Biochar production in an auger pyrolysis reactor and its amendment to soil as a tool to mitigate climate change

Patrick Brassard

Department of Bioresource Engineering, McGill University

Sainte-Anne-de-Bellevue, Québec, Canada

December 2017

A thesis Submitted to McGill University in partial fulfillment of the
requirements of the degree of Doctor of Philosophy

Abstract

Biochar is the solid product of the thermochemical decomposition of biomass at moderate temperatures (350 – 700 °C) under oxygen-limiting conditions. Not all biochars are created equal as their properties will depend on both biomass properties and pyrolysis operating parameters. Thus, the aim of this doctoral research project was to produce engineered biochars with specific properties and to evaluate their potential to be used as a tool to mitigate climate change. Based on the literature review, biochars with low O/C_{org} (< 0.2) and H/C_{org} (< 0.7) ratios would indicate high potential for C sequestration. Moreover, biochars with a low N content, and consequently high C/N ratio (> 30), are expected to be more suitable for the mitigation of N_2O emissions. A vertical auger pyrolysis reactor designed by the IRDA and the CRIQ was selected as the technology to produce the engineered biochars with the properties that were identified. Using a range of pyrolysis parameters (temperature, solid residence time and nitrogen flowrate) selected from the literature review and preliminary tests, biochars were produced from wood, switchgrass and the solid fraction of pig manure (SFPM). A Box-Benhken design based on the response surface methodology was carried out to identify the optimal pyrolysis operating parameters and the engineered biochars were produced to validate the models. For each biomass, one pyrolysis test was performed using the optimal parameters identified from the statistical models to obtain biochar with the maximum O/C_{org} and H/C_{org} ratios (scenario A). A second biochar with the properties needed to sequester C (minimum O/C_{org} and H/C_{org} ratios) was produced from each biomass (scenario B). These six biochars were amended in two agricultural soils (loamy sand and silt loam) at a rate of 2 % (w/w) with N fertilizer and incubated for 45 days. The benefits related to GHG emissions were specific to both biochar and soil properties. Biochar-C mineralisation rate over the 45-days incubation period represented only between 0.18 and 1.7% of their total C content, and was particularly low for biochar produced at a higher temperature. When compared to the control soils without biochar, N_2O emissions were only decreased in the silt loam amended with biochars made from wood and switchgrass (C/N ratio ≥ 100). The difference (-90%) was only significant with the biochar produced from switchgrass at a low temperature (459°C) and with a short residence time (78 s). Lower concentrations of NO_3^- and NH_4^+ in soil caused by the adsorption of N compounds on biochar or by N immobilisation, and a change in soil microbial abundance were identified as the mechanisms that can be responsible for the reduction of N_2O emissions. A life cycle approach was used to evaluate the GHG emissions and energy impacts of the pyrolysis of switchgrass, from the cultivation of switchgrass on marginal lands to the valorisation of co-products. The two pyrolysis scenarios were evaluated, as the experimental data from pyrolysis and from the incubation study were used as input data. Both scenarios resulted in a net reduction in GHG emissions, and this reduction was higher (-2524 kg CO_2e $t^{-1}{}_{biochar}$ yr^{-1}) in scenario B, in which pyrolysis was carried out at a higher temperature and with a longer residence time, than in scenario A (-2105 kg CO_2e $t^{-1}{}_{biochar}$ yr^{-1}). However, the energy balance of scenario B (-10,960 MJ $t^{-1}{}_{biochar}$ yr^{-1}) was more negative than in scenario A (-2401 MJ $t^{-1}{}_{biochar}$ yr^{-1}). These results suggest that pyrolysis operating parameters have a high influence on the GHG and energy impacts of biochar systems. From the results of this study, it can be concluded that only biochars produced using specific biomasses and pyrolysis operating parameters can be used as a tool to mitigate climate and only in specific soil conditions. Field studies in the presence of crops are needed to validate the results obtained from the incubation study.

Résumé

Le biochar est un résidu solide produit par la décomposition thermochimique de la biomasse à température modérément élevée (350 – 700 °C) sans oxygène. Ses propriétés physico-chimiques dépendent du type de biomasse et des paramètres de pyrolyse. Ainsi, l'objectif principal de ce projet de doctorat était de produire des biochars ayant des propriétés spécifiques et d'évaluer leur potentiel afin d'être utilisés comme outil de lutte contre les changements climatiques. La revue de littérature a permis de conclure qu'un biochar ayant de faibles ratios O/C_{org} (< 0.2) et H/C_{org} (< 0.7) a un potentiel de séquestration du carbone élevé. De plus, les biochars ayant une faible teneur en N, et donc un ratio C/N élevé (> 30) sont destinés à réduire les émissions de N_2O du sol. Un réacteur de pyrolyse à vis développé par l'IRDA et le CRIQ a été utilisé pour produire des biochars ayant les propriétés identifiées. À partir d'une gamme de paramètres de pyrolyse (température, temps de résidence et débit d'azote) sélectionnée à l'aide de la revue de littérature et d'essais préliminaires, des tests de pyrolyse ont été réalisés avec du bois, du panic érigé (PÉ) et du lisier de porc séché (FSLP). Un design expérimental Box-Behnken basé sur la méthode de surfaces de réponses réalisé afin d'identifier les paramètres de pyrolyse optimaux a été validé. Ainsi, pour chaque biomasse, un test de pyrolyse a été réalisé avec les paramètres identifiés à l'aide des modèles statistiques pour produire un biochar ayant un ratio O/C_{org} et H/C_{org} maximum (scénario A). Un deuxième biochar ayant les propriétés opposées (ratio O/C_{org} et H/C_{org} minimum) a été produit (scénario B). Par la suite, les six biochars ont été mélangés avec un sable loameux et un loam limoneux à un taux de 2% (w/w) avec un fertilisant azoté et les mélanges ont été incubés pendant 45 jours. L'effet sur les émissions de GES du sol a dépendu du biochar et du type de sol. La minéralisation du C sous forme de CO_2 a représenté seulement de 0.18 à 1.7% du C du biochar, et était particulièrement faible pour les biochars produits à haute température. Comparativement au traitement témoin sans biochar, les émissions de N_2O ont été réduites seulement dans le loam limoneux avec les biochars de bois et de PÉ (C/N > 30). Une réduction statistiquement significative de 90% a été observée avec le biochar de PÉ produit à température plus faible (459 °C) et pendant un court temps de résidence (78 s). Une diminution de la concentration en NO_3^- et NH_4^+ après la période d'incubation en raison de leur adsorption par le biochar ou de leur immobilisation, ainsi qu'une modification de la l’abondance des microorganismes sont les mécanismes identifiés pouvant être responsables de la réduction des émissions de N_2O. Une approche basée sur l’analyse du cycle de vie a permis d’étudier l’impact de la pyrolyse du PÉ sur les émissions de GES et sur la consommation énergétique, de la culture à la valorisation des coproduits. Les deux scénarios de pyrolyse ont été évalués, alors que les données recueillies précédemment dans ce projet ont été utilisées dans l’analyse. Une réduction des émissions de GES plus élevée a été obtenue pour le scénario B (-2524 kg CO_2e t^{-1}_{biochar} an^{-1}) que pour le scénario A (-2105 kg CO_2e t^{-1}_{biochar} an^{-1}). Cependant, la consommation d’énergie a été plus élevée dans le scénario B (-10,960 MJ t^{-1}_{biochar} an^{-1}) que dans le scénario A (-2401 MJ t^{-1}_{biochar} an^{-1}). Ces résultats démontrent que les paramètres de pyrolyse ont une grande influence sur les émissions de GES et sur la consommation énergétique de la production de biochar. Enfin, il est possible de conclure que seuls certains biochars ayant été produits avec des biomasses et des paramètres de pyrolyse spécifiques peuvent être utilisés comme outil de lutte contre les changements climatiques. Des essais supplémentaires au champ et en présence de cultures seront nécessaires afin de valider les résultats obtenus lors de l’étude en incubation.

Preface and Contributions of Authors

This thesis is presented as a collection of scholarly papers of which Patrick Brassard is the primary author. The following manuscripts are published or have been submitted for publication:

1- Brassard, P., S. Godbout and V. Raghavan. 2016. Soil Biochar Amendment as a Climate Change Mitigation Tool: Key Parameters and Mechanisms Involved. Journal of Environmental Management, 181: 484-497.

2- Brassard, P., S. Godbout and V. Raghavan. 2017. Pyrolysis in auger reactors for biochar and bio-oil production: A review. Biosystems Engineering. 161: 80-92.

3- Brassard, P., S. Godbout, V. Raghavan, J. H. Palacios, M. Grenier and D. Zegan. 2017. The production of engineered biochars in a vertical auger reactor for carbon sequestration. Energies. 10, 288.

4- Brassard, P., S. Godbout, J. H. Palacios, T. Jeanne, R. Hogue, P. Dubé, L. Limousy and V. Raghavan. Effect of six engineered biochars on GHG emissions from two agricultural soils: A short-term incubation study. Submitted to the journal Geoderma.

5- Brassard, P., S. Godbout, F. Pelletier, V. Raghavan and J. Palacios. Pyrolysis of switchgrass in a vertical auger reactor for biochar production: A greenhouse gas and energy impact assessment. Submitted to the journal Biomass and Bioenergy.

The elements of the thesis are original scholarship and distinct contributions to knowledge. The research work, including the review of literature, the design of experiments, experimental work, data analysis and preparation of the manuscripts, was conducted by Patrick Brassard. Prof. G.S. Vijaya Raghavan and Dr. Stéphane Godbout supervised the work and all co-authors reviewed the manuscripts. The pyrolysis experiments presented in Chapter 3 were carried out at the Laboratory on energy development for sustainable development of the *Institut de recherche et de développement en agroenvironnement* (IRDA), Deschambault (Québec), Canada, with the technical support of Joahnn Palacios and Dan Zegan (IRDA). The statistical analyses presented in Chapters 4 and 5 were realized in collaboration with Michèle Grenier (IRDA). The incubation study presented in Chapter 4 was carried out with the support of Joahnn Palacios

(IRDA). The analysis of biochars and the measurement of soil GHG emissions presented in Chapter 4 and 5 were done at the Agri-Environmental Analyses Laboratory of the IRDA, Québec (Québec) Canada, with the collaboration of Patrick Dubé. The analysis of microbial diversity and richness was carried out at the Microbial Ecology Laboratory (IRDA) under the supervision of Richard Hogue and Thomas Jeanne. The analysis of biochar porosity and surface area presented in Chapter 5 was done at the *Institut de Science des Matériaux de Mulhouse* (Université de Haute-Alsace, France) by Lionel Limousy. Finally, Frédéric Pelletier and Joahnn Palacios (IRDA) have provided guidance and suggestions on the GHG and energy impacts assessment presented in Chapter 6.

Contribution to knowledge

In the last decade, many research investigations were carried out to study the pyrolysis process for biochar production, and other studies evaluated the effects of biochar amendment in soil. It was found that biochar has properties needed to be used as a soil amendment to improve soil properties and increase crop yields, to be used as a remediation tool to adsorb pollutants in soil and water, and to mitigate climate change by sequestrating carbon in soil and reducing soil GHG emissions. However, researchers concluded that not all biochars are created equal and the effect in soil will depend on both biochar and soil properties. To the knowledge of the author, this doctoral research project is the first research work that allowed to study biochars from the production in an auger pyrolysis reactor to the use as a soil amendment, and to evaluate the global GHG and energy impacts from the life cycle approach using experimental data as inputs.

More specifically, this research work first provided knowledge regarding the pyrolysis of biomass in a new vertical auger reactor for biochar production. Statistical models based on the response surface methodology were developed to predict the yield and chemical properties (C/N, H/C_{org} and O/C_{org} ratios) of biochars from the operating parameters (temperature, biomass residence time in the reactor and N_2 flowrate) of the pyrolysis of wood, switchgrass and the SFPM. Validation experiments showed that the models fit the experimental data. Thus, the relationship between pyrolysis parameters and biochar properties are now better known.

Secondly, the results of the short-term incubation study provided evidence that biochar have an impact on soil N_2O emissions, the direction (either negative or positive) and magnitude of this change being dependent on both biochar and soil properties. Only biochars with a high C/N ratio (> 30) produced from wood and switchgrass allowed a decrease of N_2O emission in the silt loam.

The decreased N_2O emissions could be related to reduced NH_4^+ and NO_3^- concentrations in soil after biochar amendment that can be due to N immobilisation or adsorption on biochar surface, which have an influence on the N-cycle in soil. Moreover, a change in soil microbial abundance was identified and could have influenced the N-cycle.

The short-term incubation study gave an indication that biochars can be stable in soil and that stability depends on pyrolysis operating parameters. The CO_2 emissions were increased in all biochar treatments as compared to the control, but the cumulative soil CO_2 emissions represented only 0.18 to 1.68% of the total C in added biochar. The emissions were significantly lower for the biochars produced from switchgrass and the SFPM at a higher temperature and during a longer residence time.

Finally, the life-cycle concept was successfully used for GHG assessment and energy use analysis of switchgrass pyrolysis in the auger reactor. Knowing that many hypothetical data are often used in life cycle analysis, the uniqueness of this study was the use of experimental data as inputs in the analysis in order to minimize the uncertainties. The study allowed to conclude that pyrolysis operating parameters have a great influence on the energy use and GHG impacts of biochar production.

Acknowledgments

First, I would like to thank my supervisor Dr. Vijaya Raghavan who provided me all the support and the guidance throughout this doctoral project. Even if I worked on this project far away from the Macdonald campus, Prof. Raghavan always gave me his entire confidence to achieve this thesis.

I also thank Dr. Stéphane Godbout, my co-supervisor for this doctoral project and my mentor since the beginning of my graduate studies. I would not be the research scientist that I am today without his support and his confidence. I am grateful for all the advices and the resources that he provided me to complete this doctoral project successfully.

I would like to address special thanks to Joahnn H. Palacios, Dan Zegan, Jean-Pierre Larouche, Patrick Dubé, Cédric Morin, Emmanuel Gagné, Matthieu Girard, Ariane Lévesque, Étienne Le Roux, Salha Elcadhi, Martin Brouillard and Araceli Dalila Larios Martínez for their help during the implementation and the realization of the experiments at the *Institut de recherche et de développement en agroenvironnement* (IRDA).

Thanks to Frédéric Pelletier for his assistance regarding the life cycle analysis, Michèle Grenier for the statistical support, Dr. Lionel Limousy for the characterisation of biochars, and Dr. Darwin Lyew for the linguistic revision of papers.

I would like to thank all my committee members for their advices that helped me to conduct this research successfully.

I gratefully acknowledge the financial support from the *Fonds de recherche du Québec—Nature et technologie (FQRNT)*, the *Programme de soutien à l'innovation en agroalimentaire* (grant number IA113109), the Mitacs Accelerate program, IRDA and McGill University.

Finally, many thanks to the member of my family for their unconditional support and encouragement.

Table of Contents

List of Tables

List of Figures

Nomenclature

°C	Degree Celsius
% (w/w)	Percentage (weight per weight)
AEC	Anion exchange capacity
AFNOR	Association française de normalisation
Al	Aluminium
ANOVA	Analysis of variance
ASABE	American Society of Agricultural and Biological Engineers
BET	Brunauer–Emmett–Teller
C	Carbon
Ca	Calcium
C_{org}	Organic Carbon
C_{tot}	Total carbon
CEC	Cation exchange capacity
CH_4	Methane
CO_2	Carbone dioxide
CO_2e	Carbone dioxide equivalent
CRIQ	Centre de recherche industrielle du Québec
d	Day
d.b.	Dry basis
D	Diameter
DNA	Deoxyribonucleic acid
DOC	Dissolved organic carbon
FC	Fixed-carbon
g	Gram
GC-MS	Gas chromatography-mass spectrometry
GES	Gaz à effet de serre
GHG	Greenhouse gas
Gt	Gigaton
h	Hour
H	Hydrogen atom
ha	Hectare
Hg	Mercury
H_2O	Water
HDPE	High-density polyethylene
HHT	Highest treatment temperature
HHV	Higher heating value

IBI	International Biochar Initiative
IPCC	Intergovernmental Panel on Climate Change
IRDA	Research and Development Institute for the Agri-environment
K	Potassium
KCl	Potassium chloride
kg	Kilogram
L	Liter
LCA	Life cycle assessment
LHV	Lower heating value
MDF	Medium density fiberboard
m	Meter
mg	Milligram
Mg	Magnesium
min	Minute
MJ	Megajoule
MRT	Mean residence time
MSU	Mississippi State University
Mt	Megaton
N	Nitrogen atom
N_2	Nitrogen gas
N_2O	Nitrous oxide
Nb	Number
NET	Negative emission technology
NH_4^+	Ammonium
NO_3^-	Nitrate
O	Oxygen atom
OTU	Operational Taxonomic Unit
P	Phosphorus
PCoA	Principal coordinates analysis
PCR	Polymerase chain reaction
P_{sol}	Soluble phosphorus
pH	Potential of hydrogen
ppm_v	Parts-per-millions (volume)
rDNA	Ribosomal Deoxyribonucleic acid
Res. time	Residence time of biomass in the pyrolysis reactor
R_2	Coefficient of determination
R_{50}	Recalcitrance index for assessing biochar quality of C sequestration
RSM	Response surface methodology

rpm	Rotations per minute
s	Second
S	Sulfur
SEM-EDX	Scanning electron microscopy with energy dispersive X-ray spectroscopy
SFPM	Solid fraction of pig manure
SOC	Soil organic carbon
SOM	Soil organic matter
t	Ton
T	Temperature
TGA	Thermogravimetric analysis
TN	Total nitrogen
UNEP	United Nations Environment Programme
USA	United States of America
USDA	United States Department of Agriculture
VM	Volatile matter
w.b.	Wet basis
WFPS	Water-filled pore space
WSOC	Water-soluble organic carbon
WSIC	Water-soluble inorganic carbon
WSU	Washington State University
yr	Year

Chapter 1. Introduction

1.1 General introduction

In 2014, a report by the Intergovernmental Panel on Climate Change (IPCC, 2014) showed that "global emissions of greenhouse gas (GHG) have risen to unprecedented levels despite a growing number of policies to reduce climate change". GHG emissions would need to be lowered by 40 to 70% compared to 2010 values by mid-century, and to near-zero by the end of the century, to limit the increase in global mean temperature well below 2 °C above pre-industrial averages (IPCC, 2014), and to pursue effort to limit the temperature increase to 1.5 °C, which was the objective stated in the Paris agreement in 2015.

The use of negative emission technologies (NET) for the permanent removal of carbon dioxide (CO_2) from the atmosphere was reported as a solution to limit global warming (UNEP, 2016). For example, carbon sequestration from biomass conversion to biochar has been proposed as a strategy of mitigating climate change (Smith, 2016; Wang et al., 2012). Biochar is a black carbon material produced from the thermochemical decomposition of biomass in the absence of or with limited oxygen to above 250 °C (Lehmann and Joseph, 2015), which is generally achieved by pyrolysis. In fact, pyrolysis of biomass stabilizes carbon in the biochar, and when applied to soil, it can be stored for long periods of time of more than 1000 years (Haefele et al., 2011; Kuzyakov et al., 2014; Singh et al., 2012). Woolf et al. (2010) reported that biochar and its storage in soil can contribute to a reduction of up to 12% of current anthropogenic CO_2 emissions.

Moreover, many studies demonstrated that biochar amendment to agricultural soils can help reducing GHG emissions (Cayuela et al., 2014), especially nitrous oxide (N_2O), a powerful GHG with a global warming potential of 298 times in a 100 years horizon when compared to CO_2 (IPCC, 2007). Agricultural soils receiving synthetic fertilizers and organic amendment containing nitrogen (N) contribute a large part to anthropogenic N_2O emissions (Charles et al., 2017). In fact, agriculture in responsible of 60% of global man-made N_2O emissions (IPCC, 2014). For example, the agricultural sector is responsible to about 9.4% of total greenhouse gas (GHG) emissions in the province of Quebec, as 26.9% of these emissions come from agricultural soils (MDDELCC, 2016). Biochar production could be a way for carbon to be drawn from the atmosphere and a solution to reduce the global impact of farming (Verma et al., 2014).

Biochar has also many interesting characteristics to be of use as an amendment in agricultural soils, including a high carbon (C) content, a high pH, a high stability, a high porosity and a high surface area. According to numerous studies, biochar has an agronomic value through improvement of composition, water retention, and increased nutrient uptake and crop yield (Major et al., 2010; Novak et al., 2009a; Weisberg et al., 2010). Moreover, biochars with a high specific surface can be used as a remediation tool in soil to adsorb both organic and inorganic contaminants (Xie et al., 2015), heavy metals (Uchimiya et al., 2011) and pesticides (Cabrera et al., 2014), reducing leaching to water courses. Finally, pyrolysis could be a great waste management solution. For example, due to regulations in many countries that restrict use of phosphorus (P) fertilisation, swine producers are required to manage their excess manure. Solid-liquid separation and valorisation of the solid fraction by pyrolysis appears to be a sustainable way of waste management (Verma et al., 2012). Biochar can then be easily managed and transported away from the regions where P is in excess, and be used as soil amendment.

In addition to biochar, the co-products of pyrolysis are non-condensable syngas and bio-oil that can be used to substitute fossil fuels in heating appliances or to heat the pyrolysis process due to their high-energy content. Therefore, the environmental and energetic balances of the pyrolysis process is further improved.

1.2 Problem statement

It is already well known that biochar yield, physical and chemical properties depend on the conditions during pyrolysis as well as the composition of the feedstock biomass (Enders et al., 2012). According to Lehmann and Joseph (2009), the important parameters for the pyrolysis process that influence the physico-chemical properties of biochar produced from any given biomass feedstock include heating rate, highest treatment temperature (HTT), pressure, and reaction residence time. Reaction vessel design, the flow rate of inert carrier gas, and the post-pyrolysis treatment (crushing, sieving activation, etc.) are other parameters that influence biochar characteristics and properties. Therefore, not all biochars are created equal and biochars should be designed with special characteristics for their use in environmental or agronomic setting (Novak and Busscher, 2013). A limited amount of research-scale pyrolysis has been conducted using wide range of feedstocks (Sohi et al., 2010) and pyrolysis operating parameters. It is then not evident to establish the link between feedstocks characteristics, pyrolysis conditions and biochar characteristics. According to Sun et al. (2014), biochars with different properties could be developed by changing production conditions to those needed to satisfy their environmental applications; these are called engineered biochars. It is also expected that a better understanding of the relationship between feedstock, the operating parameters of the pyrolysis process, and the function of biochar in soil will ultimately enable biochar to be engineered to provide the optimal net benefit (Sohi et al., 2010). This knowledge could permit the production of a biochar optimized to enlarge the pool of stable carbon within soil (Ronsse et al., 2013) and to reduce soil GHG emissions.

Many research studies concluded that biochar amendment to soil can help reduce GHG emissions, and particularly N_2O emissions. However, Cayuela et al. (2014) reported that both soil and biochar properties have an impact on soil GHG emissions and that the mechanisms involved in soil following biochar addition are not well understood.

Finally, it is generally assumed that the pyrolysis process can provide environmental benefits and can be used as a negative emission technology. However, the environmental and energetic impact of the pyrolysis system from biomass collection to the valorisation of pyrolysis co-products is not well known, and particularly when an energetic crop is used as a feedstock.

1.3 Hypotheses

The following are the main research hypotheses of this study:

- Biochars can be created with specific characteristics when the biomass feedstock and the pyrolysis operating parameters are suitably selected.
- Soil GHG emissions are affected by biochar and soil properties. Only biochars produced with specific properties can contribute to reduce soil N_2O emissions.
- Biochars produced with specific chemical properties can be stable and sequester carbon in soil for more than 100 years.

- Biochar production in an auger pyrolysis reactor using energetic crop as a feedstock is expected to have a negative carbon balance when all operations are considered, from switchgrass cultivation on marginal land to the valorisation of pyrolysis co-products (biochar as a soil amendment and bio-oil and syngas as energy sources).
- The energy balance of the biochar production system from the pyrolysis of an energetic crop is expected to be neutral, i.e. as much energy is produced through the pyrolysis co-products than is consumed by the operations.

1.4 Objectives

Considering the hypotheses posed in the previous section, the main objective of this doctoral research project was to produce engineered biochars with specific properties needed to mitigate climate change, and to evaluate their potential to reduce soil GHG emissions and to sequester C. The specific objectives were:

1- To identify the ideal characteristics of biochar to be used for soil amendment in order to reduce soil GHG emissions and to sequester C in soil.

2- To identify the operating parameters of auger reactors which have the most influence on biochar yield and its properties and to identify their optimal range of operation.

3- To validate a response surface methodology approach used to identify the optimal pyrolysis operating parameters in order to produce engineered biochars with the ideal characteristics for mitigating climate change.

4- To evaluate the potential of the engineered biochars to be used as a tool to mitigate climate change by assessing their potential to reduce soil GHG emissions and to sequester C in soils.

5- To assess the GHG emissions and energy impacts of switchgrass pyrolysis in the auger reactor, from the cultivation of switchgrass on marginal lands to the valorisation of co-products.

Connecting text

Considering that not all biochars are created equal and that biochars with specific characteristics have to be developed to satisfy their environmental application, Chapter 2 presents a review of literature aiming at identifying key biochar properties needed for biochar to be used as a tool to mitigate climate change, to reduce soil GHG emissions and to sequester C in soil. The biomass feedstock and pyrolysis operating parameters needed to produce the biochars having the desired properties will be identified. Moreover, mechanisms involved in interactions between biochar and soils that were identified since now will be highlighted.

Chapter 2. Review of literature (Part 1) – Soil biochar amendment as a climate change mitigation tool: Key parameters and mechanisms involved

Abstract

Biochar, a solid porous material obtained from the carbonization of biomass under low or no oxygen conditions, has been proposed as a climate change mitigation tool because it is expected to sequester carbon (C) for centuries and to reduce greenhouse gas (GHG) emissions from soils. This review aimed to identify key biochar properties and production parameters that have an effect on these specific applications of the biochar. Moreover, mechanisms involved in interactions between biochar and soils were highlighted. Following a compilation and comparison of the characteristics of 76 biochars from 40 research studies, biochars with a lower N content, and consequently a higher C/N ratio (> 30), were found to be more suitable for mitigation of N_2O emissions from soils. Moreover, biochars produced at a higher pyrolysis temperature, and with O/C_{org} ratio < 0.2, H/C_{org} ratio < 0.7 and volatile matter below 80% may have high C sequestration potential. Based on these observations, biochar production and application to the field can be used as a tool to mitigate climate change. However, it is important to determine the pyrolysis conditions and feedstock needed to produce a biochar with the desired properties for a specific application. More research studies are needed to identify the exact mechanisms involved following biochar amendment to soil.

Keywords: Biochar; Soil; Greenhouse gas; Emissions; Carbon sequestration

2.1 Introduction

2.1.1 What is biochar

Biochar is a carbon rich, fine-grained, porous substance produced under oxygen-limiting conditions (Liu et al., 2014) at temperatures between 350 and 700 °C. It can be defined as the solid residue obtained from the thermochemical decomposition or pyrolysis of plant and waste feedstocks, and can be specifically used for application to soil as part of an agronomic or environmental management plan (Lehmann and Joseph, 2009). Biochar can also be burned to produce energy; however, in this case, it is called char.

In addition to biochar, the other products of pyrolysis are bio-oil and non-condensable gas. These co-products are generally used to produce energy. Pyrolysis conditions and technology determine the proportions of each product. For example, a slow pyrolysis (i.e. a long exposition to heat lasting from minutes to hours) at temperatures < 450 °C favors biochar production. Fast pyrolysis (i.e. a short reaction time of a few seconds) at high temperature (≈ 500 °C) favors the production of bio-oil (Bridgwater, 2012).

The main characteristics of biochar are its high carbon (C) content compared to the raw material, and higher stability, porosity and surface area, which generally vary between 0.5 and 450 $m^2 g^{-1}$. It is already well known that the yield, physical and chemical properties of biochar depend on operating conditions during pyrolysis, and also on the composition of the feedstock biomass (Enders et al., 2012). For example, the proportion of cellulose, hemicellulose and lignin in biomass will influence the degree of reactivity and, hence, the degree to which the physical structure is modified during processing (Lehmann and Joseph, 2009). Hemicellulose and cellulose are degraded at 200-300 and 300-400 °C, respectively, and lignin is degraded between 200-700 °C, representing a wide range in temperatures (Kim et al., 2012a).

According to Lehmann and Joseph (2009), the important parameters for the pyrolysis process that influence the physico-chemical properties of biochar produced from any given biomass feedstock include heating rate, highest treatment temperature (HTT), pressure, and reaction residence time. Reaction vessel design, the flow rate of inert carrier gas, and the post-pyrolysis treatment (crushing, sieving activation, etc.) are other parameters that influence biochar characteristics and properties. Not all biochars are created equal and biochar should be produced with special characteristics for their specific end use in environmental or agronomic applications (Novak and Busscher, 2013). A limited amount of research on laboratory-scale pyrolysis has been conducted using a wide range of feedstocks (Sohi et al., 2010). Establishing a link between feedstocks characteristics, pyrolysis condition and biochar characteristics has not been done. According to Y. Sun et al. (2014), biochars with different properties could be engineered by changing conditions for pyrolysis so as to be better suited for their applications. It is also expected that a growing understanding of the relationship between feedstock, the pyrolysis and the function of biochar in soil will direct how biochar is to be engineered in order to provide the desired benefits (Sohi et al., 2010).

2.1.2 Biochars uses

2.1.2.1 Improvement of soil fertility

When biochar is used as a soil amendment, it can alter the surface area, pore distribution, bulk density, water holding capacity and penetration resistance of the soil (Mukherjee et al., 2014). According to numerous studies, biochar has an agronomic value through improvement of composition, water retention, and increased nutrient uptake and crop yield of the soil (Major et al., 2010; Novak et al., 2009; Weisberg et al., 2010). Some research studies reported that biochar addition to soil resulted in significantly larger plants growth than in the control that were without amendment (Kammann et al., 2012; Tang et al., 2013). Depending on feedstock chemical composition and pyrolysis conditions, the resulting biochar can contain fertilizing elements (N, P, K), particularly for biochar produced from manure or sludge feedstock. However, biochar cannot be used as a fertilizer, which is generally applied onto the field every year (Maguire and Agblevor, 2010), but biochar can serve as a slow-releasing reservoir of nutrients in soils (Hossain et al., 2011). However, the impacts of biochar on nutrient dynamics, that depend on the properties of soil and biochar, are still poorly understood (Kookana et al., 2011).

2.1.2.2 Runoff and soil treatment

Biochar can be used to adsorb both organic and inorganic contaminants (Xie et al., 2015), heavy metals (Uchimiya et al., 2011) and pesticides (Cabrera et al., 2014) in soil, reducing leaching to water courses. Sohi et al. (2010) and Novak et al. (2009b) reported a decrease of nutrient leaching due to biochar application. High pH, surface area, cation exchange capacity (CEC), anion exchange capacity (AEC), hydrophobicity and negative surface charge are desirable properties of biochar for soil amelioration, contamination remediation, and wastewater treatment (Inyang et al., 2010). Relatively high pyrolysis temperatures generally produce biochars which are more effective in the sorption of organic contaminants (Ahmad et al., 2014; Tang et al., 2013). Because pollutants could be immobilized on biochar, it would then reduce the risk of pollution caused by leachate and runoff, which is beneficial from an environmental perspective. However, the sorption capacity of biochar can compromise the efficiency of some pesticides (Kookana et al., 2011; Tang et al., 2013). Therefore, a special attention has to be paid before to apply biochar to soil.

2.1.2.3 Waste management

Pyrolysis could be a great waste management solution. Due to regulations in many countries that restrict use of phosphorus (P) fertilisation, swine producers are required to manage their excess manure. For a few producers, solid-liquid separation and valorisation of the solid fraction by pyrolysis appears to be a sustainable way of waste management (Verma et al., 2012). Pyrolysis reduces the mass of the solid fraction of pig manure by 65 to 88% into a biochar in which P is concentrated. Biochar can be easily managed and transported away from the regions where P is in excess, and be used as soil amendment, because it is more stable and dryer than the raw material, and its decomposition rate is slower. In addition to manure, the following agricultural, municipal and industrial residues have been pyrolysed in order to produce biochar: biosolids, papermill waste, straw, rice husk, maize straw, barley stover, nut shell, coffee grounds, etc.

2.1.2.4 Climate change mitigation

In 2014, a report by the Intergovernmental Panel on Climate Change (IPCC, 2014) showed that "global emissions of GHG have risen to unprecedented levels despite a growing number of policies to reduce climate change". GHG emissions must be lowered by 40 to 70% compared to 2010 values by mid-century, and to near-zero by the end of the century, to limit the increase in global mean temperature to two degrees Celsius (IPCC, 2014). The association of the term "biochar" with the climate change mitigation concept did not occur until 2005 (Verma et al., 2014). Pyrolysis results in the conversion of C compounds into stable forms which can be recalcitrant to degradation. When the biochar is applied to soil, the C can be sequestered in the soil for long periods of time which according to some studies can be more than 1000 years (Haefele et al., 2011; Kuzyakov et al., 2014; Singh et al., 2012). Thus C that would normally be released as CO_2 from biomass as it is being degraded is prevented from doing so. C sequestration by the conversion of biomass to biochar has been proposed as a solution to reducing the global impact of agriculture on climate change (Wang et al., 2013). Woolf et al. (2010) reported that biochar and its storage in soil can contribute to a reduction of up to 12% of current anthropogenic CO_2 emissions. However, to be sustainable, biochars need to be produced from materials that would otherwise decompose (such as forestry slash, dead biomass, crop residues, and urban yard wastes) and that do not compete with food production (e.g. energy crops grown on productive agricultural land). Moreover, biochar must be produced in efficient reactors that produce very few or no GHG (Brewer and Brown, 2012).

According to the IPCC (2014), land is a key component for attaining the goal of limiting temperature increase to 2 °C, because agricultural land can contribute to large amounts of GHG emissions. In 2012, agriculture was responsible for 8.3% of total GHG emissions in the province of Quebec (Canada). Specifically, 3.0% was from enteric fermentation, 1.5% from manure management, and 3.8% from soil management (MDDELCC, 2016). In addition to the avoidance of CO_2 and methane (CH_4) emissions during normal decomposition of feedstock, research studies reported a decrease (Cayuela et al., 2014) or a suppression (Wu et al., 2013) of GHG emissions from agricultural soil when biochar is used as an amendment. Biochar could also reduce indirect GHG emissions by minimizing use of N fertilizer (Zhang et al., 2010).

2.1.2.5 Policy implication

Because there is no practical way to remove biochar from soil, special attention must be paid before applying it to soil. Each type of biochar is unique, having different chemical and physical characteristics depending on the pyrolysis process and on the feedstock. Some biochars could have adverse effects on the environment. For example, biochar can contain heavy metals if it is produced from a contaminated feedstock. For this reason, policy was developed and implemented to control use of biochar in agricultural fields. According to regulations, biochar can be considered as a waste or a hazardous material, and its application to field can be prohibited. For example, in Canada, in order to apply biochar to agricultural soils, special authorization must be obtained from the Canadian Food Inspection Agency. Results of analysis must prove that biochar is safe for the environment. The International Biochar Initiative (IBI) launched in 2013 the IBI Biochar Certification Program. Biochar manufacturers are now able to certify that their product meets quality standards and is safe for application to soils. This can help legislators to modify regulations in order to permit soil amendment with these certified biochars. However, long-term experiments must be carried out to add to knowledge and confirm the absence of negative side effects of soil amendment with biochar.

2.1.3 Objectives

In the last few years, many scientific articles have been published about biochar and its potential to be used as a tool to mitigate climate change. Many of the research studies focused on the effects of biochar soil amendment on GHG emissions; others aimed to evaluate the long-term stability of biochar in soil in order to determine its C sequestration potential. The objective of this paper is to carry out a systematic literature review in order to determine (1) the effect of biochar amendment on emissions of N_2O, CH_4 and CO_2 from soils, and (2) the C sequestration potential of biochar in soil. Key biochar characteristics and production conditions needed for these specific applications were identified. Moreover, mechanisms involved in soils were highlighted.

2.2 Effect of biochar on soil GHG emissions

2.2.1 Methodology

The following databases were consulted: Springer link, ASABE technical expertise database, Agricola, ScienceDirect, Engineering Village 2 and Google Scholar. Keywords used were "biochar" along with "carbon sequestration", "soil", "greenhouse gases", "climate change mitigation", "engineering", "characteristics", "production", "CH_4" and "N_2O". Only articles published after 2008 in which GHG (CH_4, N_2O and CO_2) emissions from soil amended with biochar were statistically compared with unamended soils have been retained. For each research study, biochar characteristics, pyrolysis parameters and soil conditions were compiled, when available. In the end, the characteristics of 76 biochars from 40 studies were compiled (Table 2.1). Some studies used the same biochar in many soil conditions, and others used different biochars in one or more soil conditions. For this reason, a biochar can both had a positive and a negative impact on soil GHG emissions.

Biochars were classified into three groups: biochars that significantly increased soil emissions, biochars that significantly decreased soil emissions and biochar that had no significant effect on soil emissions. Then, an average was done on the main biochar properties (surface area, bulk density, C, N, O, C/N, O/C, ash content and pH) and heating temperature.

The biochars that increased, decreased, or had no significant effect on GHG emissions following soil amendment were then grouped into categories for temperatures (≤ 400, 401-500, 501-600, > 600), surface areas (< 10, 10-100, >100), C/N ratios (≤ 10, 10-30, 30-100, > 100), pHs (< 7, 7-9, > 9), feedstocks (agricultural biomass, wood, manure, municipal waste, energetic crop, mix), production processes (fast pyrolysis, slow pyrolysis, gasification, activated biochar, others), and soil application rates that were given both in % or in t ha^{-1} depending on the studies (< 2%, 2-5 %, > 5%; < 10 t ha^{-1}, 10-19 t ha^{-1}, < 19 t ha^{-1}).

Table 2.1: Characteristics of biochars compiled from the literature review

#	Feedstock	Production conditions			Elements				Surface area	Bulk density	Volatile matter	Ash	pH	CEC	References
		Process	T	Res. time	C	N	O	H							
			ºC		%	%	%	%	$m^2\ g^{-1}$	$g\ cm^{-3}$	%	%		$cmol_c kg^{-1}$	
1	Walnut shell	Gasification	900	--	55.3	0.47	32.1	1.88	221.7	--	--	40.4	9.7	33.4	(Suddick and Six, 2013)
2	Wheat straw	Fast pyrolysis	525	--	50.4	1.2	--	--	1.6	--	--	21.6	7.4	--	(Bruun et al., 2011)
3	Spruce woodchips	Slow pyrolysis	425	--	75	0.15	--	--	209.7	--	--	--	--	--	(Kettunen and Saarnio, 2013)
4	Oak pellets	Fast pyrolysis	550	--	52	0.32	3.89	0.57	134.8	--	4.33	43.37	10.2	--	(Zheng et al., 2012)
5	Oak pellets	Fast pyrolysis	550	--	56	0.27	0.7	0.85	116.8	--	4.44	42.15	10.2	--	(Zheng et al., 2012)
6	Birch	Slow Pyrolysis	400	2-2.5 h	77.83	0.77	--	--	3.6	--	--	--	--	--	(Karhu et al., 2011)
7	Peanut hull	pyrolysis	498	--	71.6	1.84	--	--	--	0.43	--	--	8.1	--	(Augustenborg et al., 2012)
8	Miscanthus	pyrolysis	550	--	86.4	0.4	--	--	--	0.145	--	--	8.7	--	(Augustenborg et al., 2012)
9	Swine Manure digestate	Slow pyrolysis	350	10 min	39.7	2.15	--	--	--	--	29.19	2.48	10.1	--	(Ameloot et al., 2013)
10	Swine Manure digestate	Slow pyrolysis	700	10 min	35.6	1.03	--	--	--	--	10.37	2.75	11.6	--	(Ameloot et al., 2013)

11	Willow wood	Slow pyrolysis	350	10 min	67.1	1.06	--	--	--	--	35.64	0.23	8.1	--	(Ameloot et al., 2013)
12	Willow wood	Slow pyrolysis	700	10 min	80.3	1.11	--	--	--	--	14.07	1.28	11.1	--	(Ameloot et al., 2013)
13	Poultry litter	Slow pyrolysis	550	30 min	45	3.3	--	--	--	--	14.8	31.1	8.2	--	(Van Zwieten et al., 2013)
14	Green waste	Slow pyrolysis	750	25 min	67.7	0.68	8.29	--	226.4	--	--	17.7	10.1	--	(Felber et al., 2014)
15	Hardwood trees	Slow pyrolysis	400	24h	72.3	0.71	--	--	--	0.24	--	--	9.25	145	(Case et al., 2012)
16	Wood feedstock	Fast pyrolysis	410	--	65.7	0.21	--	--	2.82	--	--	2.7	7.1	10.7	(Mukome et al., 2013)
17	Wood feedstock	Fast pyrolysis	510	--	83.9	0.36	--	--	156	--	--	3.1	7.3	13.2	(Mukome et al., 2013)
18	Walnut shell	Gasification	900	--	55.3	0.47	--	--	227	--	--	46.6	9.7	10.7	(Mukome et al., 2013)
19	Peanut hull	Pyrolysis activated	498	--	71.6	1.84	--	--	--	43.0	--	--	8.43	--	(Kammann et al., 2012)
20	Wood chips	Carboniza-tion	700	--	77.1	0.73	--	--	--	26.2	--	--	10.3	--	(Kammann et al., 2012)
21	Maize	Carboniza-tion	700	--	62.7	0.88	--	--	--	26.8	--	--	9.3	--	(Kammann et al., 2012)
22	Beech	BBQ charcoal	550	--	89.5	0.25	--	--	--	26.1	--	--	8.57	--	(Kammann et al., 2012)
23	Green waste	Slow pyrolysis	700	--	51.9	0.59	--	--	303	2.0	--	45.7	9.8	10.3	(Harter et al., 2014)

24	Wheat straw	Fast pyrolysis	450	--	69	0.3	--	--	--	--	--	--	9.9	--	(Cheng et al., 2012)
25	Wheat straw	Slow pyrolysis	450	--	46.7	0.59	--	--	8.92	0.65	--	20.8	10.4	21.7	(Zhang et al., 2013)
26	Wood	Slow pyrolysis	500	24h	74.6	0.47	--	--	--	--	18.5	4.4	--	--	(Angst et al., 2014)
27	Giant reed stems	Slow pyrolysis	200	2h	48.53	0.73	39	5.86	2.46	--	--	3.99	4.96	--	(Wang et al., 2013)
28	Giant reed stems	Slow pyrolysis	600	2h	77.1	0.79	12	2.16	50.05	--	--	10.75	10.41	--	(Wang et al., 2013)
29	Giant reed stems	Slow pyrolysis	400	2h	72.28	0.95	16.5	4.04	3.04	--	--	9.65	7.88	--	(Wang et al., 2013)
30	Corn stalk	Slow pyrolysis	300	1.5 h	56.8	1.35	--	--	--	--	--	--	9.35	--	(Feng et al., 2012)
31	Corn stalk	Slow pyrolysis	400	1.5 h	51.13	1.34	--	--	--	--	--	--	9.61	--	(Feng et al., 2012)
32	Corn stalk	Slow pyrolysis	500	1.5 h	48.44	0.55	--	--	--	--	--	--	10.1	--	(Feng et al., 2012)
33	Corn silage	Slow pyrolysis	500	2h	77.88	1.99	6.45	2.29	--	--	--	11.39	9.73	--	(Malghani et al., 2013)
34	Pine	Pyrolysis	600	--	70.6	0.2	--	--	--	--	--	--	8.7	--	(Clough et al., 2010)
35	Pig manure + spruce sawdust (4:1)	Slow pyrolysis	600	15 min	62.7	2.67	--	--	--	0.19	--	27.5	9.6	--	(Troy et al., 2013)
36	Sitka spruce wood	Slow pyrolysis	600	15 min	82	0.42	--	--	--	0.18	--	3	9.3	--	(Troy et al., 2013)

37	Willow	Slow pyrolysis	450	--	78.4	0.82	--	2.03	--	--	11.2	4.3	7.3	33.4	(Nelissen et al., 2014)
38	Willow	Slow pyrolysis	650	--	84.8	1.0	--	1.14	--	--	6.0	4.9	8.1	59.1	(Nelissen et al., 2014)
39	Pine	Slow pyrolysis	450	--	86.8	0.19	--	2.8	--	--	12.1	0.9	6.7	38.6	(Nelissen et al., 2014)
40	Pine	Slow pyrolysis	650	--	92.6	0.15	--	1.68	--	--	6.0	1.1	7.7	68.8	(Nelissen et al., 2014)
41	Maize	Slow pyrolysis	350	--	67.3	1.47	--	4.25	--	--	32.6	7.7	8.3	55.2	(Nelissen et al., 2014)
42	Maize	Slow pyrolysis	550	--	72.1	1.52	--	2.21	--	--	12.1	10.9	9.8	61.9	(Nelissen et al., 2014)
43	Wood mixture	Slow pyrolysis	480	--	68.1	0.4	--	1.5	--	--	12.0	8.3	8.6	46.3	(Nelissen et al., 2014)
44	Cattle feedlot waste	Slow pyrolysis	550	45 min	44.0	--	--	--	--	--	--	--	9.7	13.0	(Scheer et al., 2011)
45	Wheat straw	Fast pyrolysis	450		72.6	0.32	15.4	2.8	--	--	5.0	13.8	9.93	--	(Wu et al., 2013)
46	Maize straw	Thermal decomposition	400	--	51.13	1.34	--	--	--	--	--	21	--	--	(Jia et al., 2012)
47	Barley stover	Slow pyrolysis	320	30 min	30.9	5.3	--	--	40.6	--	--	--	6.68	--	(Yoo and Kang, 2012)
48	Swine manure	Slow Pyrolysis	700	--	47.4	3.7	--	--	75.63	--	--	--	7.21	--	(Yoo and Kang, 2012)

49	Rice husks	Pyrolysis	450	--	46.54	0.62	--	--	--	--	--	--	9.1	17.9	(Wang et al., 2012)
50	Hardwood shaving	Slow pyrolysis	300	--	72.54	3.6	--	--	--	--	19.74	17.28	--	--	(Sarkhot et al., 2012)
51	Chicken manure	Slow pyrolysis	540	1 h	19.16	1.69	--	1.14	--	--	26.7	--	9.63	--	(Yu et al., 2013)
52	Hardwood	Slow pyrolysis (kiln)	525	1 day	90.1	0.2	8.2	1.5	--	--	12.5	2.5	7.4	--	(Spokas, 2013)
53	Wood pellets	Updraft gasifier	525	10-15 min	73.4	0.2	25.1	1.3	--	--	12.3	6.4	10.1	--	(Spokas, 2013)
54	Macadamia nut shell	Fast pyrolysis	525	30 sec	93.2	0.6	3.6	2.6	--	--	16.9	1.9	7.5	--	(Spokas, 2013)
55	Hardwood	Slow pyrolysis (kiln)	525	1 day	89.0	0.2	8.3	2.5	--	--	14.8	3	6.4	--	(Spokas, 2013)
56	Wood pellets	Updraft gasifier	525	10-15 min	76.9	0.2	20.8	2.1	--	--	23.6	8.8	5.7	--	(Spokas, 2013)
57	Macadamia nut shell	Fast pyrolysis	525	30 sec	84.3	0.7	3.6	2.8	--	--	21.0	4.8	5.4	--	(Spokas, 2013)
58	Coppiced woodlands	Slow pyrolysis	500	--	84.0	1.2	--	--	--	1.8	--	--	7.2	--	(Castaldi et al., 2011)
59	Mixed hardwood and hickory	Slow pyrolysis	475	--	71.5	0.72	--	--	19.1	--	--	13.9	7.6	--	(Rogovska et al., 2011)
60	Mixed sawdust	Fast pyrolysis	500	--	69	0.3	14.6	2.7	1.6	--	21	--	--	--	(Spokas et al., 2009)

61	Biosolid	Slow pyrolysis	550	45 min	21	2.2	--	--	--	--	--	--	7.9	--	(van Zwieten et al., 2010)
62	Poultry litter	Slow pyrolysis	550	45 min	42	2.6	--	--	--	--	--	--	8.9	--	(van Zwieten et al., 2010)
63	Papermill waste	Slow pyrolysis	550	45 min	38	2.5	--	--	--	--	--	--	6.8	--	(van Zwieten et al., 2010)
64	Green waste	Slow pyrolysis	550	45 min	75	0.24	--	--	--	--	--	--	7.3	--	(van Zwieten et al., 2010)
65	Green waste	Slow pyrolysis	350	45 min	62	0.21	--	--	--	--	--	--	4.9	--	(van Zwieten et al., 2010)
66	Wood	Slow pyrolysis	400	--	69.7	0.18	--	--	--	--	--	5.3	6.93	7.3	(Singh et al., 2010)
67	Wood	Slow Pyrolysis (activated)	550	--	80.2	0.17	--	--	--	--	--	3.5	9.49	15.8	(Singh et al., 2010)
68	Poultry manure	Slow pyrolysis	400	--	42.5	5.18	--	--	--	--	--	34.6	9.2	16.7	(Singh et al., 2010)
69	Poultry manure	Slow Pyrolysis (activated)	550	--	41.5	3.79	--	--	--	--	--	44.4	10.26	28.3	(Singh et al., 2010)
70	Woodpine	Slow pyrolysis	500	--	64.2	0.61	32	3.12	--	--	32.2	7.17	7.75	--	(Deng, 2013)
71	Poultry litter	Slow pyrolysis	550	--	45	1.9	--	--	--	--	14	45.5	7.3	--	(Van Zwieten et al., 2014)
72	Eucalyptus	Slow pyrolysis	550	--	70	0.81	--	--	--	--	20	8.6	8.4	--	(Van Zwieten et al., 2014)
73	Wheat chaff	Slow pyrolysis	550	--	58	2.8	--	--	--	--	19.8	16.2	8.9	--	(Van Zwieten et al., 2014)

74	Pine chip	Vacuum moving bed pyrolysis	550	--	71.2	0.91	23.6	--	5	--	--	17	7.9	3.2	(Angst et al., 2014)
75	Oak wood	Slow pyrolysis	650	--	90	0.3	--	--	214	0.3	--	4.3	9.4	--	(Mukherjee et al., 2014)
76	Wheat straw	Slow pyrolysis	450	--	46.7	0.56	--	--	8.9	--	--	20.8	9.4	24.1	(L. Sun et al., 2014)

2.2.2 N_2O emissions influenced by biochar amendment

2.2.2.1 Mechanisms involved in N_2O emissions from soil affected by biochar amendment

There is evidence that biochar amendment to soil can help reduce GHG emissions, and particularly N_2O emissions (Cayuela et al., 2014). N_2O is a powerful greenhouse gas, with a global warming potential of 298 (IPCC, 2007). In other words, the comparative impact of N_2O on climate change is 298 times greater than CO_2 over a 100-year period. Agricultural soils management account for about 70% of the atmospheric loading of N_2O. N_2O emissions from soils can be affected through abiotic factors, but most of the mechanisms involved in the decrease of N_2O emissions discussed in the literature are biotic (microbial response). Three main mechanisms of the nitrogen cycle are thought to be the major contributors to N_2O emissions from soil: microbial nitrification, denitrification, and nitrate ammonification (Baggs, 2011). Nitrification is an aerobic process, in which NH_4^+ is oxidized to NO_3^- with N_2O as a by-product, while denitrification is an anaerobic process, in which NO_3^- is reduced to N_2 with N_2O as an intermediary (Verhoeven and Six, 2014). These two mechanisms, contributing approximately 70% of global N_2O emissions from soils (Butterbach-Bahl et al., 2013), and can be modified with biochar, as many studies reported significant decreases in N_2O emissions following biochar application to soil (Augustenborg et al., 2012; Bruun et al., 2011; Kettunen and Saarnio, 2013; Zheng et al., 2012). These decreases are mainly attributed to changes in pH that alter the N_2O-to-N_2 ratio during denitrification, a modification of micro-organisms abundance, an increased adsorption of NH_4^+ or NO_3^-, or an improved aeration and porosity affecting soil water dynamics and leading to lower denitrification rates (Aguilar-Chávez et al., 2012; Sohi et al., 2010; Wang et al., 2012; Nelissen et al., 2014; Lehmann et al., 2011).

Biochar liming effect

The pH of biochar is generally high, with an average of 8.6 according to the literature (Table 2.1). When applied to acidic soil, biochar acts as a liming material. This could be advantageous to use biochar instead of calcium oxide, for example, which can react with $2H^+$ to produce H_2O and CO_2 (Allaire and Lange, 2013). L. Sun et al. (2014) and Deng (2013) concluded that biochar acid buffering capacity and liming effect are important factors for mitigating N_2O emissions. It was shown that when soil pH is increased, the activity of N_2O reductase enzymes of denitrifying microorganisms is encouraged, thus less N_2O is released by denitrification (Yanai et al., 2007). Soil liming under anaerobic conditions would favor nitrate reduction to N_2 or the adsorption of ammonium that prevents nitrification and denitrification (Sohi et al., 2010).

The main hypothesis posed by Cayuela et al. (2013) was that biochar's buffering capacity appears to be fundamental to decreasing N_2O emissions during denitrification, not because of a change of soil pH in itself, but because the mechanism of mitigation is connected to pH. The authors demonstrated that biochars can promote the last step of denitrification and it can also decrease total N denitrified. Similarly, Mukherjee et al. (2014) and Castaldi et al. (2011) reported that a higher pH of soils amended with biochar might have increased activity of denitrifiers or denitrifying enzymes, with a consequent decrease of the N_2O/N_2 ratio.

Impact of biochar on micro-organisms activity

The decreased N_2O emissions from soils amended with biochar might also be caused by a change in microbial abundance in the soil (Lehmann et al., 2011), and particularly to enhanced growth and activity of micro-organisms involved in denitrification (Harter et al., 2014; Bruun et al., 2011). Harter et al. (2016) concluded that biochar addition to soil can increase the relative sequence abundance of complete denitrifiers and atypical N_2O reducers restricted to N_2O reduction. Following a 30 days incubation study, Liu et al. (2014) found that biochar can potentially reduce N_2O emission by lowering the abundance of ammonia-oxidizing and nitrite-oxidizing bacteria in soil. Sun et al. (2014) made the hypothesis that biochar acts as an electron shuttle that facilitates the transfer of electrons to soil-denitrifying microorganisms, and enhances the conversion of N_2O to N_2.

Adsorption of NO_3^- and NH_4^+ in biochar

According to Case et al. (2012), the availability and form of N in the soil can strongly affect N_2O production. Due to its sorption properties, biochar can retain N compounds such as NH_4^+ and NO_3^- (Kettunen and Saarnio, 2013; van Zwieten et al., 2010), thereby affecting the N cycle in the soil (Clough et al., 2010). Kammann et al. (2012) explained that the reduced N_2O/N_2 ratio is due to the adsorption of either NH_4^+ or NO_3^-

derived from the first N fertilization and soil mineralization. Angst et al. (2013) evaluated the effect of biochar amendment on N_2O emissions from slurry, manure or chemical fertilizer. N_2O emissions from samples amended with biochar were significantly less than those from control samples. They proposed that this was due to the sorptive properties of the biochar that might decrease the availability of organic substrate and NH_4^+-N. Sun et al. (2014) also reported that free NH_4^+ can be adsorbed by biochar particles due to an enhanced physical retention, resulting in reduced N_2O emissions. The adsorption of ammonium on the surface of the biochar would prevent nitrification and denitrification (Sohi et al., 2010).

Following a nine-month experiment, both in the laboratory and in the field, Felber et al. (2014) concluded that biochar made from greenwaste limited the availability of N in soil by the adsorption of either NO_3^- or NH_4^+. The smaller amount of N available for denitrification and nitrification would explain the decreased N_2O emissions. Similarly, Van Zwieten et al. (2014) concluded that biochar limited the availability of NO_3^- to denitrifying organisms in the Tenosol since the proportion of N_2O arising from supplied NO_3 was lower than from the control soil.

Sarkhot et al. (2012) and Case et al. (2012) measured the extractable NH_4^+ and NO_3^- in a soil amended with biochar after an incubation experiment. Sarkhot et al. (2012) found that treatment of soils with enriched biochar resulted in significant reduction in KCl-extractable inorganic NH_4^+ and NO_3^- as compared to the control soil, i.e. N was immobilised. The authors concluded that biochar slowly released nutrients into the soil. Similarly, Case et al. (2012) found that extractable NO_3^- contents at the end of the experiment were lower in biochar amended soils. This was explained by the sorption of NO_3^- onto the biochar surface and by the increased immobilisation of NO_3^- within microbial biomass due to the increased C/N ratio of the soil.

However, the nutrient retention potential of biochars can differ with soil type, the properties of the biochar, as well as the age of the biochar. For example, Gronwald et al. (2015) questioned the long-term biochar sorption ability in temperate soil. After 7 months in the field, around 60% to 80% of the adsorption capacity of biochar obtained by pyrolysis of miscanthus at 750 °C was lost. Further long term studies are needed to understand the mechanisms involved.

Increased soil aeration

Enhanced aeration of the soil caused by biochar amendment may also contribute to the reductions in N_2O emissions (Augustenborg et al., 2012; Rogovska et al., 2011). Over a four months field study during the growing season, Mukherjee et al. (2014) measured GHG emissions of a silt loam amended with biochar obtained from the slow pyrolysis of oak at 650 ºC, at 0.5% w/w (7.5 t ha^{-1}). N_2O emissions were significantly reduced by 92%. Enhanced soil aeration is the suggested mechanism responsible for this difference, because the bulk density of biochar amended soils was significantly lower.

Another proposed mechanism for the suppression of N_2O from biochar amended soil revolves around modification of soil water dynamics (Sohi et al., 2010). The authors explained that soil solution (and dissolved nitrate) could be drawn into pores inaccessible to microbes and that aerobic conditions could be maintained inside inhabited pore space.

2.2.2.2 Biochar characteristics affecting N_2O emissions (results from the literature review)

A systematic literature review showed that in most of the 40 listed studies in which soil GHG emissions were measured following biochar amendment (Table 2.1), a decrease of N_2O emission or no significant effects was reported. Some studies used different biochars, while others tested only one biochar under different soil conditions. Most of the biochars (65%) were produced by slow pyrolysis. Biochar was added to different soil types, with different humidity contents, at different application rates. While some studies were done in the field, most were performed in the laboratory. A compilation of the results showed that 41 biochars had no effect on N_2O emissions, and 53 biochars significantly decreased N_2O emissions (Table 2.2). Only six biochars increased N_2O emissions when added to soil (Suddick and Six, 2013; Mukome et al., 2013; Troy et al., 2013; Yoo and Kang, 2012; Spokas, 2013 and Singh et al., 2010).

Table 2.2: Characteristics of biochars and their effect on N_2O emissions – average from the literature review

Parameter	T	Surface area	Bulk density	C	N	O	C/N	O/C molar	Ash	pH
Unit	°C	$m^2\ g^{-1}$	$g\ cm^{-3}$	%	%	%			%	
Decreased emissions										
Average	515	89	0.45	66.1	1.09	14.28	152	0.16	19.0	8.6
Standard deviation	110	103	0.46	17.2	1.09	11.52	151	0.15	36.2	1.5
Nb biochars [1]	53	15	12	53	53	13	53	15	36	48
No effect on emissions										
Average	517	50	0.32	66.0	1.22	19.29	144	0.19	13.8	8.3
Standard deviation	122	75	0.19	15.6	1.31	11.07	144	0.13	13.9	1.2
Nb biochars	41	11	7	41	39	7	39	10	29	38
Increased emissions										
Average	621	151	0.19	63.9	2.17	17.85	86	0.23	22.7	9.0
Standard deviation	169	107	0.01	20.0	2.00	20	81	0.29	19.7	1.0
Nb biochars	6	2	2	6	6	2	6	2	5	6

[1] Number of biochars found in the literature for which characteristic was given

Biochar chemical composition

Biochars that were used in studies where N_2O emissions raised significantly following amendment to soil had in general a higher N content and a lower C content, resulting in a low C/N ratio (Table 2.2). For example, Verhoeven and Six (2014) reported that soil amendment with pine chip biochar increased cover crop C and N inputs and may have contributed to increased rates of mineralization, nitrification and denitrification, and consequently increased soil N_2O emissions. The six biochars that increased soil N_2O emissions had an average N content of 2.17%. Contrarily, biochars that resulted in a reduction of soil N_2O emissions (53 biochars) and those having no effect on N_2O emissions (41 biochars) had a lower average N content of 1.09 and 1.22%, respectively. The average C/N ratios of biochars that led to either a significant decrease or no significant effect on N_2O emissions were 152 and 144, respectively. The average C/N ratio of the six biochars that resulted in a significant rise in N_2O emissions from soil, was lower, at 86 (Table 2.2). The C/N ratio of 84% of the biochars leading to decrease in N_2O emission and 79% of the biochars that had no effect on these emissions was higher than 30 (Table 2.3). In contrast, three out of six biochars that resulted in an increase of N_2O emissions when added to soil had a C/N ratio lower than 30 (Table 2.3).

This is in accordance with a meta-analysis from Cayuela et al. (2014) that indicated that the C/N ratio is a key factor influencing N_2O emissions. A higher C/N ratio resulted in a significant reduction of soil N_2O emissions. In 30 selected peer-reviewed articles, biochars with a C/N ratio lower than 30 did not affect N_2O emissions, while those with a C/N ratio higher than 30 significantly reduced soil N_2O emissions. Ameloot et al. (2013) also reported that the magnitude of N mineralization decreased with increasing biochar C/N ratio. According to Mukome et al. (2013), emission of N_2O under conditions of complete denitrification can be correlated not only with the C/N ratio, but also with the H/C ratio. They evaluated the effect of three different biochars on N_2O emissions. Not all biochars affected denitrification; effects on N mineralization being dependent on the nature of the biochar. Biochar produced from walnut shell had the lowest C/N and H/C ratios and when added to soil resulted in higher N_2O emissions as compared to biochar produced from wood feedstock.

N_2O emission is related to the use of N fertilizer. The data from Zheng et al. (2012) suggest that initial soil N and biochar N contents could be used as a predictor for N_2O emissions in laboratory studies, but this must be confirmed in field studies. Van Zwieten et al. (2014) evaluated the effect of adding biochar produced by the slow pyrolysis of poultry litter at 550°C. They found significantly lower emissions of N_2O from biochar amended soil compared to either biochar plus urea, urea alone, or poultry litter alone treatments. This was explained by the very low mineral N content in the biochar as compared to the other treatments.

Table 2.3: Effect of biochar amendment on N_2O emissions – Data compiled from the literature review

		Decrease		No effect		Increase	
		Nb biochars[1]	%[2]	Nb biochars	%	Nb biochars	%
HTT[3] (°C)	≤ 400	9	17	7	17	1	17
	400 - 500	16	30	14	34	0	0
	500 - 600	19	36	15	37	3	50
	> 600	9	17	5	12	2	33
	Total	53	100	41	100	6	100
Surface area (m^2 g^{-1})	< 10	6	40	6	55	0	0
	10 - 100	3	20	2	18	1	50
	> 100	6	40	3	27	1	50
	Total	15	100	11	100	2	100
C/N ratio	≤ 10	2	4	2	5	1	17
	10 - 30	6	12	6	15	2	33
	30 - 100	22	42	13	33	0	0
	> 100	22	42	18	46	3	50
	Total	52	100	39	100	6	100
O/C molar ratio	< 0.2	11	79	6	60	1	50
	> 0.2	3	21	4	40	1	50
	Total	14	100	10	100	2	100
pH	> 9	20	42	13	34	4	67
	7 - 9	22	46	20	53	2	33
	< 7	6	13	5	13	0	0
	Total	48	100	38	100	6	100
Feedstock type	Residue	15	28	13	32	2	33
	Wood	21	40	17	41	1	17
	Manure	4	8	6	15	2	33
	Waste	6	11	0	0	0	0
	Energetic crop	7	13	4	10	0	0
	Mix	0	0	1	2	1	17
	Total	53	100	41	100	6	100
Pyrolysis type	Fast pyrolysis	6	12	5	13	1	17
	Slow pyrolysis	37	74	28	72	4	67
	Activated[4]	3	6	1	3	0	0
	Gasification	1	2	3	8	1	17
	Other	3	6	2	5	0	0
	Total	50	100	39	100	6	100
Application rate (% w/w)[5]	Low	6	12	9	23	1	17
	Intermediate	18	36	13	33	4	67
	High	26	52	18	45	1	17
	Total	50	100	40	100	6	100

[1] Number of biochar; [2] Percentage of the total number of biochars; [3] higher treatment temperature; [4] activated biochar produced either from slow or fast pyrolysis; [5] Low: < 2% or 10 t ha^{-1}, Intermediate: 2 - 4.9 % or 10 - 19 t ha^{-1}, High: > 4.9% or 19 t ha^{-1}

pH of biochar

Many studies reported that biochar with high pH is an important factor in reducing soil N_2O emissions (Mukherjee et al., 2014; Van Zwieten et al., 2014; Castaldi et al., 2011; Kammann et al., 2012). According to the data compiled from the literature, the average pH of biochar is 8.6. There is a higher proportion of biochars with very high pH (> 9) that is associated with a reduction of soil N_2O emission (42%) than those having no effect (34%; Table 2.3). However, the pH of biochars that result in increased N_2O emissions reported in the literature review is always higher than 7, and four out of six biochars have a very high pH (> 9). Based on this information, it is difficult to correlate pH of biochar with an effect on N_2O emissions. In fact, depending on the biochar application rate and the initial soil pH, the liming effect of biochar could be insignificant.

Ash content of biochar

From the literature review, biochars that result in an increase of soil N_2O emissions was observed to have a higher average ash content (22.7%) compared to biochar having no effect on N_2O emissions (13.8%) and that decrease N_2O emissions (19%; Table 2.2). Most of the biochars resulting in higher N_2O emission have high ash content because they are produced from agricultural biomasses or manure wastes (Table 2.3), these biomasses having generally higher ash content than woody biomass. Cayuela et al. (2013) assumed that the salting-out effect of ashes can reduce the solubility of N_2O and thus favors its emission.

Porous structure of biochar

A review of the literature (Tables 2.2 and 2.3) also showed no correlation between biochar surface area and the ability of biochar to mitigate GHG emissions, even if both micro-porosity and macro-porosity of biochar play a role in soil. Micropores (< 2 nm diameter) contribute most to the surface area of biochars (750 to 1 360 m^2 g^{-1}) and are responsible for the adsorptive capacities. Macropores (> 50 nm) have a smaller surface area (51 to 138 m^2 g^{-1}) and are relevant to vital soil functions such as aeration and hydrology, for the movement of roots through soil and as habitats for a vast variety of soil microbes (Lehmann and Joseph, 2009). Because of the different distribution of micro and macro-pores in the biochar, it would be difficult to make a relation between the surface area and porosity. Using data from the literature, a graph was constructed showing the Brunauer–Emmett–Teller (BET) surface areas as a function of pyrolysis temperature (Figure 2.1). This indicated that the surface area of biochars generally increases with pyrolysis temperature. The development of micropores and increase of surface area with higher temperatures has already been demonstrated by other research groups (Lehmann and Joseph, 2009).

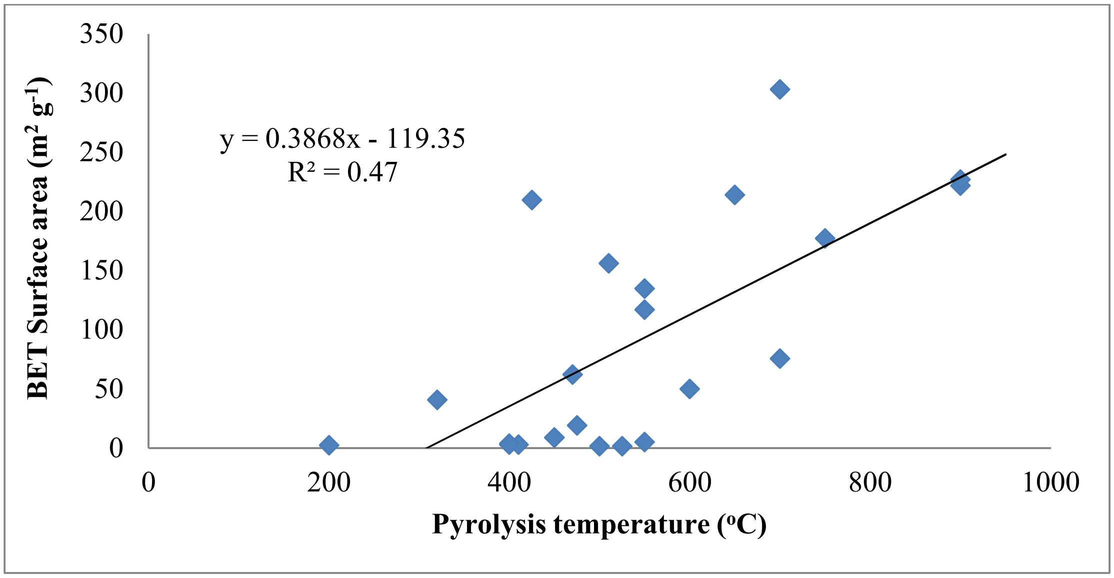


Figure 2.1: Relation between BET surface area and pyrolysis temperature – compiled data from literature

2.2.2.3 Other factors influencing N_2O emissions

Pyrolysis conditions

Although it is known that pyrolysis conditions influence biochar properties (Enders et al., 2012; Lehmann and Joseph, 2009), analysis of data obtained from the literature did not demonstrate a correlation between pyrolysis temperature and pyrolysis type and the capacity of biochar to reduce soil GHG emissions. A majority of the biochars used in these studies were produced by slow pyrolysis (52 out of 76) and most of the biochars were produced between 500 and 600 °C (Table 2.3). Spokas and Reicosky (2009) reported that pyrolysis temperature was uncorrelated to any of the observed impacts on greenhouse gas production. Similarly, following a meta-analysis, Cayuela et al. (2014) reported no significant difference among the different temperatures of pyrolysis in terms of the extent of N_2O emissions mitigation.

Feedstock

Biochars used in studies reported in the literature were mostly produced from either wood (30 biochars) or agricultural residues (22 biochars). Ten biochars were produced from manure and nine from energetic crops (Table 2.1). Four of the six biochars that caused a rise in N_2O emissions were produced from agricultural residues or manure (Table 2.3). This may be due to high N content of these biomasses (Zheng et al., 2012). However, other biochars produced from manure also did not have any effect or caused a decrease in N_2O emissions. Cayuela et al. (2014) indicated that the combination of chemical composition and physical properties related to the specific feedstock possibly defined the potential of the biochar to decrease soil N_2O emissions. The authors indicated that plant derived materials seemed to be the most promising feedstock for producing biochar for mitigation of N_2O emissions from soil.

Biochar application rates

The application rate can have an impact on soil N_2O emissions. Examination of data from the literature revealed that biochars applied at high rates ($\geq 5\%$ or ≥ 20 t ha^{-1}) resulted in a decrease in soil N_2O emissions. However, because the characteristics of each biochar are different, a high biochar application rate cannot be directly correlated to a better N_2O emission mitigation. Aguilar-Chávez et al. (2012) compared different biochar application rates on N_2O emissions and reported that higher application rate resulted in higher potential for N_2O emission mitigation. Harter et al. (2014) found that N_2O emission was reduced by up to 96% in the presence of 10% biochar, but the reduction decreased to 47% in the presence of 2% biochar. A similar conclusion was reached in a study by Wu et al. (2013), in which biochar added at 25 t ha^{-1} suppressed the emissions by 96%, while application at 10 t ha^{-1} reduced N_2O emissions by 55%. In a study by Castaldi et al. (2011), the percentage of reduction of N_2O daily flux in biochar amended plots varied between 26% and 76% for char additions at 3 t ha^{-1}, and between 59% and 88% for 6 t ha^{-1}. In an incubation study by Case et al. (2012), biochar produced by the slow pyrolysis of hardwood at 400 ºC was added to soil cores at rates of 1, 2, 5 and 10%. The cumulative production of N_2O was significantly reduced as the biochar content increased. Rogovska et al. (2011) evaluated the effects of soil biochar amendment at 5, 10 and 20 $g_{biochar}$ $kg^{-1}{}_{soil}$, with or without manure addition. At the higher rate, biochar addition reduced N_2O emissions, but no significant effect was observed at rates of 5 and 10 $g_{biochar}$ kg^{-1}_{soil}. Similarly, Spokas et al. (2009) indicated that biochar addition at high rates (20, 40 and 60%) significantly reduced N_2O emissions, but low rates of biochar addition (2, 5 and 10% w/w) did not significantly affect emissions. A research study by Liu et al. (2014) examined how applications of different doses of biochar (1%, 2%, 4% and 8%) to soil affected emissions of N_2O. They found that maximum inhibition was reached at 4% (w/w) biochar. Cheng et al. (2012) investigated the effects of direct incorporation of either wheat straw or its biochar into a cultivated Chernozem on N_2O and CO_2 emissions. N_2O emissions were not significantly influenced by biochar application. The authors proposed that the biochar application rate of 0.29 % was too low to change the N cycling in the soil. Finally, Jia et al. (2012) reported that biochar application rate in the range of 20 to 40 t ha^{-1} had no influence on decreasing N_2O emissions.

Soil characteristics

The effect of biochar on soil N_2O emissions may differ depending on the soil type to which it was added. The divergence of the results on the potential mitigation of N_2O by biochar depends on factors such as environmental conditions, and soil and crop management (Petter et al., 2016; Suddick and Six, 2013). The meta-analysis study of Cayuela et al. (2014) revealed that interactions between soil texture, biochar, and the chemical N fertilizer applied with the biochar have a major influence on soil N_2O emissions. Scheer et al. (2011) amended an intensive subtropical pasture soil with a biochar produced by the slow pyrolysis of cattle feedlot waste at 550ºC and evaluated the impacts on GHG emissions. A positive correlation between soil moisture and N_2O emissions was observed: N_2O emissions occurred when soil moisture contents ranged from 78% to 83% of water-filled pore space (WFPS). Similarly, Petter et al. (2016) found a positive correlation between N_2O emissions and soil moisture and pH in the presence of biochar. Malghani et al. (2013) indicated that the suppression in N_2O flux with char amendment was higher in the soil to which N-fertilizer was applied. Scheer et al. (2011) concluded that under only certain soil and management conditions, biochar amendment could potentially mitigate GHG emissions from soil.

2.2.3 CH_4 emissions influenced by biochar amendment

2.2.3.1 Soil CH_4 emissions mechanism

Methane (CH_4) is an important GHG, with a global warming potential of 25 (IPCC, 2007). The agricultural sector is responsible for about half of the global anthropogenic emissions of CH_4, the main source being rice production (Brevik, 2012). The total emission of CH_4 from soil is the net result of CH_4 production by methanogenesis, and CH_4 oxidation by methanotrophic processes. During methanogenesis, CH_4 is produced by the methanogenic archaea, and then, most of the CH_4 is consumed by methanotrophic proteobacteria during methanotrophy (Feng et al., 2012). Globally, soil is a net sink for CH_4 under aerobic and well-drained conditions. Anaerobic conditions, warm temperatures and the presence of labile C are expected to favor emissions of CH_4 (Lehmann and Joseph, 2009).

2.2.3.2 Results from the literature review

In the literature, CH_4 emissions were measured in 27 studies, and in most of these studies (17) in which 29 different biochars were used, no significant difference in CH_4 emissions between soils amended with biochar and controls without biochar was reported (Table 2.4). It is difficult to determine which biochar characteristics are involved in reducing CH_4 emissions from soils (Tables 2.4 and 2.5). Biochar causing a decrease of CH_4 emissions from soils have a lower average C content, and consequently a lower average C/N ratio (Table 2.4). However, the proportion of biochar in each C/N ratio category is similar (Table 2.5). Soil conditions, for example the soil water content, are also expected to have an impact on CH_4 emissions. The addition of fertilizer and biochar application rates are other important factors influencing CH_4 emissions. Application rates of biochars higher than 5% (w/w) or 10 t ha^{-1} (Table 2.5) resulted in a significant increase in CH_4 emissions. The fact that these studies were not done over the same period of time can also have an important impact on the cumulative emissions.

2.2.3.3 Mechanisms for decreasing CH_4 emissions

Only five studies reported significant decrease in CH_4 emissions after soil was amended with 8 different biochars (Table 2.4; Zheng et al., 2012; Karhu et al., 2011; Feng et al., 2012; Yoo and Kang, 2011; and Spokas et al., 2009). In the study by Feng et al. (2012), soil amended with biochar produced by the slow pyrolysis of corn stalk at 300 and 500 °C significantly decreased cumulative paddy CH_4 emission in comparison with control soils with no amendments. This led the authors to hypothesize that the increase in dissolved organic carbon (DOC) content in soil due to biochar amendment offers more carbon sources which can promote the growth of methanogenes, and causing CH_4 emissions to increase. However, they found that CH_4 utilization by methanotrophs outpaced CH_4 production, probably because of improved soil aeration. In fact, the porous structure of biochar would allow new habitats for soil microbes to form. Karhu et al. (2011) also reported that biochar amendment increased CH_4 uptake in soil due to improved soil aeration and increased CH_4 diffusion through the soil. The authors explained that the high porosity of biochar can increase soil water holding capacity, and thus fluctuations in the CH_4 flux due to changes in water content would be stabilized.

Table 2.4: Characteristics of biochars and their effect on CH_4 emissions – average from the literature review

Parameter	T	Surface area	Bulk density	C	N	O	C/N	O/C molar	Ash	pH
Unit	°C	$m^2\ g^{-1}$	$g\ cm^{-3}$	%	%	%			%	
Decreased emissions										
Average	478	62	---	54.8	1.57	6.40	106	0.07	42.8	8.6
Standard deviation	133	57	---	14.2	1.89	7.28	86	0.08	0.9	1.9
Nb biochars [1]	8	6	---	8	8	3	8	3	2	4
No effect on emissions										
Average	529	85	13.9	62.1	1.33	10.34	134	0.10	18.0	8.3
Standard deviation	94	76	16.6	19.0	1.29	8.54	132	0.09	13.8	1.6
Nb biochars	29	7	9	29	28	8	28	8	14	27
Increase emissions										
Average	503	9	0.65	61.5	0.65	12.30	190	0.12	7.9	9.0
Standard deviation	41		---	29.0	0.55	11.32	178	0.12	8.8	1.3
Nb biochars	6	1	1	6	6	3	6	3	4	6

[1] Number of biochars for which the characteristic was available

Table 2.5: Effect of soil biochar amendment on CH_4 emissions – data compilation from the literature review

		Decrease		No effect		Increase	
		Nb biochar[1]	%[2]	Nb biochar	%	Nb biochar	%
HTT[3] (°C)	≤ 400	3	38	4	14	0	0
	401 - 500	2	25	6	21	2	33
	501 - 600	2	25	15	52	4	67
	> 600	1	13	4	14	0	0
	Total	8	100	29	100	6	100
Surface area (m^2 g^{-1})	< 10	2	33	2	29	1	100
	10 - 100	2	33	2	29	0	0
	> 100	2	33	3	43	0	0
	Total	6	100	7	100	1	100
C/N ratio	≤ 10	1	13	2	7	0	0
	10 - 30	1	13	5	18	1	17
	30 - 100	2	25	9	32	2	33
	> 100	4	50	12	43	3	50
	Total	8	100	28	100	6	100
O/C molar ratio	< 0.2	3	100	6	75	2	67
	> 0.2	0	0	2	25	1	33
	Total	3	100	8	100	3	100
pH	> 9	2	50	12	44	4	67
	7 - 9	1	25	9	33	2	33
	< 7	1	25	6	22	0	0
	Total	4	100	27	100	6	100
Feedstock type	Residue	3	38	11	37	3	50
	Wood	4	50	10	33	2	33
	Manure	1	13	4	13	1	17
	Waste	0	0	4	13	0	0
	Mix	0	0	0	0	0	0
	Total	0	0	1	3	0	0
Pyrolysis type	Fast pyrolysis	8	100	30	100	6	100
	Slow pyrolysis	3	38	3	12	1	17
	Activated [4]	5	63	18	72	4	67
	Gasification	0	0	1	4	0	0
	Other	0	0	1	4	1	17
	Total	0	0	2	8	0	0
Application Rate [5] (% w/w)	Low	1	8	11	28	1	10
	Intermediate	4	31	12	30	0	0
	High	8	62	17	43	9	90
	Total	13	100	40	100	10	100

[1] Number of biochar; [2] Percentage of the total number of biochars; [3] higher treatment temperature; [4] activated biochar produced either from slow or fast pyrolysis; [5] Low: < 2% or 10 t ha^{-1}, Intermediate: 2 - 4.9 % or 10 - 19 t ha^{-1}, High: > 4.9% or 19 t ha^{-1}

2.2.3.4 Mechanisms for increasing CH_4 emissions

Significant increases in CH_4 emissions after biochar amendment to soil has been reported (Spokas, 2013; Wang et al., 2012; Yu et al., 2013; Zhang et al., 2010 and Zhang et al., 2013). In the study realized by Zhang et al. (2010), CH_4 emissions were significantly affected by the rate of biochar amendment, N fertilization and their interaction. The increase in total CH_4 emission was 31 and 49% for the low and high rates of biochar, respectively, as compared to the no-biochar treatments.

According to Zhang et al. (2013), increased CH_4 emission was due to added C substrate from biochar, which could become the predominant source of substrate for methanogenesis. Similarly, Spokas (2013) reported that fresh biochar suppressed CH_4 oxidation potential, i.e. the soil became a CH_4 emitter instead of a sink. However, weathered biochar amendment had no significant effect on CH_4 oxidation. The hypothesis was that fresh biochar samples suppressed soil methanotrophic activity. In a study by Spokas and Reicosky (2009), sixteen types of biochars were added to three types of soils in order to evaluate their effect on GHG emissions. When incubated alone, they found that some types of biochar emitted CH_4, which can be a consequence of its fresh nature and resulting off-gassing from pores and/or surface desorption. When mixed into agricultural and landfill soils, most of the biochars decreased net CH_4 oxidation rates over a 100-days incubation period, and CH_4 production increased. The authors assumed that the net soil methanotrophic activity was reduced. According to Spokas et al. (2009), this could be due to a potential inhibitor for the methanotrophs present on the biochar (e.g. organics, pH alteration or metal toxicity). Spokas et al. (2009) also made the hypothesis that methanotrophs could use sorbed organic coumpounds versus CH_4, suppressing CH_4 oxidation.

Biochar amendment can have a different impact on CH_4 emissions depending on soil moisture content. Yu et al. (2013) found that CH_4 emission from soils with low moisture content (35 and 60% WFPS) amended with biochar increased in the first week of incubation due to the increased soil pH affecting the activity of methanogens and methanotrophs. However, with soils with higher moisture content (85 and 100% WFPS), biochar amendment enhanced soil CH_4 emission throughout. The authors proposed that organic C added by the biochar provided available substrate for methanogens and created anaerobic microsites in soil favouring the CH_4 emission. Furthermore, the organic matter of biochar was probably consumed more slowly due to restricted soil microbial activity, resulting in the suppression of CH_4 oxidation. The authors concluded that different soil moisture levels and microbial communities of different soils influenced the production and consumption of CH_4 following biochar amendment.

2.2.4 CO_2 emissions influenced by biochar amendment

2.2.4.1 Results from the literature review

From the literature review, 24 studies in which 38 different biochars were used as a soil amendment reported that soil CO_2 emissions were not significantly affected. 11 studies reported significant decreases (including 14 biochars) and 12 studies (17 biochars) reported significant increases of CO_2 emissions following soil biochar amendment (Table 2.6). Biochar characteristics and pyrolysis conditions can have an impact on soil CO_2 emissions. Following the data compilation from the literature review, biochars that resulted to an increase of CO_2 emissions were produced at a lower temperature (average of 507 °C) than biochar that resulted to a decrease of CO_2 emissions (average of 580 °C; Table 2.6). Moreover, biochars that resulted in an increase of CO_2 emissions have a higher average C/N ratio (152) when compared to those decreasing CO_2 emissions (C/N = 102; Table 2.6). There is a higher proportion of biochar with a C/N ratio > 100 that resulted in an increase of CO_2 emissions (53%) when compared to biochars that resulted in a decrease in CO_2 emissions (36%; Table 2.7).

Higher biochar application rates seem to cause more increases in CO_2 emissions (Table 2.7). Biochars amendment to soil that resulted in an increase of CO_2 emissions were generally at a higher rate of application (15 out of 27 biochars with an application rate > 4.9% or 19 t ha^{-1}). Biochar's effect on CO_2 emissions can also depend on the soil type and incubation conditions. For example, Case et al. (2012) reported that depending on the humidity of the samples, CO_2 emissions were both increased and unaffected by biochar addition.

2.2.4.2 Mechanisms for decreasing CO_2 emissions

Case et al. (2012) demonstrated that biochar amendment (49 t ha^{-1}) could suppress soil GHG emissions under field and controlled conditions. They concluded that a combination of both biotic and abiotic mechanisms may explain the lower CO_2 emissions observed in biochar amended soil. Mechanisms include a reduced enzymatic activity, increased carbon-use efficiency from the co-location of soil microbes, soil organic matter and nutrients, and the precipitation of CO_2 onto the biochar surface. Aguilar-Chávez et al. (2012) assumed that a decrease in CO_2 emission after the application of biochar was due to the sorption of part of the soil organic matter on the biochar that rendered it unavailable for decomposition. According to Felber et al. (2014), the main reason for the observed reduction in CO_2 emissions after biochar application was the reduced microbial availability of C.

Table 2.6: Characteristics of biochars and their effect on CO_2 emissions – average from the literature review

Parameter	T	Surface Area	Bulk density	C	N	O	C/N	O/C molar	Ash	pH
Unit	°C	$m^2\ g^{-1}$	$g\ cm^{-3}$	%	%	%			%	
Decreased emissions										
Average	580	77	0.50	65.4	1.42	0.70	102	0.01	27.8	9.0
Standard deviation	166	62	0.64	15.2	1.28	---	98	---	11.2	1.0
Nb biochars [1]	14	6	6	14	14	1	14	1	4	13
No effect on emissions										
Average	551	110	0.34	61.4	1.34	15.14	135	0.22	17.7	8.8
Standard deviation	147	102	0.21	18.5	1.40	11.35	134	0.21	16.6	1.4
Nb biochars	38	14	8	38	37	6	37	6	20	37
Increased emissions										
Average	507	41	0.20	62.1	0.82	8.65	152	0.12	14.9	8.5
Standard deviation	89	59	0.03	18.3	0.73	7.67	129	0.10	15.1	1.7
Nb biochars	17	7	3	17	17	6	17	6	13	16

[1] Number of biochars for which the characteristic was available.

Table 2.7: Effect of soil biochar amendment on CO_2 emissions – Data compilation from the literature review

		Decrease		No effect		Increase	
		Nb biochars[1]	% [2]	Nb biochar	%	Nb biochar	%
HTT[3] (°C)	≤ 400	2	14	6	16	3	18
	401 - 500	3	21	10	26	5	29
	501 - 600	4	29	13	34	9	53
	> 600	5	36	9	24	0	0
	Total	14	100	38	100	17	100
Surface area (m^2 g^{-1})	< 10	1	17	3	21	4	57
	10 - 100	3	50	5	36	1	14
	> 100	2	33	6	43	2	29
	Total	6	100	14	100	7	100
C/N ratio	≤ 10	0	0	3	8	0	0
	10 - 30	4	28	6	16	3	18
	30 - 100	5	36	12	32	5	29
	> 100	5	36	16	43	9	53
	Total	14	100	37	100	17	100
O/C ratio	< 0.2	1	100	3	50	4	67
	> 0.2	0	0	3	50	2	33
	Total	1	100	6	100	6	100
pH	> 9	8	62	21	57	9	56
	7 - 9	5	38	12	32	4	25
	< 7	0	0	4	11	3	19
	Total	13	100	37	100	16	100
Feedstock type	Residue	3	21	13	35	4	24
	Wood	6	43	8	22	10	59
	Manure	2	14	7	19	2	12
	Waste	1	7	6	16	0	0
	Energetic crop	2	14	3	8	0	0
	Mix	0	0	0	0	1	6
	Total	14	100	37	100	17	100
Pyrolysis type	Fast pyrolysis	1	7	4	11	6	35
	Slow pyrolysis	9	64	28	74	10	59
	Activated [4]	0	0	3	8	0	0
	Gasification	0	0	3	8	1	6
	Other	4	29	0	0	0	0
	Total	14	100	38	100	17	100
Application Rate [5] (%w/w)	Low	6	32	25	46	4	15
	Intermediate	4	21	13	24	8	30
	High	9	47	16	30	15	56
	Total	19	100	54	100	27	100

[1] Number of biochars; [2] Percentage of the total number of biochars; [3] higher treatment temperature; [4] activated biochar produced either from slow or fast pyrolysis; [5] Low: < 2% or 10 t ha^{-1}, Intermediate: 2 - 4.9 % or 10 - 19 t ha^{-1}, High: > 4.9% or 19 t ha^{-1}

2.2.4.3 Mechanisms for increasing CO_2 emissions

According to many studies, the raise of CO_2 emissions following biochar addition comes directly from the biochar labile C fraction. Troy et al. (2013) reported that the increase in soil CO_2 emissions with biochar addition was most likely due to increased rates of C mineralization of the labile biochar C or through increased mineralization of the soil organic matter. In a study from Spokas et al. (2009), CO_2 emissions were increased with addition of biochar; however, this increase came from CO_2 production from the biochar alone. When CO_2 originating from the biochar was subtracted from the soil-biochar combination, biochar reduced CO_2 production for all amendment levels tested.

After 117 days of incubation, the cumulative CO_2 emissions from soil amended with the biochar produced from the slow pyrolysis of willow and swine manure digestate at 350 °C were higher as compared to the control treatment and the soils amended with biochars produced at 700 °C (Ameloot et al., 2013). Authors suggested that enhanced C mineralization of biochar amended soils may be due to (i) biochar consumption by microorganisms, to (ii) increased native SOM mineralization (priming) or to (iii) abiotic release of biochar-C. Rogovska et al. (2011) made the hypothesis that CO_2 emissions were significantly increased with biochar addition due to the decrease in soil bulk density or to inner porosity of biochar. The age of biochar can also have an impact on CO_2 emissions from soil. Spokas (2013) reported that only one fresh biochar had no significant effect on CO_2 emissions, as all other biochars significantly increased the CO_2 emissions, particularly for the weathered biochars.

2.3 Reduction of atmospheric GHG concentration through carbon removal

2.3.1 Estimation of biochar recalcitrance

During the pyrolysis process, about 50% of the C content in the raw material is retained in biochar. Contrarily to organic matter that is mostly decomposed in the first five years, biochar applied to soil is expected to remain stable for many years (Lehmann et al., 2006). According to many authors, biochar can be stable in soils from 100 up to 4000 years because of its predominantly condensed aromatic structure that is known to be highly resistant to microbial decomposition (Baldock and Smernik, 2002). Application of biochar to soil was then proposed as a novel approach to establish a significant long-term sink for atmospheric CO_2 in ecosystems (Jha et al., 2010). Globally, the potential mitigation benefit from biochar has been estimated at between 0.7 and 2.6 Gt C yr^{-1} by 2050 (Laird et al., 2009). According to Woolf et al. (2010), the production and sequestration of biomass C in the form of biochar, with co-production and utilisation of bioenergy (bio-oil and syngas) to reduce fossil fuel emissions, could help to slow climate change. The net removal of CO_2 from the atmosphere and avoiding emissions are expected to be in the order of 1.0 – 1.8 Mt CO_2e yr^{-1} at current levels of feedstock availability (Woolf et al. 2010).

Although biochar C is recalcitrant, it is not completely inert and can be slowly mineralized through biotic and abiotic processes (Enders et al., 2012). The stability of each biochar can be different depending on its characteristics. Moreover, the soil type and environmental conditions can have an impact on the stability of biochar. Based on experimental studies, some authors extrapolated residence time of biochars over long periods of time and reported that it could reach many decades. For example, Singh et al. (2012) evaluated the stability of biochar carbon in a five years incubation study under controlled conditions. The authors estimated the mean residence time (MRT) of biochar C in the reactive clay-rich soil to be from 90 to 1600 years, depending mostly on pyrolysis temperature. Major et al. (2010) measured soil respiration for two years after biochar addition to a savanna Oxisol in Colombia. Biochar was produced from old mango trees in kilns at temperatures between 400 and 600 °C for 48 hours. After two years, less than 3% of applied biochar had been respired, resulting in a calculated mean residence time of 600 years, normalized at 26 °C. Since 75% of the loss occurred during the first year, the authors expect that losses will decrease with time as the labile carbon fraction is mineralized. In a study by Knoblauch et al. (2011), rice husk biochar was added to four soil types for 2.9 years in an incubation experiment. The results indicated that between 4.4 and 8.5% of the biochar added was mineralized to CO_2 or CH_4. The authors suggested that the residence time could be several hundred if not thousands of years. In a study by Kuzyakov et al. (2014), biochar was produced by the slow pyrolysis (400 ºC, 13 h) of ryegrass that was labeled with ^{14}C to trace its decomposition to CO_2. The biochar was applied to soil and after 8.5 years of incubation under temperate conditions, the rate of biochar decomposition was calculated to be about 7×10^{-4} % d^{-1}, corresponding to decomposition of about 0.26%

per year. The mean residence time of biochar in soils in temperate climates was estimated to be about 4000 years. However, the authors suggested that more studies are needed to confirm this extrapolation of the decomposition rate obtained in the laboratory to the field conditions.

Herath et al. (2015) conducted an incubation study to investigate the evolution of CO_2 from two soils amended with either fresh corn stover or with biochars (7.18 t C ha^{-1}) produced by the slow pyrolysis of fresh corn stover at either 350 ºC or 550 ºC. After 510 days of incubation, 66% and 78% of added corn stover was mineralized in the Alfisol and Andisol, respectively. Less than 15% of the biochar amendments were mineralized. No significant difference was found between the two biochar treatments. The authors estimated that about 50% of biochar C will remain after 100 years. Zavalloni et al. (2011) also evaluated the stability of biochar when added to soil alone or in combination with crop residues in an 84-days incubation study. Biochar was produced by the pyrolysis of hardwood at 500 ºC. 56% of the added wheat straw C was decomposed while only 2.8% of the added biochar C was respired.

Harvey et al. (2012) proposed a new recalcitrance index for assessing biochar quality for carbon sequestration. The index, called the R_{50}, uses the energy required for thermal oxidation of the biochar as a measure of recalcitrance. The equation 2.1 is as shown below:

$$R_{50,\, x} = T_{50,\text{biochar}}/T_{50,\text{graphite}}, \qquad (2.1)$$

where $T_{50,\text{biochar}}$ and $T_{50,\text{graphite}}$ are the temperature values corresponding to 50% oxidation/volatilization of biochar and graphite, respectively. Those values are obtained directly from thermogravimetric analysis thermograms that have been corrected for water and ash content. Biochars with $R_{50} \geq 0.70$ would be the most recalcitrant (comparable to graphite), while biochar with $R_{50} \leq 0.50$ are the least recalcitrant, having a sequestration potential comparable to uncharred plants.

2.3.2 Biochar characteristics indicators of carbon stability

According to Manyà et al. (2014), variables that are considered as key indicators of the potential stability of biochar in soils are: the fixed-carbon (FC) yield, the fraction of aromatic carbon, and the molar H/C and O/C ratios. The ratio of FC to (FC + volatile matter (VM)) could also be indicative of the carbon stability. Higher CO_2 emissions from biochar can be related to higher content of VM and consequent lower values of the FC/(FC+VM) ratio. According to Zimmerman (2010), VM content is the most convenient method for estimating biochar C longevity. The FC ultimately shows how effectively the biochar behaves as carbon negative from the environment point of view. The more the amount of FC, higher it will be effective as a climate change mitigation tool. Also, the highest R_{50} values were observed in biochars with the highest carbon contents. Harvey et al. (2012) also indicated that the highest R_{50} values (the highest recalcitrance potential) are observed in biochars with the highest C contents.

Spokas et al. (2010) reported that O/C molar ratio could provide a reliable indicator of the stability of biochar. It has been recommended that biochars with O/C ratio < 0.4 and H/C ratio < 0.6 are best suited for soil application as a method for sequestering C (Schimmelpfennig and Glaser, 2012). Enders et al. (2012) also proposed to use a combination of VM, and O/C_{org} or H/C_{org} ratios to classify the stability of biochars. According to the authors, biochar with a VM content above 80% ($w/w_{\text{biochar ash-free mass}}$) may indicate biochars with no C sequestration potential; a VM content below 80% ($w/w_{\text{biochar ash-free mass}}$) and an O/C_{org} ratio above 0.2 or H/C_{org} above 0.4 may indicate moderate sequestration potential; and a VM content below 80% ($w/w_{\text{biochar ash-free mass}}$) and an O/C_{org} ratio below 0.2 or H/C_{org} below 0.4 may indicate high C sequestration potential.

Bai et al. (2014) determined the biodegradation of nine biochars with large potential to increase C sequestration in two soils. The results confirmed a strong linear correlation between the biodegradation of biochar ($^{13}C_{loss}$) within periods of 115 incubation days and the O/C molar ratio of biochars ($R^2 = 0.788$), and a weaker correlation with the H/C ratio ($R^2 = 0.707$). According to Sigua et al. (2014), the C/N ratio of biochar has the most important impact on C mineralization. Based on the results of their study, the authors concluded that biochar with a low C/N ratio may result in rapid mineralization. Moreover, they made the hypothesis that biochar consisting of smaller particulate materials are more readily degraded than those with larger particles. Similarly, Bruun et al. (2012) indicated that the fine particle size of biochar produced by fast pyrolysis makes it more susceptible to microbial attack than biochar with large sized particles produced by slow pyrolysis.

2.3.3 Production parameters influencing biochar stability

As seen in the previous section, some biochar characteristics (O/C, H/C and C/N ratios, extractable C, VM content) appear to have an influence on biochar recalcitrance. However, these biochar characteristics are influenced by pyrolysis conditions as well as feedstock. A decrease in the O/C, H/C, (O+N)/C, and (O+N+S)/C ratios is associated with an increased pyrolysis temperature (Al-Wabel et al., 2013). This suggests that biochar pyrolyzed at higher temperature may possess a higher C sequestration potential when applied to the soil in comparison to that obtained at lower temperatures. Following a thermogravimetric analysis (TGA), Y. Sun et al. (2014) also concluded that higher temperatures produced higher thermal stable biochars. Junna et al. (2014) found that the cumulative C mineralization decreased as the charring temperature increased from 300 to 600 ºC. They proposed that this is due to a decrease in the labile organic C content from 133 mg g^{-1} for biochar produced at 300 ºC to 68 mg g^{-1} for biochar produced at 600 ºC.

Lai et al. (2013) examined in pot experiments over 145 days the effects of biochar application on crop growth and yield, as well as on soil C sequestration and GHG emissions from soils. A lower H/C ratio in the biochar produced at 700 ºC (0.37) compared to biochar produced at 290 ºC (1.16) indicated that the biochar produced at a higher temperature had higher stability in soil. In a study by Luo et al. (2011), biochars were produced by the slow pyrolysis of miscanthus at 350 ºC and 700 ºC. The authors indicated that the biochar produced at the higher temperature had a more aromatic structure with higher aromatic C content and a higher C/N ratio, which would result in greater chemical recalcitrance and stability.

Harvey et al. (2012) found that pyrolysis conditions are the primary factors controlling thermal stability of the resulting biochar. The correlation between R_{50} and pyrolysis temperature was significant: the R_{50} increased with temperature. In fact, the less recalcitrant biochars were all produced at low temperatures (200 or 400 ºC), while the more recalcitrant biochars were produced at higher temperatures (525 or 650 ºC).

In a study by Cely et al. (2014), three different biochars were studied for their influence on soil properties and CO_2 emissions. Biochar produced by the slow pyrolysis of wood at 620 ºC was a very recalcitrant carbon material, with a FC/(FC + VM) ratio of 0.84, compared to biochar produced from paper sludge and wheat husks at 500 ºC (ratio = 0.66) and sewage sludge biochar produced at 600 ºC (ratio = 0.48).

McBeath et al. (2014) demonstrated that the combination of feedstock composition and pyrolysis temperatures influenced the composition of aromatic domains in biochars, which is related to their recalcitrance. For example, Zimmerman et al. (2011) and J. Wang et al. (2016) reported that biochars made from residues of crops grasses generally degraded faster than those made of hard woods due to their different lignin contents. Using the R_{50} method of Harvey et al. (2012), Windeatt et al. (2014) evaluated the recalcitrance of biochars made from the slow pyrolysis of eight crop residues at 600 ºC. Biochar made from palm shell (biomass with the highest typical lignin content) would be the most resistant to degradation with a R_{50} of 0.60, and biochar made from wheat straw (the lowest typical lignin content) would be the least resistant with a R_{50} of 0.45.

According to a study from Zhao et al. (2013), biochar recalcitrance (i.e. its ability to resist to decomposition) is mainly determined by pyrolysis temperature, while the potential total C sequestration (product recalcitrance combined with pyrolysis carbon yield) depends more on feedstock. Singh et al. (2012) concluded that biochars produced by slow pyrolysis at high temperature (550 ºC) are particularly stable, but even at low temperatures (e.g. 400 ºC), plant and manure-based biochars are likely to have a mean residence time (MRT) in the range of a few centuries.

2.3.4 Effect of environmental factors on biochar stability

While Harvey et al. (2012) found that some characteristics of the biochar are related to its environmental recalcitrance, both biochar properties and soil conditions (temperature, moisture, pH, mineralogy, and organic matter content) should be considered. The results presented by Bai et al. (2014) suggested that the properties of biochar are of equal importance as the environmental factors for its degradation in soils.

As an example, Sigua et al. (2014) studied the CO_2-C mineralization in two Ultisols amended with different feedstock sources (poultry litter, swine solids, switchgrass, and pine chips) and sizes (< 2 mm, < 0.42 mm) of biochars produced by slow pyrolysis at 350 ºC. They found that biochar may be more stable in well-drained sandy soils with lower SOC and TN contents than a poorly drained organic matter enriched sandy soil, and concluded that stability of biochar vary by soil types and conditions. Soils with high clay content would have a greater ability to stabilise biochar C (Keith et al., 2015; J. Wang et al., 2016). Fang et al. (2015) reported lower mineralisation of biochar produced by the slow pyrolysis of woody biomass in sandy clay loam or clayey soils than in sandy soils at 20 ºC, suggesting that clay could stabilize biochar-C via ligand exchange, cation bridging, and van der Waals' interactions. Temperature is another important factor affecting biochar stability. Fang et al. (2015) estimated that biochar can be stable over a few centuries in soil with a mean annual temperature of 20 ºC. However, at elevated temperatures (40 ºC and more), biochar produced at lower temperature (e.g. 450 ºC) may degrade over a decadal scale. This was explained by increased microbial activity and co-metabolism with the increase in temperature. According to Luo et al. (2011), more biochar C is mineralized in a soil with high pH than with low pH. The authors reported that the cumulative amount of C mineralized from biochar (350 ºC) in low pH (0.66%) and high pH (0.81%) soils were similar to the amount of water extractable C.

2.3.5 Biochar priming effect

"Priming effect" can be defined as the alteration in the mineralization of soil organic matter due to the addition of substrates, and has been observed in many studies with the addition of biochar to soil (Cely et al., 2014). Biochar properties, soil type and conditions, and the period over which measurements are made can strongly influence the priming effect (Zimmerman et al., 2011; J. Wang et al., 2016). A combination of different biochar characteristics such as ash content and FC to VM ratio may have an impact on priming (Cely et al., 2014). Moreover, soils with low levels of decomposable organic C and low mineral N can slow down the decomposition of soil organic matter resulting in a negative priming response, i.e. a reduced C mineralisation (Keith et al., 2015).

Different studies reported either an increase or decrease in mineralisation of native soil organic carbon following biochar amendment (Fang et al., 2015). The different conclusions are probably due to the different biochars, soil types, and time durations used in these studies (Keith et al., 2015). For example, Luo et al. (2011) quantified the changes in the rate of soil organic C mineralisation following addition of two wood biochars to four soils at 20, 40 and 60 ºC in a 180 days incubation study. They found that biochar produced at low temperature (350 ºC) caused a large positive priming effect, while biochar produced at high temperature (700 ºC) caused a relatively small positive priming effect, due to the very limited amount of available C.

Following a meta-analysis, J. Wang et al., (2016) reported that biochar addition generally contributes to negative priming. In a study by Cross and Sohi (2011), in which 11 biochars were amended to a silty-clay loam with three levels of organic matter and incubated at 30 ºC for two weeks, the authors reported that there was no evidence for priming of soil organic matter, suggesting that biochar could stabilise native soil organic carbon. Keith et al. (2015) proposed that the decrease of the priming effect with biochar may be due to the sorption or interaction of the soil organic C with biochar surface and the sorption of plant root exudates onto the biochar surface. Thus, biochars produced at a higher pyrolysis temperature could minimize the priming effect because they have higher surface areas and are good adsorbents (Keith et al., 2015).

2.4 Summary

To the knowledge of the authors, this is the first review article to identify the key biochar properties and environmental parameters having an impact on both soil GHG emissions and C sequestration, and to discuss the potential mechanisms involved. The chemical composition of biochar was found to have a major impact on soil GHG emissions following biochar amendment, and particularly on N_2O emissions. Biochars with lower N contents, and consequently higher C/N ratios, are more suitable for N_2O emissions mitigation. In fact, based on the results from the literature review, 84% and 79% of the biochars that decreased or had no effect on N_2O emissions, respectively, have a C/N ratio higher than 30, while 3 out of 6 biochars that contributed to an increase of N_2O emissions had a C/N ratio lower than 30. There is a tendency for biochars with higher ash content to be less efficient in mitigating soil N_2O emissions. Biochar produced from wood having low N and ash contents could be more suitable for decreasing N_2O emissions from the soil, as compared to manure or agricultural biomass feedstocks. The effect of biochar amendment on soil pH could also be a cause for reducing N_2O emissions. However, depending on soil pH and biochar application rate, the effect of biochar pH on soil could be non-significant. In fact, biochar application rate is an important factor influencing GHG emissions.

According to Aguilar-Chávez et al. (2012), biochars resulting in a significant decrease of N_2O emissions were generally applied to soil at higher rates, which also resulted in a significant rise in CH_4 emissions (Zhang et al., 2010). The porous structure of biochar is relevant to its ability to reduce soil GHG emissions. However, based on the results of this literature review, the BET surface area does not seem to be a key parameter for choosing a biochar for mitigating GHG emissions. In fact, because of the different distribution of microporosity and macroporosity in biochar, it is difficult to make a relation between the biochar surface area and porosity.

Some studies reported an increase in CO_2 and CH_4 emissions following biochar addition to soil which could be caused by the labile C fraction of the biochar, which is directly linked to the recalcitrance of the biochar. However, most of the studies reported no effect on CO_2 and CH_4 emissions, as the soil and environmental factors have a higher impact on these emissions. The chemical composition of the biochar has an important impact on the potential for C sequestration. Variables considered to be key indicators of the potential stability of biochar in soils are: the VM content, FC yield, the fraction of aromatic C, and the molar ratios of H/C and O/C. Biochars with an O/C_{org} ratio less than 0.2, H/C_{org} ratio below 0.7 and VM content below 80% may indicate high potential for C sequestration. Biochar produced at high temperatures may possess a higher potential for C sequestration when applied to the soil as compared to that obtained at low temperatures.

Since biochar characteristics are influenced by feedstock and pyrolysis conditions (e.g. treatment temperature and residence time), it is important to define these parameters to obtain a biochar with the desired characteristics for a specific application (e.g. climate change mitigation). While it is well documented that biochar yield decreases with increasing temperature, less attention has been paid to the associated changes in biochar properties (Lehmann and Joseph, 2009). For this reason, it is important to carry out pyrolysis tests with different feedstock at different pyrolysis conditions, and to determine the characteristics of the resulting biochar. Further work is needed to identify the combination of feedstock and pyrolysis conditions that would provide the most appropriate properties for biochar as a soil amendment for a desired purpose, including mitigation of climate change (Kookana et al., 2011).

In addition to biochar characteristics, the effect on GHG emissions from biochar amended soils can be influenced by the local soil conditions, as soil type and soil water content, agricultural management activities and climate. However, most of the research studies were performed in laboratory using high biochar application rates (Angst et al., 2014). Future research studies are then necessary to better understand the mechanisms and interactions among plants, soils, microbes and climate, as well as their impact on GHG emissions. Moreover, research should be focused on the effects of specific types of biochar on emissions from specific soils to further identify the exact mechanisms responsible of a change in N_2O emissions (Wang et al., 2013).

In addition to C sequestration and decrease of GHG emissions from soil following biochar amendment, there are several other ways by which biochar can offset emissions and can indirectly contribute to climate change mitigation. First, using vegetal residues as pyrolysis feedstock is a sustainable way to manage these residues and can help to avoid important emission of CH_4 and CO_2 produced by decomposition of the organic matter. Because biochar is expected to increase soil fertility, its use could reduce the need for chemical fertilizers. Chemical fertilizers production and application to fields can emit large quantities of GHG, thus by reducing the need for chemical fertilizers would result in a net gain in the GHG balance. Also by increasing crop yields, more C can be captured in plants. Finally, the co-products of pyrolysis (syngas and bio-oil) can be used as renewable energy sources, replacing fossil fuels.

Despite the numerous advantages of biochar, there are limitations to its production on a large scale. In most countries, biochar is still considered as a waste of a combustion process, thus limiting opportunities for its exploitation since it is not economically valuable. The financial viability of biochar production is often reported as an important issue. According to Galinato et al. (2011), biochar application to soil can be economically feasible if a carbon market exists that recognizes the value in avoiding GHG emissions and in sequestering C due to the application of biochar to agricultural soils. Moreover, the market price of biochar should be low enough so that farmers will earn a profit after applying biochar to the crop field. Biochar production and application to soil with the valorisation of energetic co-products (bio-oil and syngas) could then be an economically viable option and a great environmental management solution for local biomass, including dedicated energy crops, vegetal residues and excess manure.

Connecting text

Many pyrolysis technologies exist and the choice of a pyrolysis technology over others will often depend on final products targeted. For example, when high yields of bio-oil are desired, fluidized bed pyrolysis reactors, recirculating bed reactors, ablative and cone reactors are generally used. Fixed bed reactors are generally used to produce high yields of biochar. Finally, auger reactor is an intermediate pyrolysis technology that can be used successfully for the production of large quantities of both biochar and bio-oil.

The auger pyrolysis reactor was selected to achieve the objectives of this thesis because of its simplicity to operate, its mobility and its low requirement of carrier gas and energy. Moreover, the operating parameters can be controlled easily in order to obtain biochar with the desired properties. Thus, the following review of literature was carried out to identify and to list the characteristics of the pyrolysis auger reactors used in the literature. The second objective of this thesis, which is to identify the operating parameters of auger reactors which have the most influence on biochar yield and its properties, and to identify their optimal range of operation, was achieved.

Chapter 3. Review of literature (Part 2) – Pyrolysis in auger reactors for biochar and bio-oil production

Abstract

Pyrolysis is the thermochemical decomposition of biomass under oxygen-limiting conditions used for biochar and bio-oil production. Depending on biomass feedstock, pyrolysis technology and operating parameters, product yields and properties will differ. Among the available pyrolysis units, auger pyrolysis is a polyvalent and promising technology for producing both bio-oil and biochar. These reactors are simple to operate and can be mobile, they require little or no carrier gas and low energy. Moreover, the operating parameters can be controlled easily in order to obtain the desired products. Recently, many research articles on biomass pyrolysis in auger reactors have been published. Design of laboratory-scale pyrolysis units and operating parameters differ considerably. Therefore, there was a need to list the studies in which auger pyrolysis reactors are used and to collect data for experimental operating parameters and product yields. The type and the capacity of the reactor, pyrolysis temperature, solid residence time, carrier gas flowrate, vapors residence time, and biomass feedstock type and size were identified as the parameters having the most influence on product yields and their properties. Because each pyrolysis reactor is unique, it is important to establish the relationship between operating parameters and product yields and their properties for each biomass feedstock. Future work is needed in order to provide simple solutions to scale-up laboratory-scale auger pyrolysis units to industrial size.

Key words: Pyrolysis; auger reactor; biochar; bio-oil

3.1 Introduction

3.1.1 Pyrolysis and products use

Pyrolysis can be defined as the thermal decomposition of biomass at high temperatures under oxygen-limiting conditions. In the early development of pyrolysis, biochar production was the main objective of wood carbonization. It is at the end of the eighteenth century that technologies were developed for the recovery and utilization of the volatile compounds including non-condensable and condensed gases, called later bio-oil

(Garcia-Perez et al., 2010). Biomass feedstock, pyrolysis technology and operating parameters determine the proportions and characteristics of each product. For example, a slow pyrolysis (i.e. a long exposition to heat from minutes to hours) at temperatures < 450 °C favours the production of biochar. Fast pyrolysis (i.e. a short reaction time of a few seconds) at high pyrolysis temperature (≈ 500 °C) favours the production of bio-oil (Bridgwater, 2011).

Biomass pyrolysis could be a sustainable management solution for the agricultural and forest residues that would otherwise decompose and emit large quantities of GHG. The produced biochar applied to soil will have capabilities to improve its properties and thus increase crop yields (Kammann et al., 2012; Tang et al., 2013). Depending on its properties, biochar can also be used in soils to adsorb both organic and inorganic contaminants (Xie et al., 2015), heavy metals (Uchimiya et al., 2011) and pesticides (Cabrera et al., 2014). Also, biochar can be used as a negative emission technology (NET) to sequester C in soil (Smith, 2016) and to reduce GHG emissions (Brassard et al., 2016). Further, when the produced bio-oil has a water content lower than 30% (w/w) and a higher heating value (HHV) higher than 15 MJ kg^{-1} (ASTM, 2009), it could be used as a fuel source, for example, to replace no. 2 oil in heating systems. Bio-oil can also be used for transport related applications. However, in this case, bio-oil has to be upgraded to reduce its water and oxygen contents. The latter can reach 40% (Ren et al., 2017) and can be reduced through deoxygenation processes commonly used in the petrochemical industry (Brown, 2009). Moreover, the aqueous phase of bio-oil contains a multitude of value-added chemicals, such as levoglucosan and organic acids, that can be extracted and valorised (Ren et al., 2017). Finally, non-condensable gases are often used to provide heat as part of the pyrolysis process, thus making the technology independent of external energy sources.

3.1.2 Pyrolysis technologies

The choice of a pyrolysis technology over others will often depend on final products targeted (biochar, bio-oil or syngas). Fixed bed reactors through slow pyrolysis are generally simpler to conceive and are used since many years for charcoal production. For example, the use of kilns made of earth or metal is a traditional method for biochar production. Biomass is piled and heated in the airtight kiln for many hours. Other techniques based on slow pyrolysis process include retorts and convertors for processing wood logs or wood chips (Garcia-Perez et al., 2010).

Fluidized bed pyrolysis reactors are the most documented and commercially available reactor types among all fast pyrolysis technologies and are used to produce high quality bio-oil with yields around 70-75% (Verma et al., 2012). In these reactors, a hydrodynamically stable bed of smaller size biomass particles (0.5-2 mm) is maintained using an inert fluidizing gas such as nitrogen (N_2). Similarly, recirculating bed reactors are used to achieve fast pyrolysis but have a lower heat transfer due to higher gas velocities via recirculation/reflux (Verma et al., 2012).

Ablative and cone reactors can also be used for bio-oil production through fast pyrolysis and involve the thermal erosion of biomass that come into contact with a hot surface. In a rotating cone pyrolyzer, biomass is poured on a high-speed rotating cone along with hot sand in the absence of oxygen (Verma et al., 2012). In an ablative reactor, a high relative motion is achieved between the biomass particle and the hot reactor wall (Bahng et al., 2009).

Microwave pyrolysis has been applied to various lignocellulosic feedstocks in research studies (Huang et al., 2016). Contrary to conventional heating methods, microwave heats the biomass particles from within and not by external heat transfer (Bridgwater, 2011). Gas and solid yields are higher than in conventional pyrolysis, but liquid yield is lower (Huang et al., 2016).

Finally, auger reactor is an intermediate pyrolysis technology that can be used successfully for the production of large quantities of both biochar and bio-oil (Garcia-Perez et al., 2010). Pyrolysis can be performed by changing the operating conditions for varying yields and desired characteristics in the products.

3.1.3 Objectives

Pyrolysis auger reactor exists as one of the most attractive designs developed today (Garcia-Perez et al., 2010) and hence this review of literature aims to list and to describe the auger pyrolysis reactors that are used to produce biochar and bio-oil, mainly at a laboratory and pilot scales. The operational parameters used in each study and the products yield obtained will be compiled. The second objective is to identify the operating parameters of auger reactors which have the most influence on products yields and their properties, and to identify their optimal range of operation.

3.2 Methodology

During the recent years, many research studies have been carried out with a variety of auger pyrolysis reactors. Different design configurations were evaluated on a laboratory or pilot scale and the impact of pyrolysis operating conditions on product yields was studied. In order to achieve the objectives of this review, a systematic literature analysis was carried out. Databases including Springer link, ASABE (American Society of Agricultural and Biological Engineers) technical expertise database, Agricola, ScienceDirect, and Google Scholar were consulted. Keywords used were "pyrolysis" along with "reactor", "auger", "screw", "pilot-scale" or "laboratory-scale". Peer-review articles and thesis published between 2006 and 2016 in which auger reactor was used to perform pyrolysis tests were retained. In section 3.3.2, all auger reactors found in the literature and used to carry out research study are described and operating parameters and product yields obtained from the pyrolysis experiments are given. Pyrolysis auger reactors are classified into four categories: single screw laboratory-scale reactor with a small capacity (< 1 kg h^{-1}), single screw laboratory-scale reactors with a large capacity or pilot-scale (1 to 15 kg h^{-1}), single screw industrial-scale reactors (> 15 kg h^{-1}) and twin-screw reactors. A summary of key characteristics of the auger units is presented in Table 3.1 and the experimental data (operating parameters and product yields) of pyrolysis experiments are summarized in Table 3.2. In the cases where many pyrolysis tests are carried out, only those that resulted in the optimal bio-oil and biochar yields are presented.

Table 3.1: Description of auger pyrolysis reactors

Reactor	**Reactor characteristics**		**Typical operational conditions**				**References**
#	**Diameter (D) or Cross section (W x H), mm**	**Length (m)**	**Rotation speed (rpm)**	**Solid heat carrier**	**Gas carrier**	**Mass flow rate (kg h^{-1})**	
Single screw : Small capacity laboratory-scale reactors (< 1 kg h^{-1})							
1	26	0.5	12	--	N_2	0.35	Yu et al., 2016
2	--	--	--	--	N_2	0.039	Solar et al., 2016
3	--	--	17	--	N_2	0.47	Le Roux et al., 2015
4	50	0.9	1	--	N_2	0.5	Liang et al., 2015
5	100	0.585	2.2 - 13	--	N_2	0.6 - 1.5	Garcia-Perez et al., 2007
Single screw : Large capacity laboratory-scale or pilot-scale reactors (1 – 15 kg h^{-1})							
6	--	--	2	Steel shots	--	≈ 1 (20 kg d^{-1})	Schnitzer et al., 2007
7	76	1.02	12	--	No	1.0 – 2.5	Ingram et al., 2008
8	25.4	0.3	--	No / sand	N_2	3.5 - 15	Aylón et al., 2008
9	76	2.50 (1 m heated)	10-100	--	N_2	5.0	Kim et al., 2011
10	150	2.0	--	--	N_2	2.0 – 4.0	Morgano et al., 2015
11	195	2.0	1 - 14	--	--	1.4 – 1.9	Ferreira et al., 2015
Single screw : Industrial-scale reactors (> 15 kg h^{-1})							
12	--	--	--	Steel shots	--	≈ 40 (1 t d^{-1})	Azargohar et al., 2013
13	--	2.4	5	--	Helium	25.0	Bosong et al., 2014
Twin-screw reactors							
14	63.5 x 38.1	0.559	45 - 63	Steel shot	N_2	1.0	Brown & Brown, 2012
15	44	0.45	9	Sand	N_2	0.38-0.40	Sirijanusorn et al., 2013
16	--	2.30	--	--	N_2	1.33 – 4.0	Agirre et al., 2013
17	200	1.80	7	Biochar	N_2	5.0 – 6.0	Yang et al., 2014
18	100 x 100	2.50 (2.0 m heated)	--	--	N_2	10.0	Kim et al., 2014
19	40	1.50	120	Sand - steel	N_2	10.0 – 15.0	Raffelt et al., 2006

Table 3.2: Experiments carried out with an auger pyrolysis reactor: operating parameters and product yields

Reactor	**Feedstock**		**Carriers**		**Pyrolysis conditions**		**Product yields**			**References**
#	**Type**	**Diameter / size (mm)**	**Solid carrier**	**Gas Carrier (L min^{-1})**	**T (°C)**	**Solid residence time (s)**	**Pyrolysis oil % (w/w)**	**Solid Char % (w/w)**	**Syngas % (w/w)**	
1	Rice Husk	< 10	No	--	500	60	51	32	16	Yu et al., 2016
	Corn stalk						54	27	19	
2	Pine	0.5 – 2	No	--	900	1920	9.7	21	69.3	Solar et al., 2016
						3840	5.8	19.3	74.9	
3	Aspen Wood	< 2	No	3.6	450	210	56.1	19.8	24.1	Le Roux et al., 2015
4	Potato peel	< 1	No	6	450	8	22.7	30.5	--	Liang et al., 2015
	Hybrid Poplar						40.1	15.2		
5	Pine pellets	6.46 x 12.8	No	3	500	354	57.8	30	12.2	Garcia-Perez et al., 2007
	Douglas fir wood	< 2	No	20	320	60	59	18	23	Liaw et al., 2012
6	Chicken manure	--	Steel shot	--	330	--	50	27	23	Schnitzer et al., 2007
7	Oak wood	2-4	No	--	450	30	49.6 -56.3	17.5 -19.9	--	Ingram et al., 2008
	Pine Wood						48.7 -55.2	17.5 -19.8	--	
	Oak bark						43.8 -49.8	21.3 -27.8	--	
	Pine bark						42.8 -44.2	9.7 -23.2	-	
7	Pine wood	2-3	No	--	450	55	50.1	19.1	30.8	Bhattacharya et al., 2009
	Wood/HDPE (50:50)				450		38.9	25.9	35.2	
					525		9.1	11.9	79	
7	Corn stalks	0.5 – 5	No	34	400	55	35	29	13.5	Pittman et al., 2012
				--	450		35	23.5	32	
8	Tire rubber shred	2	No	1.2	600	---	43.2	38	17.1	Aylón et al., 2008
8	Tire rubber shred	5	No	0.19	600	222	41.5	40.6	17.9	Aylón et al., 2010
					700		31.3	39	29.7	
					800		27.5	41	31.5	
8	Pine	20	No	5	500	180	57	26	18	Puy et al., 2011
						90	45	41.5	15	
						300	56.5	26.4	19	
					800	300	36.6	19	44.4	

8	Waste tires	2 – 4	No	5	550	180	42.6	40.5	16.9	Martínez et al., 2013
8	Pine	< 15	Sand	5	450	420	49	26	26.5	Veses et al., 2014
8	Pine	< 15	Sand	5	400	420	41	36	23	Veses et al., 2015
					450		49	26	25	
					500		50	21	26	
9	Pine wood	< 0.85	No	10	450	30	--	26.6	--	Kim et al., 2011
					600			15.2		
					800			9,5		
	Switchgrass	4			450			31.3		
					600			16.9		
					800			11.4		
10	Beech wood	2 - 4.5	No	14	350	600	42.9	31.5	12.5	Morgano et al., 2015
					400		37.2	24.4	15.7	
					450		48.8	20.6	23.4	
					500		39.8	18	31.6	
11	MDF	< 0.21	No	--	450	2040	25	39.7	--	Ferreira et al., 2015
						900	27	30.5		
						540	26	24.9		
					600	2040	40	17.3		
						900	26	19		
						540	23.9	25.5		
	Wheat straw	0.42 - 3.36	Steel shot	--	400	900	9.2	--	--	Azargohar et al., 2013
	Saw dust						28.0	--	--	
	Flax straw						34.8	--	--	
	Poultry manure						26.8	--	--	
12	Wheat straw				475	900	19.2	--	--	
	Saw dust						52	--	--	
	Flax straw						41.9	--	--	
12	Poultry manure						30.8	--	--	
	Wheat straw				550	900	43.5	--	--	
	Saw dust						44.5	--	--	
	Flax straw						28.7	--	--	
	Poultry manure						48.0	--	--	
13	Pine wood	< 1	No	0.025	400	480	30.2	45.1	24.7	Bosong et al., 2014

					500		34	30.3	35.7	
					600		33.1	25.2	41.7	
14	Red oak	< 0.75	Steel shot	2.5	625	11	73.6	11	12.9	Brown & Brown, 2012
					425	11	42.2	35.7	22.1	
15	Cassava rhizome	0.25 – 0.425	Silica sand	7	500	--	40	22	38	Sirijanusorn et al., 2013
					550		50	23	27	
					650		44	13	43	
		< 0.25		7	650		27	20	53	
		0.25 –0.425					42	6	50	
		0.425 – 0.6					38	15	46	
16	Fruits cutting	< 8	No	--	900	7,200	--	22	--	Agirre et al., 2013
		10 - 20					--	22.8	--	
		< 5					--	21.3	--	
17	Wood pellets	--	Char	--	450	90	54.3	28.5	17.7	Yang et al., 2014
	Barley straw						49	30.1	20.9	
18	Pine	< 4	--	20	500	72	59.8	22.6	17.6	Kim et al., 2014
					525		55.2	23.2	21.5	
					550		53.6	17.5	28.9	
19	Wood sawdust	--	Sand	--	500	35	70	16	15	Raffelt et al., 2006
	Wheat straw	--	--	--			52.5	27.5	20	
19	Corn Stover	< 5	Steel balls	--	500	13	43.5	20.8	28.8	Tröger et al., 2013
	Rape Stalks						37.2	28.8	32.4	
	Sunflower Stalk						31.1	31.4	30.9	
	Wheat straw						43.9	23.7	24.8	
	Softwood						64	13.9	20.3	
19	Eucalyptus	<5	Steel	--	500	13	67.5	16.5	15.8	Joubert et al., 2015

3.3 Auger pyrolysis reactors

3.3.1 General description

Auger pyrolysis reactors are getting increased attention from many small and mid-size industries (Verma et al., 2012). The technology enjoys some popularity because of its simplicity of construction and operation (Resende, 2014). In an auger reactor, biomass is continuously fed to a single or twin-screw, and then the auger rotation moves the product along the axis until the end of the heating zone. As biomass decomposes, gases and organic volatiles leave the reactor and the biochar is collected at the bottom. Auger pyrolysis reactors are simple to operate, require little or no carrier gas and consume lower energy. Moreover, one advantage of auger reactors is that the residence time of biomass in the heated zone can be controlled easily by varying the rotation speed of the screw or the flight-pitch.

The yield of bio-oil in auger reactors is variable and depends on operating conditions, but it is typically in the range of 40 to 60% of the feedstock, which is lower than what is achieved normally with fluidized-bed reactors. Vapors residence time is much longer in auger reactors than in fluidized bed reactors, and hence increases the likelihood of secondary reactions and consequently increases the yield of char in detriment to the yield of bio-oil (Resende, 2014). Thus, gas exit ports may also be provided along the auger reactor wall in order to decrease the vapor residence time.

Heat transfer at large scales may be a problem in auger reactors (Bahng et al., 2009; Kan et al., 2016). However, it can be successful for very small-diameter reactor tubes which have limited distance between inner reactor tube surface and the internal auger shaft (Steele and Mitchell, 2012). In order to increase heating rate and to achieve fast pyrolysis for bio-oil production, some auger reactors combine a small inert solid particulate heat carrier (usually hot sand or steel shot) with relatively small particles of biomass (1 to 5 mm). Another problem that can occur with auger reactors is the difficulty to scale-up the experimental units to industrial size. In fact, Funke et al. (2017) reported that there is no simple scaling-up strategy for fast pyrolysis technology.

3.3.2 Description of auger pyrolysis reactors in the literature

3.3.2.1 Single screw - small capacity laboratory-scale reactors (< 1.0 kg h^{-1})

Yu et al. (2016) carried out pyrolysis test in a stainless-steel bench-scale auger system designed and constructed at the Bioenergy Research Institute (Aston University, U.K.). The reactor has a low capacity of 350 g h^{-1}, is compact (26 mm in diameter and 0.5 m in length) and does not use a heat carrier. The condensation system consists of one cool water condenser, two dry ice condensers, and a cotton filter. Pyrolysis of rice husks and corn stalk was performed at a constant feeding rate of 2 g min^{-1} and at temperatures of 350, 400, 450, 500, 550, and 600 °C with a solid residence time of 60 s. The atmosphere in the reactor was purged with N_2. The maximum bio-oil yield was obtained at 500 °C for both feedstocks (51% for rice husk and 54% for corn stalk). Biochar yield decreased from 46% at 350 °C to 31% at 600 °C for rice husk and from 38% at 350 °C to 27% at 600 °C for corn stalk.

Solar et al. (2016) designed and constructed a laboratory scale continuous pyrolysis plant at the University of Basque Country (Spain). The pyrolysis reactor is an externally heated tubular auger reactor split into four individual heating zones. Vapors that exit the reactor are treated at 900 °C in order to enhance gas yields and quality, and are condensed in a metal vessel kept at 1 °C. Slow pyrolysis of waste pine sieved to particle size of 0.5 – 2.0 mm was performed at a feeding rate of 0.65 g min^{-1}. Three temperature profiles were tested: 300-500-600-800 °C; 300-500-700-900 °C; 900-900-900-900 °C. Two solid residence times were also tested: 32 min (8 min in each heat zone) and 64 min (16 min in each heat zone). Biochar, bio-oil and gas yields were in the ranges of 20-30%, 6-22% and > 47%, respectively. Bio-oil and biochar yields were the lowest (5.8% and 19.3%, respectively) for the highest temperature in the four heating zones and with the longest residence time.

A lab-scale auger reactor was designed in Quebec (Canada) and is described by Le Roux et al. (2015). Heat is supplied by two external electric furnaces which cover the reactor. During each pyrolysis test, 700 g of milled wood aspen (< 2 mm) was fed into the reactor by a screw feeder and was heated at 450 °C for 210 s, corresponding to a feeding rate of 0.47 kg h^{-1}. A N_2 flow of 3.6 L min^{-1} was kept to maintain an inert atmosphere.

Pyrolysis vapors were cooled by a two condensers system, the first cooled with tap water, and the second at -10 °C. Bio-oil and biochar yield obtained were 56.1% and 19.8%, respectively.

Liang et al. (2015) developed and described a lab-scale auger reactor (tube of 50 mm diameter and 0.9 m long). Pyrolysis of potato peel waste and hybrid poplar (< 1 mm) was conducted at 450 °C and at a feed rate of 0.5 kg h^{-1}. The system was purged with N_2 (6 L min^{-1}). The auger speed was adjusted at one rpm and the residence time was 8 s. Vapors were condensed through a two-stage ice-water cooled tube and shell condensing system. Poplar pyrolysis produced bio-oil and biochar yields of 40.1% and 15.2%, respectively. Potato peel pyrolysis produced lower yield of bio-oil (22.7%) and higher yield of biochar (30.5%).

A lab-scale pyrolysis auger reactor was developed at the University of Georgia (Garcia-Perez et al., 2007). The reactor consists of a stainless-steel tube (0.1 m diameter and 0.585 m long) placed in a furnace. Pyrolysis tests to evaluate the performance of the reactor were performed at 500 °C with pine pellets (6.5 mm diameter and 12.8 mm length). Biomass was fed to the reactor with a rotary valve at 1.5 kg h^{-1}, where the auger speed was very low at 2.2 rpm, which represented a solid residence time of 5.9 min in the heated zone. A vacuum pump was used causing a slight negative pressure in the reactor (2 mm Hg) and N_2 was used as a carrier gas at a flowrate of 3 L min^{-1}. Bio-oil and biochar yields obtained were 57.8% and 30%, respectively. Liaw et al (2012) published results of experimental trials carried out with the upgraded auger reactor at the Washington State University (WSU). Douglas fir wood (< 2 mm) was fed into the reactor at a feeding rate of 10-12 g min^{-1}, with the auger speed fixed at 13 rpm, representing a solid residence time of 1 min. 20 L min^{-1} of N_2 was used as a carrier gas. The maximum bio-oil yield of 59% was reached at a wall temperature of 500 °C, as the biochar temperature was at 320 °C before leaving the auger reactor. Biochar yield was 19% and decreased to 13% at a wall temperature of 550 °C, as biochar temperature reached 370 °C.

3.3.2.2 Single screw - large capacity laboratory-scale reactors (1 to 15 kg h^{-1})

Advanced BioRefinery Inc., ABRI (Ontario, Canada) commercialized an auger reactor technology developed by Renewable Oil International, ROI (Florence, AL, USA) and described in a patent by Badger & Fransham (2006). An external heat source heats the pyrolytic reactor tube, and a heated solid inert particulate material, such as hot steel shots, are mixed with the carbonaceous feedstock. No fluidizing gas was necessary in the reactor. ABRI is manufacturing a 20 kg day^{-1} (about 1 kg h $^{-1}$) laboratory-scale apparatus that was used by Schnitzer et al. (2007). The authors characterized the composition of bio-oil and biochar obtained by pyrolysis of chicken manure with the laboratory-scale apparatus at a temperature of 330 °C. 50% of the initial biomass was converted to bio-oil, as 27% left as biochar.

A laboratory-scale auger reactor system developed at Mississippi State University (MSU) is described by Mohan et al. (2007) and Ingram et al. (2008). The auger reactor has a 76-mm diameter and 0.102 m length. The auger speed can be varied widely and the capacity of the auger reactor can vary between 1 and 7 kg h^{-1}. The reactor is externally heated in four separate zones: the pre-heat section (130-140 °C, 102 mm), an initial pyrolysis zone (400 or 450 °C, 254 mm), a secondary pyrolysis zone (100 °C less than the previous section, 203 mm), and a cooling zone (300 °C, 203 cm). In the study by Ingram et al. (2008), oak and pine (wood and bark) ground and sieved to a particle size between 2 and 4 mm were pyrolysed using the MSU pyrolysis reactor at a solid flowrate of 1 kg h^{-1} and at a temperature of 450°C. The screw rotational speed was 12 rpm, resulting in a solid residence time of 30 s in the pyrolytic zones, and about 50 s in the whole reactor. The highest biochar yield was obtained from oak bark (27.8%) as the highest bio-oil yields was obtained from oak wood (56.3%; Table 3.2). Bhattacharya et al. (2009) investigated fast pyrolysis of wood and plastic mixtures using the MSU auger reactor. The pyrolysis operating parameters of the previous studies were used. Pine wood chips (2-3 mm) pyrolysed at 450°C resulted in yields of bio-oil and biochar of 50.1% and 19.1%, respectively. Wood and high-density polyethylene (HDPE) plastic mix (50:50) pyrolysis at 450 °C resulted in the highest yield of pyrolysis oil and char (38.9% and 25.9%, respectively), as pyrolysis at 525 °C resulted in lower products yield (9.1% of pyrolysis oil and 11.9% of char). Authors concluded that pyrolysis oil from the pyrolysis of wood and plastic mix is upgraded relative to bio-oil from wood pyrolysis alone, even if the yield is lower. Pittman et al. (2012) used the same reactor with the same operating conditions for corn stalks (0.5 – 5 mm) pyrolysis, but tested with the addition of N_2 as gas carrier at 34 L

min^{-1} flowrate. Without carrier gas, bio-oil and biochar yields were 35% and 23.5%, respectively. The addition of N_2 raised the yield of biochar (29%) as the bio-oil yield was the same.

A pilot-scale moving bed screw reactor was designed and built in Spain and is described by Aylón et al. (2008). The screw reactor has an internal diameter of 25.4 mm and is 0.3 m long. It is heated by an external electrical furnace. Authors carried out a research study comparing the results of waste tire pyrolysis between fixed bed reactor and moving bed auger reactor. A constant mass flow of 6 kg h^{-1} was fed to the reactor for four hours. The pyrolysis of tire rubber shreds (particle size of 2 mm) was performed at 600 °C with a solid residence time of 3.7 min and a N_2 flow of 1.2 L min^{-1}. Pyrolysis oil and solid yields in the auger reactor were 43.2% and 38%, respectively. Using the same auger reactor, Aylón et al. (2010) carried out a pyrolysis experiment with shredded tire rubber (particle size of 5 mm), with a N_2 flow rate of 11.4 L h^{-1} and at temperatures of 600, 700 and 800 °C. Pyrolysis oil yield decreased from 41.5% to 27.5% while increasing the temperature from 600 to 800 °C, and solid yield stayed stable at the three temperatures (about 40%). In a study by Martínez et al. (2013), waste tires (2-4 mm particles) were pyrolysed at 550 °C for 180 s with a N_2 flow rate of 5 L min^{-1}. Resulting pyrolysis oil and solid yields were 42.6% and 40.5%, respectively. Puy et al. (2011) tested the moving bed screw reactor with pine wood chips (particle size of about 20 mm), a N_2 flow rate of 5 L min^{-1}, temperatures from 500 °C to 800 °C and residence times of 90, 180 and 300 s. Water content of the bio-oil ranged from 11 to 19 % (w/w) as the highest yield of bio-oil (57%) was obtained at a pyrolysis temperature of 500 °C and residence times of 180 and 300 s. Biochar yield was the highest (41.5%) at 500 °C but with a shorter residence time of 90 s. The authors stated that a larger reactor based on this technology could be designed whenever a minimum solid residence time of two min is required in order to have full biomass devolatilization. Veses et al. (2014) tested a solid heat carrier (sand) with or without catalysts (CaO, CaO.Mg) in the same auger reactor. Pyrolysis of wood chips (< 15 mm) was performed at 450 °C, with a residence time of 7 min and a N_2 flowrate of 5 L min^{-1}. Bio-oil yield varied between 48 and 50%, as biochar yield was about 25-27%. In another study, Veses et al. (2015) tested three pyrolysis temperatures (400, 450 and 500 °C) with catalyst mixed to hot sand as a solid heat carrier. The raise in temperature from 400 to 500 °C had the effect to increase the bio-oil yield from 41 to 50%, and decreased the biochar yield from 36 to 21%.

An auger reactor designed and constructed by Proton Power, Inc. (Lenoir City, TN, USA) was used by Kim et al. (2011) in order to produce biochar from fast pyrolysis. The auger pyrolysis reactor features a cylindrical reactor (89 mm in diameter x 3 m in length) with an internal single auger (76 mm in diameter and 100 mm in pitch). The auger speed can vary from 10 to 100 rpm. A condenser using flowing tap water is used for vapors condensation to produce bio-oil. Ground switchgrass (particle size of 4 mm) and pine wood (less than 0.85 mm in particle size) were fed to the pyrolysis unit at a flow rate of 5 kg h^{-1}. Three pyrolysis temperatures were tested (450, 600 and 800 °C) with a solid residence time of 30 s in the one meter long heated zone. The biochar collector was purged with 10 L min^{-1} of N_2. Results demonstrated that biochar yield decreased from 31.3% to 11.4% for switchgrass, and from 26.6% to 9.5% for pine wood, as pyrolysis temperature increased from 450 to 800 °C. Moreover, as the temperature increased from 450 to 800 °C, H/C ratio of biochar made from switchgrass and pine wood decreased from 0.62 to 0.19 and from 0.66 to 0.17 respectively, as O/C ratio decreased from 0.17 to 0.05 and from 0.24 to 0.03, respectively.

The STYX auger pyrolysis reactor is an experimental unit developed by Morgano et al. (2015) at the Karlsruhe Institute of Technology, in Germany. The screw reactor is 2 m long and has a diameter of 0.15 m. The residence time can vary between 5 to 25 min and the temperature can reach 350 to 500 °C. The reactor has a capacity of 2 to 4 kg h^{-1} and 14 L N_2 min^{-1} is used as gas carrier. The condensation train is composed of three condensers in series and an electrostatic precipitator. Pyrolysis of beech wood chips (2.0 – 4.5 mm) was performed and the maximum bio-oil yield (48.8%) was obtained at 450 °C for a residence time of 10 min, as biochar yield was 20.6%.

In a study by Ferreira et al. (2015), pyrolysis of Medium Density Fiberboard (MDF) wastes was carried out in a semi-continuous pilot screw reactor. Screw conveyor is 2 m long, 195 mm in diameter and 195 mm in pitch. Experimental tests were performed at two temperatures (450 and 600 °C) monitored at the entrance of the char collector. Pyrolysis reactions were carried out under slightly negative pressure produced by a centrifugal fan installed on top of the bio-oil separator and no carrier gas was used. Three solid residence times were tested (9, 15 and 34 min). The maximum bio-oil yield (40 %) was obtained at 600 °C for the longer residence time as biochar yield was 17.3 %. The highest biochar yield (39.7%) was obtained with the longest residence time at 450 °C.

3.3.2.3 Single screw - Industrial-scale reactors (> 15 kg h^{-1})

Advanced BioRefinery Inc., ABRI (Ontario, Canada) commercialized an auger reactor with a capacity of one ton per day (about 40 kg h^{-1}) and a larger unit that can treat 50 tons per day. Azargohar et al. (2013) tested the first reactor that was built for on-farm use. Pyrolysis of wheat straw, saw dust, flax straw and poultry manure (particle size from 0.42 to 3.36 mm) was performed at temperatures of 400, 475 and 550 °C, with a solid residence time of 15 min. The highest bio-oil yield was obtained from the pyrolysis of saw dust at 475 °C (52%) as the lowest bio-oil yield was from the pyrolysis of wheat straw at 400 °C (9.2%). The HHV of these bio-oils was 23.9 and 26.8 MJ kg^{-1}, respectively. The H/C and O/C ratios of the biochar produced from flax straw at 550 °C were the lowest (0.42 and 0.01, respectively). In fact, for each biomass, H/C and O/C ratios always decreased with increasing temperature.

In a study by Bosong et al. (2014), a combined system of auger pyrolysis reactor and fixed-bed catalytic reactor with a capacity of 25 kg h^{-1} was designed and used for continuous pyrolysis and catalytic upgrading of pine wood. Outside the auger screw, stainless-steel tube with a length of 3 m (heating zone of 2.4 m) and a diameter of 0.16 m was heated by a hot blast stove. Gases were then evacuated in a two-step condensation system including a vertical tube with cooling water coils at 25 °C and two traps in series immersed in water cooled by ice. Tests with pine wood (< 1 mm particles size) were conducted at auger speeds of 5 rpm, which corresponds to a solid residence time inside the reactor of 8 min. Helium (25 ml min^{-1}) was used as the gas carrier and the pressure inside the reactor was maintained by a vacuum pump. Bio-oil yield increased from 30.2% to 34%, and biochar yield decreased from 45.1% to 30.3%, as the temperature was increased from 400 to 500 °C. The water content of bio-oil decreased from 60.5% at 600 °C to 40.2% at 400 °C.

3.3.2.4 Twin-screw reactors

A twin-screw design can be used to ensure sufficient mixing and to limit potential for feedstock clogging that can occur in auger reactors (Brown, 2009). An auger pyrolysis reactor using two screws was developed at the Iowa State University in USA (Brown & Brown, 2012). The reactor was designed to provide the high heat transfer rate required for fast pyrolysis, using steel shots as a heat carrier and short vapors residence times. The stainless-steel auger reactor vessel was 0.559 m long, with a width and a height of 63.5 mm and 38.1 mm, respectively. The two screws have a 25.4 mm diameter. Response surface methodology was employed using a circumscribed central composite design of experiments to optimize the system. The four following factors were investigated: temperature of the heat carrier (425, 475, 525 and 625 °C), total volumetric flow rate of N_2 (1.5, 2.0, 2.5, 3.0 and 3.5 L min^{-1}), rotational speed of screws (45.0, 49.5, 54.0, 58.5, and 63.0 rpm), and mass flow rate of heat carrier (9, 12, 15, 18, and 21 kg h^{-1}). Biomass flow rate was kept constant at 1 kg h^{-1}. The authors found that conditions for maximum bio-oil yield (> 70%) and minimum char yield were high flow rate of sweep gas (3.5 L min^{-1}), high heat carrier temperature (600 °C), high auger speeds (63 rpm) and high heat carrier mass flow rates (18 kg h^{-1}). These conditions also minimized biochar yield.

An experimental twin-screw pyrolysis unit designed in Thaïland and described by Sirijanusorn et al. (2013) is composed mainly of a biomass hopper, a sand hopper, biomass and sand screw feeders, a nitrogen pre-heater, a twin screw reactor, a solid canister, a cyclone separator, a char pot, a hot filter and a bio-oil product collection system. The pyrolysis unit can treat about 0.4 kg h^{-1} at a screw rotational speed of 9 rpm. Sand is used as a solid heat carrier and N_2 as gas carrier. The two screws have a 25-mm diameter and are 0.45 m long. Cassava rhizome of different particle sizes (< 0.25 mm, 0.25 – 0.425 mm, 0.425 – 0.6 mm) was pyrolysed at three temperatures (500 °C, 550 °C and 660 °C) with three N_2 flow rates (4, 7, and 10 L min^{-1}). For a N_2 flowrate of 7 L min^{-1} and particle size between 0.25 and 0.425 mm, bio-oil yield increased while increasing the temperature from 500 to 550 °C, and reached a maximum of approximately 50 % as biochar yield varying between 22 and 23%. Intermediate particle size (0.25 – 0.425 mm) resulted in higher bio-oil yields. When increasing the N_2 flow rate from 4 to 10 L min^{-1} at a temperature of 650 °C, bio-oil yield steadily decreased from 45% to 38%, as biochar yield stayed around 20%.

A twin-screw reactor was designed at the University of Leoben in Australia (Agirre et al., 2013). The externally heated and gas-tight reactor has a length of 2.3 m and it allows the treatment of 1 to 10 kg h^{-1} of biomass. Slow pyrolysis of fruit cuttings residues was carried out using three particle sizes (< 8 mm, 40 – 50 mm, and 100 mm), at pyrolysis temperatures of 500, 786 and 900 °C, and with residence time of one, two and three hours. The objective was to obtain a biochar with a high C content and low VM. Pyrolysis temperature of 900 °C was necessary in order to produce biochar with high C contents (>85%) and low volatiles amount (< 10%). Depending on biomass particle size, biochar yields varied from 21.3 to 22.8% at a temperature of 900 °C and with a residence time of two hours.

The Pyroformer intermediate pyrolysis reactor was designed and patented at Aston University in United Kingdom (Yang et al., 2014). The auger screw reactor comprises a horizontal carbon steel vessel containing two co-axial rotating screws. During the operation, the inner screw conveys a mixture of fresh feedstock and recycled char product forward through the reactor, and the outer screw returns a portion of the char product backwards for recycle. The unit is 1.8 m in length and has a diameter of 200 mm. The condensation of hot vapors is performed through a shell and tube water cooled condenser followed by an electrostatic precipitator. Pyrolysis tests with wood and barley straw pellets at 450 °C with a residence time of 1.5 min and a char/biomass mixing ratio of 1:4 were carried out (Yang et al., 2014). The feed rates were fixed between 5 and 6 kg h^{-1}. Bio-oil yields obtained from the reaction were 54.3% and 49% as biochar yields were 28.5% and 30.1% for wood and barley straw, respectively. The HHV of bio-oil produced from wood was higher than from barley straw (18.2 vs 17.0 MJ kg^{-1}). C, H and N contents in wood biochar were 75.6%, 3.38% and 0.22%, respectively.

Kim et al. (2014) used another semi pilot-scaled auger pyrolysis system designed and constructed by Proton Power, Inc. (Lenoir City, TN, USA) in order to produce bio-oil from pine particles (< 4 mm). The auger pyrolysis reactor featured a rectangular reactor (0.1 m × 0.1 m × 2.5 m) with internal dual augers. The 2 m-long heated zone was heated using two 1 m-long electrical resistance furnace systems. The auger pyrolysis system was operated at a feeding rate of 10 kg h^{-1}, for a 72 s residence time and at three pyrolysis temperatures (500, 525, and 550 °C). The system was purged with N_2 (30 L min^{-1}). A condensation section for bio-oil recovery comprises of three condensers (0.1 m in diameter and 2 m-long) in series. The water content of bio-oils was between 37 and 39% and the yield increased from 53.6 to 59.8% as the temperature was decreased from 550 to 500 °C. The biochar yield was the highest at 500 °C (22.6%) and the lowest at 550 °C (17.5%).

Finally, LUGRI Company developed a laboratory-scale twin-screw reactor for a throughput of up to 15 kg h^{-1} (Raffelt et al., 2006). Biomass and heat carrier (sand or steel balls) are fluidized mechanically while inert gas is not necessary. The screws have a length of 1.5 m and an inner and outer diameter of 20 and 40 mm, respectively. Fine-sized char particles are separated from the gaseous phase by two cyclones and the vapors are cooled in two condensers. Raffelt et al., (2006) tested the pyrolysis of wood sawdust and wheat straw at 500 °C and solid residence time ranged from 10 to 60 s. Wood pyrolysis resulted to a bio-oil yield of 70% and a biochar yield of 14-18%. More biochar was obtained from wheat straw (25-30%) with a corresponding bio-oil yield of 50-55%. Tröger et al. (2013) used the same pyrolysis reactor with a heat carrier loop consisting of a bucket elevator. Steel balls were used as heat carrier and N_2 was purged in the unit. Pyrolysis temperature was fixed at 500°C and the residence time was 13 s. Corn stover, rape stalks, sunflower stalks, wheat straw and softwood with a particle size < 4 mm were pyrolysed. The highest bio-oil yield was obtained from softwood (64%) with a biochar yield of 13.9%. Pyrolysis of agricultural residues resulted in bio-oil yields between 31.1 and 43.9%, and biochar yields between 20.8 and 31.4%. The same reactor unit was used by Joubert et al. (2015) for the pyrolysis of milled Eucalyptus (< 5 mm) with the same operating conditions. The yield of total condensates was 67.5%, with a HHV of 22.9 MJ kg^{-1}. Biochar yield was 16.5% and its O/C and H/C ratios were 0.13 and 0.52, respectively.

3.4 Influence of auger pyrolysis reactors operating parameters on product yields and properties

3.4.1 Auger pyrolysis technology

As described in the previous section, many auger pyrolysis technologies were designed and tested in the last decade. Most of them were laboratory-scale with a biomass flowrate capacity of less than 15 kg h^{-1}. Among these auger reactors, there are mainly two types: single screw and twin-screw reactors. Depending on the desired products, it is important to select the more efficient technology and operating conditions in order to obtain the desired products. Based on the compiled data, twin-screw reactors produce more bio-oil than single screw reactors. Average bio-oil yield of 54.5% was obtained for the pyrolysis of forest biomass in twin-screw reactors (# 14 to 19; Table 3.2), as average bio-oil yields obtained from forest biomass with single screw reactors were 53.3, 42.0 and 37.3% for small capacity laboratory-scale (# 1 to 5), large capacity laboratory-scale (# 6 to 11) and industrial scale reactors (#12 and 13), respectively. Bio-oil yields lower than 15% were not included in the average calculation. The same tendency was found for the pyrolysis of agricultural biomasses, as bio-oil yield from twin-screw reactors was on average 41.5%, as compared to 42.6, 40.0 and 30.6% for the three categories of single screw reactors. On the contrary, biochar yield is generally lower in twin-screw reactors. A better biomass mixing and a most efficient heat transfer contributing to a more complete carbonization could improve bio-oil yield in the detriment of biochar in twin-screw reactors. Moreover, the fact that most of the studies carried out with twin-screw reactors use solid carrier which helps in improving heat transfer. Results also demonstrate that the bio-oil yield decreases with increased capacity of the reactor. This can be due to a lower heat transfer in larger tubes.

3.4.2 Temperature

Based on the literature review, temperature for the pyrolysis of lignocellulosic biomasses in auger reactors ranged from 320 to 900 °C, with an average of 526 °C. Pyrolysis temperature is known to have a great influence on product yields (Scott et al., 1988). In general, increasing the reactor temperature increases the conversion of biomass (Xiu et al., 2008). Bio-oil yield tends to increase up to a certain temperature and is then decreased. Moreover, biochar yield decreases with increasing temperature, as syngas yield is increased. The results reported from this review of literature confirm these tendencies for auger pyrolysis reactors. The increased temperature resulted in decreasing of char, while the bio-oil production increased (Daiane et al., 2015). For example, Veses et al. (2015) reported that the raise of temperature from 400 to 500 °C resulted in an increased bio-oil yield from 41 to 50%, and decreased the biochar yield from 36 to 21%. In the study from Puy et al. (2011), biochar yield was higher at 500 °C (26.4%) than at 800 °C (19 %) for the same solid residence time of 300 s.

In addition to yield, products properties are also influenced by pyrolysis temperature. Based on a study from Mimmo et al. (2014), pyrolysis temperature has proven to be a fundamental parameter in determining the biochar chemical structure, physical properties and stability. As reported by Demirbas (2004), contents of C in biochar increase with pyrolysis temperature while these corresponded to H and O contents decrease. Ghani al. (2013) found that pyrolysis temperature greatly influence both thermal and chemical properties of the derived biochar. Generally, surface area of biochar increases with increasing temperature at which deformation occurs. Bio-oil quality is also affected by pyrolysis temperature. For example, the number of different organic compounds and acid in the bio-oils decreases at higher temperature (Azargohar et al., 2013; Solar et al., 2016). In fact, high temperatures (> 800 °C) produce a higher proportion of water in liquids (Solar et al., 2016), and consequently a bio-oil with lower HHV.

In an auger pyrolysis reactor, it is known that the actual biomass temperature may be much lower than that of the heat source (Lédé, 2010). In fact, temperature and heating rate of a particle may differ from those of the reactor. According to Lédé & Authier (2015), the increase of the reactor temperature won't increase systematically biomass reaction temperature and hence vapour fractions. The temperature value given in research studies often corresponds to the tube wall temperature and does not correspond to the particle pyrolysis temperature. Liaw et al. (2012) illustrated the relation between wall temperature and temperature of solid residue produced. For example, at a wall temperature of 650 °C, the produced solid residue was at 450 °C. Bosong et al. (2014) found a significant temperature gradient between the biomass bed and the wall of the reactor. Time vs temperature profile of pine wood sample and the wall of the reactor revealed that when wall temperature reached 600 °C, biomass temperature was about 100 °C lower. Then, it is difficult, even impossible, to know the exact particle pyrolysis temperature in an auger pyrolysis process. According to Brown (2009), the temperature of the vapor exiting the reactor could be more useful estimate of the actual reaction temperature.

3.4.3 Carrier gas flow / vapor residence time

Carrier gas (usually N_2) flow rate reported in the literature review varied from 0.19 to 20 L min^{-1}. The carrier gas flow rate has an impact on the vapour residence time. As the pyrolysis temperature increases, any increase in vapors residence time will result in a significant reduction in the yield of oil and increase in gas production (Liaw et al., 2012). Brown (2009) determined that biochar yield is decreased for increasing N_2 flow rate for all other pyrolysis parameters held constant. This is due to decreased residence time associated with higher gas flow rates which favours bio-oil production. In fact, low gas flows provide increased opportunities for reactive volatile matter to interact with the solid carbonaceous residue of pyrolysis and produce more charcoal (Antal Jr and Grønli, 2003). Consequently, biochar characteristics can also be modified with a change of sweeping gas flow rate. In a study from Sirijanusorn et al. (2013), the maximum bio-oil yield of 45% (w/w) was obtained at the gas flow rate of 4 L min^{-1}. When increasing the flow rate from 4 to 10 L min^{-1}, bio-oil yield steadily decreased. Brown & Brown (2012) evaluated different N_2 flowrates, from 1.5 to 3.5 L min^{-1}, and found that the maximum bio-oil yield of 73% was obtained at the highest flow rate. In the study by Pittman et al. (2012), the addition of N_2 raised the yield of biochar as the bio-oil yield was the same.

3.4.4 Solid residence time

Pyrolysis tests in auger pyrolysis reactors were performed with solids residence time varying from 11 s to 120 min, most of the studies using solid residence time below 8 min (Table 3.2). Solid residence time in an auger reactor is determined by the length of the tube, the rotational speed and the pitch of the screw (Funke et al., 2017). A model realized by Di Blasi (2002) showed that for constant temperature, increased residence time resulted in increased solid char yields due to secondary reactions. Moreover, solid residence time have an influence on biochar physical and chemical characteristics. Brown (2009) concluded that the introduction of heat carrier material can provide high liquid yields by improving heat transfer, but only if the biomass contacts the heat carrier material for a short period of time. The hypothesis is that when no heat carrier material is used, longer solid residence time is required to provide sufficient reaction heat and time. For example, in the research study carried out by Puy et al. (2011), minimum solid residence time of two min was required for complete conversion, and the highest liquid yield (58.7% w/w) required a longer residence time of 5 min. Yang et al. (2014) reported that a prolonged residence time promoted the secondary cracking reaction and led to coke formation, leading to a high fraction of C in the char product. However, at a high temperature (900 °C), Solar et al.

(2016) reported that an increased residence time of 64 min vs 32 min decreased biochar and bio-oil yields as non-condensable gases yield increased.

3.4.5 Feedstock type and particle size

Wood is the most studied biomass in auger pyrolysis reactors, as 19 research studies among the 29 reported in the literature review carried out the pyrolysis of forest biomass (Table 3.2). Agricultural biomass like crop residues were pyrolysed in nine studies as manure was pyrolysed in two studies. Biomass feedstock can affect both yield and properties of pyrolysis products (Carrier et al., 2013; Kan et al., 2016). For example, the type of feedstock utilized for biochar production influences biochar yield and characteristics, including concentrations of elemental constituents, density, porosity, and hardness (Spokas et al., 2012). Biochar yield from biomass can be influenced by its lignin, cellulose, hemicellulose and extractives contents (Kim et al., 2012a). Biomass species with high lignin contents offer higher charcoal yields because lignin preferentially forms char during pyrolysis (Antal Jr and Grønli, 2003). Moreover, high extractives content could benefit bio-oil yield (Kan et al., 2016). In a study by Demirbas (2004), the higher lignin content in olive husk (50.6%) gives a higher biochar yield in comparison with oak wood and wheat straw. Pyrolysis of biomass with higher ash content will also produce higher biochar yield and lower bio-oil yield. For example, Liang et al. (2015) reported that the pyrolysis of hybrid poplar (0.8% ash content) produced higher yields of bio-oil and lower yields of biochar as compared to potato peel (9.3% ash content).

Pyrolysis of HDPE (Bhattacharya et al., 2009) and rubber tire shred (Aylón et al., 2010, 2008; Martínez et al., 2013) in auger reactors was studied (Table 3.2). Aylón et al. (2010) reported that the maximum pyrolysis oil yield (41.5%) is obtained working at low temperatures, as gases yield increases with increasing temperature. The co-pyrolysis of HDPE with wood resulted in lower pyrolysis oil and solid yields as compared to the pyrolysis of only wood with the same operating parameters (temperature of 450 °C and residence time of 55 s). An increased temperature to 525 °C decreased biochar and bio-oil yields in detriment of gases. Despite the co-pyrolysis of biomass with plastics can reduce the quantity of produced pyrolysis oil, its quality could be improved (Bhattacharya et al., 2009).

In addition to biomass type, particle size of biomass has an impact on pyrolysis product yields and characteristics. Particle size from < 0.2 mm up to 20 mm are reported in the literature, but only five studies tested particle size higher than 5 mm. Small size particles are recommended for producing more bio-oil because of the short residence time of vapours inside the solid, hence minimising the possibility of secondary reactions. Demirbas (2004) noted that an increase of corncob particle size from 0.5 to 2.2 mm increased biochar yield from 5.7 to 16.6% after pyrolysis at 677 °C. They made the hypothesis that this is because the heat flux and the heating rate are higher in small particles than in large particles. Sirijanusorn et al. (2013) reported that intermediate particle size (0.25 – 0.425 mm) resulted in higher bio-oil yields when compared to particle size < 0.25 mm and 0.425 – 0.6 mm. Lower bio-oil yield for very small particle size can be related to the high ash content of these particles (Pattiya and Suttibak, 2012).

The addition of catalyst to biomass in auger reactors was studied by Veses et al. (2014). Authors concluded that the addition of calcium-based material (CaO and CaO.MgO) improved the bio-oil properties, decreasing both O content and acidity character, while increasing both pH and calorific value. However, the addition of catalysts did not significantly affect product yields. Auger reactors have the advantage to offer a great control of catalyst-to-biomass ratio. However, due to the small particle size of the catalyst, their transportation through the screw may be a technical barrier.

3.5 Discussion

Auger pyrolysis is a promising technology for bio-oil and biochar production. Recently, many research studies were carried out using laboratory-scale or pilot-scale reactors in order to evaluate the effect of operating conditions on product yields and their properties. In this review, nineteen auger pyrolysis reactors used to produce biochar and bio-oil are listed and described. The operating parameters tested in each research study and the associated product yields were compiled. Most of the reported pyrolysis tests have been carried out with forest and agricultural biomasses with particle size generally lower than 5 mm. Temperatures for the pyrolysis of biomass ranged from 330 to 900 °C, with an average of 526 °C. Solid residence time in most of the research studies was under 8 min, with a minimum and a maximum of 11 s and 120 min, respectively. N_2 was generally used as a carrier gas at a flowrate between 0.19 to 20 L min^{-1}. Bio-oil yield from biomass pyrolysis ranged from 19.2 to 73.6% (average of 43.6%) and biochar yield ranged from 6 to 45.1% (average of 23.2%). Since the design of every reactor is different, similar operating conditions used in different research studies do not lead to the same conclusions in terms of bio-oil, biochar and gas yields and properties. For example, results showed that twin-screw reactors combined with the use of a solid carrier improve heat transfer, thus improving bio-oil yield.

In addition to pyrolysis technology, operating parameters (temperature, carrier gas flowrate and solid residence time) and biomass feedstock and particle size were identified as parameters having the most impact on product yields and properties. Thus, pyrolysis operating parameters have to be selected carefully in function of the desired products. Some compromises may be necessary to obtain great yields of the products with the desired properties. For example, bio-oil with the highest HHV and the lowest water content is not necessarily obtained when the bio-oil yield is the highest. Moreover, the desired properties are not necessarily obtained when the same pyrolysis operating parameters are used for various feedstocks. In the research study carried out by Azargohar et al. (2013)**,** the highest HHV was obtained at 550 °C for wheat straw and saw dust (29.1 and 28.8 MJ kg^{-1}, respectively), at 475 °C for poultry manure (34.0 MJ kg^{-1}), and was identical at 475 °C and 550 °C for flax straw (29.9 MJ kg^{-1}). The highest bio-oil yield was obtained at 475 °C for sawdust, and at 550 °C for the three other biomasses. Similarly, the results obtained by Bosong et al. (2014) show that bio-oil yield was the highest (34%) at a pyrolysis temperature of 500 °C, but the water content in bio-oil was the lowest (40.2%) at 400 °C when the bio-oil yield was lower (30.3%). Moreover, biochar with the desired properties to sequester C (high H/C and O/C ratios) are generally produced at higher temperatures while the yield decreases as the temperature increases (Azargohar et al., 2013).

When the ultimate goal is to produce high quality bio-oil, the produced char can be burned in a combustor to generate heat for pyrolysis (Yildiz et al., 2016). In fact, the energy content in the non-condensable gases could be not sufficient to provide the heat needed for pyrolysis (Yildiz et al., 2016). Veses et al. (2016) demonstrated the feasibility of an integrated process that consists of biomass catalytic pyrolysis in an auger reactor and char combustion in a fluidized-bed reactor for heat carrier and regeneration.

For future work, it is recommended to establish the relationship between pyrolysis operating parameters and product yields and properties through optimization studies, and to identify the parameters needed to obtain the desired products. Experimental design based on the response surface methodology (Myers et al., 2009) could be carried out (Brown & Brown, 2012). Moreover, research studies are needed to demonstrate that it is possible to scale-up the laboratory and pilot-scale auger reactors and to obtain similar product yields and properties on a larger scale. Funke et al. (2017) proposed the dimensional analysis as a tool to scale-up a pyrolysis auger reactor. However, they concluded that there is no simple scale-up on the basis of dimensionless numbers and that further research is needed in order to validate the proposed approach.

Connecting text

The literature review presented in Chapter 3 showed that auger pyrolysis is a technology designed for producing both biochar and bio-oil. It is simple to operate, it can be mobile and it requires low carrier gas and energy. Moreover, the operating parameters can be controlled easily in order to obtain biochar with the desired properties for the desired application. Based on the results of this literature review, a range of pyrolysis operating parameters (temperature, solid residence time and nitrogen flowrate) were identified and preliminary tests were carried out with a vertical auger reactor designed by the IRDA and the *Centre de recherche industrielle du Québec* (CRIQ) (Appendix 1). Thus, the ideal range of operating parameters for producing biochar from three biomasses was identified. In Chapter 4, the third objective of this thesis, which is to validate a response surface methodology approach used to identify the optimal pyrolysis operating parameters in order to produce engineered biochars with the ideal characteristics for mitigating climate change, was achieved. These engineered biochars should have the specific properties needed to sequester C in soil (i.e. low H/C_{org} and for O/C_{org} ratios), as reported in Chapter 2.

Chapter 4. The production of engineered biochars in a vertical auger pyrolysis reactor for carbon sequestration

Abstract

Biomass pyrolysis and the valorisation of co-products (biochar, bio-oil, syngas) could be a sustainable management solution for agricultural and forest residues. Depending on its properties, biochar amended to soil could improve fertility. Moreover, biochar is expected to mitigate climate change by reducing soil greenhouse gas emissions if its C/N ratio is higher than 30, and sequestrating carbon if its O/C_{org} and H/C_{org} ratios are lower than 0.2 and 0.7, respectively. However, the yield and properties of biochar are influenced by biomass feedstock and pyrolysis operating parameters. The objective of this research study was to validate an approach based on the response surface methodology, to identify the optimal pyrolysis operating parameters (temperature, solid residence time, and carrier gas flowrate), in order to produce engineered biochars for carbon sequestration. The pyrolysis of forest residues, switchgrass, and the solid fraction of pig manure was carried out in a vertical auger reactor following a Box-Behnken design and response surface models were developed. The optimal pyrolysis operating parameters were estimated to obtain biochar with the lowest H/C_{org} and O/C_{org} ratios. Biochar produced from wood and switchgrass can only present a high potential for C sequestration if the pyrolysis operating parameters are properly selected. The minimum H/C_{org} and O/C_{org} ratios predicted from the response surface models reached values lower or equal to 0.54 and 0.14, respectively, for a pyrolysis temperature ranging from 588 to 646 °C, a solid residence time from 99 to 106 s, and a N_2 flowrate from 2.0 to 3.1 L min^{-1}. Validation pyrolysis experiments confirmed that the selected approach can be used to accurately predict the optimal operating parameters for producing biochar with the desired properties to sequester carbon.

Keywords: pyrolysis; auger reactor; engineered biochar; forest residues; agricultural biomass; response surface methodology

4.1 Introduction

The Intergovernmental Panel on Climate Change recently reported that "global emissions of GHG have risen to unprecedented levels despite a growing number of policies to reduce climate change" (IPCC, 2014). GHG emissions need to be lowered by 40% to

70% compared to the 2010 values by mid-century, and to near-zero by the end of the century, in order to limit the increase in global mean temperature to two degrees Celsius (IPCC, 2014).

Pyrolysis, the thermochemical decomposition of biomass under oxygen-limiting conditions at temperatures between 300 and 700 °C, can be a sustainable management solution for agricultural and forest biomasses, and is proposed as a strategy to mitigate climate change. The resulting co-products of pyrolysis are: a liquid bio-oil, non-condensable gases, and a solid biochar. The yields and characteristics of the products depend on pyrolysis operating parameters and biomass feedstock properties. Non-condensable gases are generally used to heat the pyrolysis unit. Bio-oils have heating values of 40%–50% of that of hydrocarbon fuels (Jahirul et al., 2012), and could be used to replace fossil heating oil. Biochar can be used as a soil amendment to improve soil fertility and has been proposed as a tool for mitigating climate change (Wang et al., 2012), because of its potential for C sequestration. When biomass is converted into biochar and is applied to soil, C can be stored for more than 1000 years (Haefele et al., 2011; Kuzyakov et al., 2014). In other words, biochar production is a way for C to be drawn from the atmosphere, and is a solution for reducing the global impact of farming (Brar et al., 2014). Woolf et al. (2010) reported that biochar and its storage in soil can contribute to a reduction of up to 12% of current anthropogenic CO_2 emissions. Moreover, there is evidence that biochar amendment to soil can help reduce GHG emissions, and particularly N_2O (Cayuela et al., 2014), a powerful GHG, with a global warming potential 298 times that of CO_2 for a 100-year timescale. Specifically, agriculture is a major source of N_2O, contributing approximately 70% of Canadian anthropogenic N_2O emissions. Agricultural soils contribute to about 82% of these emissions (Environment and Climate Change Canada, 2014). Despite the many potential benefits of soil amendment with biochar, special attention must be paid to the negative side effects. For example, heavy metals (e.g., Cu, Zn, and Mo) could be found in biochar and accumulate in soil, leading to phytotoxicity problems.

The yield and characteristics of pyrolysis products are influenced by different factors, including biomass feedstock and pyrolysis operating parameters (solid residence time, vapor residence time, temperature, heating rate, and carrier gas flowrate). Thus, not all biochars are created equal and biochars should be designed with special characteristics for their use in environmental or agronomic settings (Novak and Busscher, 2013; Sun et al., 2014). Biochars with a low N content, and consequently a high C/N ratio (> 30), could be more suitable for the mitigation of N_2O emissions from soils (Cayuela et al., 2014). Moreover, biochars produced at a higher pyrolysis temperature and with an O/C_{org} ratio < 0.2, H/C_{org} ratio < 0.4, and volatile matter below 80%, may have a high C sequestration potential (see Chapter 2). In fact, a H/C_{org} ratio < 0.4 would indicate a BC_{+100} of 70% (i.e., at least 70% of the C in biochar is predicted to remain in soil for more than 100 years), as an H/C_{org} ratio in the range 0.4 – 0.7 would indicate a BC_{+100} of 50% (Budai et al., 2013).

It is also important to select the proper pyrolysis technology to obtain the desired yield and properties of the product. Among all the existing pyrolysis technologies, the auger reactor is one of the most attractive designs that has been developed (Washington State University and Department of Ecology from State of Washington, 2011). It enjoys some popularity because of its simplicity of construction and operation (Resende, 2014). In an auger reactor, biomass is continuously fed to a screw, where it is heated in oxygen-free conditions, and then the auger rotation moves the product along the auger axis to the end of the reactor. The gases and organic volatiles leave the reactor at the end of the reactor, and the biochar is collected at the bottom. Gas exit locations may also be added along the auger reactor wall, in order to decrease the vapor residence time. The yield of bio-oil (condensed gases) in auger reactors is variable, depending on the operating parameters, but it is typically in the range of 40 to 60% (w/w) of the feedstock, which is lower than what is normally achieved with fluidized-bed reactors. This is because the heat transfer in an auger reactor is lower. Therefore, small-diameter reactor tubes which have a limited distance between the inner reactor tube surface and the internal auger shaft, are needed. In order to increase the heat transfer, some auger reactors combine a small inert solid particulate heat carrier (usually sand or steel shot) with relatively small particles of biomass (1 to 5 mm). The residence time of the vapors is much longer in auger reactors than in fluidized beds, which increases the likelihood of secondary reactions and consequently increases the yield of char (Resende, 2014).

The hypothesis of this research project is that it is possible to produce a biochar with beneficial characteristics from an environmental perspective, when pyrolysis operating parameters are suitably selected in a vertical auger reactor. Thus, the main objective was to validate a response surface methodology approach used to identify the optimal pyrolysis operating parameters (temperature, solid residence time, and nitrogen flowrate), in order to produce engineered biochars with the ideal characteristics for mitigating climate change (low H/C_{org} and O/C_{org} ratios).

4.2 Materials and Methods

4.2.1 Description of the response surface methodology approach

4.2.1.1 Development of the statistical models

Response surface methodology (RSM) was selected as an approach to determine the optimal pyrolysis operating parameters, in order to produce engineered biochars that can be used to sequester C. RSM is a collection of statistical and mathematical techniques for developing, improving, and optimizing processes (Myers et al., 2016), and is used to illustrate the relationship between the response variables (dependent variables) and the process variables (independent variables). In this study, the selected independent variables were the pyrolysis temperature, solid residence time in the heater block, and N_2 flowrate, which are three parameters known to influence the yields and characteristics of products in an auger pyrolysis reactor (Brown and Brown, 2012). The biochar yield and three indicators of biochar potential for climate change mitigation (C/N, H/C_{org}, and O/C_{org} ratios), were the response variables studied. Biochars with the highest C/N ratio are expected to reduce soil GHG emissions, and those with the lowest H/C_{org} and O/C_{org} molar ratios are expected to have a high C sequestration potential, as reported in Chapter 2.

The Box-Behnken design was selected for collecting data. For an experiment of three factors, this incomplete factorial design requires three evenly spaced levels for each factor, coded −1, 0, and +1 (Table 4.1). Two variables (−1 and +1 levels) are paired together in a 2^2 factorial, while the third factor remains fixed at the center (level 0). A total of 15 experiments run in a random order are necessary, including three repetitions of an experiment, with the three independent variables fixed at their central point.

The method of least squares from the RSREG procedure of SAS (SAS Institute Inc., 2012) was used to estimate the parameters of the quadratic response surface regression models (Equation 4.1), fitted to the experimental data obtained from the Box-Behnken design:

$$Y = \beta_0 + \beta_1 T + \beta_2 R + \beta_3 N + \beta_4 T^2 + \beta_5 (R \times T) + \beta_6 R^2 + \beta_7 (N \times T) + \beta_8 (N \times R) + \beta_9 N^2 \tag{4.1}$$

where Y is the studied response variable (biochar yield, C/N, H/C_{org}, and O/C_{org} ratios); $\beta_0, \ldots \beta_9$ are the regression coefficients to be estimated; and T, R, and N are the values of the independent variables (temperature, solid residence time, and N_2 flowrate, respectively). The significance of each independent variable was determined by the analysis of variance (ANOVA). A lack of fit test was performed to check the adequacy of the model.

4.2.1.2 Determination of the stationary points

A canonical analysis (SAS Institute Inc., 2012) was used to determine the nature of the stationary point (or the point on the surface where the partial derivatives are equal to zero), which can be a point of maximum response, a point of minimum response, or a saddle point. In the case of a saddle point, a RIDGE statement (SAS Institute Inc., 2012) was used to indicate the direction in which further experimentation should be performed, to produce the fastest decrease or increase in the estimated response, starting at the stationary point.

4.2.1.3 Validation of the statistical models

In order to validate the quadratic response surface regression models, a biochar was produced with the pyrolysis operating parameters determined from the response surface analysis, for producing a biochar with the optimal properties to maximize C sequestration (i.e., the lowest O/C_{org} and H/C_{org} ratios). A second biochar with the opposite characteristics (highest O/C_{org} and H/C_{org} ratios) was produced from each biomass. Predicted values from the response surface models vs. the actual values of the O/C_{org}, H/C_{org}, C/N ratios and yield, were compared using linear regression.

4.2.2 Pyrolysis experimental setup and procedure

4.2.2.1 Description of the vertical auger pyrolysis reactor

In order to validate the selected approach, pyrolysis tests were carried out in a vertical auger pyrolysis reactor (Patent CA 2830968 and Patent US 9,486,774 B2). The pyrolysis unit (Figure 4.1 and Appendix 1) was installed at the IRDA's research facility (Deschambault, QC, Canada). It included a hopper, a horizontal feed screw, a vertical screw passing through a heater block, a canister for the biochar recovery, and a condensation system. The feedstock in the hopper was fed to the heater block by a horizontal and vertical feed screw in a 2.54 cm diameter steel tube. The rotation speed of the two screws was controlled separately by gear motors, thus controlling the biomass flow rate. An agitator was installed and fixed at the hopper lid in order to facilitate and ensure the supply to the horizontal screw when using materials with a low density. Then, the feedstock was transported through the 25.4 cm long reactor within the vertical screw. The residence time of the feedstock in the reactor was set by controlling the rotation speed of the vertical screw, and was calculated in relation to the pitch of the screw (3.8 cm). Thermal power was supplied by two heating elements of 1500 Watts, inserted in a copper block surrounding the tube in the reaction zone. A thermocouple inserted in the middle of the cooper block registered the outside tube temperature and was used as the set point to control the heating elements. Temperatures were acquired every 10 s by a data logger (CR10X, Campbell Scientific, Edmonton, AB, Canada). At the exit of the vertical screw, the solid product of the pyrolysis (char) dropped into the canister (31.4 cm high and 16.8 cm diameter). A pot (15.2 cm high) was placed into the canister in order to recover the accumulated char. A flange at the bottom of the canister gave access to the pot. Moreover, the fine particles were separated from the gas by an inner baffle (10.2 cm diameter and 10.5 cm long) placed at the exit of the vertical screw. The gas was evacuated by an opening in the upper part of the canister and was directed to the condensation system. Every flange was tightened with a high temperature graphite gasket (1034 kPa) in order to prevent the entry of oxygen into the system. The air flowing into the system was purged with N_2, which was injected from the hopper's lid at volumetric flowrates ranging from 1 to 5 L min^{-1}, controlled by a flowmeter (Aalborg Instruments, New York, NY, USA; accuracy ±2%).

While the N_2 flow ensured that the pyrolysis reaction occurred in a non-oxygen environment, it also helped to evacuate the pyrolysis gas.

4.2.2.2 Biomass selection and analysis

The type of feedstock utilized for pyrolysis (e.g., woody biomass, crop residues, grasses, and manures) influences the yield and characteristics of the biochar, including the concentrations of elemental constituents, density, porosity, and hardness (Spokas et al., 2012). Moreover, the yield of the biochar from biomass can be influenced by its lignin, cellulose, hemicellulose, and extractive contents (Antal Jr and Grønli, 2003). Three biomasses with different physico-chemical properties were selected for the pyrolysis experiments: wood pellets made from a mixture of Black Spruce (*Picea mariana*) and Jack Pine (*Pinus banksiana*), the solid fraction of pig manure (SFPM), and switchgrass (*Panicum Virgatum* L.). In Canada, forest biomass residues such as logging residues are present in large quantities. Moreover, forest biomass is the most common feedstock used for pyrolysis. Woody biomass has a high C content and low N content, which can lead to a biochar with a high C/N ratio. Switchgrass, a perennial grass, shows great characteristics for bioenergy production, because of its medium to high productivity (8 to 12 t DM ha^{-1} yr^{-1}), its sustainability, its great ability to use water and nutrients, its adaptation to the climate of Eastern Canada, and its relatively high gross calorific value, of between 18.2 to 19.1 MJ kg^{-1} (Brassard et al., 2014). SFPM was selected because pyrolysis could be a sustainable management solution for the surplus of pig manure in some regions, where phosphorus (P) spreading in fields is restricted by regulations. Pyrolysis of the solid fraction of pig manure concentrates P in biochar (Cantrell and Martin, 2012), which facilitates its exportation outside of the region in surplus.

All biomasses were ground and sieved to a particle size between 1.0 and 3.8 mm, prior to pyrolysis. The chemical properties of biomasses (proximate and ultimate analysis) were analysed at the IRDA laboratory (Quebec City, QC, Canada). The C, H, N, and ash content of the biomass were evaluated by dry combustion (Leco TruSpec, St. Joseph, MI, USA). The O content was calculated by subtracting the C, H, N, and ash contents from 100% (w/w). Chlorine (Cl) extraction with water and dosage by titration with silver nitrate

($AgNO_3$) was used to determine the Cl content. Cellulose, hemicellulose, and lignin contents were analysed according to the AFNOR method (AFNOR, 2005).

4.2.2.3 Pyrolysis experiments

A review of the literature (Chapter 3) and the preliminary pyrolysis tests presented in Appendix 1 allowed to identify the range of pyrolysis operating parameters needed to obtain typical biochar yields in the pyrolysis auger reactor, ranging from 15% to 45%. For the three selected biomasses, the range of the N_2 flowrate selected was between 1 and 5 L min^{-1}, and the range for the solid residence time was between 60 and 120 s. The range of the pyrolysis temperature found for wood and SFPM was between 500 and 650 °C, and between 450 and 600 °C for switchgrass. Each pyrolysis test was carried out with one kg of biomass. For the selected solid residence times, the biomass flowrate in the pyrolysis reactor depended on the biomass bulk density, and varied from 0.61 to 1.08 kg h^{-1} for wood, from 0.42 to 0.8 kg h^{-1} for SFPM, and was fixed at 0.57 kg h^{-1} for switchgrass. The Box-Behnken design was carried out for each biomass with the defined range of pyrolysis operating conditions (Table 4.1), for a total of 45 experiments.

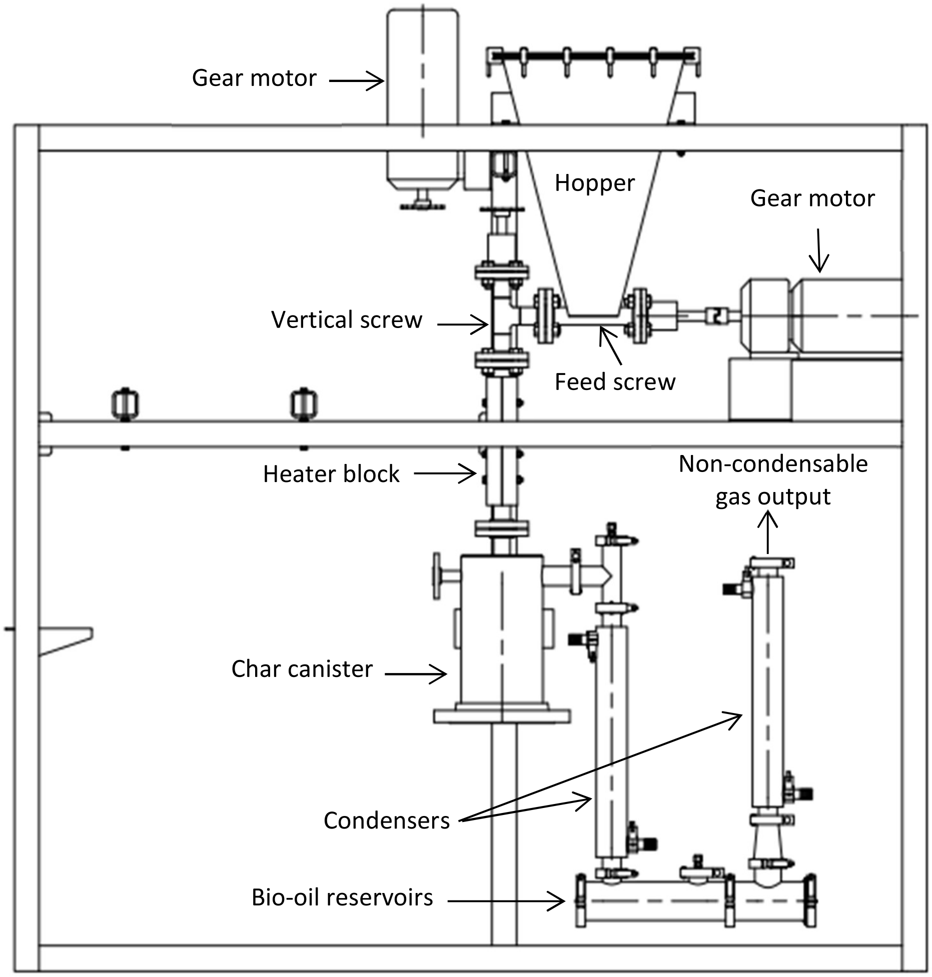


Figure 4.1: Schematic view of the vertical auger pyrolysis reactor

Table 4.1: Box-Behnken design: list of independent variables and levels

Independent variable	**Biomass**	**Values of the coded levels**		
		−1	**0**	**+1**
Temperature (°C)	Wood	500	575	650
	SFPM	500	575	650
	Switchgrass	450	525	600
Solid residence time (s)	Each biomass	60	90	120
N_2 flowrate (L min^{-1})	Each biomass	1	3	5

4.2.2.4 Products yield and biochar characteristics

Bio-oil (Equation 4.2) and biochar (Equation 4.3) yields were calculated on a wet biomass basis, the non-condensable gas (Equation 4.4) yield was calculated by the difference, and the liquid organic yield (Equation 4.5) was calculated by subtracting the water content from the bio-oil yield:

$$Yield_{bio-oil}(\%\ \mathrm{w/w}) = \frac{m_{B1}+m_{B2}}{m_f}\times 100 \tag{4.2}$$

$$Yield_{biochar}\ (\%\ w/w) = \frac{m_{Biochar}}{m_f}\times 100 \tag{4.3}$$

$$Yield_{gas}(\%\ \mathrm{w/w}) = \frac{m_f - m_{Biochar} - m_{B1} - m_{B2}}{m_f}\times 100 \tag{4.4}$$

$$Yield_{liquid\ organics}(\%\ w/w) = \frac{100 - water\ content}{100\times yield\ bio - oil} \tag{4.5}$$

where m_{B1} is the mass of bio-oil produced in the first condenser (g), m_{B2} is the mass of bio-oil produced in the second condenser (g), $m_{biochar}$ is the mass of biochar collected in the canister (g), m_f is the mass of feedstock pyrolysed (g), and the water content is the water content of bio-oil (% w/w) measured following the Karl-Fischer titration method D4928-12 (ASTM, 2012).

Biochar samples were analysed for moisture, volatile matter, and ash contents, based on the ASTM D1762-84 standard (ASTM, 2011). The organic carbon (C_{org}), total carbon (C_{tot}), hydrogen (H), nitrogen (N), and oxygen (O) were also analysed, using the same method as that employed for the analysis of biomasses.

The specific surface area of biochar was determined by gas (CO_2) adsorption according to the Brunauer, Emmett and Teller (BET) method by using a Micromeritics ASAP 2020 surface area and porosity analyser software (GA, USA). Prior to analysis, all samples were outgassed at 300°C for 24 h under vacuum to remove the adsorbed species from the surface of biochars. Analysis of the biochars was carried out at 0°C, with temperature control being achieved with an ice-water bath.

4.3 Results and Discussion

4.3.1 Analysis of biomass

The physicochemical properties of wood, SFPM, and switchgrass, are presented in Table 4.2. An ultimate analysis (C, H, N, O) shows large variations between the biomasses. The C content of wood is the highest, at 47.7%, and is the lowest for SFPM (40.0%). This is inversely proportional to the ash content, which is highest for the SFPM (11.5%), and lowest for wood (0.57%). SFPM has high N and Cl contents (2.96% and 3609 mg kg^{-1}, respectively) when compared to wood and switchgrass. The O content is low for SFPM (28.2%), when compared to wood (40.0%) and switchgrass (42.5%). The H content ranges from 3.23% (switchgrass) to 6.39% (wood). The water content of SFPM (13.0%) is higher than switchgrass (7.2%) and wood (6.5%).

Based on an analysis of the lignocellulosic components, wood could necessitate a higher temperature to decompose because of its lignin content (24%) which is higher than that of SFPM and switchgrass (12.9% and 11.2%, respectively). In fact, the proportion of cellulose, hemicellulose, and lignin in biomass, will influence the degree to which the physical structure is modified during processing (Lehmann and Joseph, 2009). Hemicellulose and cellulose, which are more volatile during thermal degradation (Yang et al., 2007), are degraded at 200–300 and 300–400 °C, respectively, and lignin is degraded between 200–700 °C, representing a wide range in temperatures (Kim et al., 2012b).

Table 4.2: Biomasses physicochemical properties

	Unit	Wood	SFPM	Switchgrass
C_{tot}	% (w/w)	47.7	40.0	45.8
N	% (w/w)	0.128	2.96	0.425
O	% (w/w)	40.0	28.2	42.5
H	% (w/w)	6.39	5.85	3.23
Water content	% (w/w)	6.5	13.0	7.2
Ash	% (d.b.)	0.57	11.5	1.6
Cl	mg kg^{-1}	10	3 609	28
Lignin	% (w/w)	24.0	12.9	11.2
Cellulose	% (w/w)	30.4	11.9	42.9
Hemicellulose	% (w/w)	29.9	22.0	30.1

4.3.2 Response surface models

4.3.2.1 Biochar yield

The yields and properties of products from the 45 pyrolysis tests carried out following the Box-Behnken design with wood, switchgrass and the SFPM are presented in Tables 4.3, 4.4 and 4.5, respectively. The highest bio-oil yields were obtained from wood (48.6% to 63.6%) and switchgrass (44.8% to 61.4%), and pyrolysis of these materials was associated with low biochar yields (17.5% to 31.2% and 16.8% to 26.4%, respectively). Conversely, the pyrolysis of SFPM produced lower yields of bio-oil (38.3% to 46.7%) and higher yields of biochar (32.1% to 40.4%).

Table 4.3: Pyrolysis of wood – Experimental data

Operational Parameters			**Products yields**				**Biochar properties**		
T	Res. time	N_2	Bio-oil	Liquid organics	Biochar	Syngas	C/N	H/C_{org}	O/C_{org}
°C	s	L min^{-1}	%	%	%	%	Ratio	Molar ratio	
500	60	3	57.6	39.0	31.2	10.9	517	0.84	0.25
500	90	1	61.9	39.9	24.6	13.2	491	0.68	0.19
500	90	5	55.2	36.3	30.2	14.2	531	0.92	0.29
500	120	3	63.6	41.9	23.4	12.4	541	0.68	0.19
575	60	1	49.1	31.8	22.6	28.0	483	0.68	0.19
575	60	5	56.8	37.8	22.2	20.5	512	0.74	0.22
575	90	3	60.0	38.1	20.7	18.8	565	0.65	0.19
575	90	3	60.6	40.6	20.6	18.2	487	0.65	0.18
575	90	3	61.5	39.4	20.2	17.8	504	0.62	0.17
575	120	1	58.8	34.4	21.2	19.6	503	0.60	0.15
575	120	5	54.4	35.2	19.9	25.2	500	0.63	0.18
650	60	3	56.0	36.8	18.3	25.2	430	0.59	0.16
650	90	1	52.4	31.3	18.0	29.0	491	0.51	0.13
650	90	5	48.8	27.8	17.5	33.1	497	0.57	0.15
650	120	3	48.6	27.4	17.6	33.3	466	0.53	0.13

T: temperature; Res. Time: solid residence time; N_2: Nitrogen flowrate.

Table 4.4: Pyrolysis of switchgrass – Experimental data

Operational Parameters			**Products yields**				**Biochar properties**		
T	Res. time	N_2	Bio-oil	Liquid organics	Biochar	Syngas	C/N	H/C_{org}	O/C_{org}
°C	s	L min^{-1}	%	%	%	%	Ratio	Molar ratio	
450	60	3	57.8	35.4	25.6	16.4	114	0.81	0.25
450	90	1	59.2	34.3	26.4	14.0	106	0.77	0.21
450	90	5	60.1	37.1	24.9	14.4	102	0.82	0.24
450	120	3	59.4	34.1	24.4	15.9	101	0.69	0.19
525	60	1	61.4	34.7	20.5	17.9	100	0.64	0.18
525	60	5	55	33.4	19.9	24.5	105	0.72	0.21
525	90	3	58.3	37.2	20.2	21.2	115	0.60	0.16
525	90	3	58.5	31.0	21.3	19.9	95	0.61	0.16
525	90	3	59	30.8	20.0	20.6	99	0.58	0.14
525	120	1	56.8	42.3	21.9	21.1	102	0.57	0.14
525	120	5	54.5	27.9	20.9	24.1	103	0.54	0.14
600	60	3	51.5	30.8	16.8	30.5	98	0.58	0.15
600	90	1	48.9	21.3	18.7	31.9	105	0.48	0.10
600	90	5	44.8	20.4	17.3	37.2	99	0.49	0.11
600	120	3	48.1	21.8	18.5	32.9	102	0.46	0.10

T: temperature; Res. Time: solid residence time; N_2: Nitrogen flowrate.

Table 4.5: Pyrolysis of the SFPM – Experimental data

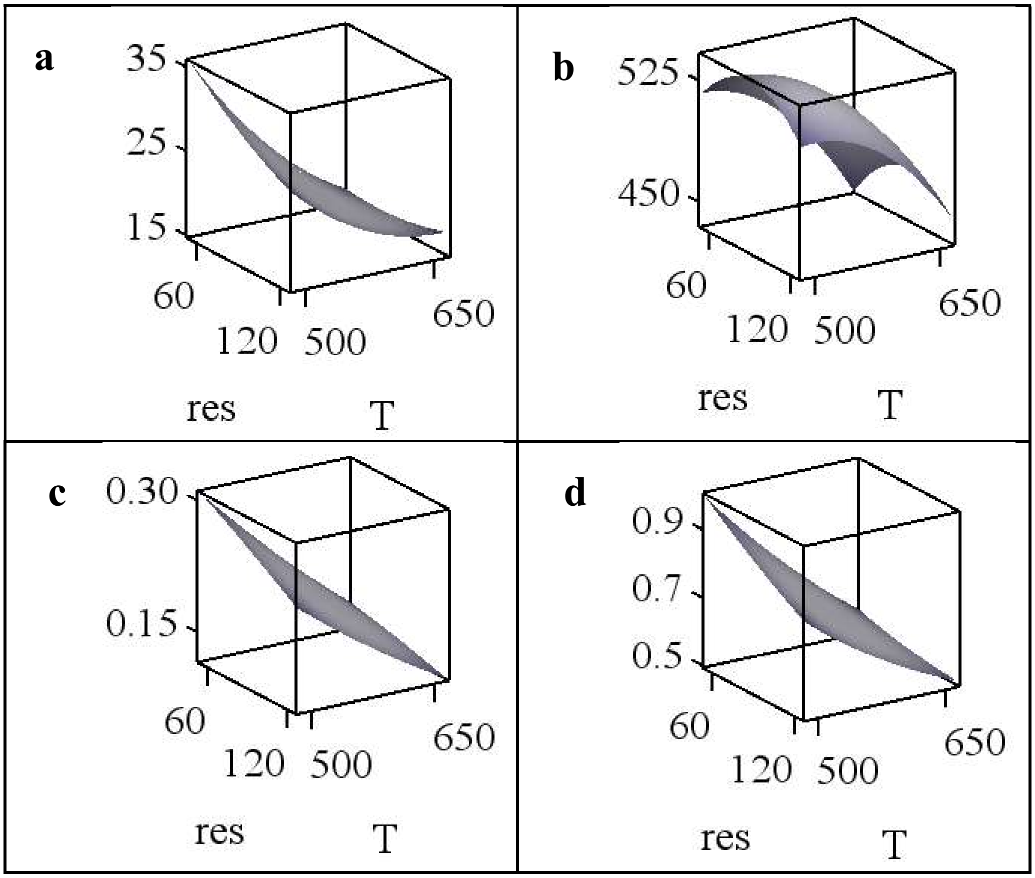
Operational Parameters			**Products yields**				**Biochar properties**		
T	Res. time	N_2	Bio-oil	Liquid organics	Biochar	Syngas	C/N	H/C_{org}	O/C_{org}
°C	s	L min^{-1}	%	%	%	%	Ratio	Molar ratio	
500	60	3	42.8	12.5	41.6	14.9	11.6	0.92	0.21
500	90	1	45.7	12.4	38.8	15.1	12.4	0.80	0.16
500	90	5	39.3	10.6	40.4	19.5	12.0	0.91	0.21
500	120	3	41.7	10.8	39.6	17.0	12.5	0.85	0.18
575	60	1	46.7	10.8	36.7	15.0	12.3	0.75	0.16
575	60	5	40.1	11.7	38.5	20.6	11.5	0.85	0.23
575	90	3	42.3	11.7	35.8	21.0	12.7	0.78	0.18
575	90	3	43.7	12.1	36.0	19.4	12.4	0.76	0.16
575	90	3	43.6	11.9	34.8	19.8	11.4	0.74	0.17
575	120	1	45.7	12.0	34.7	17.7	12.9	0.65	0.14
575	120	5	38.6	9.2	35.9	24.5	12.1	0.72	0.16
650	60	3	42.7	10.5	33.8	21.8	12.6	0.66	0.14
650	90	1	44.0	7.7	32.4	22.8	13.0	0.61	0.13
650	90	5	38.3	9.3	32.1	28.8	11.0	0.74	0.18
650	120	3	39.1	8.5	32.6	27.2	12.8	0.68	0.14

T: temperature; Res. Time: solid residence time; N_2: Nitrogen flowrate.

The canonical analysis indicated that the stationary points of the three response surface models for wood (Figure 4.2), switchgrass (Figure 4.3) and SFPM (Figure 4.4) are saddle points. Thus, results from the RIDGE analysis, indicating the direction toward which further pyrolysis experiments should be performed in order to obtain the minimal and maximal estimated values of biochar yield, are presented in Table 4.6. It is known that biochar yield decreases as pyrolysis temperature increases (Scott et al., 1988). Based on the results of the analysis of variance for the models presented in Tables 4.7 to 4.9, the biochar yield is significantly dependent on the pyrolysis temperature for the three biomass feedstocks ($Pr < 0.05$), as the solid residence time is only significant for the switchgrass biochar (Table 4.8). In contrast to what is reported in some studies (Brown and Brown, 2012; Liaw et al., 2012), the biochar yield was not significantly influenced by the N_2 flowrate, which influences the vapor residence time. The predicted biochar yield is the highest for the pyrolysis of SFPM (maximum of 40%), due to the high ash content of the feedstock, which is found in biochar after pyrolysis. The biochar yield from switchgrass and wood pyrolysis are similar. However, the predicted highest value for wood (27.8%) is higher than for switchgrass (25.2%), despite the highest pyrolysis temperature being demonstrated for wood. It reflects the higher lignin content of wood, which preferentially forms char during pyrolysis (Antal Jr and Grønli, 2003).

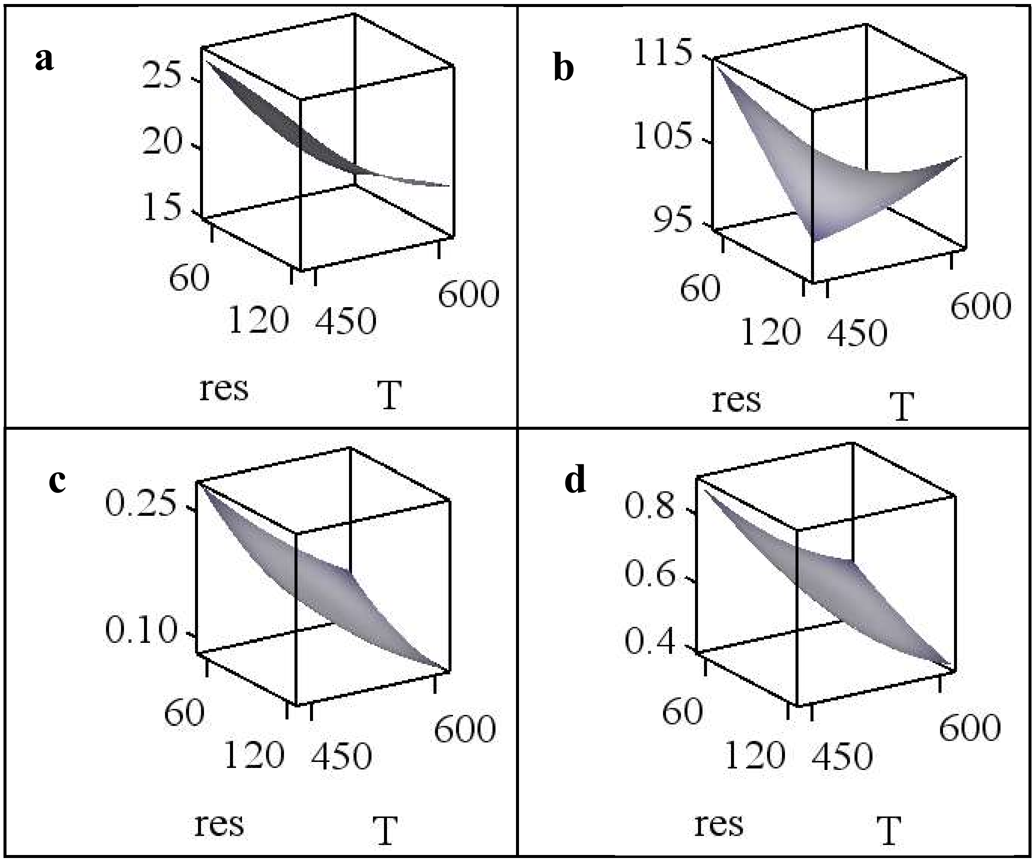
Table 4.6: Estimated values of biochar properties and estimation of optimal pyrolysis operating parameters from the response surface models

	Biochar yield (% w/w)		**H/C_{org}**		**O/C_{org}**		**C/N**	
Wood	Min	Max	Min	Max	Min	Max	Min	Max
Estimated value	17.2	27.8	0.54	0.81	0.14	0.25	477	539
Temperature (°C)	646	507	646	515	642	517	639	522
Residence time (s)	89	79	99	79	103	80	75	90
N_2 flowrate (L min^{-1})	3.6	3.4	2.9	3.9	2.8	4.1	2.8	4.4
Switchgrass								
Estimated value	17.4	25.2	0.47	0.77	0.10	0.23	100	108
Temperature (°C)	593	451	588	456	594	462	588	466
Residence time (s)	78	88	106	80	102	75	74	72
N_2 flowrate (L min^{-1})	3.3	2.8	3.1	3.4	2	3.4	3.3	3.1
SFPM								
Estimated value	32.2	40	0.66	0.90	0.14	0.21	11.5	12.8
Temperature (°C)	649	507	628	508	631	543	594	614
Residence time (s)	95	79	94	79	94	73	84	103
N_2 flowrate (L min^{-1})	3	3.4	1.6	3.6	1.7	4.4	4.9	1.5



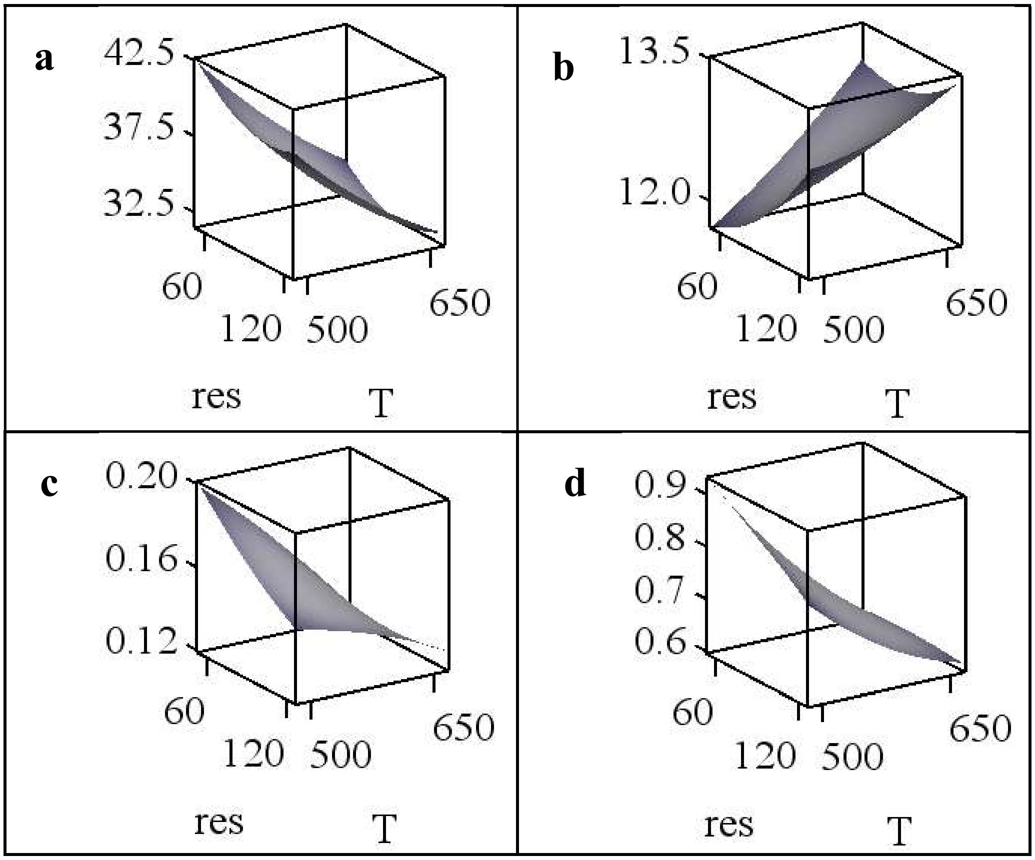
a) biochar yield; b) C/N ratio; c) O/C_{org} ratio; d) H/C_{org} ratio. res: residence time of biomass in the reactor; T: pyrolysis temperature. Nitrogen flowrate was fixed at 4.4 L min^{-1}

Figure 4.2: Response surfaces of dependant variables for biochar produced from wood



a) biochar yield; b) C/N ratio; c) O/C_{org} ratio; d) H/C_{org} ratio. res: residence time of biomass in the reactor; T: pyrolysis temperature. Nitrogen flowrate was fixed at 3.1 L min^{-1}

Figure 4.3: Response surfaces of dependant variables for biochar produced from switchgrass



a) biochar yield; b) C/N ratio; c) O/C_{org} ratio; d) H/C_{org} ratio. res: residence time of biomass in the reactor; T: pyrolysis temperature. Nitrogen flowrate was fixed at 1.5 L min^{-1}

Figure 4.4: Response surfaces of dependant variables for biochar produced from the SFPM

Table 4.7: ANOVA for the model of wood biochar

Wood	Parameter	DF	Mean Squares	F Value	Pr > F
Yield	Temperature	4	53.001	29.96	0.0011 *
	Residence time	4	8.0950	4.580	0.0632
	N_2 flowrate	4	2.9350	1.660	0.2936
H/C_{org}	Temperature	4	0.0287	18.78	0.0033 *
	Residence time	4	0.0063	4.120	0.0763
	N_2 flowrate	4	0.0070	4.580	0.0631
O/C_{org}	Temperature	4	0.0043	22.04	0.0022 *
	Residence time	4	0.0010	4.930	0.0552
	N_2 flowrate	4	0.0014	7.430	0.0247 *
C/N	Temperature	4	1452.1	1.250	0.3972
	Residence time	4	471.35	0.410	0.7982
	N_2 flowrate	4	304.41	0.260	0.8904

DF: Degrees of freedom; Residence time: solid residence time in the heating zone; * Significant at $Pr < 0.05$.

Table 4.8: ANOVA for the model of switchgrass biochar

Switchgrass	**Parameter**	**DF**	**Mean Squares**	**F Value**	**Pr > F**
Yield	Temperature	4	29.441	87.23	<0.0001 *
	Residence time	4	0.8077	2.390	0.1822
	N_2 flowrate	4	0.7911	2.340	0.1876
H/C_{org}	Temperature	4	0.0368	45.51	0.0004 *
	Residence time	4	0.0083	10.30	0.0124 *
	N_2 flowrate	4	0.0014	1.700	0.2847
O/C_{org}	Temperature	4	0.0061	72.32	0.0001 *
	Residence time	4	0.0017	20.26	0.0027 *
	N_2 flowrate	4	0.0003	3.000	0.1298
C/N	Temperature	4	29.954	0.530	0.7194
	Residence time	4	21.608	0.380	0.8125
	N_2 flowrate	4	2.1106	0.040	0.9964

DF: Degrees of freedom; Residence time: solid residence time in the heating zone; * Significant at $Pr < 0.05$.

Table 4.9: ANOVA for the model of SFPM biochar

SFPM	**Parameter**	**DF**	**Mean Squares**	**F Value**	**Pr > F**
Yield	Temperature	4	27.624	96.31	<0.0001 *
	Residence time	4	2.7895	9.730	0.0141 *
	N_2 flowrate	4	0.8267	2.880	0.1381
H/C_{org}	Temperature	4	0.0207	18.07	0.0036 *
	Residence time	4	0.0030	2.630	0.1592
	N_2 flowrate	4	0.0054	4.680	0.0606
O/C_{org}	Temperature	4	0.0009	5.020	0.0533 *
	Residence time	4	0.0008	4.470	0.0661
	N_2 flowrate	4	0.0014	8.040	0.021 *
C/N	Temperature	4	0.2138	0.850	0.5509
	Residence time	4	0.1987	0.790	0.5793
	N_2 flowrate	4	0.6988	2.770	0.1466

DF: Degrees of freedom; Residence time: solid residence time in the heating zone; * Significant at $Pr < 0.05$.

4.3.2.2 H/C_{org} and O/C_{org} ratios

The minimum values of H/C_{org} and O/C_{org} indicate a high biochar C stability (Spokas et al., 2010; Enders et al., 2012; Schimmelpfennig and Glaser, 2012; Manyà et al., 2014), and thus, a maximum potential for C sequestration. H/C_{org} and O/C_{org} ratios of biochars produced from the 45 pyrolysis tests significantly varied for a single biomass, depending on the pyrolysis operating parameters (Tables 4.3 to 4.5). The response surface models illustrated in Figures 4.2 to 4.4 demonstrated that the biochar produced from the three biomasses only shows a good potential for C sequestration if the operating parameters are properly selected. A minimum stationary point was only found for the O/C_{org} molar ratio of biochar made from switchgrass; otherwise, saddle points were identified. Minimum and maximum values of H/C_{org} and O/C_{org}, predicted from the RIDGE analysis, are presented in Table 4.6. The minimum predicted H/C_{org} ratios are 0.47, 0.54, and 0.66 for biochars produced from switchgrass, wood, and SFPM, respectively. This means that, for the optimal pyrolysis operational parameters, at least 50% of the C in biochar is expected to remain in the soil for more than 100 years (Budai et al., 2013). The predicted minimum O/C_{org} ratio below 0.2 (0.10, 0.14, and 0.14 for switchgrass, wood, and SFPM, respectively) confirms the C sequestration potential of biochars produced with similar pyrolysis operating parameters. In fact, the pyrolysis operating parameters needed to obtain the minimum H/C_{org} and O/C_{org} ratios for each biomass, are similar. Conversely, the maximum predicted H/C_{org} and O/C_{org} values for the three biomasses are always above 0.7 and 0.2, respectively. Harvey et al. (2012) found that pyrolysis conditions are the primary factors controlling the thermal stability of the resulting biochar. More specifically, Zhao et al. (2013) demonstrated that biochar recalcitrance (i.e., its ability to resist decomposition) is mainly determined by pyrolysis temperature. The ANOVA analysis confirmed this fact: the pyrolysis temperature always significantly influenced ($Pr < 0.05$) the H/C_{org} and O/C_{org} ratios (Tables 4.7 to 4.9). Moreover, the solid residence time significantly impacted the indicators of C stability for the pyrolysis of switchgrass: as the residence time increased, the H/C_{org} and O/C_{org} ratios decreased. Di Blasi (2002) also reported that the solid residence time has an influence on the physical and chemical characteristics of biochar. The addition of a heat carrier material in an auger reactor could decrease the solid residence time required to provide sufficient reaction heat and time (Brown and Brown, 2012). Finally, Antal Jr and Grønli (2003) reported that biochar characteristics can also be modified with a change in the sweeping gas flow rate, which has an impact on the vapor residence time. Statistical analysis revealed that the N_2 flowrate has a significant impact on the O/C_{org} ratio of SFPM and wood biochars. A lower O/C_{org} ratio is obtained with lower N_2 flowrates.

4.3.2.3 C/N ratio

Biochars with a C/N ratio higher than 30 could help in decreasing the N_2O emissions from soil (see Chapter 2). Results of the experimental Box-Behnken design showed that the C/N ratio markedly varies among biomasses, from 430 to 541 for wood, 95 to 115 for switchgrass, and 11.0 to 13.0 for SFPM. The Canonical analysis of the response surface models illustrated in Figures 4.2 to 4.4 show that a maximum stationary point was found for the C/N ratio of wood biochar, and that saddle points were identified for switchgrass and SFPM biochars. The minimum and maximum values estimated from the RIDGE analysis are presented in Table 4.6. The ANOVA (Tables 4.7 to 4.9) showed that none of the pyrolysis operating conditions significantly influenced the C/N ratio of biochar. In fact, because the N content of biomasses is low, particularly for wood and switchgrass (0.128% and 0.454%), the impact of pyrolysis operating parameters on the N content of biochar, and consequently on its C/N ratio, is low. Even if the C/N ratio for a single biomass does not significantly vary, depending on the pyrolysis operating parameters, there are large variations among the biomasses. In the literature, it was found that the C/N ratio is highly dependent on the type of biomass feedstock used for pyrolysis (Zheng et al., 2012; Cayuela et al., 2014). In the present study, the biomass C/N ratio (13.5, 108, and 372 for SFPM, switchgrass, and wood, respectively) is similar to the C/N ratio of biochar produced from the corresponding biomass, and the C/N ratios of biochars produced from wood pyrolysis are the highest (430 to 565), and ranged from 95 to 115 for switchgrass pyrolysis. Thus, based on their chemical composition, biochars made from these two biomasses have the potential to mitigate N_2O emissions from soil. Biochars produced from the pyrolysis of SFPM have a C/N ratio lower than 30 (11.0–13.0) and could potentially increase N_2O emissions from soil, due to their high N content (Zheng et al., 2012) and low C content.

4.3.3 Experimental validation of the models

In order to validate the quadratic response surface regression models, two biochars were produced from wood (B1 and B2), switchgrass (B3 and B4), and SFPM (B5 and B6) (Table 4.10). B2, B4 (two replicates) and B6 were produced with the pyrolysis operating parameters (temperature, residence time, and N_2 flowrate) determined from the response surface analysis for producing a biochar with the optimal properties in order to maximize the C sequestration potential (i.e., the lowest O/C_{org} and H/C_{org} ratios). B1, B3 and B5 were produced using the optimal parameters for producing a biochar with the opposite characteristics (highest O/C_{org} and H/C_{org} ratio). In fact, because the predicted optimal pyrolysis parameters needed to obtain the optimal O/C_{org} and H/C_{org} ratios are similar, the selected temperature, residence time, and N_2 flowrate, were average values. For example, the lowest H/C_{org} and O/C_{org} ratios predicted for wood biochar would be obtained at 646 °C and 642 °C, respectively (Table 4.6). Thus, the selected temperature for the production of biochar with the best C sequestration potential was 644 °C (Table 4.10). The pyrolysis operating parameters for biochar production that were used to validate the models, and the corresponding yields and properties of the resulting biochars are presented in Table 4.10. B2, B4, and B6 were produced at a higher temperature, during a longer residence time, and with a lower N_2 flowrate than B1, B3, and B5, respectively. Their ash contents are higher, whereas their H and O contents are lower. Moreover, the C and N contents of B2 and B4 are higher than B1 and B3, respectively. The water content is always low (about 1%), whereas the biochars produced at higher temperatures are more alkaline.

Table 4.10: Products yields and physicochemical properties of biochars produced with optimal pyrolysis operating conditions

	Unit	**B1**	**B2**	**B3**	**B4** [1]	**B4** [2]	**B5**	**B6**
Pyrolysis parameters								
Biomass		Wood	Wood	SG[3]	SG	SG	SFPM[4]	SFPM
Temperature	°C	516	644	459	591	591	526	630
Res. Time	s	80	101	78	104	104	76	94
N_2 flowrate	L min^{-1}	4.0	2.9	3.4	2.6	2.6	4.0	1.7
Products yields								
Biochar	% (w.b.)	26.4	18.5	26.9	18.9	18.6	46.4	34.9
Bio-oil	% (w.b.)	58.2	51.5	60.2	49.4	49.0	37.9	41.5
Biochar properties								
C_{total}	% (w.b.)	71.6	80.0	67.1	79.5	80.2	51.5	49.2
C_{org}	% (w.b.)	70.7	76.0	64.9	79.1	79.9	47.4	45.2
H	% (w.b.)	4.8	3.73	4.85	3.36	3.35	3.73	3.36
O	% (w.b.)	21.6	13.4	22.9	10.0	9.59	15.6	13.7
N	% (w.b.)	0.141	0.166	0.641	0.828	0.780	4.40	4.05
$P_{soluble}$	mg kg^{-1}	13.7	7.16	109	26.7	32.1	165	55.7
Water content	% (w.b.)	0.9	1.2	1.5	1.0	1.8	0.9	0.9
Ash (750 °C)	% (d.b.)	1.4	2.1	4.1	5.6	5.4	23.6	28.1
pH		6.8	7.6	6.4	8.7	8.9	8.6	9.3
O.M.[5]	% (d.b.)	98.6	97.9	95.9	94.4	94.6	76.4	71.9
Surface area	m^2 g^{-1}	94.2	138.1	108.7	133.2	133.2	70.9	65.1

[1] First pyrolysis test for B4 production; [2] Second pyrolysis test for B4 production; [3] Switchgrass; [4] Solid fraction of pig manure; [5] Organic matter measured at 750 °C.

The observed vs. predicted values for the biochar yield, C/N, H/C_{org}, and O/C_{org} ratios, are illustrated in Figure 4.5. A comparison of the linear regressions with the 1:1 line indicates that the models fit the experimental data for the yield ($R^2 = 0.97$), C/N ($R^2 = 1.0$), H/C_{org} ($R^2 = 0.88$), and O/C_{org} ($R^2 = 0.73$). B2 and B4 are expected to have a better potential for mitigating climate change, have a high C sequestration potential ($H/C_{org} < 0.7$; $O/C_{org} < 0.2$), and have the potential to reduce soil GHG emissions (C/N ratio > 30).

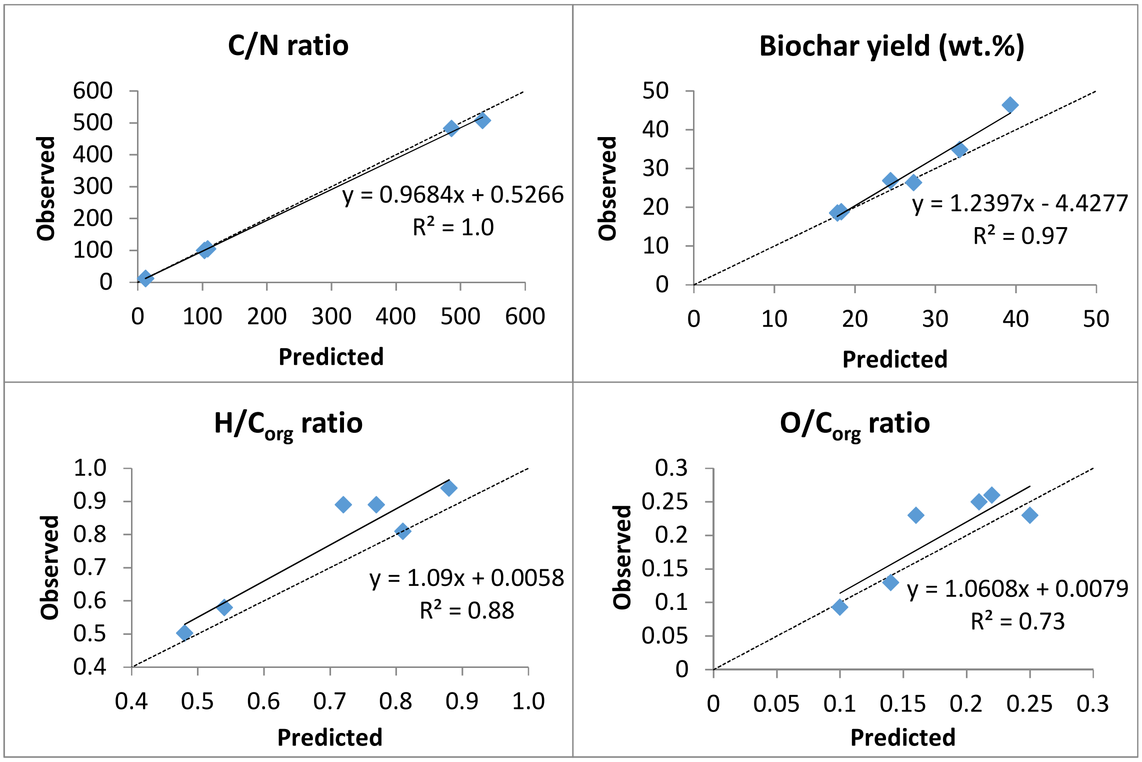


Figure 4.5: Biochar yield, C/N, H/C_{org}, and O/C_{org} ratios: observed vs. predicted values.

4.4 Conclusion

Results from this study demonstrated that the response surface methodology approach can be used to accurately predict the optimal operating parameters of a vertical auger reactor (temperature, solid residence time, and nitrogen flowrate), required to produce engineered biochars with specific characteristics for C sequestration. It was highlighted that the pyrolysis products' yields and biochar characteristics highly depend on the pyrolysis operating conditions and biomass feedstock. The response surface models did not allow to produce biochars with $H/C_{org} < 0.7$ and $O/C_{org} < 0.2$ from the pyrolysis of the SFPM. Only biochar produced from wood and switchgrass can present a high potential for C sequestration if the pyrolysis operating parameters are properly selected. In fact, the minimum H/C_{org} and O/C_{org} ratios predicted from the response surface models reached values lower or equal to 0.54 and 0.14, respectively, for a pyrolysis temperature ranging from 588 to 646 °C, a solid residence time from 99 to 106 s, and a N_2 flowrate from 2.0 to 3.1 L min^{-1}. Moreover, regardless of the pyrolysis operating conditions, the biochars produced from the pyrolysis of wood and switchgrass could help to decrease soil N_2O emissions, because their C/N ratios are higher than 30. Further experiments have to be carried out with the produced biochars, in order to evaluate their effect on soil GHG emissions and C sequestration, and to validate the hypothesis made in this study.

Connecting text

In the previous chapter, it was demonstrated that biochars can be created with specific characteristics when the biomass feedstock and the pyrolysis operating parameters are suitably selected. Six engineered biochars were produced in order to validate the quadratic response surface regression models that were developed. Two biochars were produced from wood (B1 and B2), switchgrass (B3 and B4), and SFPM (B5 and B6). B2, B4, and B6 were produced with the pyrolysis operating parameters (temperature, residence time, and N_2 flowrate) determined from the response surface analysis for producing a biochar with the optimal properties in order to maximize the C sequestration potential (i.e., low O/C_{org} and H/C_{org} ratios). B1, B3, and B5 were produced using the optimal parameters for producing a biochar with the opposite characteristics (highest O/C_{org} and H/C_{org} ratio). Moreover, based on their chemical composition, biochars made from wood and switchgrass have the potential to mitigate N_2O emissions from soil, having a C/N ratio > 30.

In the following chapter, a research study was carried out in order to reach the fourth objective of this thesis, which is to evaluate the potential of the produced engineered biochars to be used as a tool to mitigate climate change by assessing their potential to reduce soil GHG emissions and to sequester C in soils. Thus, the six engineered biochars were amended in two types of soils in an incubation study, and emissions of CO_2 and N_2O were measured over a 45-days period. In addition, the relationships between soil GHG emissions and the chemical properties, microbial diversity and abundance of the soil were studied in order to study the mechanisms involved.

Chapter 5. Effect of six engineered biochars on GHG emissions from two agricultural soils: A short-term incubation study

Abstract

Biochar production for soil amendment was recently proposed as a tool to mitigate climate change, reducing soil greenhouse gas (GHG) emissions and sequestrating carbon (C) in soil. The aim of this research project was to validate the hypothesis that only biochars with specific requirements (low H/C_{org} and O/C_{org} ratios, high C/N ratio) can be used as a tool to mitigate climate change. A 45-days incubation study was carried out, in which six engineered biochars made from wood, switchgrass and the solid fraction of pig manure (SFPM), were amended to two agricultural soils (loamy sand and silt loam) at a dose of 2% (w/w) in one liter jars. Soil moisture content was adjusted at 80% of water-filled pore space with a solution of ammonium nitrate that corresponds to 170 kg of nitrogen per hectare. N_2O and CO_2 emissions were analysed on days 2, 3, and then weekly. Soils chemical properties and bacterial richness, composition and taxonomy were analysed after the incubation period. When compared to the control soils without biochar, N_2O emissions were decreased by 42 to 90%, but only in the silt loam amended with biochars made from wood and switchgrass, these biochars having a high C/N ratio (> 30). Lower $N\text{-}NH_4^+$ and $N\text{-}NO_3^-$ concentrations in biochar treatments than in control soils and a change in microbial abundance could have led to the reduction of N_2O emissions. For each type of biochar, those produced at the highest temperature with low O/C_{org} and H/C_{org} ratios resulted in the lowest increase in CO_2 emission, which could indicate a higher biochar carbon stability. Overall, results of this study demonstrated that biochar can either increase or decrease soil GHG depending on its properties, and that the effect can differ according to soil properties. Future long-term study in the field in the presence of crop should be carried out in order to validate the conclusions of this study.

Key words: Auger Pyrolysis, Biochar, Soil Greenhouse Emissions, Carbon sequestration

5.1 Introduction

The use of negative emission technologies for the permanent removal of carbon dioxide (CO_2) from the atmosphere was reported as a solution to limit global warming below 2 or 1.5 °C by the end of the century (UNEP, 2016), which is the objective stated in the Paris agreement in 2015. The production of biochar and its amendment to soil was identified as a method to improve soil fertility and thus increase crop yields through the improvement of soil composition, water retention, nitrification enhancement and increased nutrient uptake (He et al., 2016; Major et al., 2010; Novak et al., 2009). Recently it was identified among the most promising negative emission technologies (UNEP, 2016), having a useful negative emission potential (0.7 Gt $C_{eq.}$ yr^{-1}), and potentially having the lower impact on land, water use, nutrients, albedo, energy requirement and cost (Smith, 2016). Biochar is produced from the thermochemical conversion of a biomass in an oxygen-limited environment, i.e. pyrolysis. There is a huge variability in physical and chemical properties of biochar, which depend on the feedstock and the pyrolysis operating parameters (Novak and Busscher, 2013; Y. Sun et al., 2014). Thus, not all biochars are valuable for the improvement of soil properties and as a negative emission technology. In fact, biochar can have a high carbon (C) stability when its O/C_{org} and H/C_{org} ratios are lower than 0.2 and 0.7, respectively, and thus its C content ($C_{biochar}$) will be sequestered (i.e. retained) in soils for more than 1000 years (Brassard et al., 2016). Moreover, many research studies demonstrated that biochar can reduce soil GHG emissions when its C/N ratio is higher than 30 (Cayuela et al., 2014). N_2O release by soils is driven by nitrification (oxidation of NH_4^+ to NO_3^- via NO_2^-) under aerobic conditions, and by denitrification (reduction of NO_3^- to N_2O and N_2) under anaerobic conditions (Oertel et al., 2016). The liming effect of biochar (Sohi et al., 2010; Sun et al., 2014), a change in microbial abundance in the soil (Bruun et al., 2011; Harter et al., 2014; He et al., 2016; Lehmann et al., 2011), the adsorption of NO_3^- and NH_4^+ by biochar (Kettunen and Saarnio, 2013; van Zwieten et al., 2010) and an enhancement of soil aeration (Augustenborg et al., 2012; Rogovska et al., 2011) are the mechanisms so far identified that can be responsible for a decrease of N_2O emissions after soil biochar amendment. In addition, the effect of a specific biochar on GHG emissions and on its stability will also depend on the environmental factors, i.e. soil properties, temperature and moisture (Bai et al., 2014).

The aim of this research project was to validate the hypothesis that engineered biochars with low H/C_{org} and O/C_{org} ratios can be used as a tool to mitigate climate change by reducing soil GHG emissions and sequestering $C_{biochar}$ in soil. Thus, six engineered biochars produced from wood, switchgrass and the SFPM, were amended in two agricultural soils, incubated over a 45-days period, and emissions of CO_2 and N_2O were measured. In addition, the relationships between soil GHG emissions and the chemical properties, microbial diversity and abundance of the soil were studied.

5.2 Materials and Methods

5.2.1 Biochar production and characterisation

Six engineered biochars were produced using a vertical auger pyrolysis reactor as described in chapter 4. Three biomasses with different physicochemical properties were selected for the pyrolysis experiments: wood pellets made from a mixture of Black Spruce (*Picea mariana*) and Jack Pine (*Pinus banksiana*), the solid fraction of pig manure (SFPM), and switchgrass (*Panicum Virgatum* L.). Two biochars were produced from wood (B1 and B2), two from switchgrass (SG; B3 and B4), and two from the solid fraction of pig manure (SFPM; B5 and B6). Biochars B2, B4 and B6 were produced with pyrolysis operating parameters that were chosen from a response surface methodology (RSM) and are expected to have optimal properties to maximize the $C_{biochar}$ sequestration potential (low O/C_{org} and H/C_{org} ratios). Biochars B1, B3 and B5 were produced at lower temperature and during a shorter residence time, as determine with the RSM (Chapter 4), to have the opposite characteristics (high O/C_{org} and H/C_{org} ratios). The chemical properties of biochar were analysed following the methods as indicated in section 4.2.2.4. In addition, the morphology of biochars was analysed using Scanning Electron Microscope—Energy Dispersive X-ray Spectroscopy (SEM-EDX - Philips XL 30 FEG) at the Institut des Matériaux de Mulhouse (IS2M) (Mulhouse, France).

5.2.2 Soil sampling and characterisation

Surface soil samples (0-15 cm) were collected from two important agricultural regions in the province of Quebec (Canada): a silt loam (20% sand, 55% silt and 25% clay) in St-Lambert de Lauzon (46°36’ N and 71°10’ W) and a loamy sand (82% sand, 14% silt and 4% clay) in Deschambault (46°40’ N and 71°55’ W). Soils were air-dried, ground and sieved to obtain < 2 mm fraction. Total carbon (C_{tot}) and nitrogen (N) were analysed by dry combustion (Leco TruSpec, St. Joseph, MI, USA). $N\text{-}NH_4$ and $N\text{-}NO_3$ were extracted from 5 g sample in 25 g of KCl 2M following 1 h stirring. P, K, Al and Mg were measured with the Mehlich-3 method. Moreover, soluble P (P_{sol}) was measured using the Sissingh method (Sissingh, 1971). Water-soluble organic C (WSOC) and water-soluble inorganic C (WSIC) were measured from water extraction. Organic matter content was measured at 375 °C, The pH was measured in water, and water content was determined by gravimetric method. Particle size was analysed and soil were classified according to the USDA classification.

5.2.3 Incubation experiment

A 45-days incubation study was carried out in a plant growth chamber (Conviron, Controlled Environments Ltd., Winnipeg, Canada) in order to evaluate the effect of the six engineered biochars on the emissions of CO_2 and N_2O from soil samples. In order to mimic the environmental conditions during summer in Quebec (Canada), the growth chamber was lightened for 15 hours per day while the temperature was adjusted to 22 °C during daytime and to 18 °C for the night time (9 hours).

A total of 14 treatments in three replicates (two types of soil amended with six biochars, and two types of soil without biochar as control treatments) were evaluated. The biochars were added to the soil at a dose of 2% (w/w) and mixed thoroughly. Then, 747 g (d.b) of each soil and biochar mixture was added in four jars of 1 liter capacity. The bulk density (d.b.) of the silt loam and the loamy sand without biochar was adjusted to 1.20 and 1.39 g cm^{-3}, and was slightly decreased with biochar to 1.19 and 1.37 g cm^{-3}, respectively. At the beginning of the incubation period, all treatments were fertilized with a solution of NH_4NO_3 at a dose of 75.6 mg N kg^{-1}, which corresponds to 170 kg N ha^{-1}. In order to favour N_2O emissions, water was added to fill 80% of pore space (80% WFPS). In fact, according to Ussiri and Lal (2013), denitrification becomes the main source of N_2O when water content is between 70 and 80% WFPS. As the jars were kept open in the growth chamber over the incubation period, soil humidity decreased rapidly. Therefore, the water content was adjusted again to 80% WFPS on days 23, 37 and 44, i.e. 24 hours before gas samplings.

5.2.4 Gas sampling and analysis

The N_2O and CO_2 fluxes from soil samples were measured at days 2, 3, 10, 17, 24, 31, 38 and 45 after the addition of the fertilizing solution. At those moments, the jars were closed tightly and gas samples were taken from three replicates of each treatment after 30 minutes (t_{30}) using a 60-mL gas-tight syringe inserted through septa in a through-wall connector. Then, the gas sample was injected into pre-evacuated 20-mL vials with septa. In order to calculate the flux according to the linear regression scheme (Hutchinson and Mosier, 1981), additional samples were taken over the soil surface in ten random jars before they were closed, representing the initial concentration (t_0), and a gas sample was taken from the fourth jar of each treatment after 15 minutes (t_{15}). t_{15} samples were not taken from the jars in which t_{30} were taken in order to keep the pressure constant when the jars were closed. On the same day, gas N_2O and CO_2 concentrations (in ppm_v) were analysed with a gas chromatography-mass spectroscopy (GC-MS) (Varian). Gas concentrations were converted into mg m^{-3} using the ideal gas law and the flux, in mg kg^{-1} h^{-1}, was calculated using linear regression (Hutchinson and Mosier, 1981). An example of calculation is presented in Appendix 2. Cumulative emissions of N_2O and CO_2 over the 45-days incubation period were calculated by linear integration of hourly fluxes starting on day two.

5.2.5 Analysis of soil after incubation

5.2.5.1 Chemical analysis

After the incubation period, the content of each jar was put in a plastic bag, mixed thoroughly, and kept refrigerated until the chemical analyses were performed on soil samples. The analyses that were carried out on soil samples before incubation were repeated on the soil and biochar mixtures after incubation. In addition, $P_{soluble}$ was measured in soil mixtures with biochar produced from the SFPM (B5 and B6) due to the high P content of these biochars.

5.2.5.2 Microbial analysis

DNA extraction was done on each sample of soil and soil – biochar mixtures using commercial FastDNA™ SPIN Kit for Soil (MP Biomedicals, Solon, OH) coupled with a

FastPrep®-24 (MP Biomedicals, Solon, OH) homogenization step following the manufacturer's recommendations. The quality and the quantity of the genomic DNA obtained were evaluated by spectrophotometry on the Biophotometer (Eppendorf, Mississauga, ON, Canada) with a µCuvette® G1.0 (Eppendorf, Mississauga, ON, Canada).

The bacterial diversity was determined using high throughput sequencing and involving a library preparation step with amplification of the rDNA 16S V6-V8 region of bacteria. This was performed using the sequence specific regions described by Comeau et al. (2011) using a two-step dual-indexed PCR approach specifically designed for Illumina instruments by the *Plateforme d'analyses génomiques* (IBIS, Laval university, Quebec City, Canada). More details are given in Appendix 3.

After checking the quality of the run on MiSeq instrument, the sequences obtained were demultiplexed according to the used tag and the forward and reverse fragments were joined under QIIME v1.9.1 (Caporaso et al., 2010) using the fastqjoin tools with a minimum overlap of 50 bp. The quality of the reconstituted fragments was checked by fastqc. The paired sequences were then pooled and filtered using multiple_split_libraries_fastq.py under QIIME pipeline. For the definition of OTUs (Operational Taxonomic Units), an open reference approach was used with the reference database Greengenes 13.8 (DeSantis et al., 2006) and a grouping of OTUs within 97% of similarity. The singletons were eliminated from the bacterial OTU table.

The determination of the bacterial richness was determined by the number of OTUs observed after calculating the rarefaction curves to establish an inflection of the curves and to estimate a common number of sequences making it possible to compare the microbial richness. OTU tables were standardized to 8000 sequences by samples before computing richness diversity and comparative matrices. To compare the beta diversity of bacterial communities, comparison matrix was determined by Bray & Curtis (Beals, 1984). Principal coordinates analysis (PCoA) was used to compare the bacterial diversity of the different treatments.

5.2.6 Statistical analysis

Analysis of variance (ANOVA) was performed using the mixed procedure of SAS (Little et al., 2006) in order to determine significant differences in N_2O and CO_2 emissions among treatments. The fixed variables of the mixed model include the treatment, the date and the interaction date x treatment. The random variables were the replicates, the interaction treatment x replicate, and the experimental error. The date was a factor of repeated measurements with a variance covariance matrix which has been modeled to fit the correlations among the sampling on the same experimental unit. Fixed variables were all significant. The two-by-two differences among treatments were determined by the date of the sampling. The same analysis was performed for soils properties and bacterial richness. For bacterial composition, an Anosim (Clarke, 1993) analysis on Bray & Curtis distance matrix calculating an R-test was used with an estimate of the variations with 999 permutations to evaluate the effects of the DNA extraction methods on the composition of the bacterial communities.

5.3 Results

5.3.1 Biochars characterisation

Biochar production parameters and properties (C_{total}/N, H/C_{org} and O/C_{org}) are presented in Table 5.1. Biochars B2 and B4 are expected to better resist to the decomposition process as their O/C_{org} and H/C_{org} ratios are the lowest (< 0.2 and < 0.7, respectively). Biochars produced from wood (B1 and B2) and switchgrass (B3 and B4) could help reducing soil GHG emissions since their C/N ratio is higher than 30 (Brassard et al., 2016).

Table 5.1: Pyrolysis operating parameters for the production of six biochars and their physicochemical properties

	Unit	B1	B2	B3	B4	B5	B6
Pyrolysis parameters							
Biomass		Wood	Wood	SG[1]	SG	SFPM	SFPM
Temperature	°C	516	644	459	591	526	630
Res. Time[2]	s	80	101	78	104	76	94
N_2 flowrate	L min^{-1}	4.0	2.9	3.4	2.6	4.0	1.7
Biochar properties							
C_{total}/N	Mass ratio	508	482	105	99.4	11.7	12.1
H/C_{org}	Molar ratio	0.81	0.54	0.77	0.48	0.88	0.72
O/C_{org}	Molar ratio	0.23	0.13	0.26	0.09	0.25	0.23

[1]Switchgrass; [2] Residence time of biomass in the reaction chamber

The SEM pictures of biochars are presented in Figure 5.1. Biochars B1 and B2 produced from wood show little apparent porosity. The same observation was done for B4 produced from switchgrass at high temperature. At the opposite, B3 produced at a lower temperature show a higher apparent porosity with larger pore width. Finally, B5 and B6 produced from the SFPM are more porous and their surface is covered of crystals. Larger crystals on B6 surface are K_2SO_4 and KCl. For all biochar types (wood, switchgrass and SFPM), biochars produced at a higher temperature show the most regular patterns of asperity.

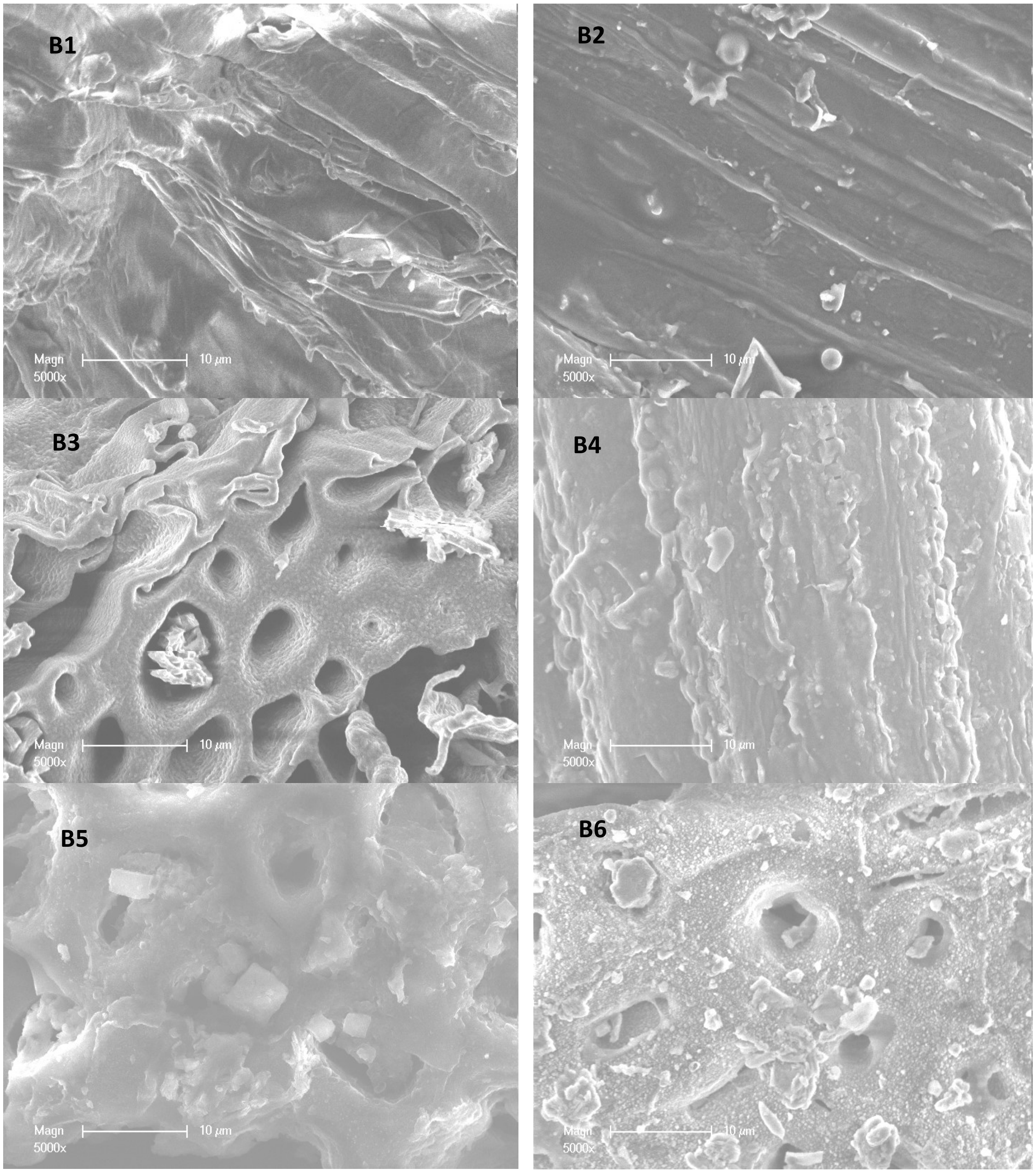


Figure 5.1: SEM/EDX pictures of biochars (B1, B2, B3, B4, B5 and B6)

5.3.2 The effect of biochar on N_2O emissions

The N_2O emissions cumulated from day 2 to day 45, averaged from the three replicates, are presented in Table 5.2. In the loamy sand, N_2O emissions were significantly increased ($P < 0.05$) in the treatments amended with biochars made from wood (B1 and B2) and SFPM (B5 and B6) as compared to the control without biochar.

In the silt loam, the cumulative N_2O emissions were also significantly increased in the presence of biochars made from the SFPM (B5 and B6). At the opposite, B3 made from switchgrass at the lowest temperature contributed to the significant reduction of soil N_2O emissions by 90% ($P < 0.05$) in the mix with silt loam. A similar tendency was observed with B1, B2, and B4 even if the difference was not significant, as these biochars contributed to reduce silt loam soil N_2O emissions by 53%, 42% and 58%, respectively. These results are similar to those reported in a meta-analysis study carried out by Cayuela et al. (2015). The authors found that the average reduction in N_2O emissions in controlled laboratory studies was of 54 ± 3%.

Figures 5.2 and 5.3 illustrate the cumulative emissions at each day of sampling. Before the irrigation on day 23, a similar trend was observed in all treatments. In fact, the hourly flux (in $\mu g\ N_2O\text{-}N\ kg^{-1}\ h^{-1}$) was the highest on day 2, decreased on day 3 and reach out very low values near zero on days 10 and 17. From day 24 to day 31, the cumulative emissions were highly increased in both soils amended with B5 and B5, which is due to the increase in the hourly flux on day 24, the next day after the soils were rewetted. For example, in the silt loam with B5, the hourly flux increased from 0.04 $\mu g\ N\text{-}N_2O\ kg^{-1}\ h^{-1}$ on day 17 to 45.33 $\mu g\ N\text{-}N_2O\ kg^{-1}\ h^{-1}$ on day 24, and it increased from 0.14 $\mu g\ N_2O\text{-}N\ kg^{-1}\ h^{-1}$ on day 17 to 21.36 $\mu g\ N\text{-}N_2O\ kg^{-1}\ h^{-1}$ on day 24 with B6. Thereafter, hourly fluxes decreased and were very low, even on the next day after the subsequent rewetting of samples on days 37 and 44.

Table 5.2: Cumulative emissions of N_2O (mg N-N_2O kg^{-1}_{soil}) and CO_2 (mg C-CO_2 kg^{-1}_{soil}) from day 2 to day 45 (mean of three replicates ± standard error)

	N_2O emissions		**CO_2 emissions**	
	Loamy sand	Silt loam	Loamy sand	Silt loam
B1	0.426 ± 0.143*	0.909 ± 0.238	62.3 ± 7.7*	122 ± 5.5
B2	0.73 ± 0.31*	0.740 ± 0.285	38.7 ± 3.8	126 ± 8.9
B3	0.216 ± 0.085	0.162 ± 0.014*	184 ± 20.5*	196 ± 17.6*
B4	0.144 ± 0.083	0.655 ± 0.244	81.3 ± 9.0*	130 ± 4.4
B5	1.14 ± 0.31*	6.08[1] *	223 ± 19.9*	273 ± 13.7*
B6	0.451 ± 0.039*	2.71 ± 0.549*	157 ± 9.4*	213 ± 3.7*
Control	0.054 ± 0.032	1.57 ± 0.186	10.2 ± 3.2	94.5 ± 7.5

*Significant difference ($P < 0.05$) when compared to control; [1] Missing data in 2 replicates.

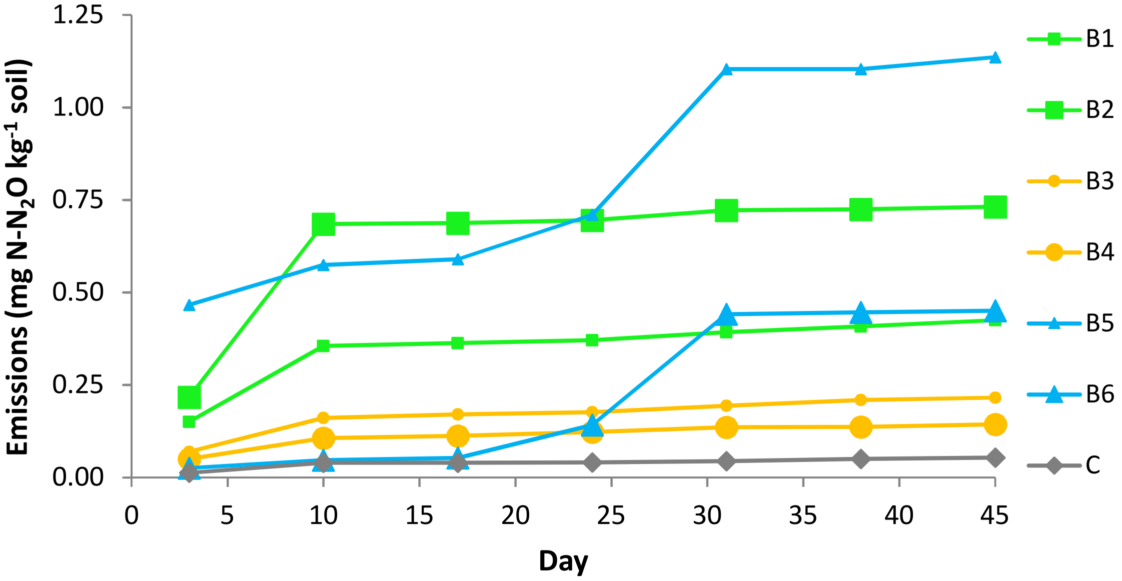


Figure 5.2: Cumulative emissions of N_2O (mg N-N_2O kg^{-1}_{soil}) after the 45-days incubation period in the loamy sand – Mean value of three replicates

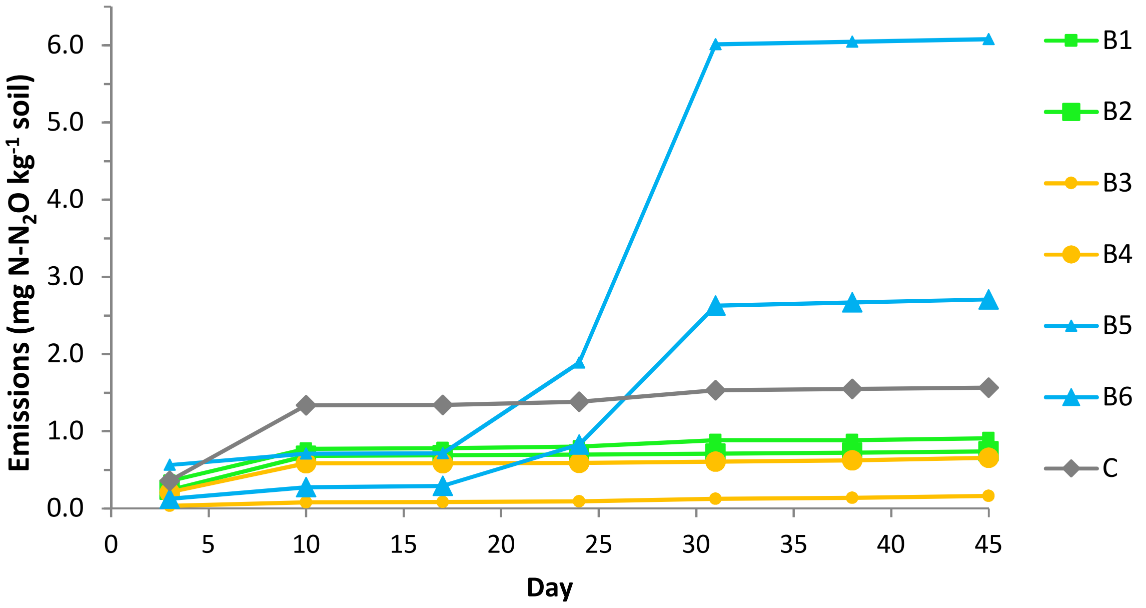


Figure 5.3: Cumulative emissions of N_2O (mg N-N_2O kg$^{-1}_{soil}$) after the 45-days incubation period in the silt loam – Mean value of three replicates

5.3.3 The effect of biochar on CO_2 emissions

The average cumulative soil CO_2 emissions from the three replicates after the incubation period of 45 days are presented in Table 5.2. In the loamy sand, biochar significantly increased CO_2 emissions ($P < 0.01$), except with B2 made from wood at high temperature. A significant increase in CO_2 emissions ($P < 0.01$) was also observed in the silt loam amended with biochars made from SFPM (B5 and B6) and from switchgrass at low temperature (B3), these biochars having H/C_{org} and O/C_{org} ratios higher than 0.7 and 0.2, respectively. In the same soil amended with B1, B2 and B4, CO_2 emissions were slightly increased but the difference was not significant.

Figures 5.4 and 5.5 show a similar trend for cumulative CO_2 emissions in both soils. For all treatments, the hourly fluxes were the highest on day 2 and decreased constantly until day 17 where they stabilised, as cumulative emissions continue to increase constantly. By day 24, the hourly fluxes in the loamy sand without biochar (control) and with B1 and B2 were reduced to near zero.

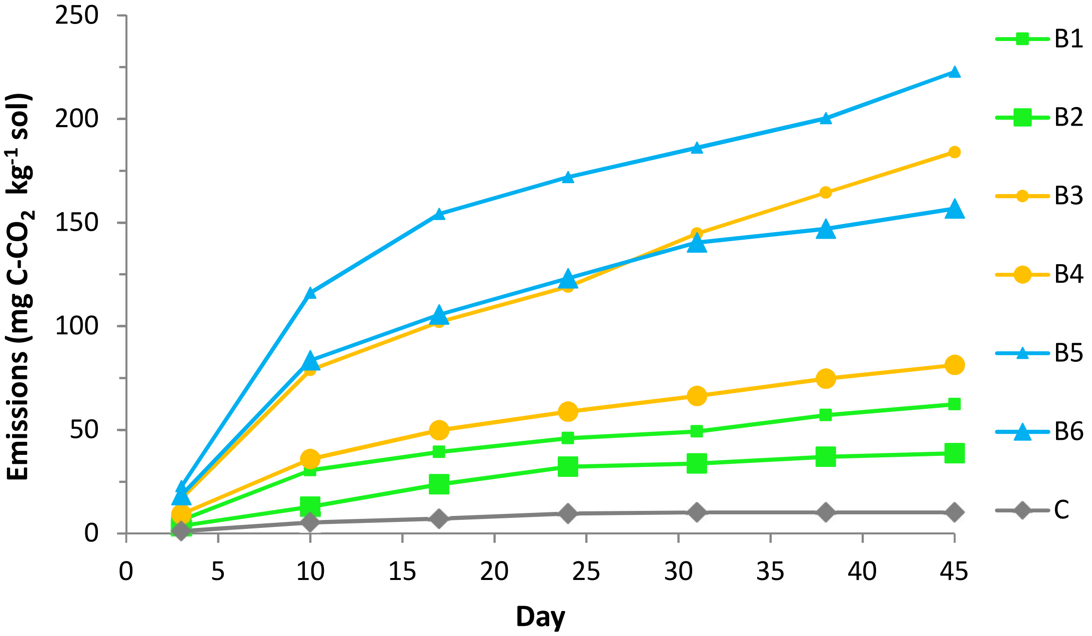


Figure 5.4: Cumulative emissions of CO$_2$ (mg C-CO$_2$ kg^{-1}$_{sol}$) after the 45-days incubation period in the loamy sand - Average of three replicates

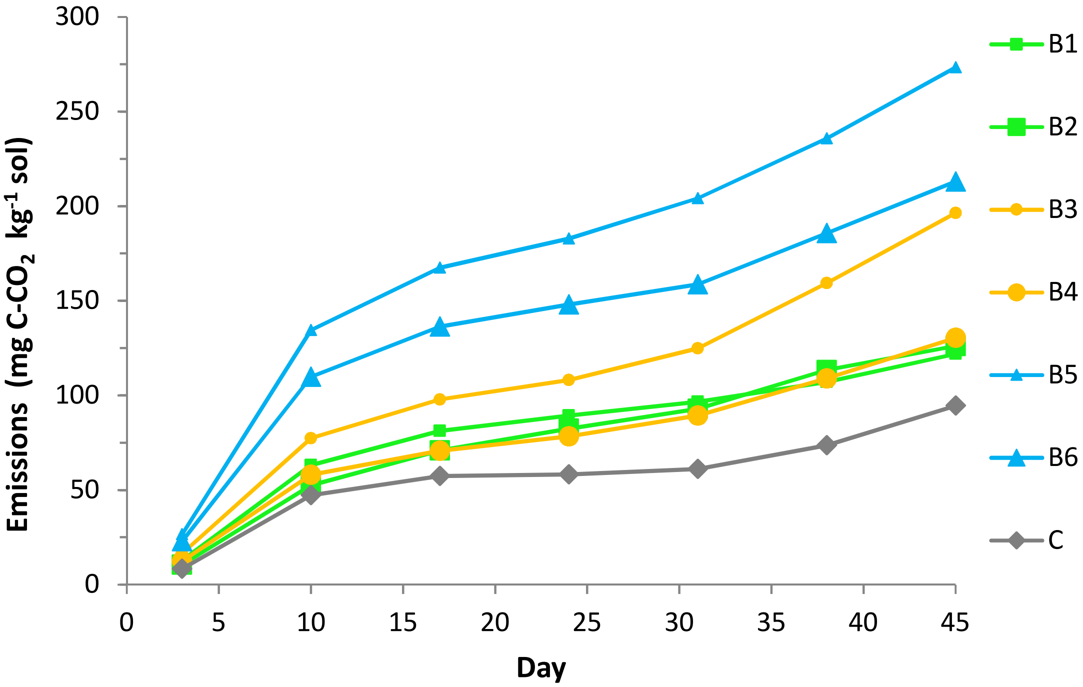


Figure 5.5: Cumulative emissions of CO$_2$ (mg C-CO$_2$ kg^{-1}$_{sol}$) after the 45-days incubation period in the silt loam - Average of three replicates

5.3.4 The effect of biochar on soil chemical properties

The chemical analysis of all treatments after incubation show that the water content in the loamy sand treatments varied from 15.3 to 16.8% (Table 5.3) and from 23.2 to 26.4% in the silt loam (Table 5.4), while it is slightly higher in biochar treatments than in the control soil. After the incubation, both control soils were acidic, with a pH of 5.4 and 4.9 in the silt loam and the loamy sand, respectively. Biochar amendment resulted to significant increase ($P < 0.05$) of pH for both soil types as compared to the treatment without biochar, except for B1 and B2 in the loamy sand. The increase was particularly high in soil amended with biochar made from the SFPM (B5 and B6).

Following the incubation period, B1, B2, B3 and B4 did not have a significant impact on NH_4^+ concentration in the loamy sand; however, it was significantly increased with biochar made from the SFPM (B5 and B6). At the opposite, NO_3^- concentration was significantly decreased with B3, B4 and B6 ($P < 0.05$). In the silt loam, all biochars significantly increased the consumption of NH_4^+ when compared to the control soil ($P < 0.05$). In the treatments amended with B1, B2, B3 and B4, the concentration of NO_3^- was also significantly lower than in the control soil ($P < 0.05$).

Total C (C_{tot}) was significantly increased in all biochar treatments as compared to control after the incubation period. However, water-soluble C (WSC) concentration after incubation was not significantly different in the treatments with biochars made from wood and switchgrass (B1, B2, B3 and B4) than in the control treatments. Only biochars made from SFPM (B5 and B6) allowed a significant increase of WSC ($P < 0.05$). Water-soluble organic C (WSOC) and water-soluble inorganic C (WSIC) show a similar tendency.

Biochar produced from the SFPM contributed to increase the available P and $P_{soluble}$ concentration in both soils. However, only 21.8 to 28.1% of the P added from biochar that became available. The percentage of $P_{soluble}$ vs $P_{available}$ in treatments with B5 and B6 varied between 7.5 and 7.8%, which is higher than in the control soils in which that percentage was 2.2% and 1.7% in the loamy sand and in the silt loam, respectively.

Other elements (K, Ca, Mg and Al) were similar in both soils amended with biochar produced from wood and switchgrass and in the control soils without biochar. However, biochar produced from SFPM increased the concentration of K, Ca and Mg ($P < 0.05$).

Table 5.3: Chemical properties of the loamy sand and of the soil and biochar mixture after the incubation period (average value of three replicates)

Properties	**Unit**	**Initial**	**Soil mixtures after the incubation period**						
		C	**SB1**	**SB2**	**SB3**	**SB4**	**SB5**	**SB6**	**C**
Humidity	%	1.24	16.3	16.1	16.6	16.8	16.7	16.7	15.3
pH		6.2	5.5	5.5	5.8	5.7	6.5	6.9	5.4
C_{total}	%	0.675	1.170	1.127	1.247	1.193	1.153	1.051	0.611
WSC	mg kg^{-1}	88.0	50.9	51.1	63.7	59.4	145	166	68.6
WSOC	mg kg^{-1}	62.4	39.6	41.1	50.7	46.4	107.6	107.4	46.6
WSIC	mg kg^{-1}	25.6	11.4	10.0	13.1	12.9	36.8	58.8	22.0
N	%	0.052	0.056	0.049	0.060	0.058	0.095	0.079	0.047
$N\text{-}NH_4^+$	mg kg^{-1}	0.871	0.513	0.573	0.515	0.542	1.09	0.953	0.602
$N\text{-}NO_3^-$	mg kg^{-1}	5.41	70.6	70.9	65.8	61.9	76.5	66.6	77.4
P	mg kg^{-1}	145	152	147	155	152	273	288	149
$P_{soluble}$	mg kg^{-1}	4.13	--	--	--	--	21.4	22.6	3.2
K	mg kg^{-1}	31.4	49.0	41.7	82.1	75.2	426	520	33.4
Ca	mg kg^{-1}	615	620	599	649	620	797	852	616
Mg	mg kg^{-1}	13.9	15.7	14.8	29.0	19.3	135	149	14.7
Al	mg kg^{-1}	1261	1288	1266	1261	1262	1224	1201	1305

SB1 to SB6 : mixtures of loamy sand with biochars 1 to 6; C: Control soil without biochar

Table 5.4: Chemical properties of the silt loam and of the soil and biochar mixtures after incubation (average value of three replicates)

Properties	Unit	Initial	Soil mixtures after the incubation period						
		C	LB1	LB2	LB3	LB4	LB5	LB6	C
Water	%	3.19	23.8	23.7	23.2	25.3	25.6	26.4	23.5
pH		5.4	5.2	5.0	5.2	5.1	5.6	6.0	4.9
C_{total}	%	1.730	2.92	2.777	2.833	2.923	2.543	2.630	1.677
WSC	mg kg^{-1}	156.1	129	113.1	139.0	140.3	207.0	215.7	124.8
WSOC	mg kg^{-1}	111.1	94.9	81.0	98.4	92.4	171.9	172.0	100.6
WSIC	mg kg^{-1}	45.0	34.4	32.0	40.7	48.1	35.2	43.7	24.3
N	%	0.145	0.147	0.137	0.158	0.157	0.209	0.215	0.152
N-NH_4^+	mg kg^{-1}	5.70	1.58	1.53	1.27	1.27	1.39	1.54	2.78
N-NO_3^-	mg kg^{-1}	42.2	140.7	133.3	140.3	134.0	152.5	156.7	152.7
P	mg kg^{-1}	30.3	32.0	31.1	35.7	32.5	133.3	176.0	30.9
$P_{soluble}$	mg kg^{-1}	0.942	--	--	--	--	10	13.7	0.5
K	mg kg^{-1}	51.7	67.7	62.6	93.2	100.8	352.7	504.3	53.8
Ca	mg kg^{-1}	950	950	971.0	1019	992.3	1171	1314	976.0
Mg	mg kg^{-1}	115	119	117.7	132.3	114.3	234.7	276.3	112.7
Al	mg kg^{-1}	1192	1270	1275	1244	1249	1187	1164	1269

LB1 to LB6 : mixtures of silt loam with biochars 1 to 6; C: Control soil without biochar

5.3.5 The effect of biochar on soil microbial community

5.3.5.1 Bacterial richness and composition

Bacterial richness index was defined with the total number of observed operational taxonomic units (OTUs) for each treatment. In both soil types, only the biochars made from the SFPM had a significant impact on the bacterial richness of soil. The alpha diversity analysis shows a significant decrease of the number of observed OTUs in the loamy sand amended with B5 and B6 as compared to the control soil without biochar ($P < 0.1$; Figure 5.6). In the silt loam, the opposite effect was observed as the number of observed OTUs was significantly higher in the soil amended with B6 as compared to the control. In both soils, the effect of biochar produced from wood and switchgrass (B1, B2, B3 and B4) was not significant as compared to the control soils.

The principal coordinates analysis (PCoA) based on Bray & Curtis distance matrix was carried out to compare the bacterial community composition (Figure 5.7). Control soil samples as well as samples from each mix of soil-biochar can be grouped in a cluster. For each soil type, the two SFPM biochars are well separated. The analysis of similarities that was done with the Anosim test (Table 5.5) revealed that the soil type and the SFPM biochars had a significant impact on the bacterial community composition ($R^2 = 1.00$, $P < 0.015$). In the loamy sand, the bacterial community compositions of soil mix with the biochars made from switchgrass or the SFPM were significantly different from the control ($P < 0.01$). In the silt loam, only the treatments with the biochars made from the SFPM had a significantly impact on the bacterial community composition ($R^2 = 1.00$, $P < 0.015$).

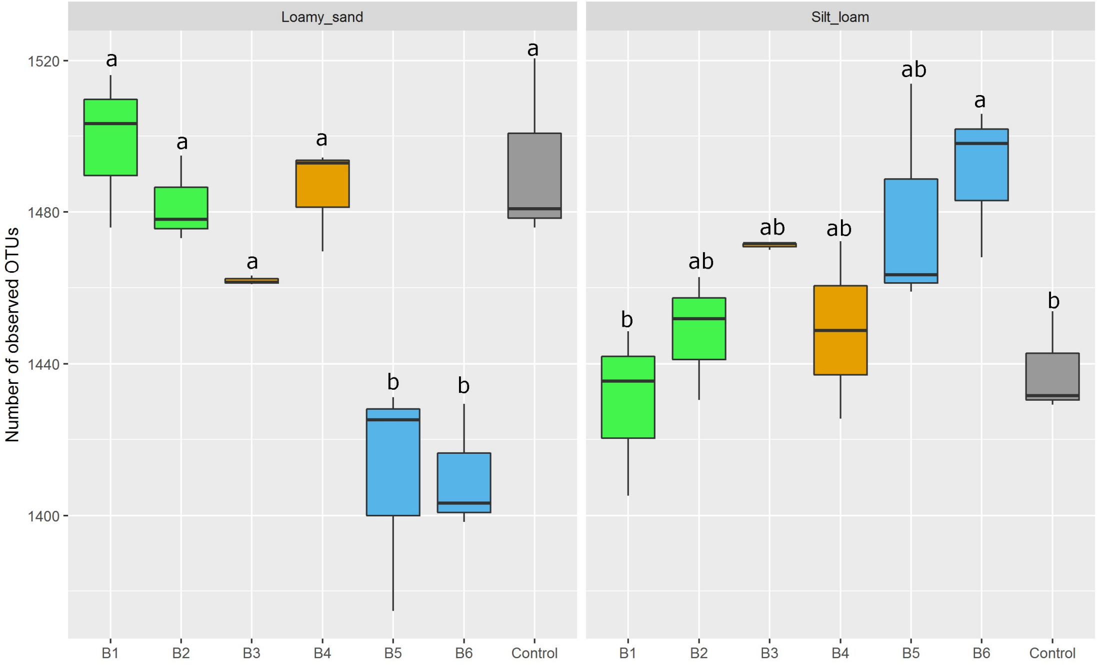
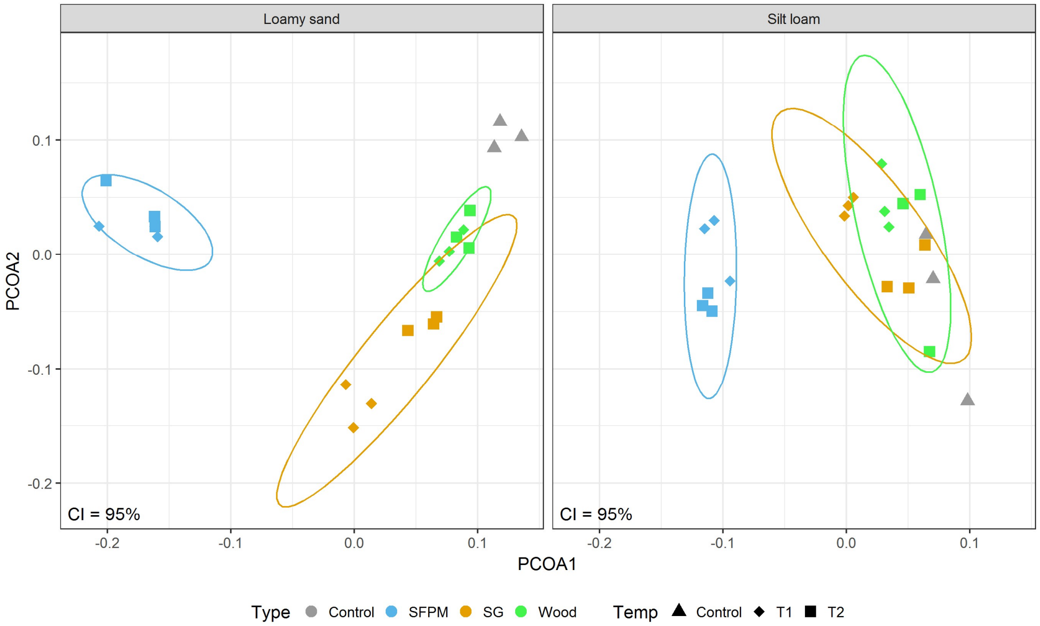


Figure 5.6: Bacterial richness index defined with total number of observed OTUs for each treatment. Different letters indicate a significant difference ($P < 0.1$)



SFPM: Solid fraction of pig manure; SG: Switchgrass. T1: Biochar produced at the lowest temperature; T2: Biochar produced at the highest temperature.

Figure 5.7: Principal Coordinates Analysis (PCoA) based on Bray & Curtis distance matrix to compare bacterial composition

Table 5.5: Analysis of similarities with Anosim index.

	Loamy sand		Silt loam	
Contrast	[1] R^2	[2] P	R^2	P
Control vs Wood	0.972	0.070	0.272	0.115
Control vs Switchgrass	**1.000**	**0.012**	0.491	0.026
Control vs SFPM	**1.000**	**0.009**	**1.000**	**0.013**
Wood vs Switchgrass	**0.719**	**0.004**	0.063	0.178
Wood vs SFPM	**1.000**	**0.005**	**0.993**	**0.002**
Switchgrass vs SFPM	**1.000**	**0.002**	**0.988**	**0.002**

Variable	R^2	P
Soil type	**1.000**	**0.001**
Biochar	0.064	0.130
Biochar type	0.116	0.021
Temperature	0.001	0.422

[1] The value represents the percentage of variation of the bacterial composition explained with the variable or between treatments; [2]Signification level: $P < 0.01$.

5.3.5.2 Bacterial taxonomy

The analysis of bacterial phylum (Figure 5.8) showed that all treatments were dominated by *Actinobacteria*, *Proteobacteria*, *Acidobacteria*, *Gemmatimonadetes* and *Chloriflexi*, but their relative abundance varied. In the loamy sand, the B5 and B6 treatments caused an increase of the abundance of *Actinobacteria*, and a decrease of the abundance of *Acidobacteria*. Proteobacteria abundance was the highest in soil amended with biochars made from switchgrass (B3 and B4), these treatments are the ones in which the N_2O emission was not significantly increased.

In the silt loam, *Firmicutes* were only reduced in B5 and B6 treatments as the N_2O emissions were significantly increased. *Proteobacteria* were increased in all biochar treatments and was the highest in B3 treatment in which N_2O emission was significantly decreased.

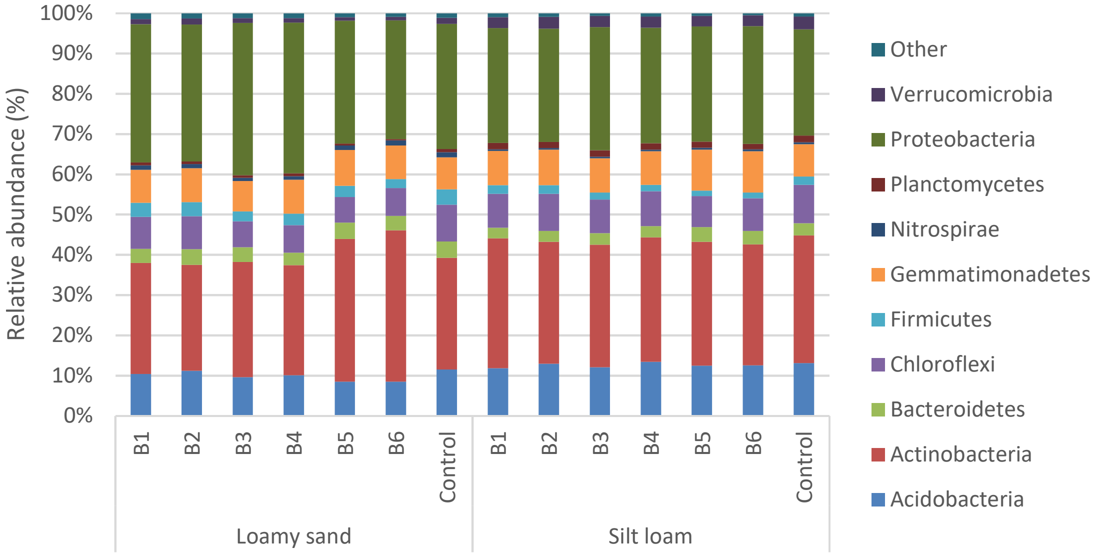


Figure 5.8: Relative abundance of bacterial phylum

5.4 Discussions

5.4.1 The selection of engineered biochars to decrease soil N_2O emissions

The results of this short-term incubation study provided evidence that N_2O mitigation depends on the biochar and soil characteristics, and that the impacts of biochar amendment on physicochemical factors, microbial metabolisms and soil nitrogen cycling are variable. Cumulative N_2O emissions in the control loamy sand were already low and were significantly increased with biochars made from wood and SFPM. Only the amendment of B3 made from switchgrass at low temperature (C/N ratio ≥ 30) in the silt loam resulted in a significant decrease in cumulative N_2O emissions. It could be explained by the lower N content in B3 as compared to B4 produced at a higher temperature, for which the decrease in N_2O emissions was not significant. Biochars made from the SFPM, having a high N content and thus a low C/N ratio (< 30), increased significantly the N_2O emissions in both soils. This could be due to enhanced N content is these soils. Feng and Zhu, (2017) reported that soil N_2O emission was affected by the ratio of biochar to N fertilizer. The authors found a negative linear relationship between the increase in N_2O emission and soil C_{total}/IN (total carbon / inorganic nitrogen) after biochar application. High C_{tot}/IN ratio (> 60) was associated to the suppression of N_2O emissions, and low C_{tot}/IN ratio (< 45) to the promotion of N_2O emission. In the present study, a similar conclusion can be drawn but with higher ratios, as significant increase of N_2O emission was found in treatments with a TC/IN ratio < 170.

Sarkhot et al. (2012) found that the addition of biochar to soil led to significant reductions in net ammonification, nitrification, and N mineralization. In fact, one important environmental factor responsible for the modification in the N cycle in biochar-amended soil, and thus for the reduced N_2O emission, could be the limited bioavailability of electron donors and acceptors (DOC, NH_4^+ and NO_3^-) for microbial nitrification and denitrification due to sorption onto biochar particles or immobilization. In the present study, as the N_2O emissions were significantly decreased in the silt loam with B3 and tended to decrease with B1, B2 and B4 as compared to the control soil without biochar, N-NH_4^+ and N-NO_3^- concentrations were significantly lower in these treatments ($P < 0.05$). Similar results were obtained in a study carried out by Harter et al. (2014): as DOC, NH_4^+ and NO_3^- concentrations decreased, N_2O fluxes declined. Similarly, after a 126-days incubation study, Case et al. (2012) hypothesised that the lower extractable N-NO_3^- content in biochar amended soil than in the control soil could explain the N_2O suppression with increasing biochar amendment. It means that N compounds could have been either adsorbed on the biochar surface or immobilised within microbial biomass, thereby affecting N cycle in soil. In fact, Burger and Jackson (2003) reported that C inputs in soil, for example through biochar amendment, often increase NO_3^- immobilization by stimulating the microbial activity.

Many studies have already reported that biochar has an impact on microbial activity in soil (Jenkins et al., 2017; He et al., 2016). More specifically, Harter et al. (2016) indicated that biochar can affect the relative abundance and taxonomic composition of N_2O-reducing functional microbial traits in soil. Anderson et al. (2011) and Harter et al. (2014) hypothesized that decreased N_2O emissions from biochar amended soil might be caused by enhanced growth and activity of microorganisms capable of complete denitrification. The results of the present study confirm that there is a difference in bacterial richness and composition between treatments, and that the effect is specific to soil and biochar type, especially the SFPM biochar. The significant difference in bacterial richness in soils amended with SFPM biochars can be linked to the increased N_2O emissions in these treatments. More specifically, the Spearman correlation between the N_2O emissions and soil bacterial groups makes it possible to complete the observations of Figures 5.7 and 5.8 by specifying the nature of the correlation (see Appendix 2). A negative correlation indicated that emissions are reduced with the increased number of OTUs of the family. Correlations are negative for N_2O for 7 bacterial OTUs : *Candidatus Solibacter*, *Chloracidobacteria*, *Catellatospora*, *Gaiellaceae*, *Elusimicrobiales*, *Gaiellaceae*, and more particularly for one of the *Hyphomicrobiaceae* family, a group of *Proteobacteria* involved in C and N cycling (Gardner et al., 2011). Under hypoxic conditions, *Hyphomicrobiaceae* can utilize N_2, NO_3^- and NH_3 (W. Wang et al., 2016). A study from Anderson et al. (2011) showed a similar conclusion, as the abundance of Hyphomicrobiacea increased by 14% in the presence of biochar.

According to Castaldi et al. (2011), an increased activity of N_2O-reducing bacteria due to an elevated soil pH could decrease the N_2O/N_2 ratio. In the present study, pH was increased with biochar amendment, especially with B5 and B6. The significant reduction in N_2O emissions in the silt loam was observed with B3, but not with B4. As these two soil samples have the same significant increase in pH, it indicates that the change in pH alone could not explain the reduction of N_2O emissions.

Improved soil aeration through biochar addition is another mechanism proposed by Augustenborg et al. (2012). The SEM-EDX pictures show that B3 has a larger macroporosity, which could have a positive impact on soil porosity, and thus could be linked to the significant decrease of N_2O emissions in the silt loam.

5.4.2 Biochar stability in soil

In the present study, soil CO_2 emission was considered as an indicator of biochar stability. CO_2 emissions were always higher in soils amended with biochar than in control soils, and the CO_2 release was particularly high in the first 10 days. According to Ameloot et al. (2013), enhanced release of CO_2 after biochar addition to soil, which occurs mainly in the first days, may result from priming of native soil organic carbon (SOC) pools, biodegradation of biochar components from stimulation of soil organisms by biochar, or abiotic release of biochar-C. In the context of the present study, it was not possible to confirm whether biochar caused a positive or negative priming effect on SOC mineralization because biochar C was not labelled. However, the hypothesis is that the degradation of the labile C in biochar caused the increased CO_2 emissions, as reported by Troy et al. (2013) and Spokas et al. (2009). The fast mineralization of fresh biochar has previously been attributed to the decomposition of labile organic C due to their lower masses and simpler structures. After mineralization of the labile biochar-C pool, mineralization rates in amended soils decrease and become nearly equal to rates in control treatments.

Despite the higher C-CO_2 emissions from the biochar treatments, C-CO_2 emitted represent a small proportion of biochar-C and does not compromise its potential to sequester C in soil (Jones et al., 2011). The quantity of C mineralized from biochar was estimated by subtracting the cumulative C-CO_2 emitted by the control soils from the cumulative C-CO_2 emitted by the biochar treatments. Quantities of C mineralized from biochar ranged from 39 to 273 mg C-CO_2 kg_{soil}^{-1}, which represent 0.18 to 1.68% of the total C in biochar. These values are in accordance with the results of other studies (Gascó et al., 2016; Luo et al., 2016; Steinbeiss et al., 2009; Zimmerman et al., 2011). A meta-analysis carried out by Wang et al. (2016) indicates that biochar addition can stimulate total soil CO_2 emissions by 28 to 32%. The same study revealed that the average biochar decomposition rate for studies lasting less than 6 months was 0.023% per day. For example, Bruun et al. (2012) carried out an incubation study of biochar amended in a sandy loam and reported cumulative C losses of 2.9 and 5.5% for biochar produced from slow pyrolysis and fast pyrolysis of wheat straw, respectively. Other studies have shown that biochar C mineralises at a very slow rate in soils, e.g. averaged 0.1 to 3% applied biochar-C mineralised per year (Fang et al., 2015).

The cumulative CO_2 emissions depended on soil type and on the type of biochar and pyrolysis operating parameters. For the treatments with biochars produced from switchgrass and the SFPM, cumulative CO_2 emissions were significantly lower for the biochar produced at the highest temperature ($P < 0.05$), these biochars having lower H/C_{org} and O/C_{org} ratios then biochars produced at the lowest temperature. The hypothesis is that the biochars with low H/C_{org} and O/C_{org} ratios resist decomposition better. This is in accordance with the conclusions of other studies in which biochars produced at different temperatures were evaluated (Al-Wabel et al., 2013; Junna et al., 2014; Luo et al., 2011; Sun et al., 2014). Moreover, CO_2 emissions from B5 and B6 treatments were particularly high as compared to the other treatments. This could be due to the high N input by the biochars made from the SFPM. In fact, soil respiration generally increases with increasing soil N content (Oertel et al., 2016). The morphology of biochar can also give an indication on the $C_{biochar}$ stability. In fact, B2 and B4 have the lowest O/C_{org} and H/C_{org} ratios (< 0.15 and < 0.55, respectively) and show the most regular patterns of asperity (Figure 5.1).

The diversity of microbial community and its abundance in soil have an influence on soil respiration. Correlations between the CO_2 emissions and soil bacterial groups were done in order to identify bacterial groups associated with lower CO_2 emissions. Correlations are negative for seven bacterial OTUs, including two *Proteobacteria* (one *alphaproteobacteria* and one *Xanthomonadaceae)*, and three *Firmicutes* (three *Clostridium*) (Appendix 2). Thus, a decrease of these bacterial OTUs could indicate lower CO_2 emissions.

5.5 Conclusion

The results of this study demonstrated that only specific engineered biochars can be used as a tool to mitigate climate change in order to reduce soil N_2O emission and to sequester $C_{biochar}$ in soil. Moreover, the benefits were specific to soil properties. When compared to the control soil without biochar, N_2O emissions were significantly decreased (-90%) only in the silt loam amended with biochar made from switchgrass at a low temperature and with a short solid residence time (B3). A similar tendency was observed with B1, B2, and B4 but the difference was not significant, as these biochars contributed to reduce soil N_2O emissions by 53%, 42% and 58%, respectively. Lower NH_4^+ and NO_3^- concentrations in soil amended with biochar as compared to the control soil and a change in soil microbial abundance were identified as the possible causes for the reduction in N_2O emissions. For example, the microbial group of *Proteobacteria*, and more specifically the *Hyphomicrobiaceae* family, was affected by biochar and could have an influence on N cycle and N_2O emissions. Soil CO_2 emissions were favoured by biochar amendment, but emissions from soils amended with biochars produced at the highest temperature were lower, indicating a higher stability. In order to validate the results of this study, long-term studies should be carried out in the field in the presence of crops.

Connecting text

The results of the research study presented in Chapter 5 demonstrated that only biochars produced with specific properties can be used as a tool to mitigate climate change to reduce soil N_2O emissions and to sequester $C_{biochar}$ in soil. More specifically, biochars made from switchgrass decreased the N_2O emissions by 90% (B3) and 58% (B4) in the silt loam as compared to the soil samples without biochar. The difference was significant only with B3 produced at a lower temperature (459 °C) and with a shorter biomass residence time in the reactor (78 s). It was demonstrated that biochars have an impact on soil chemical properties and microbial richness and abundance.

However, the global environmental and energetic impacts of the pyrolysis of switchgrass, from the cultivation of energy crop on marginal lands to the valorisation of pyrolysis co-products, is not well known. Therefore, in the following chapter, the life cycle assessment (LCA) approach was used to reach the fifth objective of this thesis, which is to assess the greenhouse gas (GHG) emission and energy impacts of switchgrass pyrolysis in the vertical pyrolysis auger reactor, from switchgrass cultivation to the valorisation of pyrolysis co-products. Experimental data from the pyrolysis of switchgrass presented in Chapter 4 and from the incubation study presented in Chapter 5 were used as input data.

Chapter 6. Pyrolysis of switchgrass in a vertical auger reactor for biochar production: A greenhouse gas and energy impacts assessment

Abstract

A life cycle approach was used to assess greenhouse gas (GHG) emissions and energy balances of switchgrass pyrolysis in an auger reactor for biochar production, with bio-oil and syngas as co-products. The system boundaries included the cultivation of switchgrass on marginal lands, handling, transport, conditioning, pyrolysis, the amendment of biochar in soil to sequester carbon (C) and to reduce N_2O emissions, and the valorisation of bio-oil and syngas as energy sources. Two pyrolysis scenarios were evaluated. Scenario A involves a lower pyrolysis temperature and a shorter solid residence in the reactor as compared to scenario B. A negative GHG emissions balance of -2105 and -2524 kg CO_2e t^{-1} biochar was obtained for scenarios A and B, respectively. Biochar C sequestration contributed the most to the reduction of GHG emissions in scenario B due to the high C content and stability in biochar. However, scenario B resulted in a higher energy consumption (10,960 MJ t^{-1} biochar) than scenario A (2401 MJ t^{-1} biochar) due to a higher energy consumption of the pyrolysis unit. These results confirm that pyrolysis of switchgrass for biochar production can be a negative emission technology, but pyrolysis operating parameters should be selected carefully.

Keyword: Greenhouse gas, energy, pyrolysis, biochar, bio-oil, switchgrass.

6.1 Introduction

The production of energetic crops as a feedstock for pyrolysis could be a solution to valorise marginal lands that cannot be used for cultivation of food crops. Switchgrass (*Panicum virgatum L.)*, a native C4 perennial grass, was identified as a potential economically viable alternative to high-input crops on these lands (Lemus et al., 2002; Samson et al., 2014) because of its high productivity and its low water and nutritional requirements. The cultivation of switchgrass would help improve soil fertility and reduce farmers' risks for crop production in marginal areas (Samson et al., 2014). Switchgrass can then be used as a feedstock in thermochemical conversion processes (e.g. combustion, pyrolysis or gasification) to produce heat and energy (Bai et al., 2010). In the case of pyrolysis, biomass is decomposed at moderate temperature (350 – 700 °C) under oxygen-limiting conditions. The resulting co-products are syngas and bio-oil, that can be used as an energy source to substitute fossil fuels or diesel (Bridgwater, 2012), and biochar, that can be used for soil amendment. In fact, biochar could sequester carbon in soil and reduce GHG emissions (Brassard et al., 2016; Cayuela et al., 2014) while improving soil properties and increasing crop yields (Novak et al., 2009a).

The United Nations Environment Program (UNEP, 2016) and Smith (2016) proposed biochar production from pyrolysis as a promising negative emission technology. Basu (2010) reported that a pyrolysis system initially requires external heat only until the required temperature is reached and afterward, the energetic products of pyrolysis, including biochar, can be used to heat the reactor. However, the global energetic and environmental impact of the pyrolysis of switchgrass, from the cultivation to the valorisation of pyrolysis co-products is not well known. Life cycle assessment (LCA) is often used in bioenergy area to address the carbon abatement and energy benefits of a technology or to select the technology resulting to the lowest environmental impact (Cherubini, 2010). LCA is defined as a "cradle-to-grave" approach used to study the environmental aspects and potential impacts of a product or a system throughout its life, from raw material acquisition through production, use and disposal (Hunkeler, 2016). Dutta & Raghavan (2014) highlighted the importance of a life cycle analysis to estimate the full life-cycle GHG emission balance and economic feasibility of biochar systems. For example, the conclusions of an LCA study realized by Roberts et al. (2010) revealed that for each ton of dry biomass waste utilized through biomass pyrolysis with biochar returned to soil, a net sequestration of about 800–900 kg of CO_2e could be provided. According to Woolf et al. (2010), biochar production can have a larger climate change mitigation potential than combustion of the same sustainably procured biomass. Similarly, Peters et al. (2015) found that coproducing biochar and heat by slow pyrolysis resulted in higher GHG savings than direct biomass combustion. von Doderer and Kleynhans (2014) presented a case study assessing lignocellulosic bioenergy systems using LCA. They found that the scenarios in which bio-oil produced in mobile fast-pyrolysis units used for energy generation and biochar sold to fertilizing industry for application to soil showed the best results on a global warming perspective, resulting in negative global warming potential

(GWP) levels of more than 32,000 t CO_2e for the electricity generated annually by a 5-MW system.

Assuming that pyrolysis of switchgrass for biochar production with bio-oil and syngas as co-products could be used as a negative emission technology and can meet its own energy demand, the goal of this study was to assess the GHG emissions and energy use of switchgrass pyrolysis in an auger reactor. The life cycle approach was used to evaluate and compare the climate change and energy impacts of two biochar systems, from the cultivation of switchgrass on marginal lands, to the use of biochar as a soil amendment in a wheat crop, and bio-oil and syngas use as energy sources.

6.2 Methods

6.2.1 Goal and scope

The goal of this study was to compare the GHG emissions and energy balances associated with two biochar production systems (scenarios A and B) in order to evaluate the impact of pyrolysis operating parameters on the global performance of the systems. Experimental data from the pyrolysis of switchgrass in an auger reactor presented in Chapter 4 and from an incubation study carried out to measure the GHG emission from soil amended with the produced biochars (Chapter 5) were used as input data in this study. The scenarios imply that biochar is used for soil amendment in a wheat crop for carbon sequestration and for the reduction of soil GHG emissions, and syngas and bio-oil are used as energy sources. The life cycle approach was followed, using a "cradle-to-grave" approach. The calculations were done using Microsoft® Excel® 2013 software (Microsoft, USA). The functional unit for the system corresponds to the production of one ton of biochar. Hot spots, i.e. the processes that are responsible for the highest contribution to climate change, were identified through a contribution analysis.

6.2.2 System boundaries

The system boundaries were defined from the switchgrass establishment on marginal lands to the final use of pyrolysis products. The following activities were considered in the system boundaries: switchgrass cultivation (soil preparation, pesticide and fertilizer applications, sowing, cutting, raking, baling), handling (loading, transport, unloading, pickup), conditioning (grinding, drying), the pyrolysis process, the valorisation of biochar as a soil amendment in a wheat crop for C sequestration and the reduction of soil GHG emissions, and the valorisation of bio-oil and syngas as energy sources. The fabrication of machinery was not included in the boundaries. However, the energy and GHG emissions associated to fuel, fertilizer, pesticides and seeds fabrication were included.

6.2.3 Inventory

6.2.3.1 Switchgrass cultivation

It was considered that switchgrass is cultivated on marginal lands in a loam soil in the province of Quebec (Canada) following the recommendations of Samson et al. (2014) during a 16-years cycle (Table 6.1). The field preparation starts in fall with a moldboard plow passing. Then, the field is sprayed with an herbicide (glyphosate – 1.2 $kg_{a.i.}$ ha^{-1}) to eliminate perennial weeds. In the spring, soil preparation includes harrowing (one pass of disk harrow and one pass of field cultivator). It is followed by seeding (cave-in-rock cultivar, 10 kg ha^{-1}) and field packing. Soon after planting, atrazine (1.34 $kg_{a.i.}$ ha^{-1}) is applied to control post-emergent broadleaf weeds. Switchgrass is cut each fall with a disk mower and conditioner, and harvested on spring. Harvesting includes a pass of side delivery rake and baling with a large square baler. By year 3, nitrogen fertilizer (NH_4NO_3) is applied at a dose of 55 kg N ha^{-1} yr^{-1}.

6.2.3.2 Switchgrass handling, transport and conditioning

The large square bales (2.6 m x 0.8 m x 0.9 m) are taken from the field using a tractor with clamps and are loaded on a wagon with a capacity of 12 bales. Bales are then transported to the storage facility next to the pyrolysis plant. Prior to pyrolysis, the bales are taken in the storage facility with a tractor and are chopped in a tube grinder. Switchgrass is then dried to reduce its water content from 13% to 7.2% in a large rotary dryer with the efficiency of 3.5 MJ kg^{-1} of water evaporated (Roberts et al., 2010).

Table 6.1: Switchgrass cultivation: Field operations for the two scenarios

Year	Operation	Equipment	Tractor
1	Herbicide application (glyphosate)	Trailed sprayer	75 kW
1	Tillage	Moldboard plow	155 kW
1	Harrowing	Disk Harrow, tandem, primary tillage	155 kW
1	Harrowing	Field Cultivator, secondary tillage	155 kW
1	Seed sowing	Grain drill w/press wheels, 2.4 m	155 kW
1	Field packing	Roller packer	75 kW
1	Herbicide application (atrazine)	Trailed sprayer	75 kW
1	Herbicide application (glyphosate)	Trailed sprayer	75 kW
2-16	Cutting	Mower, disk	75 kW
2-16	Harvesting (10.37 t ha^{-1})	Rake, side delivery	75 kW
		Baler, large square bales	155 kW
2-16	Loading and unloading	Tractor with clamp	75 kW
	Transport	Wagon for large bales	75 kW
3-15	Fertilization	Mineral fertilizer spreader	75 kW

Cultivation on a loam soil; 16-years cycle, starts in September and ends in August.

6.2.3.3 Pyrolysis scenarios

In order to collect experimental data for this study, pyrolysis of switchgrass was carried out in an auger pyrolysis reactor (capacity of about 1 $kg_{biomass}$ h^{-1}) at the research facility of IRDA (Deschambault, Quebec, Canada). Pyrolysis operating parameters (Table 6.2) were determined by using a response surface methodology approach for producing two biochars with opposite properties (Chapter 4). Biochar produced for scenario B is expected to have the optimal properties for C sequestration ($H/C_{org} < 0.7$ and $O/C_{org} < 0.2$), as the biochar produced in the scenario A has the opposite properties (high H/C_{org} and O/C_{org} ratios). The chemical properties of biochars (C, C_{org}, H, N, O) were analysed in the laboratory of IRDA (Québec, Canada). The energy consumption of the pyrolysis unit was measured and corresponded to 7510 MJ t^{-1} biomass in scenario A, and 8380 MJ t^{-1} biomass in scenario B (Appendix 4). The author posed the hypothesis that the energy consumption and the pyrolysis products will be similar to a scaled-up unit.

Based on the products yield, the quantity of switchgrass cultivated in each scenario (3.45 tons of dry matter in scenario A or 4.94 tons of dry matter in scenario B) was calculated from the quantity of feedstock needed to produce one ton of biochar per year

(Table 6.2). The yield of switchgrass is estimated to 10.27 t (d.m.) ha^{-1} yr^{-1} (3 t ha^{-1} on the year 2, 8 t ha^{-1} on year 3 and 11 t ha^{-1} on years 4 to 16). Thus, cultivated area needed is 0.336 ha in scenario A, and 0.482 ha is cultivated in scenario B.

Table 6.2: Pyrolysis scenarios, operating parameters and product yields and properties

	Unit	Scenario A	Scenario B
Pyrolysis parameters			
Temperature	°C	459	591
Solid residence time	s	78	104
N_2 flowrate	L min^{-1}	3.4	2.6
Biochar			
Yield	% (d.b.)	29.0	20.3
C/N	Mass ratio	105	99.4
H/C_{org}	Molar ratio	0.77	0.48
O/C_{org}	Molar ratio	0.26	0.09
Bio-oil			
Yield	% (d.b.)	64.9	53.0
Higher heating value	MJ kg^{-1}	11.9	10.2
Syngas			
Yield[1]	% (d.b.)	6.1	26.7
Lower heating value	MJ m^{-3}	6.63	12.86
Production scenarios			
Switchgrass	t (d.b.)	3.45	4.94
Biochar	t (w.b.)	1.0	1.0
Bio-oil	t (w.b.)	2.24	2.62
Syngas[2]	kg (w.b.)	0.127	0.214

[1] Calculated by difference; [2] Estimated from composition of syngas without N_2

6.2.3.4 Biochar use as soil amendment

The use of biochar as soil amendment is expected to be more favourable than the use of pyrolysis char as charcoal (energy use) in terms of global warming (Peters et al., 2015). Thus, it was considered that biochar is applied to soil in the top 10 cm layer (Harter et al., 2014) at a dose of 2% (w/w). Considering a bulk density of 1200 kg m^{-3}, it corresponds to 24 tons ha^{-1}. Thus, one ton of biochar covers 0.042 ha yr^{-1}. Biochar is applied to a wheat crop cultivation in a loam soil using a manure spreader and is incorporated during the usual soil preparation operations. The scenario considers that biochar is spread at the establishment of wheat at 5 years intervals. Soil GHG emissions associated with N fertilizer (120 kg N ha^{-1}) were calculated based on the method proposed by Rochette et al. (2008) and corresponds to 1210 kg CO_2e ha^{-1}.

$C_{biochar}$ could be stable in soil for more than 1000 years but its stability will depend on its characteristics and on environmental factors (Bai et al., 2014). In fact, biochars with O/C_{org} ratio below 0.2 and H/C_{org} ratio below 0.4 would have the better potential for C sequestration (Enders et al., 2012). Budai et al. (2013) proposed that highly stable biochars would have a BC_{+100} of 70% (i.e. 70% of the C in biochar will remain in soil after 100 years), as stable biochars would have a BC_{+100} of 50%. For this study, it was assumed that biochar A is stable (BC_{+100} of 50%) and biochar B is highly stable (BC_{+100} of 70%). These values are relatively conservative when compared to assumptions made in other studies, using BC_{+100} values of 68% (Hammond et al., 2011; Ibarrola et al., 2012), 80% (Roberts et al., 2010; Muñoz et al., 2017) and 90% (Peters et al., 2015).

According to Woolf et al. (2010), one of the most uncertain aspects of LCA on biochar systems is the reduction in N_2O emissions from soils. As presented in Chapter 2, biochars with a C/N ratio above 30 would have the better potential to reduce soil N_2O emissions. In the present study, percentage of reduction of soil GHG emissions associated to biochar amendment obtained from the research study presented in chapter 5 was used as an input data. In a silt loam, N_2O emissions were reduced by 90% and 58% with biochar produced for scenarios A and B, respectively, when compared to the control without biochar. These reduction values which correspond to those reported in the literature (Cayuela et al., 2014) were considered for the cultivation of wheat when biochar was applied at a dose of 2% (w/w).

6.2.3.5 Use of bio-oil for substitution of fossil fuel

The calorific value was measured using the bomb calorimeter method ASTM D7544 (ASTM, 2009). Bio-oil is expected to substitute #2 fuel oil in heating appliances. Based on the yield and HHV of bio-oil (Table 6.2), 682.2 L and 684.5 L of #2 fuel oil (36.6 MJ L^{-1}) would be replaced in scenarios A and B, respectively.

6.2.3.6 Use of syngas

During both pyrolysis treatments, exhausting syngas samples were taken in Tedlar® bags. Gas chromatograph was used for characterising the composition of the samples. Equation 6.1 was used to calculate the lower heating value (LHV; kJ m^{-3}) of the syngas (Azargohar et al., 2013), where CO_2, H_2, CH_4 and C_nH_m are the molar concentrations of gas components. The hypothesis is that syngas will substitute hydroelectricity to heat the pyrolysis process.

$$\text{LHV} = (30.0 \times \text{CO} + 25.7 \times \text{H}_2 + 85.4 \times \text{CH}_4 + 151.3 \times \text{CnHm}) \times 4.2 \qquad (6.1)$$

6.2.4 Impact assessment

The climate change impact category of LCA is one of the most important in relation to the life-cycle of biochar-soil systems (Muñoz et al., 2017). Thus, the GHG emissions balance of the system was calculated, as the impact indicator was 1 kg CO_2e. The 100 years global warming potential of CO_2, CH_4 and N_2O (1, 25 and 298 CO_2e, respectively) from the IPCC (2007) were used. The net climate change impact is the total of the GHG emissions from which are subtracted the avoided GHG emissions, in kg CO_2e $t^{-1}{}_{biochar}$ yr^{-1}. GHG emissions including the emissions from the combustion of fossil fuel in tractors (2738 g CO_2e L^{-1}), from hydroelectricity (20.7 g CO_2e kWh) (Hydro-Québec, 2017), GHG associated with the fabrication of fuel (18 g CO_2e MJ^{-1}) (Lattanzio, 2014), fertilizers (9.7 kg CO_2e $kg^{-1}{}_{N}$) (Snyder et al., 2009) and pesticides (18 kg CO_2e $kg^{-1}{}_{a.i.}$) (Meisterling et al., 2009), and soil GHG emissions in switchgrass cultivation (Rochette et al., 2008) were considered. Avoided GHG emissions included the displacement of GHG emissions associated with the combustion of #2 fuel oil (2570 g CO_2e L^{-1}; replaced by bio-oil, hydroelectricity replaced by syngas, $C_{biochar}$ sequestrated in soil and avoided N_2O emissions from soil amended with biochar. Other factors that could improve the GHG emissions balance following biochar amendment were not considered because there is too much uncertainty about these benefits. These factors include an increase in crop productivity, a decrease in the rate of soil organic decomposition, a decrease in N fertilizer requirements and a decrease in P and K fertilizer requirement (Hammond et al., 2011).

The net energy balance for the production of one ton of biochar is the addition of all energy inputs and outputs to the systems (in MJ $ton^{-1}{}_{biochar}$ yr^{-1}). Energy inputs included the use of diesel fuel for field operation (factor of 36.6 MJ L^{-1} for combustion and 4.8 MJ L^{-1} for extraction and refining) (Whitman et al., 2011) and the energy consumption for grinding, drying and pyrolysis. Energy output is the energy content of the produced bio-oil and syngas.

6.3 Results and discussion

6.3.1 Greenhouse gas emissions

6.3.1.1 Greenhouse gas emissions balance

The production of one ton of biochar and its amendment to soil resulted in a net reduction of GHG emissions in both scenarios A (-2105 kg CO_2e $t^{-1}{}_{biochar}$) and B (-2524 kg CO_2e $t^{-1}{}_{biochar}$; Table 6.3). These results are similar to those obtained by Muñoz et al. (2017), who found GHG emission reduction associated to biochar production from agricultural biomass and forestry biomass waste ranging from 2590 to 2700 kg CO_2e $t^{-1}{}_{biochar}$, and from 2670 to 2740 kg CO_2e $t^{-1}{}_{biochar}$, respectively. The authors demonstrated that the environmental benefits increase while pyrolysis temperature increases. They found similar trend for other LCA impact categories, including human toxicity, freshwater eutrophication and fossil depletion. The same conclusion can be drawn in the present study for the climate change impact. As the biochars in scenario A and B were produced at 459 and 591°C, respectively, scenario B resulted in a higher GHG reduction.

Other LCA studies considered energetic crops as a feedstock for biochar production but used a different functional unit. For example, Gaunt and Lehmann (2008) calculated total avoided emissions ranging from 12,551 to 14,109 kg CO_2e $ha^{-1}{}_{switchgrass}$ yr^{-1} when biochar produced from switchgrass is used as a soil amendment. They found lower environmental benefits when biochar was used to produce energy. In the present study, when GHG emissions (in kg CO_2e t^{-1} biochar) are divided by the total area cultivated in switchgrass for the production of one ton of biochar, net GHG emissions reach -6697 and -5714 kg CO_2e ha^{-1} y^{-1} for scenarios A and B, respectively. When emissions are converted on the basis of switchgrass production, net emissions values correspond to -652 and -557 kg CO_2e t^{-1} switchgrass for scenarios A and B, respectively. Using the LCA approach, Thornley et al. (2015) found a similar reduction of 683 kg CO_2e $t^{-1}{}_{biomass}$ for the scenario in which biochar produced from willow tree energy crop is amended in the soil. Hammond et al. (2011) found higher carbon abatement values of 900, 1100 and 1100 t CO_2e $t^{-1}{}_{biomass}$ for small, medium and large scale slow pyrolysis of miscanthus (*Miscanthus x giganteus*) for the production of biochar used as a soil amendment.

Table 6.3: GHG emissions and energy balance of the two scenarios and contribution analysis

	Greenhouse gas emissions		**Energy**	
	kg CO_2e $t^{-1}_{biochar}$ $year^{-1}$		MJ $t^{-1}_{biochar}$ $year^{-1}$	
	Scenario A	Scenario B	Scenario A	Scenario B
Switchgrass cultivation				
Field preparation	3.58	5.14	43.1	61.9
Herbicide application	1.11	1.59	16.4	23.6
Sowing	1.34	1.92	34.3	49.3
Fertilization	476.2	683.3	807.0	1157.6
Cutting	6.9	9.8	102.9	147.5
Raking	2.0	2.9	29.9	43.1
Baling	8.5	12.1	126.9	181.6
Switchgrass transport and handling				
Loading	8.1	11.6	120.7	173.1
Transport	35.7	51.2	535.2	767.7
Unloading	5.3	7.7	80.0	114.5
Pickup	11.7	16.7	174.7	250.3
Switchgrass conditioning and conversion				
Grinding	18.5	26.6	276.7	396.7
Drying	4.7	6.7	813.2	1163.4
Pyrolysis	150.6	240.4	26,172	41,761
Valorisation of co-products				
Biochar-C sequestration	-1153	-1921	--	--
Biochar-avoided soil N_2O emissions	-42.5	-27.4	--	--
Biochar spreading	0.80	0.80	-7.8	-7.8
Bio-oil	-1643.6	-1649.1	24,941	25,024
Syngas	-0.78	-4.04	1998.8	10,313
Net balance	**-2105**	**-2524**	**-2401**	**-10,960**

6.3.1.2 Contribution analysis

The emissions were classified into four stages: switchgrass cultivation, switchgrass transport and handling, switchgrass conditioning and conversion, and the valorisation of co-products (Table 6.3). The first three stages contribute towards GHG emissions as the fourth stage contributes towards avoided emissions. Due to the higher quantity of switchgrass needed in scenario B than in scenario A (4.95 vs 3.45 t), and thus to a larger field area needed (0.482 vs 0.336 ha), the GHG contribution is higher in scenario B than in scenario A regarding switchgrass cultivation (716.9 vs 499.5 kg CO_2e $t^{-1}_{biochar}$ yr^{-1}), transport and handling (87.2 vs 60.8 kg CO_2e $t^{-1}_{biochar}$ yr^{-1}) and switchgrass conditioning and conversion (273.5 vs 185.4 kg CO_2e $t^{-1}_{biochar}$ yr^{-1}). GHG emissions associated to soil fertilization are the highest, contributing to 64% of the total emissions in the first three stages, mainly due to associated soil N_2O emissions. Kim and Dale (2003) reported global warming impact associated with producing switchgrass varying from 124 to 147 kg CO_2e $t^{-1}{}_{switchgrass}$, which is similar to the value calculated in the present study for switchgrass cultivation (145 kg CO_2e $t^{-1}{}_{switchgrass}$). Emissions associated to the pyrolysis process are the second in importance and contribute to 20.2 and 22.3% of the total emissions in scenarios A and B, respectively.

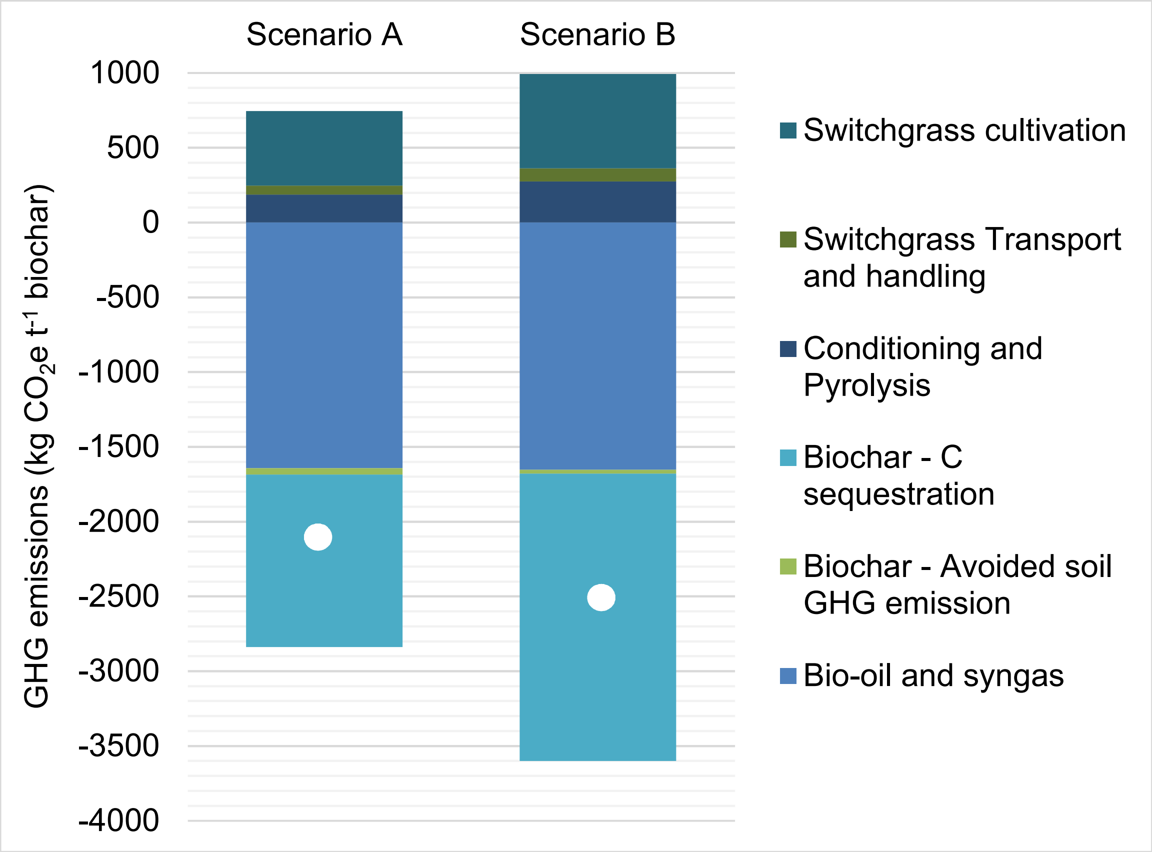


Figure 6.1: Greenhouse gas balance and contribution for scenarios A and B (kg CO_2e t^{-1} biochar)

The final stage which is the valorisation of co-products included the avoided soil N_2O emissions due to biochar amendment, the $C_{biochar}$ sequestration in soil, and the avoided emissions due to the use of bio-oil to substitute fossil fuels (Figure 6.1). The avoided GHG emissions are higher in scenario B than in scenario A, which is due to higher C content and stability of biochar produced in scenario B. In fact, $C_{biochar}$ sequestration contributes towards 53 and 41% of total avoided emissions in scenarios B and A, respectively. The decrease in N_2O emissions associated to biochar amendment is higher in scenario A than in scenarios B, as 90% and 58% of N_2O emissions associated to wheat crop were avoided, respectively. However, that represents only a small fraction of the avoided emissions associated with $C_{biochar}$ sequestration. GHG emissions avoided due to the use of bio-oil for fossil fuel substitution is similar in both scenarios A and B with -1643.6 and -1649.1 kg CO_2e $t^{-1}_{biochar}$ yr^{-1}, contributing towards 58% and 46% of avoided emissions from the valorisation of co-products, respectively.

6.3.2 Energy balance

The net energy balance of the two scenarios is negative (i.e. more energy is consumed than generated), as the net energy consumption in scenario A and B is 2401 MJ $t^{-1}_{biochar}$ and 10,960 MJ $t^{-1}_{biochar}$, respectively (Table 6.3). The higher net energy input in scenario B is due to higher energy consumption of the pyrolysis unit (41,761 MJ $t^{-1}_{biochar}$) as compared to scenario A (26,172 MJ $t^{-1}_{biochar}$; Figure 6.2). A higher pyrolysis temperature (591 vs 459°C) and a longer solid residence time (104 vs 78 s) caused this higher energy consumption. Due to the higher quantity of biomass needed to produce the same quantity of biochar, the energy consumption associated to switchgrass cultivation, handling, transport and conditioning is higher in scenario B (4530 MJ $t^{-1}_{biochar}$) than in scenario A (3161 MJ $t^{-1}_{biochar}$). However, this represents only around 10% of the total energy input, respectively. Kalita (2012) carried out a life cycle assessment of the switchgrass cultivation and found that the cumulative energy use from land preparation to baling, reached 1697 MJ $t^{-1}_{switchgrass}$, which is higher than in the present study. The energy consumption associated to cultivation (in MJ $t^{-1}_{biochar}$) divided by the quantity of switchgrass needed to produce one ton of biochar represents 337 MJ $t^{-1}_{switchgrass}$. Finally, the energy consumption for biochar spreading is negligible and corresponds to 7.8 MJ $t^{-1}_{biochar}$.

The net energy output included bio-oil and syngas (Figure 6.2). Energy production through bio-oil is the highest and is similar for both scenarios (24,941 and 25,025 MJ $t^{-1}_{biochar}$ in scenario A and B, respectively). Even though the yield and energetic content of bio-oil yield are higher in scenario A, more bio-oil is produced in scenario B, resulting in a similar energy output. The energy output through syngas is higher in scenario B (10,313 MJ $t^{-1}_{biochar}$) than in scenario A (1999 MJ $t^{-1}_{biochar}$) because the yield and energetic content of syngas is higher at a higher pyrolysis temperature. In a study by Roberts et al. (2010), the net energy balance of a biochar system, from switchgrass cultivation to biochar amendment to soil, was positive (+ 4899 MJ $t^{-1}_{\text{dry feedstock}}$). However, the energy produced through syngas was a lot higher than in the present study, with a net production of 5787 MJ $t^{-1}_{\text{dry feedstock}}$. Moreover, only a small amount of energy (58 MJ $t^{-1}_{\text{dry feedstock}}$) was needed for the initial start-up of pyrolysis.

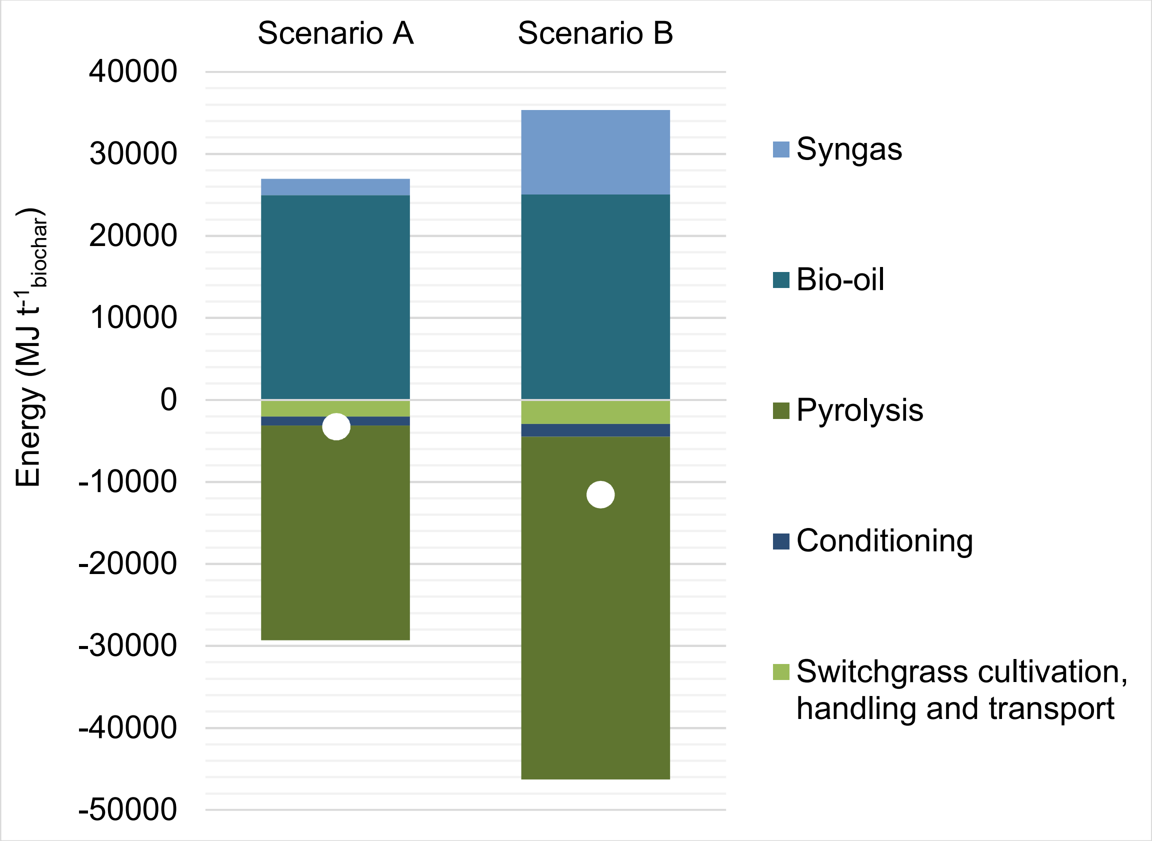


Figure 6.2: Energy balance of scenarios A and B (MJ t^{-1} biochar)

6.4 Conclusion

The life cycle approach was used in this study to evaluate the climate change and energy impacts of two biochar production systems, from switchgrass cultivation to the valorisation of pyrolysis co-products. The results confirmed that the pyrolysis of switchgrass in an auger reactor and the use of biochar for soil amendment and bio-oil and syngas as energy sources can be a negative emission technology. C_{biochar} sequestration contributed the most to GHG reduction in scenario B due to the high C content and stability in biochar, resulting in a higher net reduction of GHG emissions in this scenario. Soil GHG emissions from switchgrass cultivation and the electricity consumption of the pyrolysis unit were identified as hot spots contributing the most to GHG emissions. On the other hand, the energy balance was negative due the high-energy demand of the pyrolysis unit, and particularly in scenario B due to higher pyrolysis temperature and longer residence time of biomass in the reactor. These results suggest that pyrolysis operating parameters have a high influence on the greenhouse gas emissions and energy balances of biochar production systems. More studies are needed to confirm the stability of biochars and their long-term effect on soil GHG emissions. Moreover, the experimental auger pyrolysis unit could be scaled-up and special care should be given to its energy efficiency.

Chapter 7. Conclusions

7.1 General summary

Every sector of activity should make an effort for reducing their GHG emissions in order to limit the temperature increase to 1.5 °C above pre-industrial levels, which was the objective stated in the Paris agreement in 2015. For example, the agriculture sector shows a great potential for mitigating GHG emissions. In the province of Quebec (Canada), agricultural soils generate 26.9% of the total emissions in the agricultural sector, and most of them are in the form of N_2O emissions resulting from the nitrification and denitrification of mineral N following application of synthetic fertilizers and organic amendments. Thus, by limiting the quantity of fertilizers and by selecting the appropriate moments for spreading, these emissions could be reduced. In addition to GHG emissions mitigation strategies, negative emissions technologies resulting to the active and permanent removal of carbon dioxide from the atmosphere will be needed to achieve this ambitious objective. Technologies listed by the United Nations Environment Programme (UNEP, 2016) include sustainable afforestation and reforestation, enhanced soil carbon absorption, the combination of bio-energy with carbon capture storage, and biochar.

Biochar is the solid product of the decomposition of biomass at moderate temperature (350 – 700 °C) under oxygen-limiting conditions, which is generally achieved through pyrolysis. Due to its high C content, high porosity and high surface area, biochar can be used for soil amendment to improve soil composition, water retention, increased nutrient uptake and crop yield. In fact, about 50% of the C in biomass is found in biochar following pyrolysis, and most of this C would be sequestered in soil for more than 1000 years according to many researchers. Moreover, studies demonstrated that biochar in soil can contribute to the reduction of GHG emissions, and particularly N_2O, a powerful GHG with a global warming potential 298 times that of CO_2 for a 100-year timescale. Thus, biochar could be used both as a negative emission technology and as a tool to mitigate soil GHG emissions. However, it is known that not all biochars are created equal and that their properties will depend on both biomass properties and pyrolysis operating parameters. Therefore, biochar with specific properties should be designed for a specific application. In addition to biochar properties, soils properties and environmental conditions will have an impact on the effect of biochar in soil. Thus, the main objective of this doctoral project was to produce engineered biochars with specific properties to mitigate climate change, and to evaluate their potential to reduce soil GHG emissions and to sequester C in soil.

In Chapter 2, a literature review allowed to identify the key biochar characteristics and production conditions needed for biochar to be used as a tool to mitigate climate change. It was found that biochars with a lower N content, and consequently higher C/N ratio (> 30), are more suitable for soil N_2O emissions mitigation. Biomasses with low N and ash contents could be more suitable to produce these biochars. However, from the literature review, it was concluded that the mechanisms involved in soils resulting to a decrease of N_2O emissions are still not clear. Then, biochars with an O/C_{org} ratio below 0.2 and H/C_{org} ratio lower than 0.7 would be highly stable, and thus could have a high potential for $C_{biochar}$ sequestration. These biochars are generally produced at high temperatures.

Pyrolysis auger reactor was selected as the technology to be used to produce the biochars with the properties identified in Chapter 2. These reactors are simple to operate and can be mobile, they require little or no carrier gas and low energy. Moreover, the operating parameters can be controlled easily in order to obtain the desired products. A literature review presented in Chapter 3 aimed at listing the characteristics of the auger reactors that were used to produce biochar and bio-oil, mainly at laboratory and pilot scales. Their operational parameters and the associated products yield and properties were compiled. Based on the data compiled, pyrolysis temperature, carrier gas flowrate and biomass residence time in the reactor are the operating parameters of auger reactors which have the most influence on products yields and their properties.

A vertical auger reactor designed by the IRDA and the CRIQ was used to produce biochar in this project. Three biomasses (wood, switchgrass and the solid fraction of pig manure) were selected based on their availability and potential in the province of Quebec (Canada). Then, based on the results of the literature review presented in Chapter 3, a range of pyrolysis operating parameters (temperature, solid residence time and nitrogen flowrate) were identified for each biomass and preliminary tests were carried out (Appendix 1) in order to select the ideal range of operating parameters for producing biochars. Using the selected range of pyrolysis parameters, the research study presented in Chapter 4 was carried out to validate a response surface methodology approach used to identify the optimal pyrolysis operating parameters (temperature, solid residence time, and nitrogen flowrate) of the auger reactor in order to produce the engineered biochars. These biochars should have the specific properties identified in Chapter 2 needed to sequester carbon (i.e. low H/C_{org} and O/C_{org} ratios) and to reduce soil GHG emissions (high C/N ratio). Thus, 15 pyrolysis tests were carried out with each biomass following the Box-Behnken design. Statistical models were developed to identify the minimum and maximum values of the response variables: biochar yield, C/N, H/C_{org} and O/C_{org} ratios. Validation experiments confirmed that the developed modelled can be used to accurately predict biochar properties based on the operating parameters of the vertical auger reactor.

Using the response surface models developed in Chapter 4, for each biomass, a biochar was produced with the pyrolysis operating parameters for producing a biochar with the optimal properties to maximize C sequestration (i.e., the lowest O/C_{org} and H/C_{org} ratios; scenario B). A second biochar with the opposite characteristics (highest O/C_{org} and H/C_{org} ratios; scenario A) was produced from each biomass. These six engineered biochars were amended in two types of soil (loamy sand and silt loam) at a rate of 2% (w/w) and incubated for 45 days. The aim of this short-term incubation study presented in Chapter 5 was to validate the hypothesis that only biochars produced with specific properties can reduce soil GHG emissions and sequester C in soil. It was found that benefits are specific not only to biochar properties, but also to the type of soil. All biochars increased (significantly and non-significantly) the CO_2 emissions in both soils, but are still expected to sequester carbon for more than 100 years since their C-CO_2 mineralisation rate over the 45-days incubation period represented only between 0.18 and 1.68% of their total C content. For the treatments with biochars produced from switchgrass and the SFPM, cumulative CO_2 emissions were significantly lower for the biochar produced at the highest temperature. Then, when compared to the control soil without biochar, N_2O emissions were only decreased in the silt loam amended with biochar made from wood and switchgrass. The difference was only significant with the biochar produced from switchgrass at a low temperature and with a short residence time, resulting in a decrease of 90% of the N_2O emission as compared to the control. Reduced NO_3^- and NH_4^+ concentrations in soil associated with N immobilisation or adsorption of N compounds on biochar affecting the

N-cycle in soil and a change in soil microbial abundance were the mechanisms identified as a possible cause for the reduction in N_2O emissions.

The conclusions of Chapter 6 indicate that the pyrolysis of biomass for biochar production used as a soil amendment can be used as a negative emission technology to sequester C in soil and to reduce soil GHG emissions. The benefits of biochars produced from the pyrolysis of switchgrass, a high yield energetic crop that can be cultivated on marginal lands, was particularly interesting due to the significant decrease in N_2O emissions in the silt loam. However, the global GHG balance, from the cultivation of switchgrass to the valorisation of bio-oil and syngas as energy sources and biochar as soil amendment, is not well known. Therefore, a life cycle approach was used in Chapter 6 to evaluate and compare the climate change and energy impacts of two biochar systems. The two pyrolysis scenarios used to produce the engineered biochars from switchgrass and tested in Chapter 5 were evaluated. It was found that both scenarios result in a net reduction in GHG emissions, and this reduction was higher in scenario B (-2524 kg CO_2e $t^{-1}{}_{biochar}$ yr^{-1}) carried out at a higher temperature and with a longer residence time than scenario A (-2105 kg CO_2e $t^{-1}{}_{biochar}$ yr^{-1}). This is due to the high C content and stability in biochar of scenario B, resulting in a higher net reduction of GHG emissions in this scenario. However, the energy balance of scenario B (-10,960 MJ $t^{-1}{}_{biochar}$ yr^{-1}) was more negative than scenario A (-2401 MJ $t^{-1}{}_{biochar}$ yr^{-1}). These results suggest that pyrolysis operating parameters have a high influence on the greenhouse gas and energy impacts of biochar systems.

7.2 Recommendations for future work

This doctoral project allowed to acquire knowledge regarding biochar production, the effect of biochar on soil GHG emissions and properties, and the GHG and energy impacts of the global biochar system. However, additional research needs are identified through this work. Here are a few recommendations for future research:

1) The response surface methodology approach that was developed could be used to predict the biochar yield and properties for the pyrolysis of additional biomasses (e.g. straw, food and crop residues).

2) Research studies could be carried out to evaluate the possibility of scaling-up the laboratory-scale auger reactor and to obtain similar product yields and properties on a larger scale. For example, the dimensional analysis and similitude theory could be applied.

3) In order to validate the results of the research study presented in Chapter 5, long-term studies should be carried out in greenhouses and in field, in the presence of crops and considering the Canadian climate and the global warming. The impact of different biochars on soil GHG emissions and on soil fertility, including soil biodiversity and physico-chemical properties, and more particularly on the modification of the nitrogen cycle, should be studied. The resulting impact on crop yields have to be monitored.

4) A long-term incubation study (3-5 years) in soil is needed to confirm the carbon stability of the biochars produced in this doctoral project. Biochars should be ^{14}C-labelled in order to differentiate the soil organic carbon and biochar carbon mineralisation to CO_2.

5) Biochar has a low density thus it is difficult to spread on the field as it can be lost through wind and water erosion. A solution that is proposed is to produce densified biochar pellets, which would facilitate its spreading and incorporation in the field. The benefits of pelletized vs non-pelletized biochar in soil should be compared.

6) A complete life cycle assessment of biochar systems considering more impact categories such as acidification, ozone depletion (stratospheric), resource demand, ozone formation (near-surface), land use, eutrophication (terrestrial), eutrophication (aquatic), ecotoxicity and human toxicity should be carried out.

7) Using the life cycle approach presented in Chapter 6, additional scenarios could be evaluated and compared, including different bioenergy processes (e.g. gasification and combustion) and different biomass feedstocks.

List of References

Agirre, I., Griessacher, T., Rösler, G., Antrekowitsch, J., 2013. Production of charcoal as an alternative reducing agent from agricultural residues using a semi-continuous semi-pilot scale pyrolysis screw reactor. Fuel Processing Technology 106, 114–121. doi:10.1016/j.fuproc.2012.07.010.

Aguilar-Chávez, Á., Díaz-Rojas, M., Cárdenas-Aquino, M. del R., Dendooven, L., Luna-Guido, M., 2012. Greenhouse gas emissions from a wastewater sludge-amended soil cultivated with wheat (Triticum spp. L.) as affected by different application rates of charcoal. Soil Biology and Biochemistry 52, 90–95. doi:http://dx.doi.org/10.1016 /j.soilbio.2012.04.022.

Ahmad, M., Rajapaksha, A.U., Lim, J.E., Zhang, M., Bolan, N., Mohan, D., Vithanage, M., Lee, S.S., Ok, Y.S., 2014. Biochar as a sorbent for contaminant management in soil and water: A review. Chemosphere 99, 19–33. doi:http://dx.doi.org/10.1016 /j.chemosphere.2013.10.071.

Al-Wabel, M.I., Al-Omran, A., El-Naggar, A.H., Nadeem, M., Usman, A.R.A., 2013. Pyrolysis temperature induced changes in characteristics and chemical composition of biochar produced from conocarpus wastes. Bioresource Technology 131, 374–379. doi:https://doi.org/10.1016/j.biortech.2012.12.165.

Allaire, S.E., Lange, S., 2013. Le biochar dans les milieux poreux : une solution miracle en environnement? Vecteur Environnement 58–67.

Ameloot, N., Neve, S. De, Jegajeevagan, K., Yildiz, G., Buchan, D., Nkwain, Y., Prins, W., Bouckaert, L., Sleutel, S., 2013. Soil Biology & Biochemistry Short-term CO 2 and N 2 O emissions and microbial properties of biochar amended sandy loam soils. Soil Biology and Biochemistry 57, 401–410. doi:10.1016/j.soilbio.2012.10.025.

Anderson, C.R., Condron, L.M., Clough, T.J., Fiers, M., Stewart, A., Hill, R.A., Sherlock, R.R., 2011. Biochar induced soil microbial community change: Implications for biogeochemical cycling of carbon, nitrogen and phosphorus. Pedobiologia 54, 309–320. doi:http://dx.doi.org/10.1016/j.pedobi.2011.07.005.

Angst, T.E., Patterson, C.J., Reay, D.S., Anderson, P., Peshkur, T.A., Sohi, S.P., 2013. Biochar diminishes nitrous oxide and nitrate leaching from diverse nutrient sources. Journal of Environmental Quality 42, 672–682. doi:10.2134/jeq2012.0341.

Angst, T.E., Six, J., Reay, D.S., Sohi, S.P., 2014. Impact of pine chip biochar on trace greenhouse gas emissions and soil nutrient dynamics in an annual ryegrass system in California. Agriculture, Ecosystems & Environment 191, 17–26. doi: http://dx.doi.org/10.1016/j.agee.2014.03.009.

Antal Jr, M.J., Grønli, M., 2003. The art, science, and technology of charcoal production. Industrial and Engineering Chemistry Research 42, 1619–1640. doi: http://dx.doi.org/10.1021/ie0207919.

Association Française de Normalisation (AFNOR), 2005. Organic Soil improvers and Growing Media: Biochemical Fractionning and Estimation of Biological Stability: Method of Organic Matter Characterisation by Successive Solubilisations, Norme expérimentale. AFNOR, La Plaine Saint-Denis, France.

ASTM, 2012. D4928-12, Standard Test Method for Water in Crude Oils by Coulometric Karl Fischer Titrationle. West Conshohocken, PA. doi:10.1520/D4928-12.

ASTM, 2011. D1762-84, Standard Test Method for Chemical Analysis of Wood Charcoal. ASTM International 84, 1–2. doi:10.1520/D1762-84R07.2.

ASTM, 2009. D7544, Standard Specification for Pyrolysis Liquid Biofuel. West Conshohocken, PA. doi:10.1520/D7544-09.

Augustenborg, C.A., Hepp, S., Kammann, C., Hagan, D., Schmidt, O., Muller, C., 2012. Biochar and earthworm effects on soil nitrous oxide and carbon dioxide emissions. Journal of Environmental Quality 41, 1203–1209. doi:10.2134/jeq2011.0119.

Aylón, E., Fernández-Colino, A., Navarro, M. V, Murillo, R., García, T., Mastral, A.M., 2008. Waste Tire Pyrolysis: Comparison between Fixed Bed Reactor and Moving Bed Reactor. Industrial & Engineering Chemistry Research 47, 4029–4033. doi:10.1021/ie071573o.

Aylón, E., Murillo, R., Navarro, M. V, García, T., Mastral, A.M., 2010. Valorisation of waste tyre by pyrolysis in a moving bed reactor. Waste Management 30, 1220–1224. doi:10.1016/j.wasman.2009.10.001.

Azargohar, R., Jacobson, K.L., Powell, E.E., Dalai, A.K., 2013. Journal of Analytical and Applied Pyrolysis Evaluation of properties of fast pyrolysis products obtained , from Canadian waste biomass. Journal of Analytical and Applied Pyrolysis 104, 330–340. doi:10.1016/j.jaap.2013.06.016.

Azlina, W., Abdul, W., Ghani, K., Mohd, A., Bachmann, R.T., Taufiq-yap, Y.H., Rashid, U., Al-muhtaseb, A.H., 2013. Biochar production from waste rubber-wood-sawdust and its potential use in C sequestration : Chemical and physical characterization. Industrial Crops & Products 44, 18–24. doi:10.1016/j.indcrop.2012.10.017

Badger, P.C., Fransham, P., 2006. Use of mobile fast pyrolysis plants to densify biomass and reduce biomass handling costs—A preliminary assessment. Biomass and Bioenergy 30, 321–325. doi:http://dx.doi.org/10.1016/j.biombioe.2005.07.011.

Baggs, E.M., 2011. Soil microbial sources of nitrous oxide: recent advances in knowledge, emerging challenges and future direction. Current Opinion in Environmental Sustainability 3, 321–327. doi:http://dx.doi.org/10.1016/j.cosust.2011.08.011.

Bahng, M.-K., Mukarakate, C., Robichaud, D.J., Nimlos, M.R., 2009. Current technologies for analysis of biomass thermochemical processing: A review. Analytica Chimica Acta 651, 117–138. doi:http://dx.doi.org/10.1016/j.aca.2009.08.016.

Bai, M., Wilske, B., Buegger, F., Bruun, E.W., Bach, M., Frede, H., 2014. Biodegradation measurements confirm the predictive value of the O : C-ratio for biochar recalcitrance 633–637. doi:10.1002/jpln.201300412.

Bai, Y., Luo, L., van der Voet, E., 2010. Life cycle assessment of switchgrass-derived ethanol as transport fuel. The International Journal of Life Cycle Assessment 15, 468–477. doi:10.1007/s11367-010-0177-2.

Baldock, J.A., Smernik, R.J., 2002. Chemical composition and bioavailability of thermally altered Pinus resinosa (Red pine) wood. Organic Geochemistry 33, 1093–1109. doi:http://dx.doi.org/10.1016/S0146-6380(02)00062-1.

Basu, P., 2010. Chapter 3 - Pyrolysis and Torrefaction BT - Biomass Gasification and Pyrolysis. Academic Press, Boston, pp. 65–96. doi:https://doi.org/10.1016/B978-0-12-374988-8.00003-9.

Bhattacharya, P., Steele, P.H., Barbary, E., Hassan, M., Mitchell, B., Ingram, L., Pittman, C.U., 2009. Wood / plastic copyrolysis in an auger reactor : Chemical and physical analysis of the products. Fuel 88, 1251–1260. doi:10.1016/j.fuel.2009.01.009.

Bosong, L., Wei, L., Qi, Z., Tiejun, W., Longlong, M., 2014. Pyrolysis and catalytic upgrading of pine wood in a combination of auger reactor and fixed bed. FUEL 129, 61–67. doi:10.1016/j.fuel.2014.03.043.

Brar, S.K., Dhillon, G.S., Soccol, C.R., 2014. Biotransformation of waste biomass into high value biochemicals. Biotransformation of Waste Biomass into High Value Biochemicals 9781461480, 1–504. doi:10.1007/978-1-4614-8005-1.

Brassard, P., Godbout, S., Raghavan, V., 2016. Soil biochar amendment as a climate change mitigation tool: Key parameters and mechanisms involved. Journal of Environmental Management 181. doi:10.1016/j.jenvman.2016.06.063.

Brassard, P., Palacios, J.H., Godbout, S., Bussières, D., Lagacé, R., Larouche, J.-P., Pelletier, F., 2014. Comparison of the gaseous and particulate matter emissions from the combustion of agricultural and forest biomasses. Bioresource Technology 155. doi:10.1016/j.biortech.2013.12.027.

Brevik, E.C., 2012. Soils and Climate Change: Gas Fluxes and Soil Processes. Soil Horizons 53. doi:10.2136/sh12-04-0012.

Brewer, C.E., Brown, R.C., 2012. 5.18 - Biochar A2 - Sayigh, Ali BT - Comprehensive Renewable Energy. Elsevier, Oxford, pp. 357–384. doi:https://doi.org/10.1016/B978-0-08-087872-0.00524-2.

Bridgwater, A. V, 2012. Review of fast pyrolysis of biomass and product upgrading. Biomass and Bioenergy 38, 68–94. doi:http://dx.doi.org/10.1016/j.biombioe.2011.01.048.

Bridgwater, A. V, 2011. Review of fast pyrolysis of biomass and product upgrading. Biomass and Bioenergy 38, 68–94. doi:10.1016/j.biombioe.2011.01.048.

Brown, J.N., 2009. Development of a lab-scale auger reactor for biomass fast pyrolysis and process optimization using response surface methodology. Graduate Tehsis and Dissertations. Paper 10996. Iowa State University.

Brown, J.N., Brown, R.C., 2012. Process optimization of an auger pyrolyzer with heat carrier using response surface methodology. Bioresource Technology 103, 405–414. doi:10.1016/j.biortech.2011.09.117.

Bruun, E.W., Ambus, P., Egsgaard, H., Hauggaard-Nielsen, H., 2012. Effects of slow and fast pyrolysis biochar on soil C and N turnover dynamics. Soil Biology and Biochemistry 46, 73–79. doi:http://dx.doi.org/10.1016/j.soilbio.2011.11.019.

Bruun, E.W., Müller-Stöver, D., Ambus, P., Hauggaard-Nielsen, H., 2011. Application of biochar to soil and N2O emissions: potential effects of blending fast-pyrolysis biochar with anaerobically digested slurry. European Journal of Soil Science 62, 581–589. doi:10.1111/j.1365-2389.2011.01377.x.

Budai, A., Zimmerman, A.R., Cowie, A.L., Webber, J.B.W., Singh, B.P., Glaser, B., Masiello, C.A., Andersson, D., Shields, F., Lehmann, J., Camps Arbestain, M., Williams, M., Sohi, S., Joseph, S., 2013. Biochar Carbon Stability Test Method : An assessment of methods to determine biochar carbon stability. International Biochar Initiative 1–10.

Burger, M., Jackson, L.E., 2003. Microbial immobilization of ammonium and nitrate in relation to ammonification and nitrification rates in organic and conventional cropping systems. Soil Biology and Biochemistry 35, 29–36. doi: http://dx.doi.org/10.1016/S0038-0717(02)00233-X.

Butterbach-Bahl, K., Baggs, E.M., Dannenmann, M., Kiese, R., Zechmeister-Boltenstern, S., 2013. Nitrous oxide emissions from soils: how well do we understand the processes and their controls? Philosophical Transactions of the Royal Society of London. Series B, Biological Sciences 368, 20130122. doi:10.1098/rstb.2013.0122.

Cabrera, A., Cox, L., Spokas, K., Hermosín, M.C., Cornejo, J., Koskinen, W.C., 2014. Science of the Total Environment In fl uence of biochar amendments on the sorption – desorption of aminocyclopyrachlor , bentazone and pyraclostrobin pesticides to an agricultural soil. Science of the Total Environment, The 470–471, 438–443. doi:10.1016/j.scitotenv.2013.09.080.

Cantrell, K.B., Martin, J.H., 2012. Stochastic state-space temperature regulation of biochar production. Part II: Application to manure processing via pyrolysis. Journal of the Science of Food and Agriculture 92, 490–495. doi:10.1002/jsfa.4617.

Caporaso, J.G., Kuczynski, J., Stombaugh, J., Bittinger, K., Bushman, F.D., Costello, E.K., Fierer, N., Peña, A.G., Goodrich, J.K., Gordon, J.I., Huttley, G.A., Kelley, S.T., Knights, D., Koenig, J.E., Ley, R.E., Lozupone, C.A., McDonald, D., Muegge, B.D., Pirrung, M., Reeder, J., Sevinsky, J.R., Turnbaugh, P.J., Walters, W.A., Widmann, J., Yatsunenko, T., Zaneveld, J., Knight, R., 2010. QIIME allows analysis of high-throughput community sequencing data. Nature Methods 7, 335–336. doi:10.1038/nmeth.f.303.

Case, S.D.C., McNamara, N.P., Reay, D.S., Whitaker, J., 2012. The effect of biochar addition on N2O and CO2 emissions from a sandy loam soil – The role of soil aeration. Soil Biology and Biochemistry 51, 125–134. doi:http://dx.doi.org /10.1016/j.soilbio.2012.03.017.

Castaldi, S., Riondino, M., Baronti, S., Esposito, F.R., Marzaioli, R., Rutigliano, F.A., Vaccari, F.P., Miglietta, F., 2011. Impact of biochar application to a Mediterranean wheat crop on soil microbial activity and greenhouse gas fluxes. Chemosphere 85, 1464–1471. doi:http://dx.doi.org/10.1016/j.chemosphere.2011.08.031.

Cayuela, M.L., Jeffery, S., van Zwieten, L., 2015. The molar H:Corg ratio of biochar is a key factor in mitigating N2O emissions from soil. Agriculture, Ecosystems & Environment 202, 135–138. doi:http://dx.doi.org/10.1016/j.agee.2014.12.015.

Cayuela, M.L., Sánchez-Monedero, M.A., Roig, A., Hanley, K., Enders, A., Lehmann, J., 2013. Biochar and denitrification in soils: when, how much and why does biochar reduce N2O emissions? 3, 1732.

Cayuela, M.L., van Zwieten, L., Singh, B.P., Jeffery, S., Roig, A., Sánchez-Monedero, M.A., 2014. Biochar's role in mitigating soil nitrous oxide emissions: A review and meta-analysis. Agriculture, Ecosystems & Environment 191, 5–16. doi:http:// dx.doi.org/10.1016/j.agee.2013.10.009.

Cely, P., Tarquis, A.M., Paz-Ferreiro, J., Méndez, A., Gascó, G., 2014. Factors driving the carbon mineralization priming effect in a sandy loam soil amended with different types of biochar. Solid Earth 5, 585–594. doi:10.5194/se-5-585-2014.

Charles, A., Rochette, P., Whalen, J.K., Angers, D.A., Chantigny, M.H., Bertrand, N., 2017. Global nitrous oxide emission factors from agricultural soils after addition of organic amendments: A meta-analysis. Agriculture, Ecosystems & Environment 236, 88–98. doi:http://dx.doi.org/10.1016/j.agee.2016.11.021.

Cheng, Y., Cai, Z., Chang, S.X., Wang, J., Zhang, J., 2012. Wheat straw and its biochar have contrasting effects on inorganic N retention and N2O production in a cultivated Black Chernozem. Biology and Fertility of Soils 48, 941–946. doi:10.1007/s00374-012-0687-0.

Cherubini, F., 2010. GHG balances of bioenergy systems – Overview of key steps in the production chain and methodological concerns. Renewable Energy 35, 1565–1573. doi:http://dx.doi.org/10.1016/j.renene.2009.11.035.

CLARKE, K.R., 1993. Non-parametric multivariate analyses of changes in community structure. Australian Journal of Ecology 18, 117–143. doi:10.1111/j.1442-9993.1993.tb00438.x.

Clough, T.J., Bertram, J.E., Ray, J.L., Condron, L.M., O'Callaghan, M., Sherlock, R.R., Wells, N.S., 2010. Unweathered Wood Biochar Impact on Nitrous Oxide Emissions from a Bovine-Urine-Amended Pasture Soil. Soil Science Society of America Journal.

Comeau, A.M., Li, W.K.W., Tremblay, J.-É., Carmack, E.C., Lovejoy, C., 2011. Arctic Ocean Microbial Community Structure before and after the 2007 Record Sea Ice Minimum. PLOS ONE 6, e27492.

Cross, A., Sohi, S.P., 2011. The priming potential of biochar products in relation to labile carbon contents and soil organic matter status. Soil Biology and Biochemistry 43, 2127–2134. doi:http://dx.doi.org/10.1016/j.soilbio.2011.06.016.

Daiane, S., Roberto, C., Perondi, D., Godinho, M., 2015. Pyrolysis of Medium Density Fiberboard (MDF) wastes in a screw reactor. Energy Conversion and Management 92, 223–233. doi:10.1016/j.enconman.2014.12.032.

Demirbas, A., 2004. Effects of temperature and particle size on bio-char yield from pyrolysis of agricultural residues. Journal of Analytical and Applied Pyrolysis 72, 243–248. doi:http://dx.doi.org/10.1016/j.jaap.2004.07.003.

Deng, H., 2013. Effect of Biochar Amendment on Soil Nitrous Oxide Emission December 2013 A thesis submitted to McGill University in partial fulfillment of the requirement of the degree Master of Science.

DeSantis, T.Z., Hugenholtz, P., Larsen, N., Rojas, M., Brodie, E.L., Keller, K., Huber, T., Dalevi, D., Hu, P., Andersen, G.L., 2006. Greengenes, a Chimera-Checked 16S rRNA Gene Database and Workbench Compatible with ARB. Applied and Environmental Microbiology 72, 5069–5072. doi:10.1128/AEM.03006-05.

Di Blasi, C., 2002. Modeling intra- and extra-particle processes of wood fast pyrolysis. AIChE Journal 48, 2386–2397. doi:10.1002/aic.690481028.

Dutta, B., Raghavan, V., 2014. A life cycle assessment of environmental and economic balance of biochar systems in Quebec. International Journal of Energy and Environmental Engineering 5, 106. doi:10.1007/s40095-014-0106-4.

Enders, A., Hanley, K., Whitman, T., Joseph, S., Lehmann, J., 2012. Characterization of biochars to evaluate recalcitrance and agronomic performance. Bioresource Technology 114, 644–653. doi:10.1016/j.biortech.2012.03.022.

Environment and Climate Change Canada, 2014. National Inventory Report 1990-2014: Greenhouse gas sources and sinks in Canada Part 1 206. doi:En81-4E-PDF.

Fang, Y., Singh, B., Singh, B.P., 2015. Effect of temperature on biochar priming effects and its stability in soils. Soil Biology and Biochemistry 80, 136–145.

doi:http://dx.doi.org/10.1016/j.soilbio.2014.10.006.

Felber, R., Leifeld, J., Horák, J., Neftel, A., 2014. Nitrous oxide emission reduction with greenwaste biochar: comparison of laboratory and field experiments. European Journal of Soil Science 65, 128–138. doi:10.1111/ejss.12093.

Feng, Y., Xu, Y., Yu, Y., Xie, Z., Lin, X., 2012. Mechanisms of biochar decreasing methane emission from Chinese paddy soils. Soil Biology and Biochemistry 46, 80–88. doi:http://dx.doi.org/10.1016/j.soilbio.2011.11.016.

Feng, Z., Zhu, L., 2017. Impact of biochar on soil N_2O emissions under different biochar-carbon/fertilizer-nitrogen ratios at a constant moisture condition on a silt loam soil. Science of The Total Environment 584–585, 776–782. doi:https://doi.org/10.1016/j.scitotenv.2017.01.115.

Ferreira, S.D., Altafini, C.R., Perondi, D., Godinho, M., 2015. Pyrolysis of Medium Density Fiberboard (MDF) wastes in a screw reactor. Energy Conversion and Management 92, 223–233. doi:http://dx.doi.org/10.1016/j.enconman.2014.12.032.

Funke, A., Henrich, E., Dahmen, N., Sauer, J., 2017. Dimensional Analysis of Auger-Type Fast Pyrolysis Reactors. Energy Technology 5, 119–129. doi:10.1002/ente.201600095.

Galinato, S.P., Yoder, J.K., Granatstein, D., 2011. The economic value of biochar in crop production and carbon sequestration. Energy Policy 39, 6344–6350. doi: http://dx.doi.org/10.1016/j.enpol.2011.07.035.

Garcia-Perez, M., Adams, T.T., Goodrum, J.W., Geller, D.P., Das, K.C., 2007. Production and Fuel Properties of Pine Chip Bio-oil/Biodiesel Blends. Energy & Fuels 21, 2363–2372. doi:10.1021/ef060533e.

Gardner, T., Acosta-Martinez, V., Senwo, Z., Dowd, S.E., 2011. Soil Rhizosphere Microbial Communities and Enzyme Activities under Organic Farming in Alabama. Diversity . doi:10.3390/d3030308.

Gascó, G., Paz-Ferreiro, J., Cely, P., Plaza, C., Méndez, A., 2016. Influence of pig manure and its biochar on soil CO2 emissions and soil enzymes. Ecological Engineering 95, 19–24. doi:https://doi.org/10.1016/j.ecoleng.2016.06.039.

Gaunt, J.L., Lehmann, J., 2008. Energy Balance and Emissions Associated with Biochar Sequestration and Pyrolysis Bioenergy Production. Environmental Science & Technology 42, 4152–4158. doi:10.1021/es071361i.

Gronwald, M., Don, A., Tiemeyer, B., Helfrich, M., 2015. Effects of fresh and aged chars from pyrolysis and hydrothermal carbonization on nutrient sorption in agricultural soils. Soil 1, 475–489. doi:10.5194/soil-1-475-2015.

Haefele, S.M., Konboon, Y., Wongboon, W., Amarante, S., Maarifat, A.A., Pfeiffer, E.M., Knoblauch, C., 2011. Effects and fate of biochar from rice residues in rice-based systems. Field Crops Research 121, 430–440. doi:http://dx.doi.org/10.1016/j.fcr.2011.01.014.

Hammond, J., Shackley, S., Sohi, S., Brownsort, P., 2011. Prospective life cycle carbon abatement for pyrolysis biochar systems in the UK. Energy Policy 39, 2646–2655. doi:http://dx.doi.org/10.1016/j.enpol.2011.02.033.

Harter, J., Krause, H.-M., Schuettler, S., Ruser, R., Fromme, M., Scholten, T., Kappler, A., Behrens, S., 2014. Linking N2O emissions from biochar-amended soil to the structure and function of the N-cycling microbial community. ISME J 8, 660–674.

Harter, J., Weigold, P., El-Hadidi, M., Huson, D.H., Kappler, A., Behrens, S., 2016. Soil biochar amendment shapes the composition of N2O-reducing microbial communities. Science of The Total Environment 562, 379–390. doi:http://dx.doi.org/10.1016/j.scitotenv.2016.03.220.

Harvey, O.R., Kuo, L.-J., Zimmerman, A.R., Louchouarn, P., Amonette, J.E., Herbert, B.E., 2012. An index-based approach to assessing recalcitrance and soil carbon sequestration potential of engineered black carbons (biochars). Environmental Science & Technology 46, 1415–1421. doi:10.1021/es2040398.

He, L., Zhao, X., Wang, S., Xing, G., 2016. The effects of rice-straw biochar addition on nitrification activity and nitrous oxide emissions in two Oxisols. Soil and Tillage Research 164, 52–62. doi:http://dx.doi.org/10.1016/j.still.2016.05.006.

Herath, H.M.S.K., Camps-Arbestain, M., Hedley, M.J., Kirschbaum, M.U.F., Wang, T., van Hale, R., 2015. Experimental evidence for sequestering C with biochar by avoidance of CO2 emissions from original feedstock and protection of native soil organic matter. GCB Bioenergy 7, 512–526. doi:10.1111/gcbb.12183.

Hossain, M.K., Strezov, V., Chan, K.Y., Ziolkowski, A., Nelson, P.F., 2011. Influence of pyrolysis temperature on production and nutrient properties of wastewater sludge biochar. Journal of Environmental Management 92, 223–228. doi:http://dx.doi.org/10.1016/j.jenvman.2010.09.008.

Huang, Y.-F., Chiueh, P.-T., Lo, S.-L., 2016. A review on microwave pyrolysis of lignocellulosic biomass. Sustainable Environment Research 26, 103–109. doi:http://dx.doi.org/10.1016/j.serj.2016.04.012.

Hunkeler, D., 2016. Life Cycle Assessment (LCA): A Guide to Best Practice. The International Journal of Life Cycle Assessment 21, 1063–1066. doi:10.1007/s11367-016-1083-z.

Hutchinson, G.L., Mosier, A.R., 1981. Improved Soil Cover Method for Field Measurement of Nitrous Oxide Fluxes1. Soil Science Society of America Journal 45, 311–316. doi:10.2136/sssaj1981.03615995004500020017x.

Hydro-Québec, 2017. Taux d'émission de GES associés à l'électricité d'Hydro-Québec, (2017). [Online] http://www.hydroquebec.com/developpement-durable/centre-documentation/taux-emission-ges.html. Accessed on September 2017.

Ibarrola, R., Shackley, S., Hammond, J., 2012. Pyrolysis biochar systems for recovering biodegradable materials: A life cycle carbon assessment. Waste Management 32, 859–868. doi:http://dx.doi.org/10.1016/j.wasman.2011.10.005.

Ingram, L., Mohan, D., Bricka, M., Steele, P., Strobel, D., Crocker, D., Mitchell, B., Mohammad, J., Cantrell, K., Pittman, C.U., 2008. Pyrolysis of Wood and Bark in an Auger Reactor : Physical Properties and Chemical Analysis of the Produced Bio-oils 614–625.

Inyang, M., Gao, B., Pullammanappallil, P., Ding, W., Zimmerman, A.R., 2010. Biochar from anaerobically digested sugarcane bagasse. Bioresource Technology 101, 8868–8872. doi:http://dx.doi.org/10.1016/j.biortech.2010.06.088.

IPCC, 2014. AR5 Synthesis Report - Climate Change 2014.

Jahirul, M.I., Rasul, M.G., Chowdhury, A.A., Ashwath, N., 2012. Biofuels Production through Biomass Pyrolysis —A Technological Review. Energies 5, 4952. doi:10.3390/en5124952.

Jenkins, J.R., Viger, M., Arnold, E.C., Harris, Z.M., Ventura, M., Miglietta, F., Girardin, C., Edwards, R.J., Rumpel, C., Fornasier, F., Zavalloni, C., Tonon, G., Alberti, G., Taylor, G., 2017. Biochar alters the soil microbiome and soil function: results of next-generation amplicon sequencing across Europe. GCB Bioenergy 9, 591–612. doi:10.1111/gcbb.12371.

Jha, P., Biswas, A.K., Lakaria, B.L., Rao, A.S., 2010. Biochar in agriculture – prospects and related implications. Current Science 99, 1218–1225.

Jia, J., Li, B., Chen, Z., Xie, Z., Xiong, Z., 2012. Effects of biochar application on vegetable production and emissions of N_2O and CH_4. Soil Science and Plant Nutrition 58, 503–509. doi:10.1080/00380768.2012.686436.

Jones, D.L., Murphy, D. V, Khalid, M., Ahmad, W., Edwards-Jones, G., DeLuca, T.H., 2011. Short-term biochar-induced increase in soil CO_2 release is both biotically and abiotically mediated. Soil Biology and Biochemistry 43, 1723–1731. doi:http://dx.doi.org/10.1016/j.soilbio.2011.04.018.

Joubert, J., Carrier, M., Dahmen, N., Stahl, R., Hansie, J., 2015. Inherent process variations between fast pyrolysis technologies : A case study on Eucalyptus grandis. Fuel Processing Technology 131, 389–395. doi:10.1016/j.fuproc.2014.12.012.

Junna, S., Bingchen, W., Gang, X., Hongbo, S., 2014. Effects of wheat straw biochar on carbon mineralization and guidance for large-scale soil quality improvement in the coastal wetland. Ecological Engineering 62, 43–47. doi:https://doi.org/

10.1016/j.ecoleng.2013.10.014.

Kalita, B., 2012. Life Cycle Assessment of Switchgrass (Panicum virgatum L.) Biomass Production in Ontario. Thesis. The University of Guelph.

Kammann, C., Ratering, S., Eckhard, C., Muller, C., 2012. Biochar and hydrochar effects on greenhouse gas (carbon dioxide, nitrous oxide, and methane) fluxes from soils. Journal of Environmental Quality 41, 1052–1066. doi:10.2134/jeq2011.0132.

Kan, T., Strezov, V., Evans, T.J., 2016. Lignocellulosic biomass pyrolysis : A review of product properties and effects of pyrolysis parameters 57, 1126–1140.

Karhu, K., Mattila, T., Bergström, I., Regina, K., 2011. Biochar addition to agricultural soil increased CH4 uptake and water holding capacity – Results from a short-term pilot field study. Agriculture, Ecosystems & Environment 140, 309–313. doi:http://dx.doi.org/10.1016/j.agee.2010.12.005.

Karlsruhe, F., Chemie, T., 2006. The BTL2 Process of Biomass Utilization Entrained-Flow Gasification of Pyrolyzed Biomass Slurries K LAUS R AFFELT ,* E DMUND H ENRICH , A NDREA K OEGEL , 129.

Keith, A., Singh, B., Dijkstra, F.A., 2015. Biochar reduces the rhizosphere priming effect on soil organic carbon. Soil Biology and Biochemistry 88, 372–379. doi:http://dx.doi.org/10.1016/j.soilbio.2015.06.007.

Kettunen, R., Saarnio, S., 2013. Biochar can restrict N_2O emissions and the risk of nitrogen leaching from an agricultural soil during the freeze-thaw period. Agricultural and Food Science; Vol 22 No 4 (2013).

Kim, K.H., Kim, J.-Y., Cho, T.-S., Choi, J.W., 2012a. Influence of pyrolysis temperature on physicochemical properties of biochar obtained from the fast pyrolysis of pitch pine (Pinus rigida). Bioresource Technology 118, 158–162. doi:http://dx.doi.org/ 10.1016/j.biortech.2012.04.094.

Kim, K.H., Kim, J.Y., Cho, T.S., Choi, J.W., 2012b. Influence of pyrolysis temperature on physicochemical properties of biochar obtained from the fast pyrolysis of pitch pine (Pinus rigida). Bioresource Technology 118, 158–162. doi:10.1016/j.biortech. 2012.04.094.

Kim, P., Johnson, A., Edmunds, C.W., Radosevich, M., Vogt, F., Rials, T.G., Labb, N., 2011. Surface Functionality and Carbon Structures in Lignocellulosic-Derived Biochars Produced by Fast Pyrolysis 4693–4703.

Kim, P., Weaver, S., Noh, K., Labbe, N., 2014. Characteristics of Bio-Oils Produced by an Intermediate Semipilot Scale Pyrolysis Auger Reactor Equipped with Multistage Condensers.

Kim, S., Dale, B.E., 2003. Cumulative Energy and Global Warming Impact from the

Production of Biomass for Biobased Products. Journal of Industrial Ecology 7, 147–162. doi:10.1162/108819803323059442.

Knoblauch, C., Maarifat, A.-A., Pfeiffer, E.-M., Haefele, S.M., 2011. Degradability of black carbon and its impact on trace gas fluxes and carbon turnover in paddy soils. Soil Biology and Biochemistry 43, 1768–1778. doi:http://dx.doi.org/10.1016/j.soilbio.2010.07.012.

Kookana, R.S., Sarmah, A.K., Van Zwieten, L., Krull, E., Singh, B., 2011. Biochar Application to Soil. pp. 103–143. doi:10.1016/B978-0-12-385538-1.00003-2.

Kuzyakov, Y., Bogomolova, I., Glaser, B., 2014. Biochar stability in soil: Decomposition during eight years and transformation as assessed by compound-specific 14C analysis. Soil Biology and Biochemistry 70, 229–236. doi:http://dx.doi.org/10.1016/j.soilbio.2013.12.021.

Lai, W.-Y., Lai, C.-M., Ke, G.-R., Chung, R.-S., Chen, C.-T., Cheng, C.-H., Pai, C.-W., Chen, S.-Y., Chen, C.-C., 2013. The effects of woodchip biochar application on crop yield, carbon sequestration and greenhouse gas emissions from soils planted with rice or leaf beet. Journal of the Taiwan Institute of Chemical Engineers 44, 1039–1044. doi:http://dx.doi.org/10.1016/j.jtice.2013.06.028.

Laird, D.A., Brown, R.C., Amonette, J.E., Lehmann, J., 2009. Review of the pyrolysis platform for coproducing bio-oil and biochar. Biofuels, Bioproducts and Biorefining 3, 547–562. doi:10.1002/bbb.169.

Lattanzio, R.K, 2014. Canadian Oil Sands: Life-Cycle Assessments of Greenhouse Gas Emissions, Congress Research Service. CRS report, 7-5700.

Le Roux, É., Chaouch, M., Diouf, P.N., Stevanovic, T., 2015. Impact of a pressurized hot water treatment on the quality of bio-oil produced from aspen. Biomass and Bioenergy 81, 202–209. doi:http://dx.doi.org/10.1016/j.biombioe.2015.07.005.

Lédé, J., Authier, O., 2015. Temperature and heating rate of solid particles undergoing a thermal decomposition . Which criteria for characterizing fast pyrolysis ? Journal of Analytical and Applied Pyrolysis 113, 1–14. doi:10.1016/j.jaap.2014.11.013.

Lédé, J., 2010. Biomass pyrolysis: Comments on some sources of confusion in the definition of temperatures and heating rates 3, 886–898. doi:10.3390/en3040886.

Lehmann, J., Joseph, S., 2015. Biochar for environmental management: an introduction. Biochar for Environmental Management – Science and Technology, Second. ed. Earthscan.

Lehmann, J., Joseph, S., 2009. Biochar for Environmental Management, Biochar for Environmental Management: Science and Technology, First. ed. Earthscan.

Lehmann, J., Rillig, M.C., Thies, J., Masiello, C.A., Hockaday, W.C., Crowley, D., 2011.

Biochar effects on soil biota – A review. Soil Biology and Biochemistry 43, 1812–1836. doi:http://dx.doi.org/10.1016/j.soilbio.2011.04.022.

Lemus, R., Brummer, E.C., Moore, K.J., Molstad, N.E., Burras, C.L., Barker, M.F., 2002. Biomass yield and quality of 20 switchgrass populations in southern Iowa, USA. Biomass and Bioenergy 23, 433–442. doi:http://dx.doi.org/10.1016/S0961-9534(02)00073-9.

Liang, S., Han, Y., Wei, L., Mcdonald, A.G., 2015. Production and characterization of bio-oil and bio-char from pyrolysis of potato peel wastes. doi:10.1007/s13399-014-0130-x.

Liaw, S.-S., Wang, Z., Ndegwa, P., Frear, C., Ha, S., Li, C.-Z., Garcia-Perez, M., 2012. Effect of pyrolysis temperature on the yield and properties of bio-oils obtained from the auger pyrolysis of Douglas Fir wood. Journal of Analytical and Applied Pyrolysis 93, 52–62. doi:10.1016/j.jaap.2011.09.011.

Liaw, S.S., Zhou, S., Wu, H., Garcia-Perez, M., 2013. Effect of pretreatment temperature on the yield and properties of bio-oils obtained from the auger pyrolysis of Douglas fir wood. Fuel 103, 672–682. doi:10.1016/j.fuel.2012.08.016.

Liu, L., Shen, G., Sun, M., Cao, X., Shang, G., Chen, P., 2014. Effect of biochar on nitrous oxide emission and its potential mechanisms. Journal of the Air & Waste Management Association (1995) 64, 894–902.

Luo, X., Wang, L., Liu, G., Wang, X., Wang, Z., Zheng, H., 2016. Effects of biochar on carbon mineralization of coastal wetland soils in the Yellow River Delta, China. Ecological Engineering 94, 329–336. doi:https://doi.org/10.1016/j.ecoleng.2016.06.004.

Luo, Y., Durenkamp, M., De Nobili, M., Lin, Q., Brookes, P.C., 2011. Short term soil priming effects and the mineralisation of biochar following its incorporation to soils of different pH. Soil Biology and Biochemistry 43, 2304–2314. doi:http://dx.doi.org/10.1016/j.soilbio.2011.07.020.

Maguire, R.O., Agblevor, F.A., 2010. Biochar in agricultural systems. Virginia Cooperative Extension. Publication 442.311. [Online] http://pubs.ext.vt.edu/442/442-311/442-311.html. Accessed 10.20.14.

Major, J., Lehmann, J., Rondon, M., Goodale, C., 2010. Fate of soil-applied black carbon: downward migration, leaching and soil respiration. Global Change Biology 16, 1366–1379. doi:10.1111/j.1365-2486.2009.02044.x.

Major, J., Rondon, M., Molina, D., Riha, S.J., Lehmann, J., 2010. Maize yield and nutrition during 4 years after biochar application to a Colombian savanna oxisol 117–128. doi:10.1007/s11104-010-0327-0.

Malghani, S., Gleixner, G., Trumbore, S.E., 2013. Chars produced by slow pyrolysis and hydrothermal carbonization vary in carbon sequestration potential and greenhouse gases emissions. Soil Biology and Biochemistry 62, 137–146. doi:http://dx.doi.org/10.1016/j.soilbio.2013.03.013.

Manyà, J.J., Ortigosa, M.A., Laguarta, S., Manso, J.A., 2014. Experimental study on the effect of pyrolysis pressure, peak temperature, and particle size on the potential stability of vine shoots-derived biochar. Fuel 133, 163–172. doi:10.1016/j.fuel.2014.05.019.

Martínez, J.D., Murillo, R., García, T., Veses, A., 2013. Demonstration of the waste tire pyrolysis process on pilot scale in a continuous auger reactor. Journal of Hazardous Materials 261, 637–645. doi:http://dx.doi.org/10.1016/j.jhazmat.2013.07.077.

McBeath, A. V, Smernik, R.J., Krull, E.S., Lehmann, J., 2014. The influence of feedstock and production temperature on biochar carbon chemistry: A solid-state 13C NMR study. Biomass and Bioenergy 60, 121–129. doi:http://dx.doi.org/10.1016/j.biombioe.2013.11.002.

MDDELCC, 2016. Inventaire québécois des émissions de gaz à effet de serre en 2014 et leur évolution depuis 1990 [Online]. http://www.mddelcc.gouv.qc.ca/changements/ges/%0A2014/Inventaire1990-2014.pdf. Accessed December 2016.

Meisterling, K., Samaras, C., Schweizer, V., 2009. Decisions to reduce greenhouse gases from agriculture and product transport: LCA case study of organic and conventional wheat. Journal of Cleaner Production 17, 222–230. doi:http://dx.doi.org/10.1016/j.jclepro.2008.04.009.

Mimmo, T., Panzacchi, P., Baratieri, M., Davies, C.A., Tonon, G., 2014. ScienceDirect Effect of pyrolysis temperature on miscanthus (Miscanthus 3 giganteus) biochar physical , chemical and functional properties. Biomass and Bioenergy 39, 1–9. doi:10.1016/j.biombioe.2014.01.004.

Mohan, D., Pittman, C.U., Bricka, M., Smith, F., Yancey, B., 2007. Sorption of arsenic , cadmium , and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production 310, 57–73. doi:10.1016/j.jcis.2007.01.020.

Morgano, M.T., Leibold, H., Richter, F., Seifert, H., 2015. Journal of Analytical and Applied Pyrolysis Screw pyrolysis with integrated sequential hot gas filtration ଝ. Journal of Analytical and Applied Pyrolysis 113, 216–224. doi:10.1016/j.jaap.2014.12.019.

Mukherjee, A., Lal, R., Zimmerman, A.R., 2014. Effects of biochar and other amendments on the physical properties and greenhouse gas emissions of an artificially degraded soil. Science of The Total Environment 487, 26–36. doi:http://dx.doi.org/10.1016/j.scitotenv.2014.03.141.

Mukome, F.N.D., Six, J., Parikh, S.J., 2013. The effects of walnut shell and wood feedstock biochar amendments on greenhouse gas emissions from a fertile soil. Geoderma 200, 90–98. doi:http://dx.doi.org/10.1016/j.geoderma.2013.02.004.

Muñoz, E., Curaqueo, G., Cea, M., Vera, L., Navia, R., 2017. Environmental hotspots in the life cycle of a biochar-soil system. Journal of Cleaner Production 158, 1–7. doi:https://doi.org/10.1016/j.jclepro.2017.04.163.

Myers, Raymond H., Anderson-Cook, Christine M., and Montgomery, Douglas C.. Wiley Series in Probability and Statistics : Response Surface Methodology : Process and Product Optimization Using Designed Experiments (3rd Edition). Somerset, NJ, USA: Wiley, 20, 2016.

Myers, R.H., Montgomery, D.C., Anderson-Cook, C.M., 2009. Response Surface Methodology: Process and Product Optimization Using Designed Experiments, Wiley Series in Probability and Statistics. Wiley.

Nelissen, V., Saha, B.K., Ruysschaert, G., Boeckx, P., 2014. Effect of different biochar and fertilizer types on N2O and NO emissions. Soil Biology and Biochemistry 70, 244–255. doi:http://dx.doi.org/10.1016/j.soilbio.2013.12.026.

Novak, J.M., Busscher, W.J., 2013. Selection and Use of Designer Biochars to Improve Characteristics of Southeastern USA Coastal Plain Degraded Soils, in: Lee, J.W. (Ed.), Advanced Biofuels and Bioproducts. Springer New York, New York, NY, pp. 69–96. doi:10.1007/978-1-4614-3348-4_7.

Novak, J.M., Busscher, W.J., Laird, D.L., Ahmedna, M., Watts, D.W., Niandou, M.A.S., 2009a. Impact of Biochar Amendment on Fertility of a Southeastern Coastal Plain Soil. Soil Science 174.

Novak, J.M., Lima, I., Xing, B., Gaskin, J.W., Steiner, C., Das, K.C., Ahmedna, M., Rehrah, D., Watts, D.W., Busscher, W.J., Schomberg, H., 2009b. Characterization of Designer Biochar Produced at Different Temperatures and Their Effects on a Loamy Sand. Annals of Environmental Science; Vol 3 (2009).

Oertel, C., Matschullat, J., Zurba, K., Zimmermann, F., Erasmi, S., 2016. Greenhouse gas emissions from soils—A review. Chemie Der Erde - Geochemistry 76, 327–352. doi:https://doi.org/10.1016/j.chemer.2016.04.002.

Pattiya, A., Suttibak, S., 2012. Journal of Analytical and Applied Pyrolysis Production of bio-oil via fast pyrolysis of agricultural residues from cassava plantations in a fluidised-bed reactor with a hot vapour filtration unit. Journal of Analytical and Applied Pyrolysis 95, 227–235. doi:10.1016/j.jaap.2012.02.010.

Peters, J.F., Iribarren, D., Dufour, J., 2015. Biomass Pyrolysis for Biochar or Energy Applications? A Life Cycle Assessment. Environmental Science & Technology 49, 5195–5202. doi:10.1021/es5060786.

Petter, F.A., Borges de Lima, L., Marimon Júnior, B.H., Alves de Morais, L., Marimon, B.S., 2016. Impact of biochar on nitrous oxide emissions from upland rice. Journal of

Environmental Management 169, 27–33. doi:http://dx.doi.org/10.1016/j.jenvman.2015.12.020.

Pittman, C.U., Mohan, D., Eseyin, A., Li, Q., Ingram, L., Hassan, E.M., Mitchell, B., Guo, H., Steele, P.H., 2012. Characterization of Bio-oils Produced from Fast Pyrolysis of Corn Stalks in an Auger Reactor.

Puy, N., Murillo, R., Navarro, M. V, López, J.M., Rieradevall, J., Fowler, G., Aranguren, I., García, T., Bartrolí, J., Mastral, A.M., 2011. Valorisation of forestry waste by pyrolysis in an auger reactor. Waste Management 31, 1339–1349. doi:10.1016/j.wasman.2011.01.020.

Raffelt, K., Henrich, E., Koegel, A., Stahl, R., Steinhardt, J., Weirich, F., 2006. The BTL2 process of biomass utilization entrained-flow gasification of pyrolyzed biomass slurries. Applied Biochemistry and Biotechnology 129, 153–164. doi:10.1385/ABAB:129:1:153.

Ren, S., Ye, X.P., Borole, A.P., 2017. Journal of Analytical and Applied Pyrolysis Separation of chemical groups from bio-oil water-extract via sequential organic solvent extraction 123, 30–39.

Resende, F.L.P., 2014. Reactor configurations and design parameters for thermochemical conversion of biomass into fuels, energy, and chemicals, Reactor and Process Design in Sustainable Energy Technology. Elsevier B.V. doi:10.1016/B978-0-444-59566-9.00001-6.

Roberts, K.G., Gloy, B.A., Joseph, S., Scott, N.R., Lehmann, J., 2010. Life Cycle Assessment of Biochar Systems: Estimating the Energetic, Economic, and Climate Change Potential. Environmental Science & Technology 44, 827–833. doi:10.1021/es902266r.

Rochette, P., Worth, D.E., Lemke, R.L., McConkey, B.G., Pennock, D.J., Wagner-Riddle, C., Desjardins, R.J., 2008. Estimation of N2O emissions from agricultural soils in Canada. I. Development of a country-specific methodology. Canadian Journal of Soil Science 88, 641–654. doi:10.4141/CJSS07025.

Rogovska, N., Laird, D., Cruse, R., Fleming, P., Parkin, T., Meek, D., 2011. Impact of Biochar on Manure Carbon Stabilization and Greenhouse Gas Emissions. Soil Science Society of America Journal 75, 871–879. doi:10.2136/sssaj2010.0270.

Ronsse, F., van Hecke, S., Dickinson, D., Prins, W., 2013. Production and characterization of slow pyrolysis biochar: influence of feedstock type and pyrolysis conditions. GCB Bioenergy 5, 104–115. doi:10.1111/gcbb.12018.

Samson, R., Delaquis, E., Macinnis, G., 2014. Canadian Agricultural Adaptation Program Final Report 1–35.

Sarkhot, D. V, Berhe, A.A., Ghezzehei, T.A., 2012. Impact of Biochar Enriched with Dairy

Manure Effluent on Carbon and Nitrogen Dynamics. Journal of Environmental Quality 41, 1107–1114. doi:10.2134/jeq2011.0123.

SAS Institute Inc., 2012. SAS/STAT® 12.1 User's Guide.

Scheer, C., Grace, P.R., Rowlings, D.W., Kimber, S., Van Zwieten, L., 2011. Effect of biochar amendment on the soil-atmosphere exchange of greenhouse gases from an intensive subtropical pasture in northern New South Wales, Australia. Plant and Soil 345, 47–58. doi:10.1007/s11104-011-0759-1.

Schimmelpfennig, S., Glaser, B., 2012. One step forward toward characterization: some important material properties to distinguish biochars. Journal of Environmental Quality 41, 1001–1013. doi:10.2134/jeq2011.0146.

Schnitzer, M.I., Monreal, C.M., Facey, G.A., Fransham, P.B., 2007. The conversion of chicken manure to biooil by fast pyrolysis I. Analyses of chicken manure, biooils and char by 13C and 1H NMR and FTIR spectrophotometry. Journal of Environmental Science and Health. Part. B, Pesticides, Food Contaminants, and Agricultural Wastes 42, 71–77. doi:10.1080/03601230601020894.

Scott, D.S., Piskorz, J., Bergougnou, M. a., Overend, R.P., Graham, R., 1988. The role of temperature in the fast pyrolysis of cellulose and wood. Industrial & Engineering Chemistry Research 27, 8–15. doi:10.1021/ie00073a003.

Sigua, G.C., Novak, J.M., Watts, D.W., Cantrell, K.B., Shumaker, P.D., Szögi, A.A., Johnson, M.G., 2014. Carbon mineralization in two ultisols amended with different sources and particle sizes of pyrolyzed biochar. Chemosphere 103, 313–321. doi:http://dx.doi.org/10.1016/j.chemosphere.2013.12.024.

Singh, B.P., Cowie, A.L., Smernik, R.J., 2012. Biochar Carbon Stability in a Clayey Soil As a Function of Feedstock and Pyrolysis Temperature. Environmental Science & Technology 46, 11770–11778. doi:10.1021/es302545b.

Singh, B.P., Hatton, B.J., Balwant, S., Cowie, A.L., Kathuria, A., 2010. Influence of biochars on nitrous oxide emission and nitrogen leaching from two contrasting soils. Journal of Environmental Quality 39, 1224–1235..

Sirijanusorn, S., Sriprateep, K., Pattiya, A., 2013. Bioresource Technology Pyrolysis of cassava rhizome in a counter-rotating twin screw reactor unit. Bioresource Technology 139, 343–348. doi:10.1016/j.biortech.2013.04.024.

Sissingh, H.A., 1971. Analytical technique of the Pw method, used for the assessment of the phosphate status of arable soils in the Netherlands. Plant and Soil 34, 483–486. doi:10.1007/BF01372800.

Smith, P., 2016a. Soil carbon sequestration and biochar as negative emission technologies. Global Change Biology 22, 1315–1324. doi:10.1111/gcb.13178.

Smith, P., 2016b. Soil carbon sequestration and biochar as negative emission technologies. Global Change Biology 22, 1315–1324. doi:10.1111/gcb.13178.

Snyder, C.S., Bruulsema, T.W., Jensen, T.L., Fixen, P.E., 2009. Review of greenhouse gas emissions from crop production systems and fertilizer management effects. Agriculture, Ecosystems & Environment 133, 247–266. doi:http://dx.doi.org /10.1016/j.agee.2009.04.021.

Sohi, S.P., Krull, E., Lopez-Capel, E., Bol, R., 2010. Chapter 2 - A Review of Biochar and Its Use and Function in Soil, in: Agronomy, B.T.-A. in (Ed.), Advances in Agronomy. Academic Press, pp. 47–82. doi:http://dx.doi.org/10.1016/S0065-2113(10)05002-9.

Solar, J., Marco, I. De, Caballero, B.M., Rodriguez, N., Agirre, I., Adrados, A., 2016. Biomass and Bioenergy In fl uence of temperature and residence time in the pyrolysis of woody biomass waste in a continuous screw reactor 95, 416–423.

Spokas, K.A., 2013. Impact of biochar field aging on laboratory greenhouse gas production potentials. GCB Bioenergy 5, 165–176. doi:10.1111/gcbb.12005.

Spokas, K.A., Baker, J.M., Reicosky, D.C., 2010. Ethylene: potential key for biochar amendment impacts. Plant and Soil 333, 443–452. doi:10.1007/s11104-010-0359-5.

Spokas, K.A., Cantrell, K.B., Novak, J.M., Archer, D.W., Ippolito, J.A., Collins, H.P., Boateng, A.A., Lima, I.M., Lamb, M.C., McAloon, A.J., Lentz, R.D., Nichols, K.A., 2012. Biochar: a synthesis of its agronomic impact beyond carbon sequestration. Journal of Environmental Quality 41, 973–989. doi:10.2134/jeq2011.0069.

Spokas, K.A., Koskinen, W.C., Baker, J.M., Reicosky, D.C., 2009. Impacts of woodchip biochar additions on greenhouse gas production and sorption/degradation of two herbicides in a Minnesota soil. Chemosphere 77, 574–581. doi:http://dx.doi.org/10.1016/j.chemosphere.2009.06.053.

Spokas, K.A., Reicosky, D.C., 2009. Impacts of Sixteen Different Biochars on Soil Greenhouse Gas Production. Annals of Environmental Science; Vol 3 (2009).

Steele, P.H., Mitchell, B., 2012. Thermal transfert mechanism for an auger pyrolysis reactor. United States Patent 20120228112 A1.

Steinbeiss, S., Gleixner, G., Antonietti, M., 2009. Effect of biochar amendment on soil carbon balance and soil microbial activity. Soil Biology and Biochemistry 41, 1301–1310. doi:http://dx.doi.org/10.1016/j.soilbio.2009.03.016.

Suddick, E.C., Six, J., 2013. An estimation of annual nitrous oxide emissions and soil quality following the amendment of high temperature walnut shell biochar and compost to a small scale vegetable crop rotation. Science of The Total Environment 465, 298–307. doi:http://dx.doi.org/10.1016/j.scitotenv.2013.01.094.

Sun, L., Li, L., Chen, Z., Wang, J., Xiong, Z., 2014. Combined effects of nitrogen deposition and biochar application on emissions of N 2 O, CO 2 and NH 3 from agricultural and forest soils. Soil Science and Plant Nutrition 60, 254–265. doi:10.1080/00380768.2014.885386.

Sun, Y., Gao, B., Yao, Y., Fang, J., Zhang, M., Zhou, Y., Chen, H., Yang, L., 2014. Effects of feedstock type, production method, and pyrolysis temperature on biochar and hydrochar properties. Chemical Engineering Journal 240, 574–578. doi:10.1016/j.cej.2013.10.081.

Tang, J., Zhu, W., Kookana, R., Katayama, A., 2013. Characteristics of biochar and its application in remediation of contaminated soil. Journal of Bioscience and Bioengineering 116, 653–659. doi:10.1016/j.jbiosc.2013.05.035.

Thornley, P., Gilbert, P., Shackley, S., Hammond, J., 2015. Maximizing the greenhouse gas reductions from biomass: The role of life cycle assessment. Biomass and Bioenergy 81, 35–43. doi:http://dx.doi.org/10.1016/j.biombioe.2015.05.002.

Tröger, N., Richter, D., Stahl, R., 2013. Journal of Analytical and Applied Pyrolysis Effect of feedstock composition on product yields and energy recovery rates of fast pyrolysis products from different straw types. Journal of Analytical and Applied Pyrolysis 100, 158–165. doi:10.1016/j.jaap.2012.12.012.

Troy, S.M., Lawlor, P.G., O’ Flynn, C.J., Healy, M.G., 2013. Impact of biochar addition to soil on greenhouse gas emissions following pig manure application. Soil Biology and Biochemistry 60, 173–181. doi:http://dx.doi.org/10.1016/j.soilbio.2013.01.019.

Uchimiya, M., Klasson, K.T., Wartelle, L.H., Lima, I.M., 2011. Chemosphere Influence of soil properties on heavy metal sequestration by biochar amendment : 1 . Copper sorption isotherms and the release of cations. Chemosphere 82, 1431–1437. doi:10.1016/j.chemosphere.2010.11.050.

UNEP, 2016. The Emissions Gap Report 2016. doi:ISBN 978-92-807-3617-5.

van Zwieten, L., Kimber, S., Morris, S., Downie, A., Berger, E., Rust, J., Scheer, C., 2010. Influence of biochars on flux of N_2O and CO_2 from Ferrosol. Soil Research 48, 555–568..

Van Zwieten, L., Kimber, S.W.L., Morris, S.G., Singh, B.P., Grace, P.R., Scheer, C., Rust, J., Downie, A.E., Cowie, A.L., 2013. Pyrolysing poultry litter reduces N2O and CO2 fluxes. Science of The Total Environment 465, 279–287. doi:http://dx.doi.org/10.1016/j.scitotenv.2013.02.054.

Van Zwieten, L., Singh, B.P., Kimber, S.W.L., Murphy, D. V, Macdonald, L.M., Rust, J., Morris, S., 2014. An incubation study investigating the mechanisms that impact N2O flux from soil following biochar application. Agriculture, Ecosystems & Environment 191, 53–62. doi:http://dx.doi.org/10.1016/j.agee.2014.02.030.

Verhoeven, E., Six, J., 2014. Biochar does not mitigate field-scale N2O emissions in a

Northern California vineyard: An assessment across two years. Agriculture, Ecosystems & Environment 191, 27–38. doi:http://dx.doi.org/10.1016/j.agee.2014.03.008.

Verma, M., Godbout, S., Brar, S.K., Solomatnikova, O., Lemay, S.P., Larouche, J.P., 2012. Biofuels Production from Biomass by Thermochemical Conversion Technologies 2012. doi:10.1155/2012/542426.

Verma, M., M'hamdi, N., Dkhili, Z., Brar, S.K., Misra, K., 2014. Thermochemical Transformation of Agro-biomass into Biochar: Simultaneous Carbon Sequestration and Soil Amendment, in: Brar, S.K., Dhillon, G.S., Soccol, C.R. (Eds.), Biotransformation of Waste Biomass into High Value Biochemicals. Springer New York, New York, NY, pp. 51–70. doi:10.1007/978-1-4614-8005-1_3.

Veses, A., Aznar, M., Callén, M.S., Murillo, R., García, T., 2016. An integrated process for the production of lignocellulosic biomass pyrolysis oils using calcined limestone as a heat carrier with catalytic properties. Fuel 181, 430–437. doi:http://dx.doi.org/10.1016/j.fuel.2016.05.006.

Veses, A., Aznar, M., López, J.M., Callén, M.S., Murillo, R., García, T., 2015. Production of upgraded bio-oils by biomass catalytic pyrolysis in an auger reactor using low cost materials. FUEL 141, 17–22. doi:10.1016/j.fuel.2014.10.044.

Veses, A., Aznar, M., Martínez, I., Martínez, J.D., López, J.M., Navarro, M. V, Callén, M.S., Murillo, R., García, T., 2014. Bioresource Technology Catalytic pyrolysis of wood biomass in an auger reactor using calcium-based catalysts. Bioresource Technology 162, 250–258. doi:10.1016/j.biortech.2014.03.146.

von Doderer, C.C.C., Kleynhans, T.E., 2014. Determination of the Environmental Implications of Bio-energy Production Using a Life-Cycle Assessment Approach BT - Bioenergy from Wood: Sustainable Production in the Tropics, in: Seifert, T. (Ed.), Springer Netherlands, Dordrecht, pp. 237–262. doi:10.1007/978-94-007-7448-3_11.

Wang, J., Pan, X., Liu, Y., Zhang, X., Xiong, Z., 2012. Effects of biochar amendment in two soils on greenhouse gas emissions and crop production. Plant and Soil 360, 287–298. doi:10.1007/s11104-012-1250-3.

Wang, J., Xiong, Z., Kuzyakov, Y., 2016. Biochar stability in soil: meta-analysis of decomposition and priming effects. GCB Bioenergy 8, 512–523. doi:10.1111/gcbb.12266.

Wang, W., Wang, H., Feng, Y., Wang, L., Xiao, X., Xi, Y., Luo, X., Sun, R., Ye, X., Huang, Y., Zhang, Z., Cui, Z., 2016. Consistent responses of the microbial community structure to organic farming along the middle and lower reaches of the Yangtze River 6, 35046.

Wang, Z., Zheng, H., Luo, Y., Deng, X., Herbert, S., Xing, B., 2013. Characterization and influence of biochars on nitrous oxide emission from agricultural soil. Environmental

Pollution 174, 289–296. doi:http://dx.doi.org/10.1016/j.envpol.2012.12.003.

Washington State University and Department of Ecology from State of Washington, 2011. Methods for Producing Biochar and Advanced Biofuels in Washington State Part 1 : Literature Review of Pyrolysis Reactors, Thrombosis and Haemostasis. doi:Ecology Publication Number 11-07-017.

Weisberg, P., Delaney, M., Hawkes, J. (The Climate Trust), 2010. Carbon markets investment criteria for biochar projects. California Energy Commission. Publication number: CEC-500-02-004. 38 pp.

Whitman, T., Yanni, S.F., Whalen, J.K., 2011. Life cycle assessment of corn stover production for cellulosic ethanol in Quebec. Can. J. Soil Sci 91: 997-1012. doi:10.4141/CJSS2011-011.

Windeatt, J.H., Ross, A.B., Williams, P.T., Forster, P.M., Nahil, M.A., Singh, S., 2014. Characteristics of biochars from crop residues: Potential for carbon sequestration and soil amendment. Journal of Environmental Management 146, 189–197. doi:http://dx.doi.org/10.1016/j.jenvman.2014.08.003.

Woolf, D., Amonette, J.E., Street-Perrott, F.A., Lehmann, J., Joseph, S., 2010. Sustainable biochar to mitigate global climate change. Nature Communications 1, 56.

Wu, F., Jia, Z., Wang, S., Chang, S.X., Startsev, A., 2013. Contrasting effects of wheat straw and its biochar on greenhouse gas emissions and enzyme activities in a Chernozemic soil. Biology and Fertility of Soils 49, 555–565. doi:10.1007/s00374-012-0745-7.

Xie, T., Reddy, K.R., Wang, C., Yargicoglu, E., 2015. Critical Reviews in Environmental Science and Technology Characteristics and Applications of Biochar for Environmental Remediation : A Review 37–41. doi:10.1080/10643389.2014.924180.

Xiu, S., Wang, N., Yi, W., Li, B., Shahbazi, G., 2008. Validation of kinetic parameter values for prediction of pyrolysis behaviour of corn stalks in a horizontal entrained-flow reactor 100, 79–85. doi:10.1016/j.biosystemseng.2008.01.006.

Yanai, Y., Toyota, K., Okazaki, M., 2007. Effects of charcoal addition on N_2O emissions from soil resulting from rewetting air-dried soil in short-term laboratory experiments. Soil Science & Plant Nutrition 53, 181–188. doi:10.1111/j.1747-0765.2007.00123.x.

Yang, H., Yan, R., Chen, H., Lee, D.H., Zheng, C., 2007. Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel 86, 1781–1788. doi:10.1016/j.fuel.2006.12.013.

Yang, Y., Brammer, J.G., Mahmood, A.S.N., Hornung, A., 2014. Bioresource Technology Intermediate pyrolysis of biomass energy pellets for producing sustainable liquid , gaseous and solid fuels. Bioresource Technology 169, 794–799. doi:10.1016/j.biortech.2014.07.044.

Yildiz, G., Ronsse, F., Duren, R. van, Prins, W., 2016. Challenges in the design and operation of processes for catalytic fast pyrolysis of woody biomass. Renewable and Sustainable Energy Reviews 57, 1596–1610. doi:https://doi.org/10.1016/j.rser. 2015.12.202.

Yoo, G., Kang, H., 2012. Effects of biochar addition on greenhouse gas emissions and microbial responses in a short-term laboratory experiment. Journal of Environmental Quality 41, 1193–1202. doi:10.2134/jeq2011.0157.

Yu, L., Tang, J., Zhang, R., Wu, Q., Gong, M., 2013. Effects of biochar application on soil methane emission at different soil moisture levels. Biology and Fertility of Soils 49, 119–128. doi:10.1007/s00374-012-0703-4.

Yu, Y., Yang, Y., Cheng, Z., Blanco, P.H., Liu, R., Bridgwater, A. V, Cai, J., 2016. Pyrolysis of Rice Husk and Corn Stalk in Auger Reactor . 1 . Characterization of Char and Gas at Various Temperatures. doi:10.1021/acs.energyfuels.6b02276.

Zavalloni, C., Alberti, G., Biasiol, S., Vedove, G.D., Fornasier, F., Liu, J., Peressotti, A., 2011. Microbial mineralization of biochar and wheat straw mixture in soil: A short-term study. Applied Soil Ecology 50, 45–51. doi:http://dx.doi.org/10.1016/j.apsoil. 2011.07.012.

Zhang, A., Bian, R., Hussain, Q., Li, L., Pan, G., Zheng, J., Zhang, X., Zheng, J., 2013. Change in net global warming potential of a rice–wheat cropping system with biochar soil amendment in a rice paddy from China. Agriculture, Ecosystems & Environment 173, 37–45. doi:http://dx.doi.org/10.1016/j.agee.2013.04.001.

Zhang, A., Cui, L., Pan, G., Li, L., Hussain, Q., Zhang, X., Zheng, J., Crowley, D., 2010. Effect of biochar amendment on yield and methane and nitrous oxide emissions from a rice paddy from Tai Lake plain, China. Agriculture, Ecosystems & Environment 139, 469–475. doi:http://dx.doi.org/10.1016/j.agee.2010.09.003.

Zhao, L., Cao, X., Mašek, O., Zimmerman, A., 2013. Heterogeneity of biochar properties as a function of feedstock sources and production temperatures. Journal of Hazardous Materials 256–257, 1–9. doi:10.1016/j.jhazmat.2013.04.015.

Zheng, J., Stewart, C.E., Cotrufo, M.F., 2012. Biochar and nitrogen fertilizer alters soil nitrogen dynamics and greenhouse gas fluxes from two temperate soils. J Environ Qual 41, 1361–1370. doi:10.2134/jeq2012.0019\r10.2134/jeq2012.0019.

Zimmerman, A.R., 2010. Abiotic and Microbial Oxidation of Laboratory-Produced Black Carbon (Biochar). Environmental Science & Technology 44, 1295–1301. doi:10.1021/es903140c.

Zimmerman, A.R., Gao, B., Ahn, M.-Y., 2011. Positive and negative carbon mineralization priming effects among a variety of biochar-amended soils. Soil Biology and Biochemistry 43, 1169–1179. doi:http://dx.doi.org/10.1016/j.soilbio. 2011.02.005.

Connecting text

The vertical auger pyrolysis reactor developed by the IRDA and the CRIQ (Patent US 9,486,774B2 and Patent CA2830968) was used to produce biochar and to achieve the objectives presented in Chapter 4. Before to realize the experiments described in this chapter, it was necessary to evaluate the capacity of this new pyrolysis unit to produce biochar and to identify the pyrolysis operating parameters that would be used. Appendix 1 presents the results of preliminary tests that were carried out with wood (two particle size) with a range of pyrolysis operating parameters (temperature, solid residence time and nitrogen flowrate) that were selected from the literature review presented in Chapter 2.

Chapter 5 presented an incubation study in which N_2O and CO_2 emissions from soil samples amended with biochar were measured. Thus, the calculation method as well as an example of calculation is presented in Appendix 2.

In Chapter 5, the bacterial diversity was determined using high throughput sequencing and involving a library preparation step with amplification of the 16S V6-V8 region of bacteria. More details about this method are given in Appendix 3. Moreover, Appendix 3 presents the correlation between the N_2O emissions and soil bacterial groups.

The analysis of the energetic consumption of the pyrolysis auger reactor is presented in Appendix 4. The obtained results were used as input data in the analysis of energy impact of the biochar system which is presented in Chapter 6.

Appendix 1 Effect of operational conditions of a vertical pyrolysis auger reactor on products yields and analysis of bio-oil and biochar characteristics: preliminary tests

Introduction

As a new policy in the province of Quebec (Canada) will ban burying organic residues, the agricultural sector needs to find new and sustainable ways for managing its wastes. Pyrolysis, which can be defined as the thermochemical decomposition of biomass at elevated temperature (350-700 ºC) in the absence of oxygen, could be considered a sustainable management solution. The products resulting from pyrolysis are a solid biochar, a liquid bio-oil, and a non-condensable gas. Biochar applied to soil can increase crop yields, sequester carbon and reduce soil greenhouse gas emissions. Further, the produced bio-oil could be used, for example, to replace no. 2 oil in heating systems. Products yields and characteristics depend on feedstock, pyrolysis operational conditions and the type of pyrolysis technology used (Verma et al., 2012). In the perspective of agricultural residues local management, mobile pyrolysis reactors (e.g. auger reactor) could be established in agricultural regions and be shared by many farmers, reducing the transportation of biomass.

Objectives

The possibility of producing bio-oil and biochar from biomass pyrolysis in a mobile auger reactor was evaluated. The specific objectives were:

- To find the optimal pyrolysis operational parameters in order to produce a maximum yield of bio-oil and biochar.
- To evaluate the quality of bio-oil and biochar.

Material and Methods

Pyrolysis unit

The vertical auger pyrolysis unit (Figure A1.1) designed by the IRDA and the CRIQ was used and is described in Chapter 4. For this preliminary experiment, the pyrolytic vapors were evacuated through a 12.7 mm diameter flange in the upper part of the canister. The condensation system (Figure A1.2) includes three stages:

- Stage 1 (B1): A glass flask at ambient temperature

- Stage 2 (B2): An impinger immersed in an ice bath at 0 °C
- Stage 3 (B3): A second impinger immersed in CO_2 dry ice cooled acetone maintained at -20 to -30 °C

Figure A1.1: Picture of the pyrolysis auger reactor

Figure A1.2: Condensation system for the preliminary tests

Feedstock

Pellets made from wood (mixture of black Spruce and jack Pine) were ground and sieved to two particle sizes: 1 to 2.4 mm and 2.4 to 4 mm. Physico-chemical properties were analysed in the laboratory and the results are presented in Table 1.

Experimental design

For each trial, 1 kg of feedstock was pyrolysed. For each wood particle size, pyrolysis was performed at different temperatures, while the other operational parameters were kept constant:

- Reaction chamber temperatures: 450, 500, 550, 600 and 650 °C;
- Solid residence time in the reaction chamber: 60 seconds;
- Feedstock flow rate: 1.3 kg h^{-1};
- N_2 flowrate: 5 L min^{-1};

Yields of the pyrolysis products

Bio-oil (Eq. A.1) and biochar (Eq. A.2) yields were calculated on a wet biomass basis and non-condensable gas (Eq. A.3) yield was calculated by difference according to the following equations:

$$Yield_{bio-oil}(wt.\%) = \frac{m_{B1}+m_{B2}+m_{B3}}{m_f} \qquad (A.1)$$

$$Yield_{biochar}\,(wt.\%) = \frac{m_{Bioch}}{m_f} \qquad (A.2)$$

$$Yield_{gas}(wt.\%) = \frac{m_f-m_{Biochar}-m_{B1}-m_{B2}-m_{B3}}{m_f} \qquad (A.3)$$

Where m_{B1} is the mass of bio-oil collected in the glass flask, m_{B2} is the mass of bio-oil collected in the first impinger, m_{B3} is the mass of bio-oil collected in the second impinger, $m_{biochar}$ is the mass of biochar collected in the canister, and m_f is the mass of feedstock pyrolysed.

Products analysis

The products from the pyrolysis reaction resulting to the highest yield of bio-oil were analysed. The three fractions of bio-oil were analysed in the laboratory for water content (Karl-Fisher analysis). Other parameters were analysed, including higher heating value (HHV), pyrolysis solids content, ash content, N_{total}, pH, density, viscosity and melting point. The analysis methods used are presented in the ASTM D7544-09 standard.

Biochar sample was analysed for moisture, volatile matter and ash contents based on ASTM D1762-84 standard. Carbon (C_{tot}), hydrogen (H), nitrogen (N), oxygen (O), higher heating value (HHV), pH and density were also analysed.

Results

Feedstock

Table A1.1: Physico-chemical properties of wood

C_{tot} *(%)*	H *(%)*	O *(%)*	N *(%)*	Cl *ppm*	Moisture *(%)*	Ash (750 ºC) *(%)*	HHV *MJ/kg*
47.5	6.16	45.6	0.124	33	6.16	0.32	17.8

Yields of the pyrolysis products

A maximum bio-oil yield of 57% was obtained from the pyrolysis of wood (1 – 2.4 mm) at 600 ºC. In these conditions, biochar and non-condensable gas yields were 22% and 21%, respectively (Figure A1.3). Bio-oil yield is generally lower for the pyrolysis of larger wood particles (Figure A1.4). Bio-oil quantity collected at the first and third condensation stage was low, as the most bio-oil was collected at the second stage (88% of total bio-oil, on average).

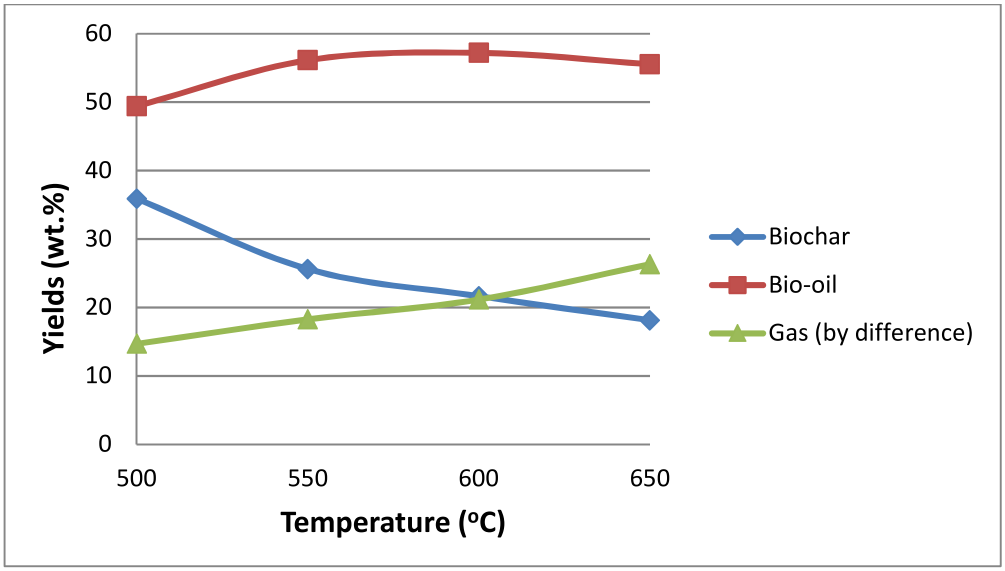


Figure A1.3: Wood pyrolysis products yields (solid residence time: 60 s; particle size: 1-2.4 mm)

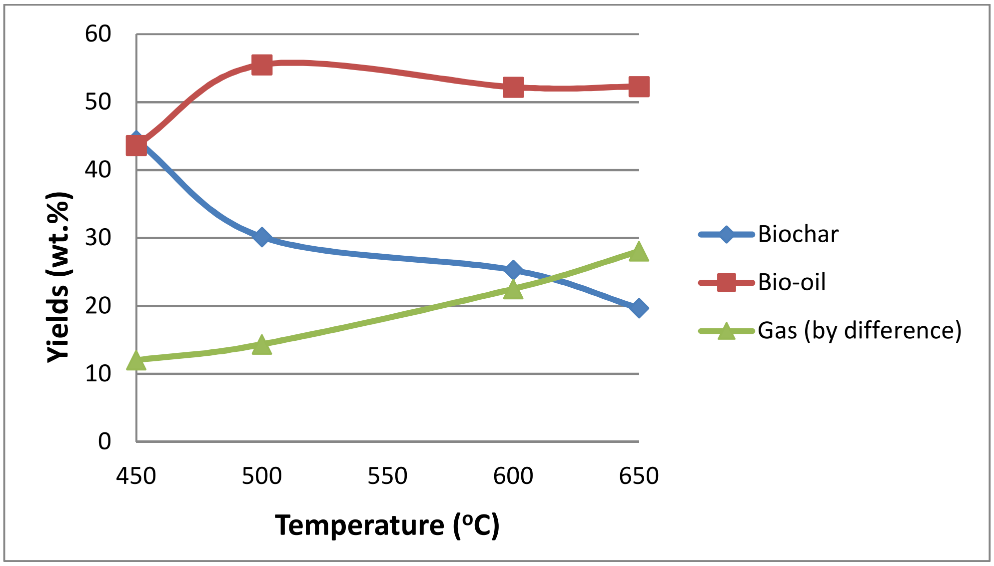


Figure A1.4: Wood pyrolysis products yields (solid residence time: 60 s; particle size: 2.4 – 4 mm)

Products analysis

Table A1.2: Physico-chemical characteristics of bio-oil produced from wood (1 – 2.4 mm) pyrolysis at 600 ºC and 60 s residence time

Parameter	Unit	B1	B2	B3	Standard specification
Water content	% (w/w)	1.8	28.1	57.9	30.0 max
HHV	MJ kg^{-1}	22.8	14.7	--	15 min
Solids content	% (w/w)	--	0.02	0.007	2.5 max
Ash (750 ºC)	% (w/w)	--	< 0.01	--	0.25 max
N total	% (w/w)	0.084	0.021	--	--
pH		--	1.98	--	--
Density (20 ºC)	g/cm^3	--	1.18	--	1.1 – 1.3
Melting point	ºC	75	--	--	--

Table A1.3: Physico-chemical characteristics of biochar produced from wood (1 – 2.4 mm) pyrolysis at 600 ºC and 60 s residence time.

Ultimate analysis				**Proximate analysis**					
C_{tot}	N	H	O	Moisture	Volatile matter	Ash (750 ºC)	HHV	pH	Density
%	*%*	*%*	*%*	*%*	*%*	*%*	*MJ kg^{-1}*		*g cm^{-3}*
74.0	0.34	4.46	18.7	0.73	54.6	1.75	27.4	6.55	0.174

Conclusions

- It is possible to produce great yields of bio-oil (>50%) and biochar (20 to 30%) from the pyrolysis of wood in the new vertical auger reactor designed by the IRDA and the CRIQ.
- Excluding the bio-oil collected at the third condensation stage, bio-oil produced from wood have a great potential to be used as an alternative fuel in industrial burners, all parameters being within the standard ASTM D7544-09 specification (Table A1.2).
- Biochar having a high C/N ratio, low O/C ratio, low H/C ratio and low volatile matter content (Table A1.3) is expected to have high carbon stability and could contribute to the reduction of soil greenhouse gas emissions when used as a soil amendment.

- Further pyrolysis tests with different agricultural biomasses are needed to establish the relation between pyrolysis operational parameters and products characteristics.

References

ASTM (American Society for Testing and Materials). 2007. D1762-84 - Standard test method for chemical analysis of wood charcoal, 2 pages.

ASTM (American Society for Testing and Materials). 2009. D7544-09 - Standard Specification for pyrolysis liquid biofuel, 7 pages.

Lehto, J., Oasmaa, A., Solantausta, Y., Kytö, M. et David Chiaramonti, D., 2013. Fuel oil quality and combustion of fast pyrolysis bio-oils. Espoo 2013. VTT Technology 87. 79 p.

Verma, M., S. Godbout, S.K. Brar, O. Solomatnikova, S.P. Lemay and J.P. Larouche. 2012. Biofuel production from biomass by thermochemical conversion technologies. International journal of chemical engineering. Article 542426. 18 pages.

Verma, M., S. Godbout, O. Solomatnikova, D. Zegan, J.P. Larouche and F. Pelletier. 2013. System and process for thermochemical treatment of matter containing organic compounds. http://brevets-patents.ic.gc.ca/opic-cipo/cpd/eng/patent/2830968/claims.html. Patent App. CA 2830968.

Appendix 2 Calculation of N_2O and CO_2 emissions

N_2O and CO_2 concentrations (in mg m^{-3} h^{-1}) were calculated from the gas concentration in ppmv (C) using the ideal gas law (Equation A2.1):

$$Concentration = \frac{C \times M \times P}{R \times T \times 1000} \qquad \text{(A2.1)}$$

Where M = molecular weight of the gases (CO_2 and N_2O = 44), P = atmospheric pressure (101325 Pa), R = ideal gas constant (8.314), T = temperature (298.15 K) and 1000 = conversion factor.

Flux (F; mg kg^{-1} h^{-1}) was then calculated on a mass basis according to the Equation A2.2:

$$F = \frac{V}{m_s} \times \frac{dC}{dt} \qquad \text{(A2.2)}$$

Where V = Volume of air in the jar (m^3), m_s = mass of the soil mixture in the jar (kg), dC/dt = slope of the regression "gas concentration (mg m^{-3}) vs time (h)". Gas concentration (mg m^3) vs time (h) was represented on a graph (e.g. Figure A2.1) for each replicate and for the average value in order to calculate the regression slope using three values: concentration at t_o and t_{15} (the same for every replicate of a treatment), and concentration at t_{30}. A complete example of calculation is presented in Table A2.1.

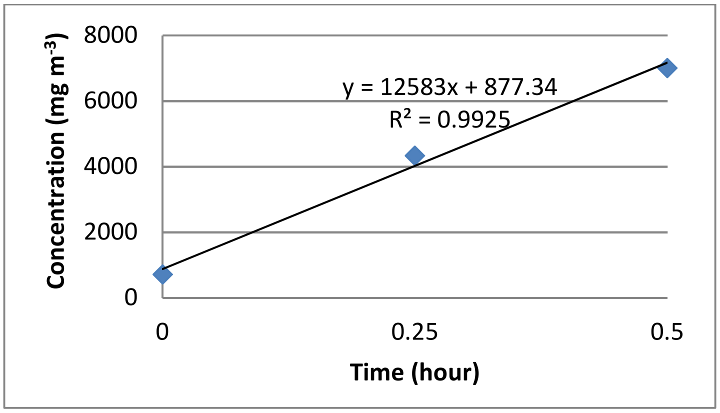


Figure A2.1: Slope of the regression CO_2 Concentration vs Time (average, 07-26-2016)

Table A2.1: Calculation example for CO_2 flux (mg kg^{-1} h^{-1}), mixture of the silt loam and biochar #5

	t	**C**	**C**	**V**	**m_s**	**Slope**	**C-CO_2 flux**							
	h	**ppm_v**	**mg m^{-3}**	**m^3**	**g**		**mg kg^{-1} h^{-1}**							
Date		*07-26*	*07-26*	--	--	*07-26*	*07-27*	*07-28*	*08-04*	*08-11*	*08-18*	*08-25*	*09-01*	*09-08*
t_0	0	400	719.7											
t_{15}	0.25	2412	4338.2											
T_{30} (R1)	0.5	3586	6448.9	0.00035	747	11458	1.10	0.75	0.26	0.09	0.01	0.12	0.19	0.10
T_{30} (R2)	0.5	4163	7487.6	0.00035	747	13536	1.08	0.79	0.21	0.08	0.00	0.13	0.21	0.09
T_{30} (R3)	0.5	3946	7096.8	0.00035	747	12754	1.16	0.86	0.24	0.07	0.00	0.11	0.21	0.17
T_{30} (Avg.)	0.5	3898	7011.1	0.00035	747	12583	1.11	0.80	0.24	0.08	0.00	0.12	0.20	0.12

t : Time after the jar was sealed (h); C : concentration; V : Volume of air in the jar; m_s : mass of soil

Appendix 3 Analysis of microbial community

Specific Methodology

Briefly, the gene specific sequence is fused to the Illumina TruSeq sequencing primers and PCR was carried out in a total volume of 50 µL that contains 1X Q5 buffer (NEB, Whitby, ON, CA), 0.25 µM of each primer, 200 µM of each dNTPs, 1 U of Q5 High-Fidelity DNA polymerase (NEB, Whitby, ON, CA) and 1 µL of template cDNA. The PCR started with an initial denaturation at 98°C for 30 s followed by 35 cycles of denaturation at 98°C for 10 s, annealing at 55°C for 10 s, extension at 72°C for 30s and a final extension at 72°C for 2 min. The PCR reaction was purified using the Axygen PCR cleanup kit (Fisher Scientific, Nepean, ON, Canada). Quality of the purified PCR product were checked on a 1% agarose gel. Fifty to one-hundred-fold dilution of this purified product was used as a template for a second PCR step with the goal of adding barcodes (dual-indexed) and missing sequence required for Illumina sequencing. Cycling for the second PCR were identical to the first PCR but with 12 cycles. PCR reaction were purified as above, checked for quality on a DNA7500 Bioanlayzer chip (Agilent) and then quantified spectrophotometrically with the Biophotometer (Eppendorf, Mississauga, ON, Canada) with a µCuvette® G1.0 (Eppendorf, Mississauga, ON, Canada). Barcoded Amplicons were pooled in equimolar concentration for sequencing on the Illumina Miseq. The following oligonucleotide sequences were used for amplification:

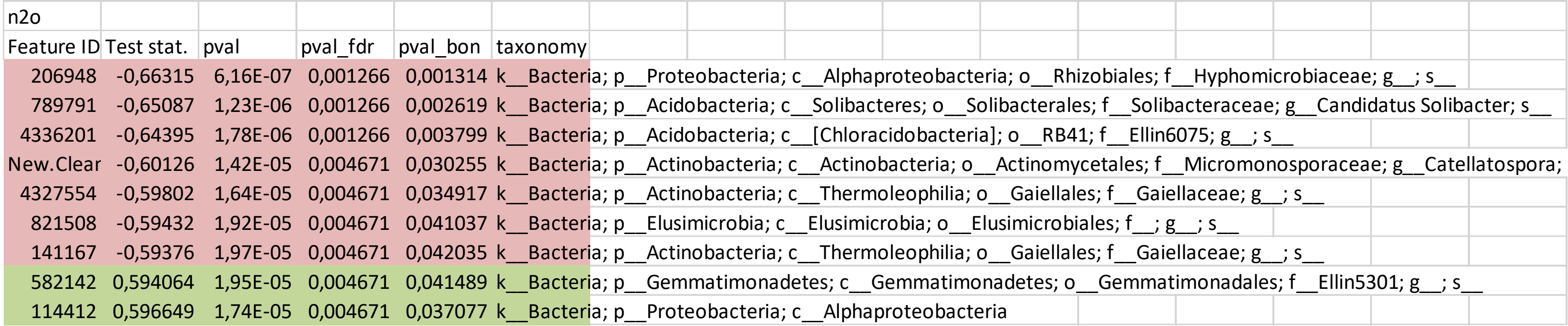
V6-V8 forward specific primer (first PCR) ACACTCTTTCCCTACACGACGC TCTTCCGATCTACGCGHNRAACCTTACC,

V6-V8 reverse specific primer (first PCR) GTGACTGGAGTTCAGACGTGTG CTCTTCCGATCTACGGGCRGTGWGTRCAA,

generic forward second-PCR primer AATGATACGGCGACCACCGAGATCTA CAC[index1]ACACTCTTTCCCTACACGAC and generic reverse second-PCR primer CAAGCAGAAGACGGCATACGAGAT[index2]GTGACTGGAGTTCAGACGTGT.

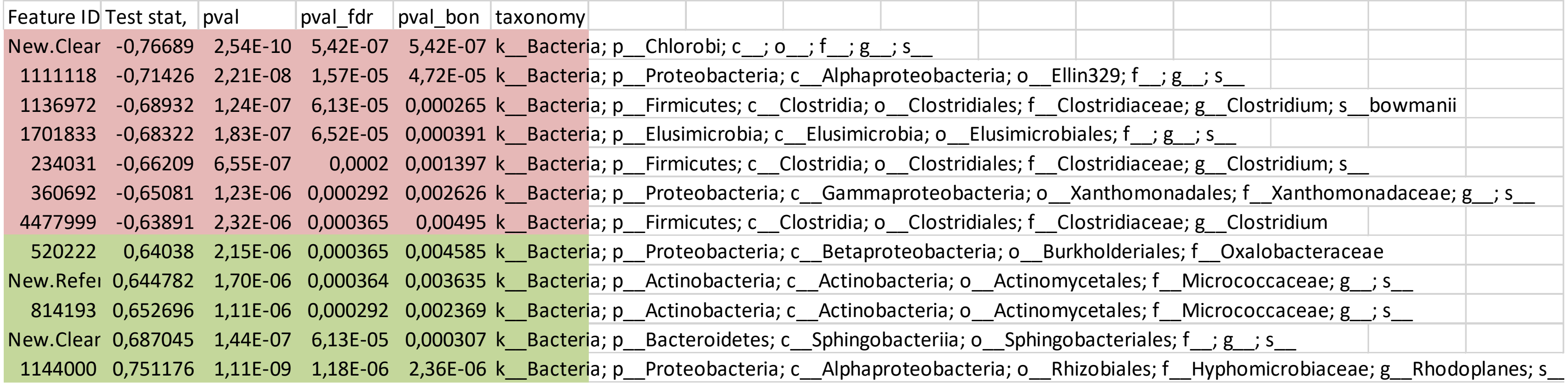
Correlations

Table A3.1: Correlation N_2O – Spearman



n2o					
Feature ID	Test stat.	pval	pval_fdr	pval_bon	taxonomy
206948	-0,66315	6,16E-07	0,001266	0,001314	k__Bacteria; p__Proteobacteria; c__Alphaproteobacteria; o__Rhizobiales; f__Hyphomicrobiaceae; g__; s__
789791	-0,65087	1,23E-06	0,001266	0,002619	k__Bacteria; p__Acidobacteria; c__Solibacteres; o__Solibacterales; f__Solibacteraceae; g__Candidatus Solibacter; s__
4336201	-0,64395	1,78E-06	0,001266	0,003799	k__Bacteria; p__Acidobacteria; c__[Chloracidobacteria]; o__RB41; f__Ellin6075; g__; s__
New.Clear	-0,60126	1,42E-05	0,004671	0,030255	k__Bacteria; p__Actinobacteria; c__Actinobacteria; o__Actinomycetales; f__Micromonosporaceae; g__Catellatospora;
4327554	-0,59802	1,64E-05	0,004671	0,034917	k__Bacteria; p__Actinobacteria; c__Thermoleophilia; o__Gaiellales; f__Gaiellaceae; g__; s__
821508	-0,59432	1,92E-05	0,004671	0,041037	k__Bacteria; p__Elusimicrobia; c__Elusimicrobia; o__Elusimicrobiales; f__; g__; s__
141167	-0,59376	1,97E-05	0,004671	0,042035	k__Bacteria; p__Actinobacteria; c__Thermoleophilia; o__Gaiellales; f__Gaiellaceae; g__; s__
582142	0,594064	1,95E-05	0,004671	0,041489	k__Bacteria; p__Gemmatimonadetes; c__Gemmatimonadetes; o__Gemmatimonadales; f__Ellin5301; g__; s__
114412	0,596649	1,74E-05	0,004671	0,037077	k__Bacteria; p__Proteobacteria; c__Alphaproteobacteria

Table A3.2: Correlation CO_2 – Spearman



Feature ID	Test stat,	pval	pval_fdr	pval_bon	taxonomy
New.Clear	-0,76689	2,54E-10	5,42E-07	5,42E-07	k__Bacteria; p__Chlorobi; c__; o__; f__; g__; s__
1111118	-0,71426	2,21E-08	1,57E-05	4,72E-05	k__Bacteria; p__Proteobacteria; c__Alphaproteobacteria; o__Ellin329; f__; g__; s__
1136972	-0,68932	1,24E-07	6,13E-05	0,000265	k__Bacteria; p__Firmicutes; c__Clostridia; o__Clostridiales; f__Clostridiaceae; g__Clostridium; s__bowmanii
1701833	-0,68322	1,83E-07	6,52E-05	0,000391	k__Bacteria; p__Elusimicrobia; c__Elusimicrobia; o__Elusimicrobiales; f__; g__; s__
234031	-0,66209	6,55E-07	0,0002	0,001397	k__Bacteria; p__Firmicutes; c__Clostridia; o__Clostridiales; f__Clostridiaceae; g__Clostridium; s__
360692	-0,65081	1,23E-06	0,000292	0,002626	k__Bacteria; p__Proteobacteria; c__Gammaproteobacteria; o__Xanthomonadales; f__Xanthomonadaceae; g__; s__
4477999	-0,63891	2,32E-06	0,000365	0,00495	k__Bacteria; p__Firmicutes; c__Clostridia; o__Clostridiales; f__Clostridiaceae; g__Clostridium
520222	0,64038	2,15E-06	0,000365	0,004585	k__Bacteria; p__Proteobacteria; c__Betaproteobacteria; o__Burkholderiales; f__Oxalobacteraceae
New.Refe	0,644782	1,70E-06	0,000364	0,003635	k__Bacteria; p__Actinobacteria; c__Actinobacteria; o__Actinomycetales; f__Micrococcaceae; g__; s__
814193	0,652696	1,11E-06	0,000292	0,002369	k__Bacteria; p__Actinobacteria; c__Actinobacteria; o__Actinomycetales; f__Micrococcaceae; g__; s__
New.Clear	0,687045	1,44E-07	6,13E-05	0,000307	k__Bacteria; p__Bacteroidetes; c__Sphingobacteriia; o__Sphingobacteriales; f__; g__; s__
1144000	0,751176	1,11E-09	1,18E-06	2,36E-06	k__Bacteria; p__Proteobacteria; c__Alphaproteobacteria; o__Rhizobiales; f__Hyphomicrobiaceae; g__Rhodoplanes; s__

Appendix 4 The energy balance of the vertical auger pyrolysis unit

Introduction

An important question that arises is whether a pyrolysis unit can meet its own energy needs or necessitate external sources of energy (Basu, 2010). Energy efficiency is an important measure for identifying the performance of a pyrolysis process (Jahirul et al., 2012). In general, pyrolysis of hemicellulose and lignin is an exothermic process, i.e. it releases energy to its surroundings, usually in the form of heat. Cellulose pyrolysis is endothermic at lower temperatures (<400 - 450 °C), and it becomes exothermic at higher temperatures (Basu, 2010). Thus, a pyrolysis system initially requires external heat only until the required temperature is reached. Afterward, the energetic products of pyrolysis (syngas and/or char) can be used to heat the reactor.

Due to the variety of pyrolysis units and to the different characteristics of the products resulting from these processes, energy consumption and production can differ among studies. The pyrolysis auger reactor is one of the most attractive designs developed today (Garcia-Perez, 2010). Recently, a vertical auger pyrolysis reactor (Patent CA 2830968) was developed by the *Institut de recherche et de développement en agroenvironnement (*IRDA) in collaboration with the *Centre de recherche industriel du Québec* (CRIQ). The experimental pyrolysis system includes the production of bio-oil intended to replace fossil fuel in heating appliance, combined with the production of biochar for soil amendment. In Chapter 4 of this thesis, an experimental design was constructed and optimal pyrolysis parameters (temperature, solid residence time and nitrogen flowrate) were determined in order to produce high quality biochar. However, the total energy needed to run this kind of pyrolysis unit was not estimated before. The different energy inputs needed to be quantified, including the electricity required to heat the pyrolysis unit, and to operate the auger screws gear motors and the water pumps of the condensers. This energy analysis will allow to answer the question of whether or not the pyrolysis unit can meet its own energy needs.

The goal of this work was to determine the energy efficiency of the vertical auger pyrolysis unit developed by the IRDA and the CRIQ. The obtained results will be used to carry out the energy balance of the global pyrolysis system, from biomass cultivation to pyrolysis products use.

Materials and Methods

In order to measure the energy consumption of the vertical auger pyrolysis reactor, pyrolysis experiments were carried out in an auger pyrolysis reactor (capacity of about 1 kg of biomass per hour) at the research facility of IRDA (Deschambault, Québec, Canada). Two scenarios (A and B) involving the pyrolysis of switchgrass were evaluated. In scenario A, pyrolysis was performed at a lower temperature (459°C) and with a shorter solid residence time (78 s) than in scenario B (temperature = 591°C; residence time = 104 s). The nitrogen flowrate was 3.4 L min^{-1} in scenario A and 2.6 L min^{-1} in scenario B. Biochar produced in scenario B is expected to have the optimal properties for C sequestration (low H/C_{org} and O/C_{org} ratios of 0.50 and 0.09, respectively), as the biochar produced in the scenario A has the opposite properties (high H/C_{org} and O/C_{org} ratios of 0.89 and 0.26, respectively). The energy consumption of the following elements was measured: the heating elements supplying thermal energy to the heater block and to the biochar canister, the two gear motors for the auger screws, the two water pumps of the condensers, the stirrer and the gas extraction fan. The power (Watts) of each element was obtained by multiplying the voltage (V) by the intensity (A). Then, the power was multiplied by the time of operation (h) to obtain the energy consumption in kWh. The operation time of each heating elements required to maintain the temperature set point was measured. Finally, the energy consumption in MJ was obtained by multiplying the energy in kWh by 3.6. The chemical properties of biochars (C, C_{org}, H, N, O) were analysed in the laboratory of IRDA (Québec, Canada) and the calorific value was calculated from Equation A4.1 (IFRF, 2014). The calorific value of bio-oil was measured using the bomb calorimeter method (ASTM, 2012) in the IRDA laboratory (Québec, Canada). The syngas heating value was calculated from the chemical composition of syngas produced in previous pyrolysis experiments carried out with similar operating parameters. Equation A4.2 was used, in which molar concentration CO, CH4, CO_2, C_2H_6 and C_2H_4 are the molar concentration in syngas (Azargohar et al., 2013).

$\mathrm{HHV_{biochar}}$ (MJ kg^{-1} dry fuel) = (34.1×C + 102×H + 6.3×N + 19.1×S - 9.85×O) / 100 (A4.1)

$\mathrm{LHV_{syngas}}$ (kJ m^{-3}) = (30.0×CO + 25.7×H_2 + 85.4×CH_4 + 151.3×C_nH_m) × 4.2 (A4.2)

Results and Discussion

The total energy consumption in scenarios A (Table A4.1) and B (Table A4.2) was 11.22 MJ kg^{-1} and 13.15 MJ kg^{-1}, respectively. The energy consumption was measured for each part of the pyrolysis unit (heating elements of the reactor, heating elements of the biochar canister, the gear motors for the two screws, the two pumps for the condensers, the gas extraction fan and the biomass stirrer). In scenario A, each element consumed 5.18, 1.48, 1.92, 0.70, 0.72 and 1.23 MJ kg^{-1}, respectively. In scenario B, they consumed 6.03, 1.93, 2.12, 0.77, 0.79 and 1.36 MJ kg^{-1}, respectively. The heating of the reactor and the biochar canister was separated in two phases: the initial phases of heating and stabilization of the temperature up to the set point (40 and 43 minutes in scenarios A and B, respectively), and the phase of pyrolysis in which the temperature is maintained at the set point (95 minutes in scenario A and 105 minutes in scenario B). Even if the phase of pyrolysis is longer than the initial phase, the latter consumes more energy (on average, 63% and 73% of the total energy consumption for heating the reactor and the biochar canister, respectively). Thus, the operation of the pyrolysis unit in continuous would contribute to decrease the energy consumption per kg of biomass.

The energy content of the co-products was evaluated in order to establish the energy balance of the pyrolysis reaction. In scenario A, the higher heating value (HHV) of biochar and bio-oil was 25.7 and 11.9 MJ kg^{-1}, respectively, and the lower heating value (LHV) of syngas was estimated to 6.63 MJ m^{-3}. The total energy output per kg of switchgrass was 14.65 MJ kg^{-1} (7.16 MJ kg^{-1}for bio-oil, 6.91 MJ kg^{-1} for biochar, and 0.57 MJ kg^{-1} for syngas). In scenario B, the HHV of biochar and bio-oil was 29.8 and 10.2 MJ kg^{-1}, respectively, and the LHV of syngas was estimated to 12.86 MJ m^{-3}. The total energy output per kg of switchgrass in scenario B was 12.69 MJ kg^{-1} (5.02 MJ kg^{-1} in bio-oil, 5.6 MJ kg^{-1} in biochar, and 2.07 MJ kg^{-1} in syngas). Thus, when the energy consumption is subtracted from the energy output, scenario A has a net energy output of 3.42 MJ kg^{-1} as the scenario B consumes 0.48 MJ kg^{-1}.

The energy balance would be improved for a scaled-up pyrolysis unit operating in continue. In fact, the initial phases of heating and stabilization of the temperature up to the set point would last the same time, as the pyrolysis phase would be longer. Thus, the author posed the hypothesis that the energy consumption and the pyrolysis products will be similar for a scaled-up unit, but larger batches of biomass could be processed. For example, if the batches of a scaled-up auger pyrolysis unit would be 8 times larger (8 kg instead of 1 kg), the total energy consumption would be 7.51 MJ kg^{-1} (2.086 kWh kg^{-1}) for scenario A, and 8.38 MJ kg^{-1} (2.326 kWh kg^{-1}) for scenario B. The net energy output would be 7.14 MJ kg^{-1} in scenario A and 4.31 MJ kg^{-1} in scenario B.

Table A4.1: Energetic consumption of the pyrolysis unit for 1 kg of biomass – Scenario A

Equipment	Stage of pyrolysis	Duration	Duration	Voltage	Electric current	Electric power	Energy	Energy
		min	h	V	A	W	W.h	MJ $kg^{-1}_{biomass}$
Reactor	Initial heating	16	0.27	240	11.6	2784	742.4	2.67
	Stabilisation phase 1	5	0.01	240	11.6	2784	34.8	0.13
	Stabilisation phase 2	19	0.04	240	11.6	2784	110.2	0.4
	Pyrolysis	95	0.2	240	11.6	2784	551	1.98
Char canister	Initial heating	12	0.2	120	7.6	912	182.4	0.66
	Stabilisation phase 1	6	0.03	120	7.6	912	27.36	0.1
	Stabilisation phase 2	19	0.09	120	7.6	912	81.83	0.29
	Pyrolysis	95	0.13	120	7.6	912	120.33	0.43
Screw 1 (8 Hz)	Pyrolysis	95	1.58	240	0.7	168	266	0.96
Screw 2 (8 Hz)	Pyrolysis	95	1.58	240	0.7	168	266	0.96
Pump 1	Pyrolysis	95	1.58	120	0.51	61.2	96.9	0.35
Pump 2	Pyrolysis	95	1.58	120	0.51	61.2	96.9	0.35
Extraction fan	Pyrolysis	95	1.58	120	1.05	126	199.5	0.72
Stirrer	Pyrolysis	95	1.58	120	1.8	216	342	1.23
Total							**3117.62**	**11.22**

Table A4.2: Energetic consumption of the pyrolysis unit for 1 kg of biomass – Scenario B

Equipment	Stage of pyrolysis	Duration	Duration	Voltage	Electric current	Electric power	Energy	Energy
		min	h	V	A	W	W.h	MJ $kg^{-1}_{biomass}$
Reactor	Initial heating	20	0.33	240	11.6	2784	928.00	3.34
	Stabilisation phase 1	4	0.01	240	11.6	2784	27.84	0.10
	Stabilisation phase 2	19	0.04	240	11.6	2784	110.20	0.40
	Pyrolysis	107	0.22	240	11.6	2784	620.60	2.23
Char canister	Initial heating	20	0.33	120	7.6	912	304.00	1.09
	Stabilisation phase 1	4	0.02	120	7.6	912	18.24	0.07
	Stabilisation phase 2	19	0.09	120	7.6	912	81.83	0.29
	Pyrolysis	107	0.15	120	7.6	912	135.53	0.49
Screw 1 (8 Hz)	Pyrolysis	107	1.78	240	0.7	168	299.60	1.08
Screw 2 (8 Hz)	Pyrolysis	107	1.78	240	0.7	168	299.60	1.08
Pump 1	Pyrolysis	107	1.78	120	0.51	61.2	109.14	0.39
Pump 2	Pyrolysis	107	1.78	120	0.51	61.2	109.14	0.39
Extraction fan	Pyrolysis	107	1.78	120	1.05	126	224.70	0.81
Stirrer	Pyrolysis	107	1.78	120	1.8	216	385.20	1.39
Total							3653.62	**13.15**

References:

ASTM. 2012. D7544-12: Standard Specification for Pyrolysis Liquid Biofuel, ASTM International, West Conshohocken, PA.

Azargohar, R., Jacobson, K. L., Powell, E. E., & Dalai, A. K. (2013). Journal of Analytical and Applied Pyrolysis Evaluation of properties of fast pyrolysis products obtained , from Canadian waste biomass. *Journal of Analytical and Applied Pyrolysis*, *104*, 330 -340. https://doi.org/10.1016/j.jaap.2013.06.016

Basu, P., 2010. Biomass gasification *and Pyrolysis : Practical Design and Theory. Elsevier. DOI: 10.1016/B978-0-12-374988-8.00003-9.*

Brassard, P., J.H. Palacios, S. Godbout, D. Bussières, R. Lagacé, J.-P. Larouche, and F. Pelletier. 2014. Comparison of the gaseous and particulate matter emissions from the combustion of agricultural and forest biomasses. *Bioresour. Technol, 155*, 300–306.

Brassard, P., Godbout, S., & Raghavan, V. (2016). Soil biochar amendment as a climate change mitigation tool: Key parameters and mechanisms involved. *Journal of Environmental Management*, *181*. https://doi.org/10.1016/j.jenvman.2016.06.063

Bridgwater, A. V. (2011). Review of fast pyrolysis of biomass and product upgrading. *Biomass and Bioenergy*, *38*, 68–94. https://doi.org/10.1016/j.biombioe.2011.01.048

Garcia-Perez, M., T. Lewis, C.E. Kruger. (2010). Methods for producing biochar and advanced biofuels in Washington State. Part 1: Literature Review of pyrolysis reactors. First project report. Department of Biological Systems Engineering and the Center for Sustainable Agriculture and Natural Resources, Washington State University, Pullman, WA, 137 pages.

Ibarrola, R., Shackley, S., Hammond, J., 2012. Pyrolysis biochar systems for recovering biodegradable materials: A life cycle carbon assessment. Waste Manag. 32, 859–868. doi:http://dx.doi.org/10.1016/j.wasman.2011.10.005

IFRF. International Flame Research Foundation (2004) Online Combustion Handbook. Method from Combustion File 24.

Jahirul, M.I., M.G. Rasul, A.A. Chowdhury and N. Ashwath. 2012. Biofuel Production through Biomass Pyrolysis – A Technological Review. Energies. 5: 2952-5001.

Kalita, B. 2012. Life cycle assessment of switchgrass (*Panicum virgatum L.)* biomass production in Ontario. Master thesis. The University of Guelph, Ontario, Canada. 105 pages.

Klöpffer, W. and B. Grahl. 2014. Life Cycle Assessment (LCA): A guide to best practice. Published by Wiley. ISBN: 978-3-527-32986-1. 440 pages.

Novak, J.M., W.J Busscher. W.J., Laird, D.L., Ahmedna, M., Watts, D.W., Niandou, M.A.S. 2009. Impact of biochar amendment on fertility of a Southeastern coastal plain soil. Soil Science 174, 105–112