Hydrothermal Carbonization (HTC) of Marine Seaweed (Macroalgae) for Producing Hydro-Char

by

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Dedicated to my,

Parents: Shankar Patel & Surekha Patel,

Wife: Dhara Patel,

and

Brother: Nisharg Patel,

for their altruistic love and encouragement.

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ABSTRACT

Seaweeds or macroalgae are mainly classified as Green, Red or Brown algae, based on their photosynthetic pigments. Some of them are edible, while others are nonedible. Most of the seaweeds that are collected at coastal regions of Prince Edward Island, Canada are nonedible and go to waste. Not only in PEI, but this waste is also creating much ecological problem in Maritime Provinces of Canada resulting in an anoxic event, which produces nearly zero dissolved oxygen in water along with hydrogen sulfide emission. Unlike microalgae, only a few works have been done for utilizing the seaweeds (macroalgae) as an advanced (third generation) biofuel for biorefineries.

The work done in this thesis attempts to address this issue by producing a coal-like solid substance (hydro-char) and nutritious liquid slurry (processed water) by employing a rather recent thermo-chemical process called Hydrothermal Carbonization (HTC), on the seaweed. The HTC was carried out in a batch reactor system for three different reaction temperatures 180 ℃, 200 ℃, and 220 ℃ and three different reaction/residence time 30, 60, and 120 minutes. Each of the produced hydro-char was characterized by different analytical methods. The effects of the process conditions on the product distribution and the properties of the products were examined.

The hydro-char that is produced at the highest reaction conditions shows the highest carbon content and fuel properties like lignite. Energy-density, the fixed carbon content, and C/N ratio in the hydro-char increased significantly. Moreover, HTC reduces the ash yield and volatile compounds of the seaweed. Thus, the hydro-char can be used as a fuel for direct combustion, in soil remediation or carbon sequestration application. Adding to that, the processed water that has nutrients leached from the seaweed during HTC was also tested for the potential biogas production from it.

LIST OF ABBREVIATIONS USED

℃	Degree Celsius
1G	First Generation
2G	Second Generation
3G	Third Generation
4G	Fourth Generation
AD	Anaerobic Digestion
AOAC	Association of Official Analytical Chemists
ASTM	American Society of Testing and Materials
B	Boron
C	Carbon
Ca	Calcium
CAO	Chief Administrative Officer
CH_3COOH	Ethanol
CH_3OH	Methanol
CH_4	Methane
CO	Carbon Monoxide
CO_2	Carbon Dioxide
Cu	Copper
db	Dry Basis
EDR	Energy Densification Ratio
FC	Fixed Carbon

g(gm)	grams
GHG	Greenhouse Gas
H	Hydrogen
H_2O	Water
HHV	Higher Heating Value
HMF	Hydroxy-methyl-furfural
HTC	Hydrothermal Carbonization
HTG	Hydrothermal Gasification
HTL	Hydrothermal Liquefaction
IEA	International Energy Agency
K	Potassium
Mg	Magnesium
MJ/kg	mega joules per kilograms
ml	milliliters
Mn	Manganese
MPa	megapascal
MSW	Municipal Solid Waste
N	Nitrogen
N/A	Not Available
NO_x	Nitrogen Oxide
O	Oxygen
P	Phosphorus

PDELJ	PEI Department of Environment, Labour and Justice
PDFAR	PEI Department of Fisheries, Aquaculture and Rural Development
PEI	Prince Edward Island
PID	Proportional-Integral-Derivative
PVC	Poly-vinyl-chloride
RPM	revolution per minutes
S	Sulfur
SCWG	Super Critical Water Gasification
toe	tonnes of oil equivalent
TS	Total Solids
VFA	Volatile Fatty Acids
VM	Volatile Matter
VS	Volatile Solids
w/v	weight by volume
w/w	weight by weight
Zn	Zinc

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CHAPTER 1. INTRODUCTION

1.1 Context of Research

Economic development combined with the increasing growth of the world population is contributing enormously to global energy consumption, which was 13865 Mtoe (toe refers to tonnes of oil equivalent; 1 toe = $4.187*10^{10}$ J) in the year 2018 (BP plc, 2019a), and has been projected to increase by 32 % by the year 2040 (BP plc, 2019b). About 85% of the world's energy consumption comes from oil (~34%), coal (~27%), and natural gas (~24%), which are non-renewable fossil fuels (BP plc, 2019a). Unfortunately, reserves of fossil fuels are finite, and their combustion produces large amounts of carbon dioxide (CO_2) and other greenhouse gases (GHGs), contributing to global warming and climate change (Bhat & Prakash, 2009; Luderer et al., 2014). Global warming is mostly transpiring in the aftermath of CO_2 release in the atmosphere, which is needed to be controlled whatsoever; otherwise, the resultant climate change due to global warming will become inevitable (Tekin et al., 2014). Furthermore, sulfur dioxide (SO_2) and nitrogen oxide (NO_X) emissions that are released during the combustion of fossil fuels are contributors to acid rain and smog (Basu, 2015). A continuous rise in such emissions also drives the future of the planet towards climatic disasters and problems associated with it, e.g., drought and flood (Kambo, 2015). Hence, rapidly exhausting petroleum reserves, proliferating demand for energy owing to increasing population, rapid industrialization for worldwide economic growth, and severe environmental concerns regarding the excessive utilization of fossil fuels are more than the required incentives to promote and invest in sustainable, renewable, and clean energy resources as well as technologies. Therefore, the researchers across the globe

have been focusing on developing energy-efficient as well as economic processes to produce fuels and chemicals, which not only heed stringent environmental regulations but also succor to fossil fuels for producing energy, thus reducing the dependence on fossil fuels and maintaining the necessary balance between supply and demand of energy simultaneously.

Bioenergy is the only renewable energy source that can address the current energy-related issues by directly integrating into existing infrastructure (Patel et al., 2016). Biomass, which is the basis for all forms of bioenergy, is considered as an attractive renewable resource of energy because of its net-zero carbon footprint, i.e., the amount of carbon absorbed during the growth of biomass is equal to the amount of carbon emitted during its combustion (Iaquaniello et al., 2017; Luderer et al., 2014; Clarke & Preto, 2011). Therefore, bioenergy based global economy can be driven by the low or negative carbon footprint of biomass-derived fuels. However, only 4% of the world energy consumption, in terms of electricity, comes from the renewable resources of energy including wind, solar, geothermal, biomass, and biofuels, among which the combined share of biomass and biofuels is merely 1%. (BP plc, 2019a).

1.2 Biomass Feedstocks and Conversion Technologies

Biomass is a collective term to describe organic materials from plants or animals, and their derived wastes as well as residues (Wang et al., 2018; Vassilev et al., 2010); the description can be extended to the by-products obtained by processing the sources mentioned above (Basu, 2018). Biomass can be broadly classified into three groups: Terrestrial biomass (forest, grasses, energy crops, etc.), Aquatic biomass (algae, marine plants, etc.), and Waste

biomass (municipal solid waste (MSW), agricultural waste, forestry residues, etc.). Bioenergy based economy, which uses eco-efficient bioprocesses for transforming biomass into more valuable biofuels, is one of the key strategic challenges of the 21st century (Naik et al., 2010; Ramirez, 2017; Khanal et al., 2010 Demirbas, 2009). Methods to convert biomass to competitive biofuels are increasingly attractive as utilization of biomass for production of biofuels show definite progress toward limiting GHG levels, improving air quality, and achieving energy independence as well as energy security (Nigam & Singh, 2011; Wei et al., 2013).

1.2.1 Biofuels

Biofuels are found in all three phases of a matter, i.e., solid (firewood, charcoal), liquid (biodiesel, ethanol), and gas (biogas) (Patzek & Pimentel, 2005; Tumuluru et al., 2011). They can be broadly termed either as primary biofuels or as secondary biofuels. Primary biofuels are biomass that can be utilized directly in the unprocessed form. Firewood, organic materials, agricultural residues are a few examples of it. On the other hand, secondary biofuels are the ones processed from biomass, such as charcoal, biodiesel, and biogas. Based on biomass feedstock and processing technology, biofuels are further classified as first, second, third, or fourth generation biofuels (Aro, 2016; Bala et al., 2016). Figure 1.1 describes the discussed classification of biofuels.
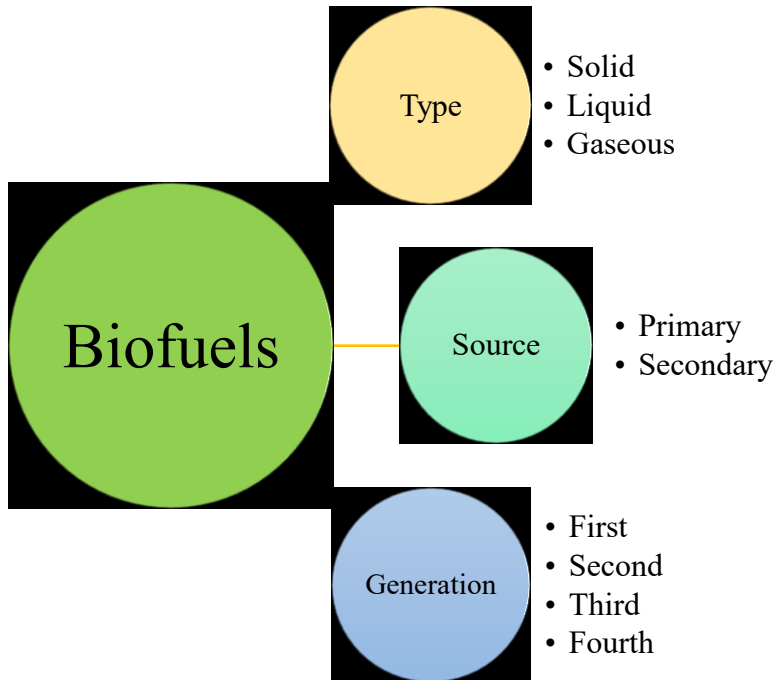
Figure 1.1 Classification of biofuels

First generation (1G) biofuels, often regarded as conventional biofuels, are derived from the food crops through relatively traditionalistic processes like fermentation and anaerobic digestion (Naik et al., 2010; Bala et al., 2016; Saladini et al., 2016). While they are the most common and widely used biofuels in the world, their long term sustainability may slump owing to well-publicized and long-standing feud considering associated competition between food crop and fuel (Patel et al., 2016; Mueller et al., 2011; Chen et al., 2015; Havlik et al., 2011).

Unlike 1G biofuels, second generation (2G) biofuels are produced from a wide range of inedible plants and agricultural residues that are primarily lignocellulosic feedstocks. Thermochemical, biochemical, and enzymatic processes are used to produce 2G biofuels,

such as bioethanol and syngas (Saladini et al., 2016; Sims et al., 2010; Naik et al., 2010). Although 2G biofuels bypass the food versus fuel conflict, they are yet to overcome the hindrances in the production cost, supply chain and logistics, and sustainability aspects, which are, unfortunately, labeling the commercialization of energy production technology based on 2G biofuels as a risky investment (Mohr & Raman, 2013; Heyne & Harvey, 2011; Smith et al., 2013; Carriquiry et al., 2011)

Biofuels that are made from non-edible microbial feedstock within algal biomass are known as third generation (3G) biofuels. 3G biofuels have emerged as an alternative and promising feedstock for producing a variety of renewable fuels such as biodiesel, bioethanol, and biogas (Dutta et al., 2014; Jambo et al., 2016, Bala et al., 2016). Algae range from unicellular or microalgae to multicellular or macroalgae (seaweeds) (Singh et al., 2014), among which a marine macroalga (seaweed) is considered in this thesis, and it will be discussed in-depth in the next chapter. Algae, compared to other biomass, have significant advantages of faster growth rate due to high photosynthetic efficiency, higher productivity without fertilizers, lower land requirement, higher CO_2 sequestration, piddling lignin content, and non-competitiveness to food resources (Menetrez, 2012; Patel et al., 2016; Raslavicius et al., 2018; Chen et al., 2015; Jones & Mayfield, 2011; Scaife et al., 2015; Biller & Ross, 2012; Chung et al., 2011). Thus, 3G biofuels, derived from the algal biomass, are considerable and viable alternative energy resources that are devoid of the major challenges associated with 1G and 2G biofuels. Moreover, existing theories claim that the petroleum reserves are majorly made up of fossilized algae combined with other organisms, which were buried inside the earth over millions of years under high pressure and temperature (Hobson, 1996; Zhang, 2010).

Development of fourth generation (4G) biofuels is at infancy. They can be engineered through genetic modification of algae (Abdullah et al., 2019; Adeniyi et al., 2018). Moreover, 4G biofuels are expected to be ultra-clean biofuels, which are carbon negative at the level of both raw material and process technology (Dutta et al., 2014; Aro, 2016).

1.2.2 Biomass Conversion

Biomass is the only renewable energy resource that can be converted into any form of fuel, including solid, liquid, and gas (Ozbay et al., 2001; Patel et al., 2016). It is relatively cheaper than fossil fuels, and it has been used for centuries to produce heat or power by direct firing (Basu, 2018). Unfortunately, diversity and seasonal characteristics in biomass feedstocks demand diverse handling techniques and expensive as well as sophisticated logistics (Yan et al., 2009). On top of that, inferior physicochemical properties such as high moisture content, low energy density, hygroscopic and fibrous nature, high volatile and ash (metallic) content, and low bulk density of biomass feedstocks are significant barriers to the direct combustion of biomass feedstocks instead of fossil fuels in the energy industries (Pimchuai et al., 2010; Jenkins et al., 1998). These reasons provide requisite motivation for developing conversion routes to make biomass superior to fossil fuels in specific ways. Each of the conversion or pre-treatment technology has specific advantages and disadvantages, but they certainly improve the energy utilization of biomass (Huber et al., 2006). The selection of conversion technology should be made on such basis that it offers a broader range of benefits for the given type of biomass and type of output. Benefits, for a given conversion or pre-treatment technology, can be summarized as follow (Huber et al., 2006; Reza, 2011):

a) Cost-effective processing with minimal pre-processing requirements such as drying and milling

b) Flexibility to use highly moist and waste biomass streams such as aquatic biomass, sewage sludge, agricultural residues and municipal solid waste (MSW)

c) Simultaneous recovering of co-products and simple downstream processing to minimize the waste production

d) Fast reactions and minimal or zero use of corrosive solvents or chemicals

1.2.2.1 Conversion Techniques for Biomass

The conversion routes or pretreatment techniques that transform biomass into a more suitable fuel form can be thermochemical or biochemical (Basu, 2018). Figure 1.2 provides a simplified overview of these conversion processes.
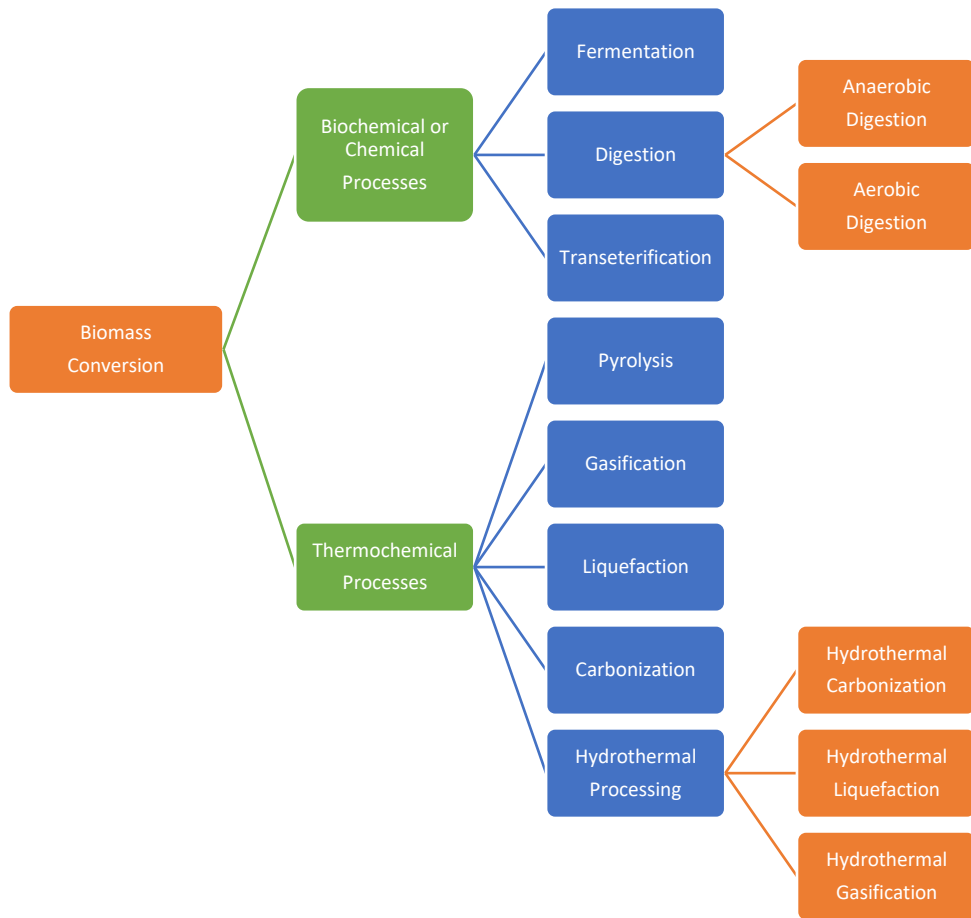
Figure 1.2 Conversion techniques for biomass

(Basu, 2018; Brown, 2019; Cheng, 2017)

The selection of a suitable conversion technique for biomass depends on the biomass type, the desired output (solid, liquid, and gas), and the desired properties of the product(s) based on its intended application, thus restricting the available pre-treatments. Therefore, the conversion processes are being developed and explored for both dry and wet biomass (Kumar et al., 2018; Cheng, 2017; Brown, 2019). Dry biomass can be transformed into a volatile matter that can be condensed to obtain liquid fuel, often regarded as bio-oil, through pyrolysis. Gasification is preferred when the product of interest is a synthetic fuel or syngas, from dry biomass. Like pyrolysis and gasification, a dry feedstock is necessary

for using the carbonization process, including torrefaction, which converts biomass into a carbon-rich and energy-dense bio-char (Basu, 2018; Brown, 2019). Nonetheless, wet biomass can surely be treated as dry biomass after drying, but such drying, most of the time, is neither an efficient nor an economical way to operate (Knezevic, 2009).

On the other side, wet biomass can be converted into biogas and ethanol through conventional processes like anaerobic digestion and fermentation (Basu, 2018; Cheng, 2017b). Of course, these methods are well-established, but environmental and socioeconomic concerns associated with the food versus fuel feud have plagued such conversion pathways. Moreover, these conventional routes are limited to particular carbohydrate fractions of biomass (Knezevic, 2009). In response, extensive research has been getting focused on using lignocellulosic and marine biomass as the feedstock (Singh et al., 2015; Adeniyi et al., 2018; Machineni, 2019; Sims et al., 2010). Thermochemical processes, when compared to biological processes, are relatively faster with higher product yield (Liu et al., 2012). However, thermochemical processes like pyrolysis, gasification, and carbonization demand dry feedstock, thus limiting their efficient and economic performance for wet biomass. Consequently, the conversion of waste as well as wet biomass like algae can be considered significant only through the techniques that do not require energy-intensive drying and water evaporation in the feedstock, e.g., hydrothermal processing which uses hot compressed water as a reaction media to produce hydrophobic solids, liquids, and gases (Kumar et al., 2018; Tekin et al., 2014; Biller & Ross, 2012). Hydrothermal processing, sometimes referred to as hydrothermal up-gradation, is further classified in hydrothermal carbonization (HTC), hydrothermal liquefaction (HTL), and

hydrothermal gasification (HTG), depending on the final product of interest which can be hydro-char(solid), bio-oil (liquid), or gas (Basu, 2018).

For the conversion of wet biomass in the processes like HTC, the biomass is mixed with water and is heated for a fixed time in a reactor vessel to produce primarily hydro-char and secondarily the processed water. The utilization of the hot compressed water allows complex reactions cascades to take place, including decomposition and depolymerization of biomass feedstock, which results in carbon-rich and energy-dense hydro-char and nutritious processed water (Roman et al., 2018; Heidari et al., In Press; Reza et al., 2013; Pavlovic et al., 2013; Funke & Ziegler, 2010). Wide variety of literature shows that both the reaction temperature and the reaction time affect the distribution and properties of the resultant products in the HTC process (Kambo & Dutta, 2015; Li et al., 2018; Nizamuddin et al., 2017; Libra et al., 2011). However, hydro-char is the desired product, which has a broad range of potential applications in various fields including energy, environment, and medical (Fang et al., 2018; Titirici et al., 2012). On the other hand, the processed water from the HTC process, although a secondary product, can be crucial as it contains the nutrients and other compounds that have leached, due to depolymerization of the biomass polymers, in the hot compressed water during the HTC process. Thus, HTC process reduces the inorganic metal content from the biomass feedstock, which shows the potential of the HTC process to mitigate the problems, associated with direct combustion of biomass, like slagging, scaling, and fouling in boilers (Makela et al., 2015; Smith et al., 2016; Reza et al., 2013). In totality, elimination of energy-intensive drying, relatively low temperature and shorter residence time, and removal of the inorganic impurities are significant advantages of the HTC process over other thermochemical processes. The HTC process of

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seaweed (macroalgae) is the primary objective of this thesis, and it is discussed in detail in the subsequent chapters.

1.3 Motivation and the Thesis Objectives

Seaweed accumulation is rapidly increasing near the town of Summerside in Prince Edward Island, Canada. It was reported that in the year 2014, a total of 4200 cubic meters of seaweed was removed from the city's shorelines; which proliferated, and it was reported that 70 cubic meters of waste seaweeds were collected within a period of less than a month in the year 2017 (MacPhee, 2017). The provincial government has identified that it is non-edible waste seaweed, and they have been trying to utilize it as compost or fertilizer since the year 2011 (PDELJ & PDFAR, 2012). However, there have been complaints regarding strong, unpleasant, and toxic smells near the farms that have been using these seaweeds as fertilizers (CBC News, 2013). The Chief Administrative Officer (CAO) of Summerside also stated about this waste seaweed that "*It is a bio-resource, and there is a potential we hope for energy production, biofuel, value-added products, nutraceuticals, other forms of fertilizers or chemicals.*" (CBC News, 2014)*.* Therefore, finding a value-added solution to address such persistent problems due to seaweeds can help the community not only by eradicating the required waste disposal for the seaweed, which of course incurs some cost to the government, but also by growing the economy by creating the source of income through biofuels from the waste seaweed.

However, it is critical to find a suitable technique for converting the waste seaweed in valuable biofuels, given that there are many conversion processes with different resultant products, as discussed earlier in this chapter. The seaweed belongs to algal biomass group,

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representing the third generation (3G) biofuels. It has very high moisture content ($\sim$ 80%), so thermochemical treatments such as torrefaction and pyrolysis, which demands dry feedstock, would be costly due to energy-intensive pre-drying. Hence, hydrothermal processing is the best option for generating biofuels out of the seaweed.

Therefore, hydrothermal carbonization (HTC) of the marine seaweed that is found near the shores of Prince Edward Island in Canada is investigated in this study to find the potential of the seaweed to produce coal-like solid (the hydro-char). Moreover, the potential of liquid product from HTC (the processed water) to produce biogas is also identified through an experimental study.

The specific objectives of the study conducted in this thesis are as follow:

a) To examine the effect of reaction temperature and reaction time on the product distribution, the mass yield of the hydro-char, and the energy density of the hydro-char.

b) To investigate the effect of reaction temperature and reaction time on H/C & O/C atomic ratios, the ash yield, and inorganic metal composition of the hydro-char samples.

c) To examine the effect of reaction temperature and reaction time on the inorganic element yield and pH of the processed water of HTC.

d) To identify the biogas yield through anaerobic digestion of the processed water from HTC.

1.4 Thesis Structure

The thesis aims to gain a better understanding of the process involved in the hydrothermal carbonization (HTC) of the seaweed (macroalgae). The work presented in the thesis also aims to elucidate the effect of the reaction temperature and the reaction time on the products, the hydro-char and the processed water, obtained through HTC of the seaweed, with particular emphasis on the hydro-char properties. Moreover, the potential of the processed water to produce biogas through the anaerobic co-digestion process is also examined. A series of experimental studies have been completed within the frame of this thesis to achieve these goals and are presented as follows:

Chapter 1 and Chapter 2 provides the context to the research objectives by conducting a review of literature relevant to the study done in this thesis. The review includes the composition of seaweed and its potential as a source of energy or as a biofuel, the hydrothermal carbonization (HTC) process, and the process of anaerobic digestion. Finally, current research gaps are identified.

Chapter 3 provides a detailed description of the experimental setup of the HTC process, which is used to obtain the results for this thesis. The collection of raw material (seaweed) and feedstock preparation are presented. A batch reactor for carrying out the HTC of the seaweed is then introduced with a detailed description of the methodology to perform the experiments. The analytical procedures including the instruments, to analyze the products of HTC, are also provided.

Chapter 4 describes the results and discussions for processing the seaweed in the batch reactor to perform HTC. It provides an investigation of the effects of processing conditions

on the properties and characterization of hydro-char and the processed water. Furthermore, the experimental setup for anaerobic co-digestion of the processed water- the secondary product from HTC of the seaweed and the results of the experiment are discussed.

Chapter 5 discusses the conclusions drawn from the study conducted in this thesis, which is followed by the recommendations for future research.

CHAPTER 2. LITERATURE REVIEW

2.1 Overview of Algal Biomass

Algae have been on earth for million years, and it differs substantially from lignocellulosic terrestrial biomass, peculiarly in cellular structure. Cellulose, hemicelluloses, and lignin are present in significant quantities in lignocellulosic terrestrial biomass. Contrary to which, algae cells are composed of carbohydrates, proteins, lipids, and nucleic acids (Adeniyi et al., 2018; John et al., 2011; Suganya et al., 2016). However, from a broader perspective, the composition of algae can be considered similar to that of plant biomass, with both containing carbohydrates, proteins, and lipids. Unlike to plant biomass, algae lack lignin crosslinking molecules in their cell structures which can be advantageous as the processing of algal biomass would bypass the lignin removal process, which is often complicated and expensive (Chen et al., 2015; Tumuluru et al., 2011). Moreover, carbohydrate profiles of algal biomass and plant or terrestrial biomass differ significantly. While both biomass contains hemicelluloses (heterogeneous polysaccharides composed primarily from xylose), algae are found to have starch content as well (Ramirez, 2017; Daroch et al., 2013; John et al., 2011; Nguyen et al., 2009). The typical difference between lignocellulosic biomass and algal biomass is illustrated in Figure 2.1.
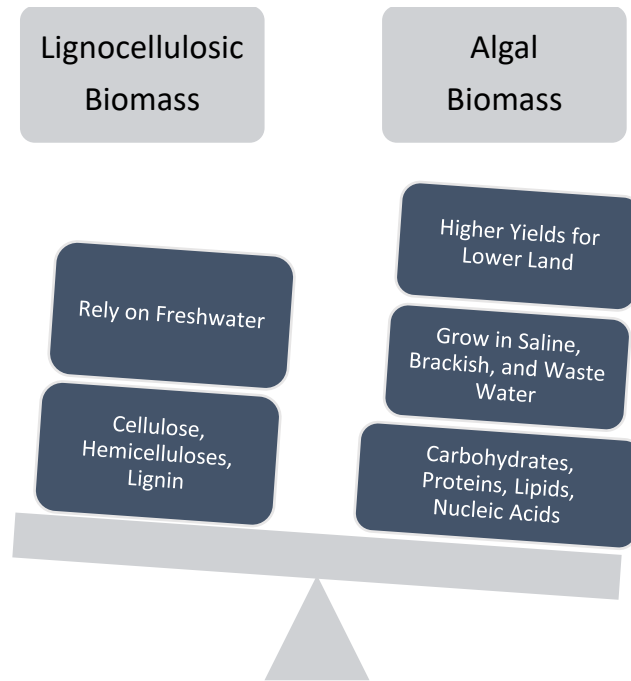
Figure 2.1 Difference between lignocellulosic biomass and algal biomass

(Adapted and modified from Singh et al., 2014)

Algae show the unique feature of high biomass yields without requiring arable land, and they have the potential to be cultivated in containment off-shore (Hallenbeck et al., 2016; Hannon et al., 2010), thus eliminating the utilization of agricultural land. Furthermore, some species of algae can also grow well in saline and waste water (Bharathiraja et al., 2015; Pittman et al., 2011; Bhatnagar et al., 2010), which makes algal biomass more promising feedstock than terrestrial biomass that relies heavily on freshwater and requires a significant portion of land. The growth of algae is estimated to be 5-10 times higher than land-based crops because algae have substantially higher photosynthetic efficiency (up to 6-8 %), in which solar energy is converted into chemical energy by fixing atmospheric carbon dioxide (CO_2), than that of conventional plant biomass (up to 3%) (Ross et al., 2008; Aresta et al., 2005; Show Jr., 1981). The potential of culturing algae in wastewater

can be beneficiary to industrial processes as it can sequester carbon, emitting in the form of CO_2 from industrial processes, to increase the growth rate of algae which further reduces CO_2 emissions and, therefore, the required inputs to cultivate algae get reduced. (Acien Fernandez et al., 2012; Pires et al., 2012; Doucha et al., 2005; Li et al., 2011).

These advantages make 3G biofuels derived from non-edible algal biomass superior to both 2G biofuels, which are processed from the lignocellulosic terrestrial biomass, and 1G biofuels that are made from the edible feedstock.

The idea of using algae as a bioresource for energy was made in the late 50s by Golueke and Oswald (Golueke et al., 1957; Oswald & Golueke, 1960). Since then, several potential applications of algae-based biofuels have been explored by researchers across the globe. Consequently, algae, nowadays, is seen as one of the promising alternatives to fulfill future demands for food, materials, and energy (Adeniyi et al., 2018; Jones & Mayfield, 2012; Suganya et al., 2016; Trivedi et al., 2015; Gao et al., 2012; Veillette et al., 2018; Lee & Lee, 2012; Kroger and Muller-Langer, 2012). Figure 2.2 illustrates the transformation of algae into various products and applications.
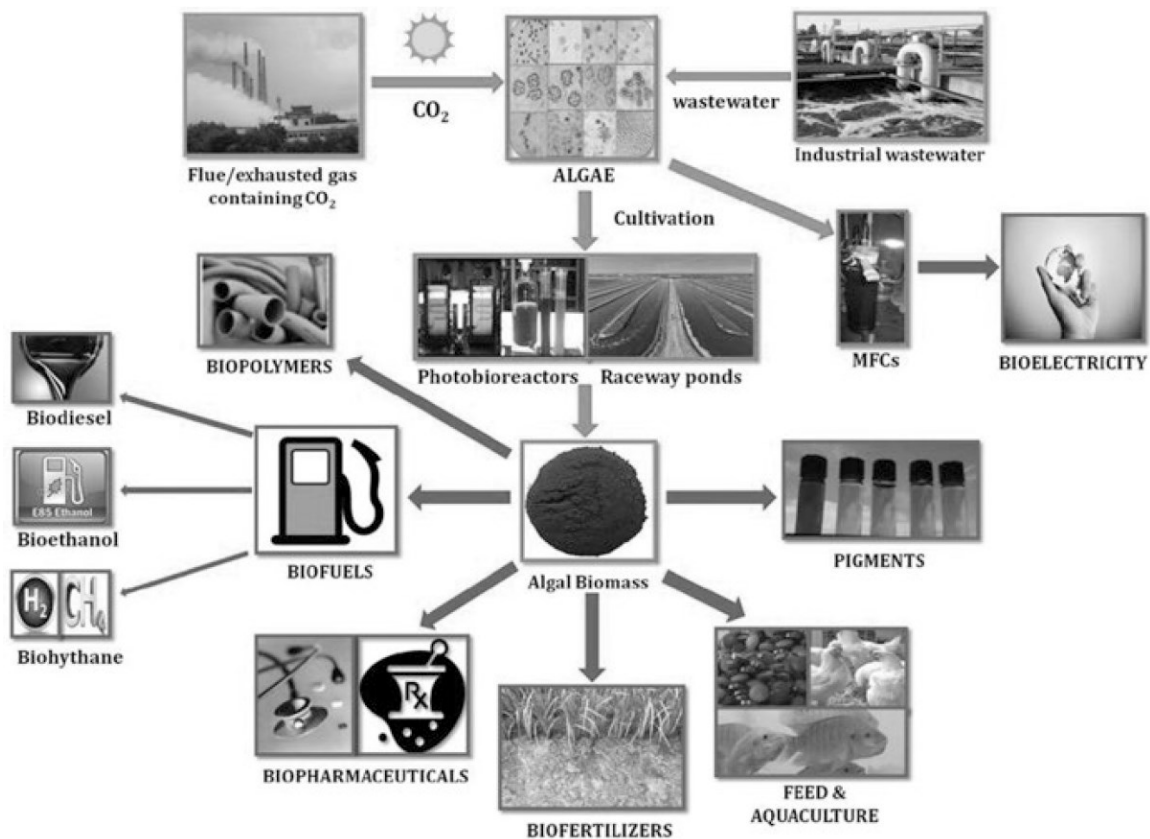
Figure 2.2 Possible utilization of algal biomass for various products

(Adapted from Das, 2015)

2.1.1 Microalgae versus Macroalgae

Algae exist in a diverse group of organisms, with hundreds of thousands of known species, which differ in size, morphology, physiology, and occurrence (Sudhakar et al., 2018). The size distribution of algae ranges from micron to several tens of meters, according to which they are subdivided into two broad categories: microalgae and macroalgae (seaweeds). The former have unicellular structure, reaching up to only a few tens of microns in size, thus limiting their visibility with the naked eye. Due to such a small size, they are very difficult to harvest and requires the removal of a significant amount of water (Chen et al., 2015; Sudhakar et al., 2018; Ross et al., 2008; Singh et al., 2014). Nevertheless, the latest report

by IEA Bioenergy shows that extensive researches have been dedicated to producing liquid biofuel from high-lipid containing microalgae, which has also led to greater development in cultivation and harvesting techniques of microalgae (IEA Bioenergy, 2017).

On the other hand, macroalgae(seaweeds) are multicellular, and they do not share the same problems as microalgae due to the significantly greater size. They are a large and diverse group of the aquatic plant-like species, yet they neither have the same structures as plants nor compete with other plants for land and freshwater (Suganya et al., 2016; Yazdani et al., 2015; Sudhakar et al., 2018). Seaweeds have a high content of polysaccharides and rapid growth rate that result in high biomass yield. Thus, they possess essential qualities for biofuels production. (Ghadiryanfar et al., 2016; Suganya et al., 2016; Yazdani et al., 2015)

However, it is found that the major residual of defatted algal biomass is under-explored (IEA Bioenergy, 2017), which is needed to be focused on achieving favorable energy balances and production costs. In particular, the use of macroalgae (seaweeds) has received less attention for energy production than that for the production of fuels and chemicals from microalgae (IEA Bioenergy, 2017). As a result, it seems that transition to utilizing macroalgae (seaweeds) for thermochemical conversion processes is rather slow, but it may catch more eyes in the global scientific community, in the future.

2.2 Seaweeds (Macroalgae)

2.2.1 General Structure and Classification of Seaweeds

Seaweeds or macroalgae belong to the lower plant, meaning that they do not have roots, stems, and leaves (Singh et al., 2014). A typical seaweed contains the following parts (Sudhakar et al., 2018; Singh et al., 2014; Suganya et al., 2016), which can also be seen in Figure 2.3.
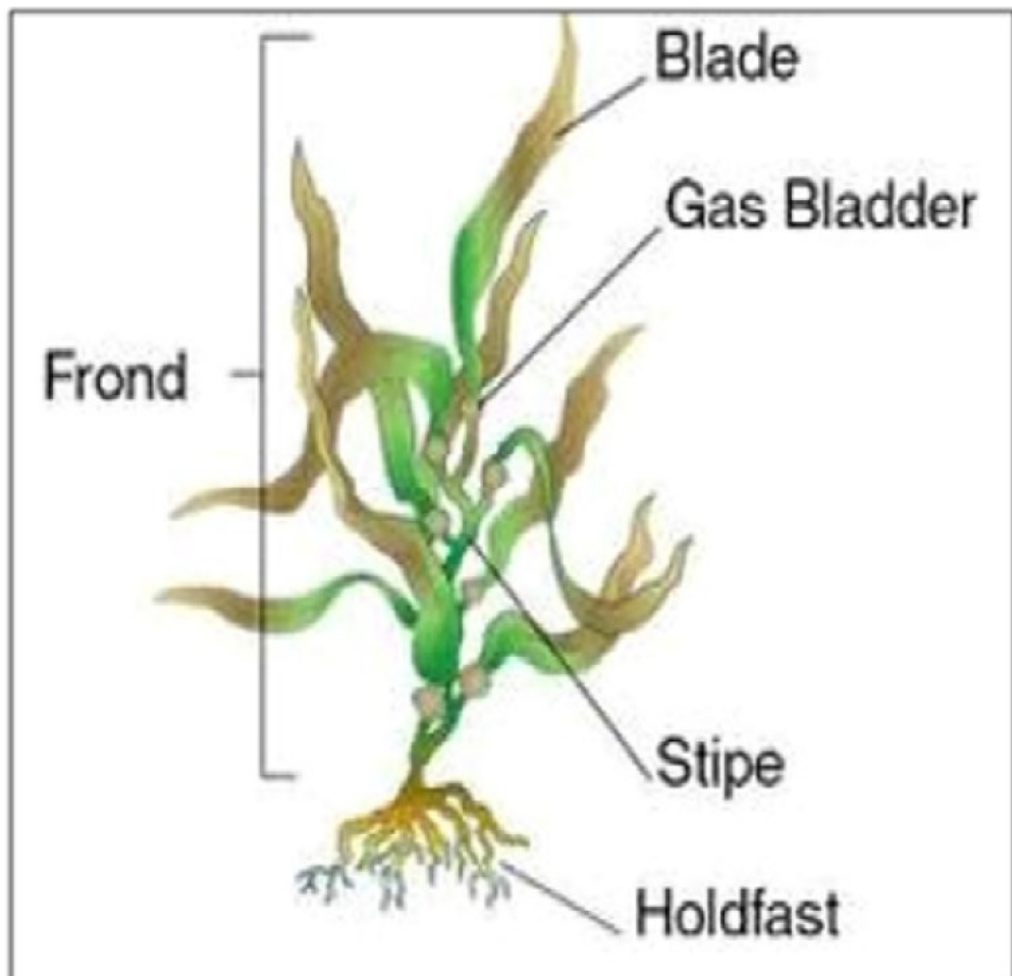
Figure 2.3 A typical structure of seaweed

(Adapted from Sudhakar et al., 2018)

a) **Thallus**: It is the algal body. All section of the thallus can photosynthesize.

b) **Lamina or Blade**: It is the leaf-like flattened portion which absorbs sunlight.

c) **Stripe**: It is a stem-like structure. It carries sugars from the lamina to the rest of the algal body while acting as an attachment for the lamina. However, it is not found in all species of seaweeds.

d) **Frond**: The combined part of blade and stripe is referred to as frond.

e) **Floats (Gas bladder)**: It is an organ between blade and stripe, which contains carbon monoxide. It aids to floating of the blades near the surface of the water where more sunlight is available for photosynthesis.

f) **Holdfast**: It is a specialized root-like structure that holds the thallus to the bottom surface or rocks. However, it does not succor to gathering nutrients. It anchors the entire structure to hard substrates in marine environments.

In the natural environment, seaweeds live near the seabed and form stable and multilayered vegetation, capturing almost all available photons (Suganya et al., 2016; Singh et al., 2014). Approximately 10,000 species of seaweeds exist in nature, and the distribution of seaweed primarily depends on the quality and quantity of the incidental solar radiation (Jard et al., 2013). Seaweeds, based on the photosynthetic pigmentation, are classified into three broad categories (Ramirez, 2017; Singh et al., 2014; Jard et al., 2013):

1) Green Seaweed *(Chlorophyceae)*

2) Brown Seaweed (*Phaeophyceae*)

3) Red Seaweed *(Rhodophyceae)*

2.2.2 Composition of the Seaweed

The chemical composition of seaweed significantly varies depending on the type, the species and cultivation conditions (Mohamed et al., 2012; Anbuchezhian et al., 2015; Hong et al., 2014). A major constituent of seaweed is the carbohydrates (between 30% and 70%); however, the composition of polysaccharides in the carbohydrates of seaweed differs across the major macroalgal groups (Ruiz et al., 2015; Cho et al., 2013; Usov & Zelinsky, 2013). The composition of the different seaweeds or macroalgae is summarized in Table 2.1. In a broad perspective, the average biomass yield and elements present in the seaweed can be presented as follow:

❖ Biomass yield: 20 tonnes per hectare per year (Sudharkar et al., 2018)

❖ Dry matter (6 - 39 %) (Chen et al., 2015; Sudharkar et al., 2018)

❖ Water content (80 – 90 %) (Sudharkar et al., 2018)

❖ Carbohydrates (mostly 30 - 65 % w/w dry basis) (Table 2.1)

❖ Lipids (mostly up to 10 % w/w dry basis) (Table 2.1)

❖ minerals (mostly 20 - 35 % w/w dry basis) and proteins (mostly around 10 - 20 % w/w dry basis) (Table 2.1)

Jung et al. reported that brown macroalgae and red macroalgae are more promising than green macroalgae for macroalgae based biorefinery technologies (Jung et al., 2013). However, they did not review the potential of any macroalgae to produce hydro-char through hydrothermal carbonization process.

Table 2.1 Chemical Composition of Green, Brown, and Red Macroalgae (Seaweeds)

(dry basis, %w/w) (Adapted and Modified from Ruiz et al., 2015; Anbuchezhian et al., 2015)

Macro Algae	Carbohydrates	Protein	Lipids	Minerals	Reference
Green Algae (Chlorophyceae)					
Chaetomorpha sp.	43.9	11.1	3.3	36.6	Neveux et al. (2014a,b)
Derbesia sp.	26.9	21.6	10.4	34.7	
Ulva sp.	43.9	16.3	1.9	30.7	
Rhizoclonium riparium	29.53	12.77	0.28	37.62	Chirapart et al., 2014
Ulva intestinalis	48.97	10.59	0.62	20.65	
Caulerpa racemose	83.2	18.3	19.10	N/A	Rameshkumar et al., 2013
Caulerpa lentillifera	44-46	11-12	1-2	N/A	Anbuchezhian et al., 2015
Ulva lectuca	70	7.06	1.64	N/A	
Ulva linza	37.4	31.6	1.8	29.2	Jang et al., 2012a
Ulva pertusa	59.07	6.30	2.39	22.86	Jang et al., 2012b
Brown Algae (Phaeophyceae)					
Bifurcaria bifurcate	N/A	10.92	5.67	34.31	Gomez-Ordonez et al., 2010
Hydroclarthus clathratus	82.26	6.39	2.18	6.47	Zafar & Chowdhury, 2009
Laminaria sp.	60	12	2	26	Fasahati et al., 2015
Laminaria hyperborea	50-52	8.9	<1	N/A	Anbuchezhian et al., 2015
Laminaria japonica	61 - 17	7 – 10	7 – 11	14 – 21	Xu et al., 2014
	50.6	10.5	37.3	1.6	Pham et al., 2013

Macro Algae	Carbohydrates	Protein	Lipids	Minerals	Reference
	54.5	7.40	1.37	28.33	Jang et al., 2012b
Sargassum fulvellum	44.5	19.9	0.5	35.1	Jang et al., 2012a
Sargassum vulgare	61	13.6	0.491	N/A	Anbuchezhian et al., 2015
Sargassum thunbergi	40.3	14.5	0.2	26.3	Li et al., 2012
Undaria pinnatifida	46.5	18.2	1.8	28	Cho et al., 2013
Red Algae (Rhodophyceae)					
Gelidium amansii	74.7	18.3	0	7.4	Jang et al., 2012a
	52.84	10.19	7.44	2.52	Malihan et al., 2014
Gracilaria Salicornia	46.22	16.28	1.69	13.49	Chirapart et al., 2014
Gracilaria tenuistipitata	54.89	6.11	0.26	22.91	
Grateloupia elliptica	59.5	13.4	1.1	26	Pham et al., 2013
Ochtodes secundiramea	45	10.10	3.5	N/A	Gressler et al., 2011
Plocamium Brasiliense	52	15.47	3.6	N/A	

N/A: Data not available

2.3 Hydrothermal Carbonization (HTC)

2.3.1 Background

The hydrothermal processing sometimes referred to as the hydrothermal upgrading, is relatively a new and versatile thermochemical process, in which characteristics of the products of the process, i.e., solids, liquid, and gases depend strongly on the feedstock and the process conditions, mainly temperature and time. The first published study on hydrothermal carbonization was conducted in 1911 by Freidrich Bergius (Bergius, 1932). The intention was to produce hydrogen via oxidation of carbon material using water as a reaction medium under high pressure (200 bars) and temperature below 600 ℃ to avoid the formation of carbon dioxide (CO_2). A vital observation that was noted through this experiment is when peat was used as the feedstock of this process. When peat was processed through hydrothermal treatment, a large amount of carbon monoxide (CO) was released, and the solid residues of the process had the elemental composition close to natural coal. Through this ground-breaking discovery, Bergius continued the research further, exposing the purpose of the hydrothermal carbonization of biomass which is to transform the biomass to carbon-rich solid, with marginal gaseous emissions, by processing the raw biomass with water at elevated pressure and mild temperature 180 ℃ – 250 ℃) (Bergius, 1932). In 1950, van Krevelen revealed the similarities between hydrothermal precursors and their respective hydrothermally processed carbons by proposing a graphical-statistical method to analyze H/C and O/C atomic ratios (van Krevelen, 1950). His model suggests that by plotting H/C atomic ratios against O/C atomic ratios, directional lines presenting the processes of demethanation, decarboxylation, dehydration, hydrogenation, and oxidation can be drawn between reactants and products.

By using such plot, which is widely regarded as van Krevelen diagram, Schuhmacher et al. investigated the carbon-rich solid products that were produced from the HTC of glucose and cellulose (Schuhmacher et al., 1960). They found that glucose is formed as an intermediate during the HTC of cellulose, and resultant solid products from both glucose and cellulose have almost indistinguishable H/C and O/C ratios when compared with each other. Thus, they concluded that both compounds undergo identical carbonization reactions.

After these initial studies, due to the oil crisis in the 1970s, the focus of the researchers shifted towards the production of high-value liquid products to find a better replacement for crude oil and derived products. These resulted in a great number of publications that intended to transform lignocellulosic biomass into liquid products by using hot compressed water as a reaction medium; such processes were labeled as a hydrothermal treatment or as a rather recent term - hydrothermal liquefaction (Latham, 2016). Nonetheless, the recent research activities show the progressive development of the HTC process for producing the carbon-rich solid (hydro-char) that have several value-added applications for the industries and environment (Ando et al., 2000; Falco et al., 2011; Titirici & Antonietti, 2010; Funke & Ziegler, 2010; Titirici et al., 2012; Arellano et al., 2016; Kambo & Dutta, 2015; Sevilla & Fuertes, 2009; Sevilla et al., 2011; Brun et al., 2013; Acharya et al., 2015; Kumar et al., 2018; Park et al, 2018; Fang et al., 2018; Bhatt et al., 2018).

Hydrothermal carbonization (HTC) differs significantly than hydrothermal liquefaction (HTL). While the product of interest for an HTC process is the carbon-rich solid (hydro-char), HTL focuses on producing a liquid product (bio-oil) that is a deoxygenated viscous product, like petroleum crude (Kumar et al., 2018; Basu, 2018). Moreover, the temperature

of the HTC process is generally in the range of 150 ℃ to 260 ℃, but the HTL is operated at moderately high temperatures (280 ℃ – 350 ℃) (Kumar et al., 2018; Basu, 2018). Besides HTC and HTL, there is an another process called hydrothermal gasification (HTG) or supercritical water gasification (SCWG), in which the feedstock is converted mainly into H_2, CO, and CH_4 gases at an elevated temperature ranging from 350 ℃ to 500 ℃ (Kumar et al., 2018; Basu, 2018). Although the processing conditions and fate of products differ substantially in all three processes, they work on the same principle that is decomposing a carbon-containing compound, typically biomass, in subcritical (HTC & HTL) or supercritical water (HTG). The classification of the hydrothermal processes with respect to the temperature and pressure is shown in Figure 2.4. The thesis aims to produce a solid product from the seaweed; therefore, only HTC is discussed in this study. More details of HTL and HTG can be found in the review done by Kumar et al. (Kumar et al., 2018), and in the book by Basu (Basu, 2018).
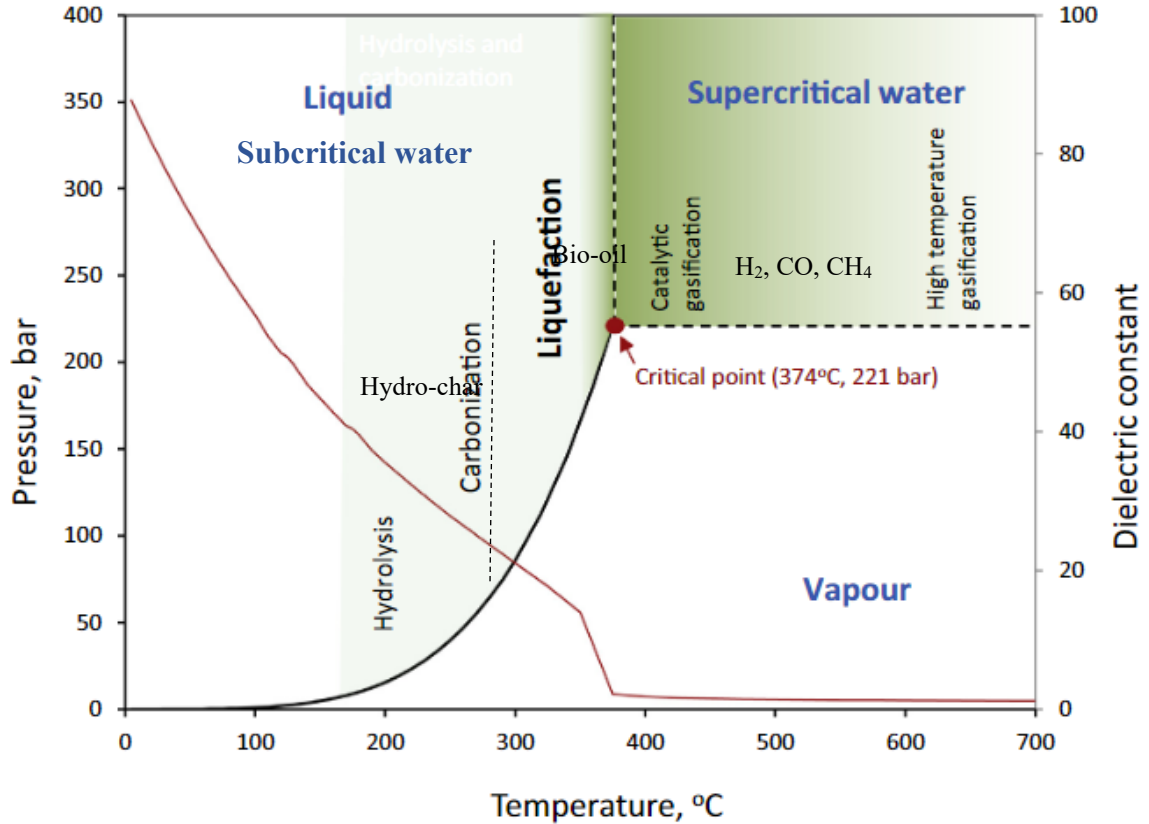
Figure 2.4 Classification of hydrothermal processes to reaction temperature and pressure.

(Adapted and modified from Tran, 2016)

2.3.2 Hydrothermal Carbonization (HTC) of Biomass

Hydrothermal carbonization (HTC), sometimes referred to as wet torrefaction, upgrades biomass into coal-like solid known as hydro-char. The HTC is operated under pressurized, inert, and aqueous environment at a relatively lower temperature (180 ℃-260 ℃) than other thermochemical processes. Reaction time for the process has been reported to be 5 minutes to several hours. Generally, the pressure is uncontrolled and is autogenous with the saturation vapor pressure of water corresponding to the temperature of the process, thus water is kept subcritical condition (in liquid form) throughout the HTC process. (Fuertes et al., 2010; Funke & Ziegler, 2010). As the HTC process uses subcritical water as reaction

medium, which can act as both reactant and solvent depending on operating conditions (Ando et al., 2000), HTC does not require pre-drying of wet biomass; thus increasing the energy efficiency the process. The resultant products of HTC process are a wet slurry, which is a two-phase mixture of solid (hydro-char) and liquid (processed water), and a very small fraction of gases (mainly CO_2 with some traces of CO and H_2). Consequently, the wet slurry requires a series of steps like mechanical dewatering, filtering, or drying to separate the hydro-char from the processed water, before using the hydro-char as fuel. However, the post-drying in the HTC process is less energy-intensive than the pre-drying which is required in torrefaction or pyrolysis, because more than half of the separation of the solid and liquid products of HTC process can be achieved by compression only (Mensinger, 1980).

Furthermore, the properties and composition of hydro-char are significantly different from the biochar that is produced from torrefaction or pyrolysis (Kambo & Dutta, 2015; Manya, 2012; Fuertes et al., 2010). Yan et al. reported that, for the equivalent mass yield, the hydro-char pre-treated at the reaction temperature of 260 ℃ has higher energy density than the torrified biochar which was pre-treated at 300 ℃ (Yan et al., 2009). Owing to high conversion efficiency, elimination of energy-intensive drying, and relatively lower operating temperature, HTC is the most suitable and recommended process over other thermochemical processes like torrefaction and pyrolysis, especially for processing highly moist biomass feedstocks such as algal biomass and sewage sludge.

During HTC, hemicelluloses and cellulose are hydrolyzed to oligomers and monomers, while lignin is mostly unaffected (Libra et al., 2011; Funke & Ziegler, 2010). The hydro-char has reduced moisture content (dry basis) than that of the raw biomass, so the hydro-

char is less likely to rot in the storage (Acharjee et al., 2011). The hydro-char is quite friable and might be able to be molded into pellets that can be fed to a gasifier or coal power plant easily (Reza, 2011). The hydro-char has a lower H/C and O/C atomic ratios than the raw biomass, and the reduction in the atomic ratios of a hydro-char depends primarily on the HTC process conditions, i.e., the reaction temperature and the reaction time. Moreover, the composition and surface functional groups of hydro-char depend on the HTC reaction temperature and reaction time, too (Fuertes et al., 2010; Nizamuddin et al., 2017; Funke & Ziegler, 2010). Bach et al. observed that increasing the pressure slightly above the saturation pressure of water increases the hydro-char yield, but it did not affect the higher heating value (HHV) of the hydro-char; further increase in pressure affected neither the hydro-char yield nor the HHV (Bach et al., 2013). The effect of the pressure in the HTC process has yet to be explored in-depth. The HTC of biomass that is ground to smaller particles results in hydro-char with larger particles due to the condensation reactions that occur during the HTC process (Parshetti et al., 2013). However, the effect of particle size has yet to be studied extensively. Such hindrances in determining the optimum parameters for HTC of biomass can be attributed to the varying chemical and physical structures among the wide variety of biomass, and they can be reduced only by conducting extensive research on HTC of different biomass. Nevertheless, it is found from the existing literature that both the reaction temperature and the reaction time significantly affect the product yields and the physicochemical properties of the HTC products, the reaction temperature remains the decisive parameter though (Landais et al., 1994; Nizamuddin et al., 2017; Volpe et al., 2018; Pruksakit & Patumsawad, 2016; Kambo & Dutta, 2015; Gao et al.,

2016; Li et al., 2018; Reza et al., 2014; Roman et al., 2018; Liu et al., 2013; Xu et al., 2013; Xiao et al., 2012; Bhatt et al., 2018).

On the other hand, the processed water has two salient features. First, it is highly rich in key nutrients of feedstock such as potassium and phosphorus with lower content of magnesium and calcium, thus opening the doors to the probable recovery of these nutrients by reusing them as fertilizers (Smith & Ross, 2016). Other is, the processed liquid carries the organic compounds such as sugars, acetic acid, 5-HMF (hydroxyl-methyl-furfural), levunic acid, and furfural, which have leached from the biomass during HTC (Funke & Ziegler, 2010; Libra et al., 2011; Levine et al., 2013; Stemann et al., 2013) and can be used for energy recovery by producing bio-methane through anaerobic digestion (Bhatt et al., 2018; Danso-Boateng, 2015; Smith & Ross, 2016); thus, aiding to the energy recovery by hydro-char. Few researchers have investigated the effects of the addition of salts and acids, and they found that the chemical properties of hydro-char improve by doing so (Lynam et al., 2011; Lynam et al., 2012). However, care must be taken as it exposes the walls of the reactor vessel to a possible threat of denting.

2.3.3 Role and Importance of Water in HTC

The thermochemical processes aim to breakdown the biomass structure into small and low molecular weight chains. The rate of degradation of the polymeric structure of biomass primarily depends on the reaction temperature and the reaction time. (Tumuluru et al., 2011).

Water is selected as a reaction medium for hydrothermal treatments because it is a cheap and non-toxic liquid, which is available in abundance in the mother nature. Moreover, the critical point for water, as can be seen in the phase diagram (Figure 2.4), is at 374 °C and

221 bars. Liquid water below the critical point is subcritical, which remains in the liquid form and acts as a non-polar solvent that exhibits greater solubility for organic and inorganic compounds of biomass during the HTC process. In addition to that, under high temperature and high-pressure conditions, water has a high degree of ionization, and it starts dissociating into acidic hydronium ions (H_3O^+) and basic hydroxide ions (OH^-), thus exhibiting both acidic and basic characteristics (Kalinichev & Churakov, 1999). The dielectric behavior of water at 200 ℃ is similar to that of methanol at ambient conditions (Kritzer & Dinjus, 2001).

The inorganic impurities in the biomass leach in the processed water of HTC and such demineralization reduce the ash yield in the hydro-char, which is not the case while processing biomass through other thermochemical processes like torrefaction (Kambo & Dutta, 2015). Subcritical water that is used as a reaction medium initiates the reaction mechanism by hydrolysis, thus lowering the activation energy level of biomass polymers such as hemicelluloses and cellulose (Fakkaew et al., 2015; Heidari et al, In Press). Consequently, these polymers are rapidly depolymerized into water-soluble products like oligomers and monomers at relatively lower temperatures (Libra et al., 2011; Reza et al., 2013a; Bobleter, 1994; Funke & Ziegler, 2010). Moreover, the degradation of biomass polymers also result in phenolic, organic, and furan compounds such as acetic acid, formic acid, glycolic acid, levulinic acid, and HMF (hydroxyl-methyl-furfural) that are found in the processed water (liquid product of HTC) (Libra et al., 2011; Levine et al., 2013; Funke & Ziegler, 2010; Stemann et al., 2013).

2.3.4 Chemical Reactions during the HTC Process

As mentioned in section 2.2.2, the hydro-char differs substantially from the biomass feedstock, and this difference can be explained by the series of reaction mechanisms that take place during an HTC process; which are hydrolysis, dehydration, decarboxylation, aromatization, and condensation (Funke & Ziegler, 2010; Libra et al., 2011; Heidari et al., In Press). It has been found that these processes occur in the order they have written, but they do not operate successively; they are interconnected with each other, thus occurring simultaneously during the HTC process (Funke & Ziegler, 2010; Libra et al., 2011). However, reactions that take place during HTC are yet to be fully understood because different components of a variety of biomass react at different rates, which, unfortunately, do not change proportionally corresponding to the change in operating condition (Minaret, 2015).

Among all the stated HTC reaction processes, hydrolysis has the lowest activation energy (Fakkaew et al., 2015; Heidari et al., In Press); therefore it can be stated the HTC reactions are primarily governed by the hydrolysis (Heidari et al., In Press). Due to hydrolysis, hemicelluloses in biomass start degrading at a lower temperature (180 ℃) compared to cellulose(200 ℃) (Funke & Ziegler, 2010; Libra et al., 2011). However, when reactions are coupled together, the degradation of cellulose occurs at lower temperature because the resulting products that are formed due to depolymerization of hemicelluloses, e.g., oligomers and xylose, increase the alkalinity of the solution, which aids in increasing the reaction rate for cellulose by reducing the activation energy required for cellulose reactions (Reza et al., 2013b). These authors also reported that, as HTC is generally operated above 180 ℃, the low degradation temperature of hemicelluloses results in the majority of

hemicelluloses being removed during the HTC process, resulting in the hydro-char with biodegradation properties similar to that of coal. As lignin remains stable at the temperatures below 260 ℃ (Zhang et al. 2008; Tumuluru et al., 2011), which is generally the maximum temperature at which HTC is performed, it can be stated that major decomposition of biomass in the HTC, operated below 260 ℃, is due to the chemical degradation reactions of hemicelluloses and cellulose only.

The next two reactions that take shape are dehydration and decarboxylation. Dehydration reduces moisture in biomass by removing the water from the biomass matrix, thus eliminating the hydroxyl groups from the biomass, thus releasing more water in the reaction medium. Decarboxylation is the process in which carboxyl and carbonyl groups are removed from the biomass structure, by the removal of CO_2 and CO. Both dehydration and decarboxylation aid in lowering the H/C and O/C atomic ratios from the hydro-char (Kambo & Dutta, 2015; Fang et al., 2018; Heidari et al., In Press). The removed single-bonded hydroxyl and carbonyl groups are then replaced by double-bonded functional groups such as C = O and C = C, leading to aromatization; thus, ultimately producing the furfural compounds that further break down into acids, aldehydes, and phenols due to hydrolysis. Ultimately, the acids generated at this stage catalyze the release of inorganic elements from the biomass into the water (Funke & Ziegler, 2010; Fuertes et al., 2010; Stemann et al., 2013). The last but important reaction in the HTC process is condensation. The compounds that are created during other HTC reactions undergo condensation regarding to their reactivity (Libra et al., 2011; Funke & Ziegler, 2010). To cite an example, the aromatized polymers from cellulose degradation are highly reactive and participates in

the condensation process (Azharul Islam et al., 2015). Such condensation in the HTC process leads to the formation of the hydro-char (Libra et al., 2011).

2.4 Anaerobic Digestion (AD)

Anaerobic digestion (AD) is a widely accepted biochemical process, in which subsequent oxidations and reductions of organic material(biomass) in an anoxic (oxygen-free) environment result mainly into methane (CH_4) and carbon dioxide (CO_2) gases, which are, collectively, known as biogas. In this anoxic environment, oxidizing agents, such as dioxygen, nitrate, and sulfate, are depleted and replaced by carbon dioxide (CO_2), resulting in the formation of methane (CH_4) (Gerardi, 2003; Klass, 1998). Such energy conversion from biomass, through the production of CH_4 gas, makes the AD process economically viable (Poschl et al., 2010). Compared to aerobic digestion, anaerobic digestion exhibits greater capability of organic matter reduction. Moreover, it has been reported that the digestate (solid residue from the AD process) can be used as an organic fertilizer for arable land (Achinas et al., 2017; Tambone et al., 2010; Holm-Nielsen, et al., 2009), which further makes the AD process attractive for commercial applications.

Several factors affect the AD process, but temperature and digester configuration are more important for successful implementation of the AD process (Chen et al., 2008; Gerardi, 2003). Increased temperature has a positive effect on the metabolic rate of microorganisms and, therefore, the rate of decomposition of a substrate increases as temperature increases, until the optimum growth temperature is reached (Chen et al., 2008). However, AD at a temperature below and above optimum growth temperature will reduce the microbial activities, thus reducing the potential gas yield of the given substrate (Chen et al., 2008).

Generally, AD process can be divided according to two widely used temperature ranges: Mesophilic AD (35 – 37 ℃), and Thermophilic AD (55 – 70 ℃) (Mao et al., 2015; Gerardi, 2003). Thermophilic AD is faster than the mesophilic AD owing to faster reaction rates at high temperature. However, it produces acids which reduce the biogas yield. Further limitations in the thermophilic AD are less stability, more susceptibility to environmental conditions, and high cost due to higher energy input. (Mao et al., 2015).

On the other hand, digesters for carrying out the AD process have several designs with a wide variety of configurations. Optimal design and configuration differ according to the substrate to be used, in which growth-supporting media can be added depending on the application. The reactors can be operated in batch, or they can be of continuous feed type.

2.4.1 Microbiology of Anaerobic Digestion

The microbial decomposition in AD is referred to the process in which microorganisms grow by metabolizing organic material in an anoxic environment, thus producing methane gas. (Gerardi, 2003; Klass, 1998). This process can be divided into four phases: Hydrolysis, Acidogenesis, Acetogenesis, and Methanogenesis (Gerardi, 2003).

2.4.1.1 Hydrolysis

Hydrolysis is the rate-limiting phase of the AD process, in which hydrolytic and fermentative microorganisms break non-soluble polymers of the biomass into soluble organic compounds such as oligomers and monomers. Pretreatment of biomass if often recommended before AD to accelerate hydrolysis phase as complex biopolymers are less likely to undergo degradation (Gerardi, 2003; Klass 1998).

2.4.1.2 Acidogenesis

In this phase of AD, diverse facultative anaerobes and anaerobes degrade the compounds that are produced in the hydrolysis phase through many fermentative processes; carbon dioxide, hydrogen, organic acids, and alcohols are the primary products of this phase. (Gerardi, 2003)

2.4.1.3 Acetogenesis

Products, mainly fatty acids and alcohols, from the acidogenesis phase are converted into acetate (CH_3COO^-), carbon dioxide, and hydrogen in the acetogenesis phase. The bacteria that aid in this phase are regarded as acetogen because they primarily produce acetate (Gerardi, 2003; Klass 1998).

2.4.1.4 Methanogenesis

Methanogenesis is the final and crucial phase of the AD process. Methanogens, the bacteria that aid in methanogenesis, metabolize the substrates to produce methane gas through three pathways: acetotrophic, hydrogenotrophic, and methylotrophic (Gerardi, 2003). The names of pathways are derived from the chemical structure of the substrate that produces methane, and they can be understood as following:

a) **Acetotrophic pathway:** Acetate that is produced in the acetogenesis phase is metabolized to form methane and carbon dioxide gases. The chemical reactions can be written as follow (Gerardi, 2003):

$$CH_3COOH \rightarrow CH_4 + CO_2$$
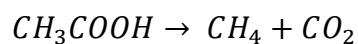
b) **Hydrogentrophic pathway:** Methanogens use hydrogen and carbon dioxide to produce methane gas and water. The chemical reactions can be written as follows (Gerardi, 2003):

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$
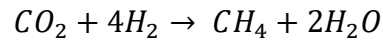
c) **Methylotrophic pathway:** Methanogens produce methane gas and water from the compounds that have a methyl group (-CH3), e.g., methanol. The chemical reaction of the process can be written as follows (Gerardi, 2003):

$$3CH_3OH + 3H_2 \rightarrow 3CH_4 + 3H_2O$$
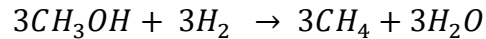
Furthermore, the methanogens are highly sensitive to the chemical and physical environment. Their performance is greatly affected by many factors such as temperature, retention time, agitation, pH, the concentration of carbon dioxide and ammonia, accumulation of volatile fatty acids (VFA), and presence of toxic compounds (Gerardi, 2003; Klass, 1998; Mao et al., 2015; Chen et al., 2008; Bacenetti et al., 2013; Karakashev et al., 2005).

2.5 Knowledge Gaps

It is clear from the section 2.1.1 that majority of the research regarding hydrothermal processing of algal biomass have been carried out for microalgae. In a latest review on the

algae-based biofuels, it was reported that the production of liquid fuels from the microalgae had been a prime focus for the majority of the researchers (Adeniyi et al., 2018). However, harvesting micro-algae is difficult and expensive than macroalgae or seaweeds. Moreover, due to the very small size of microalgae, their biomass yield is very low than that of seaweeds for a given amount of harvested algae. Such reasons have promoted the interest of researchers for using macroalgal feedstocks to produce biofuels, and the results have been getting published. These works from academia are in infancy, though; therefore, many challenges are yet to be overcome regarding the value of final products (Sudhakar et al., 2018).

Hydrothermal carbonization (HTC) process is relatively under-explored than hydrothermal liquefaction. Sudhakar et al., in a recent review of marine macroalgae as bioresource, have reported that liquid and gaseous fuels are the top priority to the researchers for using macroalgae as feedstock (Sudhakar et al., 2018). Moreover, no statement regarding the HTC process of macroalgae, whatsoever, was found in this review. Very few results are available to produce solid biofuel through the HTC process. The HTC process of biomass can provide much-needed insights into the suitability of macroalgal feedstocks for producing solid biofuel (hydro-char) that have properties like coal and the processed water, as a by-product, which contains minerals and organic compounds degraded from the macroalgae.

Golueke et al. published a study on the anaerobic digestion of algae in 1957 (Golueke et al., 1957). Since then, the potential of algae to produce biogas has been studied extensively, and the development in technologies, through these years, have solved many technical challenges associated with the AD process of algae. Consequently, AD of seaweeds or

macroalgae has also progressed excellently, and some technologies are/will be running at commercial-scale to produce energy through AD of the seaweed (SeatechEnergy, 2016; SeaGas, 2017).

The potential of the processed water of HTC to produce biogas was suggested first by Libra et al. (Libra et al., 2011), which is rather a recent time. Since then, only eight studies, which attempts to produce biogas from the processed water of HTC, have been reported in the literature (Wirth & Mumme, 2013; Oliveira et al., 2013; Poerschmann et al., 2014; Wirth et al., 2015; Erdogan et al., 2015; Danso-Boateng et al., 2015; Wirth & Reza, 2016; Smith & Ross, 2016). Hence, more comprehensive studies are required to investigate the potential methane yield from the liquid product of HTC, i.e., the processed water. Unfortunately, among these eight studies, just one study by Smith & Ross attempts to explore the potential of the processed water that has been obtained through HTC of the seaweed (Smith & Ross, 2016). However, they have only identified the theoretical yield for methane through a statistical approach. Thus, no results on the actual or experiment-based biogas yield from the processed water, which is obtained through HTC of the seaweed, have been reported to date.

Hence, HTC of the seaweed is examined, which is mentioned in the following chapters, to find the potential of the seaweed to produce coal-like solid (the hydro-char). Then, the potential of the processed water (liquid product) from HTC to produce biogas is also identified through an experimental study.

Chapter 3. EXPERIMENTS AND METHODOLOGY

The chapter provides a detailed description of the experimental setup and methodology used to obtain the results for this thesis. Firstly, the feedstock preparation, the instrument, and the experimental setup are presented. Subsequently, the methodology for the HTC process is introduced. Finally, after separation of products through gravity filtration, analytical techniques for the product yield, energy analysis of the hydro-char, proximate and ultimate analysis of the hydro-char, H/C-O/C atomic ratios of the hydro-char, inorganic material analysis of the hydro-char, and nutrient analysis of the processed water from HTC process, are described. All the experiments and analyses, except inorganic material analysis of the hydro-char and nutrient analysis of the processed water, discussed in this chapter were performed in Bioresources and Food Processing Laboratory at the Faculty of Sustainable Design Engineering in University of Prince Edward Island, Canada. The mineral (inorganic elements) analysis of the hydro-char and the nutrient solution analysis of the processed water were carried out by Prince Edward Island (PEI) Analytical Laboratories, Charlottetown, PE, Canada.

3.1 Experimental Material

3.1.1 Material: Collection and Storage

The waste seaweed growing on the surface of seawater near Summerside, Prince Edward Island, Canada was considered for this study. The same can be seen in Figure 3.1(a). Fresh seaweed was manually harvested in October 2017. For long term storage purpose, the seaweed was dehydrated in a commercially available dehydrator, as shown in Figure 3.2(a),

at 70 ℃ for 3 hours; then it was ground in a commercially available grinder, to coarse powder as shown in Figure 3.2(b). As the size of the particles is not of much importance for this research, particle size was not measured. Finally, the ground seaweed was stored in a sealed plastic bag and kept inside the commercial refrigerator until HTC treatment.

(a) The growth of waste seaweed on the surface of seawater in the town of Summerside, PE, Canada

(b) Manual harvesting of seaweed

(c) Freshly harvested seaweed

Figure 3.1 Photographs of seaweed used for the research

(a) Dehydrator for the seaweed

(b) Ground seaweed (Used for the experiments)

Figure 3.2 Photographs on dehydration of seaweed

3.1.2 Feedstock Preparation

The feedstock for every reaction was prepared just before the instance of the experiment. Three sets of experiments were performed. For the first two sets of experiments, 15 g of seaweed and 135 ml of deionized water were added in the reactor container. For the third set of experiments, 20 g of seaweed and 180 ml of deionized water were added in the reactor chamber. Thus, 1:9 (w/v) solid to water ratio or feedstock load was maintained for all the experiments performed throughout the research. The seaweed was weighed using the Cole-Parmer® Symmetry™ PA 220 balance with a tolerance of ±0.0001 g. The volume of deionized water was measured using a glass graduated cylinder of capacity 100 ml with 1 ml graduation marks. In all sets of the experiments, the mixture was manually stirred to ensure total wetting of the seaweed before closing the lid of the reactor container. The prepared feedstock that is ready for the experiments can be seen in Figure 3.3.

Figure 3.3 Photograph of prepared feedstock in the reaction container

3.2 Experimental Methodology

3.2.1 The Batch Reactor

The batch reactor system with a magnetic stirrer (PARR 4571 High-Temperature/High-Pressure Reactor System with a 4848 reactor controller, PARR Instrument Company, Moline, IL, USA) was used to carry out HTC process of the seaweed. It is a benchtop reactor, with a movable head mounted on the movable cart; the maximum temperature and pressure limits of the reactor are 500 ℃ and 34.47 MPa respectively. The reactor container is made of T316 Stainless Steel, and it is of 1000 ml capacity. A heavy lid can seal the reactor container with 12 compression bolts, along with a graphite or PTFE(Polytetrafluoroethylene) gasket inside the movable head. Besides the gasket, the movable head of the reactor consists of the magnetic drive stirrer, gas valves, a pressure gauge, two cooling coil ports for moving the external cooling fluid, and one internal

cooling line for cooling the shaft bearings of the magnetic drive stirrer. The temperature inside the reactor and RPM of the electric motor for the magnetic drive stirrer can be controlled using the 4848 controller system, which is a Proportional Integral Derivative (PID) controller system. The reactor system with the controller box, and the reactor vessel with a movable head are shown in Figure 3.4(a) and Figure 3.4(b) respectively.

(a) Batch reactor system with the controller
(PARR 4571 High-Pressure High-Temperature
Reactor System with PARR 4848 Reactor Controller)

(b) The reactor container and the movable head

Figure 3.4 Photographs of the instrument used for the HTC process

3.2.2 Hydrothermal Carbonization (HTC) of the Seaweed

3.2.2.1 HTC Process

HTC of the feedstock, with a load ratio of 1:9(w/v), was carried out in the batch reactor

system discussed in section 3.2.1. After sealing the reactor container, one of the gas valves

on the movable head was connected to a nitrogen tank to allow entry of nitrogen gas at a

pressure of 0.69 MPa in the reactor. Thus, the pressurized nitrogen gas purged the air out

from the other gas valve on the movable head. Purging is necessary to provide an inert

reaction atmosphere for the HTC process so that the water inside the reactor is maintained

above its saturated vapor pressure from the beginning of the HTC process, thus preventing

the infinitesimal probability of combustion of the seaweed. The heater was then turned on,

and the desired temperature was set using the controller box. The temperature inside the

reactor was continuously monitored and controlled by the PID controller system attached

to the batch reactor. It took about 55 mins, 70 mins, and 80 mins for the heater to reach the

setpoint temperature of 180 ℃, 200 ℃ and 220 ℃ inside the reactor. The reaction/residence time of the HTC process was calculated once the temperature inside the reactor reached to the desired value for the experiment. As a higher value of temperature would require longer heating time for the reactor, the time interval while the reactor is heated up could play a vital role in the HTC reaction. However, the study presented in this thesis defines the reaction temperature for the isothermal residence time only. On the other hand, the reactor pressure was only monitored from the pressure gauge attached to the movable head, and it was not controlled in order to keep the pressure inside the reactor autogenic with the vapor pressure of the water at the corresponding temperature. The pressure indicated from the pressure gauge, mounted on the movable head of the reactor, were 1.72 MPa, 2.56 MPa, and 3.45 MPa for the reaction temperature 180 ℃, 200 ℃, and 220 ℃, respectively.

The experiments were performed at three different reaction temperature (180 ℃, 200 ℃, 220 ℃) and three different reaction/residence time (30 mins, 60 mins, 120 mins) to study the effect of the reaction severity, i.e., the operating conditions on the seaweed. After the desired reaction/residence time, the heater was turned off and the valve for the external cooling loop, connected with a domestic cold-water line, was opened to cool the reactor quickly for preventing further reactions. Although it took about 3 hours for the temperature inside the reactor to reach down to the room temperature, it only took 2-4 minutes for the temperature inside the reactor to drop below 150 ℃. It is vital because neither the chemical nor the organic decomposition of biomass is seen below 150 ℃ (Tumuluru et al., 2011). Once the temperature inside the reactor reached room temperature, the gas valve was opened to release the gaseous products. Then, the compression bolts were unscrewed, and the movable head was removed. The two-phase mixture of solid and liquid products of the

HTC process, also called the wet slurry, was then transferred to a glass beaker, and the weight of the slurry was noted. As mentioned in section 3.1.2, three sets of the experiments were performed, and the average value of the results is taken into consideration for further analysis of the products of HTC.

3.2.2.2 Product Separation

The principle of gravity filtration was applied to separate solid and liquid products of HTC from the two-phase mixture, i.e., the wet slurry. A commercially available paper coffee filter was used for this process. Figure 3.5 (a) presents the set-up used for the separation of the HTC products by gravity filtration. While the liquid product, i.e., the processed water can be seen from Figure 3.5 (a), the solid product, i.e., the wet hydro-char, after the filtration, is depicted in Figure 3.5(b). The weight of the wet hydro-char, solid product in the filter, was recorded, then the hydro-char was transferred to the oven for drying. All the hydro-char samples were dried overnight at 105 ℃, then each dried sample, after weighing, was transferred to a falcon tube for storing the sample in the refrigerator before further analyses. On the other side, the volume of the processed water was noted for all samples, and each liquid sample was then transferred to a falcon tube for storing the sample in the refrigerator before further analyses.
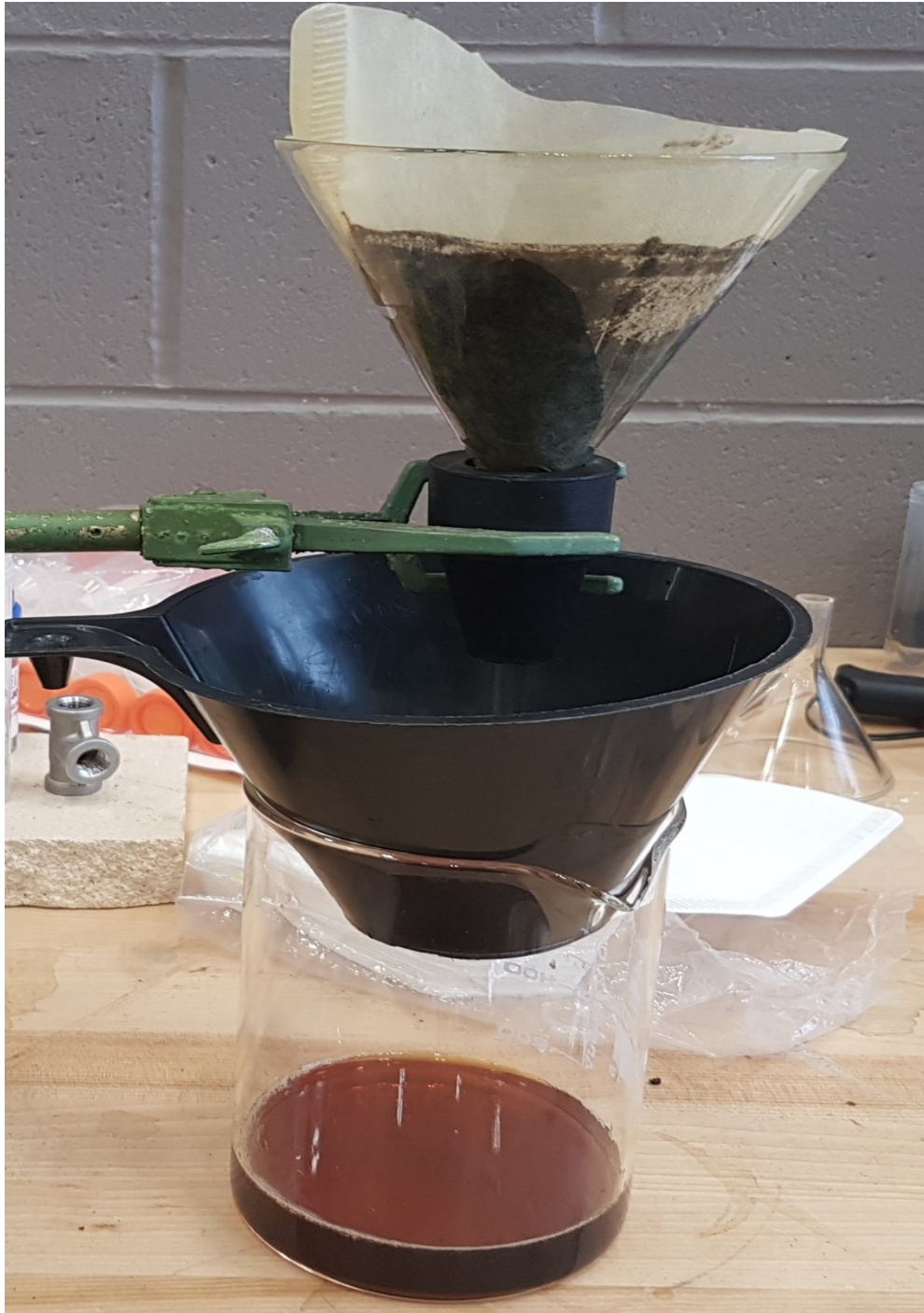
a) Gravity-Filtration setup

b) Wet hydro-char after separation

Figure 3.5 Separation process for the final products from HTC

3.3 Product Analyses

3.3.1 Proximate Analysis of the Hydro-Char

To determine the percentage of moisture content, ash content, volatile matter, and fixed carbon in the solid product, i.e., the hydro-char, the proximate analysis of the hydro-char was carried out as per ASTM (American Society for Testing and Materials) standards in a muffle furnace (Cole-Parmer StableTemp OF–33858–60, Cole-Parmer Canada Company, Montreal, QC, Canada; the same is depicted in Figure 3.6). The standards ASTM-E871, ASTM-E1755, ASTM-E872, were followed for moisture analysis, ash analysis, and volatile matter analysis, respectively. The percentage of fixed carbon is calculated by subtracting the percentage of moisture content, ash content, and volatile matter out of 100%. All the analyses were performed at least thrice, and the mean value of the results has been taken into account for further discussions.

For the moisture analysis, 1 ± 0.0001 gm of a hydro-char sample was taken into a ceramic crucible. The crucible was then kept in the pre-heated (105 ℃) muffle furnace for an hour. After an hour, the crucible was moved to a desiccator to avoid interference by the atmospheric moisture until the temperature of hydro-char reaches to the room temperature. Then, the crucible was re-weighed, and the change in the initial and the final weight of the crucible is expressed as the moisture content (ASTM- E871) in the hydro-char sample.

For the ash analysis, the crucible with a sample treated for moisture analysis was placed in the muffle furnace, and the furnace was heated to 250 ℃ for an hour. It was then heated to 575 ℃ for an hour, and finally, it was kept at 575 ℃ for two hours. After that, the crucible was moved to the desiccator for calculation of the ash percentage according to ASTM-E1755.

For the volatile matter in a hydro-char sample, the crucible with a sample treated for moisture analysis was transferred to the muffle furnace, which was pre-heated to 950 ℃, and it was kept in the furnace for 7 minutes to calculate the volatile matter in the sample according to ASTM-E872.

Figure 3.6 Muffle Furnace which was used to carry out the proximate analysis of the hydro-char samples (Cole-Parmer StableTemp OF–33858-60)

3.3.2 Ultimate Analysis of the Hydro-Char

The ultimate analysis is performed to calculate the percentage of carbon, hydrogen, nitrogen, sulfur, and oxygen in a given material. The ultimate analysis for the hydro-char samples was carried out using an organic elemental analyzer (Thermo Fisher Flash 2000 CHNS-O, Thermo Fisher Scientific, Waltham, MA, USA; depicted in Figure 3.7). The analyzer is integrated with a computer, which monitors and regulates the test runs as well as their results automatically after providing some pre-defined inputs in the software that is dedicated to the analyzer. After all the setup and inputs in the software, a maximum of 32 samples can be tested at an instance in this analyzer. Analysis for each hydro-char sample was performed twice, and the mean value of the results has been considered for further discussions.

Figure 3.7 CHNS-O Analyzer that is used to perform the ultimate analysis of the hydro-char samples (Thermo Fisher Flash 2000 CHNS-O)

3.3.3 Higher Heating Value of the hydro-char

The Higher Heating Value (HHV) for each of the hydro-char samples was calculated using the bomb calorimeter (Parr 6100 Calorimeter, PARR Instrument Company, Moline, IL, USA; depicted in Figure 3.8). Approximately 1 gm of the hydro-char sample was placed inside a steel vessel carrying 2000 gm of water. With the help of the external pressure valve connected to the oxygen tank, the vessel was then pressurized with oxygen to 3.11 MPa. The cotton thread, attached to the ignition wire on one end and the hydro-char sample on the other end, was then ignited. At the end of combustion, the computer system integrated

with the instrument records the higher heating value of the sample. The software, installed in the computer, calculates the HHV of a sample by considering the heat transfer due to the change in the temperature of the water inside the vessel. All the tests were performed twice, and the average value of the two results has been considered for further discussions.

Figure 3.8 The Bomb Calorimeter that is used for calculating the HHV of the hydro-char samples (Parr 6100 calorimeter)

3.3.4 Mineral (Inorganic Elements) Analysis of the Hydro-Char

The mineral analysis of the hydro-char was carried out by Prince Edward Island (PEI) Analytical Laboratories, Charlottetown, PE, Canada using atomic absorption spectroscopy following standard procedure (968.08) defined by the Association of Official Analytical Chemists (AOAC).

3.3.5 Nutrient Analysis of the Processed Water

The nutrient analysis and pH value calculations were performed by Prince Edward Island (PEI) Analytical Laboratories, Charlottetown, PE, Canada following standard procedure (200.7) defined by United Environmental Protection Agency.

CHAPTER 4. RESULTS AND DISCUSSIONS

4.1 Effect of the HTC Process Conditions on The Product Yields

During the HTC of biomass, solid, liquid, and gaseous products are formed. The product distribution and their physicochemical properties depend on the HTC process conditions (Yan et al., 2010). Several results on HTC of biomass are evidence that both the reaction temperature and the reaction time affect the product yields and the physicochemical properties of the HTC products, the reaction temperature remains the decisive parameter though (Landais et al., 1994; Nizamuddin et al., 2017; Volpe et al., 2018; Pruksakit & Patumsawad, 2016; Kambo & Dutta, 2015; Gao et al., 2016; Li et al., 2018; Reza et al., 2014; Roman et al., 2018; Liu et al., 2013; Xiao et al., 2012). As discussed in section 3.2.2.1, the HTC process of the seaweed resulted in gaseous products and a two-phase mixture of hydro-char and processed water, i.e., the wet slurry. Then, the final products of HTC, the hydro-char, and the processed water were obtained through gravity filtration of the wet slurry. Table 4.1 shows the results of the product yields in the HTC experiments, which were performed to study the effect of two key process parameters: the reaction temperature and the reaction/residence time. The values provided in Table 4.1 are the mean values of three experiments with a maximum error value for each entry. As the analysis of gases is not part of this research, the gaseous products of HTC were allowed to escape through a fume hood; thus, they were neither collected nor measured. Howbeit, for yield calculation perspective, the gas yield is provided in Table 4.1, which is calculated by the difference. The yield of the other products, the solid (hydro-char) and the liquid (processed

water), and the mass yield (dry basis) of the seaweed, reported in Table 4.1, are calculated from the following expressions:

$$\text{Solid (The hydro} - \text{char) Yield} = \frac{\text{Mass of the solid after HTC}}{\text{Mass of the feedstock}} \text{ X } 100 \cdots\cdots (1)$$

$$\text{Liquid (The processed water) Yield} = \frac{\text{Mass of the liquid after HTC}}{\text{Total mass of the feedstock}} \text{ X } 100 \cdots (2)$$

$$\text{Gas Yield} = 100 - (\text{Solid Yield \% + Liquid Yield \%}) \qquad \cdots\cdots\cdots\cdots\cdots\cdots\cdots (3)$$

$$\text{Mass Yield} = \frac{\text{Mass of the dried solid after HTC}}{\text{Mass of the dried, raw seaweed}} \text{ X } 100 \cdots\cdots\cdots\cdots\cdots\cdots (4)$$

Table 4.1 The Yield of the Products in the HTC process

Process Parameters		Product Yields			
Temperature (°C)	Time (min)	Solid Yield (%)	Liquid Yield (%)	Gas Yield (%)	Mass Yield (%)
180	30	40.2±1.33	54±1.67	5.8±0.33	46.9±0.89
180	60	38.45±2.05	55±1.62	6.55±0.43	45.65±0.36
180	120	35.55±1.38	59±0.90	5.45±0.47	45.3±1.39
200	30	38±0.41	56±1.66	6±1.26	45.95±2.09
200	60	33.65±2.73	60±2.85	5.58±0.12	41.8±0.08

Process Parameters		Product Yields			
Temperature (°C)	Time (min)	Solid Yield (%)	Liquid Yield (%)	Gas Yield (%)	Mass Yield (%)
200	120	30.8±0.60	64.5±1.49	4.7±2.09	39.7±0.52
220	30	28.75±2.62	65±1.68	6.25±0.93	36.1±1.08
220	60	29.4±1.01	65.50±2.84	5.1±1.83	34.65±1.65
220	120	25.6±0.77	68.50±1.86	5.9±1.08	30.5±1.61

Solid (raw seaweed) to liquid (deionized water) ratio of the feedstock was 1:9 (w/v) for each experiment.

4.1.1 Effect of Temperature on the Product Yields in HTC

Figure 4.1 shows the effect of temperature on the product yields. From the chart, it is evident that the solid yield decreased to, about, 2-5 % as the reaction temperature increased from 180 °C to 200 °C. It further dropped to, about, 5-10 % as the reaction temperature increased to 220 °C. On the other hand, the liquid yield kept on increasing, about, 2-6 % by increasing the reaction temperature from 180 °C to 200 °C, and, about, 4-9 % by increasing the reaction temperature from 200 °C to 220 °C. Gas yield, however, remained nearly constant with the change in the reaction temperature. These trends of the product yields for the change in the HTC process conditions are consistent with the findings in the literature mentioned earlier in the section. Such trends are observed in the HTC process because the activation energy level of a biomass polymer reduces due to the presence of hot compressed water (Libra et al., 2011; Bobleter, 1994). Consequently, the thermal stability of a biomass polymer reduces, and the biomass is then degraded or depolymerized in the liquid and gaseous by-products stream (Funke & Ziegler, 2010; Pavlovic et al., 2013), resulting in the

mass loss of the biomass. Hence, it is reasonable to postulate that a higher process temperature in the HTC process triggers the decomposition of the solid compounds into the liquid and the gaseous by-products, causing the lower solid yield at the end of the process.
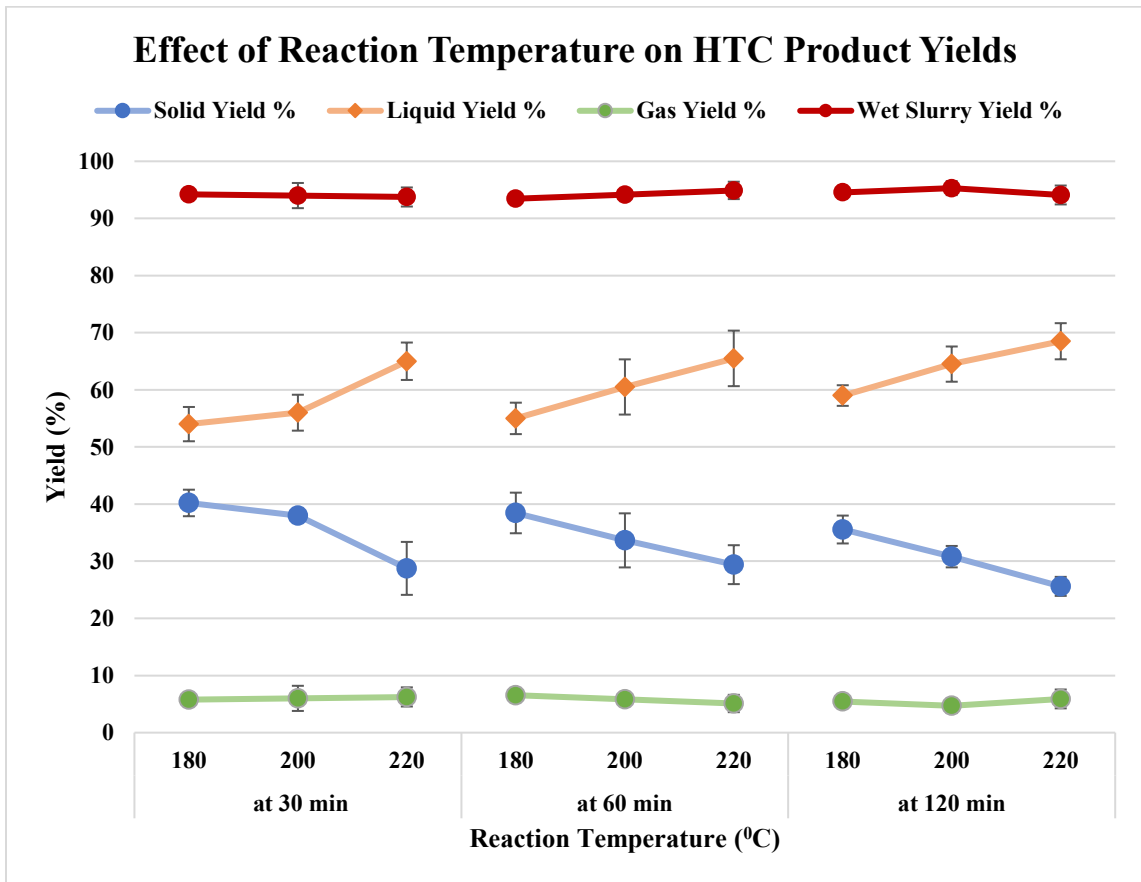
Figure 4.1 Effect of the reaction temperature on the product yields in HTC.

Like the solid yields, the mass yield (dry basis) of the hydro-char samples, as can be seen in Figure 4.2, reduced significantly as the temperature increased. At a given reaction time, the mass yield of the seaweed considerably reduced by 12-15 % with an increase in the reaction temperature from 180 ℃ to 220 ℃.
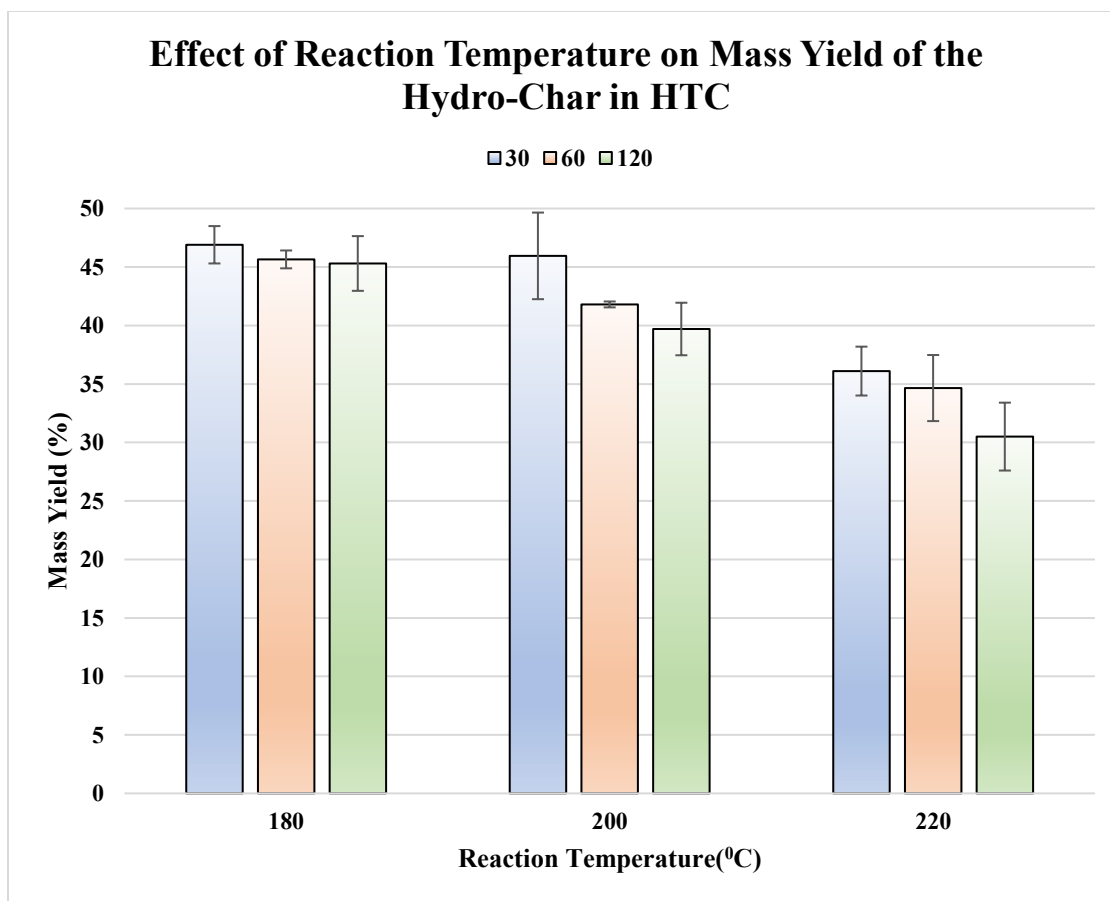
Figure 4.2 Effect of the reaction temperature on the mass yield of the hydro-char in HTC.

4.1.2 Effect of the Reaction/Residence Time on the Product Yields in HTC

Figure 4.3 depicts the trend of the product yields regarding the reaction/residence time. As can be seen, solid yield decreases as the reaction time increases from 30 minutes to 120 minutes. It was expected as longer reaction time can result in more reactions during the HTC of the seaweed, which in turn results in lower solid yield at a given temperature. Although this declining trend of solid yield is like the one due to change in the reaction temperature, yet it is less substantial than that of temperature.
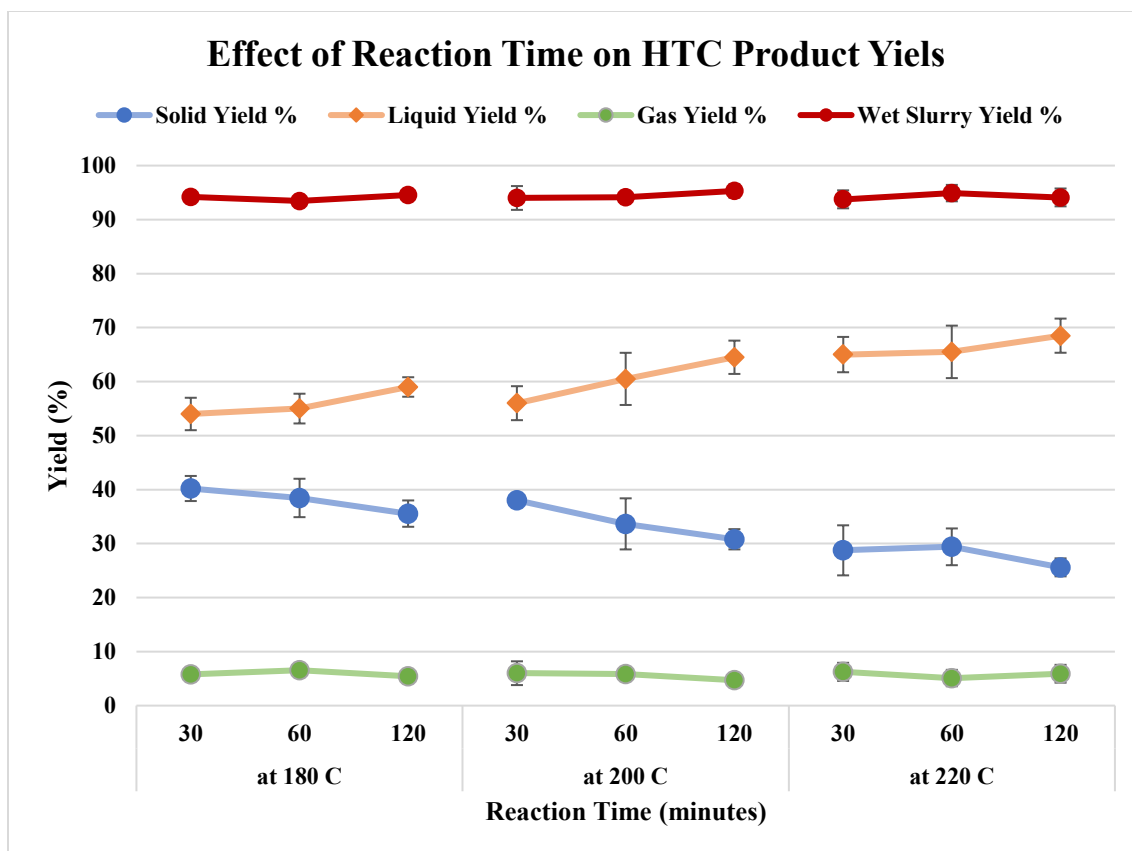
Figure 4.3 Effect of the reaction/residence time on the product yields in HTC.

Figure 4.4 shows the effect of the reaction/residence time on the mass yield of the seaweed in the HTC process. For a stable temperature, the mass yield of the seaweed decreased by, only about, 1.5 % at 180 ℃, when the reaction time increased from 30 minutes to 120 minutes. Whereas, the mass yield of the seaweed at 200 ℃ and 220 ℃ reduced significantly, about, 6 % when the reaction time increased from 30 minutes to 120 minutes. These findings show that at a higher temperature, the effect of the reaction/residence time on the mass yield of the hydro-char tends to get more severe.

Effect of Reaction Time on Mass Yield of the Hydro-Char in HTC
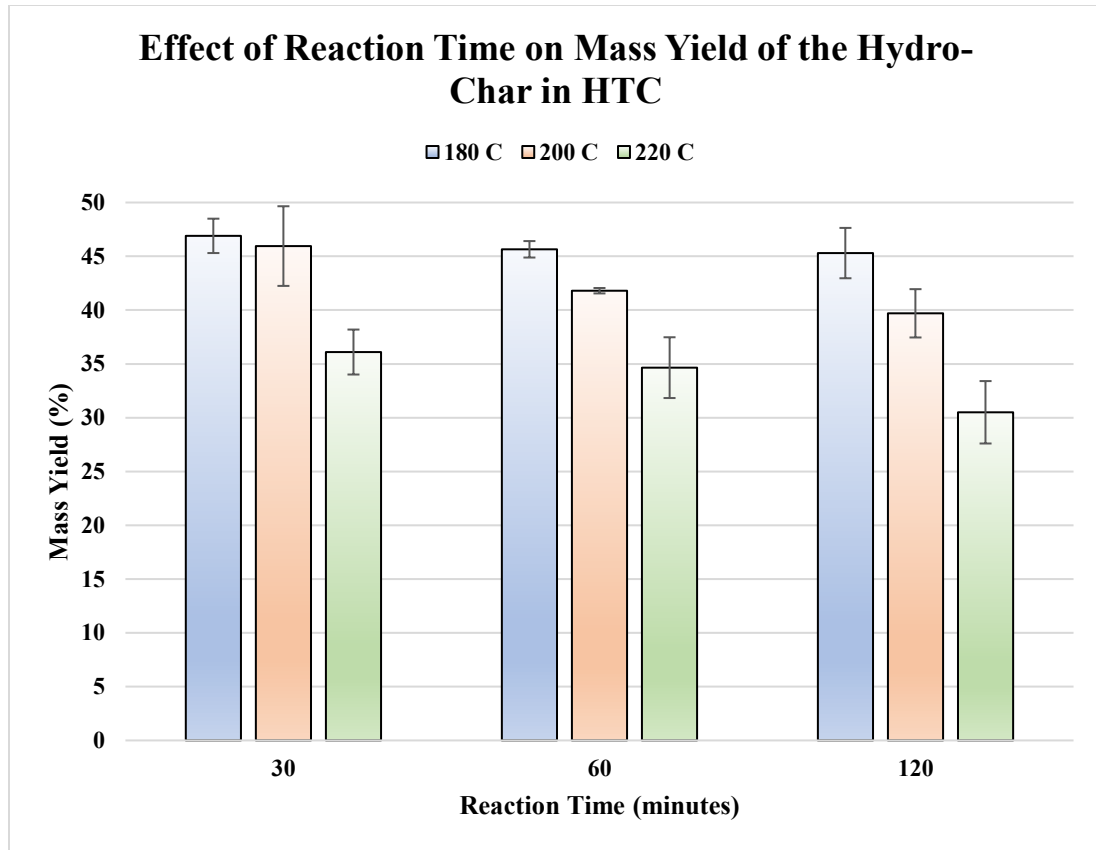
Figure 4.4 Effect of the reaction temperature on the mass yield of the hydro-char in HTC.

4.2 Effect of the HTC Process Conditions on HHV And Energy Yield of the Hydro-Char

Table 4.2 shows the energy analysis that was employed to investigate the effect of the reaction temperature and the reaction/residence time on energy properties, i.e., HHV and energy yield of the seaweed during the HTC process. The HHV provided in Table 4.2 is the mean value of the hydro-char samples from two experiments with a maximum error value for each entry. The higher heating value (HHV) of the dry hydro-char samples were measured using the bomb calorimeter, as mentioned in section 3.3.3. Energy Densification Ratio (EDR) and the energy yield are calculated from the following expressions:

$$\text{Energy Densification Ratio (EDR)} = \frac{\text{HHV of the product}}{\text{HHV of the raw seaweed}} \quad \cdots\cdots (5)$$

$$\text{Energy Yield} = \text{Energy Densification Ratio X Mass Yield} \quad \cdots\cdots\cdots (6)$$

Table 4.2 The Energy Analysis of the HTC Process

Process Parameters		Product Yields			
Temperature (°C)	Time (min)	HHV (MJ/kg)	EDR	Mass Yield (%)	Energy Yield (%)
180	30	13.81±0.26	1.13	46.9	53.09
180	60	15.76±0.71	1.29	45.65	58.97
180	120	16.63±0.32	1.36	45.3	61.75
200	30	16.39±0.61	1.34	45.95	61.73
200	60	17.58±0.27	1.44	41.8	60.23
200	120	18.12±0.06	1.48	39.7	58.96
220	30	17.55±0.39	1.44	36.1	53.11
220	60	18.27±0.25	1.50	34.65	53.51
220	120	18.93±0.24	1.55	30.5	49.65

HHV of the raw seaweed: 12.21±0.17 MJ/kg

Figure 4.5 and 4.6 show the effect of the reaction temperature and the reaction/residence time on the HHV, and the energy yield of the seaweed during the HTC process. It is evident from the graph that, the higher heating value (HHV) of the hydro-char samples increased with increasing the reaction temperature and the reaction time. Thus, the HTC process

produces energy-dense hydro-char with energy densification ratio (EDR) in the range of 1.13-1.55; that means the energy content of the hydro-char increased up to 55% than that of the raw seaweed during the HTC process. Xu et al. reported similar observations while working on the HTC of the macro-algae (Xu et al., 2013). While the HHV of all the hydro-char samples increased with increasing both the reaction temperature and the reaction time, the energy yield forwent the continuous trends, like the HHV, corresponding to the change in either the reaction temperature or the reaction time.

From Figure 4.5(a), it can be seen that by increasing the reaction temperature from 180 ℃ to 220 ℃, the HHV of the hydro-char increased by 27.08 % at the reaction time of 30 minutes, by 15.92 % at the reaction time of 60 minutes, and by 13.83 % at the reaction time of 120 minutes. On the other hand, as can be seen in Figure 4.5(b), by increasing the reaction time from 30 minutes to 120 minutes, the HHV of the hydro-char increased by 20.42 % at 180 ℃, by 10.55 % at 200 ℃, and by 7.86 % at 220 ℃. These findings suggest that the effect of the reaction temperature on HHV is more prominent for shorter reaction/residence time, and the reaction time is more influential at lower temperature. Nevertheless, for the extreme process parameters, i.e., 220 ℃ (the highest reaction temperature) and 120 minutes (the highest reaction time), the HHV of the hydro-char, as expected, was the highest.
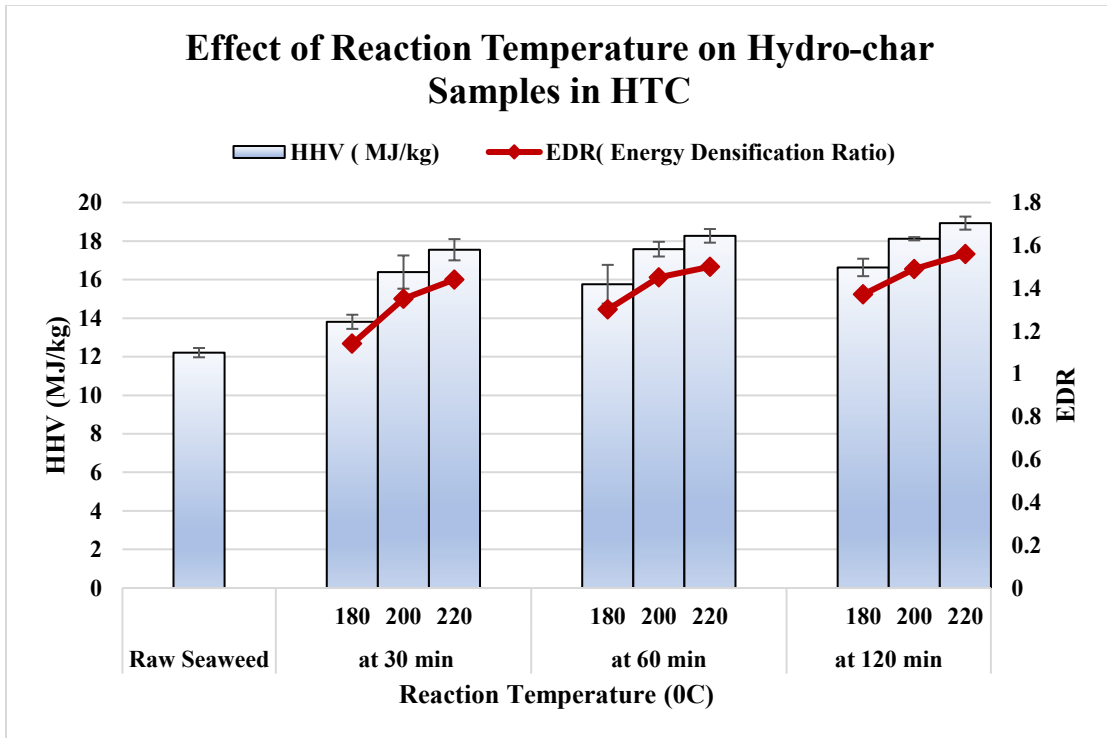
(a) Effect of the reaction temperature on HHV of hydro-char in the HTC
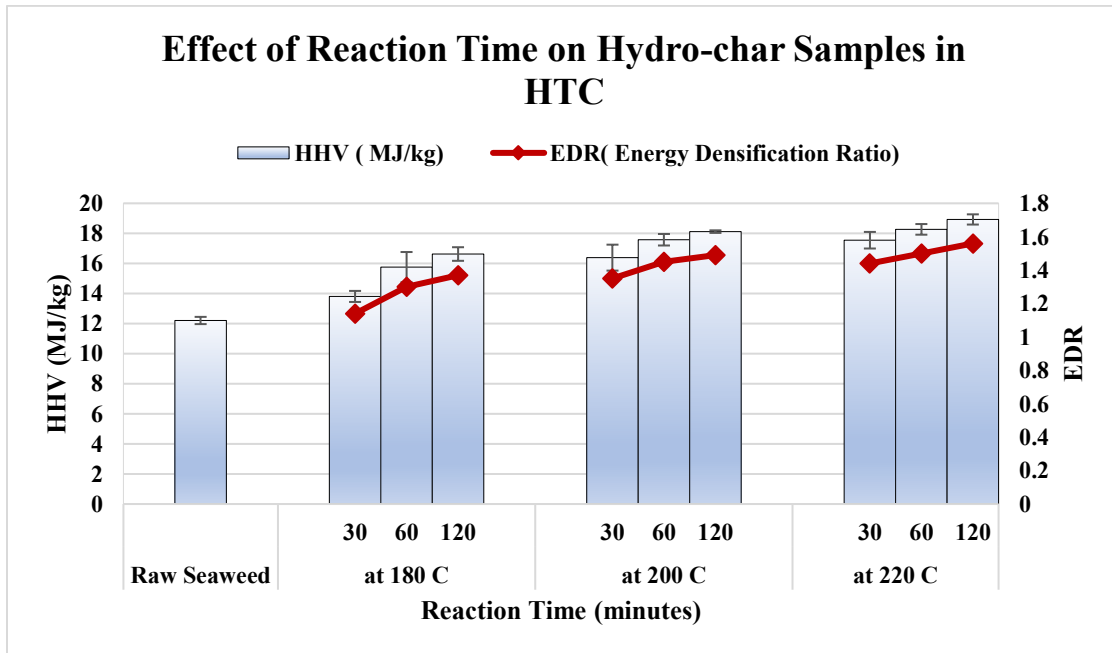
(b) Effect of the reaction time on the HHV of hydro-char in the HTC

Figure 4.5 Effect of the process conditions on the HHV of hydro-char in the HTC process.

From the Figure 4.6 (a), it can be observed that the energy yield of hydro-char increased by, about, 9%, by increasing the reaction time at 180 ℃. Contrary to which, at 200 ℃ and 220 ℃, the energy yield of hydro-char samples decreased by, about, 3%, by increasing the reaction time. At any given reaction time, as shown in Figure 4.6 (b), the energy yield of the hydro-char increased with an increase in temperature from 180 ℃ to 200 ℃, then it decreased with a further increase in temperature from 200 ℃ to 220 ℃. One plausible reason for these declining trends of the energy yield of the hydro-char at high reaction temperature can be the drastic reduction in the mass yield of the hydro-char at a reaction temperature of 220 ℃.
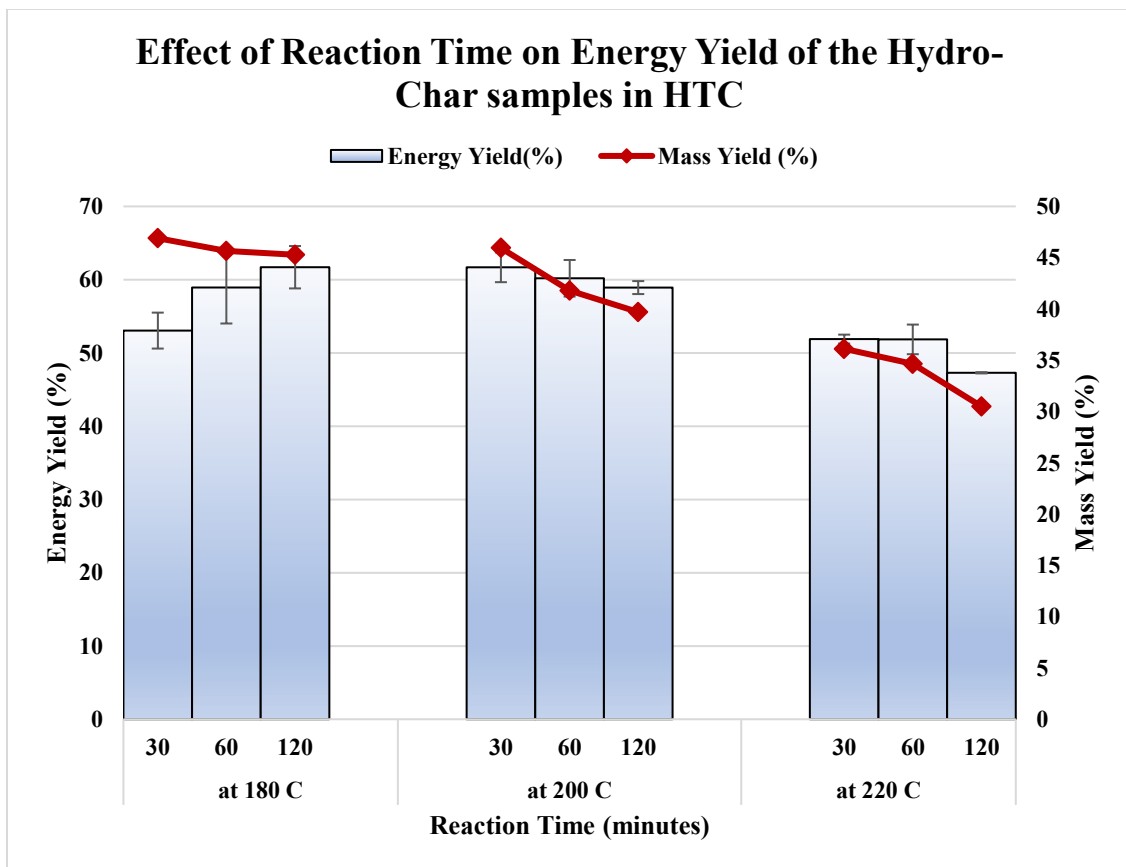
(a) Effect of the reaction/residence time on the energy yield of hydro-char in the HTC

Effect of Reaction Temperature on Energy Yield of the Hydro-Char samples in HTC

Energy Yield(%) Mass Yield (%)
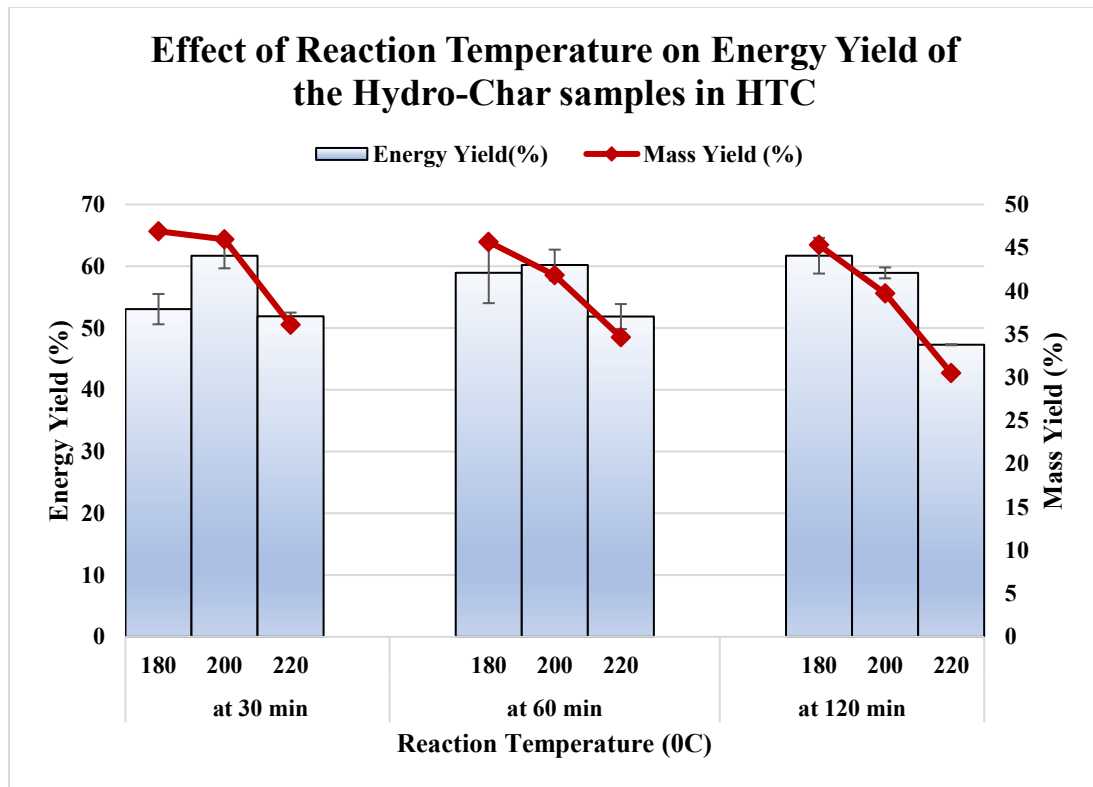
(b) Effect of the reaction temperature on the energy yield of hydro-char in the HTC

Figure 4.6 Effect of the process conditions on the energy yield of hydro-char in the HTC

4.3 Effect of the HTC Process Conditions on Physicochemical Properties of the Hydro-Char

The physicochemical properties of the dried hydro-char samples are summarized in Table 4.3. The proximate analysis is a widely accepted analytic technique that is used for investigating the quality of solid fuel like coal. Biomass is composed of a higher percentage of volatile matter than that of coal (Basu, 2006). The said fact is one of the major drawbacks for firing biomass as a fuel because the direct combustion of a fuel with a high content of volatile matter leads to poor combustion efficiency and high harmful emissions. (Broek et al., 1996; Jenkins et al., 1998). The raw seaweed that is used in this research has a high

volatile matter content of 63.19 % (db). It is evident from Table 4.3 that, the volatile matter content in the hydro-char decreases with increasing the reaction time and the reaction temperature.

The fixed carbon is the carbon that is not easily biodegraded, thus fixed carbon represents the potential of the material for ground burial for carbon credits. During HTC of the seaweed, the fixed carbon content in the hydro-char increased by increasing the reaction temperature and the reaction time. Therefore, the hydro-char produced at a reaction temperature of 220 ℃ and a reaction time of 120 minutes shows the maximum increase, from 12.44 % (db) to 24.15 % (db), in the percentage of the fixed carbon content. At the same process conditions, volatile matter content of the hydro-char has the maximum reduction from 63.29 % (db) to 54.15 % (db).

Table 4.3 Proximate and Ultimate Analysis of the Raw Seaweed and the Hydro-Char Samples

Sample	Proximate Analysis				Ultimate Analysis				
	Moisture %	VM %, db	FC %, db	Ash %,db	C %	H %	N %	S %	O %
Raw Seaweed	10.46	63.29	12.44	24.28	33.76	4.19	2.33	0.69	34.75
HC @ 180℃, 30 min	2.29	61.02	17.75	21.24	43.17	4.67	2.68	0	28.24

Sample	Proximate Analysis				Ultimate Analysis				
	Moisture %	VM %, db	FC %, db	Ash %,db	C %	H %	N %	S %	O %
HC @ 180℃, 60 min	1.81	60.53	18.42	21.05	42.58	4.91	2.66	0.1	28.70
HC @ 180℃, 120 min	1.64	57.01	21.20	21.79	42.44	4.81	2.63	0.19	28.14
HC @ 200℃, 30min	1.61	59.10	20.39	20.51	44.44	4.7	2.69	0	27.70
HC @ 200℃, 60 min	1.87	58.71	20.70	20.60	44.39	4.95	2.57	0.1	27.40
HC @ 200℃, 120 min	1.93	56.16	23.70	20.14	44.39	4.27	2.63	0	28.57
HC @ 220℃, 30 min	1.76	58.07	21.38	20.56	43.45	4.72	2.57	0.21	28.50

Sample	Proximate Analysis				Ultimate Analysis				
	Moisture %	VM %, db	FC %, db	Ash %,db	C %	H %	N %	S %	O %
HC @ 220°C, 60 min	1.63	57.70	22.11	20.19	46.86	4.89	2.8	0.13	25.13
HC @ 220°C, 120 min	1.83	54.15	24.15	21.70	48.49	4.53	2.91	0.16	22.21

HC refers to Hydro-Char; db refers dry basis

High ash content in a solid fuel is due to the high content of inorganic elements. The thermal efficiency of a system is greatly affected by using fuel with high ash content because such fuel can expose a thermal system to the risks associated with fouling, slagging, and corrosion. As the reduction in the ash yield corresponds with the removal of inorganic compounds from the solid into the liquid product during an HTC process, ash yield can be a considerable measure to compare the ash content in the hydro-char samples. Ash yield is calculated from the following expression:

$$\text{Ash Yield} = \frac{\text{Ash content in the hydro} - \text{char}}{\text{Ash content in the raw seaweed}} \text{ X Mass Yield} \quad \cdots\cdots\cdots\cdots (7)$$

Figure 4.7 shows the ash yield of the hydro-char produced at different process conditions. As can be seen, the ash yield of the hydro-char reduced significantly with increasing the reaction temperature and the reaction time. The ash yield results show exceptional reduction (at least 60%) in the ash for all the hydro-char samples. Furthermore, the ash

yield reduced by at least 10% as the reaction temperature increased from 180 ℃ to 220 ℃. The highest reduction in ash yield was around 73% at a reaction temperature of 220 ℃ and a reaction time of 120 minutes.
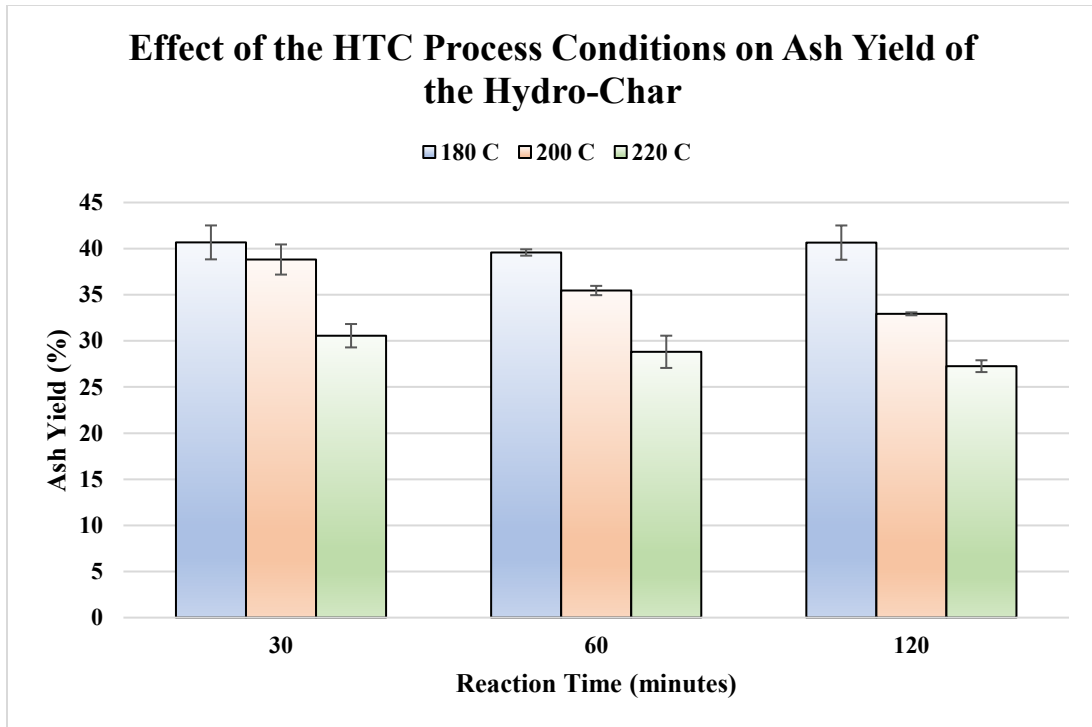
Figure 4.7 Effect of the process conditions on the ash yield of hydro-char in the HTC

Results of the ultimate analysis show an increase in carbon content and a decrease in oxygen content of the hydro-char samples than the raw seaweed. It is observed that the change in carbon content and the change in oxygen content were exceptionally low, merely 1%, for the change in reaction time at lower temperatures (180 ℃ & 200 ℃). However, both the increase in the carbon content and the reduction in the oxygen content were considerable, about 5 %, for the change in reaction time at the higher temperature (220 ℃). On the other side, an increase in either the hydrogen content or the nitrogen content of the hydro-char, with an increase in the reaction temperature, is minuscule, which is about 0.3-

0.5 % only. Though the higher percentage of nitrogen in fuel escalates the emissions of nitrogen oxides(NO_x) - contributors to the acid rain and smog (Basu, 2015), the effect of increasing such an infinitesimal percentage of the nitrogen content in the hydro-char samples can be considered insignificant for the emission-related issues. Irrespective of the process conditions, the C/N ratio in the hydro-char samples, as shown in Figure 4.8, was improved by 19% (from 14.49 to ~ 17) compared to the raw seaweed. The observed improvement of the C/N ratio in the hydro-char samples may be directly correlated with the suitability of the hydro-char for soil remediation applications those demand a higher C/N ratio.
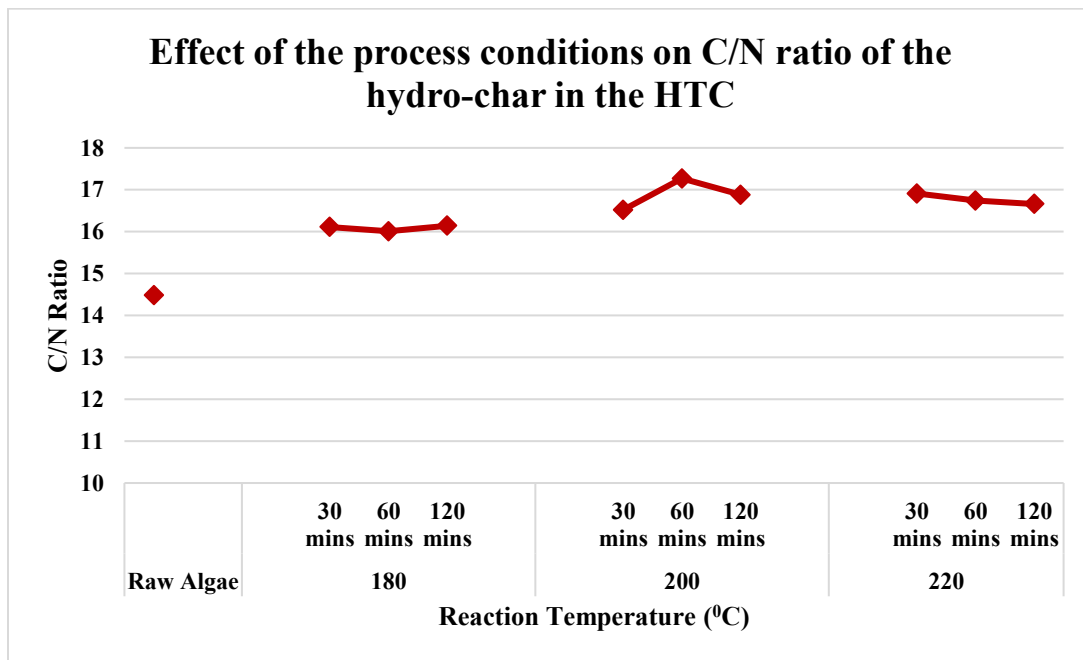

Figure 4.8 Effect of the process conditions on the C/N ratio of hydro-char in the HTC

The best approach to analyze the elemental composition of the hydro-char is through the plot of the atomic ratios H/C versus O/C. This plot, also known as van Krevelen diagram, is used to describe the quality of fuel. Low atomic ratios, i.e., proximity to the origin for a

position of fuel on van Krevelen diagram are suitable because such fuel is more energy-dense, which showcases high heating value (Basu, 2018). It means a fuel with low atomic ratio offers better combustion properties with lower energy loss during the combustion process. Biomass has a higher value of atomic ratio compared to coal because of the lower carbon content and the higher oxygen content. Figure 4.9 shows the van Krevelen diagram, in which H/C and O/C atomic ratios of the raw seaweed, the hydro-char samples, and some conventional fuels (McKendry, 2002) are described. It is noticeable that H/C and O/C atomic ratios of all the hydro-char samples are lower than that of the raw seaweed, which results in relatively high heating value for a hydro-char. This finding is consistent with the results discussed in section 3.4.2. The said improvement in the energy properties of the hydro-char can be attributed to the presence of the subcritical water as the reaction medium, which initiates hydrolysis reaction mechanism and thus exhibiting low activation energy than the other decomposition reactions (Libra et al., 2011; Bobleter, 1994).

Furthermore, the positions of every hydro-char samples on the van Krevelen diagram (Figure 4.9) are in the range of peat. However, the position of the hydro-char produced at a reaction temperature of 220 ℃ and a reaction time of 120 minutes is the closest to the range of lignite – a higher rank fuel than peat. Thus, it can be argued that the severe reaction conditions in the HTC improve the combustion properties of the hydro-char produced. Every research work cited in the thesis reported similar findings of improvement in H/C and O/C atomic ratios after the HTC of biomass. Thus, it would not be an exaggeration to characterize the HTC process as a wet pre-treatment of biomass for producing energy densified and carbon-rich solid fuel with relatively reduced volatile compounds and low H/C and O/C atomic ratios.
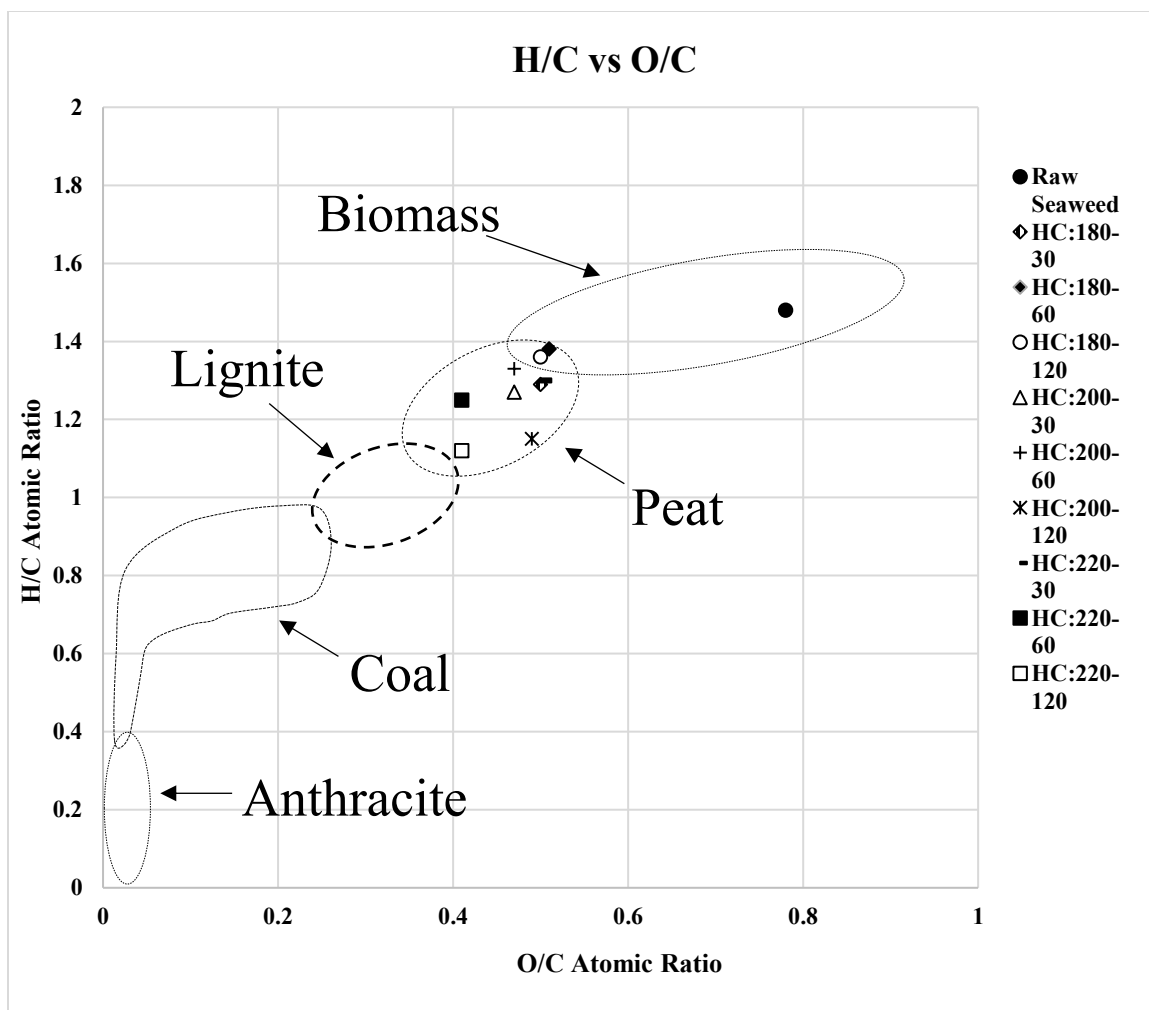
Figure 4.9 Atomic H/C – O/C ratios for the hydro-char samples and the raw seaweed.

4.4 Effects of the HTC Process Conditions on The Mineral (Inorganic) Composition of The Hydro-Char

Every biomass has several types of minerals (inorganic elements) in its structure. The inorganic composition of biomass that depends on the growing condition, type of soil, and harvesting time (Prochnow et al., 2009) differs widely among different biomass. These inorganic elements can be the alkali and alkaline earth metals such as phosphorus, potassium, magnesium, manganese, zinc, copper, iron, calcium, and sulfur those are left

behind, in their oxide form, in the ash during the combustion of biomass (Miles et al., 1996). The ash, formed of the oxides of metals mentioned above, challenges a thermal system with undesirable effects such as clinker, corrosion, fouling, and slagging (Miles et al., 1996; Basu, 2015). It is confirmed, from the discussion on the ash yield in the earlier section, that the raw seaweed is leaching inorganic elements with increasing the reaction temperature in the HTC process. This leaching can be attributed to the degradation of the biomass polymers because significant portion of the inorganic elements such as phosphorus, calcium, sulfur, magnesium, and potassium, in the biomass are held in the hemicellulose and soluble extractives (Miles et al., 1996), which degrade between 180^0 - 200 ℃ (Libra et al., 2011; Funke & Ziegler, 2010). Furthermore, this degradation and depolymerization of the biomass polymers in the HTC process are found to improve the porosity of the hydro-char (Reza et al., 2013; Funke & Ziegler, 2010).

The primary minerals, i.e., the inorganic elements present in the raw seaweed are phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), boron (B), manganese (Mn), copper (Cu), zinc (Zn), and sulfur (S). Among which, the percentage content of potassium and calcium are the highest, and the percentage content of copper and zinc are the lowest.

Figure 4.10 shows the comparison of the inorganic yield of the hydro-char at different process conditions in HTC. Inorganic yield is calculated from the following expression:

$$\text{Inorganic Yield} = \frac{\text{Inorganic content in the hydro} - \text{char}}{\text{Inorganic content in the raw seaweed}} \text{ X Mass Yield} \cdots (8)$$
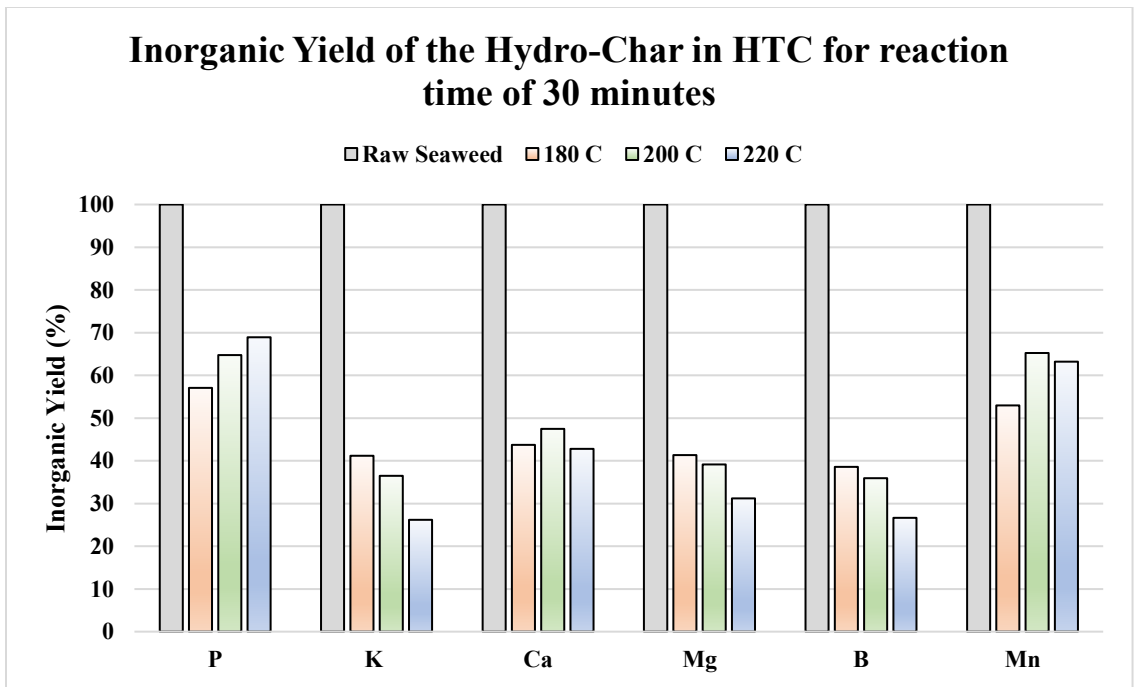
(a) Inorganic Yield of the hydro-char at a reaction time of 30 minutes in the HTC
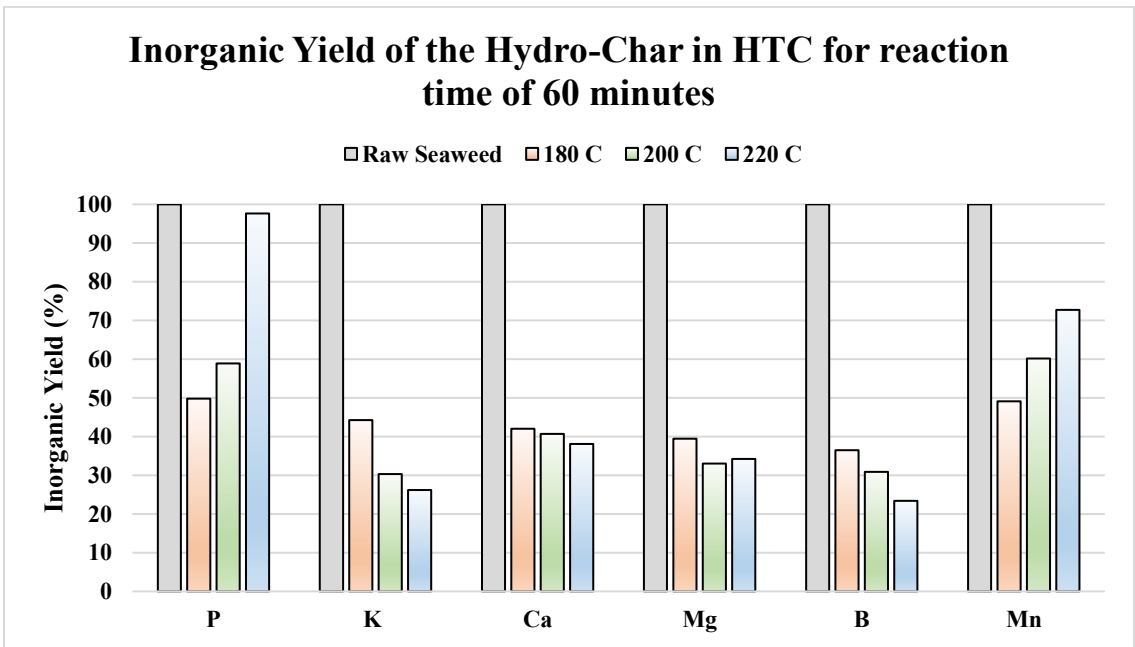
(b) Inorganic Yield of the hydro-char at a reaction time of 60 minutes in the HTC

Inorganic Yield of the Hydro-Char in HTC for reaction time of 120 minutes

□ Raw Seaweed   □ 180 C   □ 200 C   □ 220 C
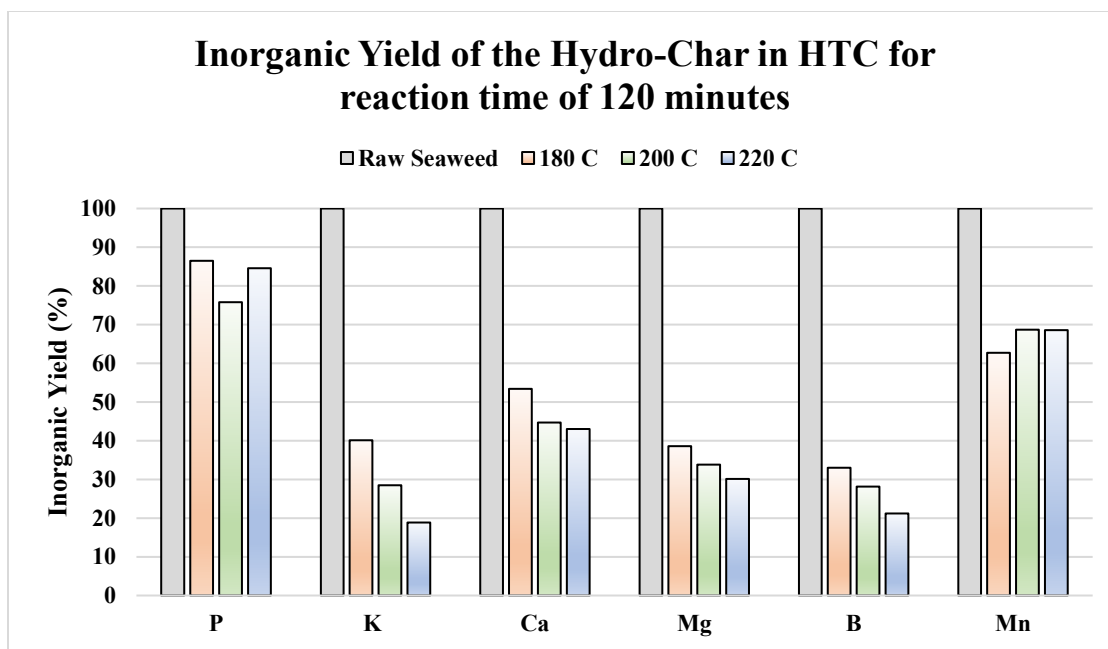
(c) Inorganic Yield of the hydro-char at a reaction time of 120 minutes in the HTC

Figure 4.10 Effect of the process conditions on the inorganic yield of the hydro-char in HTC

It can be seen from Figure 4.10 that the reduction in the percentage of the inorganic yield as the reaction temperature increased was, 31-74% (Figure 4.10(a)), 4-77% (Figure 4.10(b)), and 15-82% (Figure 4.10(c)) at the reaction time of 30 minutes, 60 minutes, and 120 minutes, respectively. It is noticeable that the reduction in the inorganic yields of potassium, calcium, magnesium, and boron were at least 50% for all the hydro-char samples, except for calcium at a temperature of 180 ℃ and a reaction time of 120 minutes. Unlike other minerals, the inorganic yield of phosphorus and manganese increased with increasing the reaction temperature. The reason behind such increase in the phosphorus content in the hydro-char at higher temperatures (specifically above 200 ℃) could be the superior surface functionality of the hydro-char that is generated at higher temperatures (Smith et al., 2016, Ekpo et al., 2016b, Heilman 2014). Increasing acidic conditions in the reaction medium increase the cation exchange capacity of hydro-char, and the divalent

cations of other inorganic metals can play a significant role in polymerization (Ekpo et al., 2016a, Wang et al., 2017). Higher content of these cations could lead to the formation of insoluble phosphates that are present in a colloidal form or electrostatically attached to proteins present in the seaweeds, and become entrapped within or precipitated on the hydro-char (Smith et al., 2016; Wang et al., 2019; Heilmann et al., 2014). Therefore, these phosphate nutrients, which are trapped within the hydro-char, can make the application of hydro-char for soil amendment challenge the application of hydro-char as a fuel, given that the hydro-chars are produced at a higher temperature during HTC.

4.5 Effect of the HTC Process Conditions on the Characteristics of the Processed Water

As mentioned in section 4.4.1, the yield of the gaseous products from the HTC of the seaweed was meager (5-6 %). In this scenario, most of the compounds, formed due to decomposition and depolymerization of the seaweed, remain in the liquid product. Thus, the study of the liquid product of HTC become essential along with the study of the solid product of HTC. It is found that the hydro-char has been the prime focus for most of the research works done on HTC of biomass; hence very few kinds of literature are available to showcase the effect of HTC process conditions on the liquid products of the HTC.

Figure 4.11 shows the effect of the reaction temperature on the inorganic element yield in the processed water of the HTC process for a reaction time of 120 minutes. The inorganic element yield in the processed water of HTC is calculated using the following expression:

Inorganic Element Yield

$$= \text{Inorganic content in processed water X Liquid Yield} \cdots (9)$$

It can be deduced from the chart that the percentage of inorganic yield of potassium and calcium are higher at the higher temperature, which shows that the reduction in the inorganic yields of potassium and calcium for hydro-char samples are more at the higher temperature. On the other hand, the percentage of phosphorus is the highest at 200 ℃, which means phosphorus that leached in the processed water from the raw seaweed tend to interact with the porous structure of the hydro-char at the higher temperature. These observations are consistent with the findings of the inorganic elemental composition of the hydro-char, as discussed in section 4.4.4.
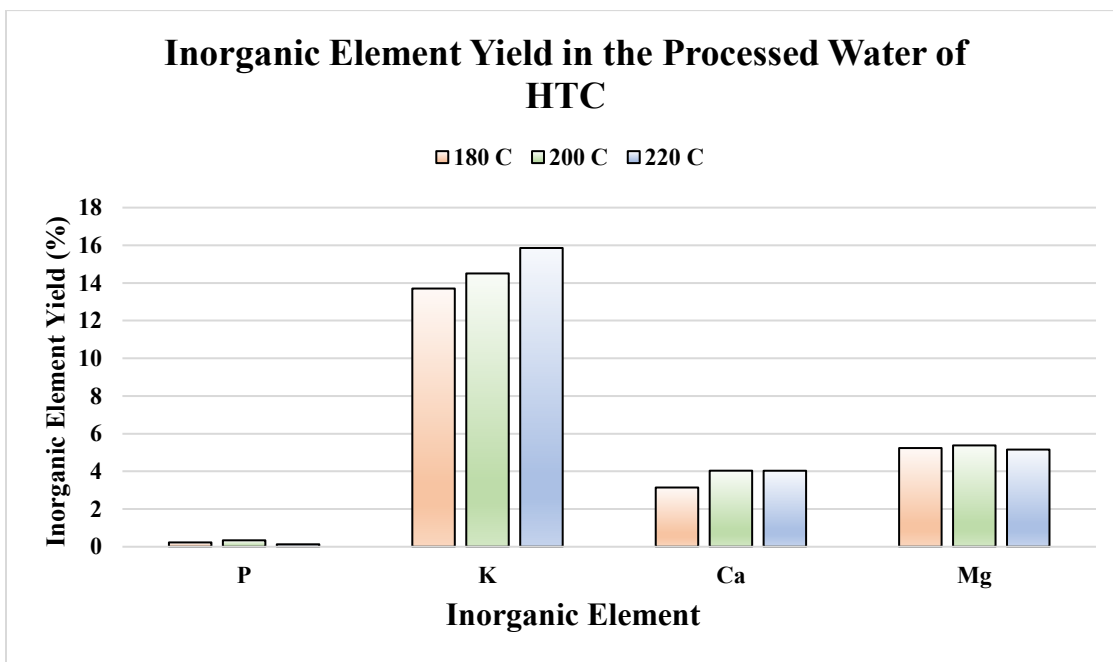
Figure 4.11 Effect of the reaction temperature on the inorganic elemental composition of the processed water in HTC.

Figure 4.12 shows the effect of the reaction temperature and the reaction time on the pH value of the processed water in the HTC process. Irrespective of the reaction severity, i.e.,

the process conditions, the pH of the processed water was on the acidic side; the acidic pH can be attributed to the formation of acidic compounds due to degradation of the biomass polymers and formation of organic acids predominantly acetic acid. Moreover, when deionized water is exposed to the atmosphere, its pH shifts to the acidic side on the pH scale because it quickly reacts with the carbon dioxide (CO_2) in the air to form carbonic acid. However, due to the marginal difference among the pH of different processed water samples, it can be argued that change in either the reaction temperature or the reaction time has no significant effect on the change in the pH of the processed water in HTC.
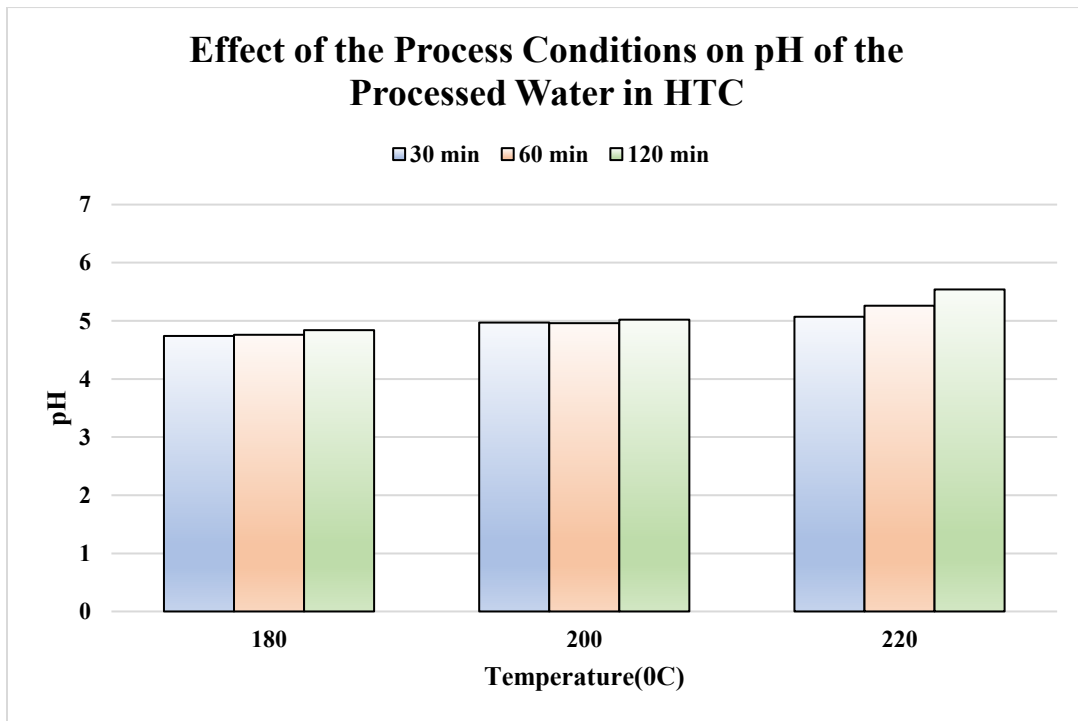
Figure 4.12 Effect of the process conditions on the pH of the processed water in HTC.

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4.6 Anaerobic Co-Digestion of the Processed Water

4.6.1 Substrate

The material used for anaerobic co-digestion of was banana, which was pureed in a commercially available grinder, with the processed water from of the HTC. The inoculum was also added to the mixture of banana and the processed water to aid the anaerobic digestion of the substrate. The inoculum used for the process was digested sludge, which was obtained from the Charlottetown Wastewater Treatment Plant, Charlottetown, Prince Edward Island, Canada. Total Solids (TS) and Volatile Solids (VS) in the inoculum and banana are given in Table 4.4

Table 4.4 Characteristics of Banana and Inoculum

Material	Total Solids (%)	Volatile Solids (%)
Banana	23.22	91.3
Inoculum	1.65	66.67

4.6.2 Batch Experiments

Batch AD experiments were carried out in 55 ml falcon tubes at Bioresources and Food Processing Laboratory, University of Prince Edward Island, Canada. The tubes were placed inside a glass chamber, in which the temperature was monitored and controlled by a PID controller. The same can be seen in Figure 4.13. The cap of each tube was drilled and, then, PVC tube was inserted into the cap. Then, a commercially available water sealant (plumbing putty) was used to seal the surrounding of the tubes. Two experiments were performed. In the first one, the other end of the PVC tubes was connected to another falcon

tube which was placed in the water bath, filled with water; thus, measuring the biogas yield with the water displacement. In the second experiment, the other end of the PVC tubes was connected to the gasbags. Both experiments were conducted simultaneously.

In each tube, 25 ml of the processed water sample was mixed with 5g of pureed banana in the falcon tube, and they were then stirred. Then, 25 ml of inoculum was added to the tube and stirred well to ensure proper mixing. Immediately after that, the tube was closed with the cap. An additional tube was used to measure the gas yield from the same amount of inoculum (25ml) and banana (5 gm). For further discussion, it is named as "blank."

Figure 4.13 Experimental Setup for Anaerobic Co-digestion of the processed water

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4.6.3 Biogas Yield

The AD was carried out for ten days; however, most of the gas production was seen within a week for all the samples. The cumulative volume of biogas from each tube was recorded as the water displaced by the gas in the respective tube in the water bath. Unfortunately, due to the very small amount of gas concerning the size of gasbags, the measurement or analysis of the biogas could not be done. For the final calculations, the amount of gas that was produced from the blank is subtracted from the amount of gas that was produced from each tube to get the actual biogas yield due to the processed water only. The results are shown in Table 4.5.

Table 4.5 Gas Yield for Anaerobic Co-digestion of the Processed Water

Sample Name	Total Gas Yield (ml)	Total Gas Yield due to PW only Total Sample (ml) – Blank(ml)
Blank	33.5	-
PW 180-30	31	-2.5
PW 180-60	33	-0.5
PW 180-120	35.5	2
PW 200-30	35.5	2
PW 200-60	34	0.5
PW 200-120	32.5	-1
PW 220-30	43	9.5
PW 220-60	35	1.5
PW 220-120	37	3.5

PW XXX-YYY refers to Processed Water – Temperature (^0C) – Time (min)

As it can be seen that, after subtracting the gas volume of the blank from the total gas volume, all processed water samples did not produce gas; for the ones who produced some gas, the gas yield was very low. Highest gas yield due to the processed water only is just 9.5 ml for the sample PW 2200-30. Moreover, samples PW 180-30, PW 180-60, and PW 200-120 has negative value, meaning they are inhibiting the anaerobic digestion. A possible reason for such a low amount of gas production can be the acidity of the processed water. As discussed in section 4.4.5, each sample of the processed water has pH in the range of 4.7 – 5.5. Most of the anaerobic bacteria, including methane forming bacteria, work best for the pH range of 6.5 to 7.5, and the methane production is reduced when the pH is out of this range (Nayono, 2010; Stronach et al., 1986) Another possible reason could the low nitrogen content in the processed water. Due to the instrumental limitation, exact nitrogen content could not be measured, but it was measured that the nitrogen content in all samples of the processed water was less than 2 ppm. Deficiency in nitrogen reduces the ammonia production (Prochazka et al., 2012; Marchaim, 1992), which is a strong base capable of balancing the acidity of the volatile acids produced by the fermentative bacteria during acetogenesis phase of AD; thus, low nitrogen content leads to an increase the acidity further. Therefore, such low gas yield or inhibition to anaerobic digestion may be attributed to the low pH and insufficiency of nitrogen as a nutrient of the processed water.

CHAPTER 5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Hydrothermal carbonization (HTC) of the marine seaweed was studied through experiments, and the results were analyzed to investigate the effect of the process conditions on the product distribution in the HTC and the physicochemical properties of the hydro-char. The conclusions that are drawn from the work mentioned in the earlier chapters of this thesis are provided below:

1. As expected, by increasing the severity of the reaction, i.e., the reaction temperature and the reaction time, the mass yield of hydro-char decreased, and the yield of processed water increased. The reaction temperature had more impact on the HTC product distribution.

2. The higher heating value (HHV) of the hydro-char also increased with increasing the severity of the reaction. The maximum value of the HHV (18.93 MJ/kg) was for the hydro-char produced at the reaction temperature of 220 ℃ and the reaction of 120 minutes.

3. Howbeit, the maximum energy yield is a variable of mass yield. So, the highest energy yield (61.75%) among the hydro-char samples was found in the hydro-char produced at the reaction temperature of 180 ℃ and the reaction time of 120 minutes.

4. The carbon content of the hydro-char increased with increasing the severity of the reaction. The highest carbon content (48.49 %) was found in the hydro-char produced at the reaction temperature of 220 ℃ and the reaction time of 120 minutes.

Thus, it could be said that the HTC process produces a carbon-rich and energy-dense solid product, i.e., hydro-char.

5. The HTC process improved the C/N ratio of the hydro-char, which can be beneficial for the application of the hydro-char for soil remediation. The highest C/N ratio (17.27) was reported in the hydro-char produced at the reaction temperature of 200 °C and the reaction time of 60 minutes.

6. The fixed carbon content in the hydro-char is significantly higher than the raw seaweed, suggesting the potential of HTC to produce carbon that can be buried underground for the carbon credits.

7. Atomic ratios (H/C and O/C) for hydro-char decreased with increasing the reaction severity. The observations that are made from the van Krevelen diagram suggests that the hydro-char, which is produced at the reaction temperature of 220 °C and reaction time of 120 minutes, is very near to the range of lignite. Moreover, the volatile matter was found to be lowest (54.15 %) for the hydro-char produced at the reaction temperature of 220 °C and reaction time of 120 minutes, and it was also lower than the raw seaweed (63.29 %); thus showcasing the enhanced fuel properties of the hydro-char produced at the severest reaction conditions.

8. The HTC process removed inorganic metals from the seaweed to the processed water quite significantly. The hydro-char showed an exceptional reduction in the ash yield (at least 60%) than the raw seaweed. The highest reduction in the ash yield (~73%) was found in the hydro-char produced at the reaction temperature of 220 °C and the reaction time of 120 minutes. The lowest reduction in the ash yield (~60%) was found in the hydro-chars produced at the reaction temperature of 220^0

°Cand 180 °Cat the reaction time of 30 minutes. Therefore, fouling, slagging, and corrosion-related challenges, related to the combustion of high ash biomass in a boiler, may be mitigated by replacing biomass with the hydro-char produced through the HTC of the biomass. Moreover, the HTC process is carried out in an aqueous environment, which allows the efficient and economical utilization of wet biomass, thus substantially increasing the process flexibility regarding suitable biomass.

9. The processed water from HTC, being acidic and deficient in nitrogen as a nutrient, produced a very low amount of gas during the anaerobic co-digestion with banana; sometimes it also inhibited the gas production.

5.2 Recommendations to Further Research

1. According to the current state of literature, reaction time and reaction temperature are the dominating factors affecting the product distribution and their properties. Moreover, throughout this study, the effects of reaction temperature and reaction time are investigated. However, the effect of other variables such as feedstock size, water to biomass ratio, use of a catalyst cannot be considered negligible, and thus, it should be further explored through implementing detailed studies on them.

2. HTC reactions are not fully understood yet. So, detailed research work on the HTC reactions may help to optimize the HTC process.

3. Present results and analysis were conducted on a batch reactor. For a commercial application, a continuous process is required. So, the research could be done for revealing the factual information of a continuous HTC process.

4. The results of the study show that the hydro-char produced at the reaction temperature of 220 ℃ and the reaction time of 120 minutes is the most promising for its application as a fuel instead of the raw biomass in boilers. However, the vapor pressure, in the reactor, would be very high for HTC process, which makes the process expensive as well as hazardous to explosions. Moreover, for a commercial-scale application, a continuous process would be required, and the high pressure inside the reactor would also incur the high cost of feeding against the pressure.

5. The hydro-char shows improvement in the C/N ratio. So, its application for the soil remediation could be explored through some field trails.

6. The processed water of the HTC contains the organic and inorganic compounds that have leached from the biomass. So, it would be interesting to investigate the effects of recirculation of the processed water in the HTC, which may exhibit hydro-char with better properties and can make the downstream processing cheaper.

7. Another approach for utilizing the processed water, which has nutrients of biomass, can be in agriculture as a nutrient for better growth of the plant. Using precision agriculture techniques, it could be possible through in-depth research. Alternatively, it can also be used to feed algae as a nutrient to increase their growth; thus, the production of the feedstock for the HTC can be done on the site, with the reduction in net carbon emissions.

8. Further research on the anaerobic digestion of the processed water should be done in details to make the HTC process an efficient and economical circular conversion route of biomass.

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