Pyrolysis of Miscanthus: process optimization and life cycle assessment

by

Vishal Lakshman

Department of Bioresource Engineering

Faculty of Agricultural and Environmental Sciences

McGill University

Sainte-Anne-de-Bellevue, Quebec, Canada

December 2021

A thesis submitted to McGill University in partial fulfillment of the requirements of the degree of **Master of Science** in **Bioresource Engineering.**

Abstract

The usage of fossil carbon (C) for heating purposes in cold areas like Quebec (Canada) poses a major threat to the environment in the long run. Cultivation of Miscanthus on marginal lands provides a biogenic C source that can be used to produce bioenergy and bio-products, switching from fossil C sources. For example, Miscanthus can be used as a feedstock for pyrolysis, which is the thermochemical conversion of biomass at high temperature in the absence of oxygen into solid (biochar), liquid (bio-crude oil and aqueous phase), and gaseous (non-condensable gases) products . The overall objective of this thesis is to study the environmental performance of a pyrolysis biorefinery using Miscanthus as a feedstock and identify the key factors affecting the environmental impact.

It is recognized that pyrolysis products' yield, and properties depend on the biomass feedstock and the pyrolysis operating parameters. Therefore, in order to establish the mass balance of the biorefinery, pyrolysis experiments with a vertical auger pyrolysis reactor were performed using a range of pyrolysis parameters (temperature, biomass residence time and N_2 flow rate) determined from literature and preliminary experiments.

Fifteen pyrolysis tests were performed following a Box-Behnken design based on response surface methodology (RSM) to identify the optimal operating parameters to produce bio-crude oil with minimal water content. Results demonstrated that the optimal parameters were a temperature of 510°C, a biomass residence time of 81s and a N_2 flow rate of 5.1 L min^{-1}. These results were used to extrapolate the mass balance of a pyrolysis biorefinery processing 1000 kg of Miscanthus (d.b.).

A consequential life cycle assessment (C-LCA) was performed to assess the environmental performance of the pyrolysis biorefinery. The system boundary included all activities from Miscanthus cultivation to the use of pyrolysis co-products. The Miscanthus considered herein is cultivated on marginal soil. The C-LCA compares a pyrolysis scenario (1 tonne of dry Miscanthus cultivated on marginal land) and a reference scenario (idle marginal land). Results demonstrated that the environmental performance of the pyrolysis scenario is better than the reference scenario in 4 out of 16 impact categories assessed. It was observed that the climate change impact of the pyrolysis scenario exceeds the reference scenario by only 79.5 kg CO_2 eq. Furthermore, a sensitivity analysis was performed to account for the variability of three parameters (the yield of biomass, C sequestration values of the biochar, and the standard soil organic carbon levels) having a significant impact on the environmental performance of the pyrolysis scenario. The results of the study exhibit that the biomass supply chain, pyrolysis parameters, as well as the choice of marginal technologies replaced, play an important role in the environmental performance of pyrolysis biorefineries.

Résumé

L'utilisation de carbone (C) fossile à des fins de chauffage dans des régions froides comme le Québec (Canada) constitue une menace majeure pour l'environnement à long terme. La culture du Miscanthus sur des terres marginales fournit une source de C biogénique qui peut être utilisée pour produire de la bioénergie et des bioproduits, remplaçant les sources de C fossile. Par exemple, le Miscanthus peut être utilisé comme intrant pour la pyrolyse, qui est un procédé de conversion thermochimique de la biomasse à haute température en l'absence d'oxygène, produisant un solide (biochar), un liquide (bio-huile et phase aqueuse) et des gaz non condensables. L'objectif principal de cette thèse est d'étudier les performances environnementales d'une bioraffinerie de pyrolyse utilisant le Miscanthus comme intrant et d’identifier les paramètres cls ayant une influence sur l’impact environmental.

Il est reconnu que les rendements et les propriétés des produits de pyrolyse dépendent de la biomasse et des paramètres de fonctionnement de la pyrolyse. Par conséquent, afin d'établir le bilan massique de la bioraffinerie, des expériences de pyrolyse avec un réacteur de pyrolyse à vis verticale ont été réalisées en utilisant une gamme de paramètres de pyrolyse (température, temps de séjour de la biomasse et débit de N_2) déterminés à partir de la littérature et d’expériences préliminaires.

Quinze tests de pyrolyse ont été effectués selon un plan expérimental Box-Behnken basée sur la méthodologie de surface de réponses (RSM) afin d’identifier les paramètres de fonctionnement optimaux permettant de produire une bio-huile ayant une teneur en eau minimale. Les résultats ont démontré que les paramètres optimaux étaient une température de 510°C, un temps de résidence de la biomasse de 81 s et un débit de N_2 de 5,1 L min^{-1}. Ces

résultats ont été utilisés pour extrapoler le bilan massique d'une bioraffinerie de pyrolyse traitant 1000 kg de Miscanthus (d.b.).

Une analyse de cycle de vie conséquentielle (ACV-C) a été réalisée pour évaluer la performance environnementale de la bioraffinerie de pyrolyse. La frontière du système comprenait toutes les activités, de la culture du Miscanthus à l'utilisation des coproduits de la pyrolyse. Le Miscanthus considéré ici est cultivé sur un sol marginal. L'ACV-C compare un scénario de pyrolyse (1 tonne de Miscanthus cultivé sur terre marginale) et un scénario de référence (terre marginale inutilisée). Les résultats ont démontré que la performance environnementale du scénario de pyrolyse est meilleure que le scénario de référence dans 4 des 16 catégories d'impact évaluées. Entre autres, l'impact sur le changement climatique du scénario de pyrolyse ne dépasse le scénario de référence que de 79,5 kg CO_2 eq. De plus, une analyse de sensibilité a été réalisée pour tenir compte de la variabilité de trois paramètres (le rendement en biomasse, les valeurs de séquestration de C du biochar et les niveaux standard de carbone organique du sol) qui ont un impact important sur la performance environnementale du scénario de pyrolyse. Les résultats de l'étude montrent que la chaîne d'approvisionnement en biomasse, les paramètres de pyrolyse, ainsi que le choix des technologies marginales remplacées, jouent un rôle important dans la performance environnementale des bioraffineries de pyrolyse.

Acknowledgements

First and foremost, I want to offer my heartfelt thanks to Prof. Vijaya Raghavan, my supervisor, for the unwavering support and encouragement throughout my studies and research. I appreciate his patience, passion, and vast knowledge. Although I worked on this project far away from the Macdonald campus, he was always eager to respond to my inquiries. his advice was invaluable throughout the duration of my experiments.

I am grateful to my co-supervisor, Dr. Patrick Brassard, for guiding me throughout my work at IRDA (*Institut de recherche et de développement en agroenvironnement*). His encouragement, vision, understanding, advice, and friendly mentorship were essential on every step of my study, during the project and for scientific writing.

I'd like to offer special thanks to Dr. Stéphane Godbout for offering me with the chance to work with his team at IRDA, and for his mentorship. I'd like to thank Dr. Lorie Hamelin for useful insights that helped in conceptualization of the pyrolysis experiments and for reviewing the article. Thanks to Michèle Grenier (IRDA) for conducting the statistical analysis.

Finally, I want to express my gratitude to my family and friends for their constant support and encouragement

Thesis format

This thesis is presented in the form of manuscripts that can be published in a journal. The Faculty of Graduate and Postdoctoral Studies at McGill University has authorised this thesis format, which adheres to the standards indicated in the Guidelines: Concerning Thesis Preparation.

The organization of this thesis consists of the following:

CHAPTER I : Introduction, the problem statement along with the hypothesis is described. Overall objectives and specific objectives of the thesis are discussed.

CHAPTER II : Review of Literature, pyrolysis technologies and the factors affecting pyrolysis yields have been discussed. The operating parameters for an auger reactor, the potential of cultivating Miscanthus for bioenergy and a tool to assess the environmental performance of a biorefinery are described.

CHAPTER III : Experimental validation of the optimal pyrolysis operating parameters for an auger reactor to produce bio-oil with minimal water content.

CHAPTER IV : Assessment of the environmental performance of a pyrolysis biorefinery using Miscanthus as a feedstock for the production of bio-based products, biochar and bioenergy.

CHAPTER V : Summary and conclusion.

Contribution of authors

The following are the manuscripts prepared for publication:

Lakshman, V., Brassard, P., Raghavan, V. 2021. Pyrolysis technologies and environmental assessment of a biorefinery using Miscanthus: a review (Pending submission)

Lakshman, V., Brassard, P., Hamelin, L., Raghavan, V., Godbout, S. 2021. Pyrolysis of Miscanthus: Developing the mass balance of a biorefinery through experimental tests in an auger reactor. Bioresource Technology Reports, 14, 100687. (Published)

Lakshman, V., Brassard, P., Raghavan, V. 2021. Consequential life cycle assessment of a pyrolysis biorefinery using Miscanthus cultivated on marginal soil. (Pending submission)

The review of relevant literature, the design of experiments, experimental work, data analysis, and manuscript preparation, was carried out by Vishal Lakshman. Prof. G.S. Vijaya Raghavan, from the Department of Bioresource Engineering, Macdonald Campus of McGill University, and Dr. Patrick Brassard, from the Institut de recherche et de développement en agroenvironnement (IRDA), supervised the work and all co-authors reviewed the manuscripts. The pyrolysis experiments presented were carried out at a laboratory of IRDA, Deschambault (Québec), Canada.

Dr. Raghavan, Dr. Brassard, Dr. Godbout, and Dr. Hamelin provided scientific advice and are directly associated with editing and reviewing the manuscript.

Table of contents

Contents

List of tables

List of figures

Abbreviations

°C	Degree Celsius
a.i.	Active ingredient
ANOVA	Analysis of variance
ASTM	American society for testing and materials
BBD	Box-Behnken design
C	Carbon
CO_2	Carbon-dioxide
d.b.	Dry basis
g	gram
GHG	Greenhouse gas
H	Hydrogen
HHV	Higher heating value
IRDA	Institut de recherche et de développement en agroenvironnement
kg	Kilogram
LCA	Life cycle assessment
LHV	Lower heating value
m	Metre
mg	milligrams
min	Minute
MJ	Mega-joule
N	Nitrogen

O	Oxygen
rpm	Rotations per minute
RSM	Response surface methodology
S	Sulfur
SOC	Soil organic carbon
t.C	Tonnes of carbon
VM	Volatile matter
w.b.	Wet basis
yr	Year

CHAPTER I

Introduction

Increasing global energy demand owing to the ever-growing population and economic growth, directly leads to the devastating impacts of global warming, which impose the need of sustainable methods for energy production. Significant efforts to be increasingly independent of fossil fuels which account to approximately 80% of the total primary energy consumption (Ahmad & Zhang, 2020) are being made. These efforts are made to reduce the greenhouse gas (GHG) emissions and to maintain the increase of global mean surface temperature to well-below 2°C from pre-industrial levels (IPCC, 2018a). The effects of temperature rise to date include, droughts, floods, rise in sea level and loss of biodiversity, posing unprecedented risks to vulnerable populations (IPCC, 2018a). A global energy transition enabled by the use of renewable energy promises a transition away from the use of fossil fuels. Contributions from renewable energy to the total primary energy supply is expected rise from 14% in 2015 to 63% in 2050 (Gielen et al., 2019). Applications of various renewable energy sources such as solar energy, wind energy, geothermal energy, hydro energy and bioenergy are being extensively researched (El Haj Assad et al., 2021). Bioenergy is obtained from biomass to produce biofuels, which are considered more appropriate than other renewable sources due to the fact that they can be used with minimal changes to the existing vehicle systems. Apart from transportation, biofuels can also be used in thermal power plants, boilers and heating systems (El Haj Assad et al., 2021).

Based on the source of feedstock used for their production, biofuels are classified into different generations. First generation biofuels constitute food crops such as, corn, sugarcane, rapeseed, etc. They are used to produce bioethanol or biobutanol through fermentation of the starch from the crops or to produce biodiesel by transesterification of oil crops (Sindhu et al., 2019). Second generation biofuels are produced from lignocellulosic biomass such as grasses, jatropha, etc. and other non-edible lipids, waste cooking oils, solid municipal waste etc. Conversion processes of non-food crops to biofuels include thermochemical (e.g. gasification, pyrolysis, torrefaction) or biochemical (e.g. saccharification, fermentation) conversion, to produce Syngas, bio-oil, etc. (Lin & Lu, 2021). Third generation biofuels use microorganisms such as microalgae or bacteria to produce biohydrogen, biomethanol, bioethanol, biodiesel, or carbohydrates, proteins or other compounds that are being used in pharmaceutical companies through fermentation and transesterification (Rodionova et al., 2017). The usage and development of technologies for second and third generation biofuels stems from the fact that first generation biofuels pose a major con through the "food versus fuel" debate. Various life cycle assessments for first generation biofuels depict a negative energy gain (Sindhu et al., 2019).

Based on their physical state, biofuels are categorized into solid, liquid, and gaseous biofuels. Solid biofuels include raw solid biomass feedstock (agricultural residues, forest residues, energy crops, and solid wastes) that is used for biofuel production along with biochar, which is a porous, carbon-enriched solid. Biochar is produced by heating biomass feedstock in the absence of air (Ruan et al., 2019). Liquid biofuels are produced using either biochemical conversion (fermentation and transesterification) or thermochemical conversion (pyrolysis, gasification, and Fischer Tropsch process). Bioethanol, biobutanol, bio-oil, etc. are some examples for liquid biofuels (Fivga et al., 2019). Gaseous biofuels include biogas, biomethane, hydrogen, and syngas, which are produced using techniques such as anaerobic digestion, photocatalytic splitting of water, pyrolysis of biomass, etc. These are used for electricity generation or as heating or transport fuel (Padilla-Rivera et al., 2019).

Energy crops are dedicated plants cultivated as biofuel feedstocks. Of the aforementioned plant-based feedstocks, a few lignocellulosic plants are considered to be energy crops because of their low cost and fast growth; perennial availability; high yield (more dry matter production per hectare); ability to grow and regenerate in marginal or degraded lands; and resistance to extreme weather conditions (Nanda et al., 2016). A few examples of such energy crops include, alfalfa, elephant grass, switchgrass, timothy grass and Miscanthus.

Pyrolysis is the thermochemical conversion of feedstock to biofuels; wherein thermal decomposition of biomass occurs in the absence of oxygen. The results of pyrolysis include a solid yield (biochar), a liquid yield (bio-oil) and a few non-condensable gases (Demirbas & Arin, 2002). Based on the heating rate and the solid residence time, pyrolysis is classified into three types. Slow (conventional) pyrolysis, which involves long residence times (hours to days), relatively low temperatures (approximately 300 to 700°C) and a relatively wide range of accepted biomass particle size (5 to 50mm). This type of pyrolysis allows the occurrence of repolymerization reactions, and thus results in higher solid yield. Fast pyrolysis requires high heating rates (10 to 200°C/s) and short residence times (typically <2 s). This type of pyrolysis enables the production of greater liquid yield (dry biomass basis) of up to 70 wt%. Flash pyrolysis entails higher heating rates of almost 10^3 to 10^4 °C/s and lower residence times (<0.5 s), enabling an elevated liquid yield of up to 75 to 80 wt% (Kan et al., 2016).

The products of pyrolysis have a wide array of uses. The bio-oil obtained could be used for electricity and heat production in boilers, engines, and turbines. They can also be used as transport fuel through upgradation processes and for chemical extraction of preservatives, resin precursors, additives in fertilisers etc. (Pattiya, 2018). The solid yield of pyrolysis commonly known as biochar, can be used for environmental remediation by reducing the leachability of heavy metals and organic pollutants, reduce greenhouse gas emissions by reducing soil organic carbon (SOC) decomposition, etc. Amongst various applications of biochar, agricultural sustainability solution is one key aspect due to their large surface area, cation exchange capacity and oxygen containing functional groups (Wang et al., 2017). Apart from these, non-condensable gases such as CO, CO_2, H_2 and light hydrocarbon gases (CH_4, etc.) are released as a result of pyrolysis (Nasir Uddin et al., 2013).

Life cycle assessment (LCA) is a commonly used methodology for environmental assessment of products and services. A well-informed evidence-based decision-making tool, such as a consequential LCA (C-LCA) is needed to come to conclusions while quantifying the environmental performance of sustainable practices. Along with the production of raw materials, a C-LCA takes into consideration the fate of all products and co-products of a process (Brassard et al., 2021). Land use change in general is driven by the need to satisfy either food or energy demands of a population. These changes are usually governed by economic profitability factors and government policies which aim to make these changes while complying with environmental goals (Albanito et al., 2016). Thus, reduction in GHG emissions is a key indicator for the energy crop production and usage.

1.1 Hypothesis and Implications

Miscanthus, a C_4 perennial grass, is deemed as an attractive option for an energy crop due to its ability to grow in poor soil conditions, the ability to use water efficiently (due to its long roots), the ability to use nitrogen in the soil with the help of rhizomes thereby decreasing agricultural inputs and having great ecological adaptability (Wang et al., 2021). Although the pyrolysis of miscanthus has been studied (Singh et al., 2020), not much information is available regarding the pyrolysis of miscanthus using an auger reactor. In this study, physiochemical characterization of the yield obtained from pyrolysis of miscanthus using an auger reactor is done and these findings are used to perform a C-LCA of the process to evaluate its environmental performance.

1.2 Objectives

1.2.1 Overall Objective:

The overall objective of this thesis is to study the environmental performance of a pyrolysis biorefinery using Miscanthus as a feedstock and identify the key factors affecting the environmental impact. Experimental data from a semi-pilot scale auger-reactor shall be used to establish the complete mass balance of the process.

1.2.2 Specific Objectives:

1) To identify the optimal pyrolysis operating parameters of an auger reactor (temperature, biomass residence time and carrier gas flowrate) for producing bio-crude oil with minimal water content.

2) To characterise the bio-oil and biochar produced with these optimal parameters.

3) To establish a mass balance of a biorefinery, providing reliable foreground data to be used in environmental life cycle and techno-economic analyses.

4) To perform a C-LCA using a land use change (LUC) scenario (marginal land to Miscanthus to determine its environmental performance in various impact categories.

Connecting text

Considering that both the yield of biomass and the pyrolysis technology used influence the physico-chemical properties of the pyrolysis yields, and since there is no standardized method to follow for pyrolysis, CHAPTER II focuses on summarizing the pyrolysis technologies available for a biorefinery. It also discusses about the pyrolysis yields and the factors affecting them. Finally, the potential of cultivating Miscanthus for bioenergy and a tool to assess the environmental performance of a biorefinery have also been identified.

CHAPTER II

Review of Literature

Pyrolysis technologies and environmental assessment of a biorefinery using Miscanthus: a review

2.1 Abstract

To reduce the long-term environmental effects of the use of fossil fuels for heating purposes it is critical to develop low-emission alternatives. Bio-oil obtained from conversion of lignocellulosic biomass, may be used for heating purposes at a lower environmental and financial impact. Many technologies have been developed for the conversion of biomass to bioenergy. These technologies can be broadly classified into thermochemical conversion and biological conversion. The technology chosen, along with the biomass feedstock used to produce bioenergy affect both the products and the environmental impact of the system. Miscanthus is a promising candidate especially for biomass-to-liquid fuel conversion because of its considerably low moisture and ash content. The purpose of this review is to outline the pyrolysis technologies available for biorefineries and describe the tools used to assess a biorefinery's environmental performance.

Keywords: Miscanthus, Pyrolysis, Biochar, Bio-crude oil, Thermochemical conversion

2.2 Introduction

The use of heavy fuel oil for greenhouse heating along with various domestic heating activities makes up a substantial amount of energy used in Quebec (Canada) (Alvarez-Chavez et al., 2019). With an aim to reduce GHG emission by switching to biogenic carbon, many conversion technologies have been studied over the past decade (Damartzis & Zabaniotou, 2011; Nanda et al., 2020; Ong et al., 2019; Osman et al., 2021). Conversion technologies for the production of bioenergy can be classified into thermochemical conversion (including combustion, gasification, pyrolysis and liquefaction) and biochemical conversion (digestion, fermentation). These have been used to produce heat, electricity, and fuels from biomass.

Direct combustion of biomass provides heat for steam production, and therefore electricity can be generated. Gasification produces a fuel gas that may be burned to generate heat or utilised to generate power in an engine or turbine. Pyrolysis is the third option, which produces a liquid fuel that may be used to replace fuel oil in a static heating or electricity production application. The benefit of pyrolysis is that it is the only renewable energy conversion process capable of converting several forms of biomass into solid, liquid, and gaseous fuels (Kataki et al., 2015). Because the yields of pyrolysis products are highly dependent on the operating parameters, they may be modified as desired.

Biofuels such as pyrolysis bio-oil can be classified into four categories, depending on the feedstock from which they are produced. First-generation biofuels are made from edible ingredients, and because they are made from edible materials there is a conflict of food versus fuel. Non-edible resources such as agricultural and forest leftovers, as well as energy crops such as Miscanthus, are used to produce the second-generation biofuels. Biofuels generated from aquatic biomass, such as algae, are classified as third-generation biofuels. Engineered plants and microbes are used to make fourth-generation biofuels (Bhaskar & Pandey, 2015).

Second generation biofuels made from energy crops have been vastly investigated. However, there is scant research on Miscanthus pyrolysis in a biorefinery setting for biofuel generation. It is very important to discuss the effects of the pyrolysis operating parameters and the biomass feedstock characteristics on the quality of pyrolysis yields. The objectives of this review are to (1) summarize the pyrolysis technologies available for a biorefinery, (2) discuss about the pyrolysis yields and the factors affecting them, (3) discuss the potential for cultivating Miscanthus for bioenergy, and (4) identify a tool to assess the environmental performance of a biorefinery.

2.3 Pyrolysis process

2.3.1 Pyrolysis reactors

Pyrolysis, which is the thermochemical breakdown of biomass at temperatures between 300 and 700 °C under oxygen-limiting settings. It can be a sustainable management option for agricultural and forest biomasses, and is advocated as a way to mitigate climate change (Thomsen et al., 2011). The products' yields and characteristics depend on the pyrolysis system and its operating parameters, and the properties of the biomass feedstock (Brassard et al., 2017a). Pyrolysis can be classified into fast pyrolysis; intermediate pyrolysis; and carbonisation (slow) (Bridgwater, 2012).

Fast pyrolysis is used to maximise the liquid production from biomass, the pyrolysis reaction temperature is carefully maintained at roughly 500 °C and short hot vapour residence periods are used to reduce secondary reactions. The most important thing is to get the reacting biomass particles to the optimal process temperature while avoiding their exposure to the lower temperatures that enhance the production of charcoal. There should be rapid removal of the bio-char to prevent secondary reactions and rapid condensation of pyrolysis vapours to maximise the bio-oil yield (Bridgwater, 2012).

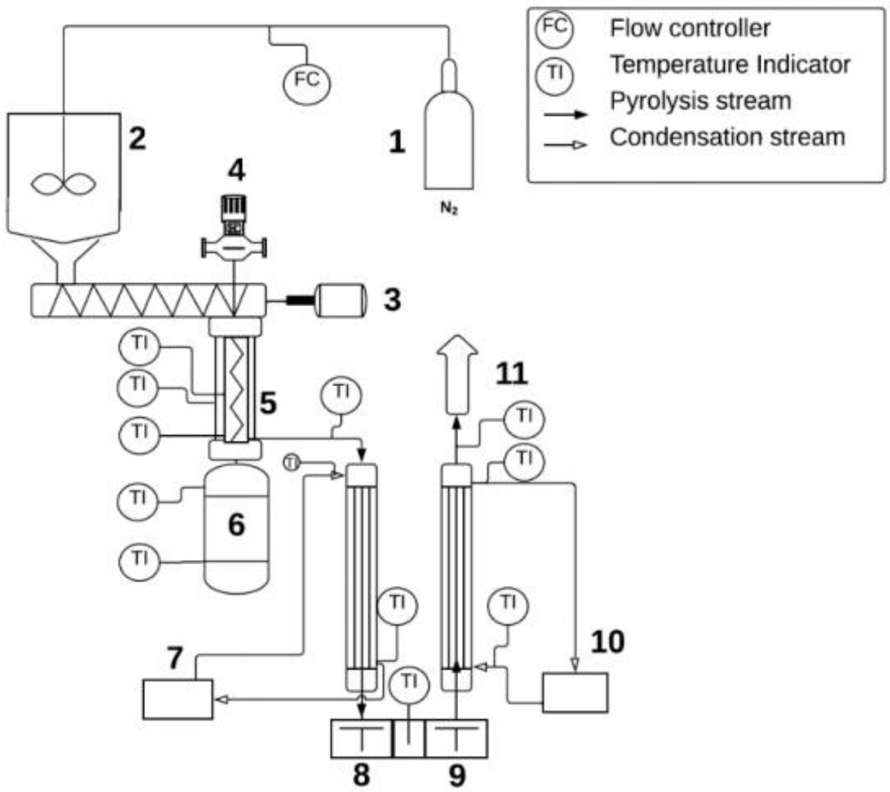

Fig 2.1: Schematic view of a vertical auger pyrolysis reactor (Álvarez-Chávez et al., 2019).

(1) N_2 tank, (2) Hopper, (3) Horizontal screw, (4) Vertical Screw, (5) Heater block, (6) Biochar Canister, (7) first condenser -glycol: water, collector, (9) second bio-oil collector, (10) second condenser – chiller, and (11) non-condensable gases exhaust

Auger reactors, fixed bed, fluidized bed reactors (bubbling, circulating, and spouted), and ablative reactors are some of the reactors that have been employed to produce bio-oil through fast pyrolysis. Most current reactors need a low particle size and a biomass moisture content of roughly 10%, which raises the cost of treating biomass before pyrolysis. In fluidized bed reactors, conduction is the primary mode of heat transport, while convection and radiation are also possible. A carrier gas is used to control the residence time of the gases and solids, resulting in a short vapor residence time (Álvarez-Chávez et al., 2019).

In an auger reactor (Fig 2.1), biomass particles come in contact with the heated surfaces of a conveyor screw and heat is transferred via conduction. The use of a carrier gas is an alternative for reducing solid residence time, although it is not required. The use of auger reactors for bio-oil production has several advantages, including lower reaction temperatures, less biomass pre-treatment processes, reactor simplicity, and the ability to build portable units, which reduces the cost of transporting the biomass. Portable auger reactors might be utilised to make less bulky bio-oil on the farm, where raw biomass is gathered, and then transported to biorefineries (Álvarez-Chávez et al., 2019).

Table 2.1: Pyrolysis product yields in previous studies using auger reactors

Feedstock	Parameters used	Products yield (wt%)	Reference
Switchgrass	Temperature: 591°C	Biochar: 20.3%	(Brassard et al., 2018)
	Biomass residence time: 104 s	Bio-oil: 53%	
	N_2 flowrate: 2.6 L/min	NCG[1]: 26.7 %	
Switchgrass	Temperature: 500°C	Biochar: 29%	(Ren et al., 2016)
	Biomass residence time: 72 s	Bio-oil: 50.0-54.4 %	
		NCG: 17-21%	
Saw-mill residues	Temperature: 400-500°C	Biochar: 19-28%	(Papari et al., 2017)

	Biomass flow rate: 1-7.5 kg/hr	Bio-oil: 39-53% NCG: not mentioned	
Black spruce	Temperature: 400-600°C Biomass residence time: 50-150 s N_2 flowrate: 2-10 L/min	Biochar: 38.61% (under optimum conditions) Bio-oil: 4.99-37.54% NCG: 36.52% (under optimum conditions)	(Álvarez-Chávez et al., 2019)
Rice husk	Temperature: 500°C Biomass residence time: 60 s	Biochar: 32% Bio-oil: 51% NCG: 16%	(Yu et al., 2016)
Corn stalks	Temperature: 400°C Biomass residence time: 55 s	Biochar: 29% Bio-oil: 35% NCG: 13.5%	(Pittman Jr et al., 2012)

From literature, most typical conditions employed in the auger reactor include temperatures in the range of 450-500°C; biomass particle sizes of 2-4 mm; biomass water content of 10%, and a nitrogen flow rate of 5 L/min. A bio-oil yield of 40-60% was observed under these conditions (Table 2.1).

2.3.2 Pyrolysis products

2.3.2.1 Bio-oil

Bio-oil is a complex mixture of water and organic chemicals which can be classified as phenols, ketones, acids, esters, aldehydes, alcohols, furans, anhydrous sugars, nitrogen-containing compounds, hydrocarbons, and carboxylic acids . The variability of differing quantities of lignin, polysaccharides (cellulose and hemicellulose), protein, triglycerides, and other compounds in the biomass determines the distribution of these components in the bio-oil (Lazzari et al., 2018). To be considered for combustion applications, the characteristics of bio-oil must fulfil the ASTM D7544-12 standards (D7544-12, 2017). The water content in the oil is the main parameter set in this standard, with a maximum value of 30 wt. % for use in industrial and commercial burners and a calorific value of at least 15 MJ/kg for a grade G or grade D bio-oil. As a result, studies have concentrated on improving the bio-oil yield and lowering the moisture content of the bio-oil generated, either by adjusting pyrolysis parameters or by pre-treating the biomass.

The composition of cellulose, hemicellulose, and lignin in the biomass are the most significant factors affecting the bio-oil produced during pyrolysis. Primary and secondary reactions during pyrolysis such as depolymerization, fragmentation, cracking, and repolymerization determine the chemical composition and properties of the resulting bio-oil and depend on these significant factors (Singh et al., 2021). During pyrolysis, hemicellulose and cellulose are degraded at 200-300 °C and 300-400 °C, respectively, and lignin is degraded between 200-700 °C, representing a wide range in temperatures (Singh et al., 2021). High quality bio-oil (i.e. low moisture, low oxygen content and low acidity) can be produced from biomasses with high content of cellulose and low ash content. High pyrolysis liquid yield and low char yield is favored by cellulose (Singh et al., 2021). Hemicellulose encourages the generation of pyrolytic gas and liquids with a greater water content, ketones and phenols. Lignin is responsible for the majority of biochar production and production of bio-oil with a high molecular weight, high oxygen content, and high viscosity. Thus, it is preferable to use biomass with higher content of free cellulose.

Pre-treatments for structural destruction of lignin and hemicellulose, on the other hand, are effective for increasing the availability of cellulose content for increased pyrolytic oil production (Alvarez-Chavez et al., 2019).

In a study by Kim et al. (2014) on the pyrolysis of Miscanthus using a fluidised bed reactor, the yields of bio-oil decreased from 57.2 to 47.7 wt% when the pyrolysis temperature increased from 350 °C to 500 °C at a constant residence time of 1.9 s. They suggested that with increasing reaction temperature, the yield of bio-oil reduced steadily, most likely due to secondary cracking of primary pyrolytic products. The Miscanthus used for these experiments had 44 wt.% of C, 72.1 wt.% holocellulose, 24.9 ± 0.3 wt.% lignin, and 4.6 ± 0.1 wt.% ash content. To check the effect of residence time on the pyrolysis yields, three tests were performed with varying residence times (1.2, 1.9 and 3.8 s) and a constant temperature of 400 °C. The results indicated a decrease in the bio-oil yield with an increase in the residence time, which could be due to the fact that increased residence times aids in secondary cracking reaction of the primary degradation products, resulting in lower bio-oil yield. They reported the lowest moisture content and highest C content in the bio-oil at 400 °C and 1.2 s residence time. In these conditions the moisture in the bio-oil was 21.1 wt%, with 43.9 wt% C and a higher heating value of 17.9 MJ/kg (Kim et al., 2014).

An experiment was conducted on black spruce using an auger reactor coupled with fractional condensation (Álvarez-Chávez et al., 2019). Fractional condensation is a technique for upgrading bio-oil by adjusting the condensing temperature of vapours to separate the bio-oil based on dew point variations between condensable components. Over a wide temperature range, a combination of 2 condensers was used. The first fraction of bio-oil produced utilising high temperature-controlled condensers (70-120°C) has a lower water content and a larger quantity of organic components. The second fraction, which was produced using low-temperature-controlled condensers, is high in water and light-oxygenated chemicals. The optimal conditions to produce bio-oil with the lowest water content was reported at 555°C pyrolysis temperature, 129 s solids residence time, 6.9 L/min carrier gas flow rate (N_2 flow), and 120°C as the temperature of the first condenser. In these conditions the total bio-oil yield was 25.4 wt.%, the amount of bio-oil recovered in the first condenser was 10.6 wt.%, with a 16.9 wt.% of moisture content. The yield of bio-oil was known to be affected significantly by both the carrier gas flow rate and the temperature of the first condenser, whereas the most significant impact on the water content of the bio-oil was due to the carrier gas flow rate which was majorly responsible for the residence time of the vapors within the pyrolysis reactor and condensers, avoiding secondary cracking reactions (Álvarez-Chávez et al., 2019).

Various biomass pre-treatments have shown technical feasibility for improving bio-oil quality. They can be chosen based on the biomass composition. They can be classified as physical, thermal, chemical, and biological pre-treatments. To increase heat transmission during the pyrolysis process, physical treatment is employed to change the structure and size of the biomass particles. Thermal treatment is used to minimise the amount of hemicellulose in biomass, resulting in a bio-oil with less carboxylic acids and oxygenates in the form of water, acetic acid, and acetals, which enhances the oil's instability. Torrefaction and hydrothermal treatment are the most common thermal pre-treatments. Torrefaction efficiently degrades hemicellulose, but it is also known to increase ash content in biomass, resulting in phase separation in bio-oil, greater acidity, and higher water content. Hydrothermal treatment, on the other hand, solubilizes hemicellulose in aqueous compounds, conserving cellulose for pyrolysis. Following hydrothermal treatment, the biomass has a lower ash content, and after pyrolysis, the bio-oil has a lower water content and yields lesser biochar (Alvarez-Chavez et al., 2019).

As mentioned above, bio-oils can be used for combustion in industrial burners or could be used to heat buildings or greenhouses that are already heated with fossil fuel oil if they meet the ASTM D7544-12 standards for grade G and D bio-oils (D7544-12, 2017). Deoxygenation and conventional refining might be used to improve bio-oils to obtain transportation fuels (Bridgwater, 2013). The aqueous phase of bio-oil obtained from the second condenser in fractional condensation could be a valuable pesticide material through conversion of the fatty acids isolated to methyl esters (Suqi et al., 2014). The aqueous phase of bio-oil containing acetic acid and polyphenols might be utilised in the pre-treatment process of the biomass to increase the amount and quality of pyrolysis bio-oil (Chen et al., 2017).

2.3.2.2 Biochar

The solid residue formed from the thermochemical breakdown or pyrolysis of plant and waste feedstocks is known as biochar. It's a carbon-rich, fine-grained, porous compound produced at temperatures between 350 and 700 °C under oxygen-limiting conditions. Biochar's key properties are its high carbon (C) content relative to the raw material, as well as its increased stability, porosity, and surface area, which ranges from 0.5 to 450 m^2 g^{-1} (Brassard et al., 2016).

Heating rate, highest treatment temperature (HTT), pressure, and biomass residence time are all essential pyrolysis process factors that determine the physico-chemical characteristics of biochar produced from any given biomass feedstock. Other factors that affect biochar features and attributes include reaction vessel design, inert carrier gas flow rate, and post-pyrolysis treatment (crushing, sieving activation, etc.) (Brassard et al., 2016). Changes in C:N (carbon to nitrogen ratio), O:C (oxygen to carbon ratio), and H:C (hydrogen to carbon ratio) ratios, cation exchange capacity (CEC), porosity, increase in aromatic carbon–carbon double bonds and a decrease in O–H and CH_3 have been observed in the biochar's composition with changes in pyrolysis operating parameters and biomass composition (Mimmo et al., 2014).

The primary use of biochar is to improve soil fertility through soil amendment. Biochar aids in improving the soil fertility by altering the surface area, pore distribution, bulk density, water holding capacity, penetration resistance of the soil, and the CEC of the soil. Biochar can also be used to adsorb both organic and inorganic contaminants, heavy metals and pesticides in soil, reducing leaching to water sources. Biochar can also be used for waste management, for example, pyrolyzing pig manure helps manage the excess manure for swine producers. The biochar from pig manure can be concentrated in phosphorous (P) and thus can be used as manure in soils with low P. Biochar is a carbon-rich stable form of biomass which can be recalcitrant to degradation. Moreover, biochar production and application in soils was recently recognised as a negative emission technology (EBI, 2020).

Biochar additions improve soil pH, cation exchange capacity (CEC), and surface area (SA), and have considerable influence on plant development, according to extensive research. On the other hand, several research found no or very minor changes in soil pH, CEC, or SA after adding biochar, which might be due to soil or biochar features (Budai et al., 2014). As a result, comprehensive biochar characterisation is required for anticipating and optimising the effects of biochar addition on soil parameters (Budai et al., 2014).

Mimmo et al. (2014) reported a decrease in the biochar yield from Miscanthus with an increase in the temperature from 360-450 °C. At these temperature ranges in a screw reactor, the biochar yield varied between 31-73 wt% of the biomass. The C% of the biochar was observed to increase with temperature ranging from 50.95 ± 0.20 to 72.61 ± 0.76. The H% and O% both decreased with an increase in temperature. The N% increased from 350 °C to 400 °C and decreased between 400 and 450 °C. With increasing pyrolysis temperature, the O:C and H:C ratios reduced, with the biggest changes in the elemental composition happening between 360 and 370 °C. Further increases in pyrolysis temperature after this "threshold" range resulted in relatively minor changes in both the H:C and O:C ratios. Following a thermogravimetric analysis (TGA), authors also concluded that higher temperatures produced biochar with higher thermal stability. They also recommended pyrolysis temperature between 400 and 600 °C for which the porosity and consequently field capacity (FC) or the ability of the soil to hold water reaches a maximum.

In a review by Brassard et al. (2016), they reported that biochar with lower nitrogen (N) contents, and consequently higher C:N ratios (>30), are more suitable for N_2O emissions mitigation. CO_2 and CH_4 emissions were not affected, as soil and environmental conditions have a greater impact on these emissions. When the biochar is applied to soil, the C can be sequestered in the soil for long periods of time. As a result, C that would otherwise be emitted as CO_2 as biomass degrades, is kept from doing so. C sequestration through biomass conversion to biochar has been advocated as a way to reduce agriculture's worldwide influence on climate change (Brassard et al., 2016). The volatile matter (VM) content, fixed carbon yield, proportion of aromatic C, and molar ratios of H:C and O:C are all regarded as critical indicators of the biochar's potential stability in soils. Biochar 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. When applied to the soil, sequestration is higher in biochar produced at higher temperatures.

2.3.2.3 Non-condensable gases (NCG)

The gaseous product of pyrolysis includes carbon dioxide (CO_2), carbon monoxide (CO), hydrogen (H_2), methane (CH_4), ethene or ethylene (C_2H_4), ethane (C_2H_6), propene or propylene (C_3H_6), and propane (C_3H_8). Additionally, certain light volatiles such as pentane, benzene, toluene, xylenes, and acetal-dehyde may be present in the gaseous stream (Rosendahl, 2017). Typically, the yield of NCG from pyrolysis is known to increase with an increase in temperature (Bridgwater et al., 1999) and an increase in the residence time (Nasir Uddin et al., 2013) as they promote secondary reactions of heavier hydrocarbon chains that are present within the pyrolyzed vapors. Due to the presence of a considerable quantity of CO as well as CH_4 and other flammable gases, NCG might be utilised as a fuel for industrial combustion or for heating the pyrolysis system itself (Bridgwater, 2012). Brassard et al. (2018) reported that the NCG produced from the pyrolysis of switchgrass in an auger reactor varied from 6.63 to 12.86 MJ/m^3 for pyrolysis temperatures of 459 °C and 591 °C, respectively.

2.4 Miscanthus for bioenergy production

Non-edible plant materials derived from lignocellulosic biomass and crop waste residues from various agricultural and forestry operations make up second-generation feedstocks. Lignocellulosic biomass derived from agricultural processes include corn cobs, corn stover, wheat straw, rice hulls, to mention a few. These wastes are combusted for heat and energy, used as pasture, or ploughed back into croplands in many developing countries (Balagurumurthy et al., 2015). In recent years, there has been a significant increase in demand for biofuels made from lignocellulosic feedstock, making it critical to discover and produce crops solely for energy generation. Fast growth rate, high tolerance to diverse environmental stresses, high energy content, and relative ease of cultivation in contrast to grain crops are some of the essential features of energy crops (Balagurumurthy et al., 2015).

Agricultural land is already under threat from a variety of factors, including present and future population growth, land degradation, and urbanisation, to name a few. As a result, marginal land for biofuel production is advocated to reduce the danger of competing for land already utilised for agricultural production of conventional food and feed crops. On marginal areas, energy crops such as Switchgrass, Miscanthus and Hybrid poplar can be cultivated. These crops were chosen as biofuel feedstock because of their higher biomass yield and lower input requirements compared to standard annual crops, along with their ability to overcome the food versus fuel debate. These characteristics have good effects on the environment, and the long-term sustainability of marginal lands. High biomass production, for example, can help to prevent erosion by providing greater surface protection and reducing runoff. These advantages are dependent on proper establishment and aboveground development (Feng et al., 2017).

Miscanthus is an attractive option for bioenergy production. The energy balance for Miscanthus cultivation was estimated by Felten et al. (2013) who obtained a 47.3 ± 2.2 output to input ratio, which was the highest amongst Miscanthus, rapeseed and maize. The energy input was the energy necessary for a specific cropping system, as well as indirect energy for provisions (transport fuels, engine oil and lubricant, seeds, fertilisers, and pesticides), while the energy output was the energy yield of the harvested biomass.

Miscanthus can be cultivated for up to 25 years. It has two growth phases, namely establishment phase and productive phase (Maxime & Fallaha, 2013). The establishment phase generally lasts for the initial two or three years of cultivation and involves the transplanting of miscanthus plugs or rhizomes. The yield during the establishment phase is lower when compared to the productive phase. Based on a study in Ontario (Canada) Maxime and Fallaha (2013) reported a yield of 13590 kg ha^{-1} of Miscanthus with 13 wt% moisture content. Hamelin et al. (2012) reported a biomass yield of 15.25 Mg DM ha^{-1} yr^{-1} in Denmark. In another study in Germany where Miscanthus was grown on marginal land, the yield was 13.5 t DM ha^{-1} yr^{-1} (Tavakoli-Hashjini et al., 2020).

The elemental composition (carbon, hydrogen, and oxygen) of biomass, as well as the variation in cell wall composition and ash content, determine its heating value. The yield of pyrolysis products is known to be affected by the compositions of lignin, cellulose, and hemicellulose. Different amounts of cellulose, hemicellulose, and lignin can be found in biomass. Cellulose and hemicellulose together makeup holocellulose. Cellulose is a glucose polymer, hemi-cellulose is made up of polysaccharides, whereas lignin is mostly made up of phenyl-propane (Brassard et al., 2016). The lignin content of the feedstock input is critical for bio-oil quality, higher lignin content means slower breakdown and lower water content in the bio-oil (Burhenne et al., 2013). Miscanthus (d.b.) typically contains 47.1- 49.7% carbon, 5.38 - 5.92 wt% hydrogen, and 41.4-44.6 wt% oxygen. The higher heating value of Miscanthus has been estimated to be between 17 and 20 MJ/kg. Holocellulose content ranges typically from 76.2 to 82.8 % and lignin from 9.2 to 12.6 % (Brosse et al., 2012).

2.5 Life cycle assessment of biorefineries

The life cycle assessment (LCA) is a well-known tool for evaluating the environmental implications of bioenergy production. In a nutshell, LCA is a standardised tool for determining and computing the possible environmental consequences throughout the life cycle of a product or process, from raw material extraction through waste management. LCA could improve the environmental implications of a product's system since it can describe environmental concerns at each stage of production without transferring the costs elsewhere. More significantly, it provides a comprehensive and all-encompassing tool for comparing the possible environmental implications of various products (Hosseinzadeh-Bandbafha et al., 2021). These features distinguish LCA as a potential tool for investigating the environmental consequences of bioenergy production.

The LCA method is classified into attributional and consequential LCA (ALCA and CLCA, respectively). An ALCA study represents the possible environmental consequences that may be ascribed to a system (e.g. a product) across the course of its life cycle, i.e., upstream along the supply chain and downstream after the system's application and end-of-life value chain (JRC IEA, 2010). A CLCA is "effect-oriented"; the goal is to determine the impact of a choice made in the foreground system on other economic processes and systems, both in the background system of the examined system and on other systems. It creates a model of the analysed system on these consequences (JRC IEA, 2010). Thus, identification of the marginal processes is an important step in the CLCA study.

According to ISO:14040 (2006), a LCA study is divided into four stages: i) goal and scope definition, ii) life cycle inventory (LCI), iii) life cycle impact assessment (LCIA), and iv) interpretation.

The goal and scope definition of a LCA study help decide the goal, the functional unit (FU), system boundaries, and allocation approach used (Hosseinzadeh-Bandbafha et al., 2021). The goal and scope of bioenergy studies vary. For example, the purpose may be to examine the historical consequences of a certain bioenergy chain or policy (retrospective analysis), or the anticipated implications of a proposed policy or planned modification in a biomass production system (prospective analysis) (Koponen et al., 2018). This step also helps in determining a reference scenario against which the current bioenergy system could be compared to make informed decisions. FU is a quantifiable description of the evaluated product's performance to which all of the system's outputs and inputs are related. Input unit related, output unit related, agricultural land unit related, and year unit related are the four types of FU observed in the LCA of bioenergy product systems (Cherubini & Strømman, 2011). Based on whether the LCA is an ALCA or a CLCA, the scope of the study can vary between by-products allocation approach or system expansion approach (Koponen et al., 2018).

LCI analyses all input and output streams to simulate a product's life cycle. It converts data into elementary flows that are measured using the FU of the assessed system (Koponen et al., 2018). Various LCI databases such as Ecoinvent v.3 (Moreno Ruiz et al., 2013) and Agri-footprint (Durlinger et al., 2017) are available to retrieve background data for the bioenergy production system. Data from these databases are generally at either the global or national level, hence local inventory data must be used where available, to produce accurate results (Hiloidhari et al., 2021).

In the LCIA step, possible environmental consequences are analysed by transforming inventory data into particular impact categories. CML 2001, TRACI, LIME, EDIP 2003, IMPACT 2002+, IMPACT world+, Eco-indicator 99, ReCiPe, Environmental Footprint (EF) 2.0 and other LCIA methodologies have been developed and published (Brassard et al., 2021; Koponen et al., 2018).

The analysis of the outcomes of the LCI and LCIA stages to give recommendations for decision-makers is the fourth step of an LCA research. The interpretation phase of LCA studies of bioenergy product systems aims to validate bioenergy production scenario while recommending measures to improve the product's environmental performance (Koponen et al., 2018). However, uncertainty in inventory data can lead to skewed conclusions thus, questioning the sustainability of bioenergy. Sensitivity analyses could be setup to tackle the uncertainty in the LCI data.

Studies have been conducted to determine the potential of Miscanthus cultivation as an energy crop on marginal lands to reduce GHG emissions, and its carbon sequestration ability (Feng et al., 2017; Maxime & Fallaha, 2013; Parajuli et al., 2013; Xue et al., 2016). In a previous study by Parajuli et al. (2013), the use of Miscanthus in a CHP plant resulted in a global warming potential (GWP) of -0.071 kgCO_2-eq. Through a comparison between production of 1MJ energy using Miscanthus in a CHP plant and the same amount of energy from natural gas, they found that Miscanthus performed better in the GWP and the Non-Renewable Energy (NRE) impact categories. In another study by Maxime and Fallaha (2013), 0.051 kg CO_2 eq/kg dry matter was calculated as a result of Miscanthus cultivation in Ontario (Canada). They also reported a loss in the SOC levels due to the cultivation of Miscanthus.

2.6 Conclusion

This chapter reviewed the technologies available for a pyrolysis biorefinery, pyrolysis yields and the factors affecting them, the potential for cultivating Miscanthus for bioenergy and a tool to access the environmental performance of a biorefinery.

This study revealed that fast pyrolysis, due to the short vapor residence time which avoids secondary cracking reactions, is an attractive option to produce larger yields of bio-oil when compared to other pyrolysis technologies available. An auger reactor, due to its simple design, ease of use and portability is a viable option for pyrolysis.

The pyrolysis product yields and their physico-chemical properties are majorly influenced by the composition of the biomass and the pyrolysis operating parameters. It was observed that the holocellulose and lignin compositions in the biomass are the driving factors for the yield and quality of the bio-oil along with pyrolysis temperature and carrier gas flow rate. The carrier gas has a major impact because it regulates the vapour residence time, which influences the secondary reactions. The biochar and NCG are both impacted by the residence time. The biochar yield decreases with an increase in the temperature, but their stability increased with an increase in the temperature.

Miscanthus was identified as a candidate for being produced as an energy crop due to its fast growth rate, high tolerance to diverse environmental stresses, high energy content, and efficient use of nutrients and water. The cultivation of Miscanthus on marginal land was also studied to address the growing threat to agricultural land due to energy crop cultivation, population growth, land degradation, urbanisation and the food versus fuel debate. LCA was recognized as an ideal tool to assess the environmental performance of a biorefinery because it uses robust data to compare all the possible environmental implications of various products. The C-LCA approach could be preferred because it considers the marginal processes replaced by the system to model the analysed system based on these consequences.

Research gaps identified in this review are:

1) Although extensive research is done for the pyrolysis of Miscanthus, to the knowledge of the authors, no attempt has been made to study the pyrolysis of *Miscanthus* in an auger reactor.

2) A comprehensive evaluation of the impact of process parameters such as temperature, carrier gas flow rate (N_2 flow) and biomass residence time on the yield and quality of

products obtained from the pyrolysis products for Miscanthus using an auger reactor is required.

3) There is a need to access the environmental performance of a pyrolysis biorefinery which uses Miscanthus through a C-LCA.

Connecting text

The desired features of the biomass and the various types of reactors to produce bio-oil and co-products of pyrolysis were highlighted in Chapter II. Auger reactors have been shown to have several benefits over other types of reactors, such as a lower temperature required for pyrolysis, durability, and the ability to be employed as portable units on site where biomass is cultivated. Despite its benefits, it has not received scientific attention.

CHAPTER III attempts to identify the optimal pyrolysis operating parameters for an auger reactor to produce bio-oil with minimal water content and to characterise the bio-oil and biochar produced with these optimal parameters.

CHAPTER III

Pyrolysis of Miscanthus: Developing the mass balance of a biorefinery through experimental tests in an auger reactor

3.1 Abstract

Miscanthus is a perennial grass that can be cultivated on marginal lands and used in multiple biobased applications. Through pyrolysis, it can be converted to bio-oil, biochar, and non-condensable gases. This study presents the mass balance and characterization results of Miscanthus pyrolysis in an auger reactor. The response surface methodology was used to identify, from empirical experiments, the optimal process parameters for producing bio-crude oil with the least water content. A response surface model was developed using a Box-Behnken design, allowing to study the impact of a range of pyrolysis temperature (425 – 575°C), biomass residence time (80 – 140 seconds) and carrier gas flowrate (2 – 7 $L_{nitrogen}$ min^{-1}). Results confirmed that the selected approach allowed identifying pyrolysis parameters for producing bio-crude oil with minimal water content. Moreover, the mass balance of the pyrolysis process was established, providing reliable foreground data to be used in life cycle and techno-economic assessments.

Keywords: Pyrolysis; Bio-oil; Biochar; Box-Behnken design; Process modelling

3.2 Introduction

Significantly lowering greenhouse gas emissions from fossil fuels to maintain the increase of global mean surface temperature to well-below 2°C from pre-industrial levels is of utmost importance (IPCC, 2018b). The use of biofuels as an alternative to fossil fuels has been intensively researched for a few decades (Demirbas, 2009). The conversion of biomass to energy can be done by either biochemical (fermentation) or thermochemical conversion (pyrolysis, gasification, hydrothermal liquefaction, and combustion). Thermochemical conversion of dry biomass (< 10% water content) via pyrolysis, wherein the biomass is subjected to moderate temperatures (≈ 400 – 700°C) with high heat transfer rates and short residence times in the reaction zones have been of great interest. Fast pyrolysis has the potential to produce up to 70-80% of liquid hydrocarbons (bio-oil) based on the feedstock and the working conditions (Bridgwater et al., 1999). Bio-oil produced from fast pyrolysis could be used as fuel for combustion in boilers and furnaces, diesel engines and turbines (Czernik & Bridgwater, 2004), or for producing chemicals such as resin precursors, additives in fertilising and pharmaceutical industries, flavouring agents (e.g. glycolaldehyde) in food industries, acetic acid, hydroxyacetaldehyde, levoglucosan, levoglucosenone, and maltol (Pattiya, 2018). Moreover, it can be upgraded to produce transport fuels by either hydrotreating or catalytic vapor cracking, used to fully deoxygenate bio-oil (Czernik & Bridgwater, 2004). For such applications, the bio-oil may undergo a multistage condensation to produce a quality bio-crude oil (input for further upgrading) and an aqueous fraction that can be used, for example, as a bio-fungicide (Brassard et al., 2020). The solid residue produced from the process, called biochar, can be used as a soil amendment in agriculture and for environmental remediation through sorption of organic and inorganic contaminants (Xie et al., 2015). Biochar applied to soils can create a long-term carbon sink (Bier et al., 2020) as around 80% of its carbon

(C) content could be stable for more than 100 years (IPCC, 2019), improving the global environmental performance of pyrolysis.

Many attempts have been made to investigate bio-oil production from pyrolysis using a wide range of lignocellulosic biomass as feedstocks, and to optimize the yield using different reactor configurations (e.g. auger, fluidized bed, etc.), mathematical modelling and variable operating parameters. The auger reactor for pyrolysis is a promising technology, majorly due to its ease of operation and mobility (Papari et al., 2017). The biomass is continuously fed into a screw and is moved towards the end of the auger axis by the rotating motion of the auger. The gases and the volatile materials exit through the end of the reactor and the biochar is collected from the bottom (Resende, 2014). In an investigation to obtain optimal pyrolysis parameters to increase the yield of bio-oil from sawmill residues as feedstock in an auger reactor (Papari et al., 2017), the lowest water content in the bio-oil was obtained at a temperature of 475°C, a reactor pressure of -200 Pa and a biomass flowrate of 4 kg hr^{-1}. Under these conditions, the bio-oil yield obtained was 50% and the water content was 24%. Ingram et al. (2008) had performed a physio-chemical analysis of bio-oil obtained from pine wood in an auger reactor. The lowest water content of approximately 20.3% in the bio-oil was observed at 475°C. In a study on the pyrolysis of *Miscanthus* using a fluidized bed reactor, the lowest water content in the bio-oil was 21.1% at 400°C and 1.2s residence time (Kim et al., 2014).

Miscanthus, a perennial grass crop is of great interest to be cultivated as a bioenergy crop due to its high yield and low input demand (Jørgensen, 2011). It has a productivity of 13-24 t (dry basis; d.b.) ha^{-1} (Lewandowski et al., 2000), a potential to optimally use water and nutrients (Cosentino et al., 2007), and has a calorific value of up to 20 MJ kg^{-1} (d.b.) (Baxter et al., 2014). Felten et al. (2013) had calculated the energy balance for *Miscanthus* cultivation and reported an output to input ratio of 47.3 ± 2.2. The energy input included the energy required for a specific cropping system and indirect energy for provisions (transport fuels, engine oil and lubricant, seeds, fertilizers, and pesticides) whereas the energy output was the energy yield of the harvested biomass.

Although the auger reactor has already been studied (Alvarez-Chavez et al., 2019; Brassard et al., 2017a), to the knowledge of the authors, no attempt has been made to study the pyrolysis of *Miscanthus* in such a reactor. It is recognized that feedstock properties, reactor configurations and operation parameters influence the pyrolysis products yields and properties. Robust process-dependant data are needed to create life cycle inventory dataset compatible with life cycle assessment standards to better quantify the environmental performance of the pyrolyzing process (Brassard et al., 2020).

In an endeavour to bridge this gap, this study attempts 1) to identify the optimal pyrolysis operating parameters for producing bio-crude oil with minimal water content; 2) to characterise the bio-oil and biochar produced with these optimal parameters and 3) to establish a mass balance of the pyrolysis process, providing reliable foreground data to be used in environmental life cycle and techno-economic analyses.

3.2 Materials and Methods

3.3.1 Feedstock

Miscanthus (*Miscanthus giganteus*) received from an agricultural producer (St-Éloi, QC, Canada) was stored before it was ground and sieved to a particle size between 1.0 and 3.8 mm using a mesh screen. Dry combustion was used to evaluate the carbon (C), hydrogen (H), nitrogen (N), and ash content of the biomass (Leco TruSpec, St. Joseph, MI, USA). The oxygen (O) content was determined after subtracting the C, H, N, and ash contents from 100 wt % (d.b.). Elemental analysis of ashes was done by acid digestion using the EPA-3500 method. The higher heating value of the ground *Miscanthus* was determined using a calorimeter (1266 Calorimeter, Parr Instrument Company, Moline, IL, USA). Cellulose, hemi-cellulose and lignin were analyzed according to the AFNOR XP U44-162 method (AFNOR, 2005). For each test, 600g of ground and sieved *Miscanthus* was fed to the hopper (Fig 3.1).

3.3.2 Pyrolysis apparatus

Pyrolysis tests were carried out in a vertical auger pyrolysis reactor (Patent CA 2830968), developed by the Research and Development Institute for the Agri-environment (IRDA, Canada) (Fig 3.1) as thoroughly described in a prior study (Brassard et al., 2017b). Briefly, the system includes a hopper (≈ 2 kg capacity), a horizontal feed screw and a vertical screw in a 2.54 cm diameter steel tube passing through a 25.4 cm long heater block, a canister for the biochar recovery, and a two-stage condensation system. Dinitrogen (N_2) was used to purge the air entering the system. It was introduced through the hopper's lid at volumetric flowrates ranging from 2 - 7 L min^{-1}, which was controlled by a single flow tube meter (Aalborg Instruments, New York, NY, USA; accuracy ±2%). The nitrogen flow served two purposes: maintaining an oxygen free environment for the pyrolysis experiment and evacuating the pyrolysis gas.

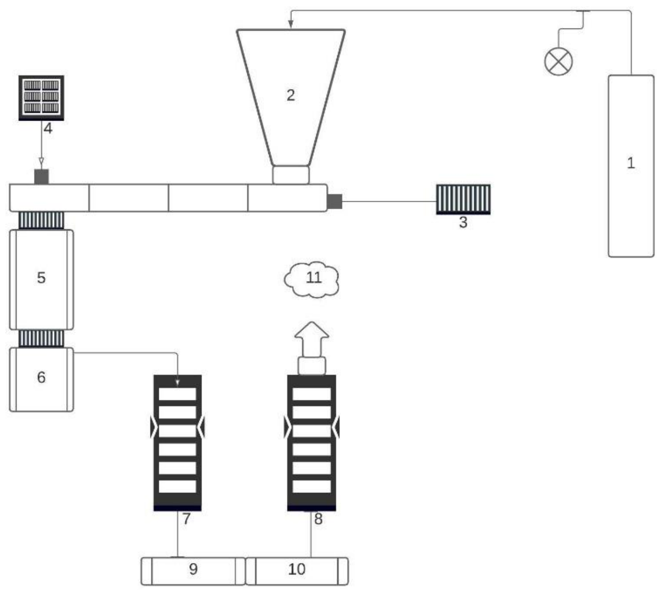

Fig 3.1: Schematic view of the vertical auger pyrolysis reactor.

1. N_2 tank, 2. Hopper, 3. Horizontal screw, 4.Vertical Screw, 5. Heater block, 6. Biochar Canister, 7. 1st condenser, 8. 2nd condenser, 9. Bio-crude oil, 10. Aqueous phase of bio-oil, 11. Non-condensable gases

3.3.3 Products yields and analysis

Yields of bio-crude oil, aqueous phase of bio-oil and biochar were calculated on a wet basis(w.b.) by weighing the mass of products in the first and second condenser and in the biochar canister, respectively. The amount of non-condensable gases was obtained by subtracting the mass of all collected products (biochar, bio-crude oil yield and aqueous phase of bio-oil) from the mass of feedstock used per test.

Water content of the liquid products (bio-crude oil and aqueous phase of bio-oil) was measured using the Karl-Fischer titration method (ASTM, 2008). The higher heating value of bio-crude oil was measured using a calorimeter (1266 Calorimeter: Parr Instrument Company Moline, IL, USA). The chemical properties of biochar (C, H, N, O and ash content) were determined using the same method as biomass, as described in section 2.1. The polyphenol content in the aqueous phase of bio-oil was measured using the Folin-Ciocalteu reagent and its acetic acid content was measured using gas chromatography in an Agilent Hi-Plex column (Santa Clara, CA, USA).

3.3.4 Experimental Design

The response surface methodology (RSM) (Sarabia & Ortiz, 2009) is a statistical approach which establishes a relationship between selected response variables (dependent variables) and process variables (independent variables) to facilitate sequential scientific discovery in a multivariate context. Here, it was used to determine the pyrolysis operating parameters to optimize the production of bio-crude oil with water content as low as possible. The relationship between the water content in the bio-crude oil (response variable) and three independent variables known to influence the yields and characteristics of pyrolysis products in an auger reactor was studied. These independent variables are the pyrolysis temperature (T), biomass residence time in the heater block (R) and N_2 flowrate (N) (Brassard et al., 2017b).

To obtain data for the RSM, a Box-Behnken experimental design was used (Ferreira et al., 2007). Three evenly spaced levels (i) for each independent variable were chosen and coded -1, 0, and +1 (Table 3.1). As prescribed by Ferreira et al. (2007), 15 initial experiments were run in a random order, including three repetitive experiments with the independent variables maintained at level 0. The quantitative values of the levels were selected based on previous experiments with lignocellulosic biomasses in this specific auger reactor (Álvarez-Chávez et al., 2019; Brassard et al., 2017b).

Table 3.1: Box-Behnken design applied to the pyrolysis tests and values of the levels (i)

Independent Variable	Symbol	Levels (i)		
		-1	0	+1
Pyrolysis temperature (ºC)	T	425	500	575
Biomass residence time (s)	R	80	110	140
N_2 flowrate ($L\ min^{-1}$)	N	2.0	4.5	7.0

The parameters of the quadratic response surface regression model (Equation 3.1) were estimated using the RSREG procedure of (SAS, 1989), by fitting the experimental data obtained from the Box-Behnken design.

$$W = \beta_0 + \beta_1 T + \beta_2 R + \beta_3 N + \beta_4 T^2 + \beta_5 (R\times T) + \beta_6 R^2 + \beta_7 (N\times T) + \beta_8 (N\times R) + \beta_9 N^2 \quad \text{(Equation 3.1)}$$

Where W is the studied response variable (water content in the bio-oil, wt.%), β_0, …β_9 are regression coefficients to be estimated; and *T*, *R*, and *N* are the values of the independent variables. The significance of each independent variable was determined by an analysis of variance (ANOVA), where a p-value lower than 0.1 was being considered significant. This procedure was repeated considering the yield of the bio-crude oil as the response variable instead of W.

In order to determine the values of T, R, N leading to a minimal W, response surface plots created using the quadratic response surface regression model were analyzed using a canonical analysis to determine the nature of the stationary points (point on the surface at which the partial derivative is zero) on the plots. The canonical analysis determines whether the point is a maxima, minima or a saddle point (SAS, 1989). In the case of a saddle point, a RIDGE analysis (SAS, 1989) was used to predict the independent variables for the additional experiments to obtain a decrease in the estimated value (dependent variable) (SAS, 1989).

Three additional experiments were performed using the pyrolysis parameters predicted by the RIDGE analysis to produce bio-crude oil with minimal water content. To validate the RSM, the average W value of the three experiments was compared against the predicted values from the quadratic response surface regression models.

3.4 Results and discussion

3.4.1 Analysis of biomass

The results of biomass characterization are presented in Table 3.2. The higher heating value was determined to be 13.6 MJ kg^{-1}. The ash content in the current study was 3.52 wt% (d.b.) as compared to a lower ash content at 2.2 wt% in related literature (Fournel et al., 2015). The higher ash content measured herein could be attributed to the loss of C and O, possibly through CO_2 and CO emissions (He et al., 2012) during storage. The water content of the *Miscanthus* feedstock was 6.0 wt% (d.b.), an important factor as it affects its thermal degradation rate during the reaction (Demirbaş, 2005). A water content below 10% is recommended for the feedstock input to the pyrolysis process (Bridgwater et al., 1999) in order to minimize the water content of the resulting bio-oil. Biomass contains varying amounts of cellulose, hemi-cellulose, and lignin. Cellulose is a glucose polymer, hemi-cellulose is made up of polysaccharides and lignin is primarily made of phenyl-propane (McKendry, 2002). The compositions of lignin, cellulose and hemicellulose are known to affect the pyrolysis products' yield (Burhenne et al., 2013). In the current study, the lignin content of *Miscanthus* is relatively high at 31.5% (Table 3.2) in comparison to the lignin content of 17.0% in previous studies (Yorgun, 2003). The lignin content of the feedstock input is of paramount importance in pyrolysis; a higher lignin content leads to a slower decomposition (Burhenne et al., 2013) and lower water content in the bio-oil (Fahmi et al., 2008).

Table 3.2: Physiochemical properties of the Miscanthus feedstock used in this study

Properties	Composition (%d.b.[1,2])
Carbon (C)	46.4
Nitrogen (N)	0.69
Oxygen (O)	39.5
Hydrogen (H)	6.2
Water Content	6.0
Ash	3.52
Lignin	31.5
Cellulose	33.3
Hemicellulose	19.4

[1]Dry basis, [2]Values are presented with significant digits

3.4.2 Optimization of bio-crude oil water content

The results of the pyrolysis tests using the Box-Behnken design are presented in Table 3.3. The yields of biochar varied from 19.0 wt% to 32.5 wt% (w.b.). Higher biochar yields were obtained at lower temperatures, aligning with observations found in previous studies (Hossain et al., 2011; Mimmo et al., 2014). The ANOVA showed that the bio-crude oil yield was significantly affected ($P < 0.1$) by the pyrolysis temperature and the N_2 flowrate. The bio-crude oil yield ranged between 11.9 wt% and 37.3 wt% (w.b.). Overall, the highest bio-crude oil yields were obtained with a N_2 flowrate of 2 L min^{-1}.

The ANOVA showed that the pyrolysis temperature, the biomass residence time and the N_2 flow rate significantly ($P < 0.1$) affect the water content in the bio-crude oil produced. On average, the lowest water content in the bio-crude oil was observed when the solid residence time was 80s while the highest was observed at 140 s. Regarding the N_2 flowrate, which inversely affects the vapor residence time, the water content in the bio-crude oil was, on average, the highest at 2 L min^{-1} and the lowest at 7 L min^{-1}. Shorter vapor residence times have been attributed to lower water content as it avoids secondary cracking reactions (Álvarez-Chávez et al., 2019). Water content in the bio-crude oil was generally the highest at the highest temperature (here 575°C), a trend that has been observed in previous studies (He et al., 2009; Heo et al., 2010). The presence of water in the bio-crude oil formed during pyrolysis could be caused by the dehydration and cross-linking reactions of cellulose and hemicellulose as well as the moisture content in the feedstock (Chaiwat et al., 2009).

The mathematical representation of the relationship between the independent variables and the water content (W) was found to be as follows (Equation 3.2):

$$W = -56.2379 + 0.2019(T) + 0.4995(R) - 2.3477(N) - 0.0004(T)^2 + 0.0028(R*T) - 0.0070(R)^2 - 0.0163(N*T) - 0.0430(N*R) + 1.2340N^2 \quad \text{(Equation 3.2)}$$

Response surface plots indicating the behavior of the system within the experimental design, depict the interaction between two autonomous variables while keeping the third variable constant at the central value (Fig A1.1, Appendix 1).

Table 3.3: Pyrolysis results for the 15 tests of the Box-Behnken design

Pyrolysis parameters			Products yields			Water content
Temperature (°C)	Biomass residence time (s)	N_2 Flowrate (L min^{-1})	Biochar (wt%)[1,3]	Bio-crude oil (wt%)[1,3]	Aqueous phase bio-oil (wt%)[1,3]	Bio-crude oil (wt%)[2,3]
425	80	4.5	33.3	18.3	15.3	20.6
425	110	2.0	29.4	37.3	11.7	41.4
425	110	7.0	28.0	22.4	16.4	24.5
425	140	4.5	27.4	27.6	16.0	24.9
500	80	2.0	24.7	37.0	14.0	38.5
500	80	7.0	23.8	22.1	15.8	26.9
500	110	4.5	24.5	24.4	15.9	32.1
500	110	4.5	22.5	23.1	15.9	37.4
500	110	4.5	23.2	24.4	16.0	33.1
500	140	2.0	26.6	33.8	14.2	50.8
500	140	7.0	24.2	20.3	17.8	26.3
575	80	4.5	20.1	11.9	15.9	13.9
575	110	2.0	21.9	26.9	12.7	61.2
575	110	7.0	21.7	15.4	16.5	32.1
575	140	4.5	21.6	18.5	14.9	43.8

[1]Percentage by mass of total input (wet basis), [2]Percentage by mass of total bio-crude yield, [3]Values are presented with significant digits

Canonical analysis performed on the stationary points indicated that they are saddle points, meaning that there are no unique minima or maxima points. The optimal pyrolysis parameters for minimum water content in bio-crude oil obtained from the RIDGE analysis were at 510°C pyrolysis temperature, 81 s biomass residence time and 5.1 L.min^{-1} N_2 flow rate, for an estimated water content of 21.3%. This result is similar to minimal water content in bio-crude oil obtained from the pyrolysis of woody biomasses in auger reactors (Ingram et al., 2008; Papari et al., 2017) and from the pyrolysis of *Miscanthus* in a fluidized bed reactor (Kim et al., 2014).

3.4.3 Experimental validation of the response surface model

Three validation runs were performed with the predicted optimal pyrolysis parameters to validate the quadratic response surface regression models (Table 3.4). The average water content observed in the bio-crude oil was 25.3 ± 1.2 %, as compared to 21.3% predicted by the response surface model. Possible reason for this difference includes errors when conducting the experiments, for example, the loss of bio-crude oil while cleaning the condensers and bio-oil reservoirs, which might have affected the uniformization of the bio-crude oil collected prior to its characterization. A second round of optimization using the optimal parameters uncovered herein as central points (i=0), and +1 and -1 levels around the central value, could improve the optimization model and predict the water content in the bio-crude oil more accurately. Physio-chemical analysis of biochar reveals average molar ratios of 0.64, 0.15 and 64 for H/C, O/C and C/N, respectively (Table 3.4). This biochar is expected to have a moderate to high C sequestration potential ($0.4 < H/C_{org} < 0.7$) (Budai et al., 2013), and the potential to reduce soil GHG emissions (C/N ratio > 30) (Brassard et al., 2017b).

Table 3.4: Products yields and physicochemical properties at optimal pyrolysis operating parameters (T=510°C; R=81 s; N= 5.1 L min^{-1})

Product Yields (wt.%)	Average value[1,2]	Standard deviation
Bio-crude oil	18.8	0.5
Aqueous phase	18.3	0.9
Biochar	22.1	0.5
Bio-crude oil properties		
Water content (wt.%)	25.3	1.2
Higher heating value (MJ kg^{-1})	15.8	0.5

Biochar properties (% d.b.)		
C	71.0	0.5
N	1.10	0.10
H	3.84	0.08
O	14.4	0.5
Ashes	9.70	0.1
Aqueous phase properties (wt.%)		
Water content	71.9	0.7
Acetic acid	5.00	0.3
Polyphenols	5.80	0.3

[1]Average value of three tests, [2]Values are presented with significant digits

3.4.4 Pyrolysis mass balance: A case-study

Bio-crude oil, biochar and the aqueous phase of bio-oil as pyrolysis co-products have the potential to be used in the bioeconomy in multiple ways. Extrapolating the results obtained herein, a mass balance was established for the pyrolysis of 1000 kg (d.b.) of stored, ground, and sieved *Miscanthus*, as illustrated on the process flow diagram (Fig 3.2). The loss of mass of *Miscanthus* due to storage is considered as 2% and the loss of mass due to grinding and sieving operations is considered to be 1% of the total mass at the inlet of the grinder (Brassard et al., 2020).

Bio-crude oil with water content in the range of 18.0% to 26.5% could be used in heating appliance to substitute fossil oil by adjusting the combustion system configuration (Gust, 1997; Lujaji et al., 2016). In the short term, the vision in the presented case-study would be to export the raw bio-crude oil to remote areas without access to gas grid nor three phase electricity power grid. It could be used to heat buildings or greenhouses that are already heated with fossil oil. Bio-crude oil produced from the pyrolysis of 1000 kg dry matter of *Miscanthus* (15.8 MJ kg^{-1}; Table 3.4) could substitute the equivalent of 82.3 kg of fossil fuel oil no. 2 (38.4 MJ kg^{-1}) ,(EPA, 2013) considering

80% efficiency for the oil boiler. Accordingly, 227 kg CO_2 equivalent (IPCC, 2013) emitted from the combustion of fossil fuel oil could be mitigated among others.

In the long term, other uses of bio-crude oil can be considered (Czernik & Bridgwater, 2004). For example, it could be upgraded to produce transportation fuels through deoxygenation and conventional refining (Bridgwater, 2013).

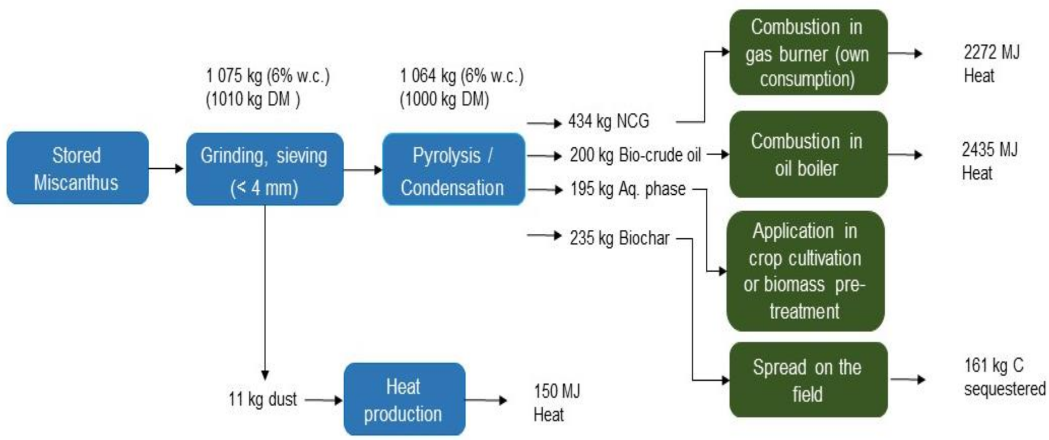

Fig 3.2: Pyrolysis process flow diagram.

NCG: Non-condensable gases; Aq. phase: Aqueous phase of bio-oil.

IPCC (2019) indicated that on average, 80% of C in the biochar can be stable for more than 100 years for pyrolysis temperatures between 450 and 600°C. On this basis, considering biochar yield of 22.1% (w.b.) and the C content of biochar (71.0% d.b.), the pyrolysis of 1000 kg dry matter of *Miscanthus* could sequester 161 kg of C in the soil for more than 100 years.

The conversion of the fatty acids isolated in the aqueous phase of bio-oil to methyl esters provides a valuable pesticide material (Suqi et al., 2014) and thus it could be used as a bio-pesticide to substitute chemical pesticides, as illustrated in the present case-study (Fig 3.2). Phenols in the bio-oil are important anti-fungal compounds (Jung, 2007). The aqueous phase of bio-oil containing acetic acid and polyphenols (Table 3.4) could also be used in the pre-treatment of biomass to improve the quantity and quality of the pyrolysis bio-oil (Chen et al., 2017). A combination of pre-treatments which include, washing the feedstock with the aqueous phase of bio-oil and torrefaction, led to less water formation in the bio-oil by removing metals, altering the degradation pathways of pyrolysis and changing the intrinsic structure and component content of the biomass. (Chen et al., 2017).

The non-condensable gases could be used to produce 2272 MJ of heat, considering 75% efficiency of gas burner and 6.98 MJ kg^{-1} as the lower heating value of NCG (Brassard et al., 2020). This heat is expected to be used for own consumption of the pyrolysis unit. In order to demonstrate the environmental benefits of the presented case-study for the pyrolysis of *Miscanthus,* a complete life cycle assessment according to the ISO international standards (ISO:14040, 2006) and (ISO:14044, 2006) needs to be performed. Accordingly, the system boundaries should include all the activities, from biomass cultivation to the use of co-products and include processes that are avoided due to pyrolysis of Miscanthus.

3.5 Conclusion

An empirical equation to predict the water content in bio-crude oil produced during the pyrolysis of *Miscanthus* in an auger reactor was derived through experimental results. The optimal pyrolysis parameters to produce a bio-crude oil with minimal water content were a temperature of 510°C, a biomass residence time of 81s and a N_2 flow rate of 5.1 L min^{-1}. The bio-crude oil water content obtained under these conditions was 25.3%. The results were further extrapolated to derive the mass balance of a biorefinery processing 1000 kg of *Miscanthus* (d.b.), which can be an input for life cycle inventories.

Connecting text

In the previous chapter, optimal conditions to produce bio-crude oil with a water content of 25.3% were identified as a temperature of 510°C, a biomass residence time of 81s and a N_2 flow rate of 5.1 L min^{-1}. The yields of the coproducts of pyrolysis were further extrapolated to derive the mass balance of a biorefinery processing 1000 kg of Miscanthus (d.b.).

In CHAPTER IV, the environmental performance of a pyrolysis biorefinery using Miscanthus as a feedstock for the production of bio-based products, biochar and bioenergy was assessed. The performance is assessed by expanding the system boundaries to marginal technologies and a C-LCA is performed to compare the performance of the pyrolysis biorefinery with a reference scenario. The performance of the biorefinery is compared over sixteen impact categories.

CHAPTER IV

Consequential life cycle assessment of a pyrolysis biorefinery using Miscanthus cultivated on marginal soil

4.1 Abstract

In efforts to accomplish GHG neutrality, reduction in fossil carbon use through evidence-based decision-making for investments in alternate energy sources is essential. Pyrolysis, the thermo-chemical conversion of biomass to liquid (bio-crude oil and aqueous phase bio-oil), solid (biochar) and gas (non-condensable gases) appears to be a viable option for an alternate source of energy. Miscanthus is a perennial plant that can grow on marginal land and is known for its resource efficiency, making it an attractive source of biomass for pyrolysis. A consequential life cycle assessment (C-LCA) is performed to quantify the environmental performance of a pyrolysis biorefinery which uses Miscanthus cultivated on a marginal land as the feedstock. Results of the C-LCA compare the environmental performance of the pyrolysis scenario to a reference scenario of an idle marginal land over 16 impact categories. Results also showed the effect of each process of the pyrolysis refinery on the various impact categories studied. Based on the results of this study, the biomass supply chain, pyrolysis parameters and technology, co-product yields, characteristics, and applications, as well as the choice of consequential technologies replaced, all have an impact on the environmental performance of pyrolysis biorefineries.

Keywords: Pyrolysis; Miscanthus; Consequential LCA; Bio-crude oil; Biochar

4.2 Introduction

The province of Quebec (Canada), has set a target of 37.5% GHG emissions reduction below 1990 levels by 2030 (Trudeau, 2018). The said target is the most ambitious GHG emissions reduction target as compared to the other 12 provinces and territories in Canada (Vaillancourt et al., 2019). In order to achieve this objective, it is necessary to get rid of fossil fuels and to adopt renewable alternatives.

The cultivation of energy crops for producing bio-based products and bioenergy has been extensively studied through the decade (Nikkhah et al., 2020; Zegada-Lizarazu & Monti, 2011). However, cultivation of energy crops on agricultural land directly competes with food production, creating a social, environmental, and economic concern. Thus, growing energy crops on marginal lands (MALs) is of popular interest as they can provide the biomass required without jeopardizing the land for food supplies (Mehmood et al., 2017; Pancaldi & Trindade, 2020; Roy et al., 2015). Approximately, 9.48 million ha of potentially useable marginal land was estimated in Canada. Of the estimated marginal land, 68.2% is covered by grassland and 31.8% by shrubland (Liu et al., 2017).

The cultivation of various energy crops in Canada such as Miscanthus, Switchgrass, Poplar, etc. has been studied over the years (Fortier et al., 2021; Marsal et al., 2016; Maxime & Fallaha, 2013). Miscanthus, a perennial rhizomatous C4 grass, due to its high water use efficiency and high nutrient use efficiency is of great interest to be used as an energy crop to be cultivated on marginal lands (Lakshman et al., 2021; Wagner et al., 2019). Due to its low water content at harvest, Miscanthus can be used as a feedstock for thermochemical conversion processes.

Pyrolysis is a thermochemical conversion technique, wherein dry biomass feedstock (generally <10% moisture content) is subjected to a high temperature (300-700°C), in limited oxygen environment to produce bio-based products and bioenergy (Bridgwater et al., 1999). The products of pyrolysis include a solid biochar, a liquid bio-oil, and non-condensable gases (NCG). Products' yields and properties depend upon the biomass characteristics and the parameters used in the operation of the reactor (Brassard et al., 2017b). Of the various available pyrolysis reactors, the auger reactor poses a certain advantage due to the use of lower reaction temperatures, fewer pre-treatment steps, the simplicity of the reactor, and the possibility to build portable units, eliminating the process of transporting the biomass to remote locations (Álvarez-Chávez et al., 2019).

Life cycle assessment (LCA) is a "cradle-to-grave" approach used to assess the environmental aspects and potential impacts of a product or a system from its start to finish, from raw material acquisition through production, usage of products and their disposal (Brassard et al., 2018). LCA studies use a functional unit which serves as the reference to which all other data in the assessment are normalised (Weidema et al., 2004). LCA is a key to answer questions about the sustainability and the environmental performance of a bioenergy production system (Hattori & Morita, 2010). LCA studies can be divided into attributional LCA (A-LCA) and consequential LCA (C-LCA). The major difference between the two being that an A-LCA does not consider the consequences of decisions, i.e. they do not provide an understanding of what the products of the system replace in the market (Brandão et al., 2017).

Although studies have been made to elucidate the potential of cultivating Miscanthus as an energy crop on marginal lands to mitigate GHG emissions, to increase the soil organic carbon and its ability for carbon sequestration (Feng et al., 2017; Mi et al., 2014; Parajuli et al., 2013; Roy et al., 2015; Xue et al., 2016), to the knowledge of the authors, no attempt has been made to perform a

C-LCA to assess the environmental performance of pyrolysis in an auger reactor to produce bio-based products from Miscanthus cultivated on marginal land. The aim of this study is to quantify the environmental performance of a pyrolysis biorefinery using Miscanthus as a feedstock. A transparent and detailed life cycle inventory was built, providing all inputs and outputs of each process, from the cultivation of Miscanthus to the production of bio-based products, biochar and bioenergy.

4.3 Methodology

4.3.1 LCA Framework

The LCA methodology is in compliance with the ISO international standards: ISO 14040 and 14044. The consequential LCA approach was selected and follows the framework suggested by Brassard et al. (2021). The background data for the life cycle inventory (LCI) were retrieved from Ecoinvent v3 (Moreno Ruiz et al., 2013) and Agri-footprint (Durlinger et al., 2017) databases. The foreground data were collected from literature, pyrolysis experiments and the characterisation of co-products. For the life cycle impact assessment (LCIA), the Environmental Footprint (EF) Method 2.0 as implemented in the SimaPro LCA software, version 9.0 (PRé Consultants B.V., The Netherlands) is applied (European Commission, 2013).

4.3.2 Goal and scope

The LCA is performed to assess the environmental performance of pyrolysis biorefineries using Miscanthus as the biomass feedstock. The biorefinery in this case is assumed to be driven by the production of bio-crude oil. It is considered that marginal land is being used for the cultivation of Miscanthus as an energy crop. The reference scenario (counterfactual case) being used for comparison of environmental performance is an idle marginal land. The functional unit considered herein is 1000 kg dry biomass at harvest, i.e. the LCA results will answer the question whether there are environmental benefits to cultivate 1 tonne of Miscanthus on a marginal land and to use it as a feedstock in a pyrolysis biorefinery. The GHG emission potential is estimated over a 100-year time horizon. A long-term temporal scope of about 30 years is considered for the selection of marginal technologies and products (i.e. technologies and products that are replaced in the pyrolysis scenario). The province of Quebec, Canada is the geographic region of interest.

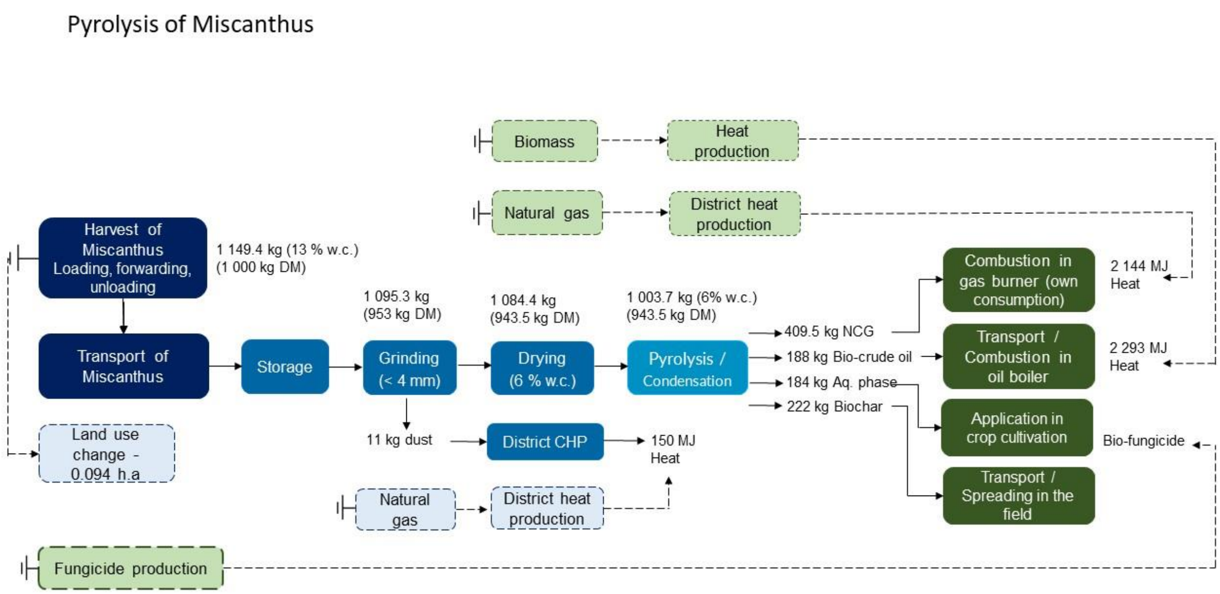

Fig 4.1: Pyrolysis process flow diagram for C-LCA

4.3.3 System boundary definition

The biomass supply chain (cultivation, harvest, transport), biomass conditioning (biomass storage, grinding, drying), pyrolysis plant installation and operation (including fractional condensation of pyrolysis gases), and the usage of pyrolysis co-products are all included in the system boundaries (Fig 4.1). The system boundaries are widened to incorporate the technologies and products that are thought to be replaced in the pyrolysis scenario, hereafter called marginal technologies and products.

Miscanthus is harvested on the idle marginal land considered as the reference scenario. The goal is to produce bio-crude oil that can be utilised in small-scale oil boilers in regions where there is no accessibility to the gas grid, avoiding the use of fossil fuel oil in the short term. The long-term goal considered is that wood chips combustion would be avoided. The aqueous phase of bio-oil is utilised as a bio-fungicide, which eliminates the need for chemical fungicides. Biochar is used as a soil amendment, and no extra operation is thought to be avoided since no soil amendment would have been applied otherwise. Non-condensable gases are thought to be burnt in a natural gas industrial furnace (>100 kW) for district heating. In the same industrial furnace, the equal quantity of heat is considered averted from natural gas combustion. Similarly, the heat produced by district cogeneration (CHP) using Miscanthus dust is thought to be a substitute for the heat provided by natural gas combustion.

4.3.4 Life Cycle Inventory

4.3.4.1 Miscanthus Cultivation

Agronomic operations included in the cultivation process are land preparation, planting, weed management, fertilization and harvesting. Data for the agricultural inputs and yields were obtained from research studies based on the production of Miscanthus and its carbon footprint (Hamelin et al., 2012; Maxime & Fallaha, 2013). The stand lifetime was considered to be 15 years including the establishment phase.

Table 4.1 LCI of Miscanthus foreground system

Input	Quantity per ha	Comments
Rhizome plantation	21000 rhizomes	
Nitrogen application as urea	60 kg N	Applied each year from year 2-15 for fertilization
Atrazine	1.1 kg active ingredient (a.i.)	Applied only during years 1 and 2 for weed control
2,4-D	1 kg active ingredient (a.i.)	Applied only during years 1 and 2 for weed control
Yield	13590 kg (13 wt% moisture content)	Tested in sensitivity analysis due to varying range of results in literature.

The yield for the first establishment year was considered zero, and the yield for the second year was assumed to be 50% of the rest of the cultivation period. The yield and input data were averaged across the whole cultivation period and the input amounts were computed on a per year basis. Standard inventory data from the Ecoinvent v.3 database was utilised for all background processes.

Table 4.2 The chemical characterisation of Miscanthus at harvest (Lakshman et al., 2021)

Chemical	Unit	Value
Carbon (C)	% (d.b)	46.4
Oxygen (O)	% (d.b)	39.4
Hydrogen (H)	% (d.b)	6.2
Nitrogen (N)	% (d.b)	0.7
Sulfur (S)	% (d.b)	0.065
Ashes	% (d.b)	7.3
Water content	% (w.b)	13

4.3.4.2 Biomass storage and conditioning

Storage of wet biomass can lead to loss of dry matter along with gas emissions. Microbial activity in stored biomass, particularly mold growth, is a major contributor to decomposition (He et al., 2014). Biomass is assumed to be stored indoors in the form of large square bales, due to lower loss in dry matter storage when compared to bales that are left uncovered (Emery et al., 2015). A 4.8% loss in dry matter was considered in the present study. The CO_2 emissions were calculated by assuming that all the C content of the dry matter lost is converted to CO_2 and 1% of N loss is considered to be emitted in the form of N_2O (Emery et al., 2015).

The particle size for the biomass fed into the auger reactor is between 1.0 and 3.8 mm (Lakshman et al., 2021). The biomass is considered to be ground using a stationary electric chipper. 1% of the total mass at the intake of the grinder is assumed to be lost in the form of dust. This dust is used for co-generation of heat and electricity.

To reduce the amount of water in the bio-oil, a common feed material specification is for the biomass to have a maximum moisture content of 10%. A high moisture level in bio-oil lowers its calorific value (Guedes et al., 2018). Thus, the water content in the biomass is considered to be reduced to 6 wt% before feeding it into the auger reactor, using a rotary dryer. The energy needed to reduce the moisture content (3 MJ kg^{-1} biomass) of the biomass was calculated using a method based on a previous study (Brassard et al., 2021).

4.3.4.3 Pyrolysis and condensation

The mass balance for the current pyrolysis biorefinery was established based on the experiments performed in an auger reactor using miscanthus as a feedstock (Lakshman et al., 2021). The operating parameters (temperature, residence time and nitrogen flowrate) were set to produce bio-crude oil with the least amount of water using the response surface methodology (RSM) approach.

Fractional condensation of bio-oil was performed in order to obtain a bio-crude oil and an aqueous phase. The condensation system uses two double shell stainless tubes in which water/glycol (50:50 mixture in the first condenser and 100:0 in the second condenser) circulates against the flow of the pyrolysis gases. In the first condenser, the cooling fluid is at a high temperature (120 °C) and is used to collect the bio-crude oil with low water content. The aqueous phase is obtained in the second condenser maintained at a lower temperature (about 4 °C) (Álvarez-Chávez et al., 2019). Electricity consumption by the pyrolysis and condensation units was calculated based on the energy consumption of the semi-pilot pyrolysis unit as described by Brassard et al. (2019).

Table 4.3 Parameters and product yields considered for the pyrolysis of Miscanthus

	value	units
Pyrolysis parameters		
Pyrolysis temperature	510	(°C)
Biomass residence time	81	(s)
Nitrogen flowrate	5	($L.min^{-1}$)
First condenser temperature	120	(°C)
Second condenser temperature	4	(°C)
Pyrolysis products yields		
Bio-crude oil	18.8	(wt.%)
Aqueous phase	18.3	(wt.%)
Biochar	22.1	(wt.%)

The current biorefinery is considered to process 20 tonnes of biomass per day, with properties similar to the auger reactor studied in the semi-pilot scale (Lakshman et al., 2021). Considering a lifetime of 50 years for the pyrolysis plant, its construction was modeled using the infrastructure process "Synthetic gas factory" from Ecoinvent database version 3.5.

4.3.4.4 Combustion of bio-crude oil and combustion of wood chips avoided

The heat produced by the combustion of bio-crude oil is considered to replace the equivalent heat provided by the combustion of softwood chips in a central or small-scale furnace (50 kW). The bio-crude oil produced has a moisture content of 25.3 wt% and a lower heating value (LHV) of 15.2 MJ/kg (Lakshman et al., 2021).

It is considered that the bio-crude oil is transported 200 km, from the pyrolysis plant to the burner location. The C, N and S compounds in the gaseous emissions from bio-crude oil combustion was modeled using the process "Heat, central or small-scale, other than natural gas {CA-QC} | heat production, light fuel, at boiler 100 kW, non-modulating | Conseq, U″ from the Ecoinvent database version 3.5.

4.3.4.5 Combustion of non-condensable gases (NCG) and avoided combustion of natural gas

The NCGs composition considered herein is derived from the sampling and characterization from the previous work of Lakshman et al. (2021). It is considered that NCGs are combusted in a natural gas industrial furnace (>100 kW) for district heat production. 2144 MJ of heat is produced in this process, which was calculated using the LHV of the NCG (Table 4.4) and with a heat conversion efficiency of syngas estimated at 75% (Roberts et al., 2010). This was considered to substitute heat produced by natural gas in the same industrial furnace with an efficiency of 85%. "Heat, district or industrial, natural gas {CA-QC} | heat production, natural gas, at industrial furnace >100 kW, | Conseq, U″ retrieved from the Ecoinvent database version 3.5 was used to model the gaseous emissions from the combustion of NCG.

Table 4.4 Characterization of pyrolysis non-condensable gases

NCG properties (% d.b.)	value	unit
CO	43.2	%vol.
CO_2	42.9	%vol.
CH_4	7.34	%vol.
C_2H_4	0.58	%vol.
C_2H_6	0.74	%vol.
H_2	5.2	%vol.
Lower Heating Value (LHV)	6.98	MJ kg^{-1}

4.3.4.6 Biochar as a soil amendment

Pyrolysis experiments on miscanthus using an auger reactor were used to determine the elemental composition of the resulting biochar (Table 4.5). In this study, the biochar is transported over a distance of 100 km to a farm from the pyrolysis plant with a freight lorry, mixed with liquid fertilizer, and applied with a conventional manure spreader. Biochar application increases the soil carbon stocks, resulting in the net CO_2 removal from the atmosphere. European Comission (2019) suggests, 80% (±11%) of the fraction of biochar carbon remains unmineralized after 100 years (BC_{+100}) for biochar produced at medium temperature (450–600 °C). In this study a BC_{+100} of 78% was calculated using an equation (Equation 4.1) proposed by Leng et al. (2019).

$$BC_{+100} = -42.4 * (H/C_{org}) + 106 \qquad \text{(Equation 4.1)}$$

The H/C_{org} ratio was considered as 0.65 (Lakshman et al., 2021).

Table 4.5 Characterization of biochar (% d.b.)

Biochar properties (% d.b.)	value
C	71.0
N	1.12
H	3.84
O	14.4
S	0.05
Ashes	9.70

4.3.4.7 Aqueous phase of bio-oil used as a biofungicide

The composition of the aqueous phase of bio-oil derived as a product of fractional condensation had a water content of 71.9 wt%, 5.8 wt% polyphenols and 5.0 wt% acetic acid (Lakshman et al., 2021). The presence of fatty acids and phenols enables the aqueous phase of bio-oil to possess anti-fungal properties. The conversion of fatty acids to methyl esters (Suqi et al., 2014) and phenols in combination with methanol and carboxylic acid are major contributors to the anti fungal properties (Jung, 2007).

In this case study, the aqueous phase bio-oil is expected to replace a typical fungicide on the market. Generic fungicide LCI data were taken from Agri-Footprint database, in which the process involves mixing 1 kg of fungicide to 370 kg of water, to attain an application rate of 0.292 kg active ingredient (a.i.) per hectare. In this study, a similar total volume with a different proportion of aqueous phase bio-oil (37.1 kg) and water (334 kg) is applied while limiting the acetic acid concentration to 0.5% to avoid damage to plants (Brassard et al., 2019).

4.3.4.8 Land use change (LUC)

Cropland use for the cultivation of energy crops result in competition for food supply(Thompson, 2012). Therefore, it is assumed that a marginal land is used to cultivate Miscanthus. From literature, the total available marginal land in the province of Quebec is estimated at 161,000 ha, of which over 68% is covered by grassland, and the remaining is covered by shrubland **(Liu et al., 2017)**.

The CO_2 emissions due to land use change were calculated in compliance with Renewable Energy Directive 2018/2001/EU (European Comission, 2018), following the commission’s decision on guidelines for the calculation of land carbon stocks (European Comission, 2010). To calculate the change in C due to land use (LU) over a 20-year period, the sum of the difference in both the soil organic carbon (SOC) and the C vegetation stocks after and before the cultivation of Miscanthus on a marginal land was calculated (Eq. 4.2).

Change in C due LUC = [(SOC miscanthus – SOC marginal land) + (Veg C stock Miscanthus – Veg C stock of marginal land)] (Equation 4.2)

SOC was calculated using equation 4.3 (European Comission, 2010), where F_{lu} is the land use factor, F_{mg} is the land management factor, F_{li} is the land input factor (appendix 2).

$$SOC = F_{lu} * F_{mg} * F_{li} * SOC_{st} \quad \text{(Equation 4.3)}$$

The value for the SOC_{st} (soil organic carbon standard) of the marginal land was chosen as 85 tonnes of carbon per hectare (t.C/ha). A range of 40.7 to 111.9 t.C/ha for the SOC of soils in Quebec was reported (VandenBygaart et al., 2003).

The vegetation C stock value for the assumed marginal land was 6.99 t.C/ha, considering the proportion of grassland (6.8 t.C/ha) and shrubland (7.4 t.C/ha) on the marginal land (European Comission, 2010). The value for the SOC after Miscanthus cultivation was calculated from literature (Maxime & Fallaha, 2013) (appendix 2). The vegetation C stocks were calculated using the percent of above ground stubble and below ground root horizon (Maxime & Fallaha, 2013). The nitrogen emissions due to land use change were based on calculations described in European Comission (2006) and Hamelin et al. (2012) (appendix 2).

4.3.5 Sensitivity analysis

Although the LCA technique is a desirable approach to identify potential environmental impacts of a system, there are some uncertainty factors that are inevitable, among others, regarding life cycle inventory data collection, impact assessment modeling choice, and the construction of scenarios. An adequate analysis of these uncertainties helps derive an informed decision using the LCA (Bamber et al., 2020; Lima et al., 2020). In this study, sensitive parameters identified after a contribution analysis were selected for a sensitivity analysis and the results of the impact assessment were analysed for each sensitivity scenario.

4.4 Results and discussion

4.4.1 Impact assessment

4.4.1.1 Climate change impact

The pyrolysis scenario produces 308.2 kg CO_2 eq and the reference scenario considered herein results in an impact of 228.8 kg CO_2 eq. The largest contributors to the climate change impact in the pyrolysis scenario are the emissions due to the combustion of bio-oil and the NCGs which account for 1021.3 kg CO_2 eq. These are followed by emissions from the storage of Miscanthus, land use change and the pyrolysis process itself. The contributions of other processes towards the climate change impact category are relatively small. Biogenic CO_2 due to combustion of biomass was considered herein, as was the CO_2 sequestered by the plant during growth and photosynthesis (negative value).

The difference between the reference and the pyrolysis scenarios is due to the land use change and the C sequestered through the biochar. The land use change for the cultivation of 1 tonne of miscanthus on an abandoned land resulted in an emission of 265.4 kg CO_2 eq. These emissions can be attributed to the soil C loss that occurred owing to the cultivation of Miscanthus on the marginal land. The soil C loss could be due to the higher decay rate of organic matter on cultivated land when compared to the marginal land. These soil C losses are very common when soils with high SOC are used for cultivation (Hamelin et al., 2012). A loss in soil C due to cultivation of Miscanthus on marginal land was recorded in previous studies (Sanscartier et al., 2014). The C sequestered through biochar accounts for 451.8 kg CO_2 eq. per tonne of Miscanthus harvested.

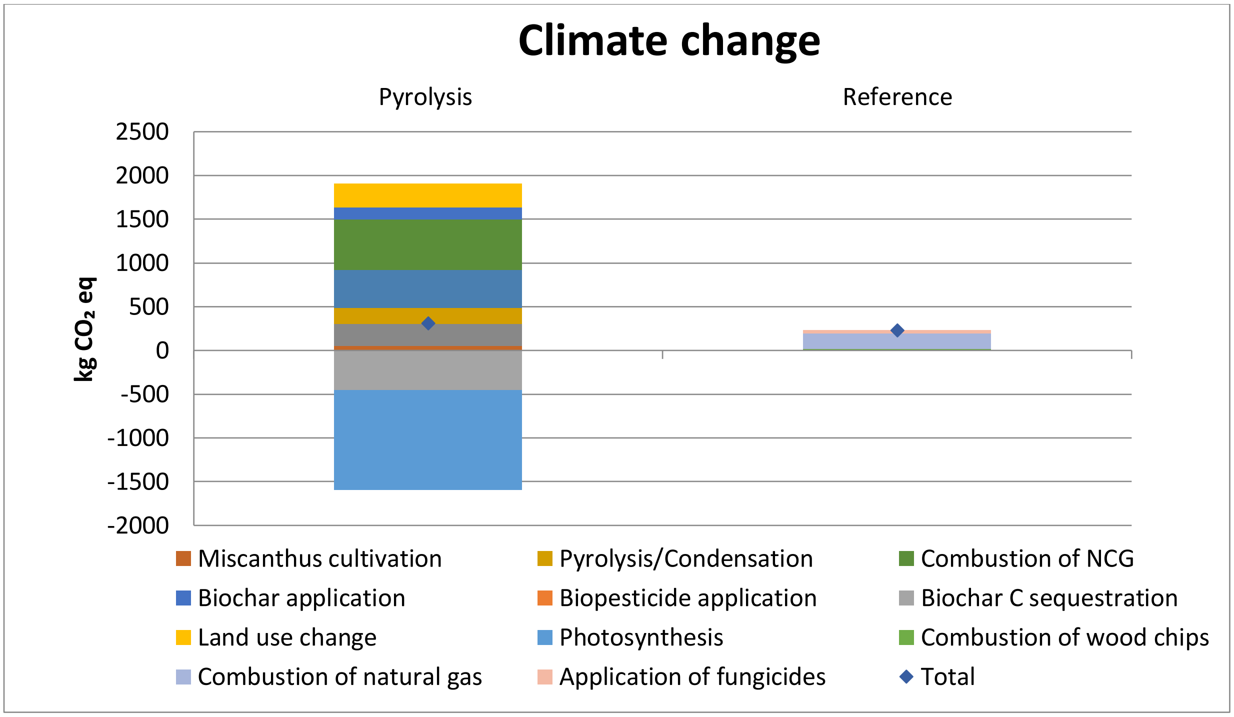

Fig 4.2: Contribution analysis for climate change impact category

(kg CO_2e Mg^{-1} dry Miscanthus harvested) NCG: Non-condensable gases

4.4.1.2 Other impact categories

From the remaining 15 impact categories studied, trade offs were observed in 11 impact categories, i.e., the reference scenario had a better performance in comparison to the pyrolysis scenario (Fig 4.3 to Fig 4.5). The storage of Miscanthus bales and its pre-treatment processes were the largest contributors in most of the impact categories wherein trade offs were observed. The pyrolysis scenario performed better than the reference scenario only in the following impact categories: land use, respiratory inorganics, ozone depletion and ionising radiation.

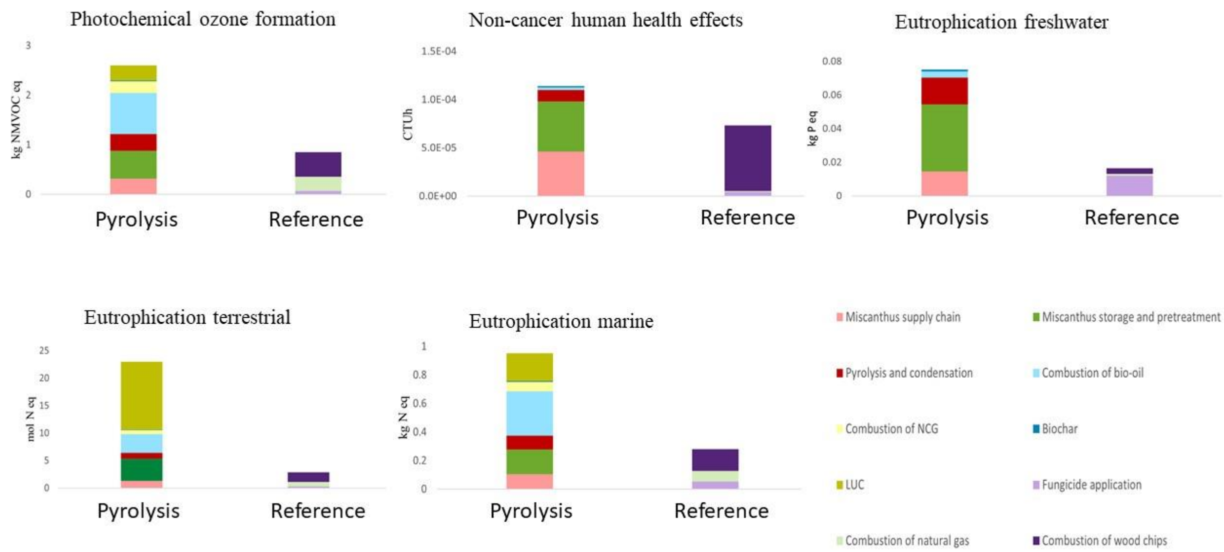

Fig 4.3: Contribution analysis for remaining impact categories (part 1)

(per dry tonne Miscanthus harvested)

4.4.1.2.1 Photochemical ozone formation

The ‘Photochemical ozone formation’ impact is higher in the pyrolysis scenario than in the reference scenario by 1.8 kg NMVOC eq (Fig 4.3). The release of nitrogen-oxides (NO_x) due to the combustion of bio-crude oil and during the use of diesel in the machines used for constructing the storage hall (used for storge of Miscanthus bales) are the major contributors in the pyrolysis scenario. The emissions from the combustion of wood chips contribute the most towards photochemical ozone formation in the reference scenario.

4.4.1.2.2 Eutrophication marine

The ‘Eutrophication marine’ impact is higher in the pyrolysis scenario than in the reference scenario by 0.68 kg N eq (Fig 4.3). NO_x released through the combustion of bio-crude oil and the combustion of wood chips, in the pyrolysis and the reference scenarios respectively are responsible for the ‘Eutrophication marine’ impact category. Miscanthus storage and pre-treatment and emissions from the combustion of bio-crude oil contribute to over 50% of the marine eutrophication effect in the pyrolysis scenario.

4.4.1.2.3 Eutrophication terrestrial

The ‘Eutrophication terrestrial’ impact is higher in the pyrolysis scenario than in the reference scenario by 20.2 mol N eq (Fig 4.3). The ammonia and NO_x released as a result of the zinc production used in the construction of the storage hall along with emissions from N-loss due to land use change contribute for almost 70% to the ‘Eutrophication terrestrial’ impact category in the pyrolysis scenario. The emissions from the combustion of wood chips are primarily responsible for terrestrial eutrophication in the reference scenario.

4.4.1.2.4 Eutrophication freshwater

The ‘Eutrophication freshwater’ impact is higher in the pyrolysis scenario than in the reference scenario by 0.06 kg P eq (Fig 4.3). The release of phosphates into water during the zinc and steel production for construction of the storage hall for the Miscanthus storage process and the steel production for wind turbines which contributes to the electricity mix considered herein for the pyrolysis process contribute the highest to the ‘Eutrophication freshwater’ impact category in the pyrolysis scenario. Emanations from the combustion of wood chips are primarily responsible for freshwater eutrophication in the reference scenario.

4.4.1.2.5 Non-cancer human health effects

The ‘Non-cancer human health effects’ impact is higher in the pyrolysis scenario than in the reference scenario by 4.0E-05 CTUh (Fig 4.3). The largest contributor to the ‘Non-cancer human health effects’ impact category is the zinc released due to zinc production for constructing the storage hall in the Miscanthus storage process and the diesel usage in tractors for harvesting and transporting biomass in the Miscanthus supply chain process in the pyrolysis scenario. In the reference scenario, discharges from the burning of wood chips are predominantly responsible for this impact category.

4.4.1.2.6 Cancer human health effects

The ‘Cancer human health effects’ impact is higher in the pyrolysis scenario than in the reference scenario by 4.0E-06 CTUh (Fig 4.4). The ‘Cancer human health effects’ impact category is mainly affected by the release of chromium from steel production for wind turbines which contributes to the electricity mix considered herein for the pyrolysis process and steel production for constructing the storage hall in the Miscanthus storage process of the pyrolysis scenario. In the reference scenario, emission from the burning of wood chips and fungicide production are accountable for this impact category.

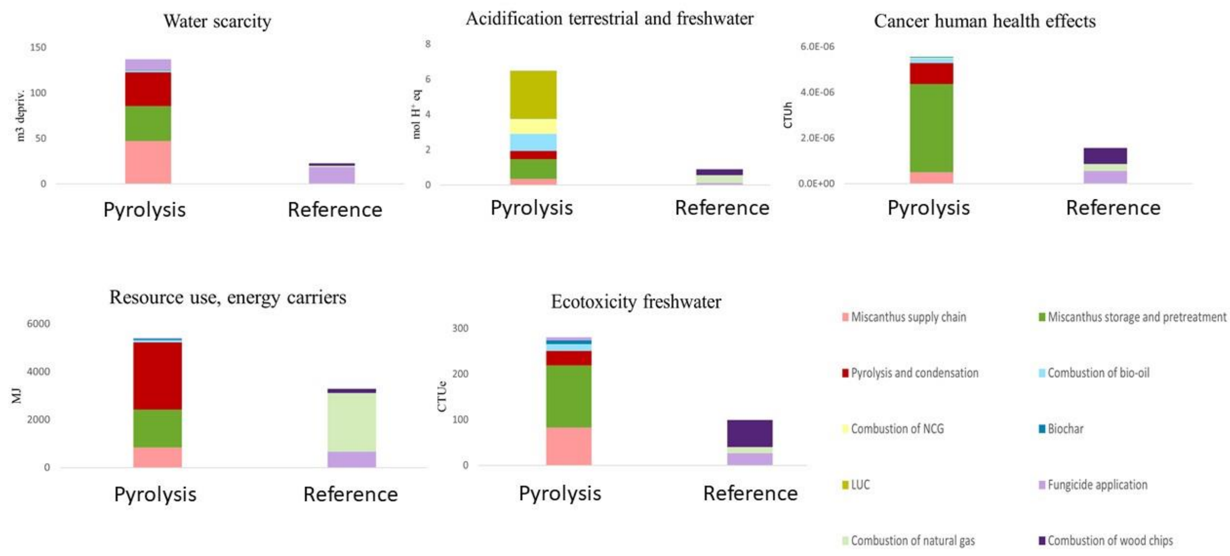

Fig 4.4: Contribution analysis for remaining impact categories (part 2)

(per dry tonne Miscanthus harvested)

4.4.1.2.7 Acidification terrestrial and freshwater

The 'Acidification terrestrial and freshwater' impact is higher in the pyrolysis scenario than in the reference scenario by 5.6 mol H^+ eq (Fig 4.4). The ammonia resulting from N-loss due to land use change process and zinc production for constructing the storage hall for the Miscanthus storage process is the largest contributor towards the 'Acidification terrestrial and freshwater' impact category in the pyrolysis scenario.

4.4.1.2.8 Ecotoxicity freshwater

The 'Ecotoxicity freshwater' impact is higher in the pyrolysis scenario than in the reference scenario by 181.4 CTUe (Fig 4.4). In the pyrolysis scenario the 'Ecotoxicity freshwater' impact category is largely influenced by the release of antimony and zinc due to the electricity mix considered in the pyrolysis process and zinc production for constructing the storage hall for the Miscanthus storage process.

4.4.1.2.9 Water scarcity

The 'Water scarcity' impact is higher in the pyrolysis scenario than in the reference scenario by 114.3 m^3 depriv (Fig 4.4). The 'Water scarcity' impact category is higher in the pyrolysis scenario predominantly due to the use of water various processes like, electricity production for the pyrolysis process, water used in the condensation process, fertilization in the Miscanthus supply chain process and the water used for the construction of the storage hall for the Miscanthus storage process.

4.4.1.2.10 Resource use, energy carriers

The 'Resource use, energy carriers' impact is higher in the pyrolysis scenario than in the reference scenario by 2126.9 MJ (Fig 4.4). The natural gas used for electricity production for the pyrolysis process and the resources used in constructing the storage hall for the Miscanthus storage process is predominantly responsible for the 'Resource use, energy carriers' impact category in the pyrolysis scenario. The emanations from the process of natural gas combustion are primarily responsible for the effect on this impact category in the reference scenario.

4.4.1.2.11 Resource use, minerals and metals

The 'Resource use, minerals and metals' impact is higher in the pyrolysis scenario than in the reference scenario by 0.014 kg Sb eq (Fig 4.5). The use of lead, cadmium and other metals for constructing the storage hall for the Miscanthus storage process are the largest contributors towards the ‘Resource use, minerals and metals’ in the pyrolysis scenario. The reference scenario did not have any process that made a significant effect to this impact category.

4.4.1.2.12 Land use

The ‘Land use’ impact category is primarily influenced by the area used for cultivating wood chips used in the electricity mix considered for the pyrolysis process along with the wood used in constructing the storage hall for the Miscanthus storage process in the pyrolysis scenario. The land use impact is 30865.9 Pt higher in the reference scenario (Fig 4.5).

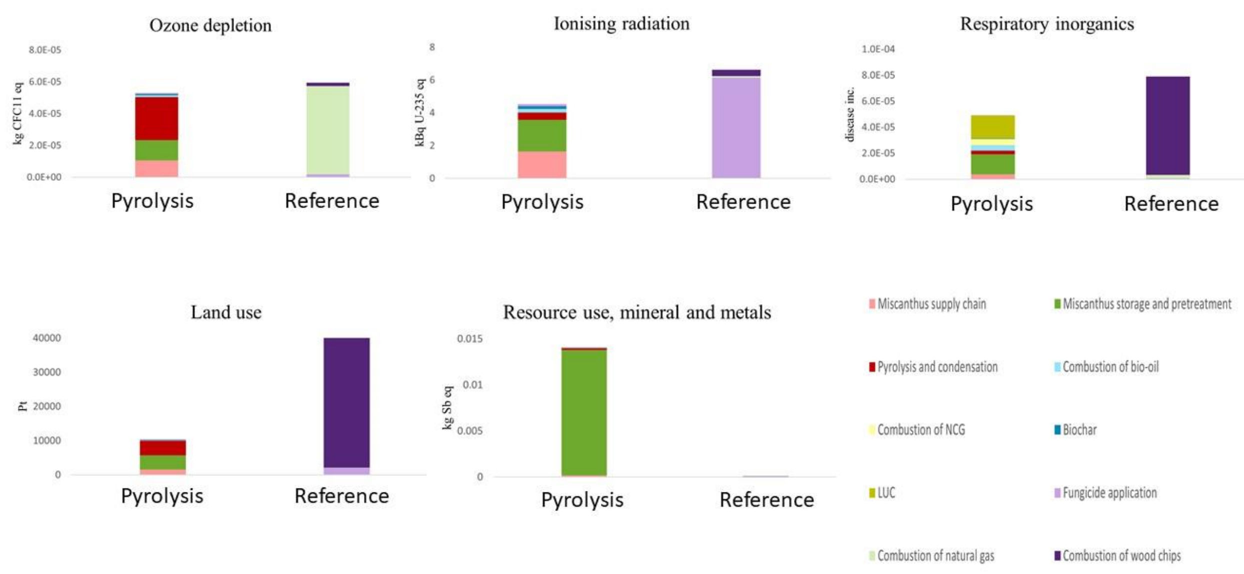

Fig 4.5: Contribution analysis for remaining impact categories (part 3)
(per dry tonne Miscanthus)

4.4.1.2.13 Respiratory inorganics

For the same amount of heat generated, particulate matter (<2.5 μm) emissions from the burning of woodchips are greater than those from the combustion of bio-crude oil. As a result, the effect of the ‘Respiratory inorganics’ impact category under the reference scenario is 2.968E-05 disease inc. higher as compared to the pyrolysis scenario (Fig 4.5).

4.4.1.2.14 Ozone depletion

The difference regarding the ‘Ozone depletion’ impact between both scenarios is relatively small (6.5E-06 kg CFC11 eq) (Fig 4.5). The main driver of the ‘Ozone depletion’ impact category is the release of Methane, bromotrifluoro-, Halon 1211 due to the use of natural gas in the electricity mix considered, for the pyrolysis process in the pyrolysis scenario. Similarly, natural gas combustion (marginal energy replacing the energy provided by dust and NCGs burning) adds to the ozone depletion potential in the reference scenario, primarily due to the emission of Halon 1211.

4.4.1.2.15 Ionising radiation

The ‘Ionising radiation’ impact of the pyrolysis scenario is 2.086 kBq U-235 eq lower than the reference scenario, in which carbon-14 released into the atmosphere during the manufacture of fungicide is the primary contributor to this impact category (Fig 4.5). The Miscanthus supply chain and the storage and pre-treatment processes generate most of the ionising radiation in the pyrolysis scenario. Carbon-14 emissions are generated by diesel production, which is utilised as an energy source for harvesting, transporting and the construction of the storage hall.

4.4.2 Sensitivity Analysis

From related literature and the observed LCA results, three parameters were found to have an important impact on the environmental performance of the pyrolysis scenario. The three parameters are the yield of biomass, C sequestration values of the biochar, and the standard soil organic carbon levels, which were chosen for the sensitivity analysis to account for any uncertainties that might occur .

The biomass yield is known to affect the carbon dynamics along with various other parameters (Kludze et al., 2013; Roy et al., 2015). The C sequestration potential of biochar (Brassard et al., 2021) and the standard SOC value (Hamelin et al., 2012) were observed to be key parameters effecting the climate change impact category.

The yield can affect the land area required to cultivate the Miscanthus needed for pyrolysis, along with the resources used for cultivation. The two scenarios considered for the sensitivity analysis of the biomass yield were, ‘Yield S1’ (decrease in yield by 20%) and ‘Yield S2’ (increase in yield by 20%) (Table 4.6). The impact categories in which changes were observed due to biomass yield include, ‘Climate change’, ‘Eutrophication terrestrial’, ‘Ecotoxicity freshwater’, ‘Land use’, and ‘Resource use, energy carriers’. Contrary to the baseline scenario in which the yield was increased (Yield S2) performed better than the reference scenario in these impact categories. The climate change impact was observed to decrease with an increase in the yield. The impact was observed to be 446.9 kg CO_2 eq and 221 kg CO_2 eq for the scenarios ‘Yield S1’ and ‘Yield S2’ respectively. The climate change impact of the scenario ‘Yield S2’ was observed to be lower than the reference scenario by 7.8 kg CO_2 eq. The scenarios considered herein for the sensitivity analysis include, ‘Biochar S1’ (decrease in C sequestration potential by 10%) and ‘Biochar S2’ (increase in C sequestration potential by 10%). For the SOC_{st} ‘SOC S1’ (decrease in standard SOC by 20%) and ‘SOC S2’ (increase in standard SOC by 20%) for the standard SOC value parameter.

Table 4.6 Parameters considered for sensitivity analysis

Parameter	units	Pyrolysis scenario	S1	S2
Biomass yield (over a 15-year cycle)	kg/ha/yr	12231 (13% w.c.)	9784.8	14677.2
C sequestration by biochar (BC_{+100})	wt %	78	68	88
SOC_{st} value	t C/ha	85	68	102

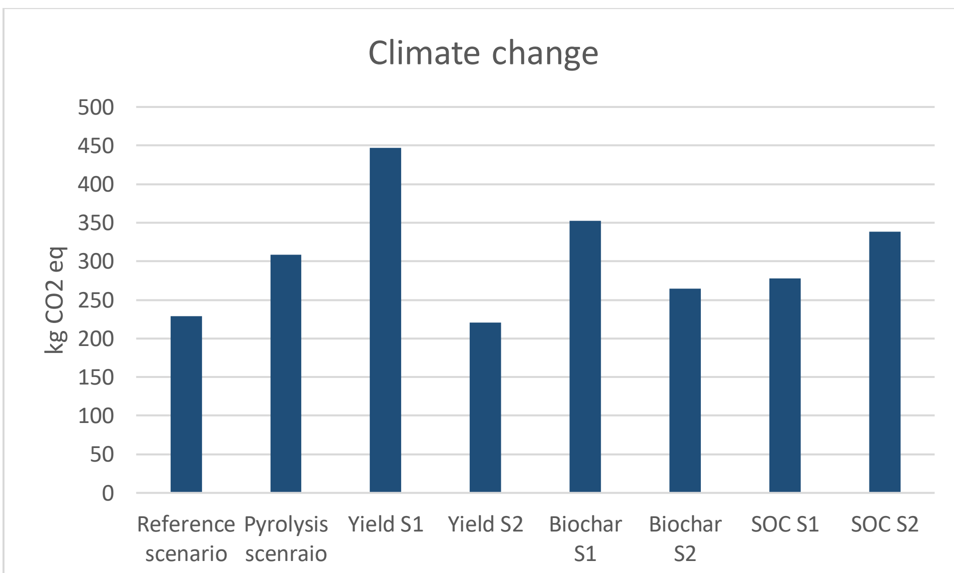

Fig 4.6: Sensitivity analysis of the climate change impact category ($kg\ CO_2e\ Mg^{-1}$ dry Miscanthus)

Changes in the climate change impact category was observed in the sensitivity analyses for both the biochar C sequestration potential and the SOC_{st} values. When compared to the 79.452 kg CO_2 eq trade-off between the baseline pyrolysis scenario and the reference scenario, the climate change impact decreased when the biochar C sequestration potential was increased by 10% (Biochar S2).

Whereas a decrease in the climate change impact category was observed with a 20% decrease in the SOC_{st} (SOC S1). The decrease in the climate change impact category could be attributed to the lower loss in soil C due LUC (Equation 4.2).

4.5 Conclusion

A consequential LCA was performed to evaluate the environmental performance of a pyrolysis biorefinery using Miscanthus. To address the counterfactual usage of biomass, the approach described involves expanding the system boundaries to marginal technologies (i.e. technologies avoided in the pyrolysis scenario). Trade-offs, wherein the reference scenario performed better than the pyrolysis scenario, were observed in twelve out of sixteen impact categories studied. The pyrolysis scenario performed better in land use, respiratory inorganics, ozone depletion and ionising radiation impact categories. The findings revealed that pyrolysis' environmental performance is dependent on a number of parameters, including biomass feedstock supply, pyrolysis technology, co-product yields, characteristics, and applications, and the identification of marginal technologies.

Sensitivity analyses revealed that the yield of biomass, C sequestration values of the biochar, and the standard soil organic carbon levels have a significant impact on the performance of the pyrolysis scenario under the climate change impact category. For example, climate change impact of the pyrolysis scenario becomes lower than the reference scenario with a 20% increase in biomass yields. These results suggests that LCA models must be improved by employing foreground data from pyrolysis, and agronomic trials. Finally, additional field experiments, as well as techno-economic studies that take into account all of the processes and products included in the LCA system boundaries, are required to validate and expand on the conclusions presented.

CHAPTER V

5.1 Summary and conclusion

The major goal of this thesis was to assess the environmental performance of a pyrolysis biorefinery that uses an auger reactor to produce bio-oil for heating applications and to identify the key factors affecting the environmental impact. The use of bio-oil was suggested to substitute fossil fuel oil used for heating purposes which produce high GHG emissions.

In CHAPTER II, a comprehensive literature review was performed to outline the pyrolysis technologies available for a biorefinery. The auger reactor was identified as an appropriate technology to produce bio-oil due to its ease of use and portability. The effect of the physicochemical properties of biomass, as well as the pyrolysis operational parameters that might affect the yield and quality of the products were studied. The chemical composition of the biomass along with the pyrolysis temperature, the vapor residence time, the biomass residence time inside the reactor and the carrier gas flow rate were identified to significantly influence the pyrolysis products yields and their quality. The possibility for growing Miscanthus for bioenergy on marginal land, and the LCA method to evaluate a biorefinery's environmental performance were studied. LCA was identified as an effective tool to aid in assessing the environmental performance of a biorefinery.

In CHAPTER III, bio-oil was produced from Miscanthus biomass using the vertical auger reactor designed by IRDA and CRIQ. The auger reactor's operating factors were optimized in order to produce bio-oil. Pyrolysis temperature, biomass residence time, and nitrogen flow were the operational variables optimized using the response surface methodology approach. The moisture content of the bio-oil was monitored since it has a significant influence on calorific value, viscosity, density, and acidity. Fractional condensation was employed to obtain two fractions of the liquid product. The first fraction was referred to as the bio-crude oil and the second as the aqueous phase. Therefore, the response analyses were performed on the first fraction of the bio-oil obtained. Statistical models were developed to identify the minimum values of the bio-crude oil moisture content. Temperature of 510°C, biomass residence time of 81s, and N_2 flow rate of 5.1 L min^{-1} were the optimal pyrolysis parameters for producing bio-crude oil with minimum moisture content. The physio-chemical characteristics of the pyrolysis yields obtained using these parameters were reported. The moisture content of bio-crude oil produced under these parameters was 25.3%. The mass balance of a biorefinery processing 1000 kg of Miscanthus (d.b.) was computed using the findings, which may be used as an input for LCI.

In CHAPTER IV, a consequential LCA was performed to evaluate the environmental performance of a pyrolysis biorefinery using Miscanthus. The pyrolysis scenario (baseline scenario) whose environmental performance was assessed considers the cultivation of miscanthus as an energy crop on marginal land. An idle marginal land is considered as the reference scenario (counterfactual case) for comparing the environmental performance of the baseline scenario. The functional unit considered herein is 1000 kg dry biomass at harvest. Results of the C-LCA compare the environmental performance of the pyrolysis scenario to a reference scenario of an idle marginal land over sixteen environmental impact categories. The climate change impact of the pyrolysis scenario was observed to be higher than the reference scenario by 79.4 kg CO_2 eq. The pyrolysis scenario performed better in four impact categories, namely land use, respiratory inorganics, ozone depletion and ionising radiation. A sensitivity analysis was performed to address the uncertainty factors regarding life cycle inventory data collection, impact assessment modeling choice, and the construction of scenarios. Sensitivity analyses revealed that the yield of biomass, C sequestration values of the biochar, and the standard soil organic carbon levels have a significant impact on the climate change impact category. The findings demonstrated that the environmental performance of pyrolysis is influenced by a variety of factors, including biomass feedstock availability; pyrolysis technique; co-product yields, characteristics, and applications; as well as the identification of marginal technologies.

5.2 Future work

This project studied the effect of a biorefinery using Miscanthus as a feedstock. However, additional research needs may be identified. A few recommendations for future research include using the response surface methodology approach to forecast pyrolysis products yield and their characteristics for other biomasses. Studies could be conducted to see if the laboratory-size auger reactor could be scaled up to provide similar product yields and characteristics on a larger scale. The bio-oil generated using this technology may be investigated for catalytic upgradation and hydrotreating, thereby improving Miscanthus' environmental and economic performance as an energy crop. Using the life cycle approach described, the environmental performance of different pyrolysis technologies and different biomass feedstocks could be analyzed and compared.

References

1. AFNOR. 2005. Organic soil improvers and growing media. Biochemical fractioning and estimation of biological stability. *Method of organic matter characterization by successive solubilisations*.
2. Ahmad, T., Zhang, D. 2020. A critical review of comparative global historical energy consumption and future demand: The story told so far. *Energy Reports*, **6**, 1973-1991.
3. Albanito, F., Beringer, T., Corstanje, R., Poulter, B., Stephenson, A., Zawadzka, J., Smith, P. 2016. Carbon implications of converting cropland to bioenergy crops or forest for climate mitigation: a global assessment. *GCB Bioenergy*, **8**.
4. Álvarez-Chávez, B.J., Godbout, S., Le Roux, É., Palacios, J.H., Raghavan, V. 2019. Bio-oil yield and quality enhancement through fast pyrolysis and fractional condensation concepts. *Biofuel Research Journal*, **6**(4), 1054-1064.
5. Alvarez-Chavez, B.J., Godbout, S., Palacios-Rios, J.H., Le Roux, É., Raghavan, V. 2019. Physical, chemical, thermal and biological pre-treatment technologies in fast pyrolysis to maximize bio-oil quality: A critical review. *Biomass and Bioenergy*, **128**, 105333.
6. Assessment WE. 2015. World Energy Assessment: Energy and the Challenge of Sustainability.
7. ASTM, E. 2008. 203-08. Standard test method for water using volumetric Karl Fischer titration. *American Society for Testing and Materials. West Conshohocken*.
8. Balagurumurthy, B., Singh, R., Ohri, P., Prakash, A., Bhaskar, T. 2015. Chapter 6 - Thermochemical Biorefinery. in: *Recent Advances in Thermo-Chemical Conversion of Biomass*, (Eds.) A. Pandey, T. Bhaskar, M. Stöcker, R.K. Sukumaran, Elsevier. Boston, pp. 157-174.
9. Bamber, N., Turner, I., Arulnathan, V., Li, Y., Ershadi, S.Z., Smart, A., Pelletier, N. 2020. Comparing sources and analysis of uncertainty in consequential and attributional life cycle assessment: review of current practice and recommendations. *The International Journal of Life Cycle Assessment*, **25**(1), 168-180.
10. Baxter, X.C., Darvell, L.I., Jones, J.M., Barraclough, T., Yates, N.E., Shield, I. 2014. Miscanthus combustion properties and variations with Miscanthus agronomy. *Fuel*, **117**, 851-869.
11. Bhaskar, T., Pandey, A. 2015. Chapter 1 - Advances in Thermochemical Conversion of Biomass—Introduction. in: *Recent Advances in Thermo-Chemical Conversion of Biomass*, (Eds.) A. Pandey, T. Bhaskar, M. Stöcker, R.K. Sukumaran, Elsevier. Boston, pp. 3-30.
12. Bier, H., Gerber, H., Huber, M., Junginger, D.H., Kray, P.D.D., Lange, D.J., Lerchenmüller, H., Nilsen, P.J. 2020. Biochar-based carbon sinks to mitigate climate change. *European Biochar Industry Consortium e.V. (EBI)*.
13. Brandão, M., Martin, M., Cowie, A., Hamelin, L., Zamagni, A. 2017. Consequential Life Cycle Assessment: What, How, and Why? in: *Encyclopedia of Sustainable Technologies*, (Ed.) M.A. Abraham, Elsevier. Oxford, pp. 277-284.

14. Brassard, P., Godbout, S., Hamelin, L. 2021. Framework for consequential life cycle assessment of pyrolysis biorefineries: A case study for the conversion of primary forestry residues. *Renewable and Sustainable Energy Reviews*, **138**, 110549.
15. Brassard, P., Godbout, S., Hamelin, L. 2020. Framework for consequential life cycle assessment of pyrolysis biorefineries: A case study for the conversion of primary forestry residues. *Renewable and Sustainable Energy Reviews*, 110549.
16. Brassard, P., Godbout, S., Palacios, J.H., Le Roux, É., Alvarez-Chavez, B.J., Raghavan, V., Hamelin, L. 2019. Bio-based products from woody biomass pyrolysis for a sustainable bioeconomy. *27th European Biomass Conference (EUBCE)-Setting the course for a biobased economy*. pp. 1234-1240.
17. Brassard, P., Godbout, S., Pelletier, F., Raghavan, V., Palacios, J.H. 2018. Pyrolysis of switchgrass in an auger reactor for biochar production: A greenhouse gas and energy impacts assessment. *Biomass and Bioenergy*, **116**, 99-105.
18. Brassard, P., Godbout, S., Raghavan, V. 2017a. Pyrolysis in auger reactors for biochar and bio-oil production: A review. *Biosystems Engineering*, **161**, 80-92.
19. 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**, 484-497.
20. Brassard, P., Godbout, S., Raghavan, V., Palacios, J.H., Grenier, M., Zegan, D. 2017b. The Production of Engineered Biochars in a Vertical Auger Pyrolysis Reactor for Carbon Sequestration. *Energies*, **10**(3), 288.
21. Bridgwater, A. 2013. 7 - Fast pyrolysis of biomass for the production of liquids. in: *Biomass Combustion Science, Technology and Engineering*, (Ed.) L. Rosendahl, Woodhead Publishing, pp. 130-171.
22. Bridgwater, A.V. 2012. Review of fast pyrolysis of biomass and product upgrading. *Biomass and Bioenergy*, **38**, 68-94.
23. Bridgwater, A.V., Meier, D., Radlein, D. 1999. An overview of fast pyrolysis of biomass. *Organic Geochemistry*, **30**(12), 1479-1493.
24. Brosse, N., Dufour, A., Meng, X., Sun, Q., Ragauskas, A. 2012. Miscanthus: a fast-growing crop for biofuels and chemicals production. *Biofuels, Bioproducts and Biorefining*, **6**(5), 580-598.
25. Budai, A., Wang, L., Gronli, M., Strand, L.T., Antal, M.J., Abiven, S., Dieguez-Alonso, A., Anca-Couce, A., Rasse, D.P. 2014. Surface Properties and Chemical Composition of Corncob and Miscanthus Biochars: Effects of Production Temperature and Method. *Journal of Agricultural and Food Chemistry*, **62**(17), 3791-3799.
26. Budai, A., Zimmerman, A., Cowie, A., Webber, J., Singh, B., Glaser, B., Masiello, C., Andersson, D., Shields, F., Lehmann, J. 2013. Biochar Carbon Stability Test Method: An assessment of methods to determine biochar carbon stability. *International Biochar Initiative*, 1-10.
27. Burhenne, L., Messmer, J., Aicher, T., Laborie, M.-P. 2013. The effect of the biomass components lignin, cellulose and hemicellulose on TGA and fixed bed pyrolysis. *Journal of Analytical and Applied Pyrolysis*, **101**, 177-184.

28. Chaiwat, W., Hasegawa, I., Tani, T., Sunagawa, K., Mae, K. 2009. Analysis of Cross-Linking Behavior during Pyrolysis of Cellulose for Elucidating Reaction Pathway. *Energy & Fuels*, **23**(12), 5765-5772.
29. Chen, D., Cen, K., Jing, X., Gao, J., Li, C., Ma, Z. 2017. An approach for upgrading biomass and pyrolysis product quality using a combination of aqueous phase bio-oil washing and torrefaction pretreatment. *Bioresource Technology*, **233**, 150-158.
30. Cherubini, F., Strømman, A.H. 2011. Life cycle assessment of bioenergy systems: State of the art and future challenges. *Bioresource Technology*, **102**(2), 437-451.
31. Cosentino, S.L., Patanè, C., Sanzone, E., Copani, V., Foti, S. 2007. Effects of soil water content and nitrogen supply on the productivity of Miscanthus×giganteus Greef et Deu. in a Mediterranean environment. *Industrial Crops and Products*, **25**(1), 75-88.
32. Czernik, S., Bridgwater, A.V. 2004. Overview of Applications of Biomass Fast Pyrolysis Oil. *Energy & Fuels*, **18**(2), 590-598.
33. D7544-12, A. 2017. ASTM D7544-12. Standard Specification for Pyrolysis Liquid Biofuel, ASTM International. West Conshohocken, PA.
34. Damartzis, T., Zabaniotou, A. 2011. Thermochemical conversion of biomass to second generation biofuels through integrated process design—A review. *Renewable and Sustainable Energy Reviews*, **15**(1), 366-378.
35. Demirbas, A. 2009. Biofuels securing the planet's future energy needs. *Energy Conversion and Management*, **50**(9), 2239-2249.
36. Demirbaş, A. 2005. Relationship between Initial Moisture Content and the Liquid Yield from Pyrolysis of Sawdust. *Energy Sources*, **27**(9), 823-830.
37. Demirbas, A., Arin, G. 2002. An Overview of Biomass Pyrolysis. *Energy Sources*, **24**(5), 471-482.
38. Durlinger, B., Koukouna, E., Broekema, R., van Paassen, M., Scholten, J. 2017. Agri-footprint 3.0. *Gouda: Blonk Consultants*.
39. EBI, T.E.B.I.C. 2020. Biochar-based carbon sinks to mitigate climate change [White paper].
40. El Haj Assad, M., Alhuyi Nazari, M., Rosen, M.A. 2021. Chapter 1 - Applications of renewable energy sources. in: *Design and Performance Optimization of Renewable Energy Systems*, (Eds.) M.E.H. Assad, M.A. Rosen, Academic Press, pp. 1-15.
41. Emery, I., Dunn, J.B., Han, J., Wang, M. 2015. Biomass Storage Options Influence Net Energy and Emissions of Cellulosic Ethanol. *BioEnergy Research*, **8**(2), 590-604.
42. EPA. 2013. 2013 Revisions to the Greenhouse Gas Reporting Rule and Final Confidentiality Determinations for New or Substantially Revised Data Elements Vol. Vol. 78
43. European Comission, T. 2019. Appendix 4 Method for Estimating the Change in Mineral Soil Organic Carbon Stocks from Biochar Amendments: Basis for Future Methodological Development.
44. European Comission, T. 2006. Chapter 11: N2O Emissions from Managed Soils, and CO2 Emissions from Lime and Urea Application
45. European Comission, T. 2010. COMMISSION DECISION of 10 June 2010 on guidelines for the calculation of land carbon stocks for the purpose of Annex V to Directive 2009/28/EC.

46. European Comission, T. 2018. Directive (EU) 2018/2001 of the European Parliament and of the Council of 11 December 2018 on the promotion of the use of energy from renewable sources (Text with EEA relevance.).
47. European Commission. 2013. RECOMMENDATION 2013/179/EU on the use of common methods to measure and communicate the life cycle environmental performance of products and organisations, Annex II (Product Environmental Footprint (PEF) Guide)–. *Official Journal of the European Union*.
48. Fahmi, R., Bridgwater, A.V., Donnison, I., Yates, N., Jones, J.M. 2008. The effect of lignin and inorganic species in biomass on pyrolysis oil yields, quality and stability. *Fuel*, **87**(7), 1230-1240.
49. Felten, D., Fröba, N., Fries, J., Emmerling, C. 2013. Energy balances and greenhouse gas-mitigation potentials of bioenergy cropping systems (Miscanthus, rapeseed, and maize) based on farming conditions in Western Germany. *Renewable Energy*, **55**, 160-174.
50. Feng, Q., Chaubey, I., Engel, B., Cibin, R., Sudheer, K.P., Volenec, J. 2017. Marginal land suitability for switchgrass, Miscanthus and hybrid poplar in the Upper Mississippi River Basin (UMRB). *Environmental Modelling & Software*, **93**, 356-365.
51. Ferreira, S.L.C., Bruns, R.E., Ferreira, H.S., Matos, G.D., David, J.M., Brandão, G.C., da Silva, E.G.P., Portugal, L.A., dos Reis, P.S., Souza, A.S., dos Santos, W.N.L. 2007. Box-Behnken design: An alternative for the optimization of analytical methods. *Analytica Chimica Acta*, **597**(2), 179-186.
52. Fivga, A., Speranza, L.G., Branco, C.M., Ouadi, M., Hornung, A. 2019. A review on the current state of the art for the production of advanced liquid biofuels. *Aims Energy*, **7**(1), 46-76.
53. Fortier, J., Truax, B., Gagnon, D., Lambert, F. 2021. Natural Drying and Chemical Characteristics of Hybrid Poplar Firewood Produced from Agricultural Bioenergy Buffers in Southern Québec, Canada. *Forests*, **12**(2), 122.
54. Fournel, S., Palacios, J.H., Morissette, R., Villeneuve, J., Godbout, S., Heitz, M., Savoie, P. 2015. Influence of biomass properties on technical and environmental performance of a multi-fuel boiler during on-farm combustion of energy crops. *Applied Energy*, **141**, 247-259.
55. Gielen, D., Boshell, F., Saygin, D., Bazilian, M.D., Wagner, N., Gorini, R. 2019. The role of renewable energy in the global energy transformation. *Energy Strategy Reviews*, **24**, 38-50.
56. Guedes, R.E., Luna, A.S., Torres, A.R. 2018. Operating parameters for bio-oil production in biomass pyrolysis: A review. *Journal of Analytical and Applied Pyrolysis*, **129**, 134-149.
57. Gust, S. 1997. Combustion Experiences of Flash Pyrolysis Fuel in Intermediate Size Boilers. in: *Developments in Thermochemical Biomass Conversion: Volume 1 / Volume 2*, (Eds.) A.V. Bridgwater, D.G.B. Boocock, Springer Netherlands. Dordrecht, pp. 481-488.
58. Hamelin, L., Jørgensen, U., Petersen, B.M., Olesen, J.E., Wenzel, H. 2012. Modelling the carbon and nitrogen balances of direct land use changes from energy crops in Denmark: a consequential life cycle inventory. *Gcb Bioenergy*, **4**(6), 889-907.
59. Hattori, T., Morita, S. 2010. Energy Crops for Sustainable Bioethanol Production; Which, Where and How? *Plant Production Science*, **13**(3), 221-234.
60. He, R., Ye, X.P., English, B.C., Satrio, J.A. 2009. Influence of pyrolysis condition on switchgrass bio-oil yield and physicochemical properties. *Bioresource Technology*, **100**(21), 5305-5311.

61. He, X., Lau, A.K., Sokhansanj, S., Jim Lim, C., Bi, X.T., Melin, S. 2012. Dry matter losses in combination with gaseous emissions during the storage of forest residues. *Fuel*, **95**, 662-664.
62. He, X., Lau, A.K., Sokhansanj, S., Lim, C.J., Bi, X.T., Melin, S. 2014. Investigating gas emissions and dry matter loss from stored biomass residues. *Fuel*, **134**, 159-165.
63. Heo, H.S., Park, H.J., Park, Y.-K., Ryu, C., Suh, D.J., Suh, Y.-W., Yim, J.-H., Kim, S.-S. 2010. Bio-oil production from fast pyrolysis of waste furniture sawdust in a fluidized bed. *Bioresource Technology*, **101**(1, Supplement), S91-S96.
64. Hiloidhari, M., Vijay, V., Banerjee, R., Baruah, D., Rao, A.B. 2021. Energy-carbon-water footprint of sugarcane bioenergy: A district-level life cycle assessment in the state of Maharashtra, India. *Renewable and Sustainable Energy Reviews*, **151**, 111583.
65. 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**(1), 223-228.
66. Hosseinzadeh-Bandbafha, H., Aghbashlo, M., Tabatabaei, M. 2021. Life cycle assessment of bioenergy product systems: a critical review. *e-Prime*, 100015.
67. 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. *Energy & Fuels*, **22**(1), 614-625.
68. IPCC. 2018a. Allen, M.R., O.P. Dube, W. Solecki, F. Aragón-Durand, W. Cramer, S. Humphreys, M. Kainuma, J. Kala, N. Mahowald, Y. Mulugetta, R. Perez, M. Wairiu, and K. Zickfeld, 2018: Framing and Context. In: Global Warming of 1.5°C.An IPCC Special Report on the impacts of global warming of 1.5°C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change, sustainable development, and efforts to eradicate poverty [Masson-Delmotte, V., P. Zhai, H.-O. Pörtner, D. Roberts, J. Skea, P.R. Shukla, A. Pirani, W. Moufouma-Okia, C. Péan, R. Pidcock, S. Connors, J.B.R. Matthews, Y. Chen, X. Zhou, M.I. Gomis, E. Lonnoy, T. Maycock, M. Tignor, and T. Waterfield (eds.)]. In Press.
69. IPCC. 2013. IPCC, 2013: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp.
70. IPCC. 2018b. IPCC, 2018: Global Warming of 1.5°C.An IPCC Special Report on the impacts of global warming of 1.5°C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change, sustainable development, and efforts to eradicate poverty [Masson-Delmotte, V., P. Zhai, H.-O. Pörtner, D. Roberts, J. Skea, P.R. Shukla, A. Pirani, W. Moufouma-Okia, C. Péan, R. Pidcock, S. Connors, J.B.R. Matthews, Y. Chen, X. Zhou, M.I. Gomis, E. Lonnoy, T. Maycock, M. Tignor, and T. Waterfield (eds.)]. In Press.
71. IPCC. 2019. IPCC. Appendix 4. Method for Estimating the Change in Mineral Soil Organic Carbon Stocks from Biochar Amendments: Basis for Future Methodological Development. Refinement to 2006 IPCC Guidel. Natl. Greenh. Gas Invent., 2019.

72. ISO:14040. 2006. International Organization for Standardization. ISO 14040: Environmental management - Life Cycle Assessment - Principles and Framework, 2nd edn. vol. 2006. Geneva, Switzerland: 2006.
73. ISO:14044. 2006. International Organization for Standardization. ISO 14044: Environmental Management – Life Cycle Assessment – Requirements and Guidelines, 1st edn. Geneva, Switzerland: 2006.
74. Jørgensen, U. 2011. Benefits versus risks of growing biofuel crops: the case of Miscanthus. *Current Opinion in Environmental Sustainability*, **3**(1), 24-30.
75. JRC IEA. 2010. International Reference Life Cycle Data System (ILCD) Handbook—General guide for Life Cycle Assessment—Detailed guidance. First edition March 2010. Publications Office of the European Union, Luxembourg.
76. Jung, K.-H. 2007. Growth inhibition effect of pyroligneous acid on pathogenic fungus,Alternaria mali, the agent of Alternaria blotch of apple. *Biotechnology and Bioprocess Engineering*, **12**(3), 318-322.
77. Kan, T., Strezov, V., Evans, T.J. 2016. Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters. *Renewable and Sustainable Energy Reviews*, **57**, 1126-1140.
78. Kataki, R., Chutia, R.S., Mishra, M., Bordoloi, N., Saikia, R., Bhaskar, T. 2015. Chapter 2 - Feedstock Suitability for Thermochemical Processes. in: *Recent Advances in Thermo-Chemical Conversion of Biomass*, (Eds.) A. Pandey, T. Bhaskar, M. Stöcker, R.K. Sukumaran, Elsevier. Boston, pp. 31-74.
79. Kim, J.-Y., Oh, S., Hwang, H., Moon, Y.-H., Choi, J.W. 2014. Assessment of miscanthus biomass (Miscanthus sacchariflorus) for conversion and utilization of bio-oil by fluidized bed type fast pyrolysis. *Energy*, **76**, 284-291.
80. Kludze, H., Deen, B., Weersink, A., van Acker, R., Janovicek, K., De Laporte, A. 2013. Impact of land classification on potential warm season grass biomass production in Ontario, Canada. *Canadian Journal of Plant Science*, **93**(2), 249-260.
81. Koponen, K., Soimakallio, S., Kline, K.L., Cowie, A., Brandão, M. 2018. Quantifying the climate effects of bioenergy – Choice of reference system. *Renewable and Sustainable Energy Reviews*, **81**, 2271-2280.
82. Lakshman, V., Brassard, P., Hamelin, L., Raghavan, V., Godbout, S. 2021. Pyrolysis of Miscanthus: Developing the mass balance of a biorefinery through experimental tests in an auger reactor. *Bioresource Technology Reports*, **14**, 100687.
83. Lazzari, E., Schena, T., Marcelo, M.C.A., Primaz, C.T., Silva, A.N., Ferrão, M.F., Bjerk, T., Caramão, E.B. 2018. Classification of biomass through their pyrolytic bio-oil composition using FTIR and PCA analysis. *Industrial Crops and Products*, **111**, 856-864.
84. Leng, L., Xu, X., Wei, L., Fan, L., Huang, H., Li, J., Lu, Q., Li, J., Zhou, W. 2019. Biochar stability assessment by incubation and modelling: Methods, drawbacks and recommendations. *Science of The Total Environment*, **664**, 11-23.
85. Lewandowski, I., Clifton-Brown, J.C., Scurlock, J.M.O., Huisman, W. 2000. Miscanthus: European experience with a novel energy crop. *Biomass and Bioenergy*, **19**(4), 209-227.

86. Lima, R.S., de Azevedo Caldeira-Pires, A., Cardoso, A.N. 2020. Uncertainty Analysis in Life Cycle Assessments Applied to Biorefineries Systems: A Critical Review of the Literature. *Process Integration and Optimization for Sustainability*, **4**(1), 1-13.
87. Lin, C.-Y., Lu, C. 2021. Development perspectives of promising lignocellulose feedstocks for production of advanced generation biofuels: A review. *Renewable and Sustainable Energy Reviews*, **136**, 110445.
88. Liu, T., Huffman, T., Kulshreshtha, S., McConkey, B., Du, Y., Green, M., Liu, J., Shang, J., Geng, X. 2017. Bioenergy production on marginal land in Canada: Potential, economic feasibility, and greenhouse gas emissions impacts. *Applied Energy*, **205**, 477-485.
89. Lujaji, F.C., Boateng, A.A., Schaffer, M.A., Mullen, C.A., Mkilaha, I.S.N., Mtui, P.L. 2016. Pyrolysis Oil Combustion in a Horizontal Box Furnace with an Externally Mixed Nozzle. *Energy & Fuels*, **30**(5), 4126-4136.
90. Marsal, F., Thevathasan, N.V., Guillot, S., Mann, J., Gordon, A.M., Thimmanagari, M., Deen, W., Silim, S., Soolanayakanahally, R., Sidders, D. 2016. Biomass yield assessment of five potential energy crops grown in southern Ontario, Canada. *Agroforestry Systems*, **90**(5), 773-783.
91. Maxime, D., Fallaha, S. 2013. Ontario Switchgrass and Miscanthus Farm Gate Carbon Footprints, Ontario Federation of Agriculture, Canada
92. McKendry, P. 2002. Energy production from biomass (part 1): overview of biomass. *Bioresource Technology*, **83**(1), 37-46.
93. Mehmood, M.A., Ibrahim, M., Rashid, U., Nawaz, M., Ali, S., Hussain, A., Gull, M. 2017. Biomass production for bioenergy using marginal lands. *Sustainable Production and Consumption*, **9**, 3-21.
94. Mi, J., Liu, W., Yang, W., Yan, J., Li, J., Sang, T. 2014. Carbon sequestration by Miscanthus energy crops plantations in a broad range semi-arid marginal land in China. *Science of The Total Environment*, **496**, 373-380.
95. Mimmo, T., Panzacchi, P., Baratieri, M., Davies, C.A., Tonon, G. 2014. Effect of pyrolysis temperature on miscanthus (Miscanthus × giganteus) biochar physical, chemical and functional properties. *Biomass and Bioenergy*, **62**, 149-157.
96. Moreno Ruiz, E., Weidema, B., Bauer, C., Nemecek, T., Vadenbo, C., Treyer, K., Wernet, G. 2013. Documentation of changes implemented in ecoinvent Data 3.0. *Ecoinvent report*, **5**, 3.
97. Nanda, S., Dalai, A.K., Kozinski, J.A. 2016. Supercritical water gasification of timothy grass as an energy crop in the presence of alkali carbonate and hydroxide catalysts. *Biomass and Bioenergy*, **95**, 378-387.
98. Nanda, S., Vo, D.-V.N., Sarangi, P.K. 2020. *Biorefinery of Alternative Resources: Targeting Green Fuels and Platform Chemicals (pp. 195-220)*. Springer Nature.
99. Nasir Uddin, M., Daud, W.M.A.W., Abbas, H.F. 2013. Potential hydrogen and non-condensable gases production from biomass pyrolysis: Insights into the process variables. *Renewable and Sustainable Energy Reviews*, **27**, 204-224.
100. Nikkhah, A., El Haj Assad, M., Rosentrater, K.A., Ghnimi, S., Van Haute, S. 2020. Comparative review of three approaches to biofuel production from energy crops as feedstock in a developing country. *Bioresource Technology Reports*, **10**, 100412.

101. Ong, H.C., Chen, W.-H., Farooq, A., Gan, Y.Y., Lee, K.T., Ashokkumar, V. 2019. Catalytic thermochemical conversion of biomass for biofuel production: A comprehensive review. *Renewable and Sustainable Energy Reviews*, **113**, 109266.

102. Osman, A.I., Mehta, N., Elgarahy, A.M., Al-Hinai, A., Al-Muhtaseb, A.a.H., Rooney, D.W. 2021. Conversion of biomass to biofuels and life cycle assessment: a review. *Environmental Chemistry Letters*, **19**(6), 4075-4118.

103. Padilla-Rivera, A., Paredes, M.G., Güereca, L.P. 2019. A systematic review of the sustainability assessment of bioenergy: The case of gaseous biofuels. *Biomass and Bioenergy*, **125**, 79-94.

104. Pancaldi, F., Trindade, L.M. 2020. Marginal Lands to Grow Novel Bio-Based Crops: A Plant Breeding Perspective. *Frontiers in Plant Science*, **11**(227).

105. Papari, S., Hawboldt, K., Helleur, R. 2017. Production and Characterization of Pyrolysis Oil from Sawmill Residues in an Auger Reactor. *Industrial & Engineering Chemistry Research*, **56**(8), 1920-1925.

106. Parajuli, R., Dalgaard, T., Nguyen, T.L.T., Sperling, K. 2013. Life Cycle Assessment of Miscanthus as a fuel alternative in district heat production. *21st European Biomass Conference and Exhibition*. ETA-Renewable Energies. pp. 388-400.

107. Pattiya, A. 2018. 1 - Fast pyrolysis. in: *Direct Thermochemical Liquefaction for Energy Applications*, (Ed.) L. Rosendahl, Woodhead Publishing, pp. 3-28.

108. Pittman Jr, C.U., Mohan, D., Eseyin, A., Li, Q., Ingram, L., Hassan, E.-B.M., Mitchell, B., Guo, H., Steele, P.H. 2012. Characterization of bio-oils produced from fast pyrolysis of corn stalks in an auger reactor. *Energy & Fuels*, **26**(6), 3816-3825.

109. Ren, S., Ye, X.P., Borole, A.P., Kim, P., Labbé, N. 2016. Analysis of switchgrass-derived bio-oil and associated aqueous phase generated in a semi-pilot scale auger pyrolyzer. *Journal of Analytical and Applied Pyrolysis*, **119**, 97-103.

110. Resende, F.L. 2014. Reactor configurations and design parameters for thermochemical conversion of biomass into fuels, energy, and chemicals. in: *Reactor and Process Design in Sustainable Energy Technology*, Elsevier, pp. 1-25.

111. 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**(2), 827-833.

112. Rodionova, M.V., Poudyal, R.S., Tiwari, I., Voloshin, R.A., Zharmukhamedov, S.K., Nam, H.G., Zayadan, B.K., Bruce, B.D., Hou, H.J.M., Allakhverdiev, S.I. 2017. Biofuel production: Challenges and opportunities. *International Journal of Hydrogen Energy*, **42**(12), 8450-8461.

113. Rosendahl, L. 2017. *Direct thermochemical liquefaction for energy applications pp. 3-28*. Woodhead Publishing.

114. Roy, P., Dutta, A., Deen, B. 2015. Miscanthus: a promising feedstock for lignocellulosic ethanol industry in Ontario, Canada. *AIMS Energy*, **3**(4), 562-575.

115. Ruan, R., Zhang, Y., Chen, P., Liu, S., Fan, L., Zhou, N., Ding, K., Peng, P., Addy, M., Cheng, Y., Anderson, E., Wang, Y., Liu, Y., Lei, H., Li, B. 2019. Chapter 1 - Biofuels: Introduction. in: *Biofuels: Alternative Feedstocks and Conversion Processes for the Production of Liquid and*

Gaseous Biofuels (Second Edition), (Eds.) A. Pandey, C. Larroche, C.-G. Dussap, E. Gnansounou, S.K. Khanal, S. Ricke, Academic Press, pp. 3-43.
116. Sanscartier, D., Deen, B., Dias, G., MacLean, H.L., Dadfar, H., McDonald, I., Kludze, H. 2014. Implications of land class and environmental factors on life cycle GHG emissions of Miscanthus as a bioenergy feedstock. *Gcb Bioenergy*, **6**(4), 401-413.
117. Sarabia, L.A., Ortiz, M.C. 2009. 1.12 - Response Surface Methodology. in: *Comprehensive Chemometrics*, (Eds.) S.D. Brown, R. Tauler, B. Walczak, Elsevier. Oxford, pp. 345-390.
118. SAS, I. 1989. SAS/STAT user's guide. *SAS Institute Inc., Cary, NC*.
119. Sindhu, R., Binod, P., Pandey, A., Ankaram, S., Duan, Y., Awasthi, M.K. 2019. Chapter 5 - Biofuel Production From Biomass: Toward Sustainable Development. in: *Current Developments in Biotechnology and Bioengineering*, (Eds.) S. Kumar, R. Kumar, A. Pandey, Elsevier, pp. 79-92.
120. Singh, A., Nanda, S., Berruti, F. 2020. A Review of Thermochemical and Biochemical Conversion of Miscanthus to Biofuels. in: *Biorefinery of Alternative Resources: Targeting Green Fuels and Platform Chemicals*, (Eds.) S. Nanda, D.-V. N. Vo, P.K. Sarangi, Springer Singapore. Singapore, pp. 195-220.
121. Singh, A., Nanda, S., Guayaquil-Sosa, J.F., Berruti, F. 2021. Pyrolysis of Miscanthus and characterization of value-added bio-oil and biochar products. *The Canadian Journal of Chemical Engineering*.
122. Suqi, L., Caceres, L., Schieck, K., Booker, C.J., McGarvey, B.M., Yeung, K.K.C., Pariente, S., Briens, C., Berruti, F., Scott, I.M. 2014. Insecticidal Activity of Bio-oil from the Pyrolysis of Straw from Brassica spp. *Journal of Agricultural and Food Chemistry*, **62**(16), 3610-3618.
123. Tavakoli-Hashjini, E., Piorr, A., Müller, K., Vicente-Vicente, J.L. 2020. Potential bioenergy production from Miscanthus× Giganteus in Brandenburg: Producing bioenergy and fostering other ecosystem services while ensuring food self-sufficiency in the Berlin-Brandenburg region. *Sustainability*, **12**(18), 7731.
124. Thompson, P.B. 2012. The Agricultural Ethics of Biofuels: The Food vs. Fuel Debate. *Agriculture*, **2**(4), 339-358.
125. Thomsen, T., Hauggaard-Nielsen, H., Bruun, E.W., Ahrenfeldt, J. 2011. The potential of Pyrolysis Technology in climate change mitigation-influence of process design and-parameters, simulated in SuperPro Designer Software.
126. Trudeau, H. 2018. Le système de plafonnement et d'échange de droits d'émission de gaz à effet de serre: l'expérience québécoise, Québec: Institut canadien du droit des ressources, Université Laval.
127. Vaillancourt, K., Bahn, O., Levasseur, A. 2019. The role of bioenergy in low-carbon energy transition scenarios: A case study for Quebec (Canada). *Renewable and Sustainable Energy Reviews*, **102**, 24-34.
128. VandenBygaart, A.J., Gregorich, E.G., Angers, D.A. 2003. Influence of agricultural management on soil organic carbon: A compendium and assessment of Canadian studies. *Canadian Journal of Soil Science*, **83**(4), 363-380.
129. Wagner, M., Mangold, A., Lask, J., Petig, E., Kiesel, A., Lewandowski, I. 2019. Economic and environmental performance of miscanthus cultivated on marginal land for biogas production. *Gcb Bioenergy*, **11**(1), 34-49.

130. Wang, B., Gao, B., Fang, J. 2017. Recent advances in engineered biochar productions and applications. *Critical Reviews in Environmental Science and Technology*, **47**(22), 2158-2207.
131. Wang, C., Kong, Y., Hu, R., Zhou, G. 2021. Miscanthus: A fas" growing crop for environmental remediation and biofuel production. *GCB Bioenergy*, **13**, 58 - 69.
132. Weidema, B., Wenzel, H., Petersen, C., Hansen, K. 2004. The product, functional unit and reference flows in LCA. *Environmental News*, **70**, 1-46.
133. Xie, T., Reddy, K.R., Wang, C., Yargicoglu, E., Spokas, K. 2015. Characteristics and Applications of Biochar for Environmental Remediation: A Review. *Critical Reviews in Environmental Science and Technology*, **45**(9), 939-969.
134. Xue, S., Lewandowski, I., Wang, X., Yi, Z. 2016. Assessment of the production potentials of Miscanthus on marginal land in China. *Renewable and Sustainable Energy Reviews*, **54**, 932-943.
135. Yorgun, S. 2003. Fixed-bed pyrolysis of Miscanthus x giganteus: product yields and bio-oil characterization. *Energy Sources*, **25**(8), 779-790.
136. Yu, Y., Yang, Y., Cheng, Z., Blanco, P.H., Liu, R., Bridgwater, A., Cai, J. 2016. Pyrolysis of rice husk and corn stalk in auger reactor. 1. Characterization of char and gas at various temperatures. *Energy & Fuels*, **30**(12), 10568-10574.
137. Zegada-Lizarazu, W., Monti, A. 2011. Energy crops in rotation. A review. *Biomass and Bioenergy*, **35**(1), 12-25.

Appendix 1

for,

Pyrolysis of Miscanthus: Developing the mass balance of a biorefinery through experimental tests in an auger reactor

Table A1.1: ANOVA for the water content in bio-crude oil

Parameter	Degrees of freedom	Mean squares	F-value	Pr>f
Temperature (°C)	4	103.38	4.30	0.0708*
Residence time (s)	4	153.69	6.39	0.0335*
N_2 flowrate (L min^{-1})	4	285.24	11.86	0.0092*

* Significant factors at Pr<0.1

Table A1.2 : ANOVA for the bio-crude oil yield

Parameter	Degrees of freedom	Mean squares	F-value	Pr>f
Temperature (°C)	4	48.656	4.29	0.0709*
Residence time (s)	4	5.3005	0.47	0.7593
N_2 flowrate (L. min^{-1})	4	121.39	10.71	0.0114*

* Significant factors at Pr<0.1

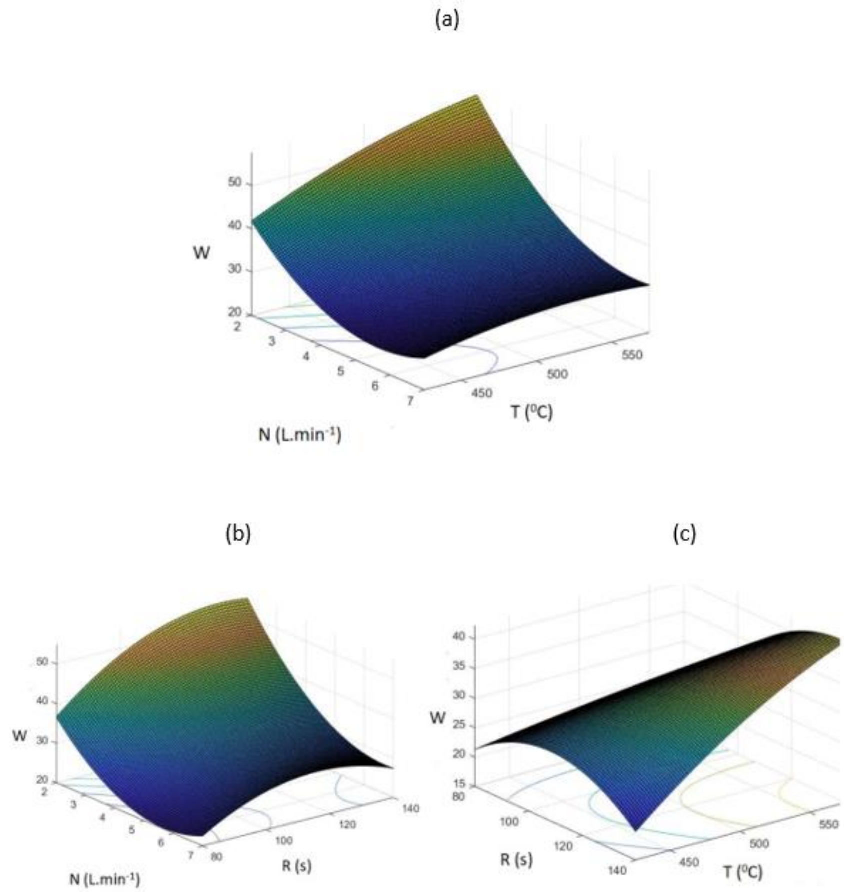

Fig A1.1: Response surface plots.

a) Combined effect of temperature (T) and N_2 flowrate (N) at constant residence time (R) of 110s , b) Combined effect of residence time (R) and N_2 flowrate (N) at constant temperature (T) of 500°C, c) Combined effect of residence time (R) and temperature (T) at constant N_2 flow rate (N) of 4.5 L min^{-1} ; W: wt% of water content in bio-crude oil

Mathematical representation of the relationship between the independent variables and the bio-crude oil yield (Y) is as follows (Equation A.1);

$$Y = -112.831 + 0.6415(T) + 0.430(R) – 13.266(N) – 0.0007(T)^2 - 0.0003(R*T) – 0.0012(R)^2 + 0.0045(N*T) + 0.0047(N*R) + 0.861N^2 \quad (A.1)$$

Where, T is the temperature (°C), N is the N_2 flowrate (L min^{-1}) and R is the biomass residence time (s).

Appendix 2

for,

Consequential life cycle assessment of a pyrolysis biorefinery using Miscanthus cultivated on marginal soil

Table A2.1: Main flows modelled in LCA

Flow #	Flow description
1	Miscanthus - Soil preparation (QC)
2	Miscanthus - Planting (QC)
3	Weed management (QC)
4	Miscanthus - Fertilizing (QC)
5	Miscanthus harvest & transport (QC)
6	Storage of Miscanthus bales (QC)
7	Miscanthus grinding (QC)
8	Drying Miscanthus
9	CHP of Miscanthus dust (QC)
10	Pyrolysis of Miscanthus (6% w.c.) (QC)
11	Condensation of vapors for the pyrolysis of Miscanthus (QC)
12	Combustion of bio-oil - Miscanthus (QC)
13	Combustion of NCG - Miscanthus (QC)
14	Biochar Application - Miscanthus
15	Application of biopesticide -Miscanthus (QC)
16	Biochar C sequestration - Miscanthus
17	Miscanthus LUC (abandoned land) - Baseline
18	Photosynthesis
19	Combustion of wood chips (Qc)
20	Combustion of natural gas (QC)
21	Application of fungides (Qc)

Table A2.2: Importance of impact for 8/16 impact categories (1/2)

Flow # [1]	CC	Oz. Dep.	Ion. Rad.	Photo. Ozone form.	Resp. Inorg.	Non cancer HH	Cancer HH	Acid. Terr.
Pyrolysis scenario								
1	Negl.	Negl.	Minor	Negl.	Negl.	Minor	Negl.	Negl.
2	Negl.	Negl.	Negl.	Negl.	Negl.	Mod.	Negl.	Negl.
3	Negl.	Negl.	Negl.	Negl.	Negl.	Negl.	Negl.	Negl.
4	Negl.	Minor	Negl.	Minor	Minor	Minor	Minor	Minor
5	Negl.	Mod.	High	Minor	Minor	Mod.	Minor	Minor
6	Minor	Mod.	High	High	High	V. high	Crucial	Mod.
7	Negl.	Negl.	Negl.	Negl.	Negl.	Negl.	Negl.	Negl.
8	Negl.	Minor	Minor	Negl.	Negl.	Negl.	Negl.	Negl.
9	Negl.	Negl.	Negl.	Negl.	Negl.	Negl.	Negl.	Negl.
10	Minor	V. high	Minor	Mod.	Minor	Minor	Mod.	Minor
11	Negl.	Minor	Minor	Minor	Negl.	Minor	Minor	Negl.
12	Mod.	Minor	Minor	High	Minor	Minor	Minor	Mod.
13	Mod.	Negl.	Negl.	Minor	Minor	Negl.	Negl.	Mod.
14	Minor	Minor	Minor	Negl.	Negl.	Minor	Negl.	Negl.
15	Negl.	Minor	Minor	Negl.	Negl.	Negl.	Negl.	Negl.
16	Mod.	Negl.	Negl.	Negl.	Negl.	Negl.	Negl.	Negl.
17	Minor	Negl.	Negl.	Mod.	High	Negl.	Negl.	V. high
18	High	Negl.	Negl.	Negl.	Negl.	Negl.	Negl.	Negl.
Reference Scenario								
19	Minor	Minor	Minor	V. high	Crucial	Crucial	V. high	High
20	Crucial	Crucial	Minor	High	Minor	Minor	Mod.	V. high
21	Mod.	Minor	Crucial	Minor	Negl.	Minor	High	Mod.

[1]Refer to Table S1 for description of flows.

CC: Climate change; Oz. Dep.: Ozone depletion; Ion. Rad.: Ionizing radiation; Photo. Ozone Form.: Photochemical ozone formation; Resp. Inorg.: Respiratory inorganics; Non cancer HHH: Non-cancer human health; Cancer HH: Cancer human health; Acid. Ter. Fresh: Acidification terrestrial and freshwater; Categorization of impact importance: Negligible (Negl.): <1% of total scenario impact; Minor: 1 to 10% of total scenario impact; Moderate (Mod.): 10 to 20% of total scenario impact; High: 20 to 40% of total scenario impact; Very High (V. high): 40 to 60% of total scenario impact; Crucial: >60% of total scenario impact.

Table A2.3: Importance of impact for 8/16 impact categories (2/2)

Flow # [1]	Eut. Fresh	Eut. Marine	Eut. Terr.	Ecotox. Fresh.	Land use	Water Scarc.	Res. use Energy	Res. use Material
Pyrolysis scenario								
1	Negl.	Negl.	Negl.	Negl.	Negl.	Negl.	Negl.	Negl.
2	Negl.	Negl.	Negl.	Minor	Minor	Negl.	Negl.	Negl.
3	Negl.	Negl.	Negl.	Negl.	Negl.	Negl.	Negl.	Negl.
4	Minor	Minor	Minor	Minor	Negl.	High	Minor	Negl.
5	Mod.	Minor	Minor	Mod.	Minor	Minor	Minor	Negl.
6	V. high	Mod.	Mod.	V. high	High	High	High	Crucial
7	Negl.	Negl.	Negl.	Negl.	Negl.	Negl.	Negl.	Negl.
8	Negl.	Negl.	Negl.	Negl.	Negl.	Negl.	Minor	Negl.
9	Negl.	Negl.	Negl.	Negl.	Negl.	Negl.	Negl.	Negl.
10	Mod.	Minor	Minor	Mod.	High	High	V. high	Minor
11	Minor	Minor	Negl.	Minor	Minor	Minor	Minor	Negl.
12	Minor	High	Mod.	Minor	Minor	Minor	Minor	Negl.
13	Negl.	Minor	Minor	Negl.	Negl.	Negl.	Negl.	Negl.
14	Minor	Negl.	Negl.	Minor	Minor	Negl.	Minor	Negl.
15	Negl.	Negl.	Negl.	Minor	Negl.	Minor	Negl.	Negl.
16	Negl.	Negl.	Negl.	Negl.	Negl.	Negl.	Negl.	Negl.
17	Negl.	High	V. high	Negl.	Negl.	Negl.	Negl.	Negl.
18	Negl.	Negl.	Negl.	Negl.	Negl.	Negl.	Negl.	Negl.
Reference Scenario								
19	High	V. high	Crucial	V. high	Crucial	Mod.	Minor	V. high
20	Minor	High	High	Mod.	Negl.	Minor	Crucial	Mod.
21	Crucial	Mod.	Mod.	High	Minor	Crucial	High	High

[1]Refer to Table S1 for description of flows.

Eut. Fresh.: Eutrophication freshwater; Eut. Marine: Eutrophication marine; Eut. Terr.: Eutrophication terrestrial; Ecotox. Fresh.: Exotoxicity freshwater; Water Scarc.: Water scarcity; Res. Use Energy: Resources use, Energy; Res. Use Material: Resources use, minerals and metals. Qualitative evaluation of impact importance by category: Negligible (Negl.): <1% of total scenario impact; Minor: 1 to 10% of total scenario impact; Moderate (Mod.): 10 to 20% of total scenario impact; High: 20 to 40% of total scenario impact; Very High (V. high): 40 to 60% of total scenario impact; Crucial: >60% of total scenario impact.

A2.1 C change due to LUC:

Change in C due LUC = [(SOC miscanthus – SOC marginal land) + (Veg C stock Miscanthus – Veg C stock of marginal land)] **(Equation A2.1)**

SOC = F_{lu} * F_{mg} * F_{li} * SOCst **(Equation A2.2)**

Table A2.4: Data used for C change calculation

Parameters	Pyrolysis scenario (Miscanthus)	source	Reference scenario (marginal land)	Source
F_{lu}	0.71	(Maxime & Fallaha, 2013)	0.82	(European Comission, 2010)
F_{mg}	1.13	(Maxime & Fallaha, 2013)	1	(European Comission, 2010)
F_{li}	0.91	(Maxime & Fallaha, 2013)	1	(European Comission, 2010)
SOCst (t C/h.a)	85 (climate region: Cold temperate, moist)	(European Comission, 2010; VandenBygaart et al., 2003)	85 (climate region: Cold temperate, moist)	(European Comission, 2010; VandenBygaart et al., 2003)
Veg C stock (t C/h.a)	6.7	(Maxime & Fallaha, 2013)	6.99 (assumed 68% is grassland and 32% is scrubland)	(European Comission, 2010; Liu et al., 2017)

SOC miscanthus = 0.71 x 1.13 x 0.91 x 85 = 62.1 tC/h.a

SOC marginal land = 0.82 x 1 x 1 x 85 = 69.7 tC/h.a

Change in C due LUC = [(62.1 – 69.7) + (6.7 – 6.99)] = -7.89 tC/h.a

Annual change in C = -7.89/20 = -0.40 tC/h.a/yr

A2.2 N emissions:

A2.2.1 F_{cr} - Annual amount of N in crop residues

F_{cr} = {crop [Area . R_{ag} . N_{ag} + Area . R_{bg} . N_{bg}]} **(European Comission, 2006) (Equation A2.3)**

	Comment	Value	Source
Crop	dry matter harvested	10641 kg/ha/yr	(Maxime & Fallaha, 2013)
Area		1 h.a	
R_{ag}	Ratio of above ground residues to total harvest	0.3	(Maxime & Fallaha, 2013)
N_{ag}	Nitrogen content of above ground residues	0.005	(European Comission, 2006)
R_{bg}	ratio of below ground residues to total harvest	1.2	(Maxime & Fallaha, 2013)
N_{bg}	Nitrogen content of below ground residues	0.0086	(European Comission, 2006)

F_{cr} = 121.31

A2.2.2 F_{som} - N mineralised due soil C loss

F_{som} = (C loss x 1/R) 1000 **(European Comission, 2006) (Equation A2.4)**

C loss = Average annual C loss due to land use = 0.4 (calculated in Appendix A.2)

R = C/N ratio of soil = 15 (European Comission, 2006)

F_{som} = 27.04

A2.2.3 F_{sn} - synthetic N fertilisers (urea)

$F_{sn} = 60$

A2.2.4 N_2O-N(direct) = {F_{sn} +F_{cr} + F_{som}}EF_1 + N_2O-N_{os} (European Comission, 2006) (Equation A2.5)

N_2O-N_{os} = Emissions from managed soils = $F_{os}.EF_2$

	Comment	Value	Source
EF_1	emission factor for N_2O emissions from N inputs and mineralised N	0.01	(European Comission, 2006)
F_{os}	Annual area of managed land	1	(European Comission, 2006)
EF_2	emission factor for marginal land (assumed as temperate and boreal organic nutrient poor forest soils from)	0.1	(European Comission, 2006)

N_2O-N(direct) = 2.18 kg N_2O-N/ha*year

A2.2.5 N_2O-N (indirect) = N_2O-N_{atd} + N_2O-N_{leach} (European Comission, 2006) (Equation A2.6)

N_2O-N_{atd} = N_2O from atmospheric deposition of N volatalised from managed soils = [F_{sn} x Fraction volatalised]EF_4

Fraction of N volatalised as NO_x and NH_3 = 0.1 (European Comission, 2006)

EF_4 = 0.01 (European Comission, 2006)

N_2O-Nleach = N_2O from leaching = [F_{sn} + F_{cr} + F_{som}] (fraction leached)(EF_5)

Fraction of N leached = 0.3 (European Comission, 2006)

REFERENCES

European Comission, T. 2006. Chapter 11: N2O Emissions from Managed Soils, and CO2 Emissions from Lime and Urea Application

European Comission, T. 2010. COMMISSION DECISION of 10 June 2010 on guidelines for the calculation of land carbon stocks for the purpose of Annex V to Directive 2009/28/EC.

Hamelin, L., Jørgensen, U., Petersen, B.M., Olesen, J.E., Wenzel, H. 2012. Modelling the carbon and nitrogen balances of direct land use changes from energy crops in Denmark: a consequential life cycle inventory. *Gcb Bioenergy*, **4**(6), 889-907.

Liu, T., Huffman, T., Kulshreshtha, S., McConkey, B., Du, Y., Green, M., Liu, J., Shang, J., Geng, X. 2017. Bioenergy production on marginal land in Canada: Potential, economic feasibility, and greenhouse gas emissions impacts. *Applied Energy*, **205**, 477-485.

Maxime, D., Fallaha, S. 2013. Ontario Switchgrass and Miscanthus Farm Gate Carbon Footprints, Ontario Federation of Agriculture, Canada

VandenBygaart, A.J., Gregorich, E.G., Angers, D.A. 2003. Influence of agricultural management on soil organic carbon: A compendium and assessment of Canadian studies. *Canadian Journal of Soil Science*, **83**(4), 363-380.