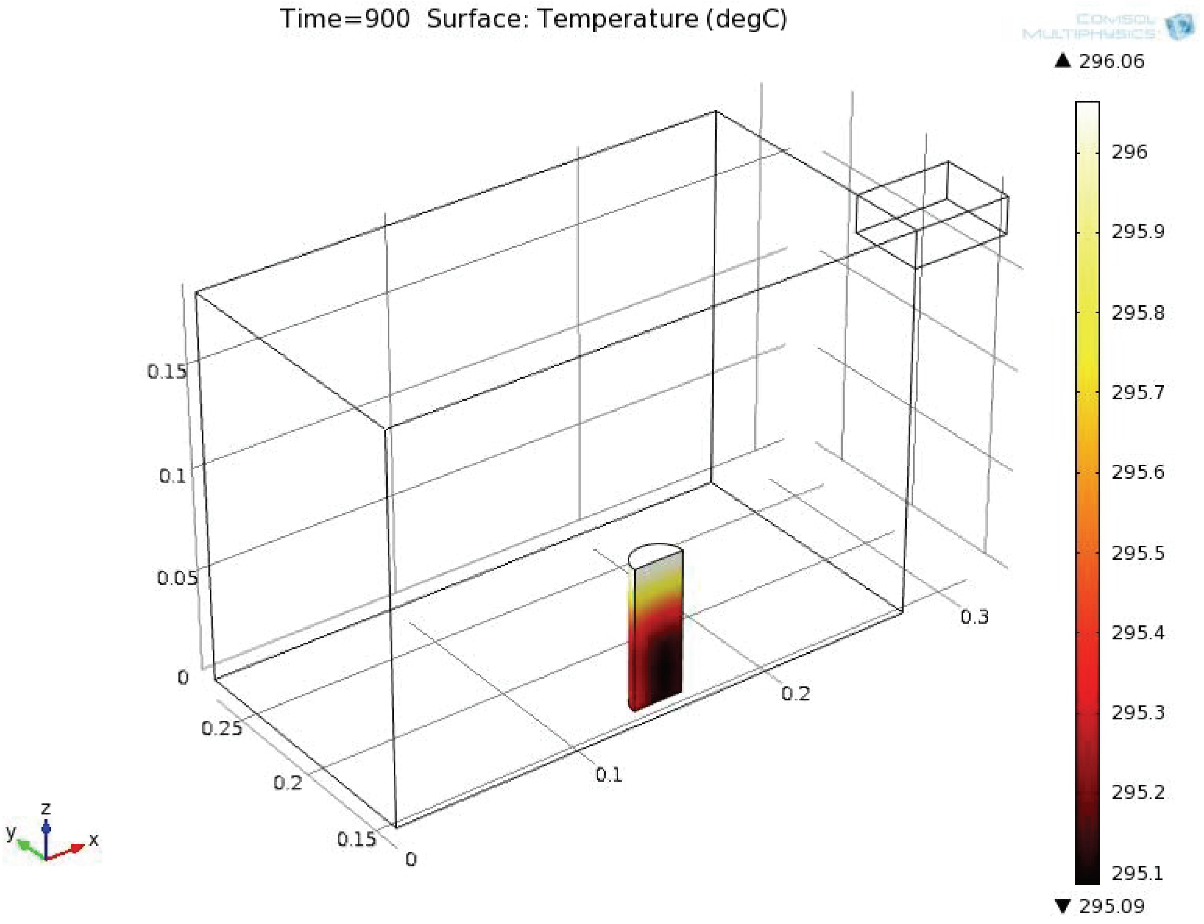


Figure 4.11: Temperature profile of non- doped biomass for microwave pyrolysis

In the case of the wood sample doped with graphite, the highest temperature attained after 15 min was ≃335°C. Heating in this case was less uniform (ΔT° ≈ 5°C) across the sample and its vertical progression in the sample was the opposite of that of the non-doped sample (Figure 4.13). The electric field distribution for the graphite doped sample is shown in Figure 4.14.

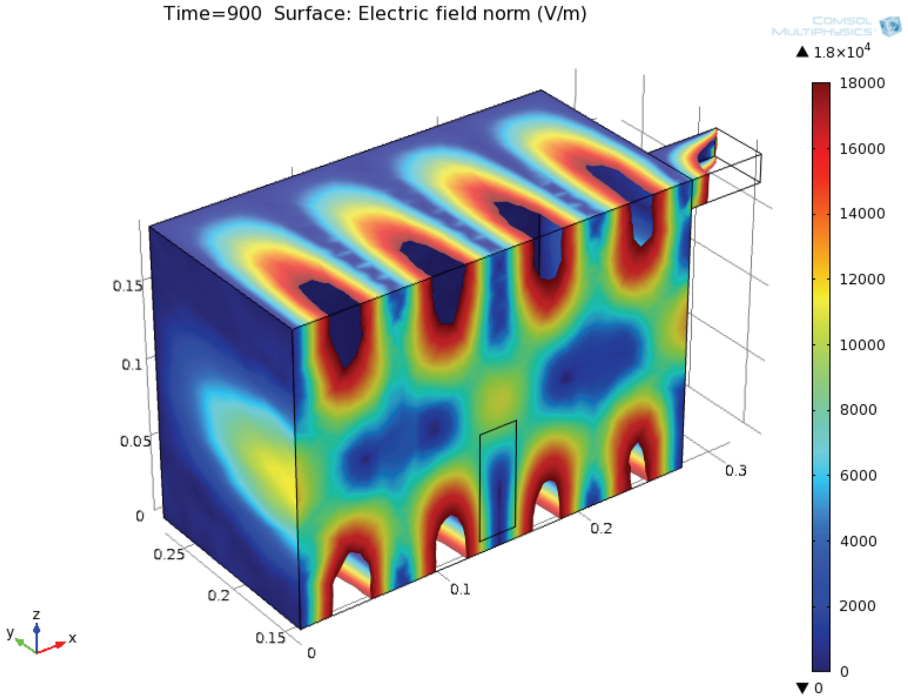


Figure 4.12: Electric field distribution of non- doped biomass for microwave pyrolysis

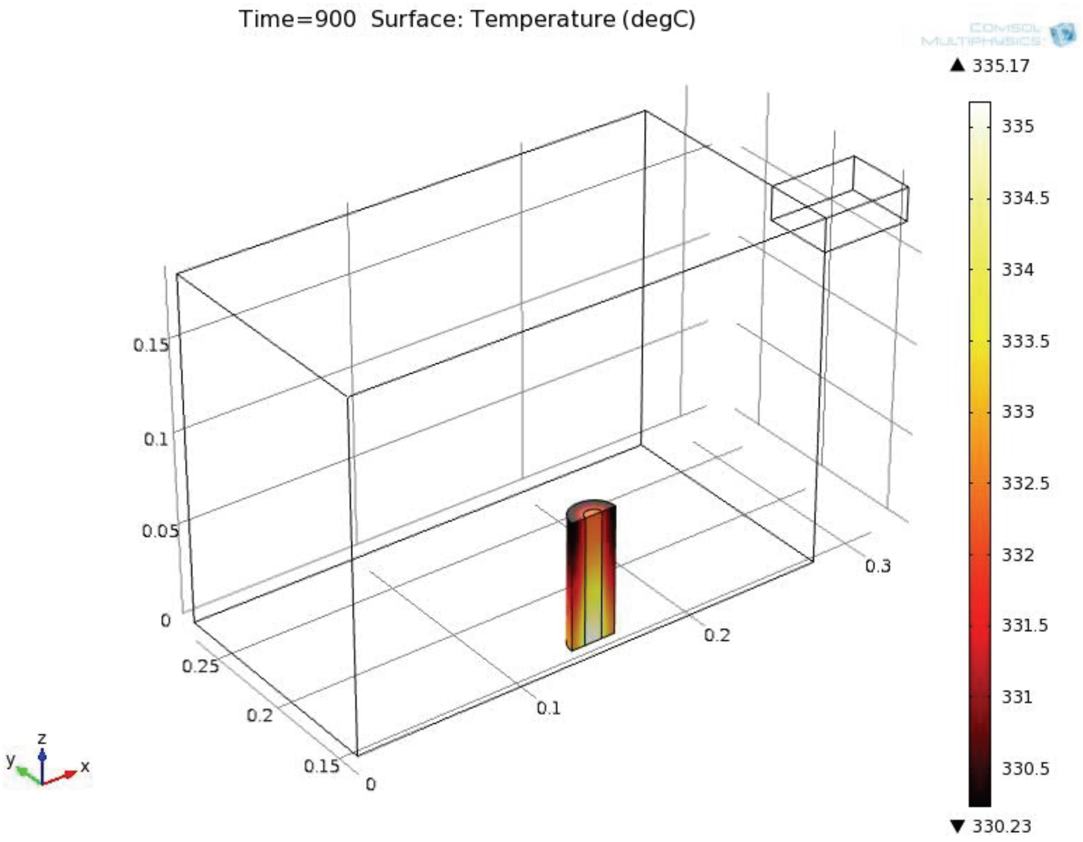


Figure 4.13: Temperature profile of graphite doped biomass for microwave pyrolysis

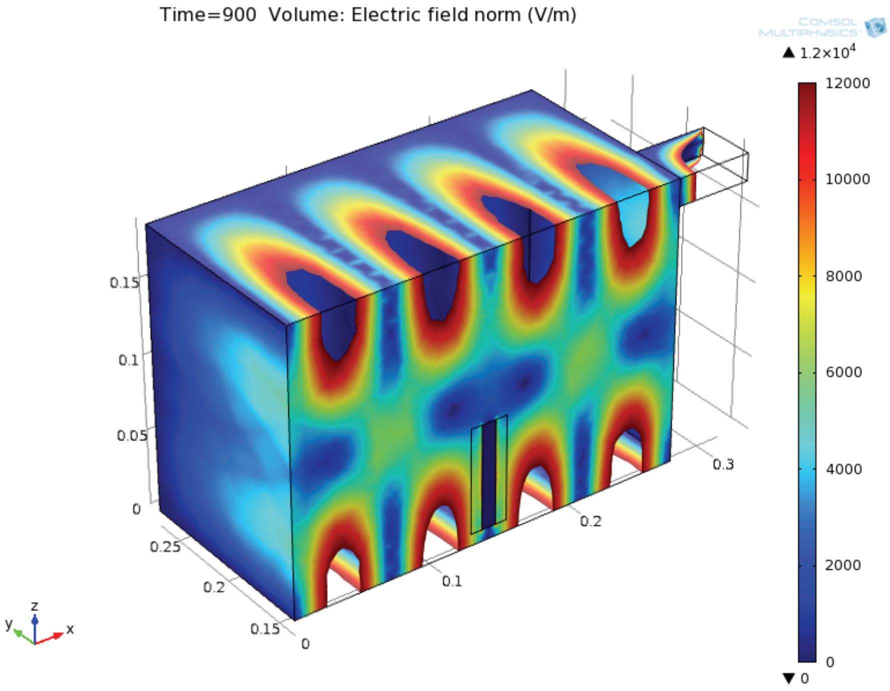


Figure 4.14: Electric field distribution of graphite- doped biomass for microwave pyrolysis

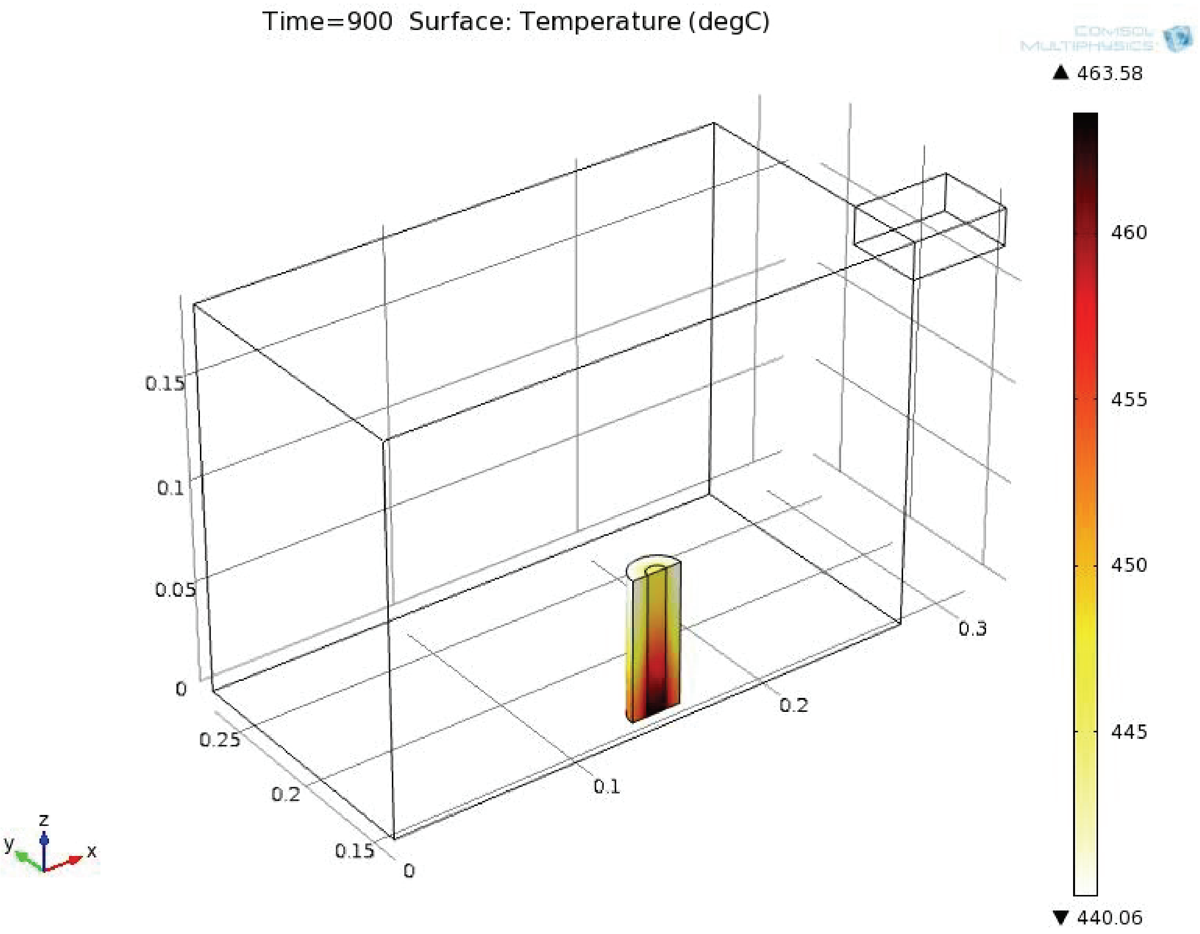


Figure 4.15: Temperature profile of char doped biomass for microwave pyrolysis

With char-doped biomass, the highest temperature reached after 15 min was 464°C. The vertical heat distribution pattern was similar to that of the graphite-doped biomass, but at overall higher temperatures. The heat distribution (ΔT° ≈ 20°C) was less uniform than for the non-doped and graphite-doped systems (Figure 4.15). The optimum biochar production temperature of 425°C, determined in a previous simulation study conducted by the same authors (Dutta et al., 2010), was attained by the char-doped biomass within 13 min (Figure 4.16). The electric field distribution within the system of the char doped sample is shown in Figure 4.17.

The radiation energy was dissipated within the sample more or less uniformly, giving rise to much greater heating rates, although significant temperature gradients may be established between the hot internal regions and the surface of the sample.

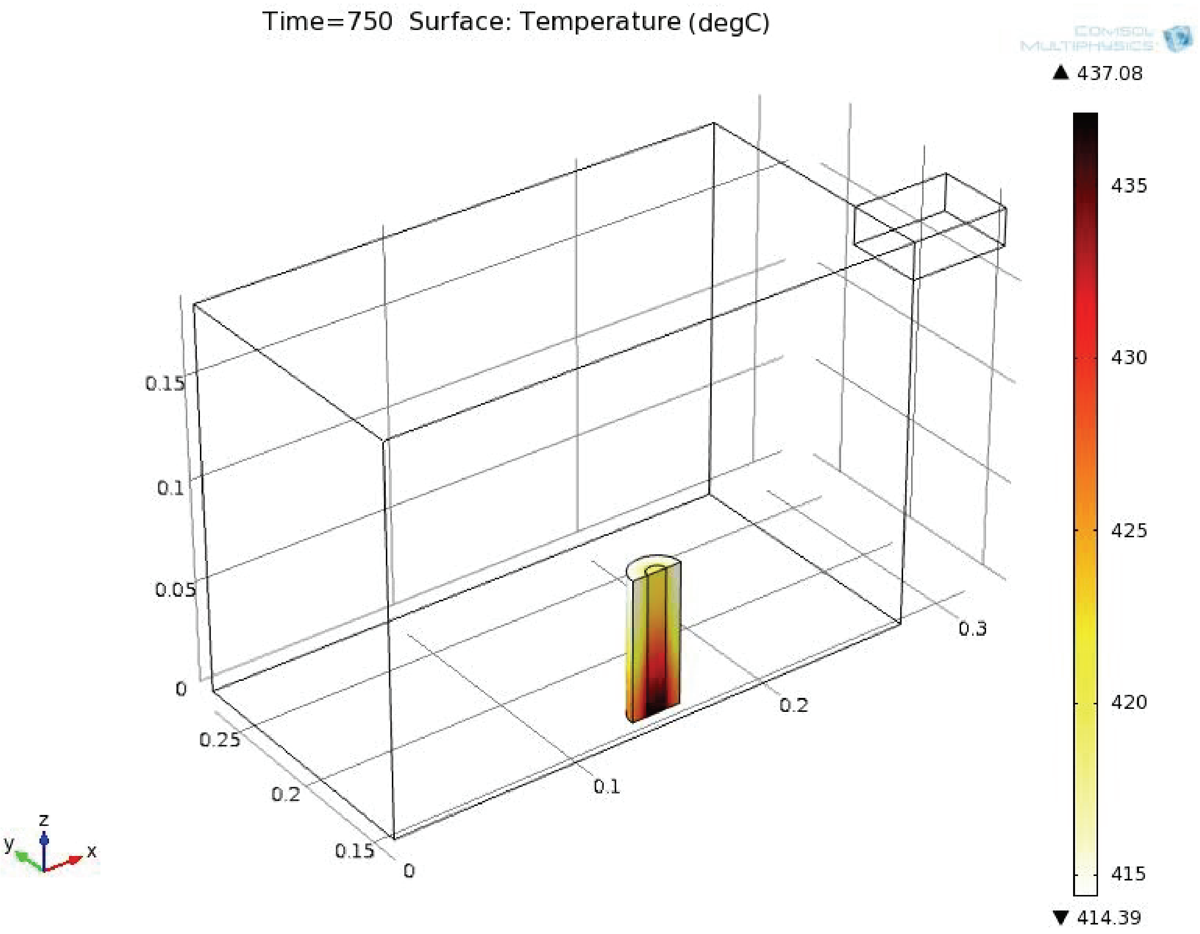


Figure 4.16: Temperature profile of char-doped biomass for microwave pyrolysis at 13 min

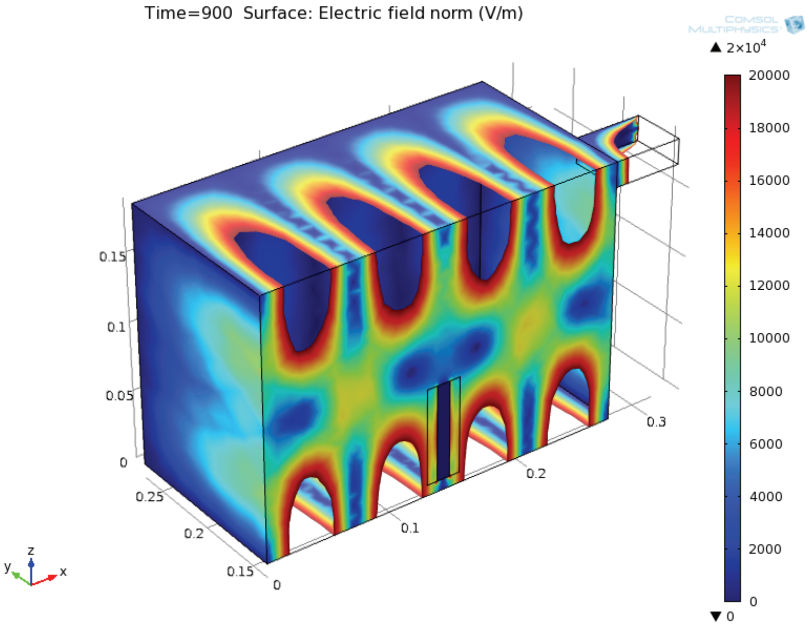


Figure 4.17: Electric field distribution of char- doped biomass for microwave pyrolysis

4.3.3. Experimental validation

The simulation results indicated that the desired temperature of 425°C was reached within 12.5 min of the onset of the reaction. The change in temperature over this time period was observed to be less than 50°C. This led to the configuration of an experimental design for the study. Based on the experimental results, the char-doped samples favored enhanced biochar formation than non-doped or graphite-doped biomass samples. Regression models ($P \leqslant 0.05$) for biochar yields *vs.* temperature under the three treatments (non-, graphite and char-doped) were derived for temperatures of 250°C, 290°C and 330°C (Figure 4.18). The measurement of temperatures > 330°C with the grounded thermocouple, even with a design improvement (Appendix 1), was restricted within the cavity due to the generation of sparks.

Figure 4.18 represents the linear relationship between yield% and temperature for each of the treatments. The correlation of determination for each model indicated that the yield% of the char-doped treatment had the best fit to the model as shown here (Equations 4.21- 4.23) and illustrated in Figures 4.19, 4.20, 4.21. The results also indicated that both the treatment conditions as well as temperature had significant effects on the yields. The effect details through an analysis of variance (ANOVA) table are shown in Table 4.3.

$$\text{Yield}_{\text{non-doped}} = 60.27 - 0.12\text{T}^\circ \qquad \mathbf{(R^2 = 0.85;\ P \leq 0.01)} \tag{4.21}$$

$$\text{Yield}_{\text{graphite}} = 78.25 - 0.15\text{T}^\circ \qquad \mathbf{(R^2 = 0.79;\ P \leq 0.01)} \tag{4.22}$$

$$\text{Yield}_{\text{char}} = 134.49 - 0.29\text{T}^\circ \qquad \mathbf{(R^2 = 0.80;\ P \leq 0.01)} \tag{4.23}$$

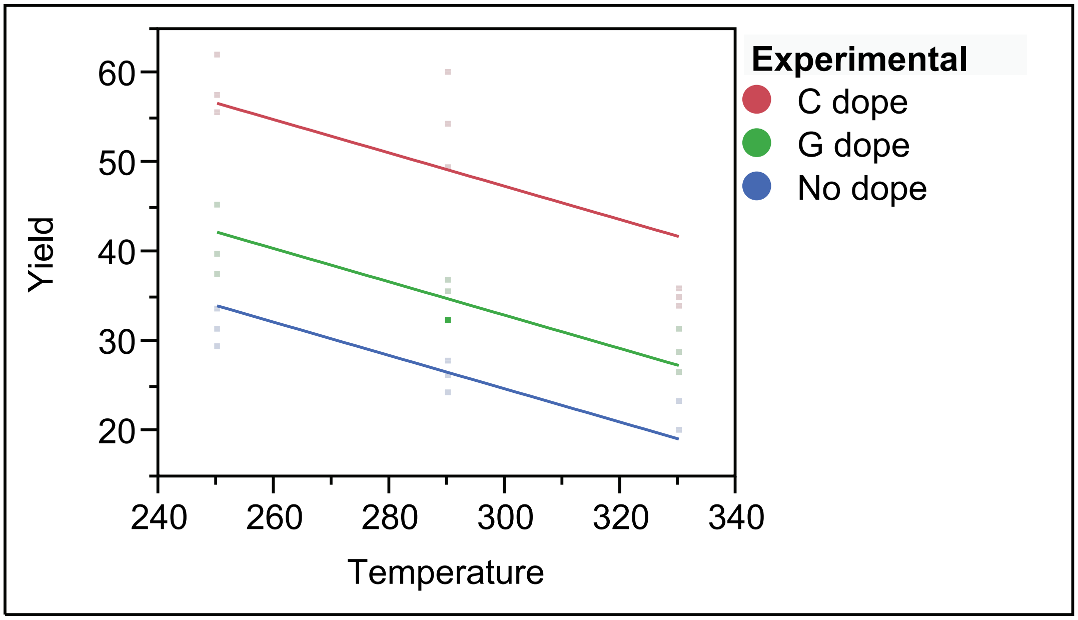


Figure 4.18: Regression analysis of Yield vs. Temperature (P ≤ 0.01) for different treatments of biomass sample

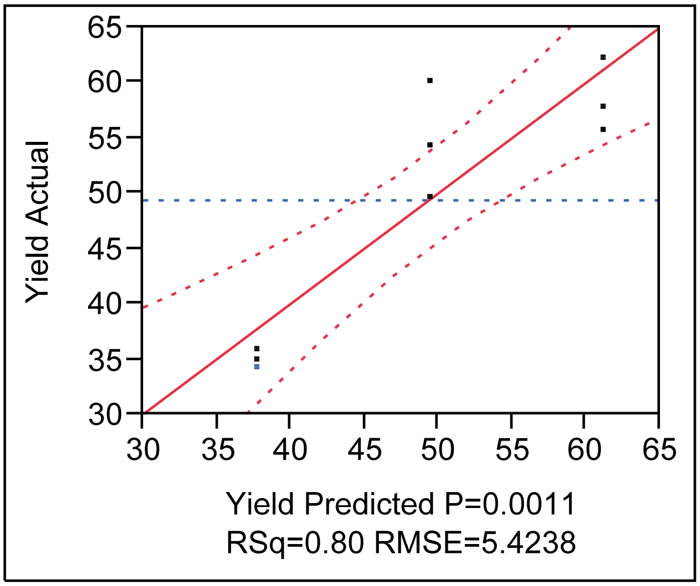


Figure 4.19: Regression analysis of Actual vs. Predicted biochar yields (P ≤ 0.01) for non doped biomass sample

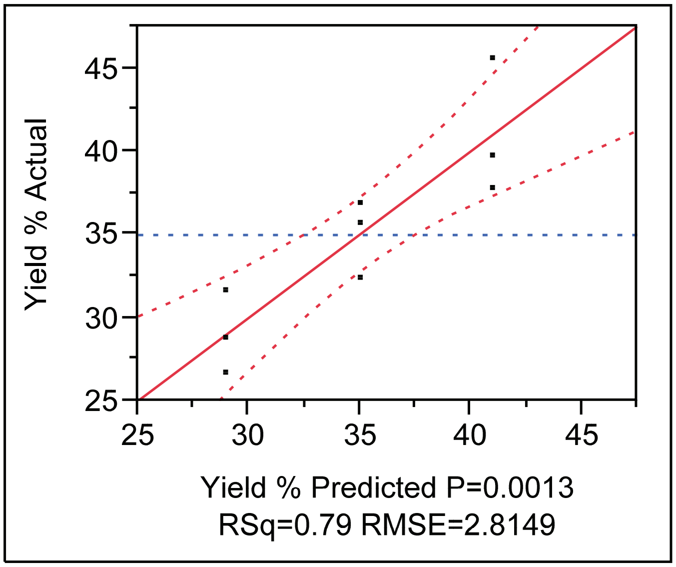


Figure 4.20: Regression analysis of Actual vs. Predicted biochar yields (P ≤ 0.01) for graphite doped biomass sample

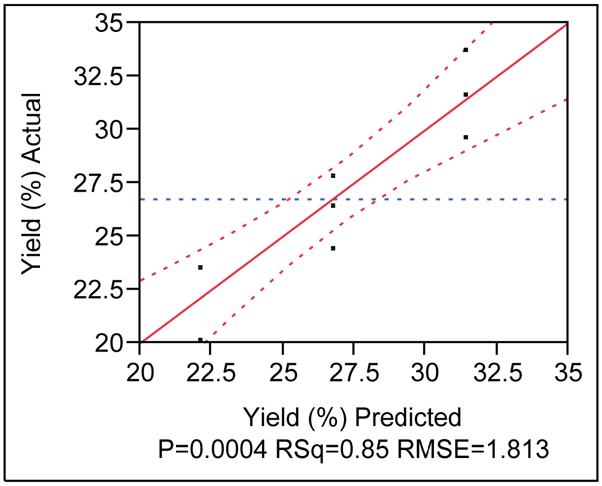


Figure 4.21: Regression analysis of Actual vs. Predicted biochar yields (P ≤ 0.01) for char doped biomass sample

Table 4.3: Testing of the effects of experimental parameters on the yields of the three configurations of the maple wood samples

Source	Nparm	DF	Sum of squares	F	Pr > F
Temperature	1	1	622.2291	47.2854	<.0001
Use of Doping agent	2	2	1525.2809	57.9558	<.0001

A multiple comparison of yields of the three types of configurations (non doped, graphite doped and char doped) of the maple wood samples, treated at three different temperatures (250°C, 290°C and 330°C) was conducted through an ANOVA and Duncan's Multiple Range test ($P \leq 0.05$). The ANOVA results are presented in Table 4.4.

Table 4.4: Analysis of variance (ANOVA) results for multiple comparison of yields of the three configurations of the maple wood samples

Source	DF	Sum of squares	Mean squares	F	Pr > F
Model	8	3221.882	402.735	55.595	<0.0001
Error	18	130.393	7.244		
Corrected Total	26	3352.275			

Char-doping at 330°C showed the lowest biochar yield than either of the other two doping treatments at that temperature (Figure 4.22) while treatments of 250°C produced greatest yields. However, biochar yields of non-doped biomass treated at 330°C and graphite-doped biomass treated at 290°C were not significantly different ($P > 0.05$). The results of the present study prove the effect of pyrolysis temperatures on the final biochar yield. It can be seen from Figure 4.22 that with increase in temperature, biochar yields decrease. Similar observations have been reported by several research studies (Yu et al., 2010, Demirbas, 2004, Dutta, 2010, Uemura et al., 2012). Microwave pyrolysis of corn cob carried out at temperatures ranging from 300 to 600°C indicated that the char yield decreased significantly to 23% with an increase in temperature to 600°C (Yu et al., 2010). The effect of treatment conditions such as temperature, particle size, lignin and inorganic matter contents on bio-char yield and reactivity were investigated by Demirbas (2004). The results of the elemental analysis show that high temperature and smaller particles led to an increase in the heating rate resulting in a decreased bio-char yield. On the other hand, carbon contents in the biochar increase with increasing pyrolysis temperature.

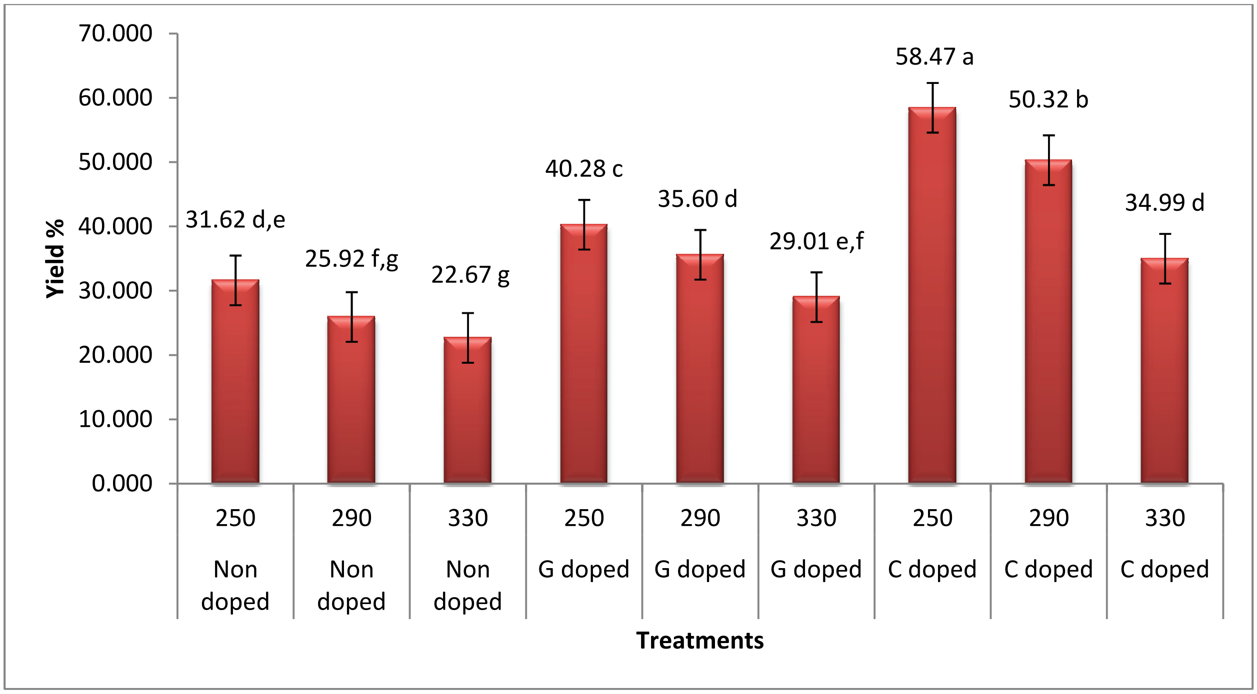


Figure 4.22: Duncan's multiple range test comparative analysis of experimental microwave pyrolysis yields (R^2 >0.95) representing statistical significance among the treatments. The means followed by the same letter are not significant at $P \leq 0.05$ level

The present experimental results clearly corroborate the simulations, and confirm the hypothesis that as a microwave receptor doping of biomass could have an influence on the pyrolysis products. Doping of the wood was instrumental in sustaining greater temperature uniformity and faster heating rates, thus improving the material's pyrolysis rate. Previous studies have indicated that the incorporation of receptors in the material can also be used to modify the pyrolysis process for maximization of a particular pyrolysis product (Fernández et al., 2011). The effects of char and graphite as microwave receptors on yield and the properties of oil products was investigated by Domínguez et al. (2003). Their results indicated that the bio-oil yields obtained from microwave pyrolysis with char as a receptor were higher than those obtained with graphite. Moreover, they showed that the use of graphite instead of char as a microwave receptor favored the cracking of large aliphatic chains to lighter species of oil products. Previous studies have shown that the solid residue or char produced through the pyrolysis also contributes to the final pyrolysis temperature. Therefore, the use of char as a doping agent could prove to be useful (Fernández et al., 2011).

4.4. Conclusions

This study investigated the advantages of using doping agents such as char and graphite to improve heat transfer during microwave pyrolysis of lignocellulosic biomass. A finite element model (FEM) was developed using the dielectric properties of the doping agents. The regression models developed from the dielectric property measurements indicated that char doping was better suited for microwave heating than graphite. The model developed during the simulation study found that doping helped to achieve a more efficient heat transfer within the biomass compared to non-doped samples. Char-doping resulted in rapidly reaching optimal temperatures, resulting in greater biochar yields. Laboratory-scale trials were conducted to test the validity and effectiveness of the simulation results. Statistical analysis of the yields of the biochar indicated that char doping was very efficient in terms of reducing heating time and raising temperature compared to graphite doping. The numerical simulation model could be used to inform the design of a microwave-assisted bioreactor capable of achieving maximum biochar formation.

4.5. Acknowledgements

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Connecting text

The results of the Finite Element Modelling (FEM) were instrumental in visualizing the heat transfer mechanism inside the pyrolysis reactor inside the microwave chamber during the pyrolytic reactions. The results of the previous chapter indicated the advantages of using doping agents such as char and graphite to improve heat transfer during microwave pyrolysis of lignocellulosic biomass. 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 process parameters of temperature, time and doping ratio on 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 5

A Study of Effects of Process Parameters and Selective Heating on Microwave Pyrolysis of Lignocellulosic Biomass

Abstract

Biochar has successfully emerged as a solid biofuel to address the concerns of greenhouse gas emissions. This study investigated microwave pyrolysis of maple wood in a laboratory-scale microwave pyrolysis reactor. The effects of final pyrolysis temperature, holding time and selective heating through doping on the biochar yield were investigated. A model was developed to predict the biochar yield as a function of pyrolysis temperature, time and doping ratio. The results of this research work indicate that microwave heating can fasten the process of pyrolysis conversion reactions. Results showed that the yield of the pyrolysis products increased with increase in holding time and decrease in process temperature. On the other hand, doping ratio did not have a significant effect on the biomass conversion to biochar. The resulting biochar was tested through proximate analysis and differential scanning calorimetry to determine its thermodynamic potential.

Keywords. Biochar, Biomass, Pyrolysis, Microwaves, Thermodynamics

5.1. Introduction

The past century has seen average surface temperature increase of 1.3 degrees Celsius on the Earth. However, it has been projected that this temperature increase would be raised by an additional 3.2 to 7.2 degrees over the 21st century by the Intergovernmental Panel on Climate Change (IPCC, 2007). These seemingly slight changes in temperature could have profound implications for farmers. This temperature increase has been attributed to a rise in carbon dioxide and other greenhouse gases released from the burning of fossil fuels, deforestation, agriculture and other industrial processes (Schahczenski and Hill, 2009).

Biomass, as an energy source, has two striking characteristics of being the only renewable organic resource and having the ability to capture 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 (Demirbas, 2000).

In general, the thermochemical conversion of biomass leads to the formation of biochar 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. 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 (Dutta et al., 2012).

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 (Lehmann, 2007).

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 good efficiency standards is the use of microwave or microwave assisted pyrolysis methods to form biochar and other useful volatiles. Results obtained through several investigations and largely the technology patented by the prototype microwave oven invented by the New Zealand Company, Carbonscape have established microwave assisted pyrolysis to be a technology which could enhance biochar production. Each patented industrial-scale oven will convert 40-50% of the wood sent through it into charcoal (Gaunt, 2012).

The concept of using microwave radiation to carry out pyrolysis of biomass for the production of biochar is still in its nascent stages. The inherent nature of dielectric heating could be taken advantage of in this process which would lead to higher yields of pyrolytic products. Microwave heating benefits from the fact that it is very efficient at only heating the material which is targeted wherein microwave chamber walls and exterior surfaces are not directly heated (Dai et al., 2010; Gaunt, 2012). Moreover, the microwave process has very short residence times compared with conventional non-microwave processes, improving efficiency and also reducing the process time from hours to minutes (Orsat et al., 2007).

Most of the specific research on microwave pyrolysis has been focussed on the maximization of bio-oil or syngas production such as in the case of Menéndez et al., (2004) which 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 yields of bio-oil, syngas, and biochar. Specific research activities on microwave pyrolysis of biomass include pyrolysis of fir pine wood sawdust (Wang et al., 2009), corn stover (Yu et al., 2007), rice straw (Huang et al., 2008, 2010), fir sawdust (Guo et al., 2006), biomass (Wan et al., 2009), coffee hulls (Domínguez et al., 2007) and wheat straw (Budarin et al., 2009).

Important research questions, therefore, for microwave pyrolysis are optimizing size and configurations of various feedstock materials in order to maximize heating efficiency. In addition, the manipulation and optimization of the process parameters could also be useful in increasing efficiencies so as to maximize biochar production through microwave assisted technology (Gaunt, 2012).

Many researchers have concluded that the optimum pyrolysis conditions for by product maximization cannot be attained without adding microwave susceptible doping agent (Robinson et al., 2010; Al Sayegh et al., 2010), which has been found to have significant impact on the pyrolysis conditions and the products formed. The advantages of the use of a doping agent is to absorb maximum microwave radiation in the initial phase and then to help sustain the pyrolysis process and final temperatures (Dominguez et al., 2008). Salema and Ani (2011) investigated the effect of microwave irradiation on oil palm biomass pyrolysis and found that char could be used as a microwave absorber to initiate the pyrolysis reaction and enhance the heating process. However, the effect of a microwave absorber or doping agent on the temperature profiles and yield of biochar has been found lacking in the literature. Therefore, the present research work holds interest to investigate the performance of char as a microwave absorber to initiate the pyrolysis reaction and enhance the heating process for microwave pyrolysis of wood biomass. The objective of the present study was to investigate the effect of microwave absorber to biomass ratio on the yield of biochar and heating characteristic through the temperature profiles of maple wood biomass under microwave radiation. Further, the effects of the pyrolysis conditions 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.

5.2. Material and Methods

5.2.1 Sample preparation

The biomass taken into consideration for simulation was maple wood of 25 mm diameter and 33 mm length with a moisture content of ≃ 7% was mounted on the sample stand. The biomass sample was doped with char of three variable diameters for the required doping to biomass ratio and 33 mm length having dielectric properties obtained from the previous chapter.

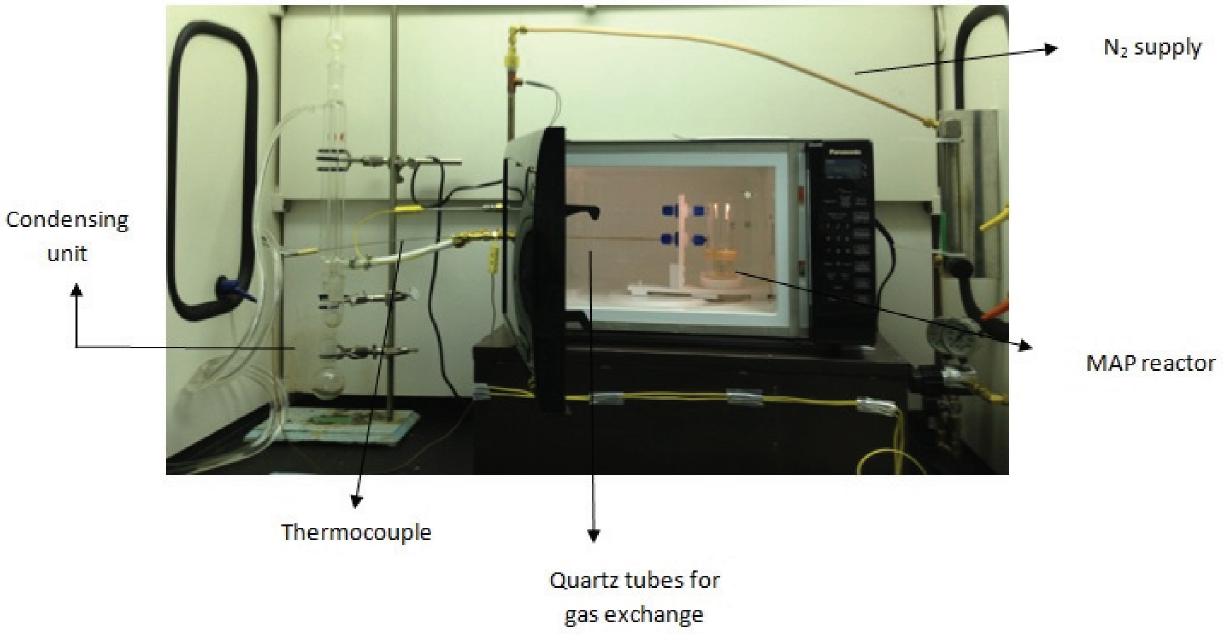
5.2.2 Microwave Pyrolysis Experimental set up

The microwave pyrolysis of maple wood was carried out in a custom built microwave pyrolysis unit within a regular domestic multimode microwave oven configuration of dimensions 205 mm × 335 mm × 180 mm operating at 2.45 GHz in the laboratories of Department of Bioresource Engineering, McGill University as shown in Figure 5.1.

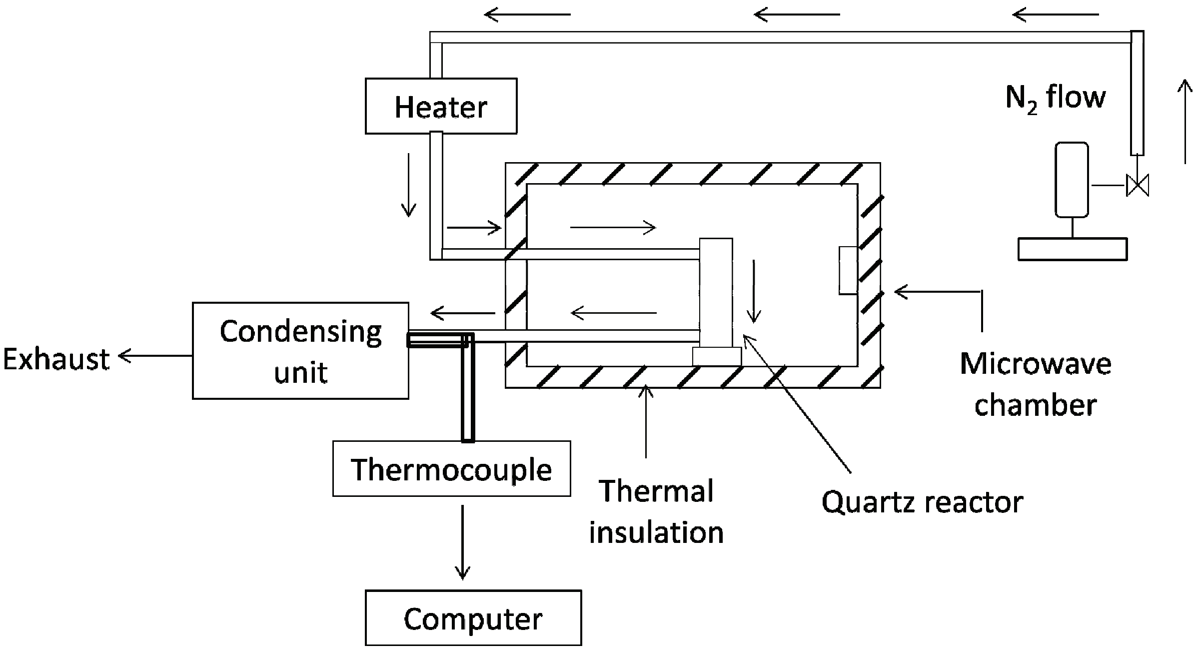
The pyrolysis reactor made of quartz consisted of three parts: an upper cylinder, a lower cylinder and a sample stand. The upper cylinder has 40 mm inner diameter and a length of 90 mm length. This was connected to the lower cylinder with an inner diameter of 50 mm and 42 mm height by a tapered ground joint. The sample stand had a diameter of 35 mm and 25 mm height. The air inside the reactor is purged with nitrogen at a flow rate of 0.003 l/s to create an oxygen free inert atmosphere using two quartz tubings of 6.3 mm diameter and 25.4 mm length.

The reactor was placed at the center of the microwave chamber and was connected to the two quartz tubings connecting the nitrogen gas purge and the gaseous product release. A K-type thermocouple was inserted into the reactor through the gaseous product release tube to monitor the biomass temperature continuously throughout the experiment. The thermocouple was inserted in a cylindrical copper shield of 5 mm diameter and 14 mm length to prevent signal interruption by microwaves (Ramaswamy et al., 1998) with a design described in Appendix 1. The gaseous product release pipe was then connected to a condensation unit with continuous rotation of cooling water at $\leqslant$10°C.

The experimental conditions were established through a three factorial central composite design obtained from JMP software (version 10) with the pyrolysis temperature, holding time and doping ratio as the three factors as shown in Table 5.1. Although 20 treatments were identified through the experimental design, the central point was replicated 6 times and the averages of the replicates were considered for the quantitative and qualitative analysis. The wood sample was then subjected to microwave heating at 2.45 GHz frequency and 300 W with a heating rate of 30°C/min as shown in Figure 5.2. After each run, the reactor was cooled to the ambient temperature under a nitrogen atmosphere. 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 product.



(a)



(b)

Figure 5.1: Microwave Pyrolysis Setup (a) Lab scale; (b) Schematic

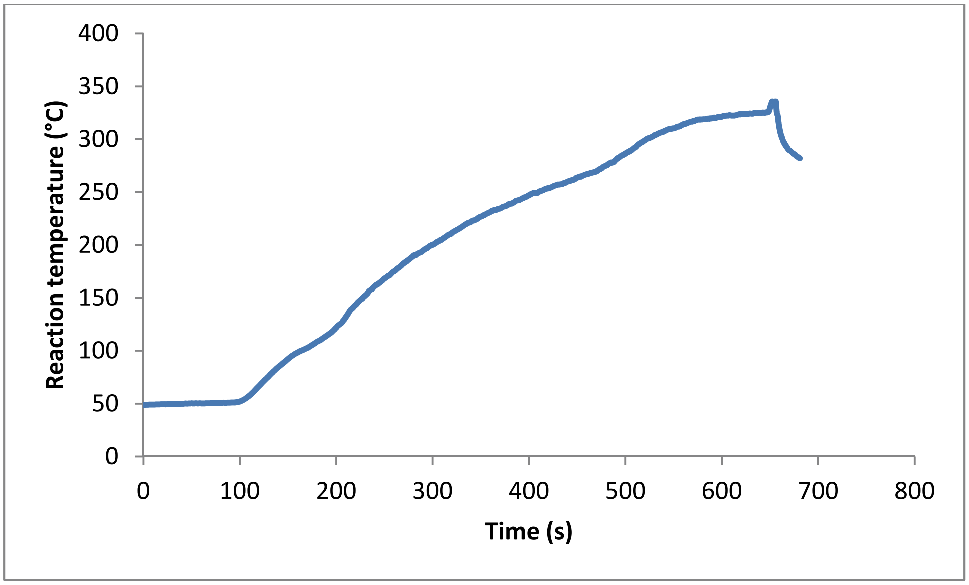


Figure 5.2: Microwave pyrolysis of maple wood with heating rate of 30 °C/min at 300 W with a desired reaction temperature of 330 °C

Table 5.1: Experimental conditions with a three factorial central composite design

Run	Pattern	Temp (°C)	Time (min)	Dope ratio (%)
1	0	290	3	24
2	+++	330	5	32
3	0A0	290	5	24
4	−−−	250	1	16
5	0	290	3	24
6	++−	330	5	16
7	0	290	3	24
8	+−−	330	1	16
9	0	290	3	24
10	A00	330	3	24
11	00a	290	3	16
12	0	290	3	24
13	−−+	250	1	32
14	00A	290	3	32
15	+−+	330	1	32
16	0	290	3	24
17	−+−	250	5	16
18	−++	250	5	32
19	0a0	290	1	24
20	a00	250	3	24

5.2.3 Biochar characterization

5.2.3.1 Proximate analysis

The biochar products were analyzed through proximate analysis of the char using modified ASTM methods (McClaughlin, 2009) 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.

5.2.3.2 Differential scanning calorimetry

The instrument used to measure the exothermic enthalpy of the biochar samples was a TA Instruments Q100 Differential Scanning Calorimeter (NewCastle, DE, USA) operated with the TA Instruments Q100 DSC 7.0 Build 244 software. The samples were first placed in aluminium pans (2 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.

5.3. Results and Discussion

5.3.1 Statistical comparison of biochar yields

The interpretation of the experimental results was achieved by the use of the response surface design technique. In this technique, the influence of the three experimental variables and their interactions on the results was investigated. Based on the experimental results, the following biochar yields were obtained from the microwave pyrolysis of the maple wood samples as shown in Figure 5.3.

The trend of decreasing biochar yield with increase in temperature has been corroborated in several studies (Masek et al., 2013; Yu et al., 2010). This trend has been reported by many researchers who have attributed this either to greater primary decomposition of the wood at higher temperatures or to secondary decomposition of the char. The parametric relations concluded in the current investigation are also consistent with previous studies of cellulose and lignocellulosics (Sensoz and Can, 2002, Valenzuela-Calahorra et al., 1987).

Using the results of the experiments, the biochar yield was represented through the following second-order polynomial equation (Equation 5.1) as a function of pyrolysis temperature (°C), holding time (min) and dope ratio (%).

$$Yield\% = 38.71 + 12.99 \times T + 2.85 \times t + 1.39 \times D + 0.98 \times T^2 + 3.96 \times t^2 - 3.32 \times D^2 + 2.13 \times T \times t - 2.76 \times T \times D + 1.71 \times D \times t \tag{5.1}$$

where, T is the pyrolysis temperature; t is pyrolysis time and D is the doping ratio (%).

The biochar yield was found to have a range of 37 to 77% variation with different pyrolysis conditions. A regression analysis indicated that the predicted biochar yield had a good correlation to the model with the correlation coefficient of determination of $R^2 = 0.82$ ($P \leq 0.01$). The predicted biochar yield is given in Figure 5.4 with the corresponding experimental value. This implies that the quadratic regression model can be used to explain the variation in biochar yield and can be attributed to the independent variables of pyrolysis temperature, holding time, dope ratio and their interaction.

The corresponding analysis of variance (ANOVA) is presented in Table 5.2. The predicted optimum levels of the experimental variables of pyrolysis reaction were obtained by applying the regression analysis to the model. This model indicated that the highest biochar yield was 80.5% at the pyrolysis temperature of 250°C, holding time of 3.3 min and dope ratio of 16% with a desirability of 0.99 as shown in Figure 5.5. The validation of these optimized conditions indicated a difference of 1.2% with the predicted value.

On the other hand, the maximum yield of biochar from the experimental results was 78% for pyrolysis conditions of pyrolysis temperature of 250°C, holding time of 1 min and dope ratio of 16%, presenting a relative difference of 1.3% with the predicted highest yield obtained from the model. The pyrolysis conditions of pyrolysis temperature of 250°C, holding time of 1 min and dope ratio of 32% also produced a high yield of 70.3%. This in turn also corroborates the model indicating that dope ratio was not found to be a significant parameter for maximization of biochar yield for microwave pyrolysis.

The response surface optimization for the results of the biochar yields are represented by the surface and contour plots for the pyrolysis conditions in Figures 5.6, 5.7, 5.8. It was evident from the response surface plots that the treatments with lower temperatures produced higher yields of biochar which confirms the findings of a number of studies (Di Blasi, 1996; Domı´nguez et al., 2007; Maˇsek et al., 2013; Dutta, 2010).

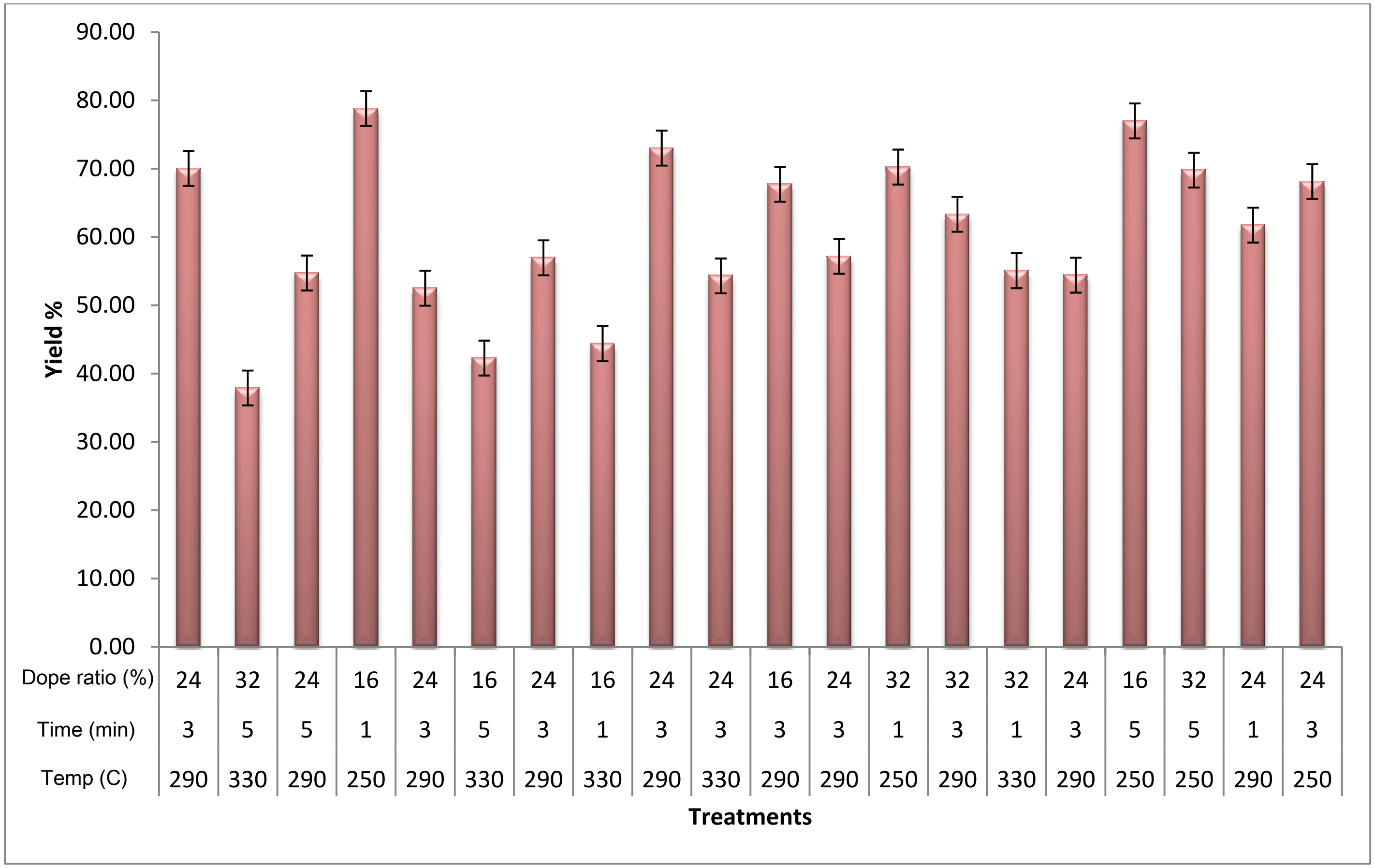


Figure 5.3: Fischer's multiple comparison test results for yields for microwave pyrolysis of biochar with statistical significance among treatments

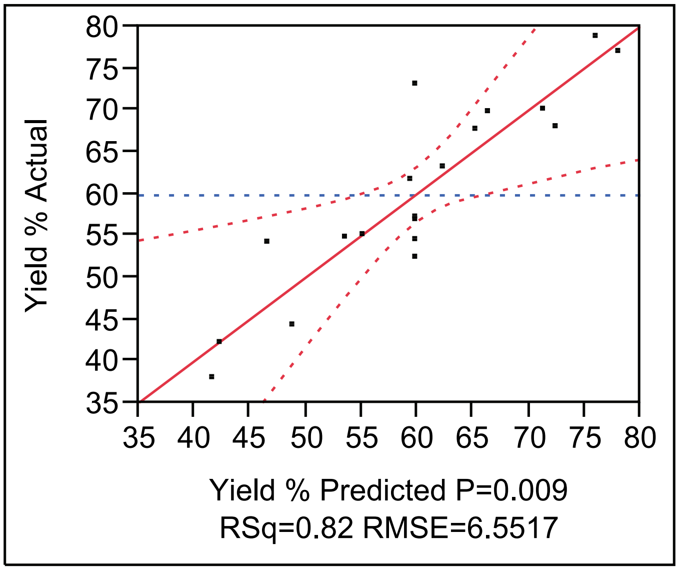


Figure 5.4: Regression analysis of Actual vs. Predicted biochar yields ($P \leq 0.01$)

Table 5.2: Analysis of Variance of Regression model for biochar obtained through microwave Pyrolysis of maple wood

Source	DF	Sum of squares	Mean square	F ratio	Prob > F
Model	9	1974.1776	219.353	4.3135	0.0161
Error	10	508.5283	50.853		
C. Total	19	2482.7059			

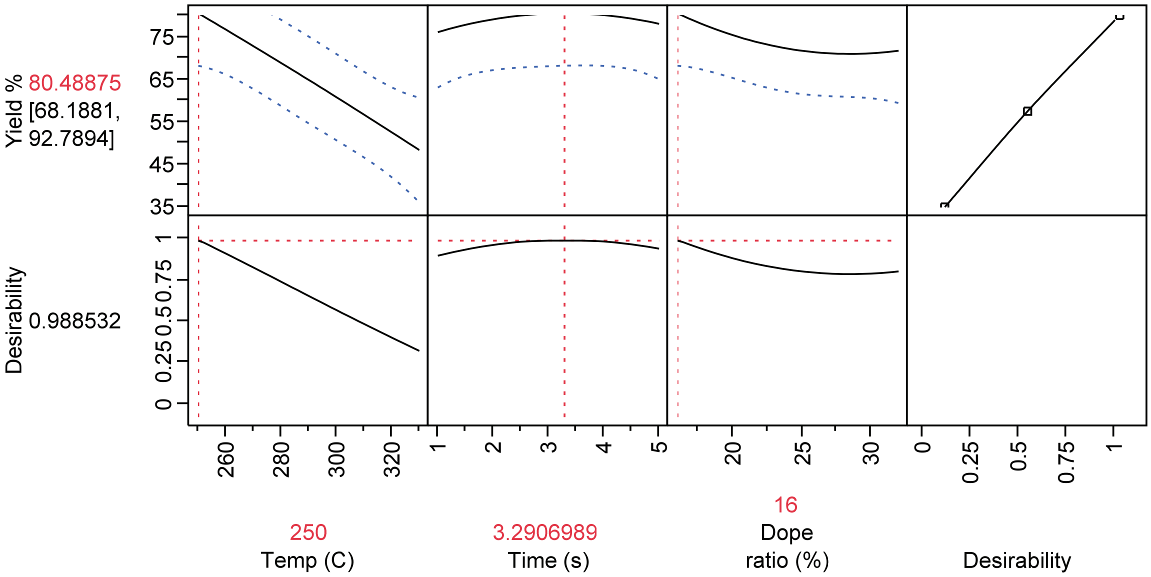


Figure 5.5: Optimum pyrolysis parameters for maximization of biochar through the regression model ($R^2 = 0.91$; $P \leq 0.05$)

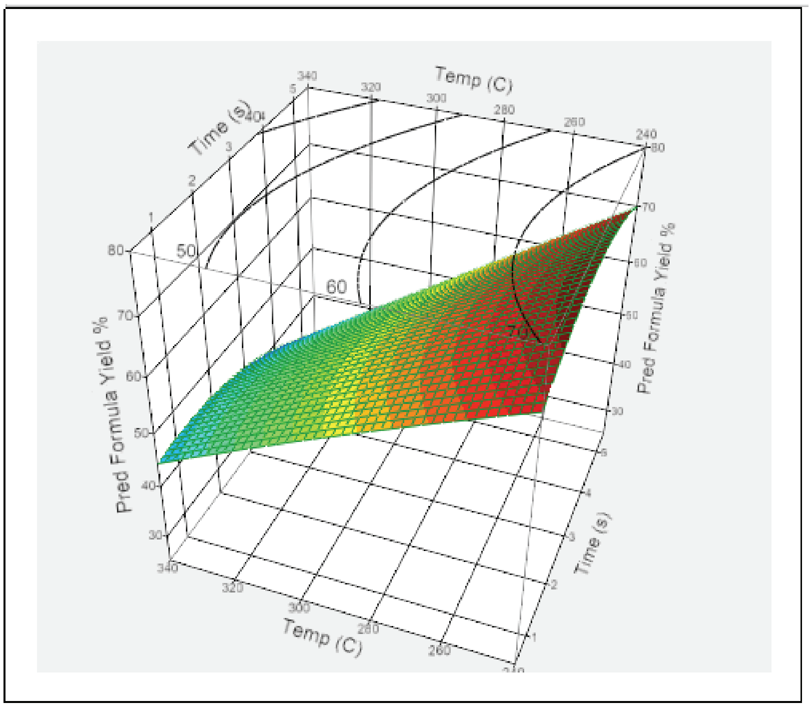


Figure 5.6: Response surface plot of biochar yield for microwave pyrolysis from regression model (Y: Temperature; X: Time)

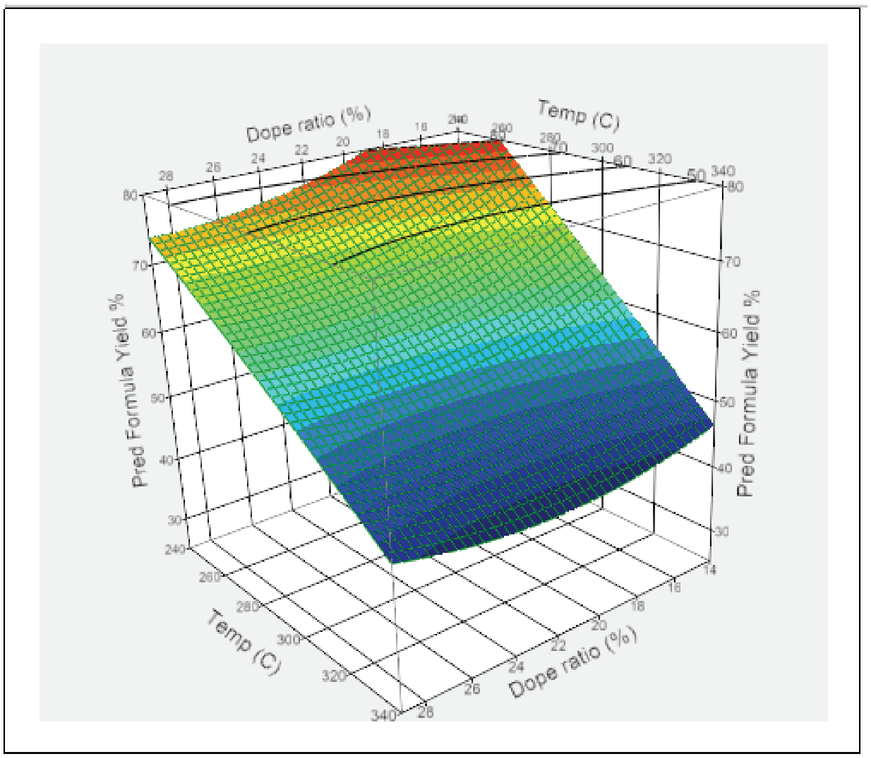


Figure 5.7: Response surface plot of biochar yield for microwave pyrolysis from regression model (Y: Temperature; X: Dope ratio)

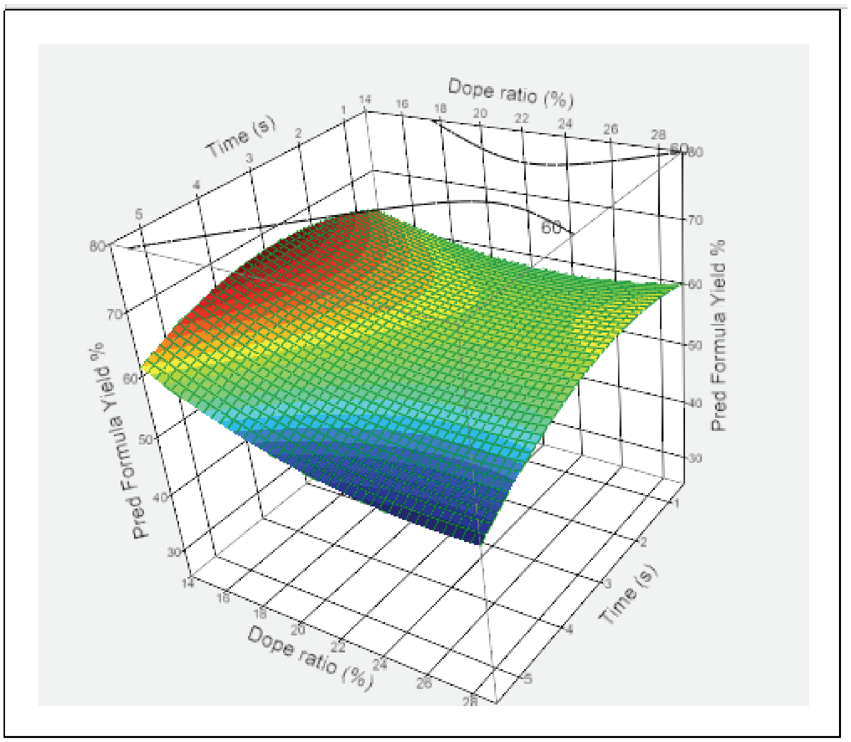


Figure 5.8: Response surface plot of biochar yield for microwave pyrolysis from regression model (Y: Time; X: Dope ratio)

The dope ratio (from 16- 32%) did not affect the pyrolysis process significantly as shown through the regression analysis by the insignificant model terms (P > 0.50). This in turn indicates that microwave pyrolysis of maple wood was not affected by the variation in doping of the biomass using char. Thus, it would be possible to attain desired biochar yields through doping for various microwave pyrolysis conditions with better heat distribution and reduction in processing times.

5.3.1.1 Validation of Regression Model

The accuracy of the regression model was also validated using five random experimental conditions as shown in Table 5.3 in an independent experiment and compared to the corresponding predicted biochar yields. The validation results indicated a % difference between the experimental and predicted value of ±4.6%. Thus the technique of central composite design enables us to evaluate the accurate values of the pyrolysis parameters for the maximization of biochar from maple wood by using microwave pyrolysis.

Table 5.3: Regression model validation: Comparison of Experimental and Predicted Biochar Yields

Temp (°C)	Time (min)	Dope ratio (%)	Exp Yield%	Predicted yield %	% Diff
250	3	24	65.60	70.03	6.33
290	5	24	51.28	54.47	5.85
290	3	24	66.16	61.29	-7.95
290	1	24	55.51	60.18	7.77
330	3	24	42.09	47.30	11.02
				Avg	**4.60**

5.3.2 Biochar properties as a fuel

Table 5.4 summarizes the main chemical characteristics of the maple wood and its biochar component obtained through varying treatments. Results indicated that the biochar obtained treatments at 290°C had higher ratio of residual to mobile matter in comparison to all other treatments of all pyrolysis durations and doping ratios. The highest residual matter% with comparatively lowest mobile matter% was found with the treatment at pyrolysis temperature of 290°C, pyrolysis time 1 min and doping ratio of 24% having 32.94% mobile matter and 59.14% residual matter. The treatment also had the lower ash% value of 7.92%. The treatment at 250°C, pyrolysis time 1 min and doping ratio of 32% had the highest mobile matter% of 97.20 and low residual matter% of 2.25 but had the lowest ash% of 0.55.

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, 2007). The presence of higher ash contents occurs at the expense of the carbon content in the biochar sample. Research in relation 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 char 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.

Table 5.4: Proximate analysis of maple wood and biochar samples obtained through microwave pyrolysis

Temp (°C)	Time (min)	Dope ratio (%)	Ash%	Mobile matter (MM) %	Residual matter (RM) %	MC%	Ratio of RM/MM
330	5	32	5.64	53.68	40.68	4.14	0.76
290	5	24	15.50	48.68	35.82	3.42	0.74
250	1	16	5.48	91.09	3.43	4.13	0.04
330	5	16	10.64	53.37	36.00	2.27	0.67
330	1	16	11.11	84.12	4.77	1.18	0.06
330	3	24	2.80	56.19	41.01	6.47	0.73
290	3	16	18.25	64.30	17.45	2.87	0.27
250	1	32	0.55	97.20	2.25	3.60	0.02
290	3	32	3.05	74.12	22.83	5.89	0.31
330	1	32	10.18	66.68	23.14	1.13	0.35
250	5	16	3.55	68.51	27.94	6.41	0.41
250	5	32	13.33	77.34	9.33	2.79	0.12
290	1	24	7.92	32.94	59.14	1.82	1.80
250	3	24	1.02	80.43	18.55	3.85	0.23
290	3	24	11.64	65.84	33.00	2.10	0.30
Wood			2.05	75.26	22.68	7.24	0.50

5.3.3. Differential Scanning Calorimetry

A Differential Scanning Calorimetry (DSC) was also conducted for the maple wood samples maintaining the central composite experimental design matrix as shown in Table 5.5 taking the average for the 6 central points (Run 1). The calorimetric study was conducted for a temperature range of 0°C to 550°C with a heating rate of 50°C/min. The objective of this investigation was to compare the exothermic enthalpy of the biochar samples produced from microwave pyrolysis and carry out a response surface optimization.

The results of the DSC study are shown in Figure 5.9. The highest exothermic enthalpy was found to be at the pyrolysis temperature, holding time and dope ratio of 250°C, 1 min and

32% respectively. The following equation (Equation 5.2) for the optimization of the DSC results for the microwave pyrolysis was obtained with the help of JMP:

$$Exothermic\ energy = 94.23 - 14.37 \times T + 9.06 \times t + 9.50 \times D + 6.31 \times T^2 + 3.94 \times t^2 + 27.29 \times D^2 + 7.23 \times T \times t - 17.25 \times T \times D - 19.99 \times D \times t \quad (5.2)$$

where, T is the pyrolysis temperature; t is pyrolysis time and D is the doping ratio (%).

Table 5.5: Central composite experimental design matrix for DSC of maple wood biochar treatments

Run	Temp (°C)	Time (min)	Dope ratio (%)
1	290	3	24
2	330	5	32
3	290	5	24
4	250	1	16
5	330	5	16
6	330	1	16
7	330	3	24
8	290	3	16
9	250	1	32
10	290	3	32
11	330	1	32
12	250	5	16
13	250	5	32
14	290	1	24
15	250	3	24
Wood	No treatment		

A regression analysis was carried out in order to compare the predicted and actual biochar exothermic enthalpy (Figure 5.10). This comparison showed that the experimental values had a good correlation to the model with $R^2 = 0.90$ ($P \leq 0.05$). Thus the variation in biochar yield can be attributed to the process variables of pyrolysis temperature, holding time, dope ratio and their interaction. The corresponding analysis of variance (ANOVA) is presented in Table 5.6.

The predicted variables of pyrolysis reaction were optimized to be at the pyrolysis temperature of 250°C, holding time of 1 min and dope ratio of 32% by applying the regression analysis to the model. The highest exothermic energy of 191.05 J/g with a desirability of 0.91 was obtained as shown in Figure 5.11. The optimization results of the exothermic enthalpy of the biochar samples are represented by the surface and contour plots for the pyrolysis conditions in Figures 5.12, 5.13, 5.14, relating the three factors of pyrolysis temperature, holding time and dope ratio.

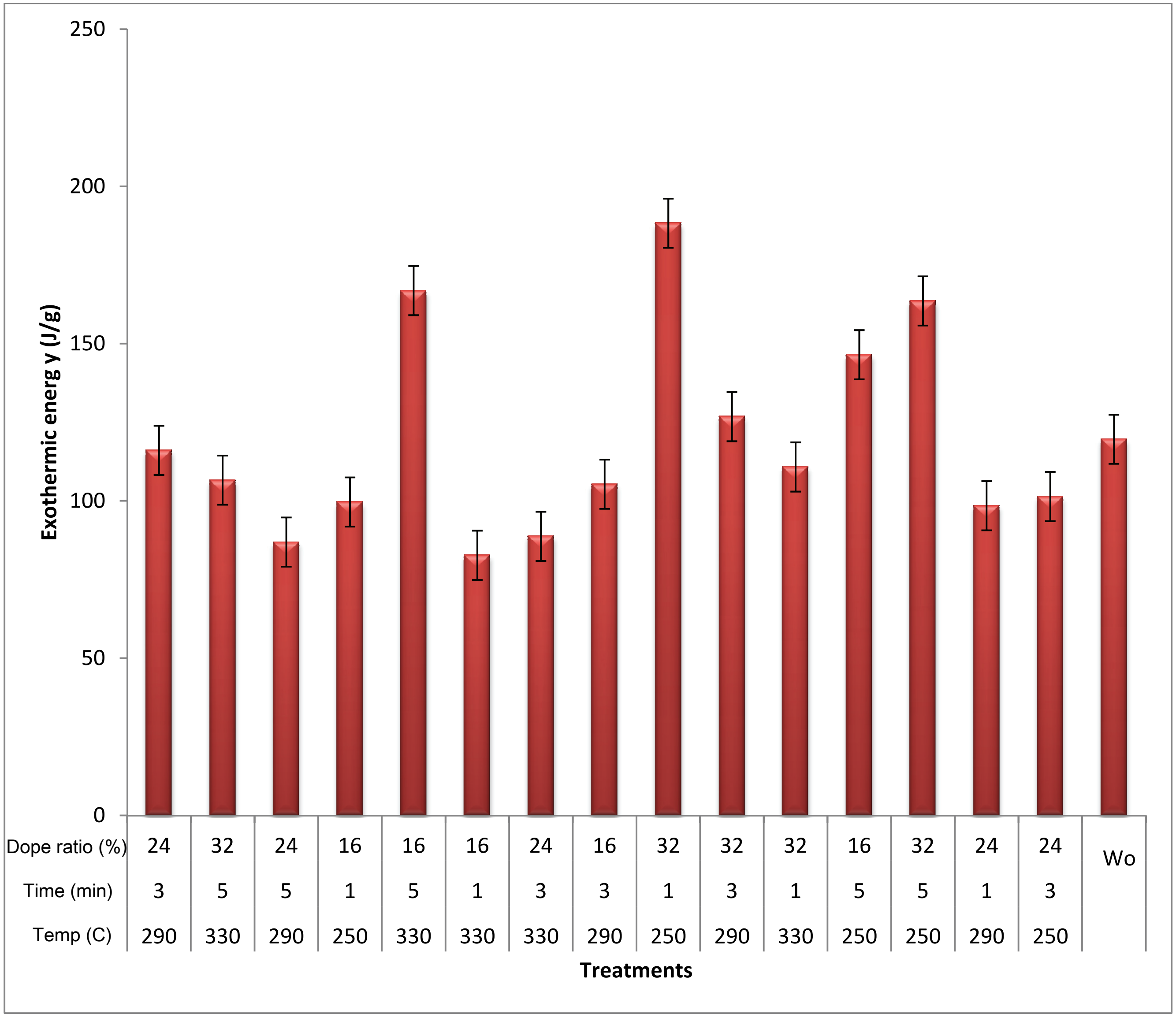


Figure 5.9: Differential Scanning Calorimetry results indicating the thermodynamic potential for the maple wood biochar

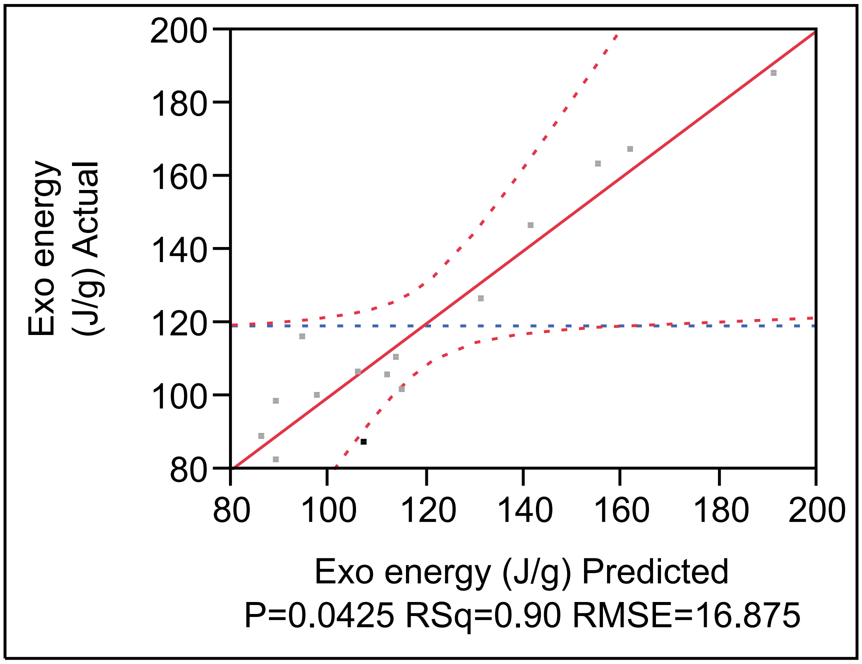


Figure 5.10: Regression analysis of Actual vs. Predicted exothermic energy (J/g) of maple wood biochar treatments ($P \leq 0.05$)

Table 5.6: Analysis of Variance of Regression Model for exothermic energy of biochar obtained from Microwave Pyrolysis of maple wood

Source	**DF**	**Sum of squares**	**Mean square**	**F ratio**	**Prob > F**
Model	9	13261.288	1473.48	5.1746	0.0425
Error	5	1423.767	284.75		
C. Total	14	14685.055			

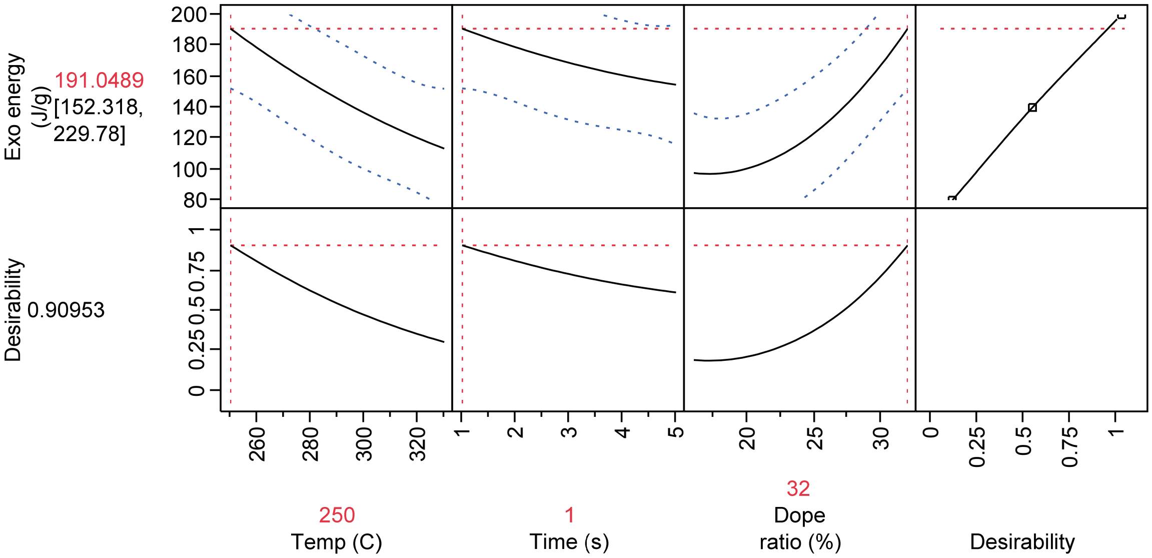


Figure 5.11: Optimum pyrolysis parameters for maximization of exothermic energy (J/g) of maple wood biochar treatments through the regression model

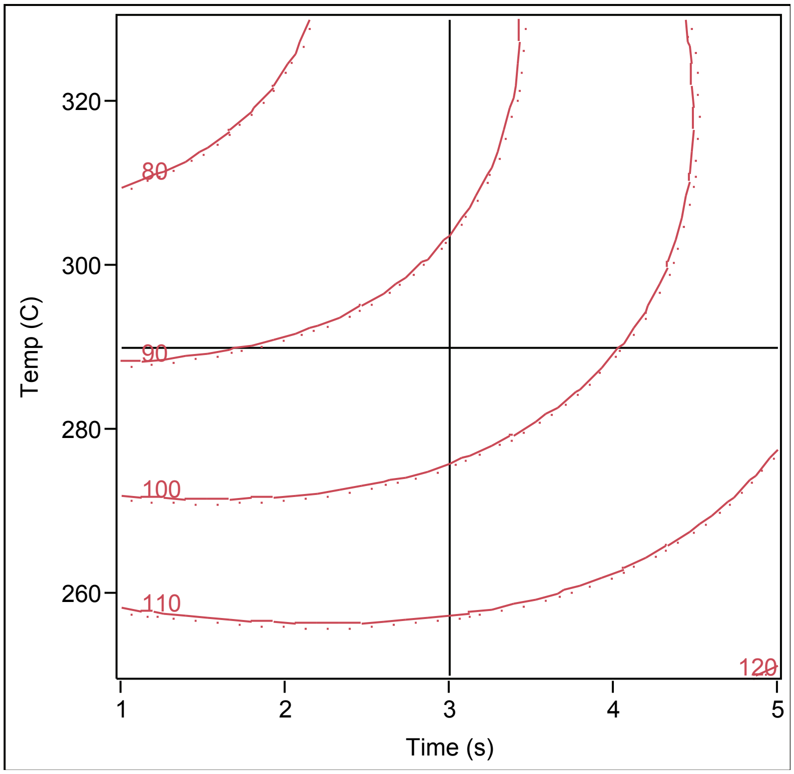


Figure 5.12: Response contour plot of exothermic energy (J/g) of maple wood biochar microwave pyrolysis treatments from regression model (Y: Temperature; X: Time)

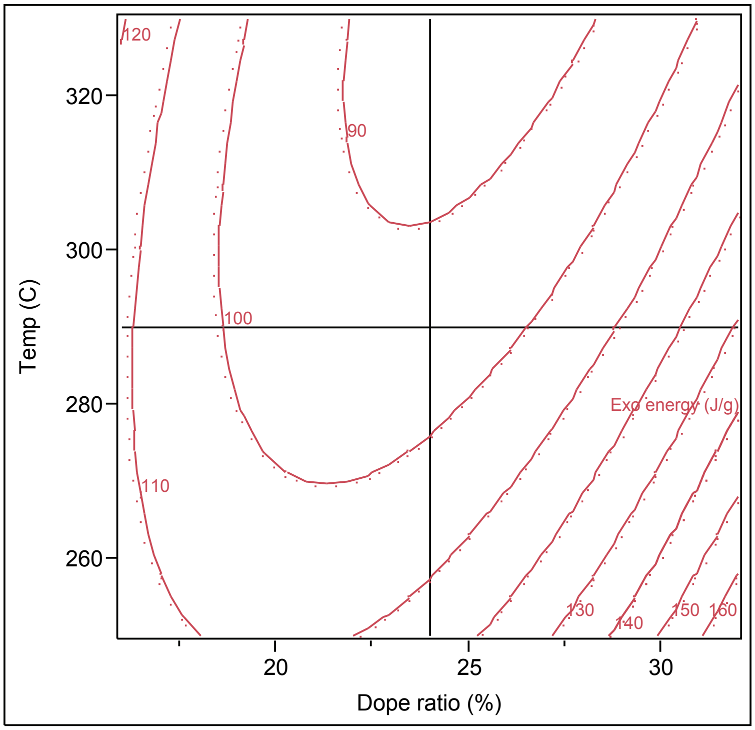


Figure 5.13: Response contour plot of exothermic energy (J/g) of maple wood biochar microwave pyrolysis treatments from regression model (Y: Temperature; X: Dope ratio)

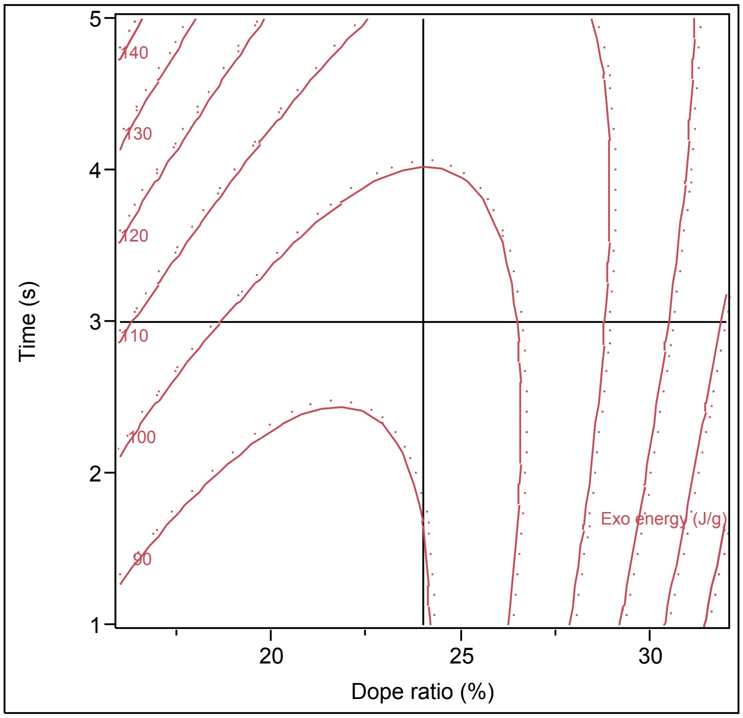


Figure 5.14: Response contour plot of exothermic energy (J/g) of maple wood biochar microwave pyrolysis treatments from regression model (Y: Time; X: Dope ratio)

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 et al. (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 510°C. Similarly, in the current study, the DSC curves ended 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 should be investigated.

5.4. Conclusion

In this study, the effects of pyrolysis conditions such as temperature, time and dope ratio on the biochar yields and fuel properties of biomass samples were investigated by using statistical design techniques. Results showed that the yield of the decreased with increasing pyrolysis temperature and time while doping ratio did not have a significant effect on the biochar yields. The maximum predicted value of yield for microwave pyrolysis was optimized to be at the pyrolysis temperature of 250°C, holding time of 3.3 min and doping ratio of 16%. The regression analysis showed good correlation between the experimental and predicted results. Through the results obtained from the Differential Scanning Calorimetry, the highest exothermic enthalpy of 188.31J/g was found to be at the pyrolysis temperature, holding and dope ratio of 250°C, 1 min and 32% respectively, which had good agreement with the optimization results.

5.5. Acknowledgements

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Connecting text

The previous section dealt with the establishment of a design and fabrication of a lab scale microwave assisted pyrolysis reactor which aims at the production of high yield of biochar from biomass doped with microwave receptors not only to enhance the heat transfer but also to provide a point of concentration for microwave radiation for initiating the pyrolytic process. It also evaluated the roles of process parameters such as pyrolysis temperature, time and doping ratio of the receptors on the biochar yields. After quantification of the pyrolysis reactions for yield, it was essential to carry out the qualitative analysis of the biochar product. Also to understand the extent of the chemical reactions from microwave pyrolysis it would be beneficial to determine the influence of these process parameters on the structural composition of biochar. Porosity measurements and their relation to reflectance, scanning electron microscopy and FTIR studies in the biochar samples can be used as an index for further evaluation of the products formed in the pyrolytic process in terms of their physical characteristics.

Chapter 6

Surface Characterization and Classification of Microwave pyrolysed Maplewood Biochar

Abstract

The maple wood biochars produced by microwave pyrolysis were analysed and compared in relation to their physical properties such as porosity and reflectance of chars. The aim of this research was to investigate the feasibility of the selection of relevant wavelengths in Visible/Near Infra-Red spectroscopy by combining Maximum R^2 (MAXR) with Multiple Linear Regressions (MLR) method to build a predictive model. The porosity and yields data of the resulting biochar were used to test the model. Based on the spectral information, different mathematical techniques were used to group the biochar based on their physical properties. Scanning electron microscopy imaging of the biochar samples showed that pyrolysis temperatures and doping ratio played a major role in the formation of microporous structures within the biochars formed due to the devolatilization process during microwave pyrolysis. The FTIR analysis was consistent with the scanning electron microscopy conclusions indicating evidence of aliphatic group stretching with increase in temperature and doping ratio. The FTIR profile of the control (fresh maple wood) sample had a more complex spectrum. With increase in pyrolysis temperature functional group activities decreased indicating breaking up of weaker bonds.

Keywords. Biochar, Pyrolysis, Porosity, Pycnometry, Hyperspectral imaging, Scanning electron microscopy, FTIR

6.1. Introduction

In general, the thermochemical conversion of biomass leads to the formation of biochar at temperatures above 300°C. Biochars are more or less amorphous, nanostructured with localized crystals of highly conjugated aromatic compounds with 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 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). Reaction parameters can be varied easily to alter the relative quantities and qualities of the resulting products (Avenella et al., 1996). The rate of cooling also significantly contributes to the final structure of the biochar. It has been stated that slow cooling results in further pyrolysis and this in turn, results in loss of carbon. As a result of this, a hardened hydrophobic biochar is formed. This kind of biochar, although ideal for furnaces, does not have much application in soil. Hence quick cooling or quenching makes it easily breakable and hydrophilic instead of hydrophobic (Reed, 2009).

The heating mechanism in the case of conventional pyrolysis is from the surface towards the center of the material while in case of microwave pyrolysis, the heat is generated through a volumetric method by the conversion of electromagnetic energy to thermal energy. This results in increased penetration leading to higher temperature of the core of the material than the surface. Thus the use of microwaves for pyrolysis favours devolatilization reactions of biomass. In addition microwave heating is a faster process compared to conventional pyrolysis yielding desired temperatures for pyrolysis. Additionally, the lower temperatures in the microwave cavity can be useful to avoid undesirable reactions and condense the final pyrolysis vapours in this area.

The devolatilization of the biomass is linked to the process of volatile matter generation, where significant changes to the physical structure of the char take place. The chemistry of 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 native configuration 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 impact of pyrolytic reactor conditions on the char reactivity for biomass fuels (Cetin et al., 2004; Chitsora et al., 1987; Gale et al., 1996). 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 process. However, only a limited number of studies have dealt with the relation between the pyrolytic conditions and char structure (Hu et al., 2009).

The comparison between the pyrolysis and gasification of eucalyptus sawdust under different conditions was undertaken by Pindoria et al. (1998). Their study highlighted the importance of biomass pyrolytic conditions 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 comparison of the physical properties of biochar produced through slow conventional pyrolysis and microwave pyrolysis, as measures of the degree of conversion, based on porosity and true density were assessed by Masek et al., (2013).

Helium pycnometer employs the general method of gas displacement and the principle driving this is a volume: pressure relationship stated in Boyle's Law (Shea, 1954; Turner et al., 1977; Furuse, 1988). Pycnometers have always been recognized as density measuring devices but they are in fact devices for measuring volume displacement only. Density is merely calculated as the ratio of mass to volume. The mass of the sample in question is usually measured on a separate device, usually by weighing. The volume measured in a gas pycnometer is the amount of volume within the sample chamber from which the gas is excluded. Hence, the volume measured considering the finest scale of surface roughness will depend on the atomic or molecular size of the gas. Helium is the gas commonly used as the measurement gas, owing to its small size and its inherent inert nature (Tamari, 2004). The determination of density by gas pycnometer (volumetric) using helium as the measuring gas is also a well known technique for testing of carbon materials (DIN, 2001). Helium pycnometry was used to study the carbons and the subsequent tailoring of high performance carbon adsorbents at the Sigma-Aldrich laboratories (Betz et al., 2011).

Visible/ Near Infrared Spectroscopy (Vis/NIRS) is a rapid, non-invasive and in-line method, increasingly being used for testing the quality of many agricultural products. This technique has been found to be quite effective in assessing the internal quality of fruits and vegetables. The detailed chemical composition, moisture profile 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). Infrared spectroscopy has been used to analyse the structure of biochar and to draw relations with porosity of the microstructure within. Fourier transform infrared (FTIR) spectroscopic analyses have come to be an important and popular tool for biochar study. Karaosmanogˇlu et al., (1999) performed FTIR spectroscopic analyses of the second group of biochar samples of straw-stalk of rapeseed plants to identify and compare their functional groups. Reeves et al., (2010), investigated the effect of adding biochar to soil on the spectra of mixed biochar and soil in the near- (NIR, 10,000 to 1000 cm^{-1}) and mid- infrared (mid-IR, 4000 to 400 cm^{-1}) regions.

Hyperspectral imaging is part of a class of techniques commonly referred to as spectral imaging or spectral analysis. Hyperspectral images are produced by instruments called imaging spectrometers (Smith, 2012), a technique that combines both conventional imaging and spectroscopy (Venkatesh, 2007). Hyperspectral imaging is extremely advantageous in terms of its data, presenting the information in the spatial direction which is useful for extracting information with minimum loss of data. Reflectance is the most common mode of hyperspectral imaging and is usually carried out in the Vis–NIR (400–1000 nm) or NIR (1000–1700 nm) range, and has been used to detect defects, contaminants and quality attributes of fruits, vegetables and meat products (El Masry et al., 2007; Qiao et al., 2007; Lu & Peng, 2006). Adopting the same concepts of hyperspectral reflectance imaging, an investigation could be conducted to relate the structure of biochar and the different pyrolysis conditions such as the pyrolysis temperature and residence time. Moreover, an analysis of the influence of porosity on the reflectance of the biochar samples could also be accomplished. Birchwood biochar produced by slow as well as fast pyrolysis were analysed and compared according to their physical characteristics of porosity and reflectance. A relation between char porosity and the reflectance of the biochar structure was found wherein porosity is inversely proportional to reflectance (Dutta et al., 2012).

The aim of this study was to investigate the structure of biochar produced by microwave pyrolysis. The effects of different pyrolysis conditions such as the pyrolysis temperature, residence time and doping of the biomass on the porosity and reflectance of the resulting biochar were characterized using Helium pycnometry techniques, hyper spectral imaging in the near-IR range, scanning electron microscopy and Fourier transform infrared radiation.

6.2. Material and Methods

6.2.1. Production of biochar by microwave pyrolysis

The microwave pyrolysis of maple wood was carried out in a custom built microwave pyrolysis unit within a regular domestic multimode microwave oven configuration of dimensions 205 mm × 335 mm × 180 mm of 2.45 GHz in the laboratories of Department of Bioresource Engineering, McGill University (Figure 6.1). The pyrolysis bioreactor system made of quartz consisted of three parts: an upper cylinder, a lower cylinder and a sample stand as illustrated. The air inside the reactor is purged with nitrogen with a flow rate of 0.003 l/s to create an oxygen free inert atmosphere. The wood sample was then subjected to microwave heating at 2.45 GHz frequency and 300 W with a heating rate of 30°C/min. After each run, the reactor was cooled to the ambient temperature under a nitrogen atmosphere. The volatiles produced during the process were constantly displaced with nitrogen gas purged into the system and then condensed in a water- bath. The experimental conditions were established through a three factorial central composite design obtained from JMP software (version 10) with the pyrolysis temperature, holding time and doping ratio as the three factors as shown in Table 6.1. Although 20 treatments were identified through the experimental design, the centre point of the cube was replicated 6 times and the averages of the replicates were considered for the quantitative and qualitative analysis.

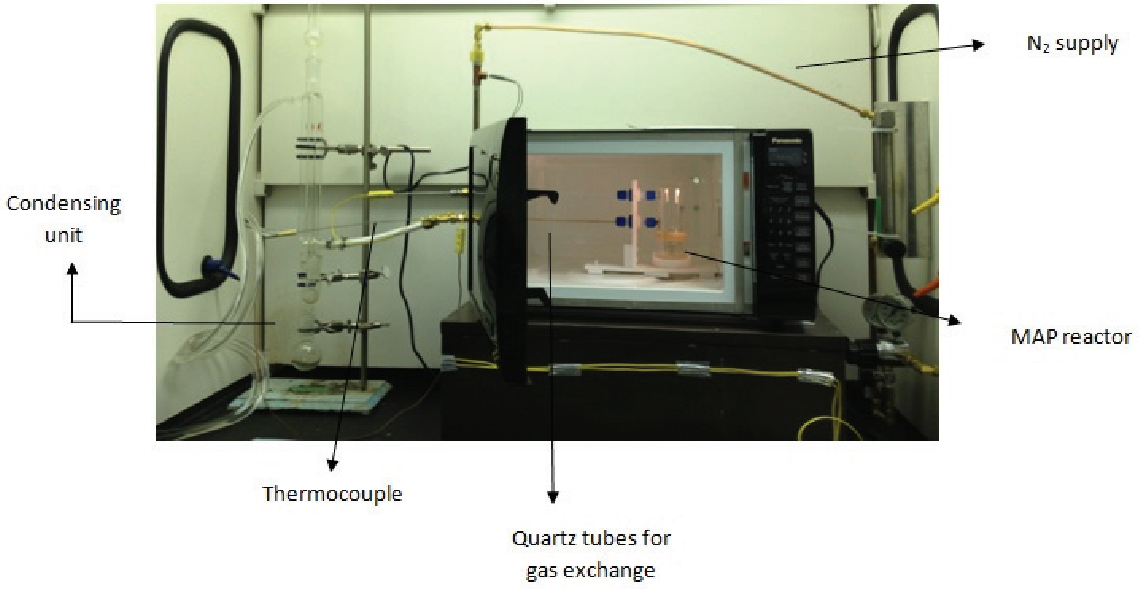


Figure 6.1: Microwave Pyrolysis Setup

Table 6.1: Experimental conditions with a three factorial central composite design

Run	Pattern	Temp (°C)	Time (min)	Dope ratio (%)
1	0	290	3	24
2	+++	330	5	32
3	0A0	290	5	24
4	−−−	250	1	16
5	0	290	3	24
6	++−	330	5	16
7	0	290	3	24
8	+ − −	330	1	16
9	0	290	3	24
10	A00	330	3	24
11	00a	290	3	16
12	0	290	3	24
13	−−+	250	1	32
14	00A	290	3	32
15	+−+	330	1	32
16	0	290	3	24
17	−+−	250	5	16
18	−++	250	5	32
19	0a0	290	1	24
20	a00	250	3	24

6.2.2. 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 6.2. The samples were weighed prior to measurement of porosity. No pretreatments were carried out. The solid volume of the samples excludes pores within the sample material.

The gas pycnometer usually consists of two chambers, one to hold the sample and a second chamber of fixed internal volume referred to as the reference volume. The device additionally comprises a valve to admit a gas under pressure to one of the chambers. The working equation of a gas pycnometer wherein the sample chamber is pressurized first is given in Equation 6.1 (Lowell et al., 2004):

$$V_s = V_c + \frac{V_r}{1 - \frac{P_1}{P_2}}$$

(6.1)

where Vs is the sample volume, Vc is the volume of the empty sample chamber (known from a prior calibration step), Vr is the volume of the reference (again known from a prior calibration step), P_1 is the first pressure (i.e. in the sample chamber) and P_2 is the second (lower) pressure after expansion of the gas into the combined volumes of sample chamber and reference chamber. Using the pycnometry method, the sample was placed in the 50 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 (Kassama and Ngadi, 2005).

Figure 6.2: Helium Pycnometer (Model 1305 Multivolume, Micromeritics Instrument Corporation, Norcross, GA)

The bulk density of the biochar was calculated by dividing the mass of the char samples with its bulk volume. As the char samples were perfectly cylindrical in shape, the bulk volume was calculated using the mathematical formula for the volume of a cylinder ($\pi d^2 l/4$) by measuring the diameter (d) and length (l) of the sample.

6.2.3. 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 of the pores or interstices of a substance in a material matrix and is expressed as a percentage or ratio. It is commonly computed based on the measured bulk and apparent density as described above and calculations based on the following relationship as given in Equation 6.2:

$$\varepsilon = 1 - \frac{\rho_b}{\rho_p} \tag{6.2}$$

where ε is the open pore porosity, ρ_b is the bulk density, and ρ_p is the particle density of the biochar sample (Pastor-Villegas et al., 1998).

6.2.4. Hyper- spectral imaging of biochar

6.2.4.1. Hyperspectral image acquisition set up

The hyperspectral imaging system used for the study consists of a line-scan spectrograph called HyperspecTM (Headwall Photonics Inc. Model No. XS-100, USA) which included the spectral range of 900 to 1730 nm (Figure 6.3). 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). Two tungsten halogen lamp (150 Watts) was used to illuminate the samples as they are moved across the field of view of the cameras.

The camera controlled by the software (Remote Sensing Cube, Specim Ltd. and Auto Vision Inc. Finland) captures the image in the visible/near infrared wavelength range of 400 nm to 1000 nm. The images are recorded as three dimensional arrays with spatial and spectral components. The spatial components are measurements in x and y directions and spectral component wavelength (λ) in the third direction. The camera records the spatial information by scanning a single line in the x direction, while the conveyor moves the sample in the y direction to form a 512x512 pixels image size. An exposure time of 30 ms was used for the study.

The spectral imaging system was calibrated with a dark image, collected by blocking the light from lens and a white image collected from a standard white reference board. Image acquisition was done on the inner charred body of the sample after removing the doping agent.

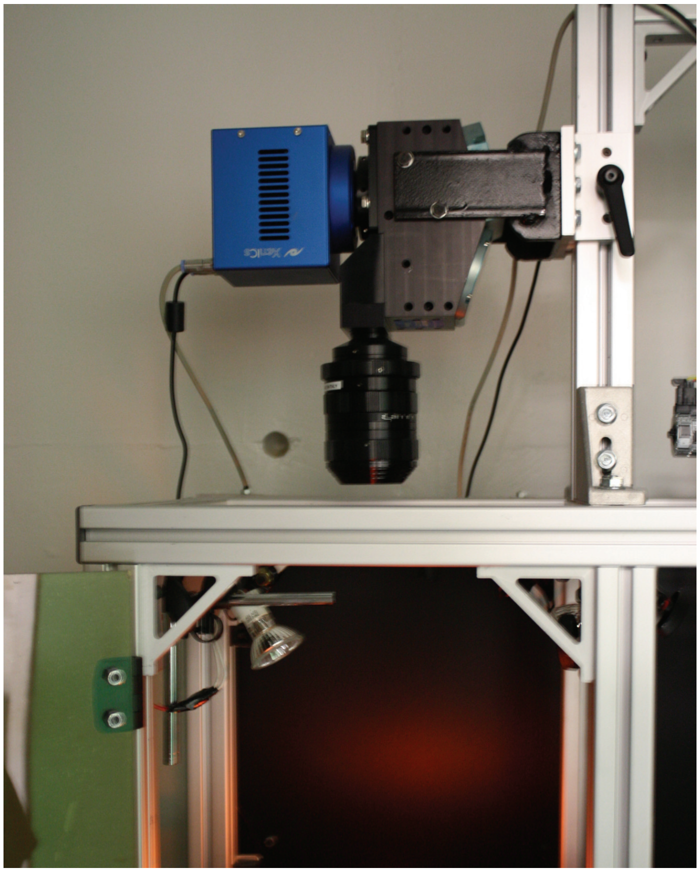


Figure 6.3: Hyperspectral imaging system (HyperspecTM) for the classification of biochar

6.2.4.2. Data Analysis

The software ENVI (Version 4.7, ITT Visual Information Solutions, Boulder, CO, USA) was used to preprocess the spectral images and to extract the spectral information from the biochar samples. Classification of the spectral data was performed by mosaicking the images of the slow pyrolysis images together. The spectral data were collected from the biochar samples by selecting an area of 2 cm diameter as region of interest (ROI) using the software. The data contains the reflectance values of the spectra in the wavelength range of 900-1730 nm from the biochar samples. The reflectance was calculated for each pixel in the ROI or any selected pixel using the following Equation (6.3) (Servakaranpalayam, 2006):

$$R_{ci} = \frac{Sample_{ci} - Dark_{ci}}{White_{ci} - Dark_{ci}} \tag{6.3}$$

This is done to remove noise and to compensate for offset due to dark current, light source colour temperature drift and lighting spatial non-uniformity across the scene line. The mean spectral values obtained by averaging each pixel values in the region of interest (ROI) from 900-1730 nm were used as spectral features of the image. Multiple linear regressions (MLR) were used for the wavelength selection in order to obtain the maximum classification of the biochar samples. The spectral data were analyzed by using principle component analysis (PCA) for classifying the biochar samples in terms of porosity and reflectance using the statistical software JMP (Version 10).

6.2.4.2.1. Mosaicking

Mosaicking is a very effective tool in hyper-spectral imaging analysis to categorize images of samples. It involves combining multiple images into a single composite image. This tool provides interactive capabilities for placing images within a mosaic, and automated placement of images within an output mosaic (ITTVIS, 2011)

6.2.4.2.2. Multiple linear regressions (MAXR technique)

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 selection of wavelength for extracting maximum information from whole spectra is an important step which needs to be done with accurate and reliable methods. This was carried out by using the technique of MAXR, which chooses the wavelengths by producing the MLR model with highest coefficient of determination or R^2 value through an iterative process.

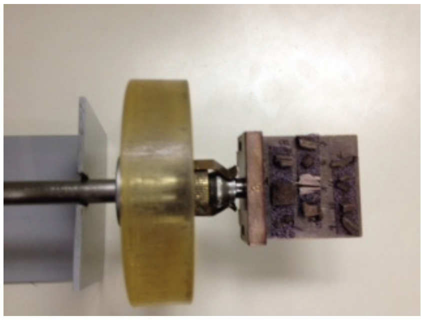
6.2.4.2.3. Principle component analysis

The averages of the spectra for each wavelength were the input to the PCA and the outputs were the principle components at all wavelengths. The number of principle components was selected based on the percentage explained by the principle components which represents the maximum correlation.

6.2.5. Scanning electron microscopy

Scanning electron microscopy (SEM) was carried out for the char samples by placing them on an aluminium stub. A coating of Au film was applied to the sample for >1s time period using a Cressington sputter coater with a gold target (Cranberry Twp., PA). The coated samples were then examined and imaged under a JEOL JSM electron microscope model – 840A (École Polytechnique Montréal, QC) (Figure 6.4).

(a)



(b)

Figure 6.4: (a) JEOL JSM electron microscope model – 840A; (b) Au coated char samples

6.2.6. Fourier transform infrared spectroscopy (FTIR)

The diffuse reflectance spectra of the char samples under dry nitrogen atmosphere were recorded by a Fourier transform infrared spectroscopy (FTIR) spectrophotometer (Nicolet Magna

750 FTIR, Nicolet Instrument Corp., Madison, WI) equipped with a liquid-nitrogen-cooled mercury-cadmium-telluride detector and Windows-based OMNIC software (Thermo Nicolet Co., Madison, WI) for data collection and analysis. Spectra in the mid-infrared region (4,000-600 cm^{-1}) were collected with 50 scans at a spectral resolution of 2 cm^{-1}. A background spectrum of dry nitrogen atmosphere without the sample was recorded under the same instrumental conditions and was subtracted from each sample spectrum.

6.3. Results and Discussion

6.3.1. Porosity

The porosity results obtained through the pycnometer readings were analyzed using a multiple comparison test by analysis of variance (ANOVA) and Fischer's multiple comparison analysis. The ANOVA results as shown in Table 6.2 indicated that the porosity values of the biochar samples obtained through microwave pyrolysis of maple wood fit the model well with an R^2=0.99 for $P \leq 0.05$. The differences between the porosity values (Figure 6.5) of all the biochar samples as obtained through the experimental design in Table 6.1 and the fresh maple wood were found to be significant using a Dunnett (two sided) test at $P \leq 0.05$.

Table 6.2: Analysis of Variance of Regression Model for porosity of biochar obtained from Microwave Pyrolysis of maple wood

Source	DF	Sum of squares	Mean squares	F	Pr > F
Model	20	201.858	10.093	242.199	< 0.0001
Error	42	1.750	0.042		
Total	62	203.608			

The highest porosity was found to be for the microwave pyrolysis conditions of reaction temperature of 330°C for 5 min with doping ratio of 16%. A regression analysis indicated that the biochar porosity had a good correlation to the model with the correlation coefficient of determination of $R^2 = 0.75$ ($P \leq 0.05$). The predicted porosity is given in Figure 6.6 with respect to the experimental value. This implies that the model correlates to the independent variables of pyrolysis temperature, holding time, dope ratio and their interaction. The predicted optimum levels of the experimental variables of pyrolysis reaction were obtained by applying the regression analysis to the model. According to the model, the highest biochar porosity value of 94.5% was found to be at the pyrolysis temperature of 330°C for 5 min with doping ratio of 20.9% with a desirability of 0.98 as shown in Figure 6.7. The response surface optimization for the results of the biochar porosity was represented by the surface and contour plots for the pyrolysis conditions in Figures 6.8, 6.9, 6.10.

In general, during the pyrolysis reactions, the biomass undergoes a change in phase leading to the creation of void spaces. In slow pyrolysis, as the name implies, this process happens relatively slower resulting in greater collapse of the structure of the char closing the created void space. The longer the duration of pyrolysis, the greater would be the chances of such structural collapse. The number of closed pores was not accounted for in helium pyconometry; therefore the measured porosity of the samples indicates there is less number of open pores in the samples that are pyrolysed for a longer duration.

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. These results were found to be in agreement with the findings of Hu et al., (2008) which was conducted for rapid pyrolysis.

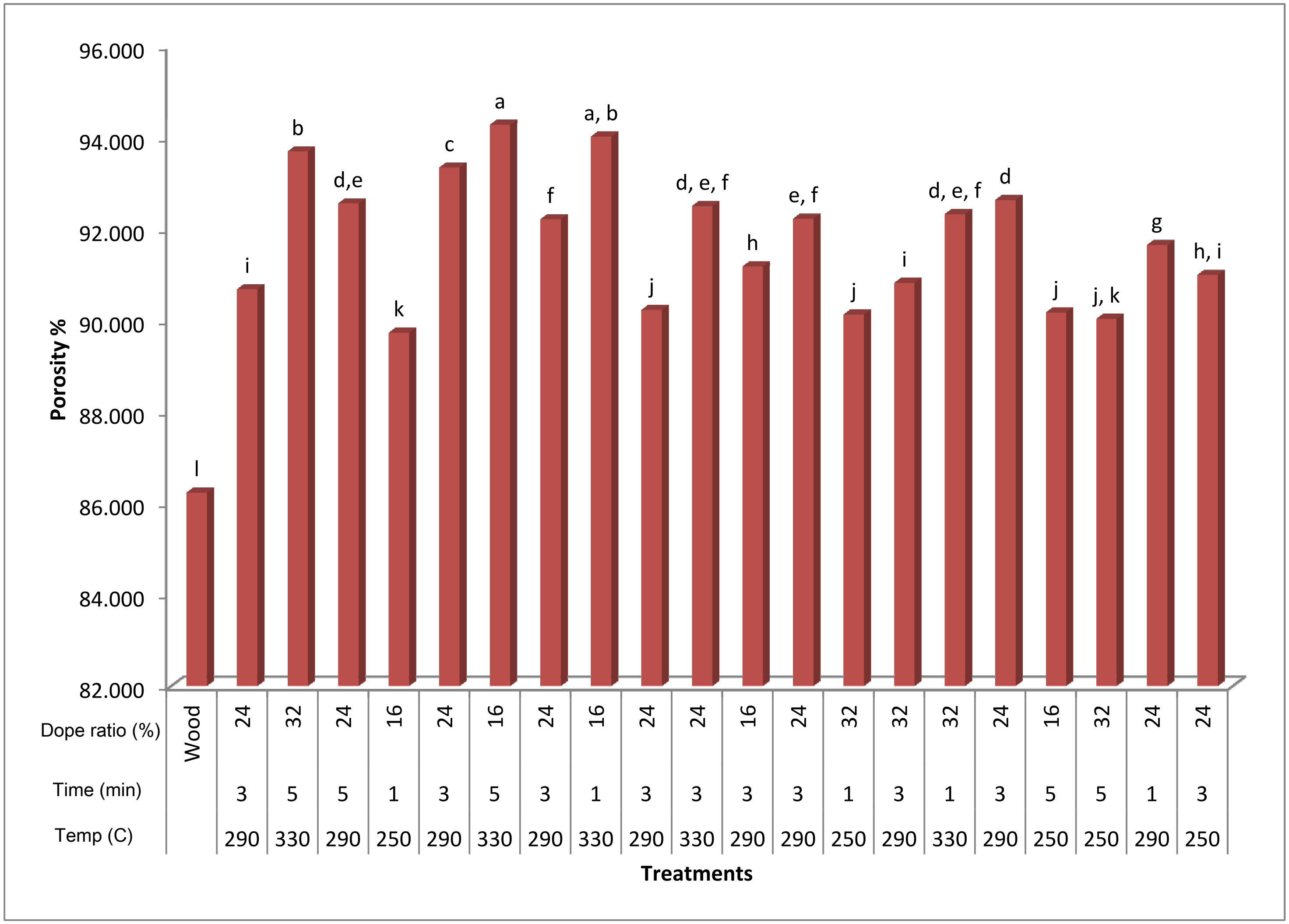


Figure 6.5: Fischer's multiple comparison test results for porosity of microwave pyrolysed biochar with statistical significance among the treatments. The porosity with the same letter are not significant at P<0.05 level

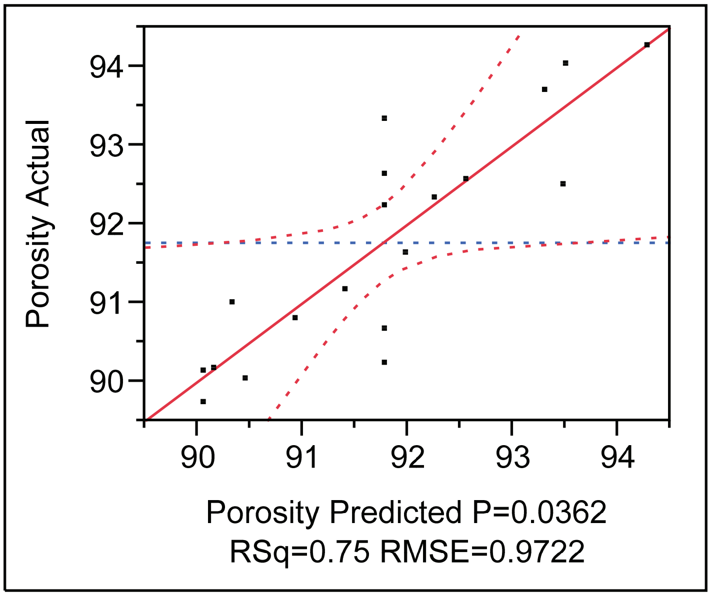


Figure 6.6: Regression analysis of Actual vs. Predicted porosity (%) of maple wood biochar treatments ($P \leq 0.05$)

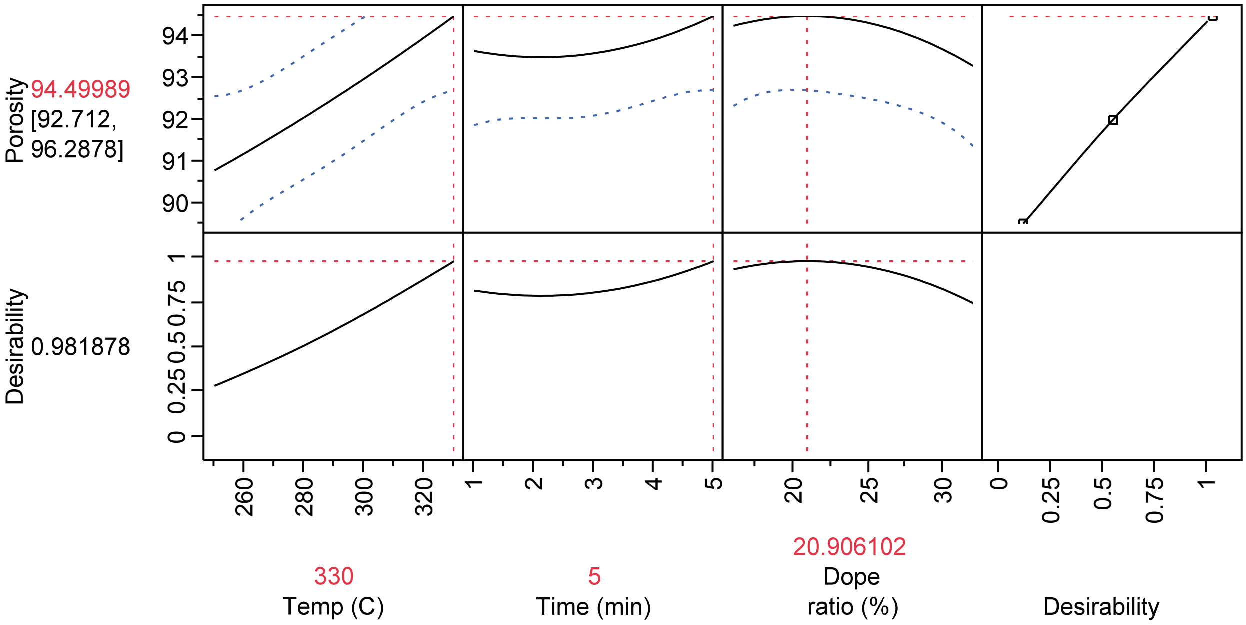


Figure 6.7: Optimum pyrolysis parameters for maximization of porosity (%) of maple wood biochar treatments through the regression model

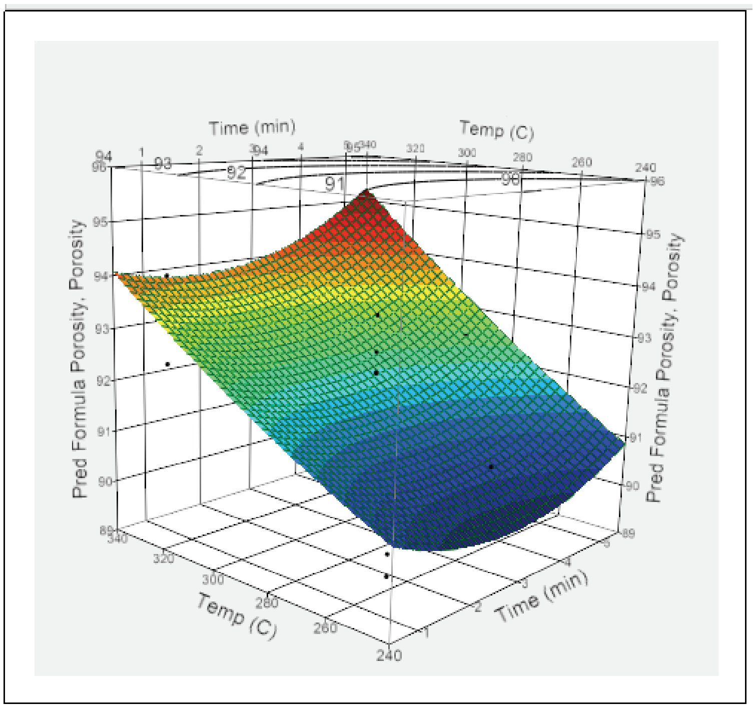


Figure 6.8: Response surface plot for predicted porosity (%) of microwave pyrolysed biochar from maple wood (Y: Temperature; X: Time)

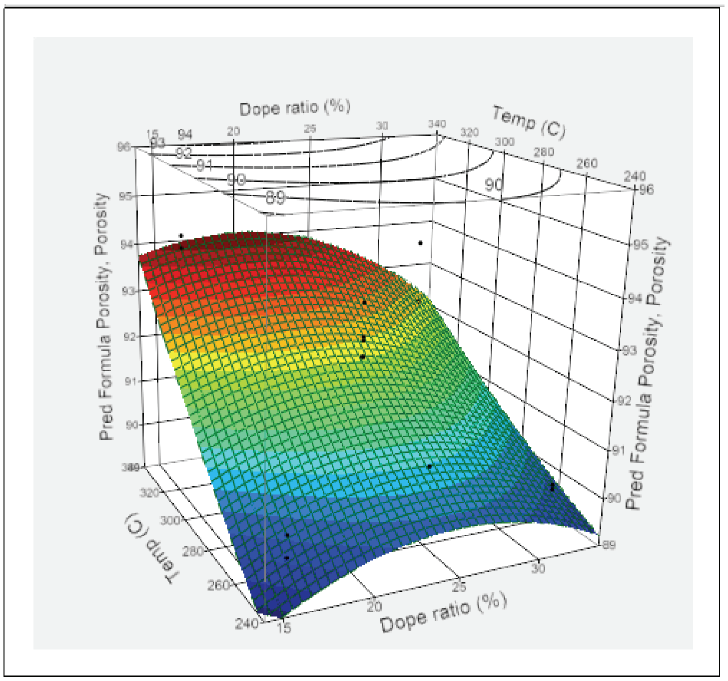


Figure 6.9: Response surface plot for predicted porosity (%) of microwave pyrolysed biochar from maple wood (Y: Temperature; X: Doping ratio (%))

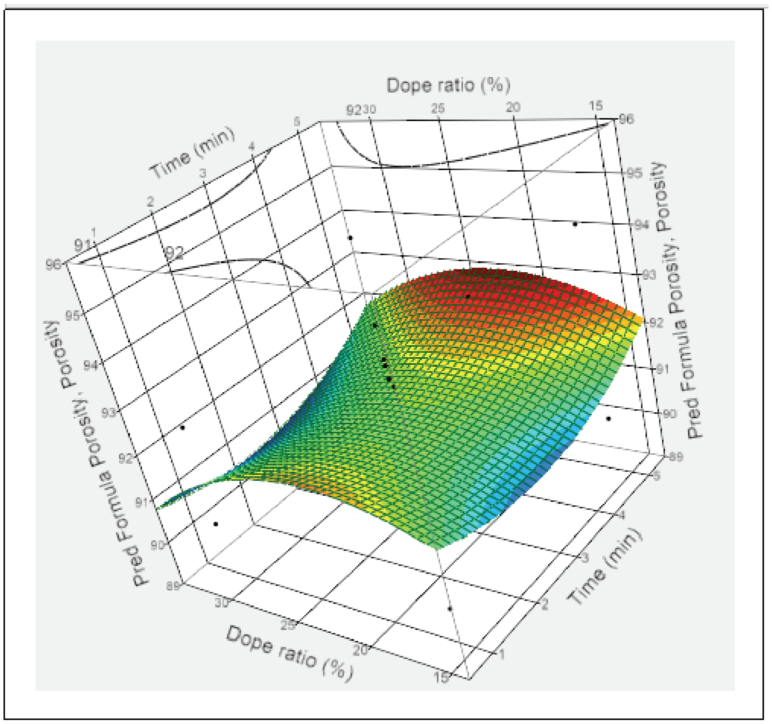


Figure 6.10: Response surface plot for predicted porosity (%) of microwave pyrolysed biochar from maple wood (Y: Doping ratio; X: Time)

It was seen in earlier studies that helium density values of the biomass/chars increase gradually in the whole process, especially at the end of the reaction. In their study, Pastor-Villagens et al., (1998) reported the increase of helium density which is used during pycnometry analysis 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 of devolatilization and structural shrinkage 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. Hence while devolatilization plays a much greater role during slow pyrolysis, shrinkage of the internal structure of the biochar has a higher impact during fast pyrolysis.

Hu et al., (2008), 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.

Masek et al., (2013) compared slow pyrolysis and microwave pyrolysis of two different feedstocks (willow chips and straw) in their study with particular focus on physical properties of resulting chars and their relation to biochar soil function. For both feedstocks, the study found that microwave pyrolysis considerably promotes porosity development, as both the surface area and pore volume were considerably higher for materials prepared by MAP than for those prepared by conventional heating at comparable temperature. The authors attribute high porosity of MW chars even at these low temperatures to the volumetric nature in MW heating.

In microwave pyrolysis, the volatiles formed within the particle can escape more freely with the absence of a clear high temperature front. Devolatilization is the main cause of porosity development at lower temperatures which results in higher porosity in MAP. As in the case of Masek et al., (2013), this study also used lower heating rates in microwave pyrolysis for the production of biochar which reduces the extent of secondary reactions that could cause formation of deposits and thus blockages in pores were minimized. Moreover, the promotion of secondary reactions was minimized by the constant purging of nitrogen during the pyrolysis process as well as continuous displacement of volatiles from the reactor.

6.3.2. Hyper-spectral imaging of biochar

6.3.2.1. Selection of wavelength

The averaged spectral curves representing reflectance from the surface of the biochar samples are shown in Figure 6.11. The difference in the curves showed the variation in reflectance values for the different classes of the samples. Porosity and yield as physical attributes are predicted in the wavelength range of 900 – 1730 nm.

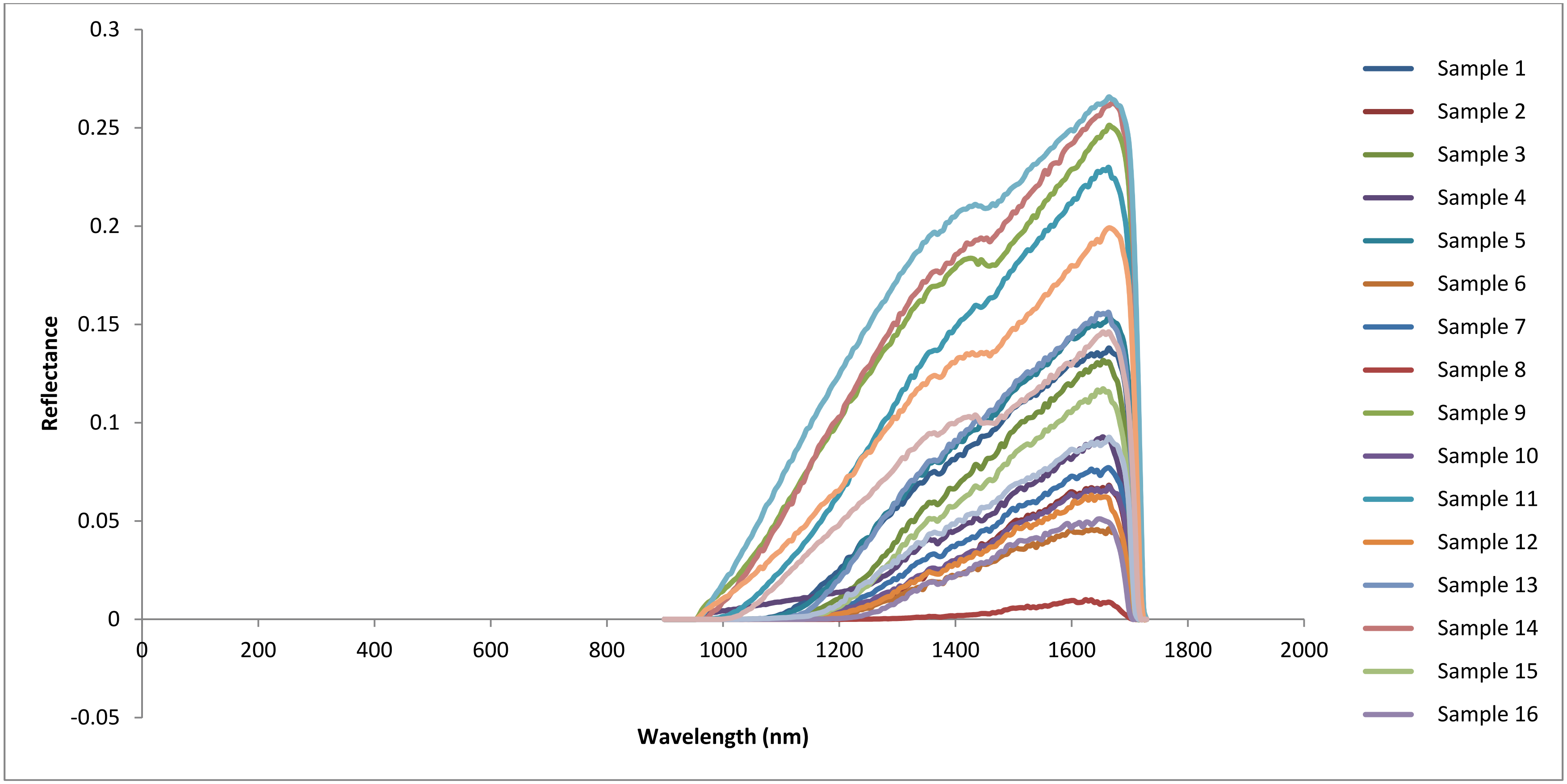


Figure 6.11: Spectral curves for reflectance of biochar samples from microwave pyrolysis of maple wood for full spectral range (900 – 1730 nm)

Samples	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Temp(C)	290	330	290	250	290	330	290	330	290	330	290	290	250	290	330	290	250	250	290	250
Time (min)	3	5	5	1	3	5	3	1	3	3	3	3	1	3	1	3	5	5	1	3
Dope ratio (%)	24	32	24	16	24	16	24	16	24	24	16	24	32	32	32	24	16	32	24	24

The classification of the spectral data was performed by mosaicking the images of the biochars formed under different conditions. The reflectance measurements from 900 - 1180 nm were eliminated from the analysis because of extreme noise. Using the MAXR technique, a set of 25 wavelengths were chosen which gave high R^2 values as well as low Root Mean Square Error (RMSE) for the reflectance values of all the 20 microwave pyrolysed biochar samples ($P \leq 0.1$). The regression analysis for the selected wavelengths showed an $R^2 = 0.996$ (Figure 6.12) with the analysis of variance (ANOVA) as presented in Table 6.3 and Table 6.4. The regression model of the reflectance in terms of the selected wavelength (1190 – 1310 nm) is presented in Equation 6.4. The observed reflectance values for the given spectral range showed good correlation to the predicted values obtained from the model as seen in Figure 6.13.

$$R = -0.38 + 3.74\,W \tag{6.4}$$

Where, R is reflectance and W is wavelength.

Table 6.3: Analysis of Variance of Regression Model for reflectance of biochar obtained from Microwave Pyrolysis of maple wood

Source	DF	Sum of squares	Mean square	F ratio	Prob > F
Model	1	0.004552	0.004552	6644.367	<.0001
Error	23	1.58E-05	0.000001		
C. Total	24	0.004567			

Table 6.4: Regression Model statistics for reflectance of biochar obtained from Microwave Pyrolysis of maple wood

Regression Statistics	
R Square	0.99655
R Square Adjusted	0.9964
Root Mean Square Error	0.000828
Mean of Response	0.084629
Observations (or Sum Wts)	25

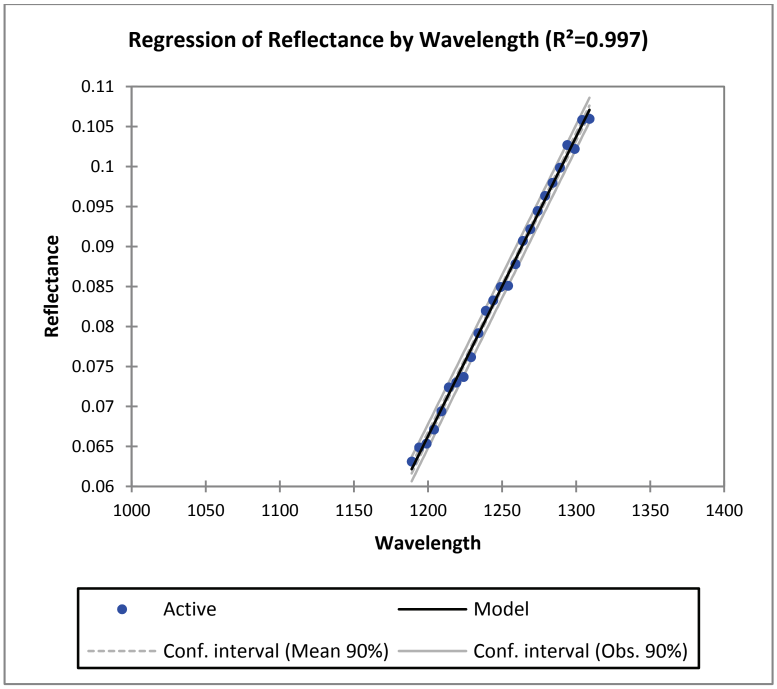


Figure 6.12: Regression model for reflectance values of biochar obtained from Microwave Pyrolysis of maple wood (R^2=0.997; $P < 0.1$)

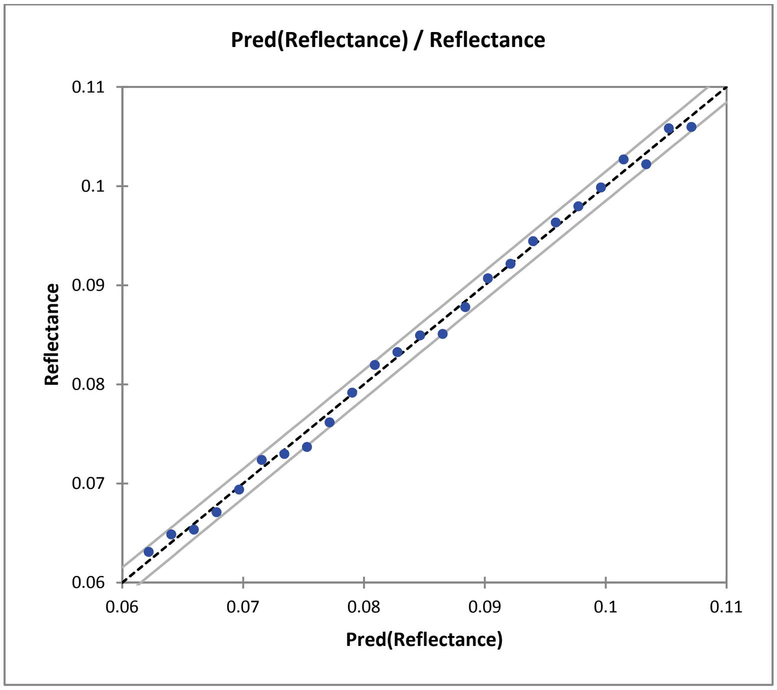


Figure 6.13: Regression model for reflectance values of biochar obtained from Microwave Pyrolysis of maple wood (Actual vs. Predicted)

Goel (2003) used the MAXR criterion with PROC REG procedure of SAS software to choose the best model for estimations of various crop's biophysical parameters. The feasibility of an automated selection of sets of relevant wavelengths in Visible/Near Infra-Red (VISINIR) spectroscopy by combining Maximum R^2 (MAXR) method with Partial Least Squares (PLS) regression (MAXR-PLS) to build a PLS predictive model was investigated by Abdel- Nour et al. (2009) for the determination of albumen pH and Haugh Unit (HU) as tools to test egg quality.

A regression model was built to evaluate the relation between the spectral data with the porosity and yield of the biochar samples in the selected wavelength range of 1190 – 1310 nm. The correlation data as shown in Figure 6.14 indicated that both the chosen physical attributes had similar trend with the best correlation value of 0.67 at a wavelength of 1309 nm.

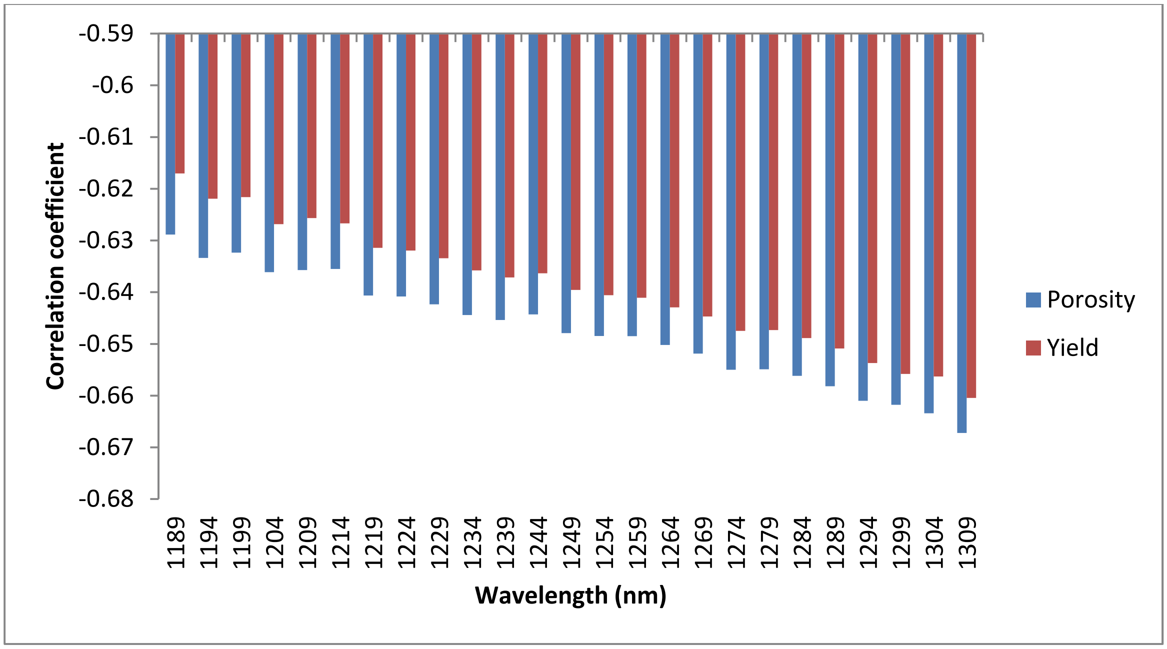


Figure 6.14: Correlation of first derivative spectral data with physical attributes

6.3.2.2. Principal component analysis

Figure 6.15 shows the results of the principle component analysis for the full spectral range of 900–1730 nm. The different biochar samples were clearly separated based on their yields and porosity values represented by first two principle components. The first two principle components constituted 99.41% of variation among the groups.

The biochar samples were classified based on their physical attributes of yield and porosity when the selected wavelength region of 1190 – 1310 nm spectra was analyzed, which indicated a similar variability due to clear distinct grouping of the samples. Here also the first two principle components constituted for the maximum variability with 99.65%. The different treatments of biochar samples were clearly differentiated by the principle component analysis as shown in Figure 6.16. Both PCA results showed a similar grouping of the central pyrolysis conditions of pyrolysis temperature of 290°C, reaction time of 3 min and doping ratio of 24%.

It has been suggested by researchers Tang et al., (2005) that with the increase of coal reflectance, the porosity of formed char decreases. The chars were produced in a Drop Tube Furnace (DTF) at 1400 °C under N_2 environment with 1% oxygen to burn tar at a heating rate of 10^5°C/min which was considered to be fast pyrolysis. The average porosity and the porosity distribution of the char sample were then obtained by the volume average of all particles.

Also, models were 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.

The hyperspectral imaging was conducted earlier for birch wood biochar samples produced through slow and fast pyrolysis by the same authors. The results showed that certain infra-red wavelengths had very high reflectance resulting in poor visibility of the biochar samples. 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 other char samples (Dutta et al., 2012).

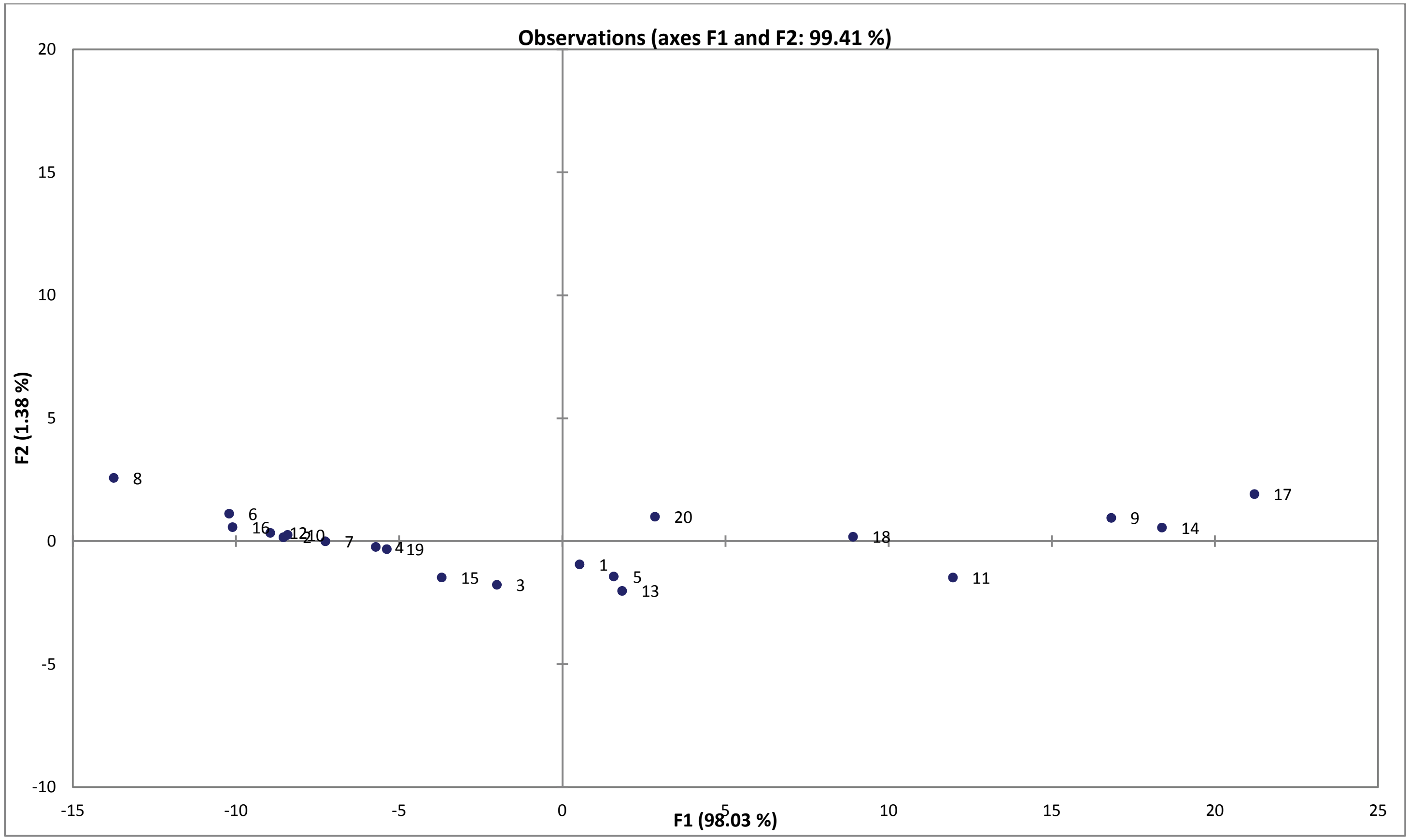


Figure 6.15: Principle component analysis of biochar samples from microwave pyrolysis of maple wood for full spectral range (900 – 1730 nm)

Samples	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Temp (C)	290	330	290	250	290	330	290	330	290	330	290	290	250	290	330	290	250	250	290	250
Time (min)	3	5	5	1	3	5	3	1	3	3	3	3	1	3	1	3	5	5	1	3
Dope ratio (%)	24	32	24	16	24	16	24	16	24	24	16	24	32	32	32	24	16	32	24	24

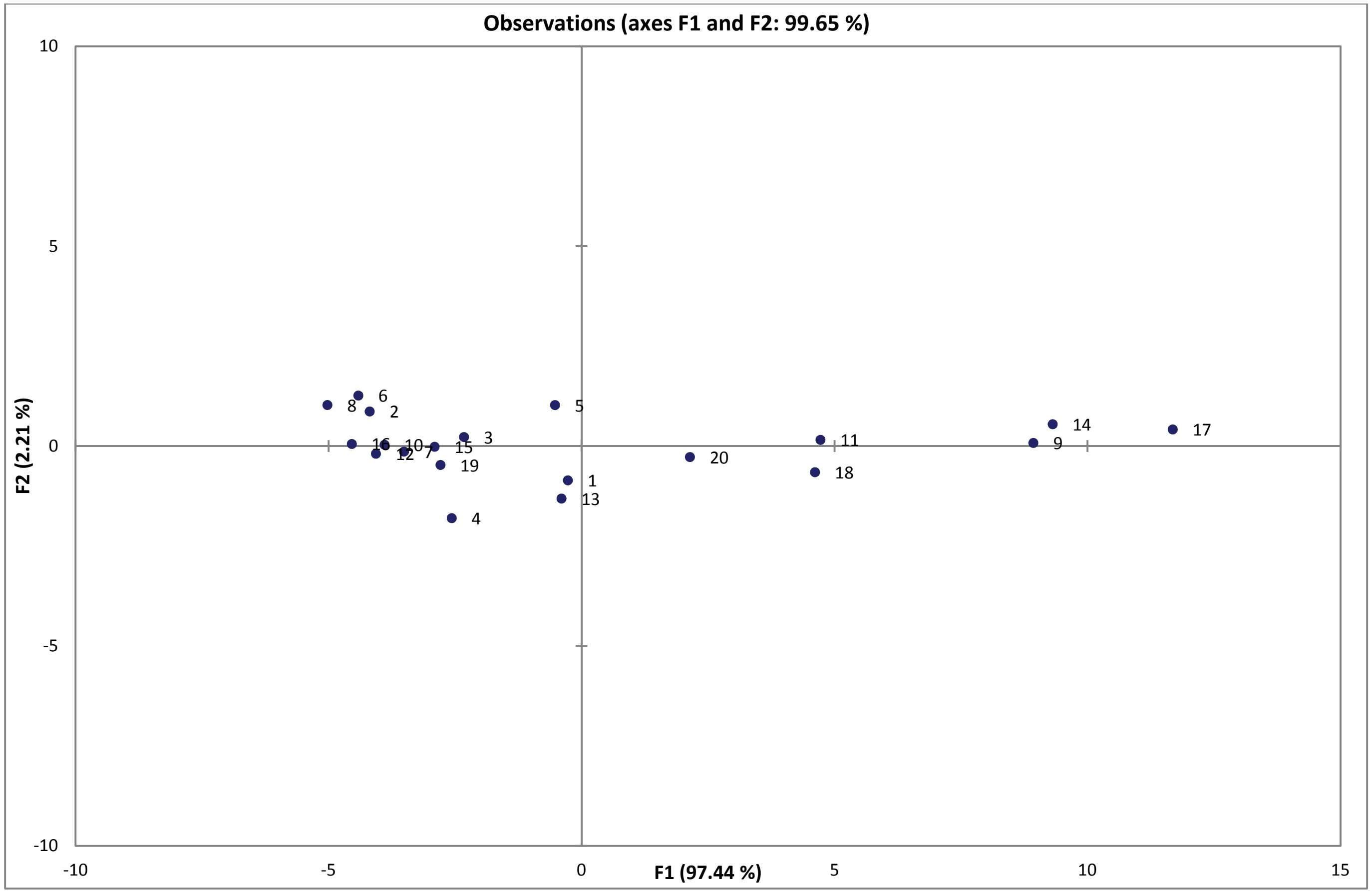


Figure 6.16: Principle component analysis of biochar samples from microwave pyrolysis of maple wood for 1190 – 1310 nm spectra

Samples	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
Temp (C)	290	330	290	250	290	330	290	330	290	330	290	290	250	290	330	290	250	250	290	250
Time (min)	3	5	5	1	3	5	3	1	3	3	3	3	1	3	1	3	5	5	1	3
Dope ratio (%)	24	32	24	16	24	16	24	16	24	24	16	24	32	32	32	24	16	32	24	24

6.3.3. SEM Analysis

The SEM images of the biochar obtained through the microwave pyrolysis of maple wood are given in Figure 6.17. The SEM images showed that the pyrolysis temperature had an effect on the structure of the biochars during microwave assisted pyrolysis process. As shown in Figure 6.17b with the onset of the pyrolysis process at 250°C, there are significant morphological changes in comparison to the control maple wood sample (Figure 6.17a). Porous structures were found at the surface of the biochar formed. At low temperature (250°C), the surface of chars was found to have more irregular porous structures while at higher pyrolysis temperatures of 290°C and 330°C, surface morphological changes were apparent (Figures 6.17c and 6.17d). The pores developed at 290°C were found to be more uniform and appeared to have a microporous network structure (Figure 6.17c). On the other hand, the porous nature of the biochar structure produced at 330°C was more prevalent but had a number of debris as shown in Figure 6.17d.

The SEM images also indicated that the dopant ratio also played a role in the microstructural formation of the biochars which needs to be further investigated in detail. A comparison of the biochars produced at the same pyrolysis temperature of 290°C with varying doping ratio indicated that while low doping ratio (16%) produced irregular porosity in the biochar structure with greater proportion of debris (Figure 6.17d), the microstructure of biochar at 24% doping ratio was found to be more uniform as mentioned earlier (Figure 6.17b). While lamellar-shaped particles were found for biochar produced with 32% doping ratio with under developed pores (Figure 6.17e).

These results, indicating a correlation to pyrolysis process parameters such as temperature, are in good agreement with previous investigations (Tsai et al., 2001, Yu et al., 2010, Sharma et al., 2002). In general, it has been revealed through SEM images that biochar structures were not homogeneous (Karaosmanogˇlu et al., 2000). The formation of these porous structures have been attributed to evolving volatiles due to a stepwise accumulation of inorganic matter onto the exposed surface with subsequent melting of organic matter (Yu et al., 2010).

Due to the experimental constraints of the present study which did not allow for experimental trials at higher temperatures than 330°C, it would not be possible to discuss the effect of higher temperatures on the porous structure of maple wood biochar. But the presence of a well-developed porous network indicates that maple wood biochars formed at 290°C with 24% doping ratio, could be further investigated for potential applications mimicking properties of activated charcoal.

6.3.4. FTIR analysis

FTIR was used to investigate the changes in the chemical composition in maple wood biochar due to pyrolysis conditions of temperature, time and doping ratio. The various functional bonds which were found in the pyrolysed biochar were in the region of 1250 – 1335 cm^{-1} (C–N), 1600–1585 cm^{-1} (C–C stretch in–ring) and 3100–3000 (C–H) representing aromatics; aliphatic regions are represented by 1760–1665 cm^{-1} (C=O) corresponding to carbonyls, 2260–2210 (C(triple bond)N) to nitriles, 3300–2500 (O–H) to carboxylic acids and 3640–3200 (O–H) to alcohols, phenols.

In Figure 6.18 it is shown that the fresh Maplewood biomass has increased functional group spectra compared to that for the biochars produced through microwave pyrolysis. Various bands in the spectra for pyrolysed biochar were identified corresponding to stretches for aliphatic hydrocarbon groups (2050- 3600 cm^{-1}), aromatic hydrocarbons (1100- 1300 cm^{-1}; 2050- 3300 cm^{-1}) and phenols (3300 – 3600 cm^{-1}). At 250°C, the number of aromatic groups was more prevalent compared to aliphatic groups as seen in Figure 6.19. However, with increase in pyrolysis temperature, only aliphatic group stretching vibration was found in the spectra and band shifts occurred (Figure 6.20 and Figure 6.21). Aliphatic amino acid salts (C=O) stretch was seen at 1550-1650 cm-1 for unpyrolysed maple wood and biochar at 250°C that shifted to 2850-2950 cm^{-1} at 290 and 330°C. Aromatic groups were in general not seen to undergo any changes in wave numbers with increase in temperature (e.g. Aromatic sulfonic acids at 1100- 1200 cm^{-1}). However, aromatic mercaptans were found to be absent at the highest pyrolysis temperature of 330°C.

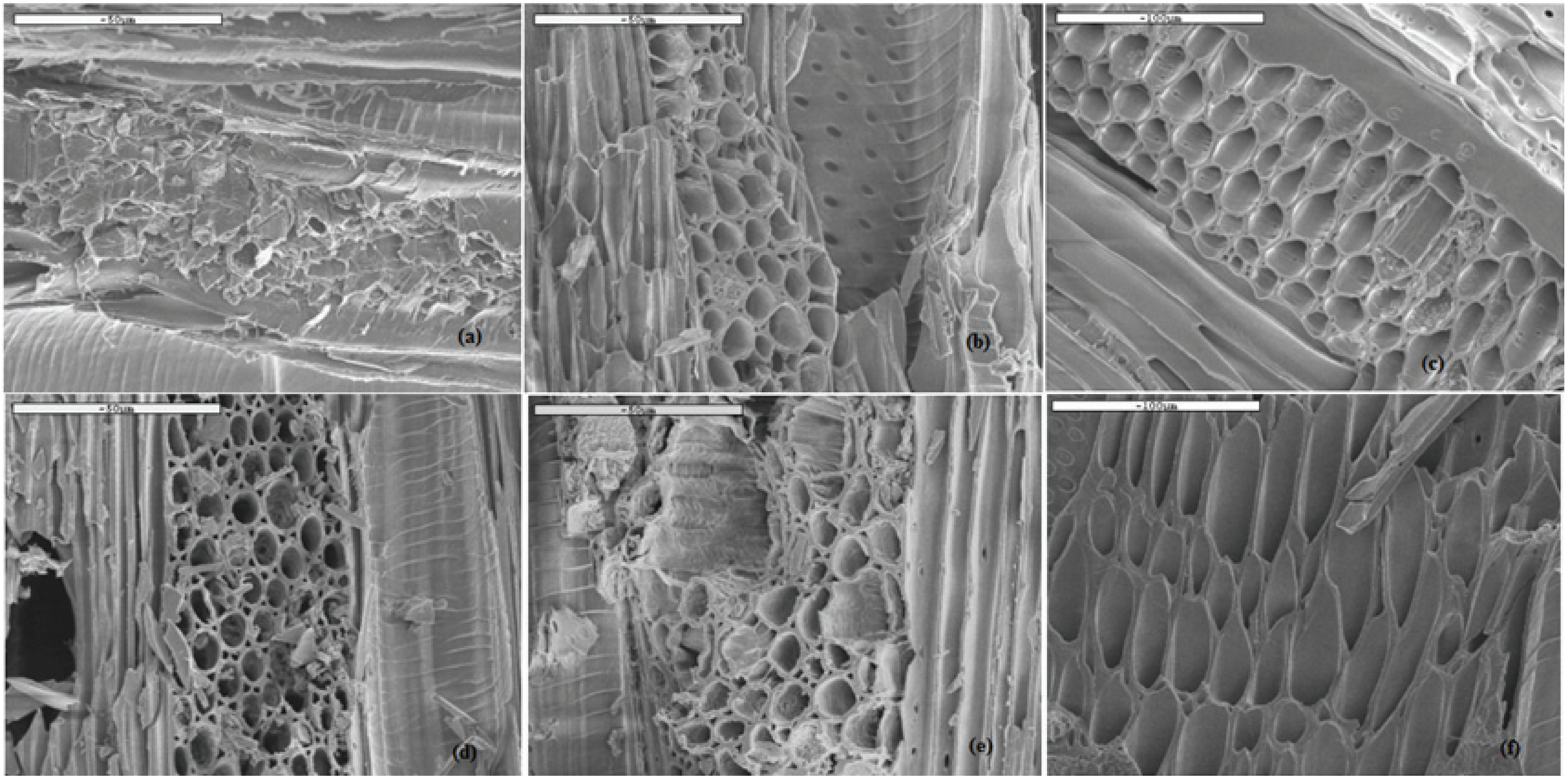


Figure 6.17: SEM micrographs (1kx) of (a) maple wood, (b) MW pyrolysis biochar at 250°C (24% doping ratio), (c) MW pyrolysis char at 290°C (24% doping ratio), (d) MW pyrolysis biochar at 330°C (24% doping ratio), (e) MW pyrolysis biochar at 290°C (16% doping ratio), and (f) MW pyrolysis biochar at 290°C (32% doping ratio)

Similarly increase in doping ratio at the same pyrolysis temperature had the same effect as that of increasing temperature. A comparison of Figures 6.22, 6.20, 6.23 indicated that as the doping ratio was increased from 16 to 32% at 290°C, there was evidence of stretching of the aliphatic groups. A number of spectral peaks indicating characteristic hydrocarbons, such as alkynes (–C≡C– stretch) at 2260–2100, nitriles (C≡N stretch) at 2260–2210 were found at 16% doping ratio which were absent in biochar produced using higher doping ratios of 24 and 32%.

As such, this study indicates that the FTIR spectrum of maple wood was more complex and showed various peaks indicating the presence of several heterogeneous components compared to the biochars produced. Biochar formed at lower temperatures had similar characteristics as that of the sample wood. These observations are consistent with results of Yu et al. (2010) who found that as the pyrolysis temperature increased; the bands became weaker, which lowered functional group activity. This result is consistent with the scanning electron microscopy (SEM) results which also illustrated influence of temperature on the increased surface characteristics of biochars.

6.4. Conclusion

The aim of this study was to investigate the structural development of the biochar and the influence of the pyrolysis temperature, residence time and doping ratio on these changes. The structure of the chars was characterized using Helium pycnometer as well as hyper spectral imaging to study the influence of porosity on the reflectance of the biochar samples. From the pycnometry data gathered, it was observed that the treatments with the highest temperatures and longest holding times had the highest porosity compared to the other biochar samples. A regression analysis was applied which found the predicted optimum levels of the experimental variables of pyrolysis reaction. The highest porosity of biochar was found to be at the pyrolysis temperature of 330°C for 5 min with doping ratio of 20.9%, which also indicated that doping ratio was not a significant factor towards the determination of porosity. 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. The hyperspectral imaging experiments showed that certain infra-red wavelengths had very high reflectance resulting in poor visibility of the biochar samples. Using the multiple linear regression technique to obtain the maximum R^2 value (MAXR), a set of 25 wavelengths was chosen. A regression model was built to evaluate the relation between the spectral data with the porosity and yield of the biochar samples in the selected wavelength range of 1190 – 1310 nm, which showed good correlation between the predicted and observed porosity. A principal component analysis was also done to differentiate between the biochar samples according to their physical attributes. These findings corroborate with previous studies which indicate that with the increase of reflectance, the porosity of formed char decreases. Scanning electron microscopy imaging indicated that the pyrolysis temperature and doping ratio most likely plays a major role in the formation of a microporous biochar structure with 290°C at 24% doping ratio presenting uniform porosity. The FTIR analysis also indicated that with increase in temperature and doping ratio, there was evidence of aliphatic group stretching which were in good agreement with the SEM results. The fresh maple wood FTIR profile showed more complex spectra and as the pyrolysis temperature increased; the bands became weaker, which lowered functional group activity.

6.5. Acknowledgements

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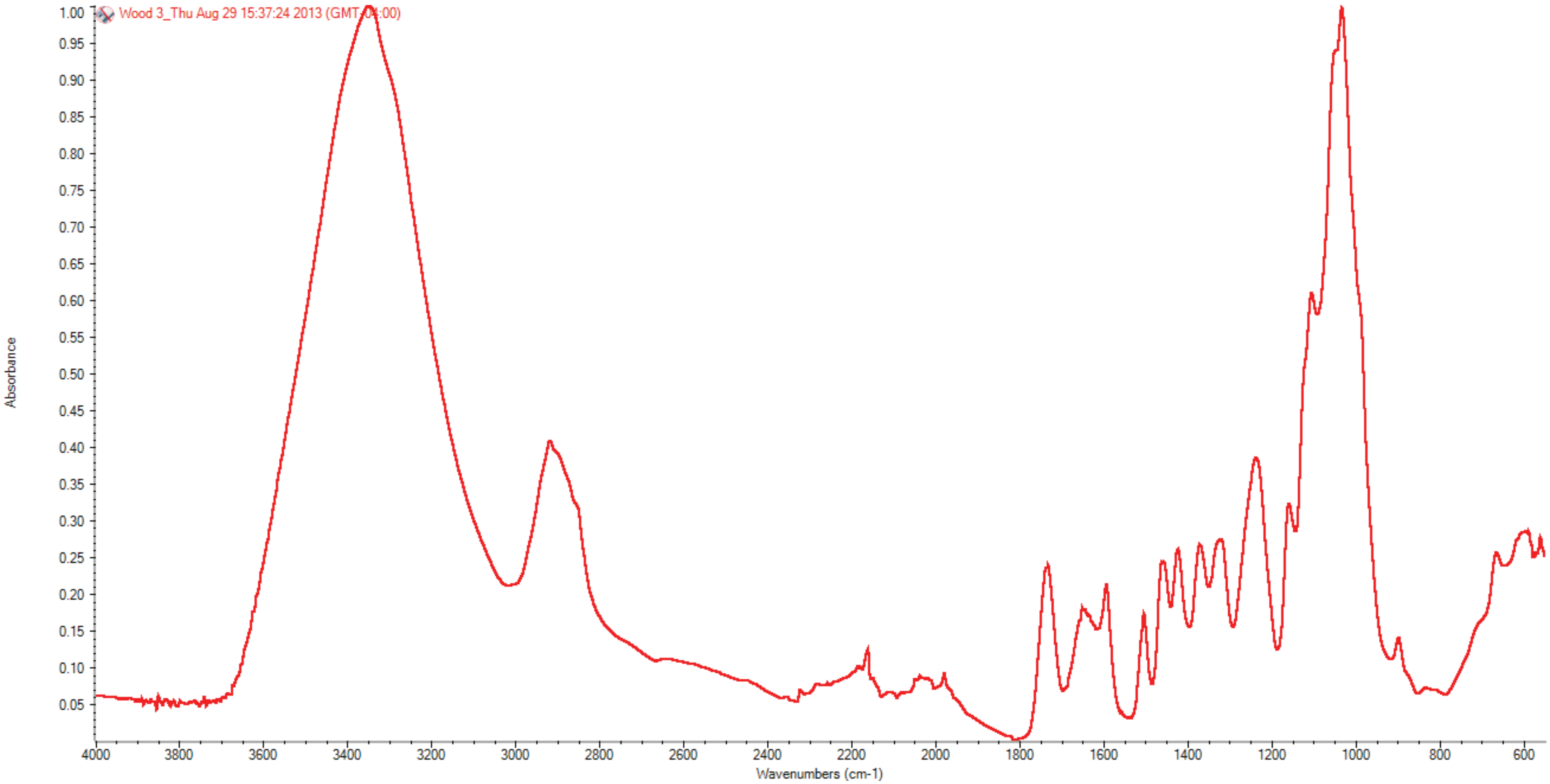

Figure 6.18: FTIR profile for maple wood

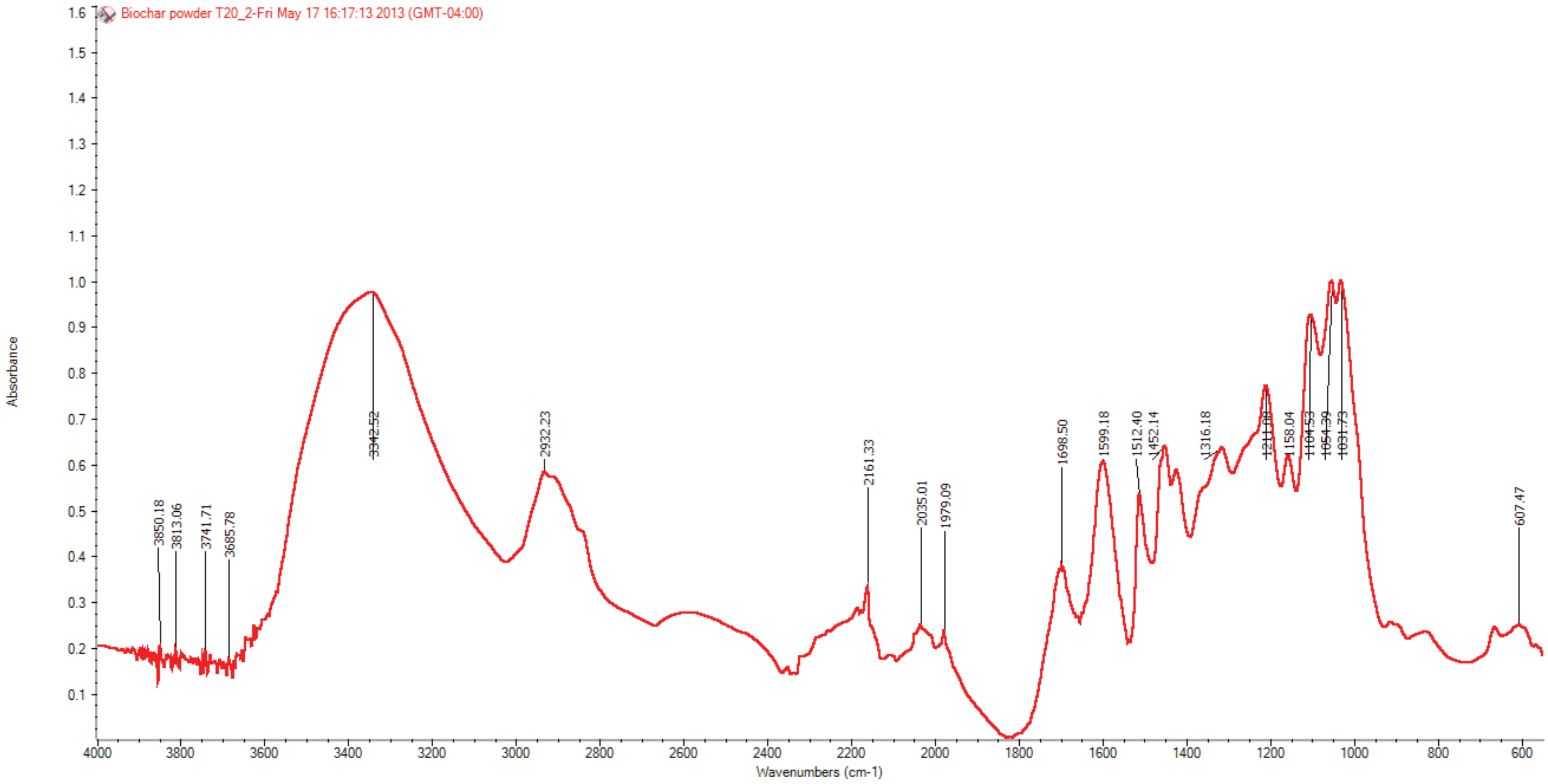

Figure 6.19: FTIR profile for MW pyrolysis biochar at 250°C (24% doping ratio)

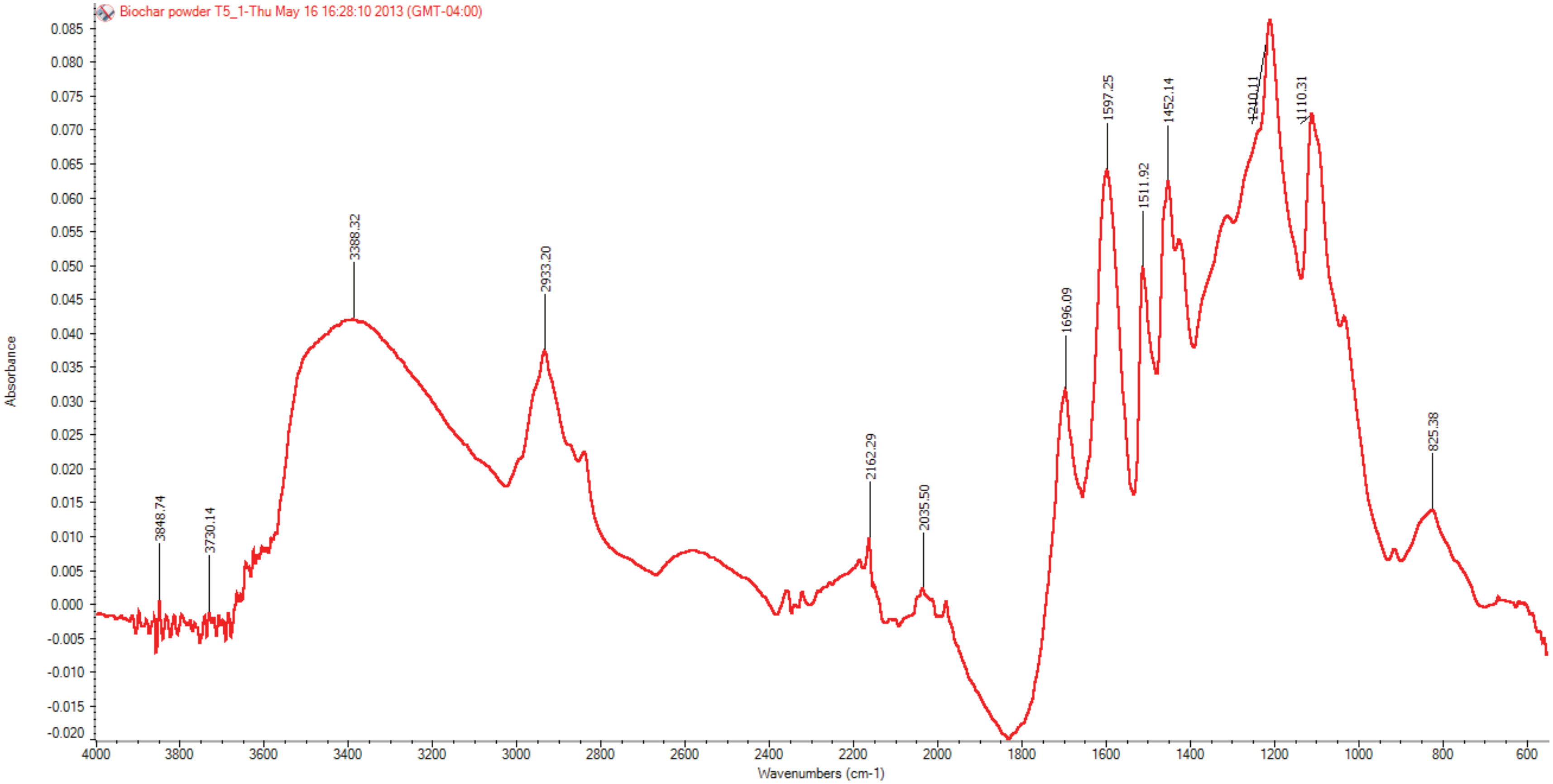

Figure 6.20: FTIR profile for MW pyrolysis biochar at 290°C (24% doping ratio)

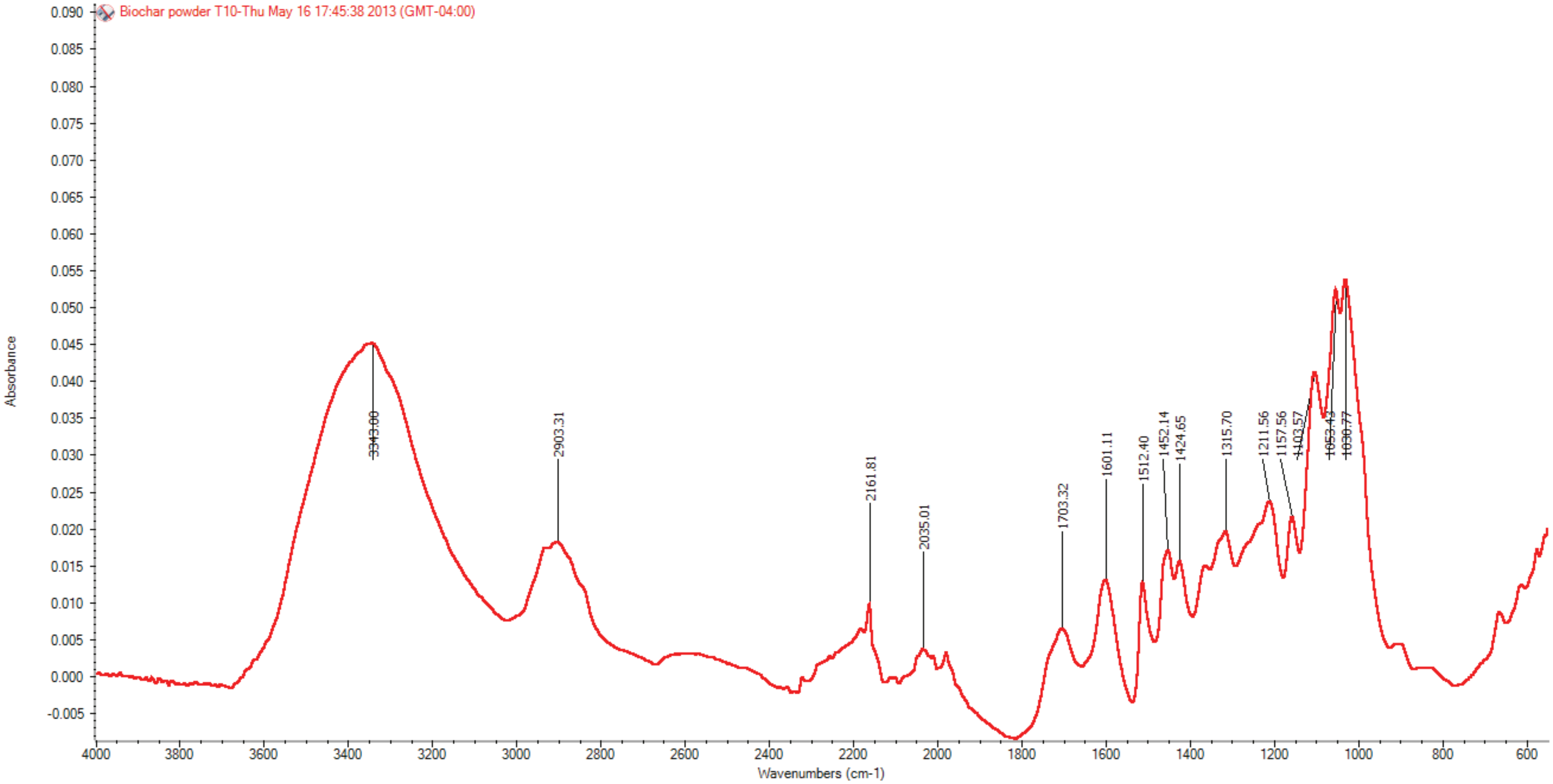

Figure 6.21: FTIR profile for MW pyrolysis biochar at 330°C (24% doping ratio)

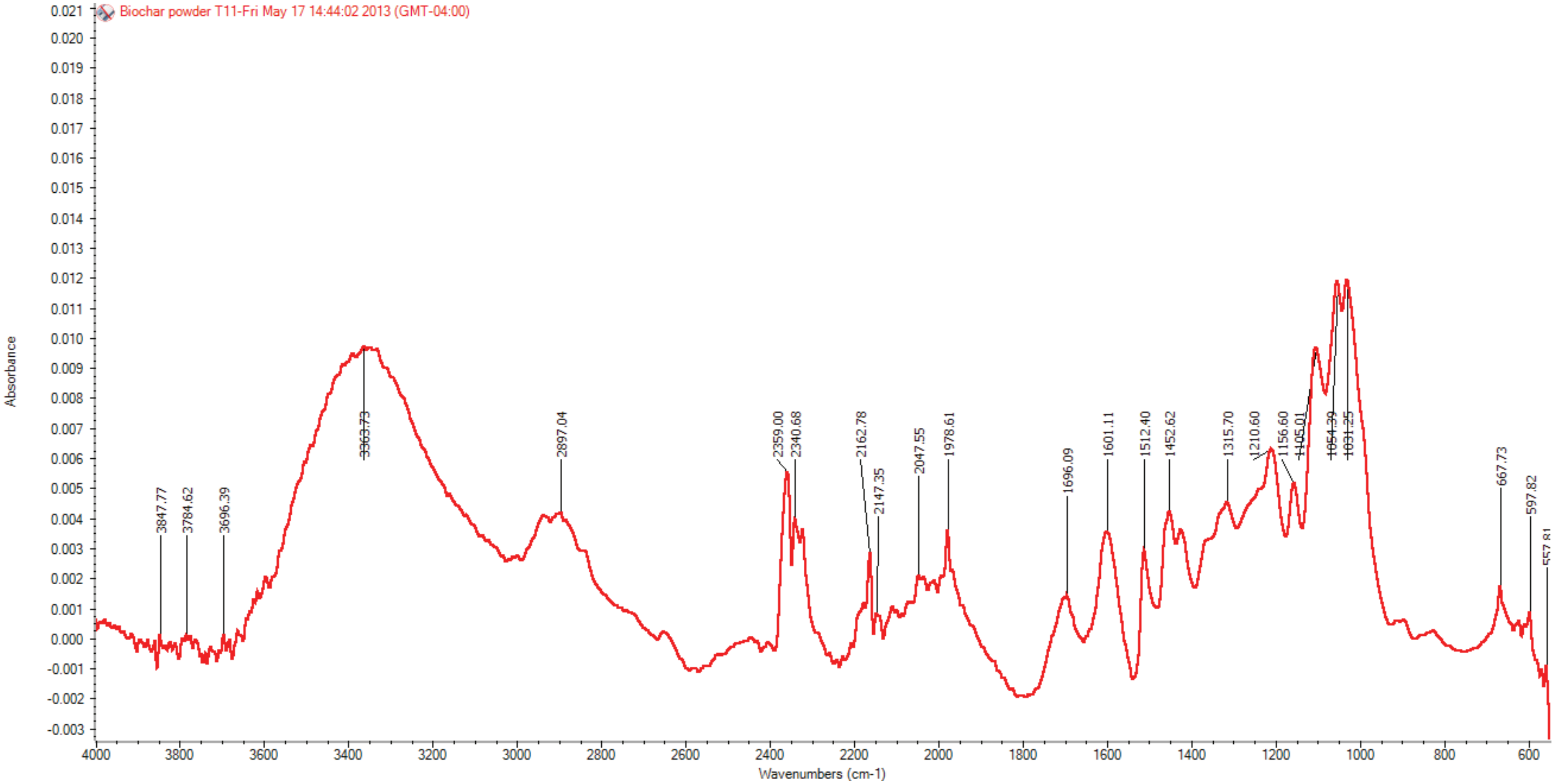

Figure 6.22: FTIR profile for MW pyrolysis biochar at 290°C (16% doping ratio)

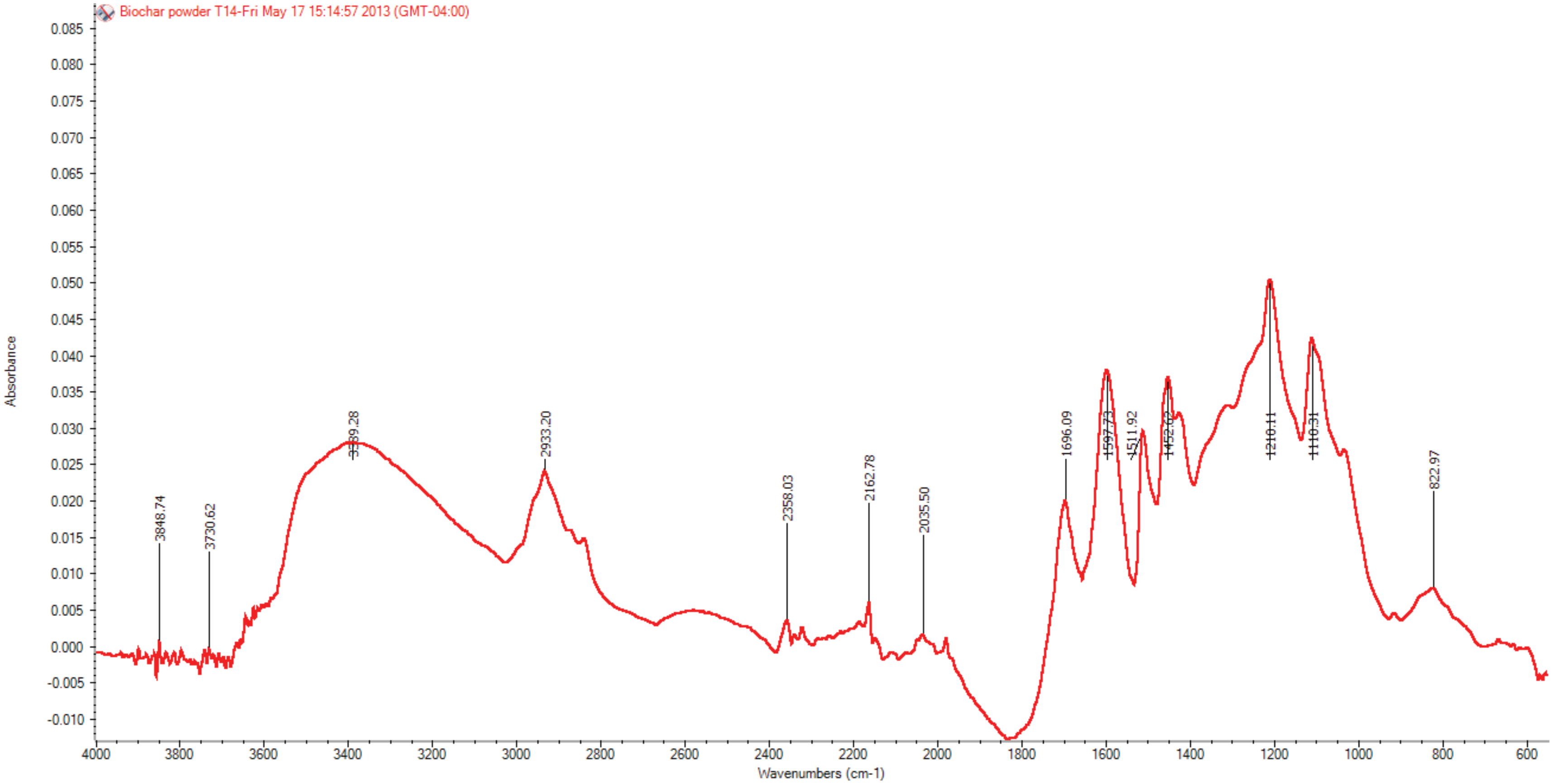

Figure 6.23: FTIR profile for MW pyrolysis biochar at 290°C (32% doping ratio)

Connecting text

It has been generally accepted that biochar is a highly stable form of carbon and has the potential to form an effective carbon sink, therefore sequestering atmospheric carbon dioxide. The carbon dioxide capture in soil in the form of stable biochar would in turn help in reducing associated global warming threats. It is important to conduct the assessment and monitoring greenhouse gas emissions in fields amended with biochar. In this thesis, microwave pyrolysis has been shown as a competent technology for production of biochar from agricultural biomass. However, to avoid unintended consequences of a new technology or mitigation strategy, it is necessary to conduct analyses of potential life-cycle impacts of biochar pyrolysis systems, as it would be undesirable to have the system actually emit more GHG than sequestered or consume more energy than is generated. Hence to ascertain the optimum potential of biochar systems, it is important to understand the dynamics of the application of biochar systems on climate security, soil regeneration, and economic recovery. Life cycle analysis (LCA) which evaluates a particular system from its "cradle-to grave" is an appropriate tool for estimating the energy and climate change impacts of pyrolysis-biochar systems.

Chapter 7

A Life Cycle Assessment of Environmental and Economic Balance of Biochar Systems in Quebec

Abstract

A life cycle analysis (LCA) for pyrolysis biochar systems was carried out to determine greenhouse gas balance, carbon cycling, and the economics of biochar production from different agricultural residues and wastes. Investigating a range of feedstocks (forest residues, corn stover, etc.) provided insight into the use of biomass residues rather than bioenergy crops as biochar production substrates and the resulting energy and climate change impacts. The analyses were conducted based on various optimized pyrolysis parameters for corn fodder and forest residue. The observed reductions of greenhouse gas (GHG) emissions (CO_2 equivalent per Mg dry feedstock) for both corn fodder and forest residue were mainly contributed by the stable carbon in the biochar. Corn fodder showed a greater reduction in emissions than forest residue, indicating the corn fodder's greater economic potential for soil sequestration of stable carbon. The relative GHG emission analysis found that the optimization of a biomass pyrolysis system for biochar production is better suited for soil sequestration of stable carbon than as a fuel source. The economic viability of the pyrolysis-biochar system is largely dependent on the costs of feedstock production, pyrolysis, and the value of C offsets. The LCA reported in this study can be instrumental in assessing the environmental potential of biochar production and its application in the region.

Keywords

Life cycle analysis, Biochar, Climate change, Economics, Greenhouse gas

7.1. Introduction

Combating global climate change and meeting the world's ever-rising energy demands are concerns which have occupied researchers all around the world. The global greenhouse gas emissions were estimated at approximately 32 Pg in 2008 (Boden et al., 2010). Adding to this dilemma is an ever-increasing world population which is creating an enormous stress on our fragile planet. While carbon emissions increased 6 times since

1950 (Boden et al., 2010), the same 75-year span has seen the world population increase by 3¼-fold to almost 7 billion in 2011, and it is expected to reach the 9 billion mark by 2050 (U.S. Census Bureau, 2013).

Canada's total GHG emissions for 2008 were estimated at 702 Tg of CO_2 equivalents (CO_2e), of which nearly 10% was contributed by the agricultural sector (Environment Canada, 2013). This sector generates roughly 300 Tg of agricultural waste (AAFC, 2010; StatCan, 2009). Assuming 50% recovery of carbon from this biomass (Lehmann, 2007), one could sequester nearly 150 Tg of carbon dioxide from the atmosphere, in the form of biochar, or about 20% of Canada's GHG emissions.

An increased need of technologies with long-term sustainable implications in the bioenergy sector has been widely acknowledged. Biochar's use as an energy source (Wu and Abdullah, 2009), as a fertilizer when mixed with soil (Lehmann, 2007), and as a means of reducing greenhouse gas emissions through the soil-sequestration of carbon (Joseph et al., 2009), have gained enormous attention in recent years. Moreover, biochar can also have potential positive effects on food security by reducing the amount of food crops used for biofuel production (Kleiner, 2009).

One of the most important current thermochemical biomass-conversion technologies, pyrolysis is a process of thermal decomposition of biomass under conditions ranging from low oxygen (<1% O_2 v/v) to anoxia (no oxygen). It converts organics to solid (charcoal), liquid (organics) and gas (CO, CO_2, CH_4, H_2) products. Their range and relative amounts depend on process variables such as the nature of the feedstock and the heating rate (Brownsort, 2009; Dutta et al., 2011). Biochar production through pyrolysis has become an extremely efficient and popular technology in recent years.

Life-cycle analysis (LCA) is a technique to assess the potential environmental impacts associated with all the stages of a material, service or product's life. The approach involves careful calculation and evaluation of parameters which might influence such impacts. As LCA consists of the assessment and characterization of products, systems, processes and design (Smith Cooper and Vigon, 2001); it can be said to follow a "cradle to grave" approach. Highly useful in post facto determination of the unwanted outcomes of a product's use or technology's implementation, LCAs can also serve a priori in facilitating appropriate decision-making to avoid unwanted outcomes.

A LCA was carried out by Whitman et al., (2011) to evaluate corn stover feedstock production for cellulosic EtOH production in three corn-producing regions in Quebec for energy and greenhouse gas (GHG) impacts. In this study, in-field processes such as corn stover production, collection, transport, soil organic carbon (SOC) loss, and N_2O emissions, as well as background processes of herbicide, fertilizer, seed, and fuel production and transport were considered as the system boundaries. The sensitivity analyses included the variation of the percentage of corn stover collected, contrasted a multiple-pass with a one-pass stover-grain collection system, and compared mass, economic and system expansion allocation methods. Their results showed that the total energy impact was 931-1442 MJ t^{-1} dry stover collected under 15% stover collection, with stover harvest, transport, and field operations contributing most strongly to the total impact. Total GHG emissions from corn stover production and transport of stover to the ethanol facility were found to be 320- 488 kg CO_2e t^{-1} dry stover under 15% stover collection, with SOC loss, N_2O emissions, and stover harvest contributing the most to the total impact. A sensitivity analysis carried out by this research revealed that the energy and GHG impacts of stover production are strongly influenced by the mass of stover collected, the use of a one-pass system, and the choice of allocation methods. Scaling-up results from the modelled system suggest that 100% of Quebec's EtOH targets could technically be supplied using corn stover feedstock, but would have negative impacts on GHG emissions and soil health (Whitman et al., 2011).

Although biochar is known for its enormous potential as an alternate energy source, the environmental implications of its potential role as a tool for mitigation of greenhouse gas emissions through C sequestration has not been fully assessed. Consequently an LCA of biochar production (pyrolysis) and sequestration (soil amendment) systems is warranted, as it would be undesirable to have the system actually emit more GHG than it sequesters, or consume substantially more energy than it generates (Krull, 2010).

There have been very few LCAs conducted to assess pyrolysis biochar systems or to quantify the GHG mitigation potential of biochar. Roberts et al. (2010) conducted an LCA to estimate the energetic, economic, and climate change mitigation potential of various agricultural residue or energy crop pyrolysis feedstocks (corn stover, residential yard waste, and switch grass). They found that corn stover yielded greater energy generation and lesser GHG emissions than switchgrass, as well as showing a moderate potential to be profitable. This evaluation was dependent on the value of C offsets and feedstock collection costs.

An LCA carried out by Gaunt et al., (2008) on the energy and climate impacts of biochar systems operating with bioenergy crops or crop wastes as feedstocks, showed soil amendment with biochar to reduce GHG emissions 2- to 5-fold more than if used solely as fossil energy offsets. Roughly half the magnitude of these reductions arose through the retention of C in biochar. They found the ratio of energy produced per mass of feedstock to that supplied to produce biochar through slow pyrolysis were 2- to 7-fold greater than that of comparable technologies (e.g., ethanol from corn). In particular low-temperature slow pyrolysis offers an energy-efficient strategy for bioenergy production (Gaunt et al., 2008).

The overall impacts of biochar for agricultural use were evaluated by Sparrevik et al., (2012) through a LCA for field sites in Zambia. The study evaluated three different biochar production methods of traditional earth-mound kilns, improved retort kilns, and micro top-lit updraft (TLUD) gasifier stoves with cultivation growth basins and precision fertilization and compared to conventional agricultural methods. Although the study found beneficial aspects of biochar use in conservation farming, conservation farming plus biochar from earth-mound kilns was found to have certain negative health impacts due to the particle emissions originating from biochar production. The use of cleaner technologies such as retort kilns or TLUDs could however overcome this problem. The authors emphasized the need for a holistic view on biochar use in agricultural systems (Sparrevik et al., 2012).

Woolf et al. (2010) estimated the maximum sustainable technical potential of biochar to mitigate climate change. Their results show that biochar application has the maximum potential of reducing the annual net emissions of CO_2, methane and nitrous oxide by 1.8 Pg CO_2 equivalent (CO_2e), and total net emissions over the course of a century by 130 Pg CO_2e, without endangering food security, habitat or soil conservation.

Given the limited extent of these studies, an LCA was carried out to assess the GHG balance, carbon cycle, and economics of biochar production from different agricultural residues, using different pyrolysis biochar systems in the Quebec region.

7.2. Methodology

Using original spreadsheets and data derived from a wide review of literature, carbon flows, greenhouse gases expressed as carbon equivalents, and energy generated were monitored. The factors taken into account were type of feedstock, transport, electricity generation through pyrolysis and heat use.

7.2.1. Goal and scope

Assuming biochar production to occur through slow pyrolysis, total emissions, and emission factors used in preparing emission inventories and calculating emission reductions for particular fuels, along with the economics of biochar production from corn stover or forest residues were estimated. For a given pyrolysis system the LCA estimated the production of biochar based on 1.0 Mg of dry biomass. The reference flows for this system, as implemented through a methodology developed in Microsoft Excel, were considered to be the mass and carbon content in the biomass feedstock.

i. Feedstocks

As suggested by Hammond et al. (2009), feedstocks were selected on the basis of their suitability for pyrolysis, and the quantity of source material available in Quebec presently, and over the past 5 years.

ii. System boundaries

Studies of biochar systems' wide-ranging applications—including carbon sequestration, reduction of carbon-containing GHG emissions, energy production, soil enhancement, and in some cases, waste disposal—have highlighted such systems' importance (Hammond et al., 2009; Roberts et al., 2009). It was beyond the scope of this study to consider all possible boundaries associated with the production and application of biochar to soils. The objective of drawing such boundaries was to allow for the determination of factors in three categories: sources of GHG, GHG sinks, and variables (GHG emissions, Avoided emissions, Energy offsets) considered in the LCA (Figure 7.1).

7.2.2. Inventory

The biochar considered for this LCA finds its use as a soil amendment produced through slow pyrolysis in pyrolysis units. The biochar produced is then transported to the farm for sequestration in soil. The LCA considered the following processes:

a) Feedstock analysis: The feedstocks considered were corn fodder (corn stalk without the kernels and the ears; treated as waste) and forest residues. Biochar production data for Quebec was drawn from Statistics Canada (2012). Energy use/production and greenhouse gas emissions were calculated according to IPCC guidelines (1996) for GHG estimation.

b) Pyrolysis: The pyrolysis conditions and parameters chosen for this study were those of slow pyrolysis as optimized by Dutta et al., (2011). Slow pyrolysis conditions constituted heating rate of 20°C/min at optimal pyrolysis temperature and residence time of 400°C for 12 min.

c) Transport: The transport data were gathered from the North East Biofuel Supply Chain Carbon Intensity Assessment (Mortimer and ElSayed, 2006) and calculations were based on the transport of 25.5 Mg of feedstocks from the field to the pyrolysis facility using a heavy duty diesel truck with no backhaul (Hammond et al., 2009). The return trip loaded with the finished biochar product was accounted for in the biochar application process. Though the transport distance varied, based on requirements in Quebec, a return trip baseline of 200 km was used.

d) GHG sinks: Heat and electricity generation were considered to be the two main GHG sinks in the present study and were included as energy offsets or co-products in the biochar production process.

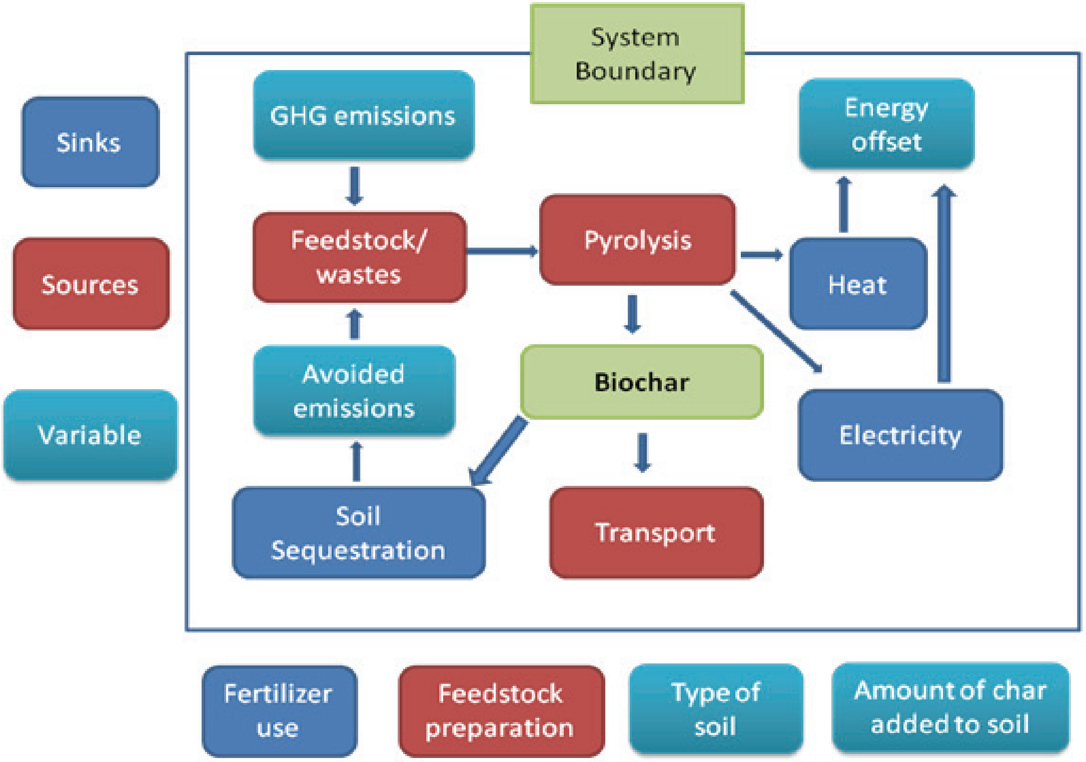

Figure 7.1: Biochar LCA Flow Diagram

7.2.3. Impact assessment

Computational spreadsheets were developed around the factors defined in the goal and scope, and drawing upon data derived from a wide review of the literature. The impact assessment consisted of deriving the GHG carbon equivalent and net energy generated or consumed during the progression of biochar production through the steps of feedstock accumulation, transport, and pyrolysis. In turn, this was used to calculate the climate change impacts of each process. The net climate change impact was calculated as the sum of "CO_2e sequestered" and "CO_2e emissions".

7.2.4. Economic assessment

An economic assessment estimated the cost/revenue contribution of each process in the biochar life cycle. As in earlier studies (Roberts et al., 2009; Hammond et al., 2009), the main costs arose from feedstock collection, pyrolysis and transport, while the revenues generated arose from the value of the biochar and the reduction in GHG emissions. In valuing GHG offsets, only the stable carbon in the biochar was considered.

Two revenue scenarios were investigated: low revenue (\$20 $\mathrm{Mg^{-1}}$ CO_2e) and high revenue (\$80 $\mathrm{Mg^{-1}}$ CO_2e) based on the IPCC definitions. The net profit of the biochar production system was calculated on the basis of a unit biomass of 1.0 Mg dry weight (d.w.) (Roberts et al., 2009) in Equation 7.1:

$$\mathrm{NP} = \mathrm{BC} + \mathrm{E} - \mathrm{F} - \mathrm{T} - \mathrm{O} - \mathrm{C} - \mathrm{A} \tag{7.1}$$

where,

NP	is the profit associated with 1.0 Mg d.w.,
BC	is the value derived from the biochar,
E	is the value of the energy created in the process,
F	is the cost of producing and collecting the feedstock,
T	is the transportation cost for both the feedstock and the biochar product,
C	is the capital cost associated with processing a unit of the feedstock,
O	is the operating cost incurred for processing a unit of feedstock,
A	is the cost of applying the biochar to the field.

The BC value was calculated as in Equation 7.2 (adapted from Roberts et al., 2009):

$$\mathrm{BC} = \mathrm{pPqcP} + \mathrm{pKqcK} + \alpha\delta(\mathrm{pPqBaseP} + \mathrm{pKqBaseK} + \mathrm{pNqBaseN}) + \mathrm{pGHGqGHG} \tag{7.2}$$

where,

pK, pN, pP	are, respectively, the price of potassium, nitrogen and phosphorus fertilizers
qGHG and pGHG	are, respectively, the quantity of GHG reductions associated with the biochar, and the value of these reductions
qBaseK, qBaseN and qBaseP	are, respectively, the average quantities of potassium, nitrogen and phosphorus fertilizers applied to a corn crop under standard, biochar-free cultural conditions.

qcK, and qcP	are, respectively, the quantity of potassium and phosphorus in the biochar,
α	is a conversion factor (0.14 ha Mg^{-1} biochar) based on the assumption of a biochar having a 67.68% carbon content (w/w) being applied at a rate of 5 Mg C ha^{-1},
δ	is the difference in fertilizer uptake efficiency between soil amended with biochar and soil without biochar,

In calculating the biochar's value, all of the biomass' P and K were assumed to remain present in the biochar, but made available to plants when the biochar was used as a soil amendment. The quantities of N, P and K for forest residues and corn fodder were collected from various sources (McHargue and Roy, 1932; Fernández, 2007), while their prices were determined based on fertilizer prices of \$0.80 kg^{-1} P_2O_5, \$1.60 kg^{-1} N and \$0.75 kg^{-1} K_2O (AAFC, 2012).

The energy generated through biochar production served to counterbalance the energy spent during the pyrolysis process, and was expressed as equivalents of a conventional form of energy, in this case, natural gas. The Canadian mean natural gas prices for all sectors (Henry Hub pricing for December, 2012) were \$2.88/mm BTU or \$1.04 m^{-3} (CGA, 2013). Syngas energy was valued at \$42.81 Mg^{-1} (d.w.) for corn fodder feedstock (Roberts et al., 2009) and \$30.0 Mg^{-1} (d.w.) for forest residue feedstock (Koch, 2008). Transport costs accrued with the progress of biomass transport from the field to the pyrolysis unit and of biochar from the pyrolysis unit to the field. The total transport costs for corn fodder and forest residues were \$20.22 Mg^{-1} (d.w.) and \$15.17 Mg^{-1} (d.w.) (Roberts et al., 2009; Conversion and Resource Evaluation Ltd, 2009).

Biochar application costs (A) included implement cost, fuel, and labor, at \$26.69 ha^{-1} or 5 Mg C ha^{-1}, or \$3.62 Mg^{-1} biochar. The operating and capital costs were calculated collectively based on figures reported by McCarl et al. (2007), which included both pretreatment and pyrolysis operational costs. These figures were chosen as being the highest among the most conservative estimates of pyrolysis facility costs.

7.2.5. Improvement assessment

The results of this study were used to quantify the effects of the application of biochar produced in the pyrolysis process in soil sequestration as well as a tool for climate change mitigation through reduction of GHG emissions. Thus the improvement assessment was carried out in the context of biochar production.

7.3. Results and Discussion

7.3.1. Greenhouse gas emissions balance

A comparison of total GHG emissions from corn fodder and forest residue feedstocks and conventional fuel sources (natural gas and petroleum) (Environment Canada, 2012), showed the former to generate much lower emissions than the latter (Figure 7.2). Expressed on a percent reduction basis, GHG emissions from corn fodder and forest residues, respectively, were 94.2% and 92.9% less than those for natural gas, and 89.4% and 87% less than those for petroleum. It is interesting to note that a complete consideration of all emissions from using natural gas would place it at a far less attractive position than petroleum and not significantly better than coal in terms of the consequences for global warming. Some of these considerations are: natural gas obtained from hydrofracking which is estimated to have 60% more emissions than for diesel fuel and gasoline, additional emissions of greenhouse gas occur during the development, processing, and transport of natural gas as well as the leakage of methane gas during production, transport, processing, and use of natural gas (Howarth, 2010).

Greenhouse gas (GHG) emissions are most commonly calculated using emissions factors, whose values relate the quantity of an emission with an associated activity (Environment Canada, 2013). Emissions factors for corn fodder and forest residues were marginally lower than that for natural gas, but substantially lower than that for petroleum (Figure 7.3).Although GHG emissions were greater for natural gas than petroleum, the burning of natural gas emits less carbon dioxide than from burning coal per unit of energy generated, which results in lower emissions factors for natural gas (Howarth, 2010).

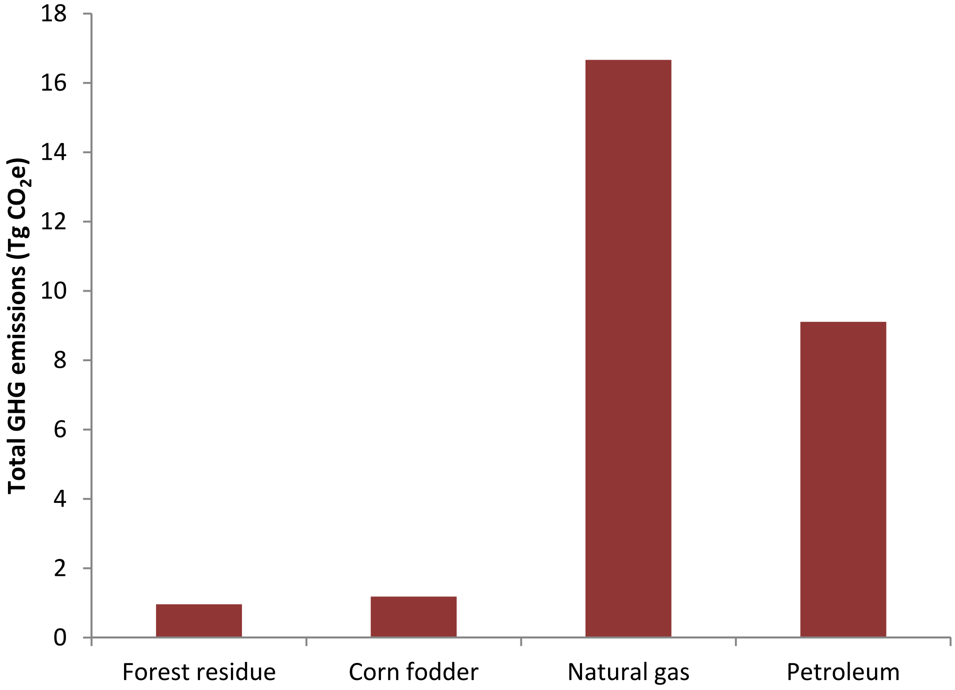

Figure 7.2: Comparison of total emissions (per Mg of fuel) between traditional fuel sources and biofuels

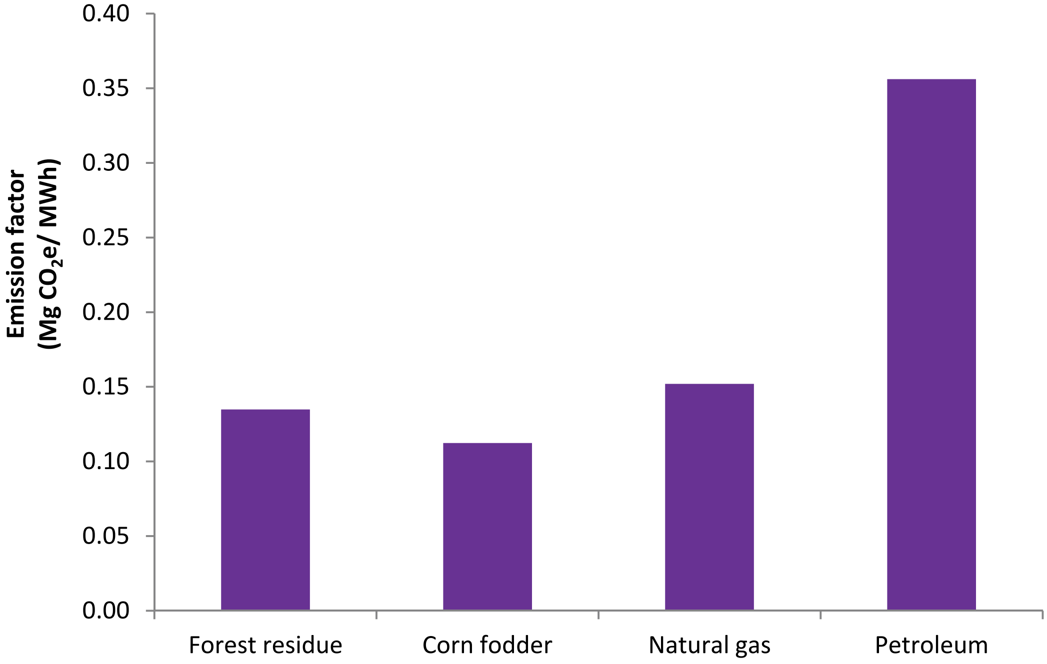

Figure 7.3: Comparison of emission factors of traditional fuel sources and biofuels

7.3.2. Improvement assessment

The effect of the balance of biochar vs. syngas as primary end product of biofuel production on GHG emissions from the chosen feedstocks was evaluated by calculating the percent difference between GHG emissions associated with the production of biochar and that of biofuels produced without biochar coproduction. Percent abatement of GHG emissions with biochar vs. syngas production were 1.47% and 1.77% for corn fodder and forest residues, respectively (Figure 7.4). In the context of the 14% of global CO_2 emissions coming from agriculture, this reduction of approximately 2% through the incorporation of biochar co production would play a significant role in the climate change mitigation efforts. In the case of emission factors, the percent reduction in emission factors for biochar (vs. syngas) production was roughly 13% for both feedstocks (Figure 7.5).

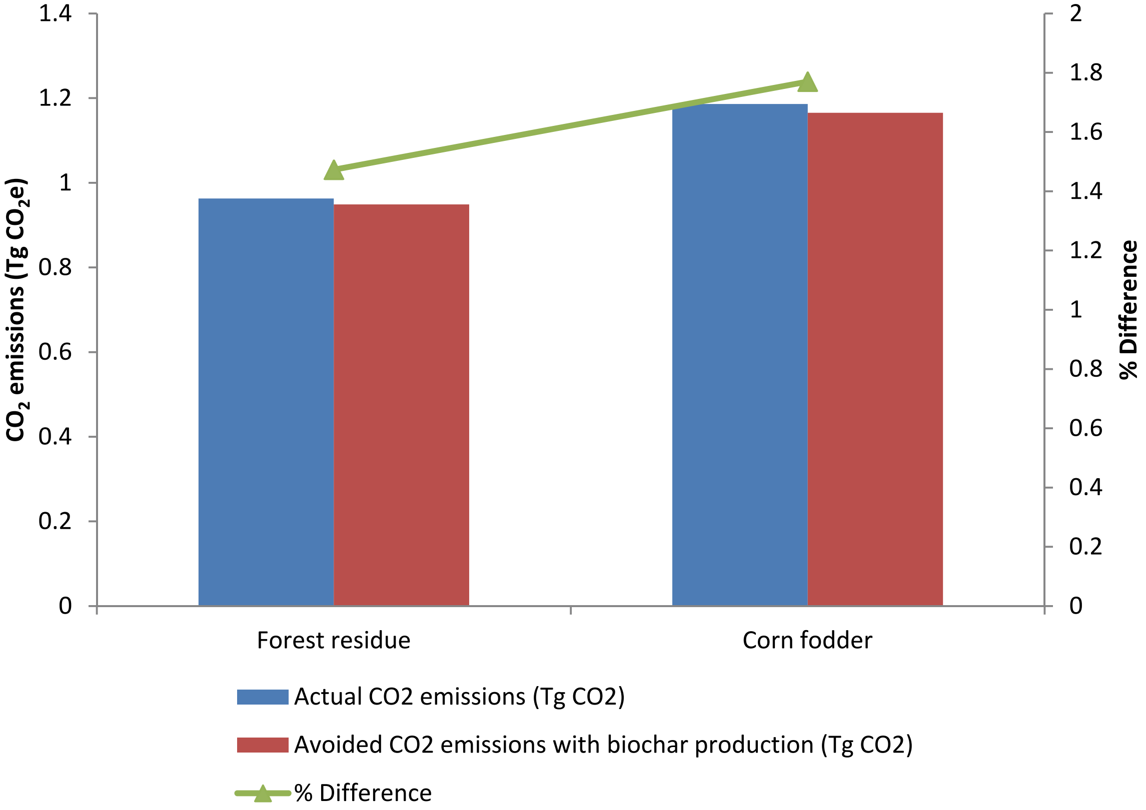

Figure 7.4: Effect of Biochar Production on Biomass Fuel Net GHG Emissions

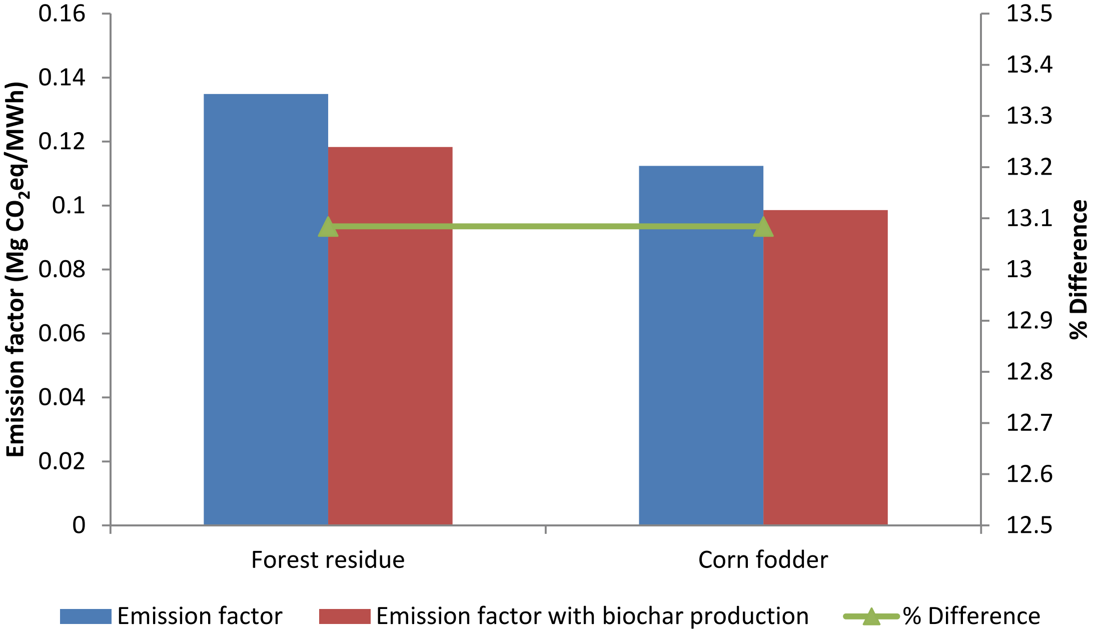

Figure 7.5: Effect of Biochar Production on Biomass Fuel Emission Factors

7.3.3. Contribution analysis

A contribution assessment of the processes involved in these biochar systems indicated that GHG emissions associated with the pyrolysis stage were the highest, contributing 51.2% and 47.3% of total emissions for forest residues and corn fodder, respectively (Figure 7.6). This corroborates the findings of studies in which different feedstocks were compared (Roberts et al., 2009, Gaunt et al., 2008). While a number of studies have shown that land-use changes and field emissions associated with feedstock production were the dominant processes contributing to GHG emissions (Roberts et al., 2009, Gaunt et al., 2008), the present research did not consider land-use change as a part of the feedstock production process. Other factors which may contribute to GHG emissions include transportation of biomass and biochar, and the use of machinery involved in biochar production and biochar application.

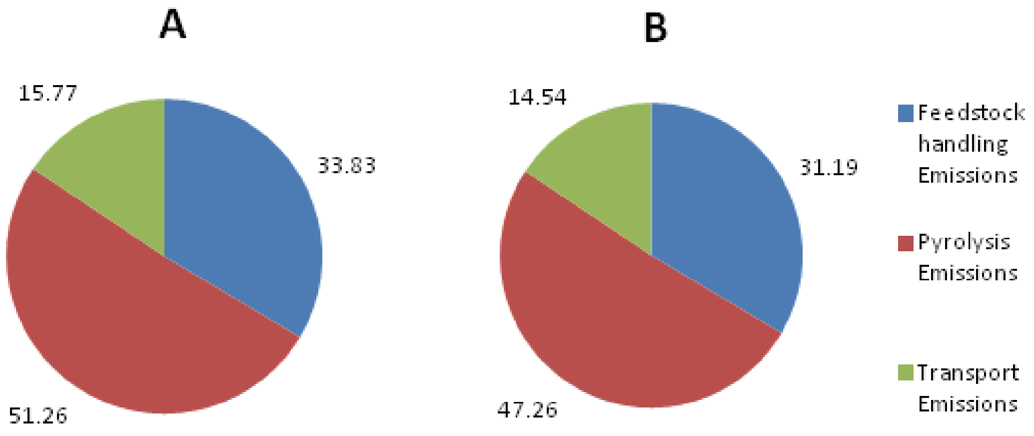

Figure 7.6: Analysis of life cycle stages contributing to GHG emissions (kg CO_2e Mg^{-1} feedstock d.w.): A. forest residues, B. corn fodder

It has been suggested that the pyrolysis stage's proportionately greater contribution to GHG emissions arises from the gaseous emissions which make up part of the syngas during pyrolysis. In general, the process of pyrolysis is endothermic for temperatures <280 °C and becomes exothermic between 280-350°C, where char formation takes place. Beyond >350°C, the process once again becomes endothermic, consisting of a devolatilization stage (McClaughlin et al., 2009; Brownsort, 2009).

During the endothermic processes, initial energy loss is linked to the initiation of pyrolysis as well as emissions during the devolatilization process. It is assumed that roughly 10% of total energy available for conversion to electricity is required in the process, and that a further 10% to 15% is lost in the process, partially accounting for startup fossil fuel (Brownsort, 2009).

7.3.4. Emissions avoided balance

The net GHG emission reductions or carbon sinks in the life cycle of biochar systems included are: reductions due to the avoidance of fossil fuel production and combustion, the generation of electricity and heat by the pyrolysis process, and the sequestration of stable biochar-C upon its use as a soil amendment. Reduction in emissions from corn fodder pyrolysis associated with soil sequestration of stable carbon and the sink represented by the electricity and heat generated were 38.6% and 44.3% greater, respectively, than those achieved with forest residues (Figure 7.7).

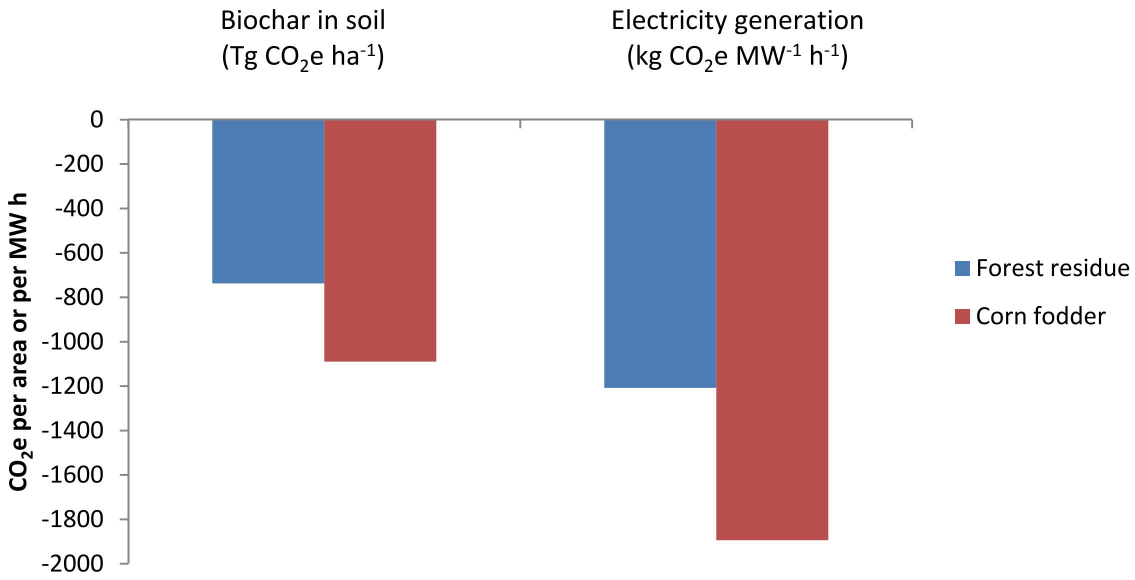

Figure 7.7: Comparison of reduction in emissions (Carbon sinks) for forest residue and corn fodder

A GHG emissions balance for the different components of the biochar system cycle (Figure 7.8) shows that in the case of both feedstocks, transport emissions accounted for very little of the overall emissions. Barely noticeable alone, heat offsets were combined with the electricity generation offset to become a significant source of GHG emissions reduction. Thus the GHG emissions balance analysis found that the optimization of a biomass pyrolysis system towards biochar production is better suited for soil sequestration of stable carbon than for the production of a fuel source. These findings concur with the conclusions of several other studies (Hammond et al., 2009; Gaunt et al., 2008). This in turn would support the implementation of biomass pyrolysis units associated with biochar amendments to agricultural soil as a strategy to reduce greenhouse gas emissions and deliver environmental benefits.

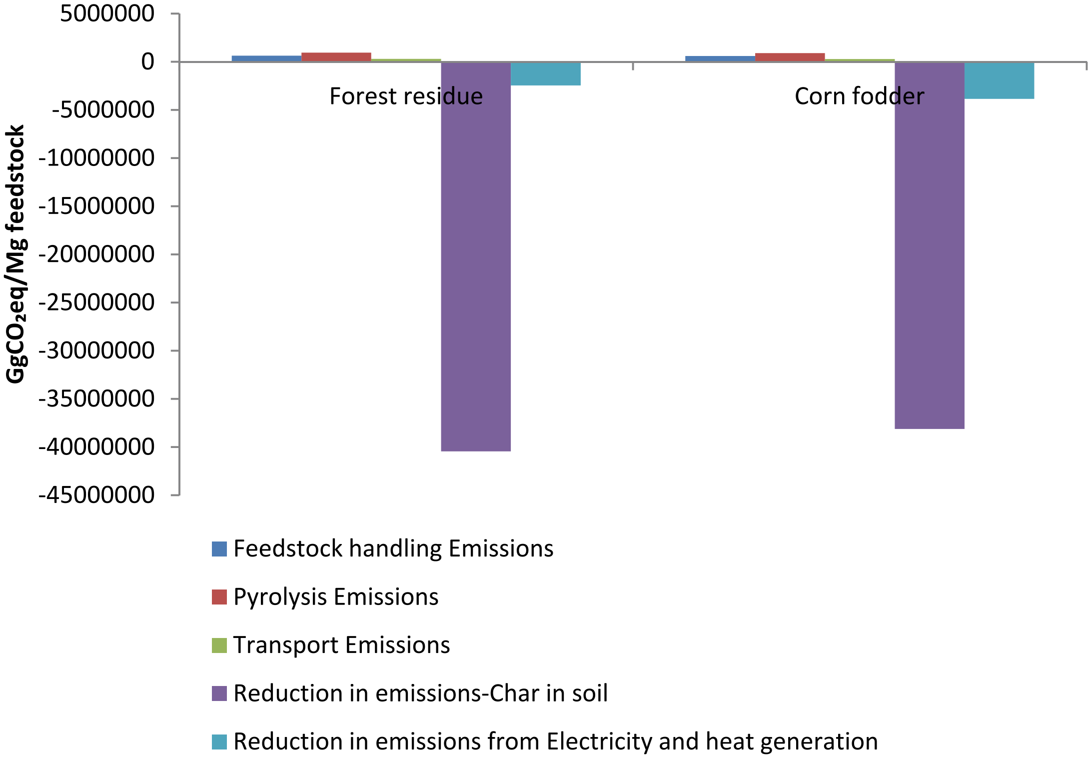

Figure 7.8: Relative GHG emissions for different components of the biochar system cycle

The net avoided emissions were calculated as the total emissions abatement from biomass generating pyrolysis with biochar applied to soil and electricity generation minus the sum of emissions from feedstock handling, pyrolysis emissions and transport emissions.

While total GHG emission reductions through soil amendment with biochar and electricity and heat generation during pyrolysis were higher for corn fodder than forest residue (Figure 7.9), total emissions were also higher for corn fodder. As a result, the net reduction in emissions (Gg CO_2e Mg^{-1} of feedstock) for forest residue was greater, making it a more suitable source for biomass pyrolysis for GHG reductions.

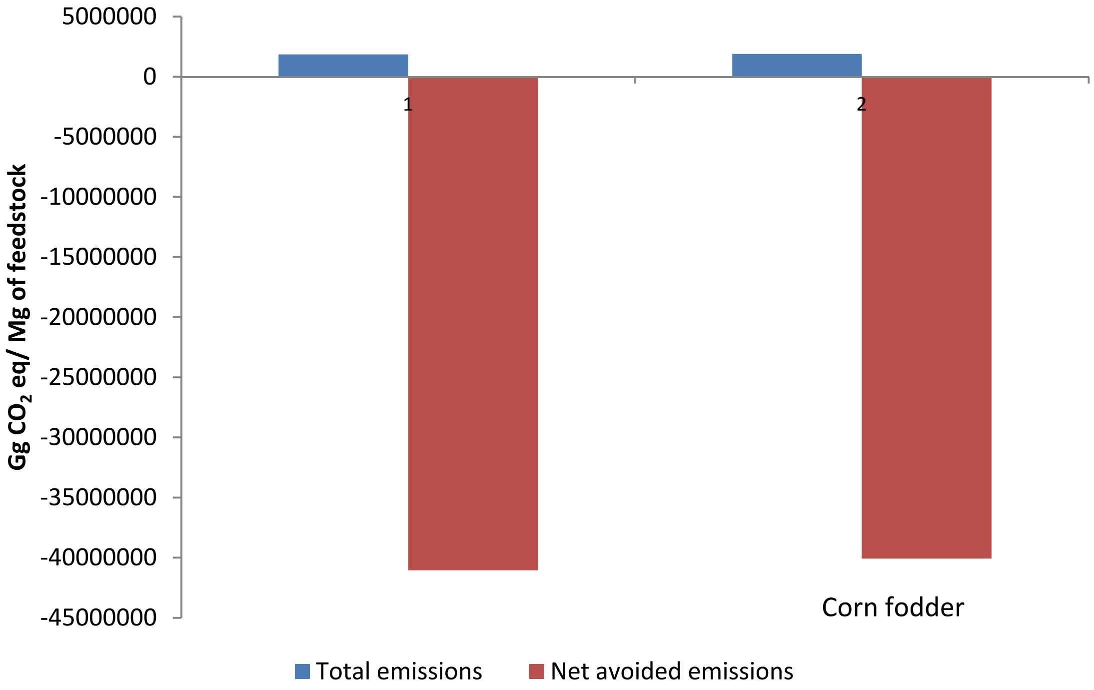

Figure 7.9: Comparison of GHG balance for corn fodder and forest residue

7.3.5. Economic assessment

In the low revenue scenario ($20 Mg^{-1} CO_2e; Figure 7.10), net costs incurred for biochar production through pyrolysis of both corn fodder and forest residue were $43 Mg^{-1} and $66 Mg^{-1} biomass (d.w.), respectively, indicating that these systems' economic viability remained quite poor. Comparatively, for the high revenue scenario ($80 Mg^{-1} CO_2e), forest residue continued to be a poor economical option with net costs of $9 Mg^{-1} biomass, whereas corn fodder showed gains of $26 Mg^{-1}, indicating a moderate potential for economic viability (Figure 7.10).

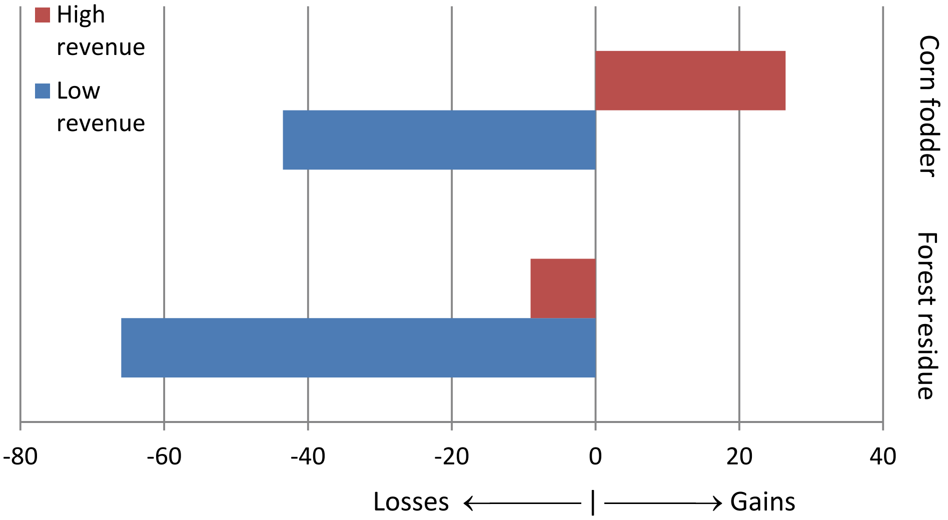

Figure 7.10: Net gains or losses ($\$ \text{ Mg}^{-1}$) for each feedstock

Although the biochar systems for both feedstocks do provide energy offsets in terms of electricity and heat as well as help in GHG abatement, their economic potential requires further improvement. An analysis of the net costs of each life cycle stage for the low and high revenue options (Figure 7.11) indicates that the cost of feedstock collection and operating costs of the biochar production unit were the main impairment to financial viability. Despite both the feedstocks incurring similar levels of costs during the "expenditure" stages, corn fodder is a more suitable candidate given its higher biochar value (Figure 7.11). It is interesting to note that transport costs have very little effect on the net costs for either revenue scenario.

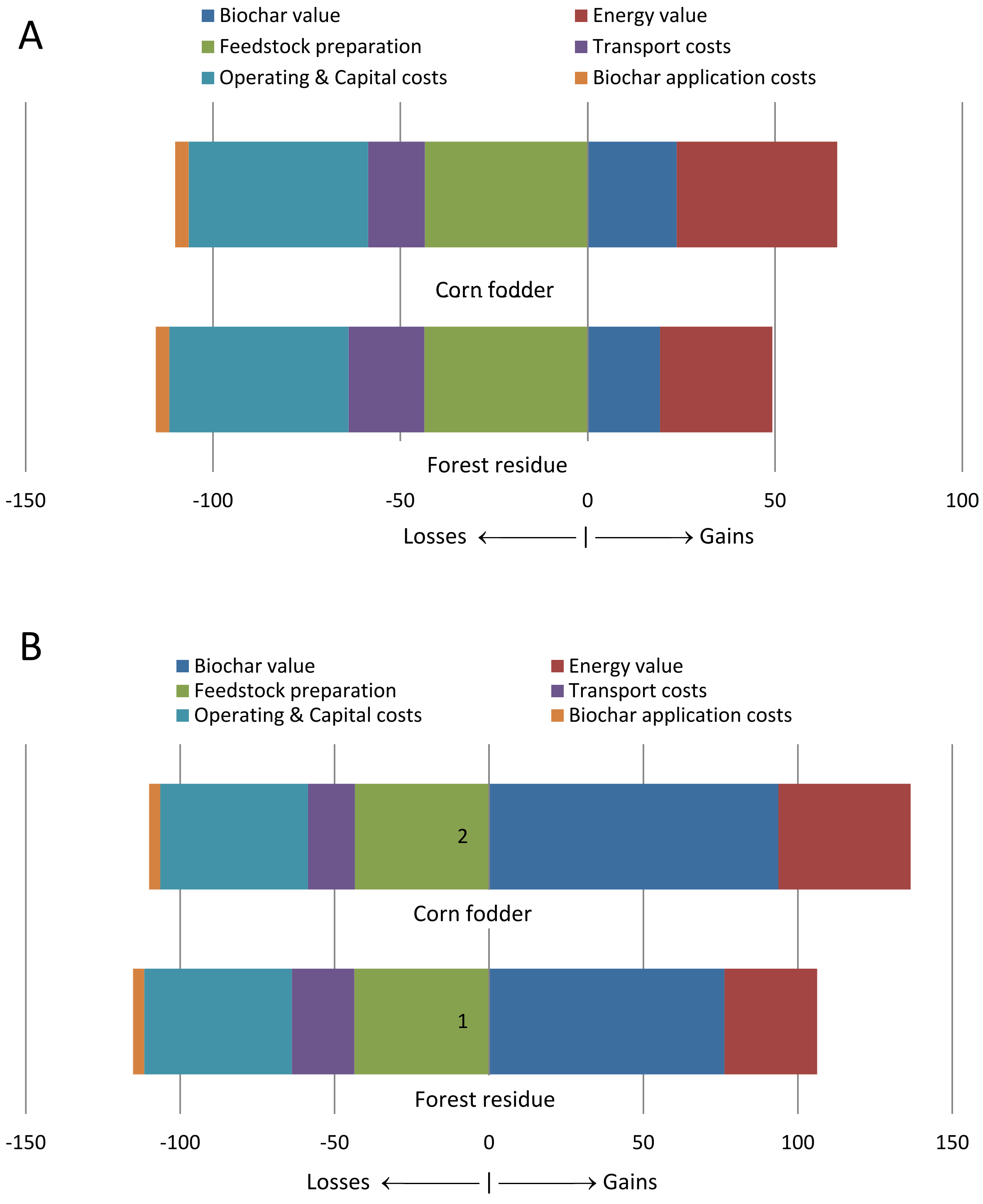

Figure 7.11: Comparison of net costs (\$ Mg^{-1}) by life cycle stage for two feedstocks and two revenue scenarios: A: Low, B High.

Results indicating that corn fodder is one of the more economically feasible feedstocks have been widely reported. Roberts et al. (2009) found that the late corn stover had a greater economic viability compared than even high energy alternatives like switchgrass, which was not found to be profitable. The authors surmised that this was due to the low value associated with the latter's reduction of CO_2e units.

Furthermore, if we compare the biochar systems of corn fodder and forest residue (Figure 7.12), it is interesting to note that although their potential to reduce GHG emissions is almost equivalent, the net terms of profits associated with corn fodder makes it a more suitable candidate and would allow it to gain better carbon credits in a competitive market scheme.

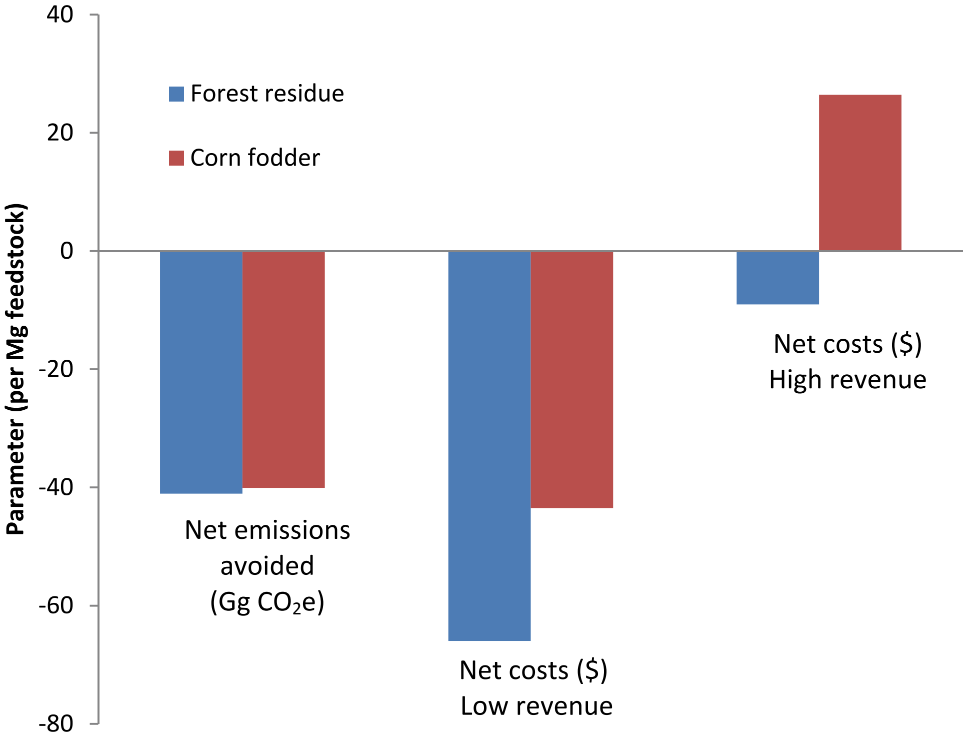

Figure 7.12: Comparison of feedstocks: Economic vs. GHG balance

7.4. Conclusion

This research highlights the importance of a life cycle analysis to estimate the full life-cycle GHG emissions balance and economic feasibility of biochar systems. This analysis was conducted based on various optimized pyrolysis parameters for agricultural wastes of corn fodder and forest residue. The GHG emissions avoided for both corn fodder and forest residue showed a reduction in emissions (CO_2e Mg^{-1} feedstock d.w.). The stabilized carbon in the biochar was the main contributor to these reductions. The reductions in emissions attributable to soil sequestration of stabilized carbon in biochar (C sink) and to electricity and heat generation during pyrolysis were respectively 38.6% and 44.3% greater for corn fodder than forest residue. A relative GHG analysis found that the optimization of a biomass pyrolysis system for biochar production to be better suited to soil sequestration of stable carbon than as a fuel source. The economic viability of the pyrolysis-biochar system is largely dependent on the costs of feedstock production, pyrolysis, and the value of C offsets. Corn fodder at a net cost of \$26 Mg^{-1} feedstock showed a moderate potential for economic viability compared to forest residue.

7.5. Acknowledgements

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Chapter 8

General Summary and Conclusions

The originality and significance of this research lie in its contribution to both the limited research undertaken so far in the assessment of novel biochar production technology of microwave assisted pyrolysis as well as the application of biochar as a sustainable agricultural practice in the context of a changing climate. There are several advantages to the use of microwave energy for the pyrolysis of agricultural feedstocks such as uniformity of heating, reduction of the duration of pyrolysis. Despite these benefits, there are several uncertainties associated with the application of microwave assisted pyrolysis relating the heat and mass transfer characteristics, coupling of electromagnetic radiation, and the energy considerations. Moreover, the geometry, heterogeneity and orientation of the biomass within the microwave reactor also play an important role in the extent of the pyrolysis process and the product formation. To realize the full potential of this technology and the subsequent beneficial application of biochar for mitigation of greenhouse gas emissions, it is essential to address these challenges. An overall schematic of the objectives of this thesis is summarized in Figure 8.1.

In this thesis, the goals were to improve upon the design of the microwave assisted pyrolysis reactor and to fabricate such a unit aimed towards increasing yields of biochar. The first step towards this was to develop process models through which it would be easier to visualize the process and to facilitate design optimization. Another goal was to investigate the design of the biomass sample optimized for maximization of biochar yields. The secondary goals of the research were to explore innovative methods which would assist in the characterization of the biochar produced as well as develop a life cycle analysis of biochar systems aimed at investigating elements of economic benefits and energy consumption in the biochar systems which will in turn enhance sustainable development of green energy and sequestration of carbon.

In the first two chapters of the thesis, the concept of biochar and its applications as a tool for sequestration of carbon in soil as well as reduction of greenhouse emissions is introduced. Of the various biochar production strategies, the focus of this thesis was microwave assisted pyrolysis which offers several advantages over traditional production methods such as kilns etc. which are based on convection or conduction heat transfer within the biomass. Microwave assisted techniques have the inherent properties of volumetric heating resulting in more uniform transfer of heat as well as being a faster process due to the penetration depth of the radiation inside the material. In chapter two, the advantages of these properties in terms of reducing process time, energy and cost efficiency and uniformity in heating has been described. Despite these advantages, there are several challenges such as control of the process parameters like temperature, process time, power density of the microwaves, penetration depth for a specific biomass etc. The two chapters describe the design considerations which are necessary in microwave assisted pyrolysis to overcome these challenges. Another recommendation of this section of the thesis is to develop robust numerical models which can be simulated in order to attain better visualization of the pyrolysis process in a microwave environment.

The third chapter of the thesis is based on the conclusions of the first two chapters which highlight the necessity of building simulation techniques. A finite element model (FEM) was developed in order to couple thermal heating and heat and mass transfer phenomena in order to simulate the microwave heating of biomass and to predict the optimal conditions for the maximization of biochar using the process. These models take into consideration various parameters like the mass, geometry, power density and orientation to determine the energy distribution and heating rate of the biomass undergoing microwave pyrolysis in a multimode cavity.

The simulation studies were conducted for biomass subjected under microwave radiation at the frequency of 2450 MHz for 3 to 15 minutes (with increments of 3 minutes) with power densities of 5 W/g, 7.5 W/g and 10 W/g in order to visualize and investigate the energy distribution within the biomass. The results of simulation model developed in this chapter indicated 425°C to be the optimum temperature and optimum power density of 7.5W/g at which highest yield of biochar is found based on the kinetics of the model taken into consideration. It also showed that the rate of reaction would vary at this temperature for different power densities applied to the microwave set up. The desired temperature was reached in 4 min of the reaction time at the power density of 7.5W/g while the entire pyrolysis of the biomass sample took place in approximately 6 min. At higher power densities although the optimum temperature was attained in less time, it was a very unstable reaction with greater temperature variation. The experimental validation of the simulation model was carried out using a two factor response surface design with pyrolysis temperature and time at the optimal power density of 7.5 W/g. There were several challenges encountered during the experimental work such as non uniform heating resulting in the creation of hot spots in the biomass, generation of sparks in the cavity. This led to severe instabilities which caused inaccuracies in the temperature control of the process. The validation results showed that the biochar yields of the maple wood biomass increased with increase in duration of the pyrolysis and decreased with increasing temperature. The highest biochar yield of 65.24% was found at the pyrolysis temperature and time of 250°C and 5 min respectively and was in good agreement with the regression model built through the experimental design. These new approaches using Maxwell's equations can be used to simulate the microwave heating of any complex and heterogeneous object. This type of simulations will be very useful in the microwave process equipment design and development.

The two inherent properties of microwave assisted technologies are volumetric heating and selective heating of materials, which are directly influenced by the material's dielectric properties. Hence in the fourth chapter of the thesis the influence of the dielectric properties of two microwave-susceptible doping agents, i.e., char and graphite were evaluated to comprehend their role in optimum pyrolysis conditions for product maximization. The dielectric properties of the doping agents (i.e., char and graphite) were assessed over the range of 25°-400°C and used to further develop the finite element model (FEM) introduced in the previous chapter. This model served to couple electromagnetic heating, combustion, and heat and mass transfer phenomena and evaluated the advantages of selective heating of woody biomass during microwave pyrolysis. The dielectric properties of the doping agents had a linear correlation to the increase in pyrolysis temperature. Regression analysis of the model indicated that char had more uniform susceptibility to microwaves than graphite. The simulation study found that doping helped to provide a more efficient heat transfer within the biomass compared to non-doped samples. Moreover samples doped with char resulted in better heat transfer compared to graphite doping and also produced optimal temperatures for maximization of biochar production. The model was then validated through experimental trials in a custom-built microwave pyrolysis unit which confirmed that the addition of a microwave-susceptible doping agent (particularly char doping) would assist in reaching optimum pyrolysis conditions for maximization of biochar.

In the fifth chapter, the conclusions of the third and fourth chapters were used as guidelines for the design and subsequent fabrication of a custom built microwave assisted pyrolysis chamber aiming toward increase of biochar yield from maple wood. An interesting feature of the reactor was that it provided the means for the continuous disposition of secondary gases, which is an unwanted outcome of the pyrolysis process aimed at biochar production. The objective of the fifth chapter was to investigate the effect of microwave absorber to biomass ratio on the yield of biochar and heating characteristic through the temperature profiles of the maple wood biomass under microwave irradiation. Further, the effects of the pyrolysis conditions 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. In this study, the effects of pyrolysis conditions such as temperature, time and dope ratio on the biochar yields and fuel properties of biomass samples were investigated by using statistical design techniques. Results showed that the yield of the increased with decreasing pyrolysis temperature and increasing pyrolysis holding time while doping ratio did not have a significant effect on the biochar yields. The maximum predicted value of yield for microwave pyrolysis was optimized to be at the pyrolysis temperature of 250°C, reaction time of 1 min and doping ratio of 16%. The regression analysis showed good correlation between the experimental and predicted results. Through the results obtained from Differential Scanning Calorimetry, the highest exothermic enthalpy of 188.31J/g was found to be at the pyrolysis temperature, holding and dope ratio of 250°C, 1 min and 32%, which had good agreement with the optimization results.

The aim of the fifth chapter was to investigate the structural development of the biochar produced in the study undertaken in the fourth chapter as well the influence of the pyrolysis conditions such as temperature, residence time and doping ratio on these changes. The structure of the chars was characterized using helium pycnometry and hyper spectral imaging in order to ascertain the correlation between the degrees of porosity on the reflectance of the biochar samples. The results showed that with the increase of reflectance, the porosity of formed char decreases. From the pycnometry data gathered, it was observed that the treatments with the highest temperatures and longest holding times had the highest porosity compared to the other biochar samples. 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. Through the hyperspectral imaging experiments, certain infra-red wavelengths were selected which provided maximum structural information of the biochar. A regression model was built to evaluate the relation between the spectral data with the porosity and yield of the biochar samples in the selected wavelength range of 1190 – 1310 nm, which showed good correlation between the predicted and observed porosity. A principal component analysis was also done to differentiate between the biochar samples according to their physical attributes. Scanning electron microscopy imaging was also used for structural determination which indicated that the pyrolysis temperature and doping ratio plays a role in the formation of a microporous biochar structure with 290°C at 24% doping ratio presenting uniform porosity. FTIR analysis was also included in the structural investigations in this chapter which indicated that a correlation to increase in temperature and doping ratio and thus substantiated the SEM results. The fresh maple wood FTIR profile showed more complex spectra and as the pyrolysis temperature increased; the bands became weaker, which lowered functional group activity.

A life cycle analysis (LCA) for pyrolysis biochar systems was carried out in the sixth chapter of the thesis to determine greenhouse gas balance, carbon cycling, and the economics of biochar production from different agricultural residues and wastes with a special focus on Quebec, Canada. Investigating a range of feedstocks (forest residues, corn stover) provided insight into the use of biomass residues rather than bioenergy crops as biochar production substrates and the resulting energy and climate change impacts. The amount of stable carbon in the biochar was found to be the main contributor of the observed reductions of greenhouse gas (GHG) emissions (CO_2 equivalent per Mg dry feedstock) for both corn fodder and forest residue. The conclusions of the chapter found 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. Although corn fodder was found to be moderately successful as an economic option, it showed a greater reduction in emissions than forest residue, which in turn presents corn fodder to have a higher potential as an alternate feedstock option for biochar production seeking reduction in greenhouse gas emissions through soil sequestration. A relative GHG emission analysis was conducted which indicated that a pyrolysis system for biochar production is better suited for soil sequestration of stable carbon than as a fuel source.

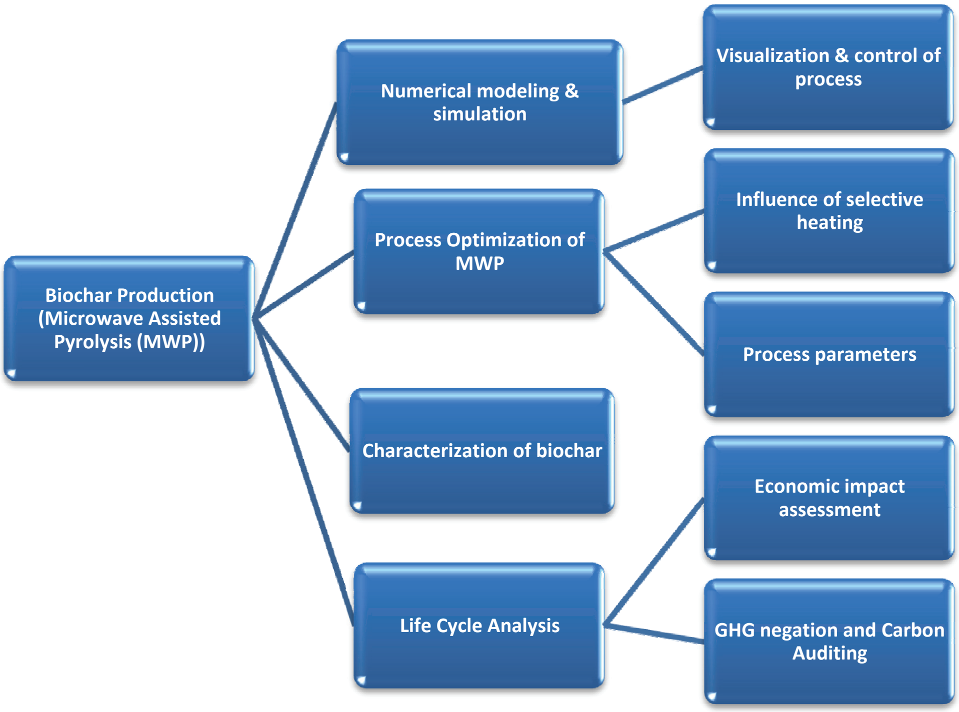

Figure 8.1: Schematic representation of the theories and methodologies of the overall objectives of the research undertaken in the thesis

Chapter 9

Contribution to Knowledge and Recommendations for Future Research

9.1. Contribution to Knowledge

In a broad-spectrum, the goals of this research work were to shed more light on the least understood aspects of microwave processing for bioenergy applications. The following are a few of the several contributions of this research:

1. Simulation techniques of finite element model (FEM) were developed in order to couple electromagnetic heating and the thermochemical conversion process during microwave pyrolysis involving simultaneous heat and mass transfer phenomena. This numerical modelling and simulation approach will be very useful in the visualization of these novel processes such as microwave pyrolysis and leads to the optimization of the product formation.
2. The numerical models developed in this research work and their validation take into consideration various parameters like the mass, geometry, power density and orientation to determine the energy distribution and heating rate of the biomass undergoing microwave pyrolysis in a multimode cavity. These new approaches using Maxwell's equations can be used to simulate the microwave heating of any complex and heterogeneous object.
3. Numerical modeling and simulations were also used as a tool to study the advantages of selective heating of lignocellulosic biomass during microwave pyrolysis. The outcomes of this research indicated that the application of a doping agent leads to more uniformity in heat transfer in the biomass during microwave pyrolysis. These simulations can be a guideline towards the design of biomass aimed at higher yields of different co products of the pyrolysis process in a microwave environment.
4. Traditionally microwave pyrolysis has been carried out mainly for obtaining higher yields of bio-oil. This study elucidated the different parameters and the conditions under which the microwave pyrolysis at 2.45 GHz of different biomass can be carried out for the maximization of biochar. A microwave pyrolysis unit was designed and fabricated with the novel concept of continuous

disposition of the secondary syngases and liquids as a method to improve the yields of biochar.

5. The study explored new techniques like hyperspectral imaging and pycnometry for the quantitative and qualitative assessment of the biochar obtained through microwave pyrolysis which can be compared to those from conventional pyrolysis. These techniques along with other established methods of Scanning electron microscopy (SEM), Fourier Transform Infrared Radiation (FTIR) spectroscopy provide a comprehensive representation of the surface characteristics of the biochar produced through microwave pyrolysis with selective heating as a tool for better uniformity.
6. The authors found through their literature survey that the environmental implications of the potential role of biochar as a tool for mitigation of greenhouse gas emissions through C sequestration have not been fully assessed. The life cycle analysis (LCA) carried out in this thesis evaluated the potential of common biomass sources in the province of Quebec in Canada to estimate the energy and climate change impacts and the economics of biochar systems using a cradle to grave approach. These methods would help in the determination of the unwanted outcomes of a product's use or technology's implementation and facilitate appropriate decision-making to avoid such outcomes.

9.2. Recommendations for further research

The research undertaken in this thesis developed simulation techniques of finite element model (FEM) to design and carry out microwave pyrolysis of lignocellulosic biomass (maple wood) in a custom built microwave pyrolysis reactor in order to improve yields of biochar. In addition, the biochar produced under different process parameters were then characterized using various quantitative and qualitative techniques. In order to make these outcomes comparable for commercial purposes, further research is essential for the optimization of the reactor design and microwave pyrolysis process conditions. A few of the recommendations for future research are:

1. Dielectric properties of any material play a major role in the extent of microwave energy absorption in different biochemical species. In this study, it has been

proven that dielectric properties have a correlation to variation in temperature. Hence, it would prove to be useful to have a robust model illustrating the relationship between the dielectric properties and increase in temperature inside a microwave environment during the pyrolysis process.

2. Biological materials such as biomasses possess inherent non-homogeneous structural characteristics, or that contain different chemical species with different dielectric properties dispersed into a homogeneous environment. This results into a possible selective heating of some areas, or components of these systems. In this study, this characteristic feature was applied to improve the heat transfer within the biomass resulting in faster increase of temperature and higher yields of biochar. Further research could also focus on exploring other materials with higher potential as a doping agent allowing for better heat distribution within the biomass.
3. The instability in the measurement of temperature within the microwave cavity during the pyrolysis of the biomass presents the major barrier towards the development of an optimum design. Further studies should focus on investigating alternates such as non invasive techniques, like infrared or optical methods for the measurement of the variation in temperature within the biomass inside the microwave chamber.
4. Further studies could also be focussed towards pretreatment processes for the biomass and the optimization of the auxiliary pyrolysis process conditions such as nitrogen flow rate or the rate of removal of secondary co products which could play a role in the degree of biochar yield. The microwave pyrolysis of the lignocellulosic biomass in this study was carried out in a multimode microwave cavity operating at 2450 MHz. Dielectric properties of a heterogeneous biological material also have been found to vary with variation in frequency. Hence it is recommended that in order to determine the potential of other commercially viable microwave frequencies such as 915 MHz may be investigated for improving biochar yields. Practical applications of microwave pyrolysis technology would benefit from the investigation of these operating frequencies which facilitate design of large scale reactors for commercial implementation.

The design principles of the lab scale microwave pyrolysis unit could be applied as a model to design and develop the pyrolysis production systems that can be used either as a mobile unit at the farm or as a stationary unit at a central site to be used by small scale local industries.

5. Further research could be undertaken into the novel characterization techniques of hyperspectral imaging and pycnometry developed through this study along with other techniques to distinguish biochar produced from other feedstocks and also assist in the production of optimal or desired product formation through better energy utilization.
6. The life cycle analysis developed in this study could further be extended to include several other important parameters which were excluded from the system boundaries, such as, fertilizer use, consideration of type of soil, mineral content of the soil etc. Moreover, this LCA could be made more robust by carrying out a sensitivity analysis with the inclusion of various other feedstock sources (switchgrass, nut shells), inclusion of other scenarios with variation in pyrolysis operating conditions which might help in determining a more comprehensive understanding of biochar’s potential as a soil sequestration tool for greenhouse gas abatement.

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3

Appendix 1

Connecting text

The results of the Finite Element Modelling (FEM) were instrumental in visualizing the heat transfer mechanism inside the Maplewood biomass during the microwave pyrolytic reactions. However evidence of non uniform heating resulting in the creation of hot spots in the biomass was also observed during the microwave pyrolysis process. Temperature control and monitoring carried out by the thermocouple during the process interfered with the electromagnetic field and resulted in the concentration of microwave energy at the tip of the probe. This ended up in producing erroneous temperature measurements. Hence it was essential to resolve this problem by analysing the existing design of the temperature quantification and control system.

Development of design principles for increasing accuracy in temperature measurement in microwave pyrolysis of biomass for biochar production

The response to an applied electric field is dependent on the dielectric properties of the material (Thostenson & Chou, 1999). As discussed in previous chapters, the ability of a material to absorb microwave energy, resulting in an increase in temperature is determined by its dielectric properties. Moreover, constructive and destructive interferences of the microwaves occur due to the geometry of multimode cavities through their reflections off the cavity walls and the conductor elements of the sample. Hence there is no well-defined electric field but the field acts over a much larger volume, allowing larger samples to be treated.

One of the most important considerations regarding monitoring of pyrolysis or any heating applications in a microwave environment is the design of the temperature measurement feedback control device. Temperature sensors of two kinds, namely, non-contact or contact with the material can be used for this purpose. In recent pyrolysis work, infrared optical pyrometers have been used which can carry out high temperature measurements but have the disadvantage of measuring only the surface temperature. Temperature sensors in contact with the sample, such as thermocouple probes which consist of two dissimilar metals joined together, are simpler in design and are cost effective (Fernández et al., 2011). However, accurate measurement of temperature is difficult even in the case of thermocouple probes, which measure an over-temperature (Cloete et al, 2001). However it has been generally accepted that temperature measurement corresponds to the average temperature of the bulk. When heating non-polar substances, the temperature registered on the probe will in fact be that of the probe itself and not of the specimen. Thus, in this respect it is particularly difficult to determine the temperature in nonwater-soluble substances (Fernández et al., 2011). In the present thesis work, a contact measurement with material/biomass technique through K-type thermocouple was chosen for temperature measurement as this presents a better indication of the heat distribution inside the biomass.

In the validation of the simulation models for the microwave pyrolysis of lignocellulosic biomass, a K-type thermocouple was inserted into the reactor through the gaseous product release tube to monitor the biomass temperature continuously throughout the experiment. The major challenge that was faced during the validation of the simulation of microwave pyrolysis of lignocellulosic biomass was the evidence of non uniform heating resulting in the creation of hot spots in the biomass observed during the process. The pyrolysis process was hard to control due to the non uniformity of heating and the generation of sparks in the cavity. This led to severe instabilities in the temperature control of the process as seen in Figure A1.1. The measurement of temperature interfered significantly with the generation of electromagnetic waves within the cavity and resulted in uneven heat distribution inside the biomass sample. Hence it was essential to modify the design of the thermocouple for better temperature measurement and control.

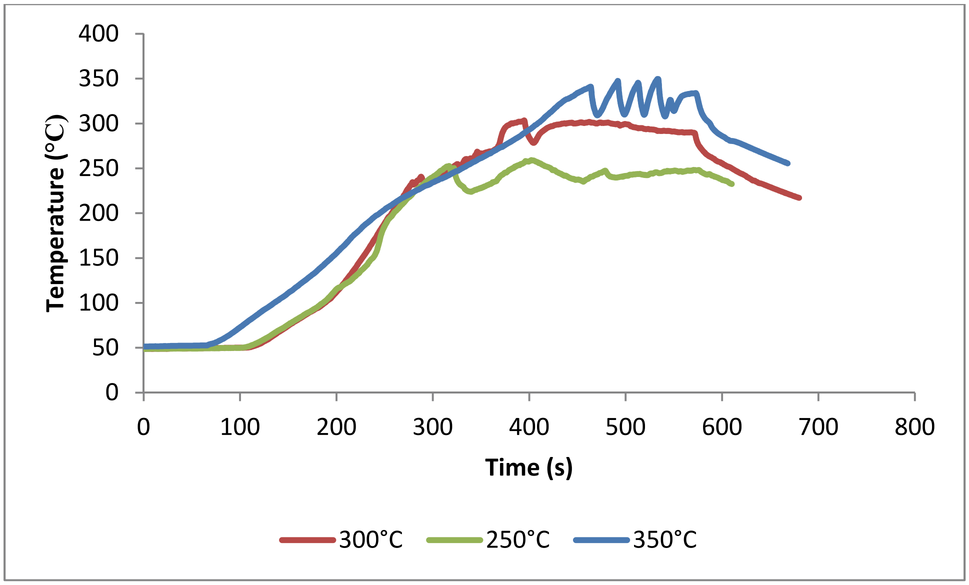

Figure A1.1: Variation in temperature measurement observed at various pyrolysis temperatures during experimental validation of simulation model

During the microwave pyrolysis process, it was observed that localized heating was occurring at the location where the tip of the thermocouple probe was inserted into the biomass sample. This observation led to the hypothesis that this localization of microwave energy was causing the interruption in temperature signals through the thermocouple and resulted in the final design of the probe through a number of trial and error experimental work as well as simulation studies.

It was hypothesized that if the localized microwave energy gets dissipated from the tip of the probe, it would offer better control of the process and more accurate temperature readings. This challenge of inaccuracy in temperature measurement and control has been reported in a few studies. The suitability of using mobile metallic temperature sensors was evaluated in applications of continuous microwave assisted sterilization (MATS) systems. This study also utilized simulation models with finite difference time domain method to study the influence of microwave field on the accuracy of mobile metallic temperature sensors in a MATS system in which food packages with embedded sensors traveled on a conveyor belt. Contrary to simulation results which showed negligible effect of the metallic temperature sensors on the overall heating patterns within food samples, experimental work showed that high electric field intensity at the sensor tip and caused localized overheating within microwave cavities similar to the present study. This was avoided by altering the orientation of the sensor to the electric field and verified with experimental results (Luan et al., 2013).

In another work, shielding of the thermocouple junction in an aluminium tube grounded to the microwave cavity wall has been reported to prevent electrical perturbations and permit measurement of temperatures. Several shielded thermocouples were evaluated for temperature measurement inside a microwave cavity and compared with a standard fibre optic temperature sensor. Results indicated that proper design such as shield isolation and body insulation of the thermocouples can be used for temperature measurement in microwave ovens and shield heating to yield reasonably accurate values of temperatures (errors <2°C) (Ramaswamy et al., 1998).

Taking these into account, a simulation model was developed using finite element modeling for MAP with a K type thermocouple inserted in a cylindrical metallic shield of diameter 5 mm and 14 mm length embedded in the biomass to prevent signal interruption by microwaves (Ramaswamy et al., 1998). The metallic shield had rounded edges to avoid microwave interruptions. In this simulation, only the microwave heating was simulated with a focus on the effect of the thermocouple on the temperature distribution.

The simulation results showed that the insertion of the probe in the shield helped in avoiding signal interruptions and localized heating of the tip. At the same time, the new design did not change the temperature distribution within the biomass as compared in Figure A1.2 and Figure A1.3. The simulated heating patterns and temperature profiles were then verified with experimental results. A single factor full factorial design with three replicates was chosen for the validation of the simulation. Probe design was the single factor (i.e., with or without shield) at the pyrolysis temperature and time of 300°C and 5 min respectively. Table A1.1 shows the experimental design drawn for validation purposes with 1 indicating the insertion of probe into the shield and -1 indicating absence of shield in temperature design.

Table A1.1: Experimental design for the validation of the simulation model to study the effect of temperature measurement design

Runs	Pattern	Presence of shield
1	+	1
2	−	-1
3	−	-1
4	+	1
5	−	-1
6	−	-1
7	+	1
8	+	1

The validation results using the regression analysis of the experimental design clearly indicated that the presence of the metallic shield did not significantly affect the biochar yield during microwave pyrolysis as illustrated in the ANOVA shown in Table A1.2 and Figures A1.5, A1.6.

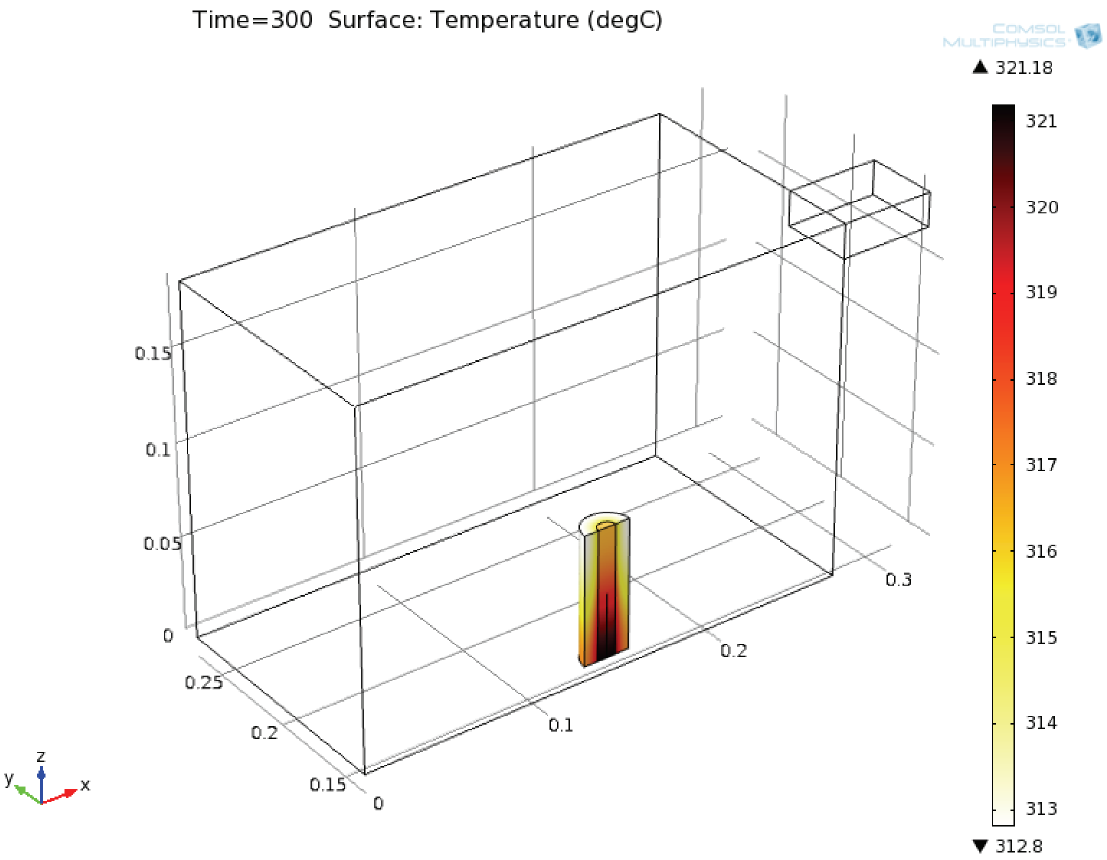

Figure A1.2: Temperature profile of char doped biomass with thermocouple (without shield) for microwave pyrolysis of biomass

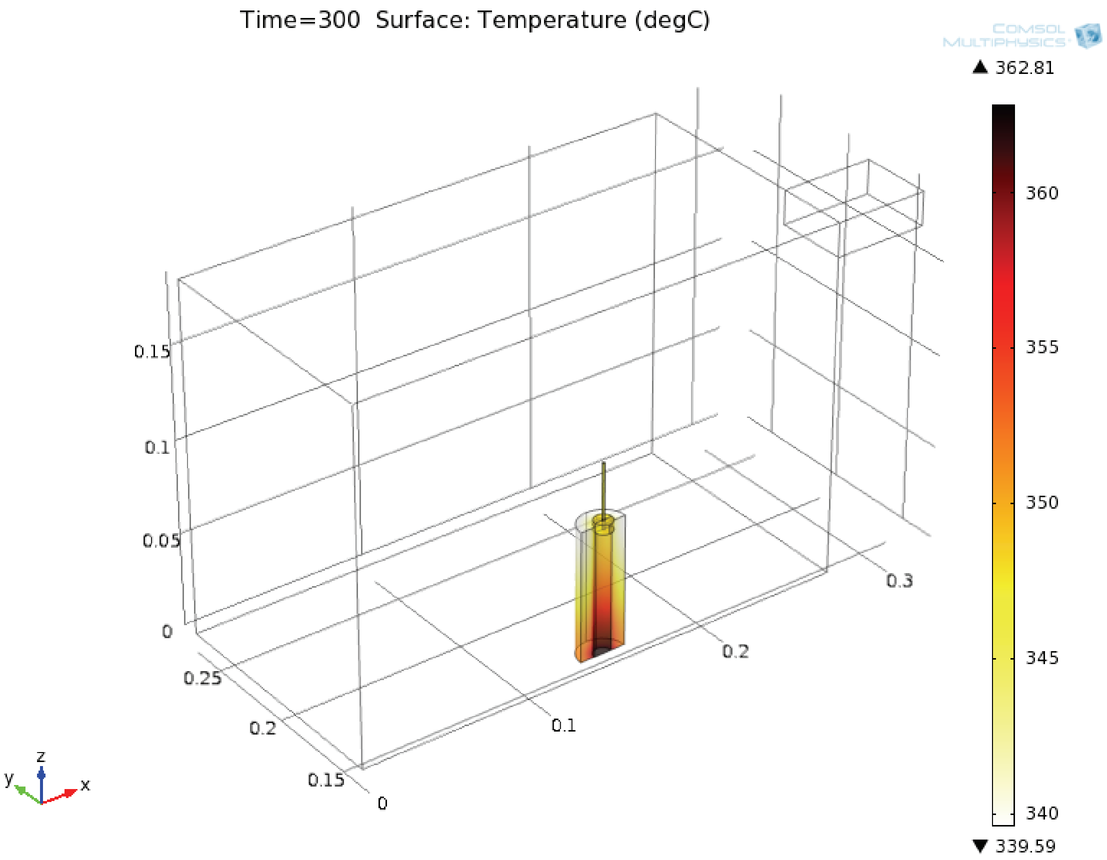

Figure A1.3: Temperature profile of char doped biomass with thermocouple (with shield) for microwave pyrolysis of biomass

Although it was evident from both simulated and experimental results that the metallic temperature sensor could be used to capture temperature profile in a MAP process but an illustration of the radial temperature distribution with the biomass using a slice of the xy plane in the simulation showed that the highest temperature reached was about 190°C in 5 min (Figure A1.4).

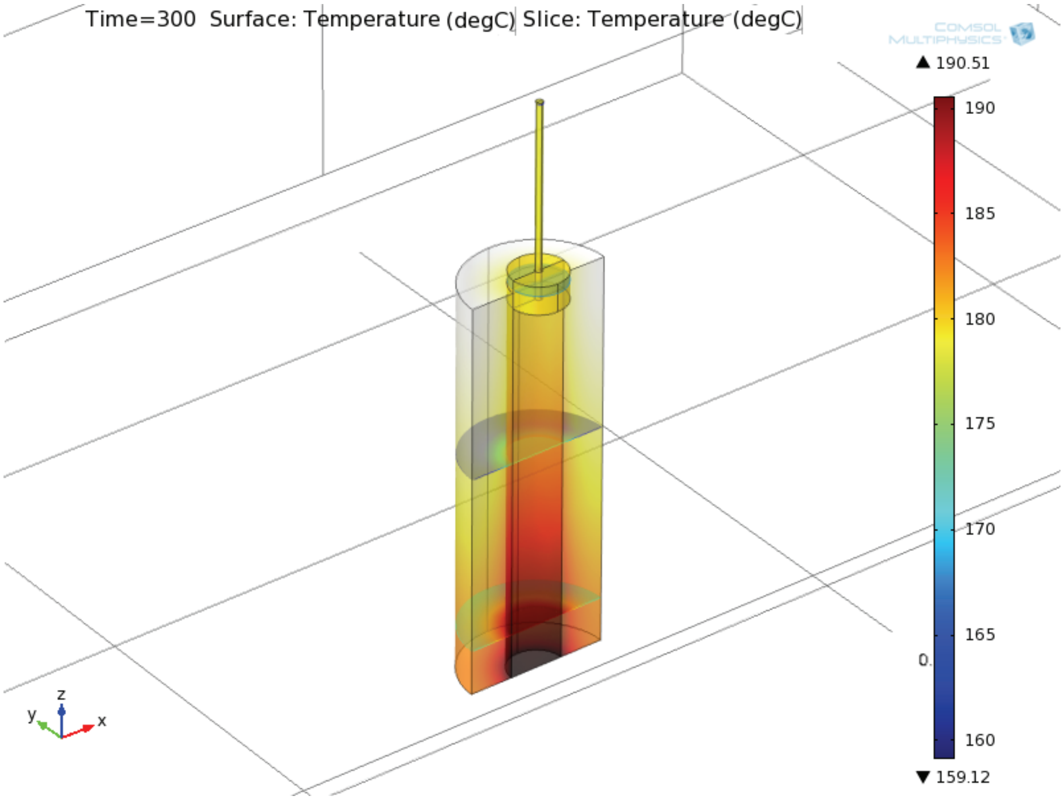

Figure A1.4: Temperature profile of char doped biomass with thermocouple (with shield) for microwave pyrolysis of biomass: radial slice view

Table A1.2: Analysis of variance (ANOVA) of regression (validation) model for biochar yields obtained with thermocouple (with shield) during microwave pyrolysis of biomass

Source	DF	Sum of squares	Mean square	F ratio	Prob > F
Model	1	9.49038	9.4904	0.1609	0.7022
Error	6	353.8864	58.9811		
C. Total	7	363.37678			

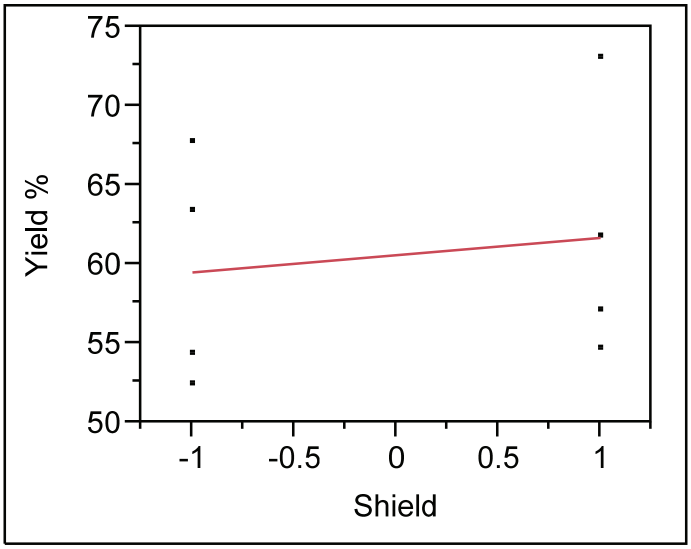

Figure A1.5: Effect of presence of shield on biochar yield for experimental validation of microwave pyrolysis of biomass

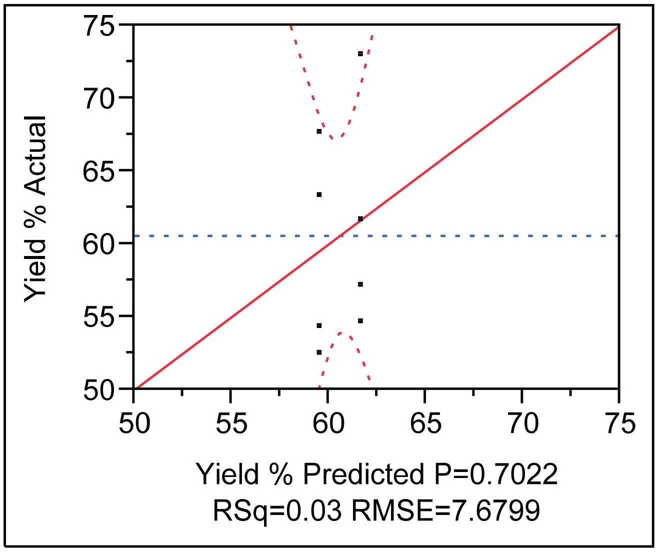

Figure A1.6: Regression model for actual vs. predicted biochar yields to indicate effect of thermocouple (with and without) shield (R^2= 0.03; P> 0.5)

In order to improve this, a change in the orientation of the shielded probe with the biomass was carried out in the simulation so that the thermocouple was placed perpendicularly to the electric field component as in the case of Luan et al. (2013). This resulted in similar pattern of heat distribution within the biomass but reaching higher temperatures as demonstrated in Figure A1.7. The same experimental design was applied as in the previous case which presented similar results indicating negligible effect of the shield on temperature measurement but producing higher yields of biochar as illustrated in Figures A1.8, A1.9 and the ANOVA carried out for the regression analysis as shown in Table A1.3.

Table A1.3: Analysis of variance (ANOVA) of regression (validation) model for biochar yields obtained with thermocouple (with shield) including orientation change during microwave pyrolysis of biomass

Source	DF	Sum of squares	Mean square	F ratio	Prob > F
Model	1	25.69541	25.6954	1.1183	0.331
Error	6	137.86342	22.9772		
C. Total	7	163.55883			

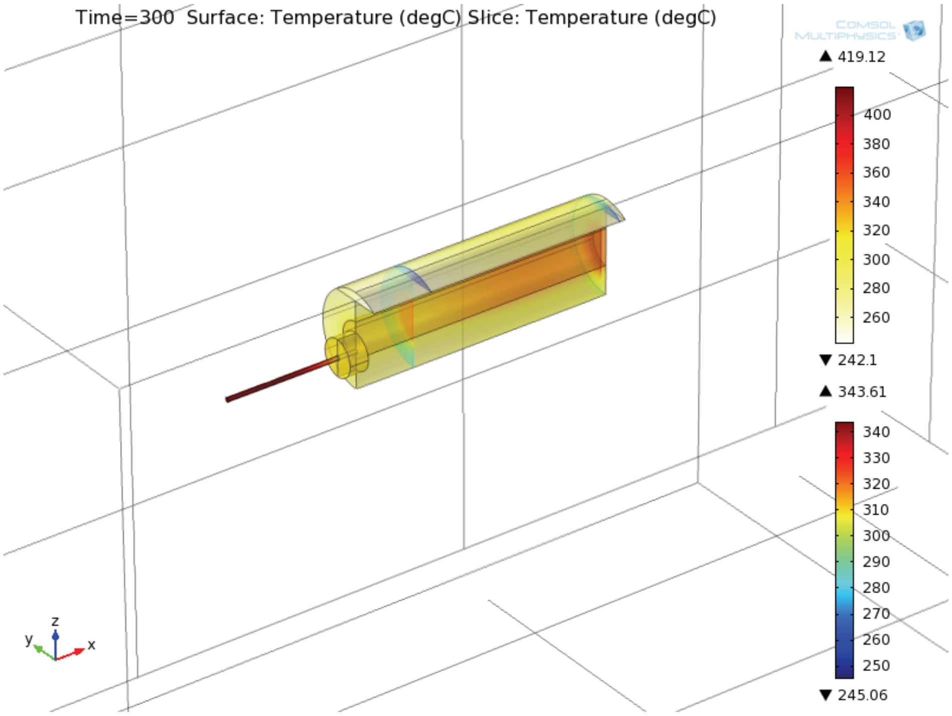

Figure A1.7: Temperature profile of char doped biomass with thermocouple (with shield) including orientation change for microwave pyrolysis of biomass: radial slice (zoom)

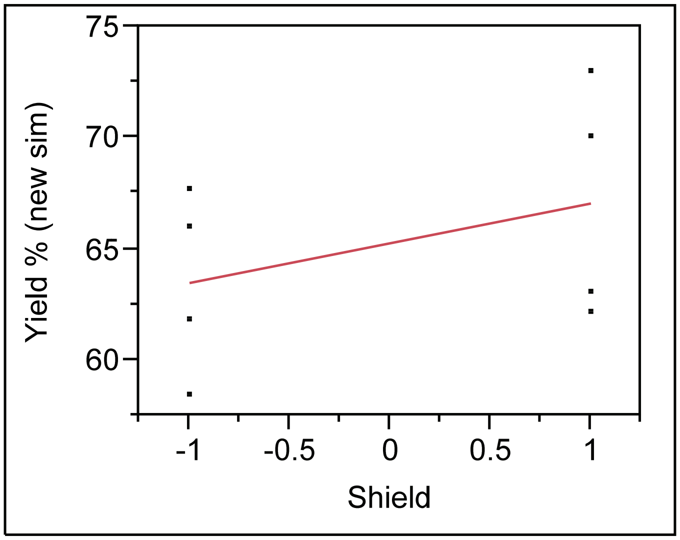

Figure A1.8: Effect of presence of shield with orientation change on biochar yield for experimental validation of microwave pyrolysis of biomass

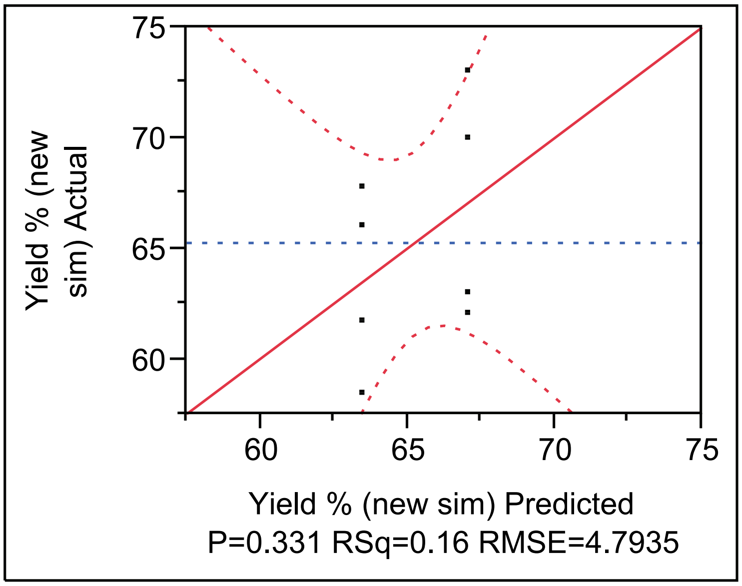

Figure A1.9: Regression model for actual vs. predicted biochar yields to indicate effect of thermocouple (with and without shield including orientation change) (R^2= 0.16; P> 0.3)

Hence the final design of the temperature measurement unit for microwave pyrolysis of maple wood consisted of a K type thermocouple inserted in a cylindrical metallic shield of diameter 5 mm and 14 mm length embedded in the biomass with orientation perpendicular to the electric field within the microwave cavity.

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Appendix 2

Connecting text

There are several research gaps with the successful adoption of biochar as a tool for long term carbon sequestration and mitigation of greenhouse gases. The research related to biochar has so far been limited to its individual benefits such as the unique elements of soil-char interactions, long term char stability, and effect upon crop yields. This is particularly true for developing nations like India, wherein the challenges associated with a technology such as pyrolysis for the production of biochar for environmental usage are many-folds. The complexity and heterogeneity of woodfuel-related issues in India present policy-makers with major challenges. Hence it becomes essential to understand the extent to which the production strategies for biochar production and biochar as a means of long term sequestration can be subject to policy making and the priorities which would drive these policies in these tropical countries. The following manuscript provides a map of the challenges related to biochar/charcoal production in a developing country like India.

Socio-economic Assessment of Implementation of Policy Options for Biochar Systems as a Mitigation Strategy for Greenhouse Gas Emissions-India as a Case Study

Introduction

Combating global climate change and meeting the ever-rising energy demands of the world are closely linked challenges which have occupied researchers all around the world. In 2010, speaking at the Technology, Entertainment, Design (TED) conference, Mr. Bill Gates, chairman of Microsoft Corporation, mentioned that the annual carbon dioxide (CO_2) emissions had reached over 26 billion tons (approximately 23.6 Tg) (Gates, 2010). Adding to this dilemma is the ever increasing population which has created enormous stress on our fragile planet. The stark reality is that, since 1935, both carbon emissions (Figure 1a), and world population (Figure 1b) have increased roughly 3.5-fold, with the latter expected to reach 10 billion by 2100.

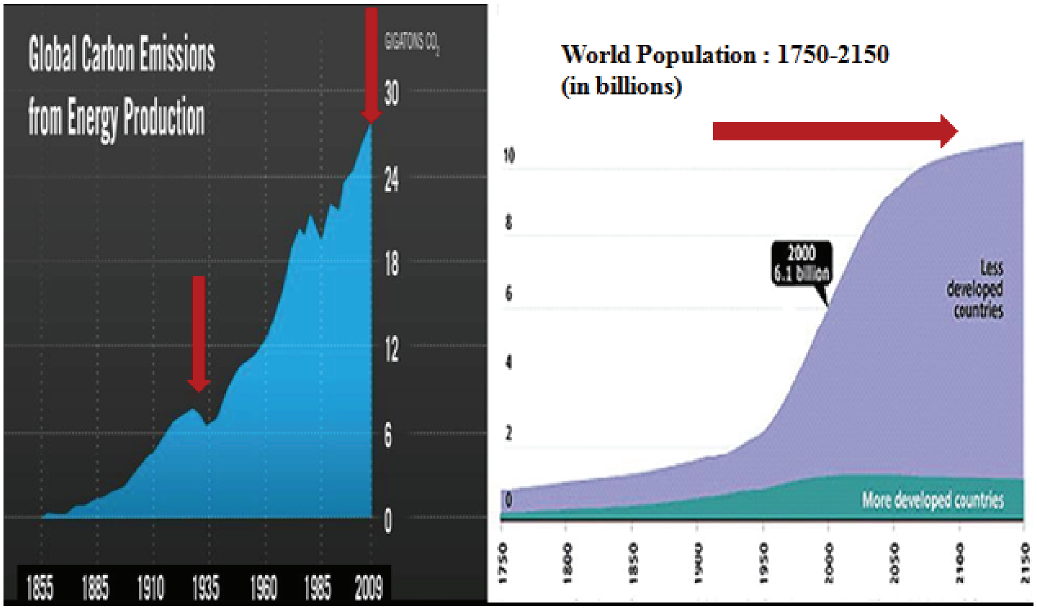

Figure 1. (a) State of global carbon emissions (b) World Population: 1750-2150
(Source: Bill Gates, 2010; UN, 1998)

India is one of the fastest growing economies in the world. Its increasing population presents enormous demands on its energy sector. Contributing 5-6% of total global GHG emissions, India has emerged as one of the largest contributors to world greenhouse gas (GHG) emissions (Figure 2; UN Stats Div., 2012). This will not only lead to increased environmental problems, but will also result in vast social problems such as inequalities between rural and urban populations, health-related disorders, and other community-level issues (UK BRC, 2012). With the struggle to meet the increasing demands of the urban sector, developments in emerging bioenergy technologies could provide a solution to these concerns.

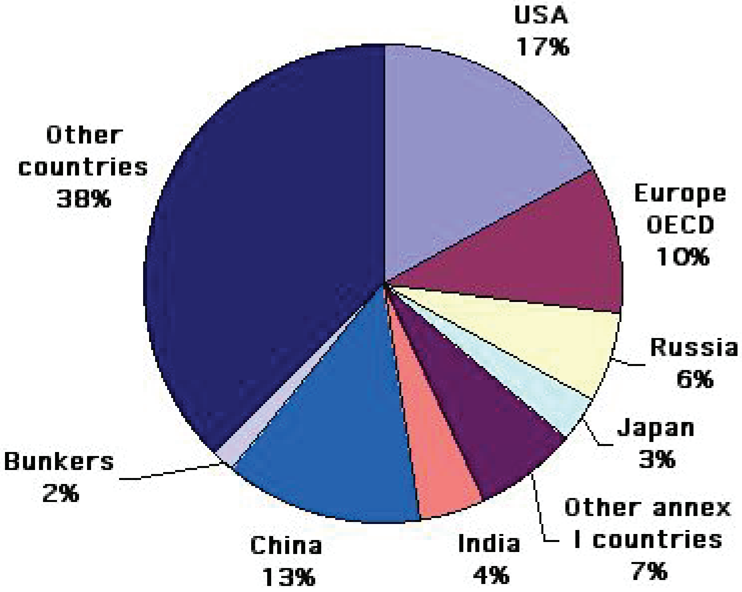

Figure 2. Greenhouse Gas world emissions

(Jancovici, 2003)

Bioenergy production has the potential to play a prominent role in meeting increasing energy needs, particularly in rural India. It is estimated that 90% of rural energy needs and 40% of urban energy needs are met by biomass (TERI, 2010). The share of biomass energy ranged from 36–46 per cent. Biomass is considered an important source or sink of CO_2, the conversion of which to bioenergy could help to neutralize all the net emissions due to forestry and land-use change. In addition it could also partly offset emissions due to the burning of fossil fuels to meet India’s energy needs. Furthermore, electricity generation from biomass is a carbon-neutral option for power generation leading to no net emissions. Large quantities of woodfuels can be produced sustainably through the recycling process of growing and harvesting (FAO, 2010).

India contributes to approximately 4% towards the total charcoal production (Figure 3). Woodfuel converted into charcoal is the most prominent source of biomass used for energy needs in India and it alone accounts for 30–40 per cent of the total energy consumption in the country (Figure 4) (Ghilardi and Steierer, 2011; IEA, 2010). This high energy consumption results from the abundant use of woodfuel not just in the rural areas but also by the urban poor and middle classes in India. Woodfuel was chosen as the bioenergy source following the oil crisis in the '70s which resulted in a reassessment of the energy options in favour of biofuels (Saxena, 1997).

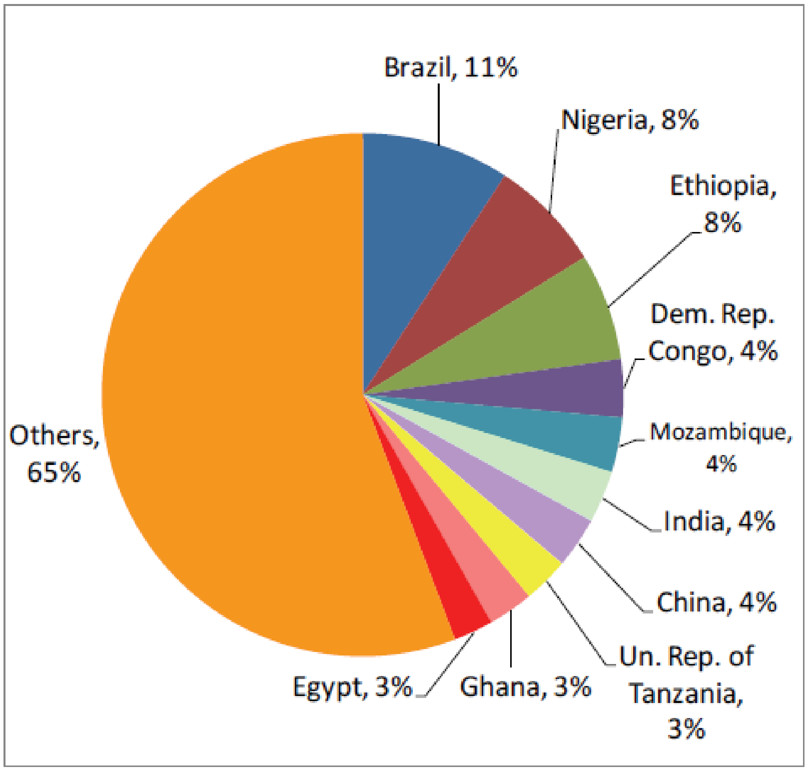

Figure 3. Percent of world charcoal production by nation

(Steierer, 2011)

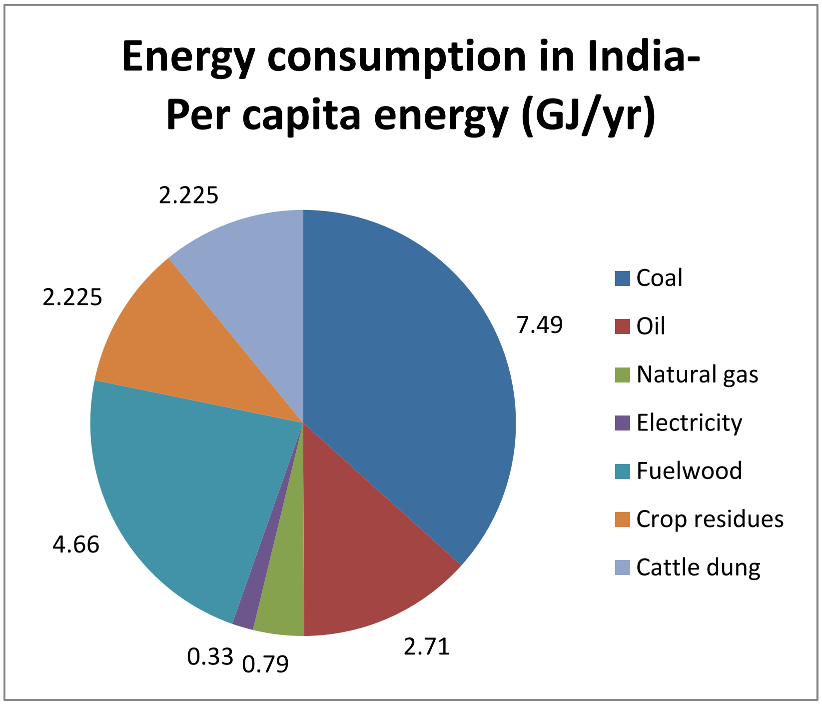

Figure 4. Energy consumption by source in India

(Saxena, 1997)

One of the important thermochemical conversion techniques of biomass is known as pyrolysis. It is the thermal decomposition of biomass in reduced concentrations of oxygen. Pyrolysis converts organics to solid, liquid and gases by heating in the absence of oxygen. The process of pyrolysis produces solids (charcoal), liquids (organics), and gases (CO, CO_2, CH_4, H_2). The production of this solid residue, also known as biochar through the process of pyrolysis has become an extremely efficient and popular technology in recent years (IBI, 2011).

Biochar has slowly but surely gained the reputation as a potential mitigation strategy applicable to the global climate challenge. The production of biochar has come under a lot of focus in recent years due to its many advantages in terms of its use as an energy source (Wu and Abdullah, 2009), a fertilizer when mixed with soil (Lehmann *et al.* 2003), and as a means for reducing GHG in the atmosphere by sequestering carbon in soil (Joseph *et al.* 2009). As an alternative, biochar can increase food security by reducing the amount of food crops used for biofuel production (Kleiner, 2009).

Globally about 60 Pg of carbon dioxide (CO_2-e) is taken up annually by photosynthesis. Of the biomass generated approximately 10% becomes available as agricultural residue. If all such residues, 6 Pg of carbon were put through the pyrolysis process; approximately 3 Pg of biochar would be produced every year, reducing atmospheric carbon emissions by the same amount (Amonette *et al*., 2007). This could offset a substantial proportion of the 4.1 Pg of excess CO_2-e that accumulates annually in the atmosphere. It is predicted that this simplistic, yet powerful, approach can be used to store up to 2.2 Pg of carbon annually by 2050. It is one of the few technologies that are relatively inexpensive, widely applicable, and quickly scalable (IBI, 2010).

India's total GHG emissions for 2008 were estimated at 4.177 Pg of CO_2-e (UN Stats Div., 2012), of which nearly 18% originated from the agricultural sector (INCCA, 2010). India produces 350 Tg yr^{-1} of organic agricultural waste (Pappu *et al.,* 2007). Assuming 50% recovery of carbon from this biomass, nearly 0.175 Pg of carbon dioxide could be sequestered from the atmosphere, in the form of biochar, representing about 5% of India's GHG emissions.

Biochar technology

Biochar is carbonaceous material produced specifically for application to soil as part of agronomic or environmental management. Biochar is the product of pyrolysis, which is the decomposition of C-bearing organic compounds at elevated temperatures in the absence of oxygen. This decomposition process is not perfectly understood, especially for complicated polymeric materials such as biomass from which charcoal is traditionally derived. In addition to biochar, other products of pyrolysis include condensable vapours (that yield insoluble tars and pyroligneous acid) and gases (Figure 5). The quantity of these products depends upon the composition of the biomass and the conditions under which pyrolysis occurs. The pyrolysis products and their yields depend on the composition of the biomass (i.e., cellulose and hemicelluloses, lignin, protein and ash contents) and on the process settings (i.e., pyrolysis temperature, process pressure, vapour residence time, particle size, heating rate and heat integration) (Evans and Milne, 1987).

However, there are still a number of uncertainties associated with the environmental and economic performance of different biochar production pathways. Many questions regarding biochar production and use; and its potential environmental risks remain unaddressed. As a result, estimates of the potential for biochar production and carbon sequestration remain highly uncertain and largely premature at this time (Brick, 2010). An attempt has been made in this paper to highlight the challenges related to biochar/charcoal production in a developing country like India. It then evaluates and critiques the existing policies related to different biochar production strategies already in place and the viability of these policies in carrying out the successful adoption of such biochar systems as an important tool for GHG abatement. This research analyzes the barriers and proposes recommendations to overcome them.

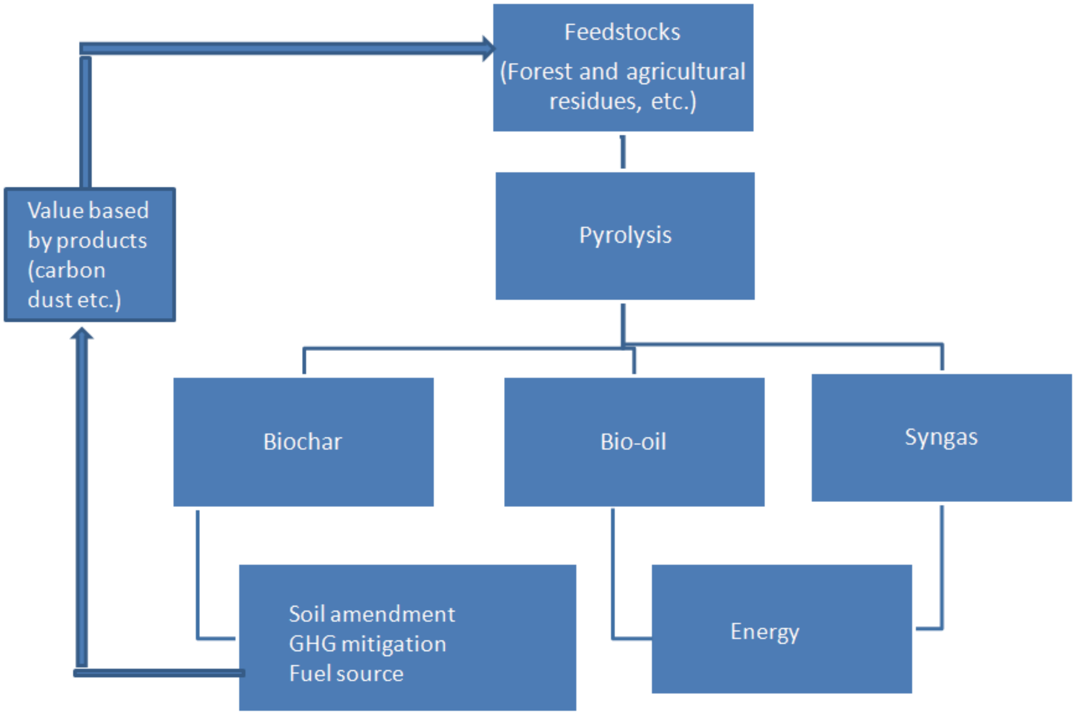

Figure 5. Overview of biochar technology

Biochar success stories in India

The tradition of the application of biomass residue in various agricultural practices has existed for hundreds of years. In particular, rural regions of India still depend largely on biomass resources as their only energy forms (Saxena, 1997).

An NGO, Geo-ecology Energy Organization (GEO) has been developing a number of biochar stoves, and carrying out biochar soil improvement on a pilot scale basis. Similarly, another NGO, Social Change and Development (SCAD) has been working with Mysore University, distributing their Anila pyrolysis stoves and carrying out soil research with biochar (Whitfield, 2010). The Society of Biochar Initiatives (TSBI) works to highlight and support biochar projects and organizations in India. One of the first endeavours they supported was that of the Organization of Development Action and Maintenance (ODAM), an organization based in Tamil Nadu, India, which, along with support from Finland's Siemenpuu Foundation, conducted a series of biochar field trials in Southern India using common feedstocks to produce the biochar (IBI, 2012a).

In 2010, a workshop on biochar innovation, supported by the UK *Brassica* Research Community (UK-BRC), and in collaboration with the Appropriate Rural Technology Institute (ARTI), India, was held in Phaltan, India. The objectives of this project were to evaluate the potential of biomass gasification stoves as a solution to the difficulties faced by the rural poor, with respect to smoke inhalation from indoor air pollution, which leads to ill-health of occupants. It also addressed gender inequalities and hunger, as well as the use of biochar as a soil amendment tool (UK BRC, 2012). However, as yet, active engagement with biochar in India is limited.

The success of these biochar systems is to a large extent dependant on the implementation of appropriate driving policies, which requires an understanding of the local conditions. However, such essential and comprehensive studies have been mostly limited to the western hemisphere.

Biochar policy options- Developments around the globe

The Natural Resources Defense Council (NRDC), USA, has recently (2010) released a report addressing biochar production pathways, energy co-products resulting from biochar production and their potential uses. The report highlights i) key environmental risks associated with biochar production and utilization systems; ii) estimates of global technical and economic potential for biochar production and carbon sequestration; iii) provides a brief overview of existing domestic and international policies on biochar (Brick, 2010).

The viability of biochar as a carbon sequestration tool at both a global and Canadian scale was investigated from two perspective. Firstly, an assessment was made as to whether sufficient biomass was present for its conversion to biochar to have significant impact on the atmospheric CO_2 levels. Secondly, appropriate soil areas for biochar dispersal were identified when present. The successful adoption of this technology is largely dependent on proper recognition of the carbon sequestration impact of biochar and its potential to improve soils. Many organizations and agencies, such as the Canadian Biochar Initiative are actively promoting biochar-related research and associated policy frameworks (Matovic, 2010).

Bracmort (2010) recognizes, in their CRS Report to the US Congress, that biochar research and development is in its infancy. In spite of this, biochar could equip agricultural and forestry producers with numerous revenue-generating products related to carbon offsets, soil amendments, and energy. This report brings to light the fact that, although various climate change bills have been proposed, many of these do not directly address mitigation and adaptation technologies in their developmental stages, such as biochar technology. It has been stated that obstacles such as technology costs, system operation and maintenance, feedstock availability, and biochar handling may stall rapid adoption of biochar production systems.

The Water Efficiency via Carbon Harvesting and Restoration (WECHAR) Act was introduced in 2009 to establish loan guarantee programs that would develop biochar technology. The act aims to use excess plant biomass and establish biochar demonstration projects on public lands. The primary focus of the legislation was to address research and development needs for biochar production with specific concentration on woody biomass. However, the argument remains that the legislation lacks specific actions regarding technology transfer or commercial development of biochar production systems (Bracmort, 2010). The farm bill put through during the 110th US Congress in 2008 promoted biochar development. The research areas of this bill include biochar production and use, co-production with bioenergy, soil enhancements, and soil carbon sequestration (Bracmort, 2010).

As a result of the impediments inherently related to this technology, the development of a comprehensive and meaningful policy on biochar requires further research. In particular, it needs to be recognized that the performance parameters of various biochar production systems would vary significantly between developing and developed nations. The production, transport and energy efficiency of biochar constitute a critical energy and economic cycle in the economies of many developing nations. The use of biochar has remained constant or grown in a number of countries, including India, Brazil, and Mexico, as well as several regions of Africa. Various studies have been conducted to address the issues and implications of biochar production and end-user applications in these countries (Kammen and Lew, 2005, Smith *et al.*, 2000)

In one such study, the authors discuss the harvesting and transport of biomass for biochar production, the efficiency of pyrolysis in various kilns, trace gas emissions, and the relative economics of biochar and its fuel substitutes for a range of urban African biochar markets. This analysis was critical to the design of sensible biomass energy policies at the national and international level (Kammen and Lew, 2005). Another review examined particulate emissions from a range of household stoves in common use in India using different biomass sources. This work also investigated possible policy options for international investment in rural energy development that would achieve cost-effective GHG reduction as well as substantial local benefits (Smith *et al.*, 2000).

Barriers to biochar policy reforms in India

An understanding of the extent to which local policy making influences the development of biochar technology, as a means of long term carbon sequestration, is essential. It is also important to evaluate the priorities which would drive such policies in tropical countries.

United Nations Framework Convention on Climate Change (UNFCCC) is the main body responsible for the implementation and adoption of energy and climate legislation and policies around the world. Although the inclusion of biochar in the

UNFCCC as a mitigation option was advocated by various organizations, specific references to biochar were dropped from the negotiating texts. The United Nations Convention to Combat Desertification (UNCCD) has been a strong supporter of including biochar as a mitigation option at the UNFCCC (IBI, 2012b).

There are several research gaps holding back the successful adoption of biochar as a tool for long term carbon sequestration and mitigation of GHG. The research related to biochar has so far been limited to its individual benefits such as the unique elements of soil-char interactions, long term char stability, and its effect upon crop yields. Crop studies have mainly focussed in tropical countries because soils are poorer and biomass resources more quickly replenished, thus offering greater potential benefits (Lehmann *et al.* 2006).

This is particularly true for developing nations like India, where challenges associated with a technology, such as pyrolysis, for the production of biochar for environmental usage are many-fold. The complexity and heterogeneity of woodfuel-related issues in India present policy-makers with major challenges. However, India's total annual woodfuel consumption, currently estimated at 220–300 million tonnes, and valued at 9 billion US dollars, is ever increasing (Saxena, 1997).

Another barrier to the adoption of large-scale biochar systems is the lack of a significant number of in-field tests of different chars. This makes it difficult to fully understand the potential agronomic costs and benefits. Further research on the stability of biochar-based carbon in soils is needed to validate long-term carbon sequestration claims (Whitfield, 2010).

Additionally concern related to determining the portion of the sustainably-produced biomass resource to be devoted to biochar systems needs to be addressed. As there are many promising biomass conversion technologies, competition for the same biomass resource will influence the adoption or abandonment of biochar systems. An important but often neglected barrier in many studies which investigate the potential contribution of such technologies is that a lack of competition for primary feedstocks is often assumed. Given the shortage of feedstock in many parts of the country great care would be required to ensure that the feedstock used meets emerging sustainability standards. In this regard, the major driver would be incentives to individuals or industries for the generation of carbon credits.

Among the major issues which could impair the adoption of biochar technologies in India are the discrepancies between centralized and state-level parameters to fix tariffs for biomass gasification projects. The Central Electricity Regulatory Committee (CERC) has indicated that the tariff for combustion would also hold for gasification. However, these tariffs were not devised to keep the attributes of biomass gasification projects in view, thus perpetuating incorrect assumptions (Ravindranath and Rao, 2011). Moreover, the land-tenure policy acts as a barrier for farmers and communities entering into any long-term contract to supply wood-fuel to the bioenergy utility (Rao and Ravindranath, 2002).

Another factor playing a role in the implementation of comprehensive policies for biochar adoption is the nature of agricultural practices in India. Traditionally, agricultural practices become an integral part of the culture of the farming community. Adoption of new practices would bring forth significant sociological impacts in the community which would have both short and long term economic implications.

Recommendations

The existence of the barriers noted above prevents the large-scale adoption and implementation of biochar technology as a mitigation source of GHG in India. An assessment of policy options and consequent recommendations on how to overcome these barriers are extremely important. These recommendations would include categories of technical, institutional, educational, awareness and regulatory interventions. In addition to international policy on biochar, regional policies strengthen the standing and potential funding for biochar projects.

i) Technical

Biochar's success rate would benefit from its increased status as a potential clean development mechanism (CDM) technology. A CDM, monitored by the UNFCCC, allows developed countries to invest in and receive credit for activities that reduce GHG emissions in developing countries.

UNFCCC has recognized biochar as a vital tool in reducing GHG emissions in both developed and developing countries, with food security, energy security, and other environmental co-benefits. In lieu of this, many organizations, including the International Biochar Initiative (IBI), are working towards quantifying and verifying emission reductions achieved through biochar technology, in order to seek related carbon credits. Additionally, the development of standardized tests and classification systems and whole-system sustainability criteria for biochar production and utilization systems would benefit efforts towards large scale biochar technology adoption.

Building on the National Biomass Resource Atlas, an inventory of local feedstocks and soils throughout the different regions in India, would greatly benefit farm-scale application of biochar, by quantifying and giving credit for carbon sequestration in the soil. Different pyrolysis unit designs could then be tested to establish the optimum solution for any given region of India.

ii) R&D and educational

It is very important for efforts to focus on a biochar R&D agenda which would further enhance scientific understanding of this technology, as well as boost the advocacy for and identification of public and private R&D funding of biochar systems at different scales. Research should be focussed on the evaluation of the economic potential of on-farm biochar production, and its application in agricultural waste management. Care should be given towards reducing handling and transportation costs.

A coordinated programme of communication, capacity building and deployment of the stoves could be launched, potentially with EU support. The establishment of institutional linkages for developing micro-enterprises for production/dissemination of biochar pyrolysers/gasifiers is also essential. These R&D efforts should also include monitoring and service centres to allow smooth technology transfer at the grass root levels. Hence capacity building is essential.

iii) Regulatory and societal

Community-based social marketing could grow to make a significant contribution towards biochar production, although linking such activity into a system of formal incentives may prove problematic. Farm-level agricultural production should thus be adjusted to meet the farmers', requirements rather than the nation's priorities. Wastelands should also afforest or cropped, so as to increase the availability of appropriate biomass in the shortest possible time and with little investment.

Increasing farmers' awareness and understanding of an optimal balance in the many potential uses of biochar should be encouraged, as it would help them to reduce their total carbon footprint, while maintaining financially viable agricultural production practices.

Conclusions

Biochar production is an age-old technology which may prove to be powerful but simple tool to bring about significant mitigation of GHG emissions. In order to achieve this paper's objective of evaluating the policies which govern the deployment of sustainable biochar production and utilization systems in India, an analysis of the opportunities and challenges presented by biochar technology in India was completed.

In order to facilitate the adoption of biochar systems, the barriers identified in the report need to be discussed further with various stakeholders so that targeted policies can be developed. These policies would not only establish, but also help in demonstrating the effectiveness of biochar in a large developing country such as India. They would also help the government and individuals to generate appropriate carbon credits or Certified Emission Reduction (CER).

Some of the recommendations provided by this analysis include the development of a suitable field trial program to be coordinated with existing national and international efforts to develop a meaningful classification scheme for biochar. Moreover, policy options aimed towards large-scale biochar deployment should be focussed towards the development of R&D, targeting performance enhancement of biochar in soil, large-scale demonstrations targeting rural participants, capital cost subsidies and other performance-based financial incentives, competitive tariffs, as well as the creation of a network of skilled personnel.

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