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Fuel Characterization and Process Analysis of Hydrothermal Liquefaction of Algae

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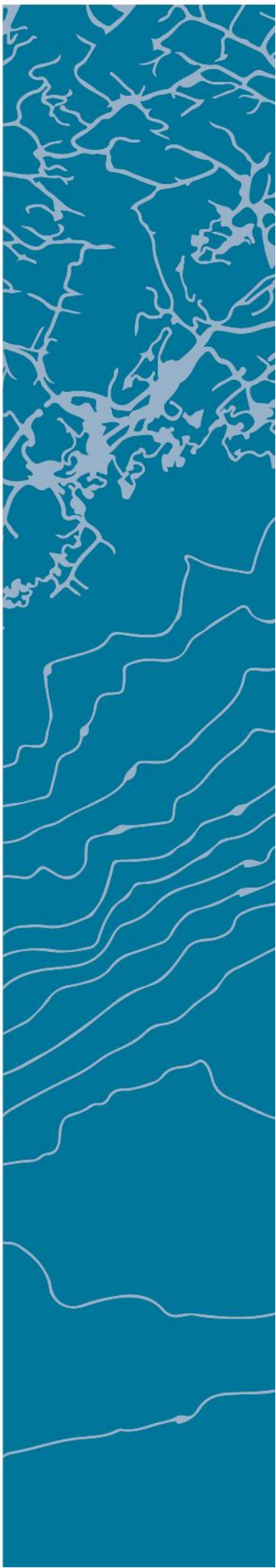

Abstract

The conversion of microalgae to biocrude by hydrothermal liquefaction (HTL) is a technology that could reduce the use of fossil fuels. The aim of this study was to provide insight in the fuel characterization and process analysis of algae HTL. Three microalgae species were provided for the fuel characterization. The *Phaeodactylum tricornutum* algae were received as a slurry, while the *Spirulina platensis* and *Chlorella vulgaris* were received as dried powders. Experiments by TGA, proximate and ultimate analysis were performed on the three algae species. A process analysis of algae HTL was carried out in Aspen Plus. Properties from the algae analysis was used in the simulation model.

Great improvement of the process efficiency was obtained by implementing a heat exchanger in the simulation model. The *S. platensis* and *P. tricornutum* algae obtained 83 % energy efficiency in the process analysis, when all the products from the process were utilized. Water recycling or district heating could further improve the energy efficiency of the system. For fuel characterization, the *C. vulgaris* algae had the best properties. In the process analysis, the *P. tricornutum* algae obtained the best results. In future work a kinetic simulation should be designed in order perform yield optimization and increase the accuracy of the system.

Sammendrag

Omdannelsen av mikroalger til råolje ved hydrotermisk flytendegjørelse (HTL) er en teknologi som kan redusere bruken av fossile brensler. Målet med dette studiet var å gi innsikt i drivstoffkarakterisering og prosessanalyse av alger i en HTL prosess. Tre mikroalger ble brukt for brensel karakterisering. *Phaeodactylum tricornutum* algene som ble benyttet var i form av en tyktflytende masse. *Spirulina platensis* og *Chlorella vulgaris* algene var i form av tørkede pulver. Eksperimenter ved TGA, proximate og ultimate analyse ble utført på de tre algene. En prosessanalyse av HTL ved bruk av alger ble utført i simuleringsprogrammet Aspen Plus. Egenskaper fra alge analysen ble brukt i simuleringsmodellen.
Stor forbedring av prosessens effektivitet ble oppnådd ved å implementere en varmeveksler i simuleringsmodellen. *S. platensis* og *P. tricornutum* alger oppnådde 83% energieffektivitet i prosessanalysen, da alle produktene fra prosessen ble utnyttet. Vanngjenvinning eller fjernvarme kunne forbedret systemets energieffektivitet ytterligere. For drivstoffkarakteriseringen hadde *C. vulgaris* algene de beste egenskapene. I prosessanalysen oppnådde *P. tricornutum* algene de beste resultatene. I fremtidig arbeid bør en kinetisk simulering utformes for å kunne utføre utbytte optimalisering og for å øke systemets nøyaktighet.

Acknowledgements

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Chapter 1

Introduction

This chapter starts with the background, a brief explanation about the subject of focus. Problem definition in chapter 1.2, states the objectives, limitations and assumptions. Then in chapter 1.3, a brief literature review is given on the most relevant work. Chapter 1.4 describes the problem solution and chapter 1.5 is the report outline, describing the chapters in this master thesis.

1.1 Background

In 2010 the European Union launched the Europe 2020 strategy, which is a job and growth strategy for a ten-year period [1]. The headline targets to achieve by the end of the period is poverty reduction, education, climate, energy, research and development. EU's aim in the climate and energy package is to achieve 20% of EU energy from renewables [2]. In the transport sector, use of fuels from renewables such as biofules was set to 10 % [3]. During the negotiation of the state budget 2017 in Norway, an agreement of achieving 20 % biofuels in the road going traffic was made as the target within the year 2020 [4]. From the total, eight percentage is to be advanced biofuel.

The EU strategy increased interest in research and development in the biofuel industry. This shed light on the method of producing crude oil by hydrothermal processing of biomass, that has been of interest since the first oil crisis in the mid-1970s. The term direct biomass liquefaction used in the 1970s and 1980s later changed to hydrothermal liquefaction (HTL) [5].

One of the main differences between HTL and other biocrude production processes, is the capability of handling wet biomass. Algae is a fast growing biomass with high lipid content suitable for the HTL process, and as a non-food biomass the algae biomass is classified as a third generation biofuel [6]. The HTL process has not been commercialized yet. This due to complicated reactions, high energy consumption and water demand. But the process is seen on as a promising contribution in future biofuel production.

1.2 Problem Definition

Microalgae is a fast growing organism with a high content of oil. The hydrothermal liquefaction process capable of producing biocrude from wet biomass, is suitable for microalage because of its high moisture content. The high pressure and temperature in HTL leads to a high energy demand in the conversion of the biomass. Selection of biomass for the process is important in order to obtain an energy gain as high as possible. Aspen Plus is a simulation tool that makes it possible to obtain valuable information of a process or plant, and is suitable for modeling HTL. Using the Aspen Plus tool for HTL of algae would help addressing optimization potential and problems that may occur. Process simulation is an important step in the development of the HTL to a sustainable process for future biofuel production.
In this master thesis, different microalgae species available is to be analyzed in relevance to biocrude production, by hydrothermal liquefaction. A simulation of a continuous algae HTL process is to be designed and analyzed using Aspen Plus. The energy used in the process, the algae biomass energy and biocrude energy are of main interest. The main objectives of this thesis are listed below.

- Objective 1: Provide algae biomass of different species, suitable for analysis by proximate, ultimate and thermogravimetric analysis.
- Objective 2: Perform proximate, ultimate and thermogravimetric analysis of the algae biomass.
- Objective 3: Characterize algae in terms of biocrude production by HTL, and compare results of the algae analysis with results from literature.
- Objective 4: Design an Aspen Plus model of HTL, using properties of the algae species analyzed in previous objective. Execute optimization of the model.
- Objective 5: Perform process analysis of the Aspen Plus simulation.

1.2.1 Key Assumptions and Limitations

Assumptions made for this master thesis are the following:

- The simulation model is based mainly on relevant literature.
- Algae analysis are based on 3 samples in each test, measurements are assumed to be representative for the use in simulation model.
- Simulation model is ideal with no pressure loss.

The following limitations in this master thesis are:

- Algae species selection are limited, due to requirement of low moisture content.
- Only the RYield reactor is considered for the simulation, no kinetics involved.
- Data for continuous flow HTL is limited.

1.3 Brief Review of Related Work

In this section, some of the relevant research on the HTL process is reviewed and mentioned in two separate parts. Microalgae in chapter 1.3.1, and simulation of the hydrothermal liquefaction in chapter 1.3.2. These two parts are considered as the main focus of this thesis. Whenever algae are mentioned in this thesis, it refers to microalgae.

1.3.1 Microalgae

Properties of different species algae is found both in books and in publications on the internet. There are many studies on analysis of microalgae for biofuel purposes, often of the same species algae. These studies use algae slurry or powder that is easily obtained, due to the low concentration of microalgae cultivated in water.
A review of microalgae for biofuel in HTL [7], was carried out to bring together published work by performing a literature research. This kind of research points out the differences in analysis and results, published by the different authors.

A review of biodiesel production of microalgae by Mata et al. [8], contains these properties for several species of algae. Experiment on continuous HTL is the next step in the process of biofuel production. The works of Jazrawi et al. describing the behavior of the algae in continuous HTL pilot plant, is an example of work critical for further development of continuous systems [9].

1.3.2 Simulation of Hydrothermal Liquefaction

The simulation model made in this master thesis, was mainly based on studies found in literature. Properties and yield of biocrude and other products are important for modeling and should be obtained from experiments of HTL. There was little literature related to HTL simulation found in books, but there were several journals which have published simulation mechanism by using different software.
The works of Pacific Northwest National Laboratory [10], was used as the main frame to define components in the simulation. Although their work was mainly focused on the economics of the HTL of algae, the work is thoroughly, containing valuable information that often is excluded in similar publications. The composition of components used is equal in simulations of two species of algae, which leads to equal heating value. This is not the case in a real case scenario, and should be considered.

In literature, yield products from HTL, both in batch and continuous flow applications, was only found for a few number of species. The *Chlorella* and *Spirulina* are two algae species used in supplements and are easy to provide, these are therefore commonly seen in literature of algae analysis for energy use. A study on the influence of strain-specific parameters on HTL by Barreiro et al. [11], is one of few

that reveals yield of components on several species of algae in four phases crude, aqueous, gas and solids. Vardon et al. studied thermochemical conversion by HTL and slow paralysis [12]. In the study the yield balance of HTL products was reported for *Spirulina*. These values are crucial for this master thesis, as no real HTL was conducted and analyzed. A study of HTL of manure using Aspen Plus simulation by Pedersen el al. [13], was completed by using an RYield reactor. Yield and composition used for the reactor was found in literature based on GC/MS analysis. This is a common approach in the few simulations of HTL found in literature.

1.4 Problem Solution

The objectives of this work will be achieved by the following process. First an assessment of the available and suitable microalgae will be done. Then the algae will be ordered or gathered from the producer. An analysis of the algae will be performed in the laboratory at the University of Agder. Results will be collected and calculated using Excel. The Aspen Plus software is to be installed on the author's computer and experience using the program will be gained by completing tutorials and examples. Finally, the HTL simulation will be designed and tested, before further optimization of the model and analysis of the results.

1.5 Report Outline

This report consists of two main parts, the algae characterization and the process analysis of algae HTL. Each chapter starts by presenting with the fuel characterization part, before the process analysis part.

Chapter 2 presents the theoretical background for this work, with a view on literature relevant for the algae characterization and process analysis.

Chapter 3 describes the method, instruments, algae biomass and simulation tool. Assumptions used in the process analysis of the Aspen Plus Model is defined, and a flow sheet of the process is presented.

Chapter 4 presents the results of the algae analysis and process simulation.

Chapter 5 gives the discussion of the results and literature relevant for the report.

Chapter 6 presents the conclusion of this master thesis.

Appendixes, introduce additional information on the TGA, microalgae literature and the Aspen Plus model.

Chapter 2

Theoretical Background

In chapter 2.1, a short description is given of the microalgae, harvesting methods and the main properties for fuel utilization. Chapter 2.2 introduce the common methods of analysis for fuel characterization, and literature found on analysis of several species microalgae. Chapter 2.3, introduces hydrothermal liquefaction in general, and microalga in HTL. Batch and continuous reactor systems and main products from the HTL process is also presented. Chapter 2.4 gives a short background information on the Aspen Plus simulation software.

2.1 Microalgae

Microalgae also called phytoplankton are unicellular algae species, existing in groups, chains or individual. In size, the microalgae range from one micrometer up to a few millimeters. Living both in freshwater and seawater, thousands of species have been reported, though numbers differs in literature. Photosynthesis is the transformation of light energy into chemical energy which organisms and plants make use of. Using the light energy, the microalgae turns CO_2 into carbohydrates by utilizing water and producing oxygen. The microalgae consist of elements of nitrogen, oxygen, hydrogen and carbon, in the form of proteins, lipids and carbohydrates.

The *Chorella* algae species has several stains, one of the most common in literature is the freshwater microalgae *Chlorella vulgaris*. Some strains of this algae have the ability to thrive in seawater. The algae have a medium content of carbohydrates, and a high content of proteins and lipids [14]. It is used as human food supplement and as an aquaculture feed [15]. According to Figueira et al. [16], *Chlorellavulgaris* is the most widely grown microalgae species on an industrial scale.

Spirulina is a cyanobacteria, that has been used as human food for decades. One advantage with this microalga is the easy of harvesting due to the algae tendency to aggregate. Another is the high protein content. *Phaeodactylum tricornutum* is a marine algae strain within the *Phaeodactylum* algae species. A high biomass productivity and ease of cultivation is some of the advantages of this algae [7].

2.1.1 Harvesting and Pretreatment

The harvesting of microalgae is a complicated process due to their small size and the water mass fraction of about 80-90 % [7]. The amount of dry biomass in a dilute suspension depends on the species and the growth conditions, it varies in the range of 0.02-0.05 % [17], or 0.02-0.06 % [8]. Most common used harvesting methods are filtration, centrifugation and coagulation/flocculation [18]. Other methods for harvesting are magnetic separation [18], gravity sedimentation [19] and flotation [17]. These methods could in some applications be used in combination to obtain the desired moisture content. Dehydration or drying after the harvesting process could be used to further decrease the moisture content of the algae [19].

2.1.2 Microalgae as a Fuel

Protein, carbohydrate and lipid components of algae biomass vary for each species, and can be influenced by growing conditions. These components are considered important in the determination of species for fuel use. Composition of protein, carbohydrates and lipids of four species algae is shown in table 2.1.1. The Kjeldahl method could be used to determine the crude protein content, phenol-sulfuric acid method for the carbohydrate content and Soxhlet-extract method for the crude fat content [20].

Table 2.1.1: Protein, carbohydrate and lipid content, as wt.% of dry algae biomass [14, Table 1].

	Proteins	Carbohydrates	Lipids
Chlorella Sp.	30	15-17	9.0-13
Chlorella vulgaris	42-58	12-17	14-22
Spirulina maxima	60-71	13-16	6.0-7.0
Spirulina platensis	46-63	8.0-14	4.0-9.0

In table 2.1.2, the oil content of fourteen algae species are shown. In general algae species with high oil content are desired for biodiesel production, but due to variations in the kinds of complex oils, lipids and hydrocarbons in the algae, not all species will be suitable [21].

Table 2.1.2: Oil content of algae, as wt.% dry [21, Table 2].

Microalgae	Oil %
Botryococcus braunii	25-75
Chlorella sp.	28-32
Crypthecodinium cohnii	20
Cylindrotheca sp.	16-37
Dunaliella primolecta	23
Isochrysis sp.	25-33
Monallanthus salina	>20
Nannochloris sp.	20-35
Nannochloropsis sp.	31-68
Neochloris oleoabundans	35-54
Nitzschia sp.	45-47
Phaeodactylum tricornutum	20-30
Schizochytrium sp.	50-77
Tetraselmis sueica	15-23

For the production of bio-diesel from microalgae, the lipid content which ensure a high oil content is important. Different microalgae species have different quantity and productivity of lipids, and there are significant differences. Low lipid content of 1 % to as high as 70 %, or even 90 % under certain conditions is shown from research [8]. Usually most lipid-rich strains have slow grow rates.

Strains with high lipid productivity have been preferred in research of biodiesel production, but as the HTL process utilizes the entire microalgae not only the lipid content, it appears that the biomass productivity is more important [7]. For bio-diesel production, the species *Chlorella* is mentioned as a good option [8]. The major component of carbon, hydrogen, nitrogen, oxygen and sulfur, in the microalgae are important parameters in terms of fuel potential. Biomass with a high carbon and hydrogen content, low in sulfur and nitrogen is desirable [22].

There are many parameters when considering an algae species for processing and biofuel usage. In the following list, some of the parameters are presented:

- Productivity of biomass
- Ease of cultivation
- Harvesting and separation from water
- Resistance to contamination
- Nutrient requirements
- Ease of processing
- Possibility of obtaining high value products

- Freshwater or seawater
- Lipid content
- Lipid production
- Size and shape

2.2 Analysis of Microalgae

In literature, different methods are used in the analysis of microalgae biomass, for the purpose of biofuel products. Most common are the thermogravimetric analysis (TGA), proximate analysis and ultimate analysis. The bomb calorimeter method is commonly used to measure the heating capacity.

2.2.1 Proximate Analysis

The proximate analysis is used to designate the structural elements of the biomass. Moisture content (MC), volatile combustible matter (VCM), fixed carbon (FC) and ash are the four structural elements.

To determine the moisture content of a biomass, small amounts of sample is placed in crucibles and weighted. Then it is placed in a forced convection oven at a temperature according to the chosen standard. The sample is retrieved and weighted when all moisture has evaporated and the weight of the sample is constant. Often the sample is placed over night or for a duration of 16 hours.

Depending on the biomass, different standards uses different temperature settings. For wood $103°C$ by standard ASTM E871-82. For coal $104°C$ and coke $110°C$, by standard ASTM D 3173-03 [23, p. 93]. There are also a European Standard for moisture content in solid bio-fuels, EN 14774-1,2,3:2009. The percent moisture content is calculated by Equation 2.2.1, on as received basis [23]. Initial weight m_i as received, final weight m_f as the bone-dry biomass.

$$Moisture\ content\ (\%MC) = \frac{m_i - m_f}{m_i} \times 100\% \tag{2.2.1}$$

Volatile combustible matter also referred to as volatile matter (V_d), is measured by placing a small amount of sample in a crucible with lid, before it is placed in a tube furnace for 7 minutes. The sample is retrieved from the furnace, cooled and reweighed. Temperature setting for the ASTM E872-82 standard for wood or the ASTM D 3175-07 for coal or coke, is $950 \pm 20°C$. Initial sample is to be bone-dry biomass. The percentage of volatile combustible matter is determined by equation

2.2.2, v_i initial weight bone-dry, v_f final weight [23]. Using the EN 15148 standard the temperature setting is $900\pm10°C$, and the initial sample could either be oven-dry or in moisture equilibrium with the atmosphere of the laboratory. EN standard equation 2.2.3, m_1 weight of empty crucible and lid, m_2 initial weight of crucible with lid and sample, m_3 final weight of crucible with lid and rests of sample, M_{ad} moisture percentage determined by EN 14774-3 [24].

$$Volatile\ combustible\ matter\ (\%VCM) = \frac{v_i - v_f}{v_i} \times 100\% \tag{2.2.2}$$

$$V_d = [\frac{100(m_2 - m_3)}{m_2 - m_1} - M_{ad}] \times (\frac{100}{100 - M_{ad}}) \tag{2.2.3}$$

To measure the ash and fixed carbon, the sample biomass and crucible is weighted and placed in a furnace at the specific time and temperature setting. Sample is then retrieved, cooled in a desiccator and then reweighed. Remaining material in the crucible is the ash, and the weight difference is the fixed carbon. For the ASTM the ash content is measured on the sample after the VCM test is conducted, only removing the lid of the crucible.

The standard for wood (ASTM D 1102-84) uses a temperature setting of $600°C$ for about one hour. While for coal and coke (ASTM D 3174-04) the temperature setting is respectively 700-750$°C$ and $950°C$, and about 4 hours. Equation 2.2.4 and 2.2.5 determines the fixed carbon and ash for the ASTM standard, f_i is the initial sample weight before sample is placed in the furnace and f_f is the final weight afterword's [23, p. 95-96]. The European Standard used to determine the ash content in solid biofuels is EN 14775. A sample is placed in a cold furnace, either using the same bone-dry samples from the MC measurement, or sample that is dried by the same procedure. The furnace temperature increases evenly for 30 or 50 min to a temperature of $250°C$. This temperature is then kept constant for one hour, before the temperature is increased evenly to $550\pm10°C$ and kept at that temperature at least for two hours. A_d is the ash content on dry basis calculated by equation 2.2.6, m_1 weight of empty crucible, m_2 initial weight of crucible and sample, m_3 final weight of crucible and ash, M_{ad} moisture percentage [25].

$$\%FC = \frac{f_i - f_f}{v_i} \times 100\% \tag{2.2.4}$$

$$\%Ash = 100 - \%VCM - \%FC \tag{2.2.5}$$

$$A_d = \frac{(m_3 - m_1)}{(m_2 - m_1)} \times 100 \times \frac{100}{100 - M_{ad}} \tag{2.2.6}$$

2.2.2 Ultimate Analysis

The ultimate analysis is used to measure the chemical elements of the biomass. Carbon (C), hydrogen (H), nitrogen (N), sulfur (S) and oxygen (O). Depending on the method or instrument used, the content of carbon, hydrogen, nitrogen and sulfur is measured. If the ash content of the biomass has been measured by proximate analysis, then the oxygen content is calculated by the difference between the sum of C, H, N, S, ash and 100 % [23][5]. From the chemical composition measured by the ultimate analysis the parameters of atomic C/H and O/C ratio could be calculated. The ultimate analysis is also useful for the calculations of heating value and to determine the chemical formula. Apparatus used in elemental analysis burns a small sample of the biomass. The chemical elements are measured by analyzing the exhaust gases and the combustion process.

The EN 15104 standard [26], determine the C, H and N of solid bio-fuels by instrumental method. The ASTM E 777 standard is for carbon and hydrogen content, ASTM E 775 is for sulfur and ASTM E 778 is for nitrogen content [23]. ASTM are standards by the international organization for standards ASTM International [27]. EN is standards by the European Committee for Standardization [28]. In figure 2.2.1, the PerkinElmer 2400 series II CHNS/O elemental analyzer is displayed. The ultimate analysis should be performed on dry basis, as moisture would give an increase in oxygen and hydrogen.

Figure 2.2.1: PerkinElmer elemental analyzer [29].

2.2.3 Heating Value

The heating value or calorific value is a measure of the energy content in the biomass. Expressed either by higher heating value (HHV), lower heating value (LHV), gross calorific value (GCV), or net calorific value (NCV). It could either be calculated using the elemental composition, or performed experimentally by calorimetry. Using a bomb calorimeter to measure the heat of combustion, is a common method used in calorimetry. A commonly used equation in calculation of the heating value of algae biomass is Dulong's equation 2.2.7 [23, eq. 3.13], as used in [30][31][32][33][34][12], the Boie equation 2.2.8 [23, eq. 3.12] has also been used [35][11]. Elements used in the equations is percentage dry weight.

$$HV = 33823 \times C + 144250 \times (H - O/8) + 9419 \times S \; [kJ/kg] \tag{2.2.7}$$

$$HHV = 35160 \times C + 116225 \times H - 11090 \times O + 6280 \times N + 10465 \times S \; [kJ/kg] \tag{2.2.8}$$

The Dulong equation 2.2.7, uses the C, H, O and S elements, and are valid if the oxygen content is below 10 % [23]. Boie equation 2.2.8 uses C, H, O, S and N elements. There is a difference in the heating value reported in Europe and USA, the LHV that is the NCV is used in Europe, while the HHV that is the GCV is used in USA. Equation 2.2.9 and 2.2.10 determines the GCV and NCV of biomass [36], where w is the weight percentage moisture content on wet basis, h is concentration of hydrogen and X_i is content of the elements and ash.

$$GCV = 0.3491 \cdot X_C + 1.1783 \cdot X_H + 0.1005 \cdot X_S - 0.0151 \cdot X_N$$

$$- 0.1034 \cdot X_O - 0.0211 \cdot X_{ash} \; [MJ/kg, \; d.b.] \tag{2.2.9}$$

$$NCV = GCV \left(1 - \frac{w}{100}\right) - 2.444 \cdot \frac{w}{100} - 2.444 \cdot \frac{h}{100} \cdot 8.936 \left(1 - \frac{w}{100}\right) \; [MJ/kg, \; w.b.] \tag{2.2.10}$$

2.2.4 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is a technique used to characterize materials based on the composition. Thermogravimetry and thermal gravimetric analysis (TG) is other common names for this measurement. The technique measures the weight change of a sample and is used in characterization of physical and chemical properties. Measurement is conducted as the sample is heated at a constant temperature rise, or kept at a constant temperature. An inert gas atmosphere or an oxidative gas atmosphere [37], is used to ensure higher accuracy and the possibility for analysis of different materials above the normal flash point. The DTG curve is the derivative of the TGA curve and could be used to determine temperature of which the main decomposition stages occur [38].

Differential scanning calorimetry (DSC) is a technique that measures the ability of the sample to release or absorb energy. The technique characterizes the endothermic and exothermic behavior of the sample material, and measure its heat capacity [39]. This technique is implemented in some particular TGA instruments. An example of an TGA instruments is the METTLER TOLEDO TGA/DSC 1, with temperature range up to $1600°C$, temperature accuracy of $\pm 0.5K$, weight resolution $0.1\mu g$ and sample size from $20\mu L$ to $900\mu L$ [40]. In figure 2.2.2, a TGA/DSC instrument is displayed.

Figure 2.2.2: METTLER TOLEDO TGA/DSC thermogravimetric analyzer [41].

2.2.5 Literature Review on Thermogravimetric Analysis

Two different ways to perform the TGA is found in the literature. To characterize the main steps in the weight loss curve, a constant heat rate starting at room temperature and ending at around 800-1000$°C$ is used. Another method for analysis uses steps of constant heat rate, followed by a constant temperature before another heat rate step. The first method mention could be used to customize the heat rate and constant temperatures for the second method. If the heating cycle is conducted with an inert gas, then air is usually introduced to complete the combustion of the sample leaving only ash left. In order to determine the ash content of the microalgae biomass by TGA, the combustion must be complete. The use of different methods and standards to determine the ash content of algae biomass leads to different results, not only may the biomass content be different but due to incomplete combustion, the results may vary.

A study of the ash content temperature in TGA of four microalgae species ($Isochrysis zhangjiangensis$, $Arthrospira platensis$, $Tetraselmis subcordiformis$, $Nannochloropsis oceanica$), proposed the optimized terminal ashing temperature of 600$°C$ [42]. This was in conjunction with a heat rate of 20$°C/min$, air atmosphere and retention time of 30 min, for samples of 5-10 mg. Higher temperatures that were tested, showed only negligible results.
Sandhakar and Premalatha used biomass from microalgae *Scenedesmus* sp. in TGA, to characterize the three main decomposition phases [43]. Samples of 7-8 mg was heated from room temperature to 800$°C$, in air atmosphere with heating rate of 10 and 30$°C/min$. Results was dehydration at 190$°C$, devolatilization with peaks at 280$°C$, 350$°C$, 470$°C$, and a third step of slow decomposition at 730$°C$.

Zhang et al. conducted a study on the *Chlorella* algae, analyzing the structure and properties of the algae [44]. Measurements of the thermal stability of the algae using TGA was carried out by three different methods. Heating rate of 5$°C/min$ both in air and in nitrogen atmosphere, or at constant temperatures at 140, 160, and 180$°C$ in oxygen atmosphere. The TGA curve presented in figure 2.2.3 shows a slightly weight loss below 150$°C$, from loss of water and volatiles. Further weight loss from 250$°C$ to 550$°C$ in air, while in nitrogen the rate of weight loss decreases after 400$°C$.

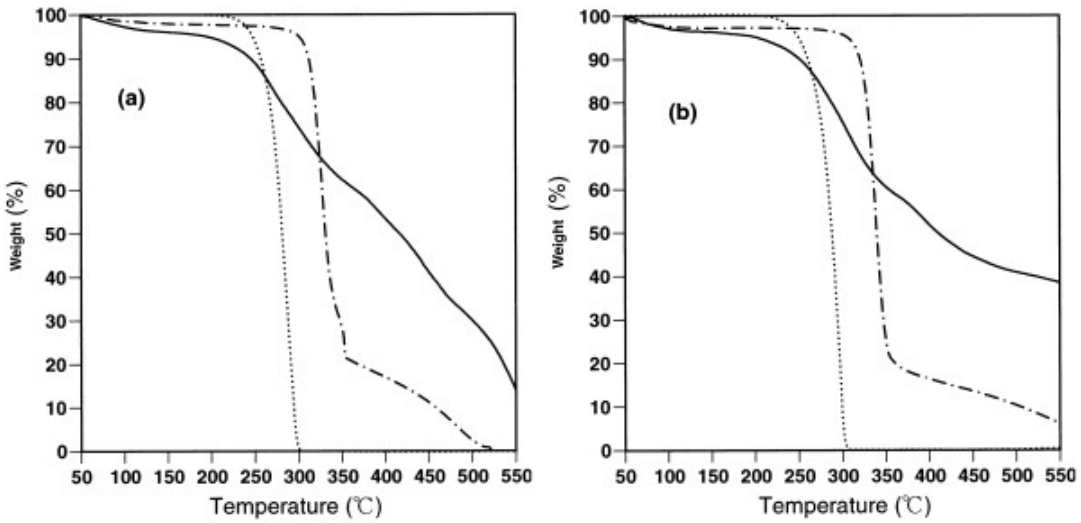

Figure 2.2.3: TGA graph. The continuous line is *Chlorella* algae. Oxygen atmosphere used in left graph, nitrogen in right graph [44, Fig. 5].

In a study of slow pyrolysis of *Spirulina* sp. for bio-char and bio-oil production, Chaiwong et al. used TGA to characterize the pyrolytic properties and algae components [45]. In a nitrogen atmosphere, the biomass was first heated at a heating rate of $10°C/min$, from 50 to $135°C$ where it remained for 5 min. Then a heating rate of $100°C/min$ raised the temperature to $900°C$. In this study three stages describes the pyrolysis process in TGA, first stage was dehydration from 50-$200°C$, second stage was devolatilization and the third stage was decomposition at 600-$900°C$.

A study of the microalgae *Chlorella* and *Spirulina* for energy application by Chen and Torii [46], used the TGA and bomb calorific meter. TGA results showed rapid weight loss as the temperature increased above $300°C$, and 80 % loss of mass at $900°C$. The test was started at a constant temperature of $90°C$ to remove water, followed by an increase of $50°C/min$, until $900°C$ was reached.

Instruments capable of simultaneous TGA and DSC measurements makes the analysis faster and easier for comparison and characterization of biomass.
Nannochloropsis gaditana, *Scenedesmus almeriensis* and *Chlorella vulgaris* was characterized by TGA and DSC in a study by Lopez-Gonzalez et al. [38]. The analysis of each sample started at a heating rate of $40°C/min$ until $105°C$ was reached and held for 10 min. Next a heating rate of $40°C/min$ increased the temperature from $105°C$ to $1000°C$. Initial sample weight of 8 mg, was tested in an oxygen and Argon atmosphere of respectively 21 % and 79 %.
The first decomposition started at 170-$180°C$, with a peak decomposition at 284-$311°C$ and a final decomposition at 378-$453°C$. The second decomposition at 478-$725°C$, and an additional decomposition for *N.gaditana* at around 826-$998°C$. Final burnout temperatures for *N. gaditana*,
S. almeriensis and *C. vulgaris* was respectively 716, 696 and $725°C$. Results were presented for *C. vulgaris*, *S. almeriensis* and *N. gaditana* as initial decomposition

temperatures, respectively 172, 125 and 142°C. Ignition temperature 265, 276 and 237°C. Burnout temperature 725, 696 and 716°C. The DSC analysis results were presented by temperature of the sample and heat released. Two exothermic regions from the samples was obtained. The first exothermic region occurred at around 300-400°C, and the second around 530-630°C. Total heat released during combustion of *C. vulgaris*, *S. almeriensis* and *N. gaditana*, was respectively 7.9, 7.8 and 8.8 kJ/g.

A thoroughly study of the microalgae *Nannochloropsis gaditana* was performed by Sanchez-Silva et al. to investigate pyrolysis, combustion and gasification characteristics of the algae by TGA and DSC [47]. The study aimed to investigate operation conditions and their effects in the TGA, by using three different methods for the three processes of pyrolysis, combustion and gasification.

- Pyrolysis analysis performed in an Argon atmosphere, at a heating rate of 40°C/min from 40 to 1200°C.
- Combustion analysis performed in a pure oxygen atmosphere, sample heated to 125°C and maintained for 10 min then heated from 125 to 1000°C. Heat rate 40°C.
- Gasification analysis performed in three steps, first drying in a pure Argon atmosphere at a heating rate of 15°C/min from 30 to 125°C. Next step, pyrolysis at a heat rate of 40°C/min from 125°C to 850°C. Final step, gasification of the char produced in the pyrolysis step gasified by Argon and H_2O mix for one hour at test temperature.

In all three analysis, a varied gas flow rate, particle size and sample weight was used for optimal operating conditions. Main results from pyrolysis and combustion in the study presented, devolatilization during the pyrolysis process at 160-450°C, and oxidation during the combustion process at 450-600°C. Dividing the pyrolysis and combustion of the microalgae in three main stages, dehydration, polysaccharides and proteins degradation, and char decomposition.

Standard ASTM E1131, describes the standard test method for compositional analysis by thermogravimetry [48]. The method measures the moisture content, volatile compounds and carbon of a sample by TGA. In using this method, the sample is heated to 900°C in a nitrogen atmosphere, then the atmosphere is changed to oxygen for the combustion of the sample [49]. Pedersen et al. [13], used results from TGA of *S. platensis* and *Nannochloropsis salina* comparing it to results of proximate analysis. Similar results of moisture and volatile matter was shown.

2.2.6 Microalgae Analysis in Literature

In literature, results from microalgae analysis is well reported both for *Spirulina* and *Chlorella* species algae. Proximate and ultimate analysis, are common methods used for in biomass characterization. In a study by Chaiwong et al. [45], the *Spirulina* sp. algae in powder form, was characterized by ultimate and proximate analysis. Another example is a study conducted by Lopez-Gonzalez et al. [38]. Using the proximate and ultimate analysis on three different algae species, among them the *Chlorellavulgaris*. Results from ultimate and proximate analysis found in literature, is presented in table 2.2.1. Ultimate analysis represented by carbon (C), hydrogen (H), nitrogen (N), sulfur (S) and oxygen (O). Proximate analysis results are moisture content (M), ash content (Ash), volatile matter (VM) and fixed carbon (FC).

Table 2.2.1: Chemical and structural element of microalgae from literature, presented as wt.% [45][50][9][51][31][52][38][53][54][11].

	C	*H*	*N*	*S*	*O*	M	Ash	VM	FC
Spirulina sp.	39.26	6.11	6.65	0.57	47.41	8.45	13.99	65.48	12.08
$Spirulina_1$	55.7	6.8	11.2	0.8	26.4	7.8	7.6	-	-
$Spirulina_2$	53.7	7.7	12.1	0.6	25.9	5.7	7.6	-	-
$Spirulina_3$	54.4	7.6	10.9	0.83	26.3	7.8	7.6	-	
$Spirulina_4$	45.61	6.66	10.21	0.79	36.74	7.8	8.2	-	-
S.platensis	46.87	6.98	10.75	0.54	34.86	-	6.60	78.15	15.25
Chlorella	53.5	7.4	11.0	0.5	27.6	5.2	6.0	-	-
$C.\,vulgaris_1$	52.6	7.1	8.2	0.5	32.2	5.9	7.0	-	-
$C.\,vulgaris_2$	40.8	6.5	6.7	1	43.1	4.4	15.9	67.2	12.4
$C.\,vulgaris_3$	53.6	7.3	9.2	0.5	29.4	5.2	6.8	-	-
$P.\,tricornutum_1$	38.0	4.8	5.2	0.7	51.3	-	5.2	-	-
$P.\,tricornutum_2$	57.03	7.46	8.00	1.28	24.97	-	12.45	-	-
Nannochloropsis	49.27	7.27	6.29	0.83	36.34	3.1	8.9	-	-
Nannochloropsis sp.	51	7	9	0.6	28.8	-	3	-	-

The weight percentages reported in table 2.2.1, for each specific alga are as follows: *Spirulina* sp. as % dried algae [45]. Freeze dried $Spirulina_1$ and $Chlorellavulgaris_1$, daf. (dry ash free) by ultimate analysis [50]. $Spirulina_2$ and *Chlorella* powder, elemental composition wt.% daf, proximate analysis wt.% as received [9]. $Spirulina_3$ and
$Chlorella\,vulgaris_3$, ultimate analysis daf. [51]. $Spirulina_4$ and *Nannochloropsis*, ultimate and proximate analysis results[31]. *Spirulina platensis* wt.% [52]. Oven dried $Chlorella\,vulgaris_2$, ultimate analysis wt.%, proximate analysis wt.% [38]. $Phaeodactylum\,tricornutum_2$ by wt.% on dry basis [53]. *Nannochloropsis* sp. values reported as wt.%, with 0.6 % P not presented in table [54]. Oxygen content of $Phaeodactylum\,tricornutum_1$ is calculated on difference and not given by in reference, values reported on wt. % dry basis [11]. In table 2.2.1 oxygen content is

reported by difference without the ash content. In the books [23] and [5], the ash content calculation is done by subtracting the ash content in the calculation, thus a lower value of oxygen.

The volatile combustible matter, fixed carbon and ash are important in fuel characterization. A high percentage of VCM leads to more combustible gases during thermal conversion. The FC generate hydrocarbon fuels when matched with hydrogen, which is important for conversion of biomass into liquid fuels. A high ash content may cause problems in thermal conversions by fouling because of slag formation [23].

Jazrawi et al. [9] used *Spirulina*$_2$ and *Chlorella* algae species received as powders, in their study of a continuous flow HTL. The biochemical content as shown in table 2.2.2 was provided by the supplier. Both strains were grown for food supplement, and thus is rich in protein and low in lipid. The volume median diameter of the two powders was 48.8 and 62.2μm for *Chlorella* and *Spirulina*.

Table 2.2.2: Biochemical content of *Spirulina*$_2$ and *Chlorella* powders (wt.%) [9, Table 1.].

	Carbohydrates	Protein	Lipids
Spirulina$_2$	11	68	8
Chlorella	25	60	4

In comparison to the lipid content presented in table 2.2.2, the *Phaeodactylum tricornutum* algae are rich in lipids, containing 18 % lipids, 26 % carbohydrates and 36 % proteins [7]. Variations in the biochemical composition is found in literature. Reported values might be of algae collected in the wild, grown in pawns or bioreactors. The *Chlorella vulgaris* estimated composition $C_{106}H_{181}O_{45}N_{15}P$ roughly containing 37.5 % protein, 31 % carbohydrates and 30 % lipids [55], differs from the *Chlorella* algae in table 2.2.2.

Peng et al. conducted a study on the pyrolytic characteristics of *Spirulina platensis* and *Chlorella protothecoides* by TGA [20]. Three methods were used to determine the main chemical components of protein, carbohydrate and fat. These were the Kjeldahl method, Soxhlet-extract method and phenol-sulfuric acid method. Results from the chemical analysis is presented in table 2.2.3.

Table 2.2.3: Main chemical components of *S. platensis* and *C. protothecoides* cells [20, Table 1]. The percentage of others are determined by difference.

Component %	*S. platensis*	*C. protothecoides*
Protein	61.44±0.31	52.64±0.26
Lipid	10.30±0.10	14.57±0.16
Carbohydrate	10.57±0.13	10.62±0.14
Ash	4.34±0.03	7.38±0.05
Moisture	8.04±0.06	8.74±0.07
Others	5.31±0.63	6.05±0.68

From the TGA conducted at various heat rate, stages of the pyrolysis were characterized as well as the reaction rates. The moisture, volatile and final residue percentage of the initial biomass was calculated using the TGA results, shown in table 2.2.4. Using the ash percentage from table 2.2.3, the char percentage of the final residue in table 2.2.4 was determined to be 17.18-17.46 % and 14.00-15.14 % respectively for *S. platensis* and *C. protothecoides*.

Table 2.2.4: Moisture, volatile and final residue of *S.platensis* and *C.protothecoides* [20].

Microalgae	Moisture (%)	Volatile (%)	Final residue (%)
S. platensis	6.68-7.57	71	21.52-21.80
C. protothecoides	6.85-7.64	71	21.38-21.52

The heating value of algae biomass is commonly reported as the HHV. This due to the variation in the water content of various slurry's, compared to dry powders. In table 2.2.5 the higher heating value of a few algae species are presented. The three values presented for the *Spirulina* algae might differ in the real heating value of the biomass or by the equations or tests used to determine the value.

Table 2.2.5: Higher heating value of algae species and strains.

	HHV (MJ/kg)	
$Spirulina_2$	24.9	[9]
$Spirulina_3$	21.2	[51]
$Spirulina_4$	18.4	[31]
Chlorella	24.3	[9]
$Chlorella\ vulgaris_3$	23.2	[51]
Nannochloropsis	20.5	[31]

2.3 Hydrothermal Liquefaction

Hydrothermal liquefaction (HTL) is a thermochemical conversion that produces biocrude from biomass. If biomass is exposed to a water environment, heat and high pressure for sufficient time, the solid structure breaks down to form biocrude, aqueous, solid and gaseous products. Typical process conditions of HTL ranges from 245 to 375°C and from 4 to 22 MPa [56]. The biocrude produced can either be used as an alternative to heavy fuel oil, or upgraded to petroleum fuels. At temperatures below 245°C the process is not hydrothermal liquefaction, but hydrothermal carbonization. Above 375°C the process is hydrothermal gasification. The difference in the process of hydrothermal carbonization and hydrothermal gasification, is that carbonization produces hydrochar, while gasification produces synthetic fuel gas.

Subcritical water or superheated water is the term referred to when water is kept in its liquid phase under higher temperatures in the range 100-374°C [57]. This is done by obtaining a pressure high enough to keep the water in the liquid phase. If water is heated above 200°C, the concentration of $H_3O^+$and OH^- is increased by several magnitudes of order [58], while the pH remains neutral [57]. This makes the water act as an acid or base catalyst, making it possible to use the subcritical water as a solvent for wet biomass. Thus, reducing or eliminating the need of an added base or acid, for a reaction that normally would need an added catalyst.
Holding time or retention time, is the period in the HTL process where the maximum temperature in maintained. A low reactor temperature requires a longer holding time to obtain the same biocrude yield compared to a higher temperature.

Upgrading the biocrude is done mainly by removing the oxygen in the crude. Hydrotreating and hydrocracking of the biocrude, is used to produce similar hydrocarbon fuels to the petroleum products currently available on the marked [35]. Biocrude processed by catalytic hydrotreating produce liquid hydrocarbon products such as low sulfur diesel.

The HTL process seems to be an interaction between several reactions that is cross-linked, thus the products are difficult to predict. Barreiro et al. [7], describes the reactions by two main occurrences.

- The Millard reaction between the carbohydrates and proteins.
- Condensation occurring in the degradation products of lipids and protein.

The reaction mechanism of HTL is complicated due to interactions among reaction intermediates, and more effort is needed in the study of these interactions to illustrate the complete reaction pathway [59]. A pathway scheme of the simplified reaction for HTL of microalgae, is shown in figure 2.3.1.

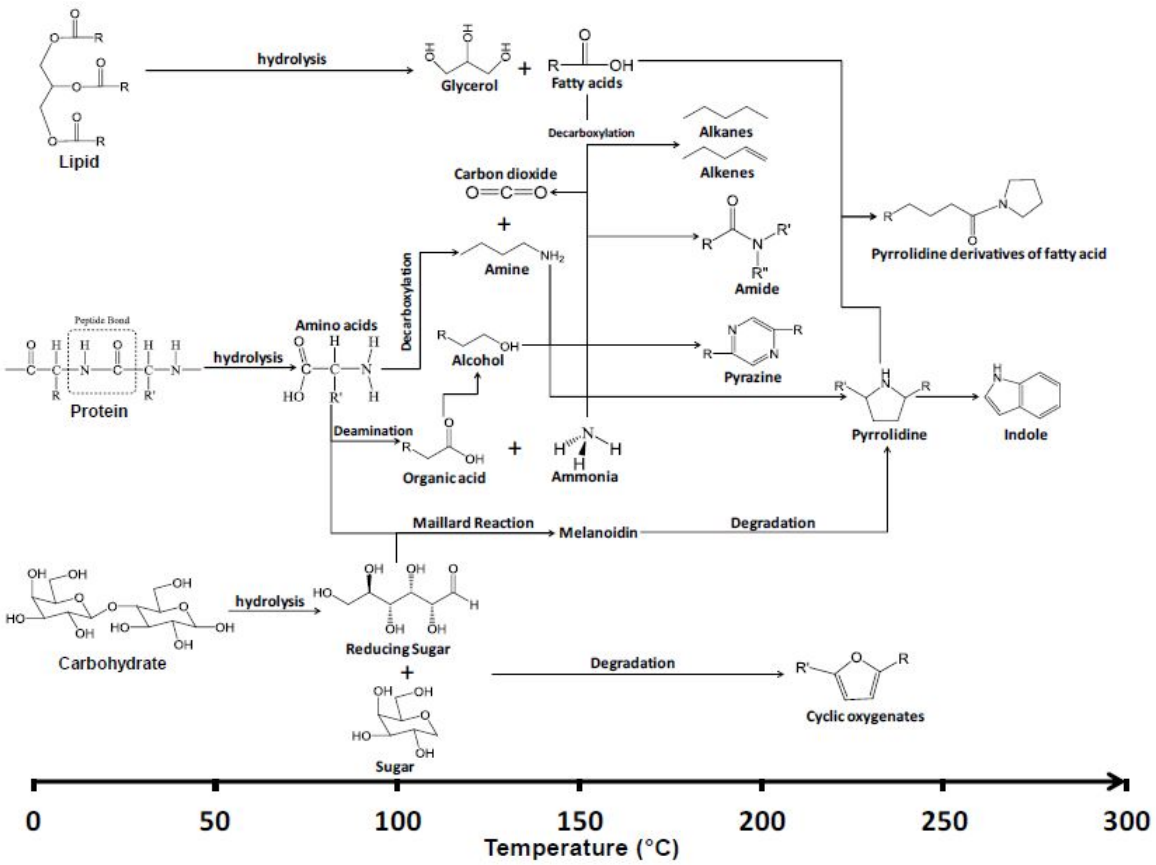

Figure 2.3.1: A simplified reaction pathway of microalgae HTL, from [59, Figure 9-16]. Temperature axis represent the lowest temperature of which reactions take place.

The simplified reactions in figure 2.3.1, is shortly explained in the following text:

- Hydrolysis is a chemical process that splits bonds of a molecule by addition of water molecule, creating two molecular fragments. H^+ is collected by one fragment, and OH^- by the other fragment [60]. There are three main types of hydrolysis in chemistry; salt, acid and base hydrolysis [61].
- The Maillard reaction is a temperature dependent chemical reaction that occurs between carbohydrates and amino acids [62].
- Decarboxylation is a chemical reaction that releases carbon dioxide by removal of a carboxyl group [63]
- Deamination occur when an amino group is removed from a molecule [64].

Dehydration and decarboxylation reduces the oxygen content of the biomass producing CO_2 and H_2O. In production of biocrude, decomposition of biomass relies on solvolysis and depolymerization. During HTL water is used as a solvent, this solvolysis reaction is named hydrolysis. Other reactions occurring is dehydration, condensation and isomerization [22]. The temperature helps the depolymerization, pressure maintains the single-phase medium and residence time is crucial for biomass

decomposition and biocrude composition. Particle size of biomass and heat rate are also significant variables in HTL.

2.3.1 Hydrothermal Liquefaction of Microalgae

A high yield of biocrude is obtained by HTL of algae, not only the lipids are converted but also the carbohydrates and proteins [56]. Biller and Ross [50] state that the trend of biocrude formation follows lipids>proteins>carbohydrates. The lipid content is converted into fatty acids. Proteins produce heterocycles, indoles and pyrroles while carbohydrates produce phenols and cyclic ketones.

Different methods for HTL has been found in literature, some of the work only focus on a main goal of obtaining biocrude, while others implement the upgrading to further optimize the total system of biocrude production. The reactor setup varies and though batch reactors is widely used in experiment testing, a few continuous reactor systems has also been tested and reported in literature. Different algae species, reactor temperatures, retention time, and catalysts are parameters considered in literature. The mass fraction of algae in the initial mixture feed to the reactor ranges from 4-50 % [7], though a value of about 80 % seems to become a commonly used value.

Vo et al. suggest that a microalga rich in lipid content, will produce a high yield of biocrude with a high content of fatty acid [65]. Analysis of HTL experiments on the *Aurantiochytrium* species algae at different temperatures and retention time, showed a trend of fast conversion of solids to biocrude, gas and aqueous phase at higher temperatures. At longer retention time the biocrude and aqueous phase percentage would decrease, and the gas percentage increase. The highest yield of biocrude was 51.22 wt.%, obtained after 10 min at $400°C$.

A study by Toor et al. on the HTL of *S.platensis* and *N.salina* concluded that subcritical water in more effective than supercritical water for extracting biocrude [66]. Suggesting optimal temperature of $310°C$ and 11.5 MPa pressure for *S.platensis*, $350°C$ and 17.5 MPa for *N.salina*.
Albrecht et al. [67], used a two-step process to make hydrocarbon fuel. First an intermediate biocrude was made by HTL of algae biomass. Then the biocrude was upgraded by HT (catalytic hydrotreating). HLT was conducted at $350°C$ and 20 MPa, while HT was conducted at $400°C$ and 10 MPa.

The composition of the biocrude from HTL is complex and strongly affected by the process conditions and biomass feed. A detailed chemical analysis of *Desmodesmus* sp. algae [68], characterized some of the main reactions and main behavior of the specific algae in HTL treatment. At low temperature, the main compounds are classified as lipids, with some hydrophbic protein and algaenan. Results at temperatures from 300 to $375°C$, shows that a reaction which converts the proteins, cellulose and carbohydrates to biocrude. At the higher temperature, the reaction causes higher

oil yield and nitrogen content in the oil. Reactions similar to pyrolysis breaks down cellulose and protein, to form amino acids side chains and cyclic dipeptides. The cellulose and protein also form carbohydrate derivatives, and from a cross reaction of carbohydrates and proteins, formation of pyrazines, pyrroles, alkyl-pyrrolidinones and melanoidin-like form.

A life cycle comparison of HTL and lipid extraction (LE) for diesel production from algae biomass [69], identify the main advantage of HTL compared to LE. That is the efficient utilization of algae biomass, not only the lipid content is converted into oil but also parts of the protein and carbohydrate. In terms of the life cycle analysis key variables was oil yield, nitrogen content in oil and hydrogen demand for upgrading.

2.3.2 Batch Reactor

The batch reactor is the most common reactor type for experiments on HTL of algae. A rather simple construction, consisting of a high-pressure tank and appropriate heating equipment leads to a low investment cost and easy of maintains. Different gases could be used to flush the air from the reactor, helium was used by Barreiro et al. [11].

Biller and Ross used a batch reactor to conduct HTL experiments on biochemical components, microalgae and cyanobacteria [50]. At $350°C$ and about 20 MPa the algae biomass was converted to biocrude, using either distilled water, formic acid ($HCOOH$) or sodium carbonate (Na_2CO_3). The most efficient conversion of lipid and protein was shown to be without the use of catalyst, while conversion of carbohydrates was most efficient with the use of Na_2CO_3. The same type of reactor, an unstirred bomb type design was used in similar experiments at $300°C$ and $350°C$ by Ross et al. [51]. By using an organic catalyst, a higher biocrude yield, improved flow properties and lower boiling point was achieved from *Chlorella vulgaris* and *Spirulina* algae. Increasing the temperature from 300 to $350°C$ increased the bio-crude yield of the *Chlorella vulgaris* algae, as Ross et al. conclude that an alga containing a higher lipid content will have a higher yield of bio-crude.

Raikova et al. used the *Spirulina platensis* algae in batch reactor tests [70]. Metal sulphates was added to the process to simulate metal remediation. Results from analysis of the biocrude produced, verify that algae used in acid mine drainage cleaning, could be used in HTL. Valdez et al. investigated the impact of time, temperature and biomass loading in HTL batch reactor experiments of *Nannochloropsis* sp. algae [54]. At temperatures from 250 to $400°C$, retention time from 10 to 90 min and biomass loading of 5 to 35 wt.%. The study suggests that HTL at shorter times than 10 min should be examined, since about half of the of the converted material was biocrude products at 10 min. Generally, temperatures of 300 to $350°C$ showed a greater yield of biocrude than at 250 and $400°C$, with a yield between 40 and 50 %. By increasing the temperature from 250 to $400°C$, the gas produced increased

from about 1 wt.% to 13 wt.%.

A batch reactor study of *C. protothecoides* and *Scenedesmus* sp. at different temperatures and retention time, conclude that the biocrude yield of the *Scenedesmus* sp. algae could reach a value four times larger than the lipid content of the initial algae biomass [71]. This verify that the HTL process utilizes more than the lipid content of the biomass. Huang et al. conducted batch reactor experiments of *Cyanobacteria* sp. and *Bacillariophyta* sp. algae, achieving energy recovery percentages in the range of 27-51% [72]. Variations in the results was established by varying the retention time and reactor temperature.

2.3.3 Continuous Flow Reactor

The continuous flow reactor is more complicated than the batch type reactor, and there are few studies on this reactor found in literature. A pump able to pump slurry at a higher pressure, heating equipment, a reactor and a valve for retaining the appropriate pressure is needed. Experiments are often run only over a short period of time, and difficulties due to clogging is one of the main concerns.

A thoroughly study was conducted by Elliott et al. of a continuous flow HTL process [73]. Four algae of *Nannochloropsis* sp. grown differently were used. A high levels of carbon conversion was achieved at $350°C$ and 20 MPa, slurry concentrations of up 35 wt.% dry solids. Analysis of the biocrude suggest that the phosphorus in the solid, oil and aqueous products from the process was quite low compared to the initial concentration in the feed, as only 27 % was accounted for. About 75 % of the phosphorus in the products was solid, 15 % in oil and 10 % in aqueous components. A minor decrease of nitrogen content in the HTL products at about 86 % of the initial biomass, was accounted for in the analysis. About 56 % in aqueous, 11 % in oil, 0.1 % in solid and 33 % in gas components.

Jazrawi et al. conducted tests of a continuous HTL pilot plant using *Spirulina* and *Chlorella* biomass [9]. A higher biocrude yield was obtained as the temperature and residence time was increased. This showed that more of the protein content of the algae was liquefied and thus increasing the nitrogen in the biocrude. The cell size of solids in the HTL process was examined by scanning electron microscopy (SEM). The initial *Chlorella* algae cells about $55\mu m$ in diameter, would aggregate to a compact structure up to $500\mu m$ in diameter at $250°C$. Increasing the temperature to $275°C$ the cells appeared to be less compact but approximate the same size. At a temperature of $300°C$ using the same residence time, the sell structure is destroyed and fragments of 10-15μm was left. Concluding that the breakdown temperature which gives the highest biocrude yield is $300°C$, at a residence time of 3 min. A reduction of the solid residue and pressure fluctuations in the process system after the reactor was also noticed. A maximum biocrude yield of 41.7 wt.% was reached for a solid concentration of 10 wt.% *Chlorella*, at 20 MPa, temperature of $350°C$

and residence time 3 min.

Zhu et al. used a lipid-extracted microalgae (LEA) of the *Nannochloropsis salina* strain, in a bench-scale continuous flow rector [35]. Lipid extraction is a process used to convert only the lipid fraction of the biomass to biodiesel, LEA is a by-product from this process. Water and LEA was mixed to a slurry with a moisture content of 83 wt.%, with LEA lipid content of 19.9±3 wt.%. The slurry was continuous fed into a continuous stirred-tank reactor at 20.9 MPa, with a temperature of 348°C at the outlet of the reactor. Biocrude produced was upgraded in a fixed-bed reactor. Elemental analysis showed an increase in the carbon wt.% on dry basis from 49.0 in LEA, 79.2 in biocrude to 85.0 in the upgraded bio-oil. The energy recovery percentage of bio-oil in continuous HTL calculated by Elliott et al. [56], was in the rage of 52-78 % based on several pilot plant experiments. Similar values were established by the *Chlorella* species in a study by Biller et al., with energy recovery percentages of 54.9 and 55.8 at residence time of 1.4 and 5.8 min [33].

2.3.4 Products from Hydrothermal Liquefaction

Product yields of HTL varies in different studies. Some report the yield as a weight percentage on a dry ash free basis of the algae feed weight percentage, while other report on the dry basis containing ash. Equation 2.3.1 was used by Barreiro et al. in the analysis of HTL products, from batch experiments [11]. The yield is established by the weight of the mass of each product (m_i), and the initial microalgae mass ($m_{microalgae}$) on a dry and ash free basis.

$$Yield_i(wt\%,\, daf) = (\frac{m_i}{m_{microalgae}}) \times 100 \tag{2.3.1}$$

The product yields of water solubles, solid residue, gas and biocrude is effected by the reaction temperature, holding time, and the solid concentration feed to the HTL reactor. Jena et al. used the *Spirulina platensis* algae in powder form, to show the effects of different temperatures, holding times and solid concentration on the HTL products [52]. The effects on the products is stated in the following text:

- The water content of the initial slurry is seen in most experiments to be about 60-90 %. With a water content of 80 %, the water solubles as a percentage of the total product yield decreases from 56.3 to 30.2 % when the temperature was increased from 200 to 380°C. By increasing the holding time from 0 to 120 min, the water solubles yield at 350°C decreased from 44.4 to 34.9 %. Increasing the solid concentration from 10 to 50 % resulted in a decrease from 44.6 to 30.9 % of the water solubles.

- The percentage of solid residue of the total product yield change with temperature, holding time and solid concentration (Feed). The most significant

effect on the solid residue is by temperature change, with the largest decrease from 200 to 300°C, and a total decrease from 22.0 to 5.7 % by an increase in temperature from 200 to 380°C. Holding time and solid concentration had little effect on the solid residue.

- A gas yield of about 5 % at 200°C and 28 % at 380°C, shows that the gases produced increase at higher temperature. At holding time from 0 to 60 min the gas yield is about 18 %, and at 90 and 120 min the yield has increased to 24 and 27 % respectively. The increase in solid concentration had no noticeable effect on the gas yield.
- The biocrude yield at 200°C was shown to be below 20 %, while at 350°C a maximum biocrude yield of 39.9 % was obtained. Above 350°C the yield decreased slightly. Holding time between 0 and 60 min had an increase in biocrude yield from about 30 to 40 %, while holding times above 60 min resulted in a decrease in yield. An increase in biocrude yield from 32.5 to 39.9 % was shown by increasing the solid concentration from 10 to 20 %. The yield at 20 to 50 % solid concentration had no further increase.

The higher heating value of biocrude from different microalgae species and strains in table 2.3.1, shows variations obtained by experiments found in literature.

Table 2.3.1: Higher heating value of biocrude.

	HHV (MJ/kg)	
Chlorella	33.8	[9]
Chlorella vulgaris	35.0	[11]
Spirulina	32.0	[9]
Spirulina	35.8	[12]
Spirulina platensis	35.27	[52]
Nannocholorpsis gaditana	37.2	[11]
Phaeodactylum tricornutum	35.9	[11]
Phaeodactylum tricornutum	37.4	[74]

The main gas products from HTL increases when the retention time or the temperature is increased, in conjunction with a decrease of biocrude [52]. Tang et al. found the main gas products of CO_2, H_2 and CH_4, from HTL of *Spirulina* and *Nannochlororpsis* [31]. Another study of *Spirulina* and *C. vulgaris*, suggest main gas products of CO_2, CH_4, CO [51]. Common in these studies is the major percentage of CO_2, and relatively small percentages of other gases. Jazrawi et al. consider about 95-99 mol% of the gas steam to be CO_2, in HTL experiments of *Spirulina* and *Chlorella* [9].

Li et al. detected an increase in the gaseous products from 1.1 % to 2.8 % (*Chlorella* sp.), and 2 % to 6.6 % (*Nannochlororpsis* sp.), by increasing the reaction temperature from 220°C to 300°C [75]. Main components by gas chromatography (GC)

was CO_2, H_2, CO, CH_4 and N_2. With 87 % CO_2, H_2 of 0.2-1.5 % for *Chlorella* and 0.1-0.6 % *Nannochlororpsis*. Both H_2 and CH_4 was shown to increase as the reaction temperature was increased.
In a batch reactor purged with N_2, Jene el al. detected the main gaseous components from HTL of *Spirulina platensis* [52]. Gaseous products consisted of 71.00 mol% N_2, 0.39 H_2, 0.79 CH_4, 1.10 CO, 26.00 CO_2 and 0.75 $C_0 - C_5$. The products in the range of $C_0 - C_5$, was higher hydrocarbon gases such as ethane, propane, butane, pentane, acetylene, butane and propylene.

The biocrude chemical compounds is highly affected by the temperature of the HTL process. Optimal temperature in terms of biocrude yield from *Spirulina* and *Nannochloropsis* was respectively 260°C and 280°C in batch reactor [31]. The solid residue from HTL of *Spirulina platensis* at 350°C, 60 min holding time and 20 % solid concentration was analyzed by elemental composition: C 11.82 %, H 2.41 %, N 1.61 %, S 1.81 % and O 82.43 % [52]. At temperatures above 350°C the biocrude yield decreased while the gas yield increase, due to decomposition of intermediate compounds that form gas.

Products of biocrude and gas obtained from HTL are valuable products and is the main focus in literature. The waste water, solids and organics in aqueous phase products are rarely considered valuable, but there is suggestion of recycling the solids and aqueous products. Recycling of nutrients in the HTL process for further cultivation of microalgae is possible by recycling the solids in the process water [56], and is considered a key element in optimization of HTL.

2.4 Aspen Plus

The Aspen Plus software is used in chemical process design, operation and optimization. This simulation tool from AspenTech is capable of modeling fluids and solids. With a large model library, the software is capable of modeling complicated chemical processes.

Designing a process in Aspen Plus starts by drawing a flow sheet, next the components is entered and the various operation conditions defined. The various pieces of equipment such as mixers, separators, heat exchangers, columns, and reactors are represented by blocks. Steams connecting the blocks could be chosen as heat, work or material streams. In each stream the work, temperature, pressure, flow rate and components could be defined depending on the stream type selected.

The various reactors perform calculations based on the different parameters as listed in the following text:

- RYield reactor requires the yield of components.
- RStoic and REquil reactor requires reaction stoichiometry.
- RGibbs reactor require detailed stoichiometry or yield.
- RCSTR and RPlug reactor require specific process conditions
- Batch reactor require specific operation specifications and reaction stoichiometry.

2.4.1 Process Simulation of HTL

There are few studies conducted on HTL of microalgae using Aspen Plus. Jones et al. performed process design and economic evaluation of microalgae hydrothermal liquefaction and upgrading [10]. It is a comprehensive study by the Pacific Northwest National Laboratory, with the main purpose of economic evaluation. A simulation model was made in Aspen Plus, where hydrothermal liquefaction produces biocrude from the microalgae feed, the biocrude is catalytic upgraded to produce renewable diesel fuel. The model is based on laboratory experiments and does not represent the current state of technology for commercial production of biofuel.

Zhu et al. designed an Aspen Plus model to evaluate the economic feasibility of a large-scale HTL process, using lipid-extracted algae (LEA) [35]. The model was based on results from bench-scale reactor experiments both for the hydrothermal liquefaction and the upgrading. About forty components was used in the simulation for the products of the HTL. These were based on the GC/MS analysis or elemental analysis from the experiment results obtained.

In both the previous mentioned studies on HTL in Aspen Plus, the RYield reactor was used. Algae or LEA was entered as user defined by the elemental and structural composition. Other components were chosen based on analysis or of equal properties.

Chapter 3

Method

In chapter 3.1, the microalgae species chosen for analysis is introduced. Chapter 3.2-3.4 describes the procedures and equipment used in proximate, ultimate and thermogravimetric analysis. Chapter 3.5 outlines the process description and key elements of the Aspen Plus simulation.

3.1 Algae

Microalgae biomass of three different algae species were analyzed using TGA, proximate analysis and ultimate analysis. *Chorella vulgaris* and *Spirulina platensis* algae were bought from an online health store, sold as ecological super-food. The two powders had different consistence, the *C. vulgaris* as a fine dust like powder and the *S. platensis* as a chunkier powder. The *Phaeodactylum tricornutum* algae were collected as a slurry from Truls Haugsrud, at J Kristiansen Gartneri AS in Grimstad. A total of three samples were provided, one with less water content than the two others. Variation of moisture was due to different filters used in the filtration process at their facility. The algae are grown in a tubular photobioreactor in one of their many greenhouses.

Since both *C. vulgaris* and *S. platensis* were bought as food, the content of these two algae might differ from what is seen in wild grown species. This is because the algae might be stressed in such way that it produces more protein and less lipids. The packaging of the two powders are shown in figure 3.1.1, and in table 3.1.1, the nutritional content is presented.

Table 3.1.1: Nutritional content of *C. vulgaris* and *S. platensis* powder.

		C. vulgaris	*S. platensis*
Protein	wt.%	59.1	63.5
Carbohydrates	wt.%	5.22	9.1
Fat	wt.%	13.4	8.2
Energy	kJ/kg	1.686	1.594

Figure 3.1.1: Packaging of the *Chorella vulgaris* and *Spirulina platensis* powder.

3.2 Proximate Analysis

The proximate analysis was conducted in the laboratory called Brænderiet at the University of Agder, Grimstad. This was done to measure the moisture content, volatile combustible matter, fixed carbon and ash content of algae samples.

Method

Two separate tests were conducted. Both tests were performed on the *C. vulgaris*, *S. platensis* and *P. tricornutum* algae. Test 1 was used to measure the moisture content and the ash content, test 2 was used to measure the volatile matter. Different crucibles were used for the two tests, big crucibles in test 1 and small crucibles with lid in test 2.

Test 1 First the crucibles were weighted and the number and weight noted, then approximately 3 g of sample was placed in each crucible. The crucibles containing the sample were weighted once more before they were placed in the heating cabinet at $105°C$. Samples were obtained in the oven until they were dry, and weight was stable. Crucibles containing the dry sample were removed from the heating cabinet and placed in a glass desiccator to cool, before once again being weighted. Next the crucibles were placed in the oven and the following program were used for the oven:

1. Oven heated from ambient temperature to $250°C$, over a period of between 30 and 50 min.
2. The oven temperature was kept at $250°C$ for one hour.
3. Temperature increased from $250°C$ to $550°C$, over a period of 30 minutes.

4. The oven temperature was kept at 550°C for a minimum of two hours.

Crucibles only containing the ash left after complete combustion, were placed in a glass desiccator to cool. Samples are weighted again after they have cooled.

Test 2 Small crucibles with lid were weighted before approximately 1 g of algae sample was placed in each crucible and they were once again weighed. One or more crucibles were placed in a crucible bracket and placed in the oven at 900°C for 7 min. Next, the samples were placed in a glass desiccator to cool. When the samples had cooled the crucibles and lid containing the rest of the sample were weighted again. The loss of weight in this test is due to the loss of moisture and volatile matter.

All the notes taken during the proximate analysis was entered in an excel document. From test 1, the initial weight of the sample and the sample weight after drying was used to calculate the moisture content by equation 2.2.1. An average value of each species was calculated based on three samples. The ash content was calculated using equation 2.2.6, and the average moisture content of the species. From test 2 the volatile matter was calculated using the initial weight of the crucible and lid, the weight of sample and the crucible with lid, the weight after heating and the moisture content.

3.3 Ultimate Analysis

Element analysis of the algae biomass was conducted on the PerkinElmer 2400 Series II CHNS/O Elemental Analyzer, available at the University of Agder. The instrument burns a small sample and analyze the combustion gases from the combustion. Thus, the percentage of carbon, hydrogen, nitrogen and sulfur were measured. Depending on the sample type and the elements of interest, different type of analysis is possible. The PerkinElmer was used in CHN mode, but was capable of CHNS and oxygen mode.

Method

When the element analysis was conducted, a tin cup was first put on the weight and the weight was set to zero by pressing tare. The tin cup was removed from the weight and an algae biomass of approximately 1.5-2.5 mg was placed in the cup. The cup was then weighed a second time. If the weight of the sample was within the rage, the cup was folded around the sample mass. Next, the cup was weighted, the name of the sample and weight was entered into the instrument, and the cup was placed into the respectively numbered chamber of the instrument. The elemental analyzer would run the sample and the results appear on the computer connected to the analyzer.

Before element analysis, samples were dried to maintain accurate results. To verify that the element analyzer was working properly, a cycle of blank samples and two samples containing specific test material were executed. The cycle was conducted as follows: Three tin cups of blank samples, one tin cup containing an organic analytic standard material, one tin cup of blank, one tin cup of the analytic material. The results from this cycle was checked to match the specification on the container of the organic analytic standard material, where the accurate percentage of carbon, hydrogen and nitrogen is stated.

Test Before the test started the samples of algae was dried in a heating cabinet at 105°C. The *S. platensis* and *C. vulgaris* was dried overnight while the *P. tricornutum* was dried for about 3 hours. After the samples was collected from the heating cabinet the test on the PerkinElmer elemental analyzer was started. The First a blank was used, then three samples of the *S. platensis*, another blank followed by three samples of *C. vulgaris*. Due to some error, the blank that was supposed to be before the three samples of *P. tricornutum*, was not executed correctly. It would happen because of the blank had gotten into the same chamber as the first *P. tricornutum*, another sample of that algae was executed to have a total of three results without errors.

The results from the ultimate analysis was exported to an excel document where mean values from the three samples of each algae was calculated. Oxygen content is usually calculated by subtracting the sum of H, C, S, N and ash from 100 %. But since no sulfur test was conducted, the oxygen content was calculated by subtracting H, C, N and ash from 100 %.

3.4 Thermogravimetric Analysis

The thermogravimetric analysis was performed using the Mettler Toledo TGA/DSC 1, available at the University of Agder in Grimstad. The instrument is capable of simultaneous thermogravimetric analysis and differential scanning calorimetry.

Method

The first step in using the TGA instrument, was to create an appropriate method for the chosen sample material. Since the main interest was the components of the biomass, a step method was created. The first step is the drying process referred to as the volatile step, the second step is the decomposition by pyrolysis. The third step is the combustion step in which the fixed carbon is released, leaving mostly ash as the remaining mass. Using the results from the TGA, the amount of fixed carbon was calculated.
The following method was used for the TGA instrument:

1. Sample weight was stabilized at 30°C for 1 min in N_2 atmosphere. N_2 flow rate 50 ml/min.
2. Heated from 30°C to 110°C, heat rate 20°C/min in N_2 atmosphere, 50 ml/min.
3. Isotherm step, 110°C for 15 min in N_2 atmosphere, 50ml/min.
4. Heated from 110°C to 900°C, heat rate 100°C/min in N_2 atmosphere, 50 ml/min.
5. Isotherm step, 900°C for 7 min in N_2 atmosphere, 50 ml/min.
6. Isotherm step, 900°C for 10 min in oxygen atmosphere, oxygen flow rate 50 ml/min.

The test on the algae samples were started by entering the information into the instrument. Method parameters, run blank, sample names and crucible type was chosen. Nitrogen supply to the TGA instrument was checked and adjusted to approximately $0.02NL/min$. Coolant supply was verified by a look at the turning wheel in the coolant pipe, coolant level in the cooling machine and the operation display. Air supply to the TGA machine was verified by lifting the air pump, hearing the pump and feeling the vibration of the pump.

The crucible chosen was the Alumina 150µl, one crucible was placed on the crucible holder for the DSC measurement. Seven crucibles were placed on the turn table, the first used as the blank sample while the six other was used for the biomass samples. Next, the weight procedure of the crucibles was started by the computer, first the blank was weighted two times then the seven empty crucibles. When the weight procedure was finished crucible 2-7 was removed from the turn table and algae biomass was placed in its respective crucible. In number 2, 3 and 4 samples of *C. vulgaris*. In number 5, 6 and 7 *S. platensis*. Crucibles containing the algae was placed back on the turn table in their correct positions and the experiment started by running the blank two times before the algae samples.

After the experiment the crucibles was removed, only small amounts of ash were left in the crucibles. Black ash from the *C. vulgaris*, light brown or yellow ash from the *S. platensis*. An error occurred in all three samples of *C. vulgaris*, three new samples were conducted with a smaller amount of sample in each crucible.

Next up for the TGA was the *P. tricornutum* algae, three samples were first used but the results showed that the water content was not fully removed before the second step (decomposition). There was also a difference in each sample, showing that the last sample dried while waiting on the two others. To correct this error, three more samples was conducted, these were placed in the TGA instrument one day, and dried to the next day in the laboratory atmosphere before the experiment was conducted. The results showed a lower moisture content and water content fully removed giving stable values for the three samples.

Results from the first experiment of the *S. platensis* algae, the second experiment of the *C. vulgaris* and the second experiment of the *P. tricornutum*, was used in in further analysis. Results from the TGA was exported as a text file from the computer of the TGA instrument. The text file was imported into an excel sheet, where the results from each test-sample was calculated and checked for errors before the average value of each species was determined. Three samples of each algae were used to create a mean value.

3.5 Simulation Model

A simulation in Aspen Plus was used in this master thesis, for the simulation of a pilot plant size HTL process. Aspen Plus is a simulation software used in chemical process design, operation and optimization. This tool developed by AspenTech, is capable of modeling complicated chemical processes and offers several different thermodynamic property methods. In this thesis, the main task for the simulation was to make a yield based model of the HTL process, in terms of the energy required to turn the slurry into products of solids, aqueous, gas and biocrude.

3.5.1 Process Description

The design of the HTL plant started by drawing the main flowsheet for the process, consisting of the main components, a pump, heater and reactor. Input, output, and streams between the components was drawn. The reactor was modeled as a RYield reactor for the HTL. In terms of simplifying analysis of the components in the product stream, a separator was added. The feed entering the system is considered as an algae slurry containing a high water content. Products are separated in separator into products of gases, solids, aqueous and biocrude. A second plant was made by adding a heat exchanger. The two different systems were named plant 1 and plant 2.

Plant 1 The layout of the plant 1 is shown in figure 3.5.1, the following operations takes place: A slurry containing water and biomass (FEED) is pressurized to the specified pressure by the feed pump (PUMP). The mixed stream is heated to the specified reactor temperature by the heater (PREHEAT), before entering the reactor (RYIELD). In the reactor, the water and biomass mixture is converted to HTL products in the fluid, solid, and gas phase. The separator (SEP) distribute the components in the products stream into the streams of biocrude, solids, aqueous and gas.

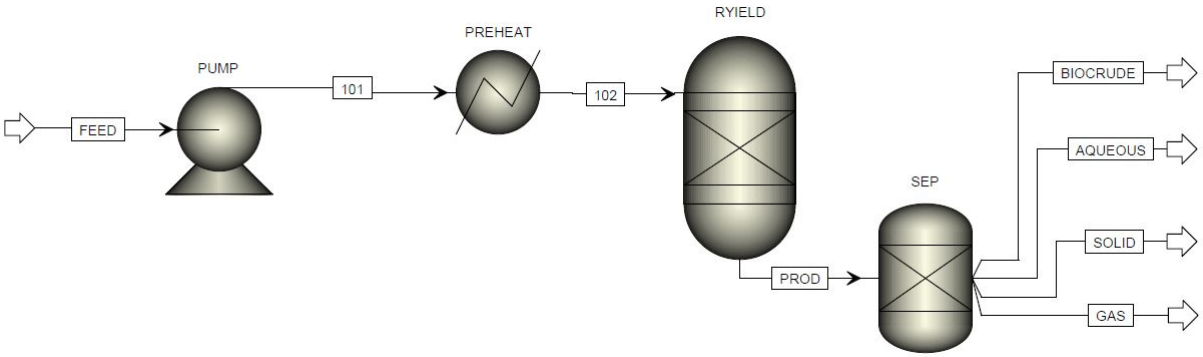

Figure 3.5.1: HTL flowsheet, plant 1.

Plant 2 Layout of the plant 2 is shown in figure 3.5.2 the following operations takes place: A slurry containing water and biomass (FEED) is pressurized to the specified pressure by the feed pump (PUMP). The mixed stream is heated in the heat exchanger (HX) by the hot products in the stream from the reactor. Next, the mixed stream in heated to the specified reactor temperature by the heater (PREHEAT), before entering the reactor (RYIELD). The hot stream from the reactor is cooled as it flows through heat exchanger, the products in the stream are separated into appropriate streams of biocrude, solids, aqueous and gas in the separator (SEP). The counter current heat exchanger (HX) implemented in the plant has a heat transfer area of 2 m^2.

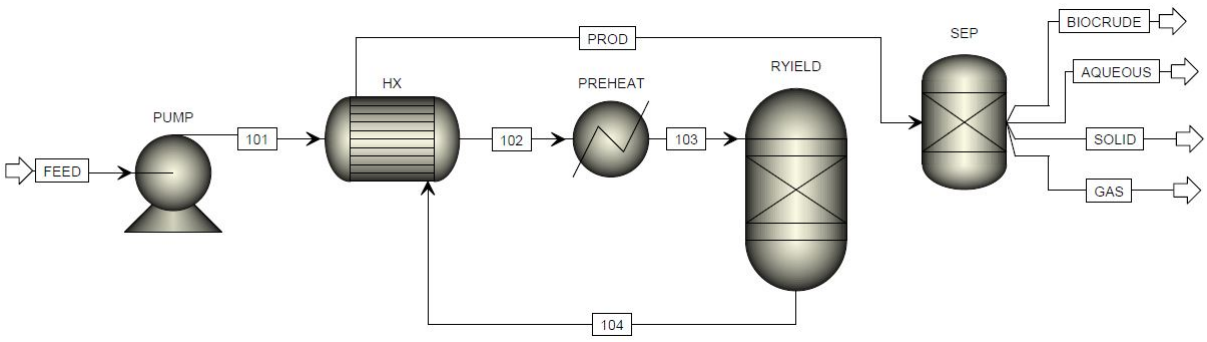

Figure 3.5.2: HTL flowsheet, plant 2.

Components in the Aspen Plus model is added as conventional or non-conventional. Water in the feed and components in the crude, gas and aqueous phase are conventional with data available in the Aspen Plus software. Algae and solid phase components are user defined, non-conventional components. The enthalpy and density of the non-conventional components are calculated using special models designed for coal-derived materials, named HCOALGEN and DCHARIGT. For the HCOALGEN the Boie correlation is used in calculation of the heat of combustion. Kirov correlation is used to calculate the heat capacity, and heat-of-combustion-based correlation is used for the calculation of standard heat of formation. For the DCHARIGT the density is determined by the components attributes, based on IGT equations (Institute of Gas Technology).

The elemental composition entered in ULTANAL, SULFANAL and PROXANAL are the components attributes from ultimate, sulfur and proximate analysis used for HCOALGEN and DCHARIGT. The four output stream from the separator, are defined as biocrude, aqueous, solid and gas phase. Biocrude phase contains seventeen different components of different yields. Aqueous phase is a mix of twelve different components, with a major part being water. Biocrude and aqueous phase components, and yield of each component in these two phases are taken from [10]. Since the yields of the three algae species used differ, the yields of components had to be calculated and fitted to each simulation. The gas phase consists of five gas components, CO_2 being the major contributor. Due to little research on the solid phase products found in literature, the solids are chosen as ash and char. Yield, component and properties used in each simulation of the various algae species is listen in appendix C. For the *P. tricornutum* algae a moisture content of 7.5 % was used in the simulation model.

For the three species of algae, temperature, pressure and yield are the main differences. In the Aspen Plus model the following operation conditions was used for HTL:

- *S. platensis*, pressure 12 MPa, temperature 300°C, biocrude yield 31 wt.%.
- *C. vulgaris*, pressure 20.2 MPa, temperature 348°C, biocrude yield 38 wt.%.
- *P.tricornutum*, pressure 27 MPa, temperature 375°C, biocrude yield 54 wt.%.

3.5.2 Assumptions

The key assumptions in the Aspen Plus simulations performed in this master thesis, is presented in the following list.

- Steady-state operation
- Uniform heat distribution

- Instant reaction and full conversion of biomass
- Homogeneous mixing
- Ideal separator
- No pressure drop
- Uniform particle size of algae species

3.5.3 Evaluation of Heat and Energy

The energy conversion efficiency η biomass to biocrude on a LHV basis are calculated by equation 3.5.1. With mass m_i, lower heating value LHV, heat Q_{Heater} and pump work W_{Pump} from Aspen Plus model.

$$\eta = \frac{(m_{Biocrude} \times LHV_{Biocrude})}{(m_{Algae} \times LHV_{Algae}) + Q_{Heater} + W_{Pump}} \times 100\ [\%] \tag{3.5.1}$$

Energy conversion efficiency of the HTL process, is calculated by equation 3.5.2. Were the energy content in gas and aqueous phase components is included. Solid components are not included as they were selected as pure ash with no valuable heating value.

$$\eta_{HTL} = \frac{(m_{Biocrude} \times LHV_{Biocrude}) + (m_{Aquous} \times LHV_{Aquous}) + (m_{Gas} \times LHV_{Gas})}{(m_{Algae} \times LHV_{Algae}) + Q_{Heater} + W_{Pump}} \times 100\ [\%] \tag{3.5.2}$$

Production of biocrude is the main objective of HTL, converting the biomass into a biocrude with a higher heating value than the initial biomass. Equation 3.5.3, shows the energy recovery of biocrude as a ratio of the heat content of biocrude and algae. Similar equations have been found in literature [72][74][13][31].

$$Energy\,recovery\,biocrude = \frac{m_{Biocrude} \times HHV_{Biocrude}}{m_{Algae} \times HHV_{Algae}} \times 100\ [\%] \tag{3.5.3}$$

Chapter 4

Results

4.1 Algae Characterization

The result section of the algae analysis is sectioned into four subsections. First the proximate analysis results are presented, then ultimate analysis, calculations of heating value and last the thermogravimetric analysis. Three species of algae was used *Chlorella vulgaris*, *Spirulina platensis* and *Phaeodactylum tricornutum*.

4.1.1 Proximate Analysis Results

Results from proximate analysis is presented in table 4.1.1, as mean values based on the three samples of each species. The amount of fixed carbon was calculated based on the mean values. Test 2 was to determine the volatile combustible matter (VCM), while moisture content (MC), ash and fixed carbon (FC) was determined in test 1.

Table 4.1.1: Proximate analysis results. VCM, FC and ash reported on a dry basis.

	% MC	% VCM	% Ash	% FC
S. platensis	5.7	79.6	8	12.4
C. vulgaris	5.5	82.4	5.4	12.2
P. tricornutum	83.2	77.9	15.8	6.3

Both *S. platensis* and *C. vulgaris* show promising values in terms of high VCM and FC percentage, with a low ash percentage. *P. tricornutum* algae has shown low FC and high ash percentages compared to the two other algae. The remaining ash of samples in test 1 were different for each algae species. *S. platensis* ash was a white porous lump, *C. vulgaris* ash was a small solid black lump, and the *P. tricornutum* ash was a porous powder. The remaining ash in the crucibles from the three algae species is presented in figure 4.1.1.

Figure 4.1.1: Remaining ash in crucibles after test 1. *S. platensis* (left), *C. vulgaris* (center), *P. tricornutum* (right).

The first experiments used for the VCM in test 2, did not give any results. This was due to the expansion of the *C. vulgaris* biomass, lifting the lid of the crucible. New experiments were conducted with less sample mass in each crucible. These experiments were successful, and results was used in calculation of VCM. In figure 4.1.2 and 4.1.3, the transparent crucible show how the three different algae samples reacted, leaving marks on the crucibles.

Figure 4.1.2: Crucibles used in test 2, of the *C. vulgaris* (left) and *S. platensis* (right).

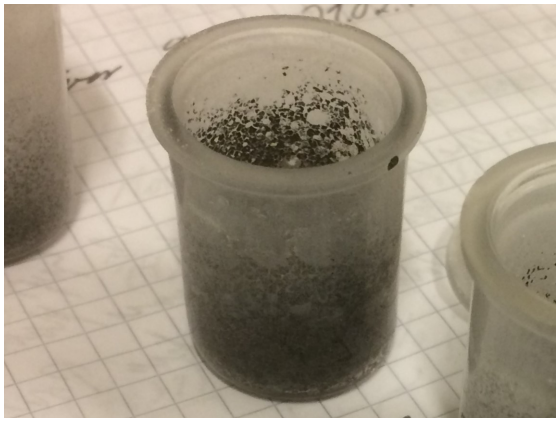

Figure 4.1.3: Crucible used in test 2, of *P. tricornutum*.

4.1.2 Ultimate Analysis Results

The results from the ultimate analysis are presented in table 4.1.2. Oxygen content is calculated as the difference between 100 % and the sum of the percentage C, H, N, S and ash content. The ash content used is from proximate analysis. No measurement of sulfur was conducted; thus it was neglected in the calculations. The oxygen percentage is higher than the real value of the algae. The *C. vulgaris* algae contains the highest percentages of carbon and hydrogen. *P. tricornutum* algae has the lowest nitrogen percentage of the three algae species.

Table 4.1.2: Ultimate analysis results, oxygen calculated by difference.

	C %	H %	N %	O %
S. platensis	48.5	6.8	11.2	25.5
C. vulgaris	51.0	7.0	9.5	27.1
P. tricornutum	44.2	6.9	7.4	25.7

4.1.3 Heating Value Calculation

Four different calculations for the heating value of the three algae species were conducted and values is presented in table 4.1.3. Using the GCV, NCV, Dulong and Boie equation, based on element composition from ultimate analysis and percentages from proximate analysis. Sulfur content was neglected in calculations due to no sulfur content measurement available. If sulfur content would have been examined and used in calculations, a higher value of all four heating values would have been the outcome. The *P. tricornutum* slurry had a high moisture content, giving a low value of NCV. Heating value of *C. vulgaris* was shown to be greater than for the two other species, *P.tricornutum* had the lowest heating value. Gross calorific value (GCV) is calculated on the dry basis, net calorific value (NCV) is on the wet basis.

Table 4.1.3: Heating value of different algae species (MJ/kg).

	GCV d.b.	NCV w.b.	HV Dulong eq.	HHV Boie eq.
S. platensis	21.97	19.44	21.62	22.83
C. vulgaris	22.99	20.46	22.46	23.66
P. tricornutum	20.46	1.20	20.27	21.17

4.1.4 Thermogravimetric Analysis Results

Thermogravimetric analysis (TGA), heat flow and derivative thermogravimetric analysis DTG, are the three main graphs made in Excel. These were obtained by the results from the TGA instrument, collected as data. The TGA graph of the *S.platensis*, *C.vulgaris* and *P.tricornutum* algae is shown in figure 4.1.4. A slightly dip in the curve due to drying of the sample is noticed from 0 to 500 seconds as the temperature increase from 30 to 110°C. The major weight decrease by pyrolysis at time 1300-2000 seconds, occur when temperature increase from 110 to 900°C. A last rapid weight decrease occurs approximately at 2150 seconds. This last step is the combustion of the sample when the atmosphere is changed from nitrogen to oxygen.

In figure 4.1.4, the graph of the *P. tricornutum* slurry has a kink at the start of the decomposition step and combustion step. Graphs for *S. platensis* and *C. vulgaris* powder has a more rounded profile at the start of the decomposition step and combustion step. The kink and the rounded profile is one of the main differences in the graphs, and reflect the behavior during rapid temperature change. The *S. platensis* and *C. vulgaris* powders had a steeper weight-loss curve in the decomposition step starting at a slightly higher temperature. In the combustion step differences verify the variation in FC as seen in proximate analysis. *S. platensis* and *C. vulgaris* seem to behave quite equal, with a slight difference in the combustion step. The dotted line was the temperature of the atmosphere surrounding the sample during TGA analysis. Specific heat rate and temperature was defined by the method used for the TGA instrument, and are presented in chapter 3.

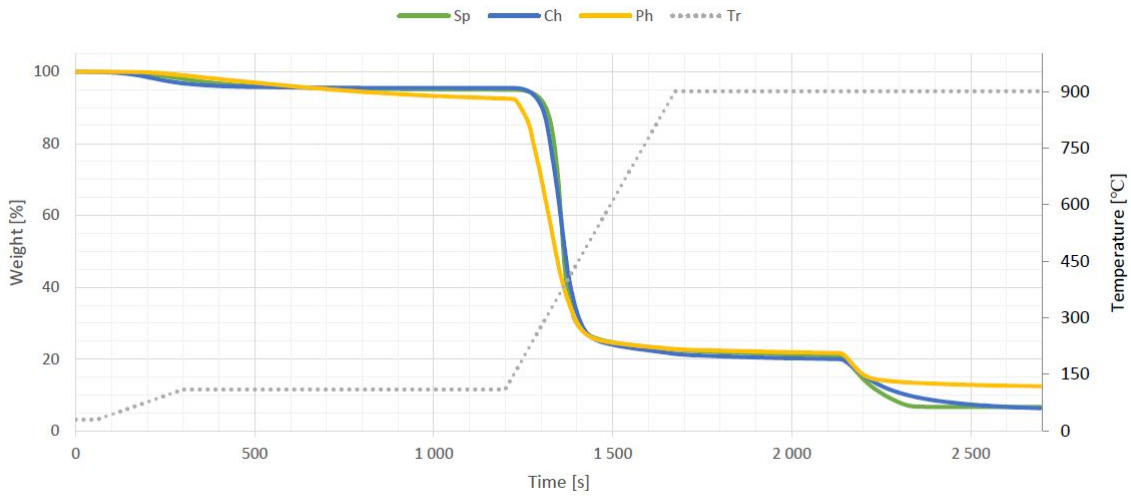

Figure 4.1.4: TGA results of *S.platensis* (Sp), *C.vulgaris* (Ch), and *P.tricornutum* (Ph). Dotted line (Tr) is the temperature setting.

From the TGA results the VCM, MC, FC and ash was calculated, values shown in table 4.1.4. These values are not valid in terms off the reel value of the biomass, but in comparison to the values from proximate analysis the volatile combustible matter only show minor differences. Moisture content in TGA of *P. tricornutum*, is lower than results in proximate analysis because the biomass was dried in the laboratory atmosphere overnight before TGA. The reduction in moisture content from dying was 75.7 %, from the moisture content of 83.2 % in proximate to 7.5 % in TGA.

Table 4.1.4: Structural elements by TGA. VCM, FC and ash on a dry basis.

	% MC	% VCM	% Ash	% FC
S. platensis	5.0	77.9	7.0	15.1
C. vulgaris	4.6	79.1	6.6	14.3
P. tricornutum	7.5	76.5	13.4	10.1

Heat flow as endothermic and exothermic regions during TGA is shown as a differential scanning calorimetry (DSC) graph, in figure4.1.5. The behavior of the *P. tricornutum* which is a slurry, differs from the two powders of *S. platensis* and *C. vulgaris*. There are two main exothermic regions, the first is occurring in the volatile step and the second one in the combustion step. In the first region, the *P.tricornutum* algae releases the highest amount of heat, while in the second region the *S. platensis* releases the highest amount.

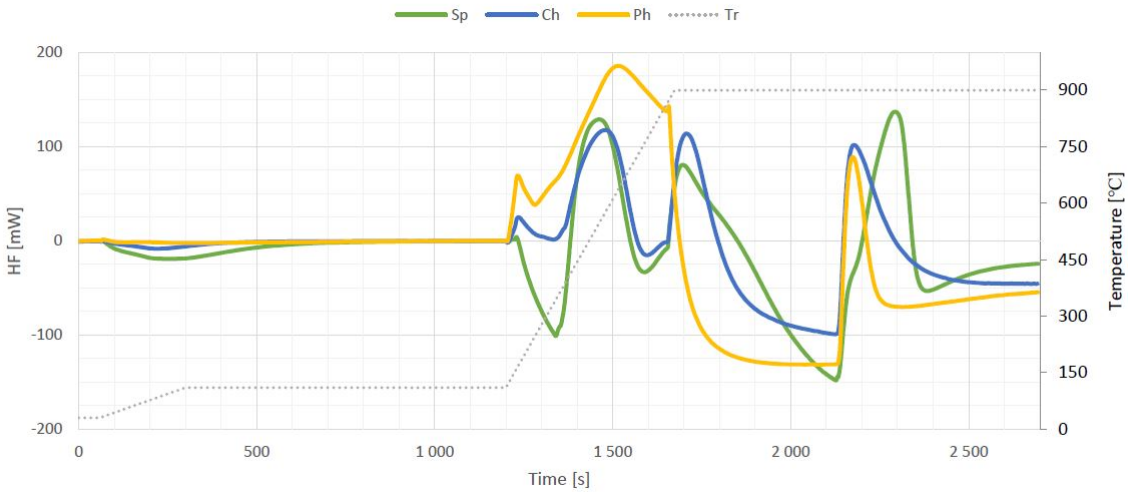

Figure 4.1.5: Heat flow graph (DSC), of *S. platensis* (Sp), *C. vulgaris* (Ch) and *P. tricornutum* (Ph). Dotted line (Tr) is the temperature setting.

The DTG graph of TGA is shown in figure 4.1.6. Three regions are visible, a minor bump in the drying step, several large peaks in the decomposition step and a minor peak in the combustion step.

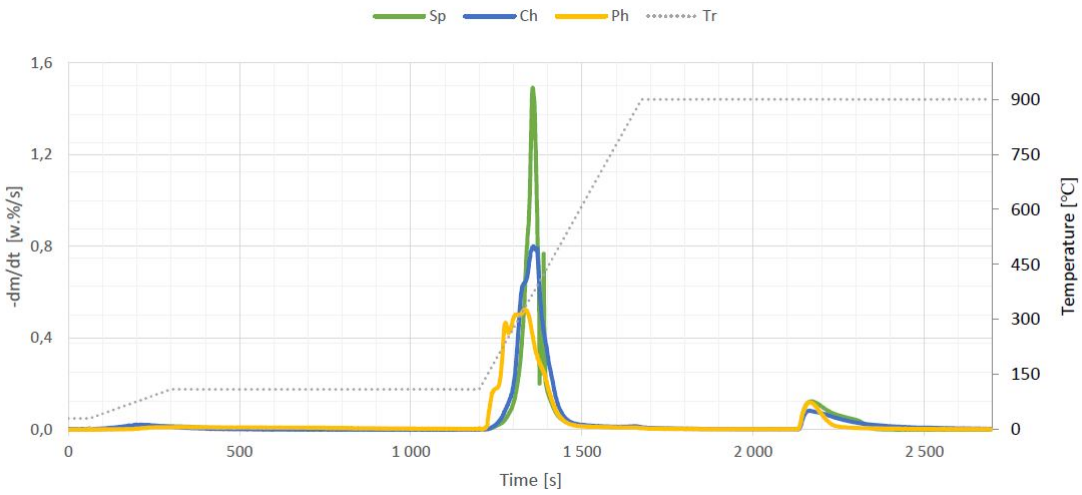

Figure 4.1.6: DTG graph, *S. platensis* (Sp), *C. vulgaris* (Ch) and *P. tricornutum* (Ph). Dotted line (Tr) is the temperature setting.

A detailed graph of the main peaks of the DTG graph is shown in figure 4.1.7. Main peak occurs at 370°C and some roughness in the graph at around 400-420°C, for *S. platensis*. Decomposition of *C. vulgaris* shows first a peak at 320°C, then a main peak around 370-390°C. For *P. tricornutum* a small peak occurs at 180°C, then a a second peak at 230°C and the largest at 335°C.

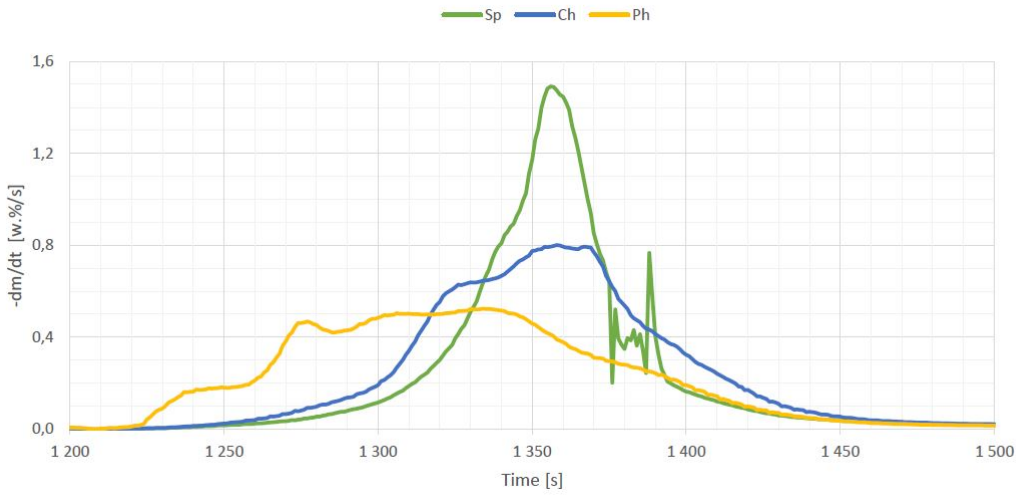

Figure 4.1.7: DTG graph, in the time span of 1200-1500 seconds from figure 4.1.6. *S. platensis* (Sp), *C. vulgaris* (Ch), *P. tricornutum* (Ph).

The peak of the DTG graph in the combustion step is shown in figure 4.1.8. At a temperature of 900°C the atmosphere is changed from nitrogen to oxygen and the combustion starts. The fixed carbon of the *P. tricornutum* algae disappear faster than in the *S. platensis* and *C. vulgaris* algae.

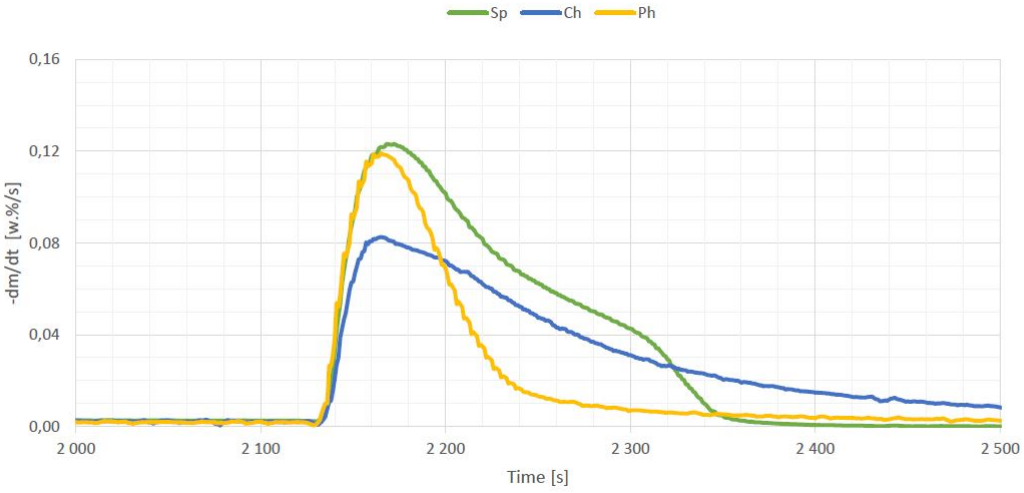

Figure 4.1.8: DTG graph, in the time span of 2000-2500 seconds from figure 4.1.6. *S. platensis* (Sp), *C. vulgaris* (Ch), *P. tricornutum* (Ph).

In appendix A more figures and results are shown. A figure explaining the temperature of the sample and atmosphere is introduced, and figures for the three samples conducted for each species are presented by TGA and DSC graphs.

4.2 Process Analysis

In this the two following chapter the results from the Aspen Plus simulation of continuous hydrothermal liquefaction of microalgae is presented. Starting with results of the mass balance and then the process energy result.

4.2.1 Mass Balance

The mass balance of HTL for each algae species is given in table 4.2.1. The mass balance of output and input, is arranged according to equation 4.2.1 and 4.2.2. Water is separated from the other aqueous phase organics in the aqueous phase product, this is done in the result section to simplify the evaluation.

$$\sum \dot{m}_{In} = \sum \dot{m}_{Out} \tag{4.2.1}$$

$$\dot{m}_{Algae} + \dot{m}_{Water} = \dot{m}_{Biocrude} + \dot{m}_{Aquous} + \dot{m}_{Water} + \dot{m}_{Solids} + \dot{m}_{Gas} \tag{4.2.2}$$

From the input of 60 kg/h *S. platensis* algae, 18.6 kg/h of biocrude output was obtained. For the *C. vulgaris* algae the input of 56.1 kg/h, resulted in a biocrude output of 21.3 kg/h. The input of 21 kg/h of *P. tricornutum* algae, resulted in the output of 11.3 kg/h of biocrude. Water was by far the largest part of the products from HTL of algae. A major difference in the gas phase products and aqueous products is shown in table 4.2.1. The yield of components in the solid phase was low, and had a minor variation. If considered twenty-four hour operations, the annual production of biocrude would be about 180,000 liters from *S.platensis* algae, 211,000 from *C. vulgaris* and 124,000 from *P. tricornutum*. The ratio of water and algae in the feed was based on the reference studies used for the specific yield of each algae.

Table 4.2.1: Mass balance in HTL simulation.

		S. platensis	*C. vulgaris*	*P. tricornutum*
Input: $\dot{m}$ (kg/h)	Algae	60	56.1	21
	Water	240	243.9	279
	Total	300	300	300
Output: $\dot{m}$ (kg/h)	Biocrude	18.6	21.3	11.3
	Aqueous	13.8	33.1	2.5
	Water	240	243.9	279
	Solids	6.6	1.1	1.5
	Gas	21	0.6	5.7
	Total	300	300	300

4.2.2 Energy

The energy consumption of the heater, pump and as a total of each plant is shown in table 4.2.2. In plant 2, the heat exchanger decreases the energy demand of the heater. Difference in pump and heater consumption, reflects the difference in pressure and temperature of each process. The temperature and pressure of each HTL process used in the simulation was $300°C$ at 12 MPa for the *S. platensis* algae, $348°C$ at 20.2 MPa for *C. vulgaris* and $375°C$ at 27 MPa for *P. tricornutum*.

Table 4.2.2: Energy consumption plant 1 and 2.

		S. platensis	*C. vulgaris*	*P. tricornutum*
Pump	(kW)	2.7	4.6	7.0
Heater Plant 1	(kW)	114.7	154.8	242.9
Heater Plant 2	(kW)	19.3	35.2	84.5
Total Plant 1	(kW)	117.4	159.4	249.9
Total Plant 2	(kW)	22.0	39.8	91.5

Aspen Plus used the components in each stream to estimate the HHV and LHV. In the biocrude product streams the simulation results gave a HHV of 33.2 MJ/kg, and

LHV of 30.8 MJ/kg. With a 46.9 % energy recovery percentage, the *S. platensis* algae had the lowest value. A medium recovery percentage of 54.9 % was found for *C. vulgaris*, while a high percentage of 87.7 % for *P. tricornutum* algae. This high percentage is due to the high yield and low HHV of the algae feed compared to *S. platensis* and *C. vulgaris*. The Energy conversion efficiency biomass to biocrude, and HTL process energy conversion efficiency is presented in table 4.2.3. By implementing the heat exchanger, efficiency increased by a minimum of 10 %, and a maximum of 53 %.

Table 4.2.3: Energy conversion efficiency, η (biomass to biocrude) and η_{HTL} (HTL process).

		S. platensis	*C. vulgaris*	*P. tricornutum*
Plant 1				
Energy efficiency η	(%)	36	38	28
HTL energy efficiency η_{HTL}	(%)	41	45	30
Plant 2				
Energy efficiency η	(%)	46	52	78
HTL energy efficiency η_{HTL}	(%)	83	61	83

The main idea of HTL is to increase the energy of the biomass when converted into biocrude. By establishing the relation of $E_{Biocrude}/E_{Algae}$ the increase of energy in one kg of fuel is stated. Based on the LHV, $E_{Biocrude}$ is the energy content of the biocrude and E_{Algae} is the energy content of the algae. For *S. platensis* the relation was 1.59, for the *C. vulgaris* algae it was 1.51, and for *P. tricornutum* it was 1.85. In table 4.2.4, several equations and results are shown. The first equation is the energy recovery of biocrude on the LHV. In table 4.2.4 equations 2 and 3, based on the energy flow are presented. The third equation shows the energy flow of the output product of main focus, when the consumption of the heater and pump is considered.

Table 4.2.4: Energy equations plant 1 and plant 2.

Equation	*S. platensis*	*C. vulgaris*	*P. tricornutum*
1. $(\frac{\dot{E}_{Biocrude}}{\dot{E}_{Algae}}) \times 100\,(\%)$	49.2	57.3	99.8
Plant 1			
2. $[\frac{(\dot{Q}_{Heater}+\dot{W}_{Pump})}{\dot{E}_{Biocrude}}] \times 100\,(\%)$	73.6	87.3	257.2
3. $\dot{E}_{Biocrude} - \dot{Q}_{Heater} - \dot{W}_{Pump}\,(kW)$	42	23	-153
Plant 2			
2. $[\frac{(\dot{Q}_{Heater}+\dot{W}_{Pump})}{\dot{E}_{Biocrude}}] \times 100\,(\%)$	13.8	21.8	28.1
3. $\dot{E}_{Biocrude} - \dot{Q}_{Heater} - \dot{W}_{Pump}\,(kW)$	137	143	70

Results from the sensitivity analysis of the heat exchanger in plant 2, is presented in figure 4.2.1, 4.2.2 and 4.2.3. For the heater, a heat duty curve marked as a black line in the figure, show how the energy demand decreases as the heat exchanger area increases. The decrease in heat duty reflects the effect of heat exchanger area and difference in operation temperature of the three HTL processes.

At a HTL operation temperature of 300°C for *S. platensis*, a decrease in heat duty of 55 % was obtained by increasing the heat exchanger area from 2 to 4 m^2.
In figure 4.2.1, the rapid decrees of heat duty are presented.

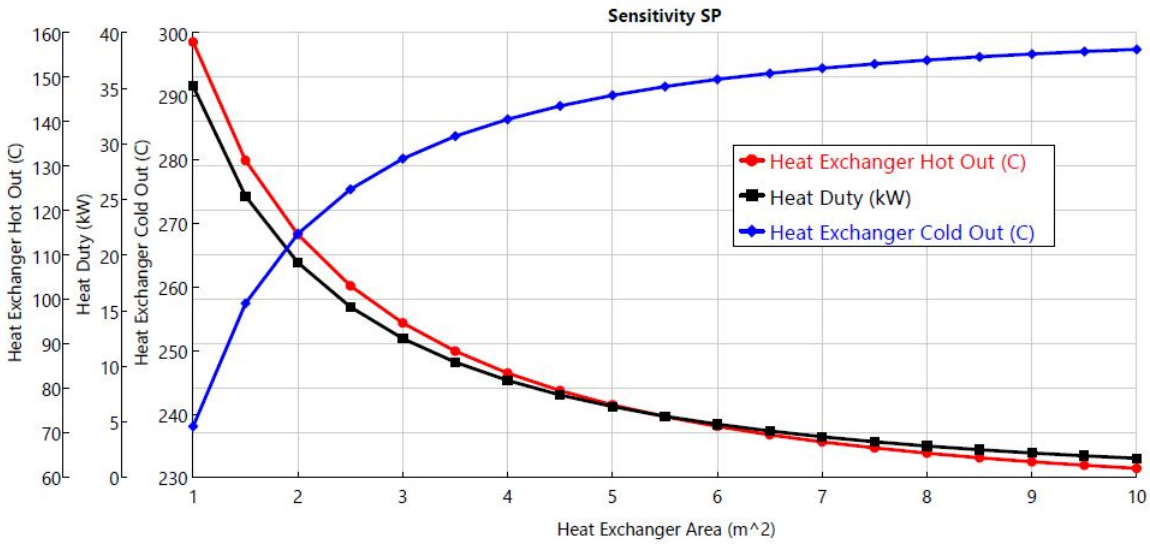

Figure 4.2.1: Sensitivity analysis of heat exchanger, *S. platensis*.

For the operation temperature of 348°C in HTL of *C. vulgaris*, a decrease in heat duty of 45 % was obtained for an increase from 2 to 4 m^2 in heat exchanger area. Figure 4.2.2 shows the change in heat duty, as area of the heat exchanger increases or decreases.

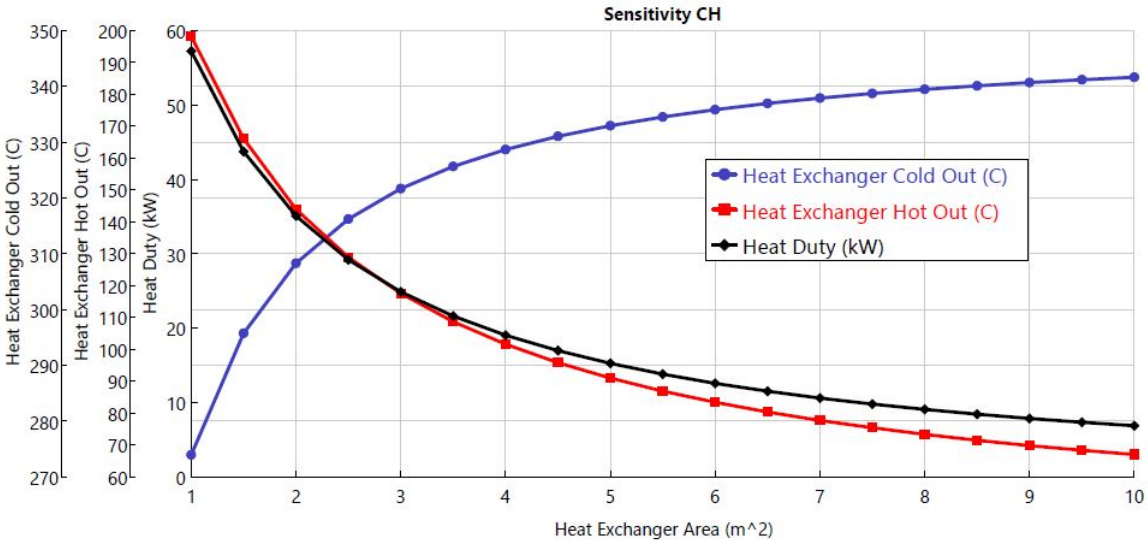

Figure 4.2.2: Sensitivity analysis of heat exchanger, *C. vulgaris*.

In HTL of *P. tricornutum* at an operation temperature of 375°C, a decrease in heat duty of 34 % was obtained for an increase from 2 to 4 m^2 in heat exchanger area. Figure 4.2.3 shows the mild decrease of heat duty as area increases.

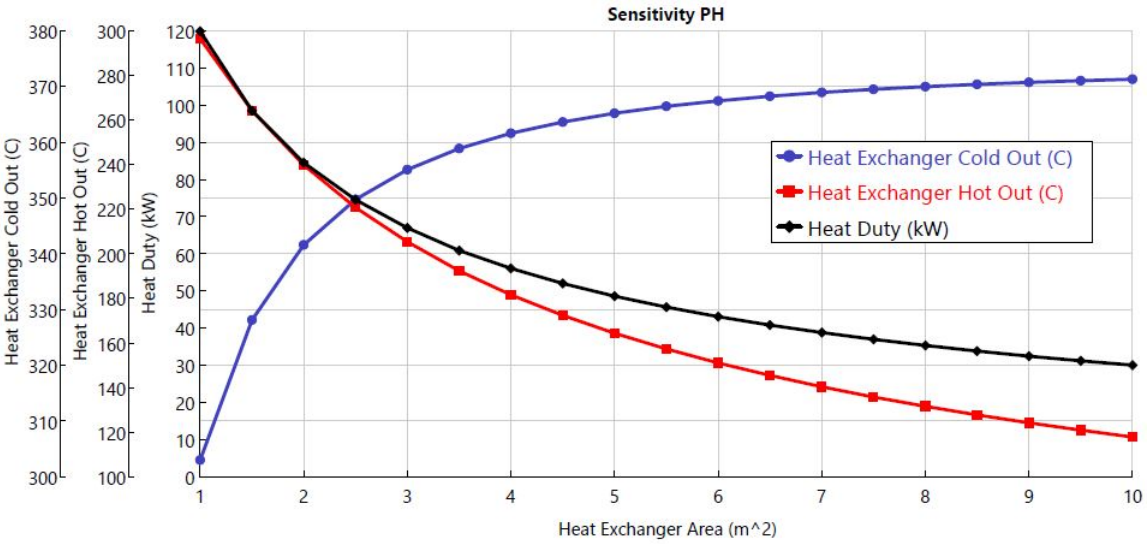

Figure 4.2.3: Sensitivity analysis of heat exchanger, *P. tricornutum*.

Chapter 5

Discussion

This chapter presents the discussion of the results and main findings, from the analysis and simulation performed. Chapter 5.1, introduces the discussion of the algae analysis and characterization. Chapter 5.2, presents the discussion on the process analysis of the Aspen Plus model.

5.1 Algae Characterization

Algae powders used as food supplements might be grown in such a way that the algae are rich in protein. Increased protein content converted in HTL would increase the nitrogen content in the biocrude, which causes high NO_x emissions if used directly as a fuel. It may also cause problems in the refining process.

There are two main standards found in literature, used in analysis of algae. One is testing by the coal standard, the other one is testing by the biomass standard. In this thesis, the coal type analysis was used. The temperatures in coal analysis are commonly higher than the one used in biomass analysis. If both standards would have been tested a comparison could have been made.

In proximate analysis, the *C. vulgaris* algae showed the best values in terms of high VCM and FC, with a low value of ash. The *S. platensis* showed a FC percentage only slightly higher than the *C. vulgaris*, but with a higher ash content. With an even higher ash content and lower FC content, the *Phaeodactylum tricornutum* may not be the optimal choice of the three algae species in terms of the VCM, FC and ash comparison.

In the ultimate analysis, results were obtained as the content of nitrogen, oxygen and carbon. The lack of the sulfur test, caused a small increase in the calculated oxygen percentage. Sulfur content of various species of algae is presented in table 2.2.1. The sulfur content in the table is 0.54 % for *S. platensis*, 0.5-1 % for *C. vulgaris* and 0.7-1.28 % for *P. tricornutum*.

The *C. vulgaris* algae had the highest carbon and hydrogen content of the three algae species. Results of hydrogen, carbon and nitrogen content of the *S. platensis*

and *C. vulgaris* algae is equal to the values found in literature. In literature values for the *P. tricornutum* algae differs quite a bit, but results from this study is in the range of values found from literature. A comparison of the results obtained in this thesis and values from literature in made and presented in table 5.1.1.

Table 5.1.1: Comparing the carbon (C), hydrogen (H) and nitrogen (N) from literature with results obtained from ultimate analysis. Ultimate analysis from table 4.1.2, literature from table 2.2.1.

		C %	H %	N %
Ultimate analysis:	*S. platensis*	48.5	6.8	11.2
	C. vulgaris	51.0	7.0	9.5
	P. tricornutum	44.2	6.9	7.4
Literature:	*S.platensis*	46.87	6.98	10.75
	$C. vulgaris_1$	52.6	7.1	8.2
	$C. vulgaris_2$	40.8	6.5	6.7
	$C. vulgaris_3$	53.6	7.3	9.2
	$P. tricornutum_1$	38.0	4.8	5.2
	$P. tricornutum_2$	57.03	7.46	8.00

In this thesis, the oxygen content was calculated as the difference of 100% and the C, H, N and ash. Thus, the sulfur was neglected. The oxygen content obtained was 25.5 % for *S. platensis*, 27.1 % for *C. vulgaris*, and 25.7 % of *P. tricornutum*. In table 2.2.1, the oxygen for *S.platensis* species is 34.86 %, *C.vulgaris* in the range of 29.4-43.1 %, and *P.tricornutum* of 24.97-51.3 %. The variations are due to different calculations used. Oxygen content of the values in table 2.2.1, is mainly based on the difference of 100 % and C, H, N and S. Thus, the ash is not accounted for.

The heating value calculated from results of ultimate analysis shows reasonable values. The *C. vulgaris* algae had a heating value higher than the *S. platensis* and *P. tricornutum* algae. Four equations were used to confirm the variation and compare to values reported in other studies. One of the differences of Dulong's equation and the gross calorific value (GCV) equation, is that the GCV includes the ash content. Common in literature on algae is the use of Dulong's equation, thus a high oxygen content due to the calculation used for results in ultimate analysis. A high oxygen content has a larger impact on the decrease in heating value then the ash content if the GCV equation is used. Also for the Dulong's equation, a high oxygen content will decrease the heating value of the algae.

When conduction TGA the main decomposition temperatures was obtained at $370°C$ for *S. platensis*, $390°C$ for *C. vulgaris* and $335°C$ for *P. tricornutum*. The quite high heating rate used in TGA was not optimal for characterizing the decomposition, as the biomass was heated quite rapidly. In terms of the behavior of the algae biomass, more TGA experiments could have been done at different temperature setting and heating rates for a more complete analysis of the DTG and DSC

graphs. This would provide the information on temperature of start and end of pyrolysis, or the VM release rate.

A slurry or paste from a culture medium should be the preferred biomass used in analysis. Reason being that the slurry will be used in future full size HTL production facilities. The paste or slurry is a more accurate input for this process, than powder or other types of processed biomass. There were few reports found in literature on the behavior of various species algae in HTL, and the use of slurry compared to powder. From analysis of the three species of algae conducted in this thesis, differences in the biomass behavior was observed. The *C. vulgaris* algae biomass expanded or spread, both in TGA and proximate analysis, causing error in measurements. A second round of experiments was required because of this behavior. No further investigation of the cause was done. One reasonably cause for this behavior could be the particle size, the *C. vulgaris* was a fine dust like powder.

5.2 Process Analysis

The steady-state system in Aspen Plus, was created as a base model without the complex dynamics. Components were kept as simple as possible. Only one pump was used to pump the slurry from atmospheric pressure to a pressure of 12-27 MPa. Due to the properties of the slurry, this could cause problems in a real scenario. Using two pumps in series might be a better option. One pump as a low-pressure pump, and the second as a high-pressure pump. The type and design of heater and heat exchanger, was not specified in the simulation. Since both streams in the heat exchanger contains liquids and solids, a plate or tube design would be more appropriate than a shell and tube type. A reason for this, is that a continuous process with streams containing solids could cause pressure fluctuations or clogging. Thus, the design of reactor, separator, heater, valves and heat exchanger is critical. More research is needed on the properties and behavior of the slurry and products from HTL, for more appropriate component selection.

In the simulation model, components in the feed and product stream was mainly chosen from the components library. Only the algae, and components in the solid phase were user-defined, modeled as non-conventional solids. The number of these components were kept at a minimum, as recommended when using Aspen Plus.
The same components for the biocrude and aqueous phase, were selected for the three species of algae. Thus, results obtained from these phases were also quite equal. A common heating value of biocrude are a consequence of this selection. When selecting components, a GS-MS analysis should be conducted of the biocrude obtained by each specific algae species. Knowledge of petrochemical classification is important in the selection process, as the components in Aspen Plus library is limited. The mixture of the biocrude in the model, could be modeled with other components. If the composition of the components where specified in the simulation

by fewer components, the yield calculations would be simplified. Output values would likely not change much if the suitable components would have been chosen.

From literature, the higher heating value of biocrude were 35.27 MJ/kg for the *S.platensis*, 35.0 MJ/kg for *C.vulgaris* and in the range 35.9-37.4 for *P.tricornutum* algae. Thus, a value of about 35 MJ/kg would be preferred in the simulation to maintain correct calculation. The value in the simulations model was 33.2 MJ/kg, and equal for all three algae. For a more accurate simulation the components selected for the biocrude should have a HHV that match the value obtained in experiments.

Due to equal heating value of the biocrude, the energy recovery percentage is only varied by the heating value of the algae and the mass flow of algae. The low heating value of the *P. tricornutum* algae and high yield resulted in the highest energy recovery of 87.7 %. This high energy recovery value, was higher than common values found in literature, as presented in chapter 2. For *S. platensis* and *C. vulgaris* the energy recovery of 46.9 and 54.9 %, were within the range of the presented values. The heating value was calculated without the sulfur, and is a bit lower than the real value of the biomass. This results in a larger gap in the difference of the heating value of biomass and biocrude, thus the conversion efficiency and other calculations were affected.

The energy consumption of HTL is one of the main barriers in terms of commercializing the technology. The energy used in cultivation, harvesting, conversion and upgrading, of the biofuel from algae, should be as low as possible to compete with fuels available on the commercial marked. Biomass to water ratio, temperature, pressure and residence time were parameters well presented in literature. Several studies have also been performed on the effects of the use of catalysts. But literature on the effects of particle size, heating rate and the slurry versus powder was limited.

In the Aspen Plus model, energy consumption was due to pump work and heating. The consumption of the pump was low compared to what the heater required. By implementing a heat exchanger in the simulation a large reduction in the energy demand was obtained. A specific heat transfer area and overall heat transfer rate for the heat exchanger, were defined and equal in the HTL plant for the three algae species.

The largest increase in energy conversion efficiency and HTL energy efficiency were obtained by the *P. tricornutum* algae, with 50 and 53%. Main reason of the improvement is the potential of heat recovery. From the results, a trend of higher energy demand due to higher pressure and temperature is obtained. The yield of the three species in the simulation correlates to the heat and pressure. Even if the *S. platensis* has the lowest energy demand, the yield on a weighted percentage of the algae feed, was lower than for the two other algae species.

There is a potential for heat integration and optimization of the system. By im-

plementing a recycling loop, the water in the aqueous stream could be used in the input stream mixed with the algae to decrease the heat duty. Or the water could be implemented in the stream after the pump or heat exchanger.

In future work, a kinetic model of microalgae HTL should be developed. This would make it possible to report the specific yields at different temperatures, retention time and pressure.

Chapter 6

Conclusion

The aim of this work was to provide insight in the fuel characterization and process analysis of hydrothermal liquefaction of algae. In fuel characterization three species of algae was provided for experiments by proximate, TGA and ultimate analysis. The simulation tool Aspen Plus, was used in the process analysis of hydrothermal liquefaction. Properties from algae analysis was used in the simulation model.

Three algae species, a slurry of *P. tricornutum*, and powders from *S. platensis* and *C. vulgaris*, were analyzed in this thesis. The algae with the best properties for fuel utilization was the *C. vulgaris*, with a net calorific value of 20.46 MJ/kg and the highest percentage of carbon and hydrogen. *C. vulgaris* was also low in ash and nitrogen content. The only concern of the *C.vulgaris* was the behavior of the powder during rapid heating. *S. platensis* powder was quite equal in most parameters if compared to the *C. vulgaris* algae, but a higher content of nitrogen and ash makes it less appropriate. The *P. tricornutum* slurry was low in fixed carbon and high in ash content.

In literature, hydrothermal liquefaction is mentioned as a promising process for future biofuel production. Complex reactions that occur during the process is not fully understood, thus accurate simulations are not yet attainable. Several batch reactor experiments have been reported in literature, but only few of the continuous flow reactor.
The Aspen Plus simulation tool was used to model the continuous HTL of algae. Simulations were performed for each algae species, using properties of the algae biomass obtained from the algae analysis performed in this thesis.

The energy of the main components was considered, and a process optimization was done by implementing a heat exchanger. Without the heat exchanger, a large amount of waste heat was not utilized and the system showed poor efficiency. The heat exchanger showed great improvement. Still there was potential for heat integration and optimization of the system. Water recycling, district heating or other options could be considered.
The efficiency of the system was improved when products in all the streams were utilized. *S. platensis* and *P. tricornutum* algae obtained 83 % energy efficiency for

the HTL process. The annual production of biocrude in the simulation was 180,000 liter from *S. platensis*, 211,000 from *C. vulgaris* and 124,000 from *P. tricornutum*.

The outcome of the simulation was mainly determined by the composition of components in the product stream. To increase the accuracy of the simulation, the selection of components should be specific for each algae species. In the simulation model, equal components selected for the biocrude, resulted in an equal heating value of the biocrude for each algae species. Because the simulation was yield based, it was not possible to vary the temperature or pressure in terms of yield optimization. This would be possible by using the reaction kinetics. In future work a kinetic simulation should be designed and tested against a real HTL process.

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Appendixes

Appendix A

TGA

In this appendix, the thermogravimetric analysis results are explained by several figures. The TGA, heat flux and DTG graphs is shown and commented.

A.1 Thermogravimetric Analysis of Microalgae

In figure A.1.1 the TGA results from a single sample of *S. platensis* is presented. The yellow curve (Sp1) is the weight loss, with measure on y-axis on the left. Red (Tr) curve is temperature of the atmosphere in the closed chamber of the TGA instrument, where the sample is placed during a run. Purple (Ts) curve is the sample temperature. For both temperature of sample and chamber, the measure is showed on the right y-axis. Time on x-axis and atmosphere temperature curve, is determined by the method used. Since the same method was used in all the TGA samples in this study, the red (Tr) curve represent the method for all TGA results.

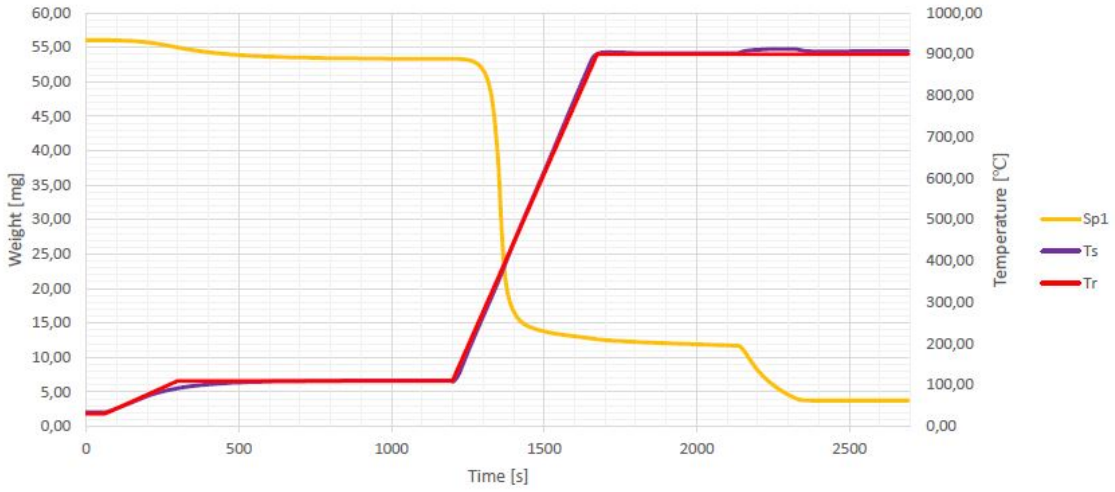

Figure A.1.1: TGA of one sample *S. platensis* algae, weight (Sp1), sample temperature (Ts) and atmosphere temperature (Tr).

The values of moisture (MC), volatile combustible matter (VCM), fixed carbon (FC) and Ash as determined by TGA is shown in table A.1.1. Usually these contents in

the biomass are measured by proximate analysis as the TGA results are not intended for this purpose. Still a comparison of values is possible in that the trend is often quite equal.

Table A.1.1: Results from the TGA of three algae species. VCM, FC, Ash on a dry basis.

	%MC	%VCM	%Ash	%FC
S. platensis	5.0	77.9	7.0	15.1
C. vulgaris	4.6	79.1	6.6	14.3
P. tricornutum	7.5	76.5	13.4	10.1

The weight loss of the *S. platensis* algae samples in TGA is shown in figure A.1.2, *C. vulgaris* in figure A.1.3, and *P. tricornutum* in figure A.1.4. Time is presented in seconds on the x-axis, and are equal for all figures. Weight in milligrams is presented on the y-axis, and different on the three figures due to change in the initial sample weight. Almost equal initial weight of two samples of *S. platensis* shown in figure A.1.2 as Sp1 and Sp2, show little difference on the weight loss curve. Due to reactions causing problems with the measurement of the *C. vulgaris* algae species, the initial weight of the samples was reduced. A high moisture content in the *P. tricornutum* algae slurry caused problems in duplicating using the method chosen. The solution was to let the samples dry in laboratory atmosphere overnight, before testing. Results shown in figure A.1.4.

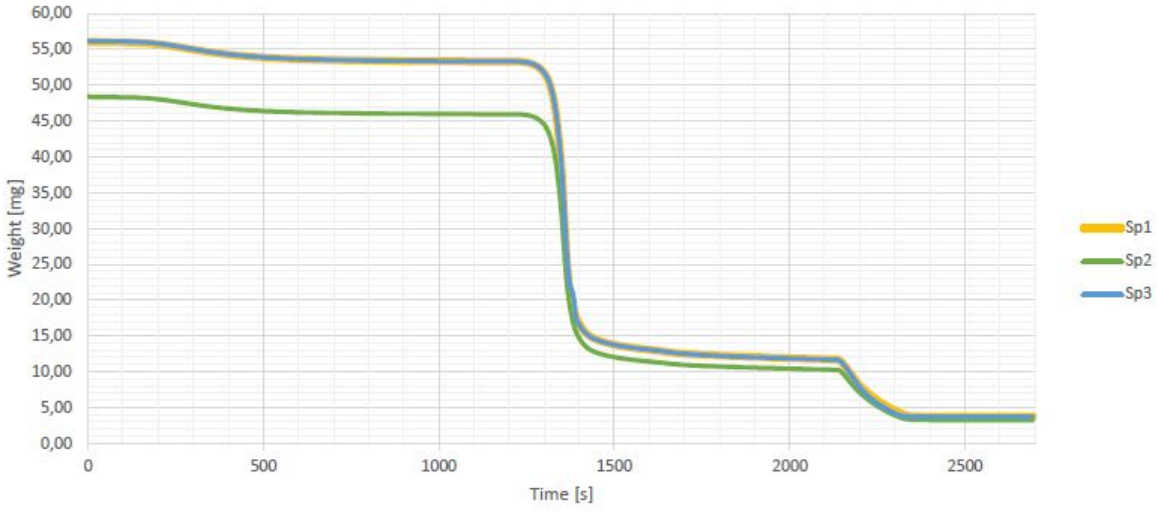

Figure A.1.2: Weight loss of three samples of *S. platensis* algae from TGA.

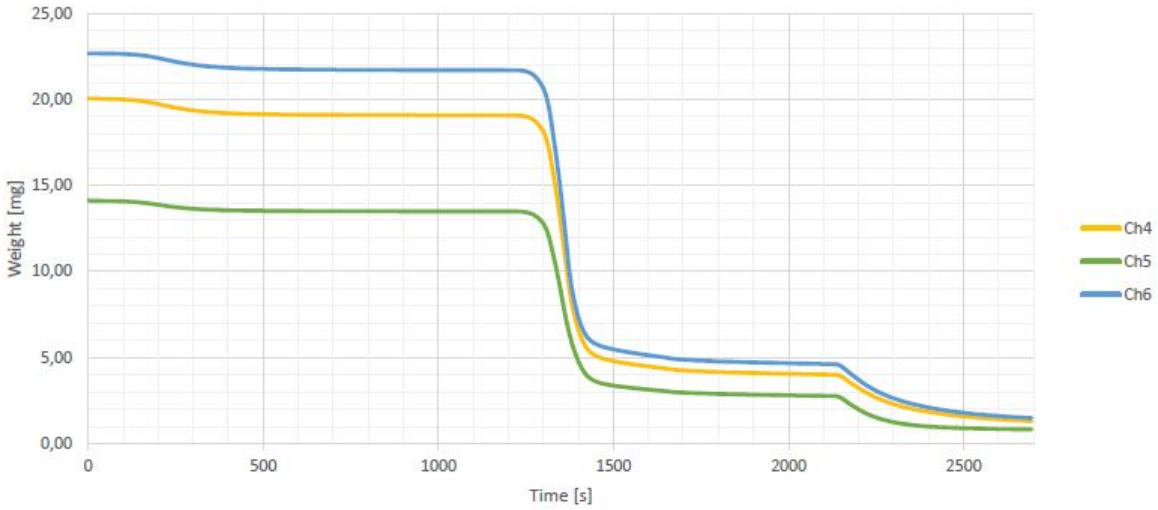

Figure A.1.3: Weight loss of three samples of *C. vulgaris* algae from TGA.

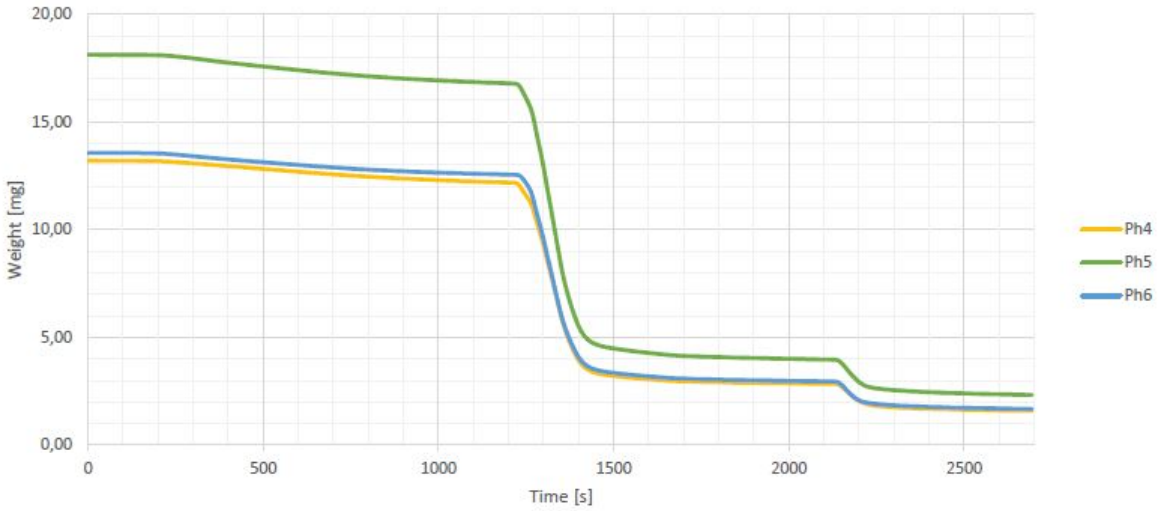

Figure A.1.4: Weight loss of three samples of *P. tricornutum* algae from TGA.

An average weight loss percentage from the three samples of each algae species is shown in figure A.1.5.

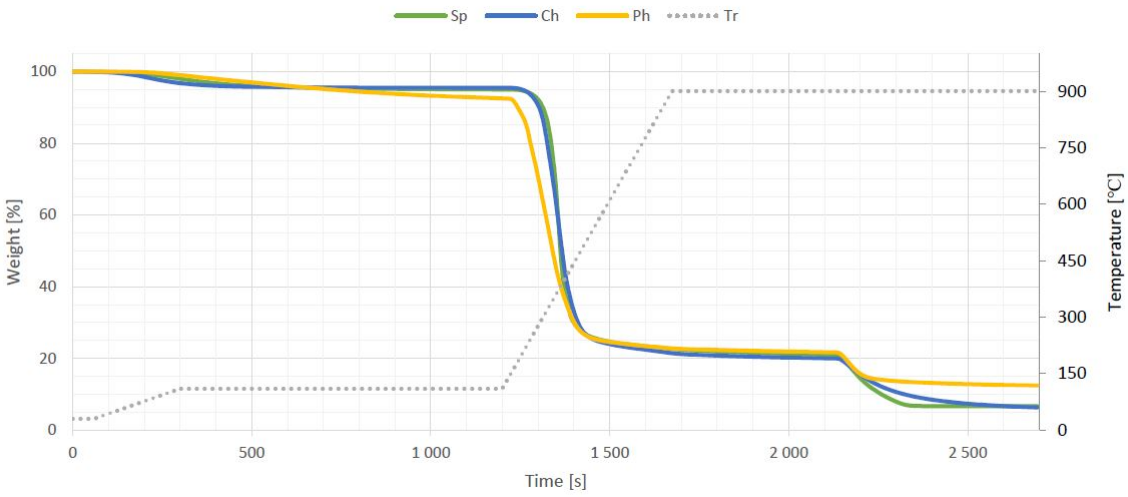

Figure A.1.5: TGA of algae species *S. platensis* (Sp), *C. vulgaris* (Ch) and *P. tricornutum* (Ph). Temperature curve of the chosen method, shown by the dotted line.

The heat flow from DSC shows the exothermic and endothermic behavior of the algae sample. *S. platensis* algae in figure A.1.6, *C. vulgaris* in figure A.1.7 and *P. tricornutum* in figure A.1.8. Time is presented in seconds on the x-axis, and are constant for all three figures. Heat flow is presented on the y-axis and are constant for all three figures. The powders have similar heat flow curves while the heat flow curve of the slurry differs. A slight decrease in the curve from 0 to 500 seconds show the required heat for moisture removal. *S. platensis* samples show that the larger initial sample weight, requires more heat for moisture removal than the smaller samples as used in *C. vulgaris* and *P. tricornutum*.

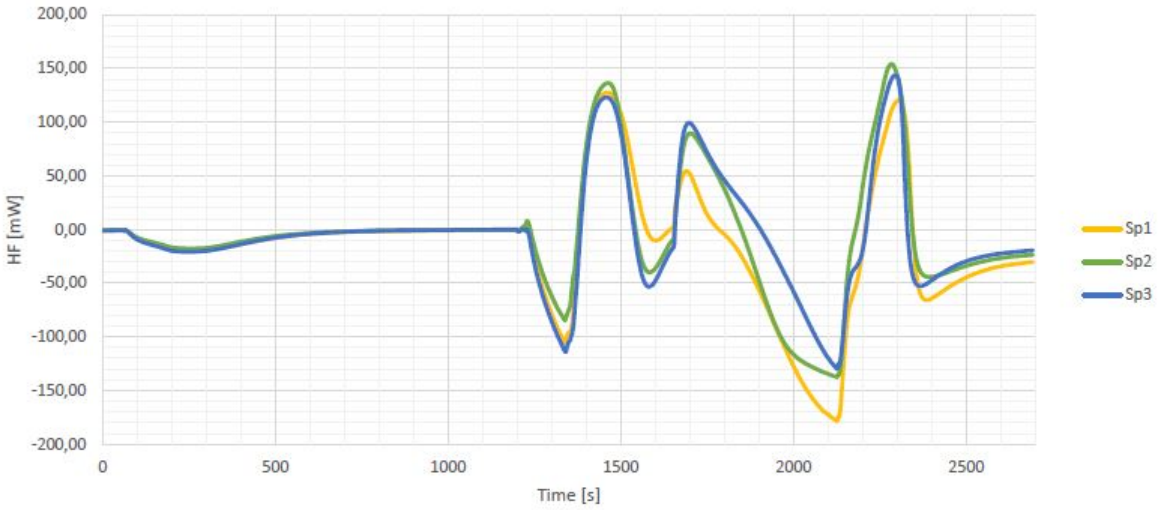

Figure A.1.6: Heat flow of *S. platensis* samples.

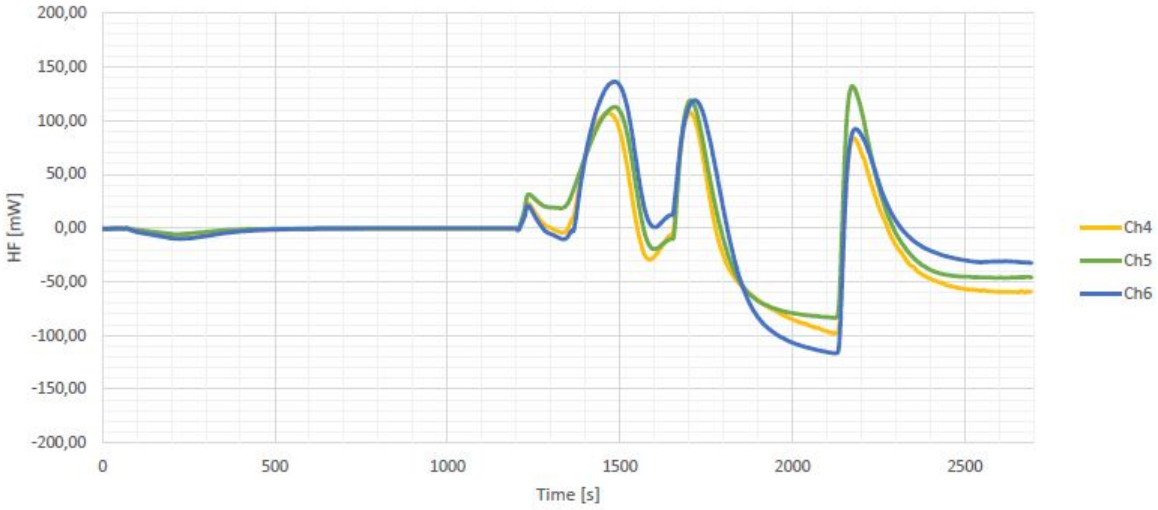

Figure A.1.7: Heat flow of *C. vulgaris* samples.

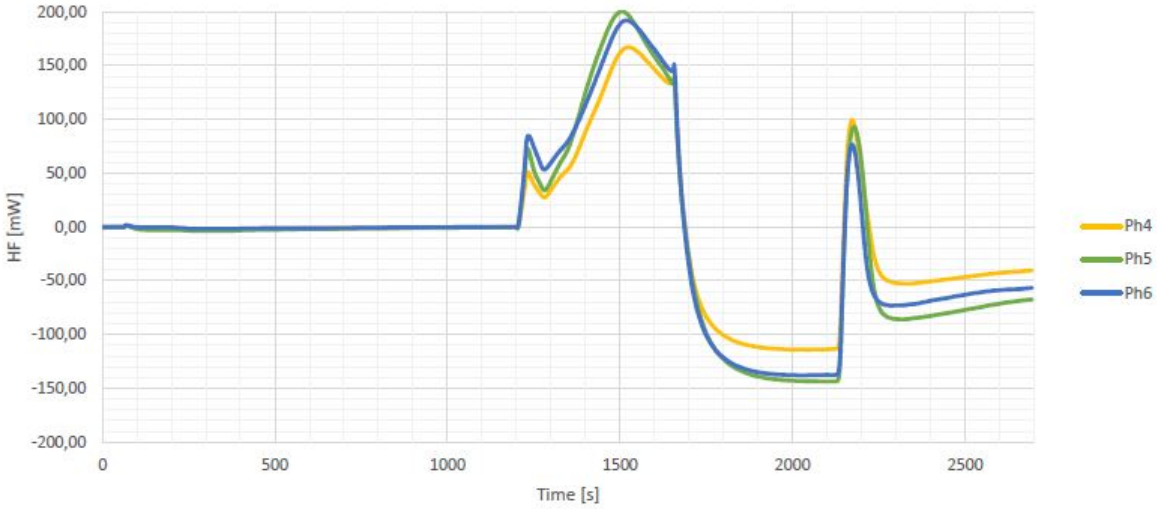

Figure A.1.8: Heat flow of *P. tricornutum* samples.

Averages of the heat flux is shown in figure A.1.9. Peaks of heat flux occur because of reactions, due to temperature increase or change of atmosphere. An example of this is the combustion of the sample when oxygen is introduced into the chamber. This reaction is visual in the figure, as the last peak starting at about 2150 seconds.

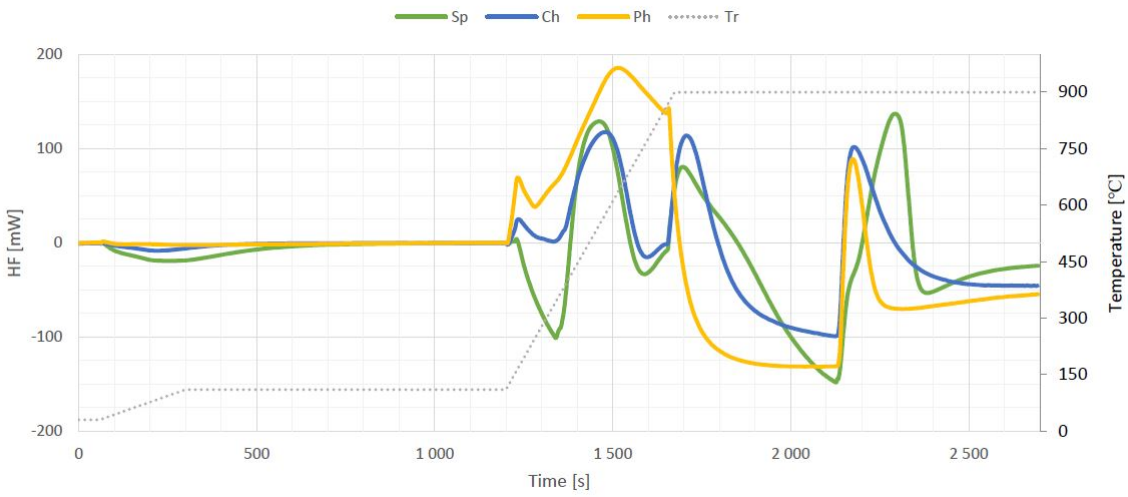

Figure A.1.9: Heat flow in TGA of *S. platensis*, *C. vulgaris* and *P. tricornutum* algae.

The derivative thermogravimetric analysis DTG, by percentage weight loss is shown in figure A.1.10.

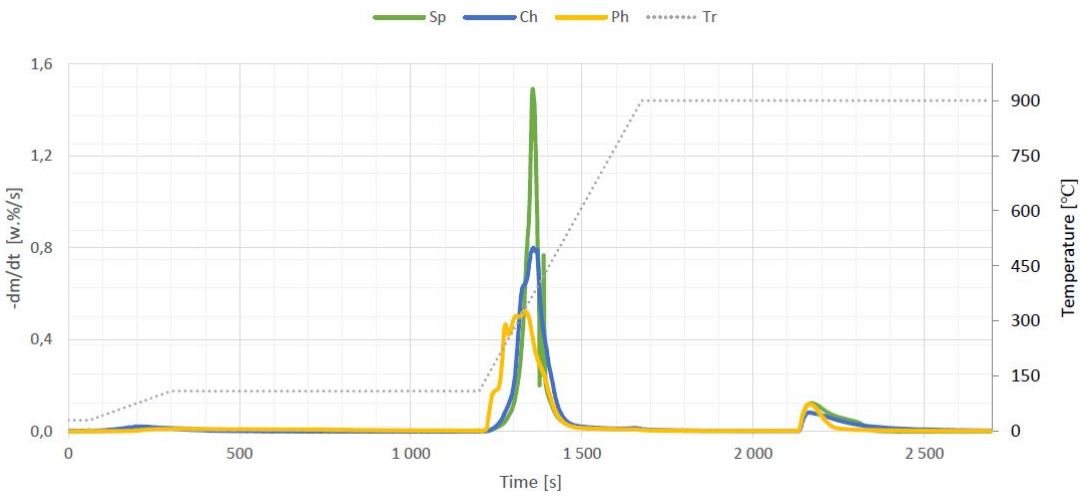

Figure A.1.10: DTG of *S. platensis*, *C. vulgaris* and *P. tricornutum*.

Figure A.1.11 is an enlarged picture of the peaks from figure A.1.10. The peaks occur during temperature increase from 110° C to 900° C.

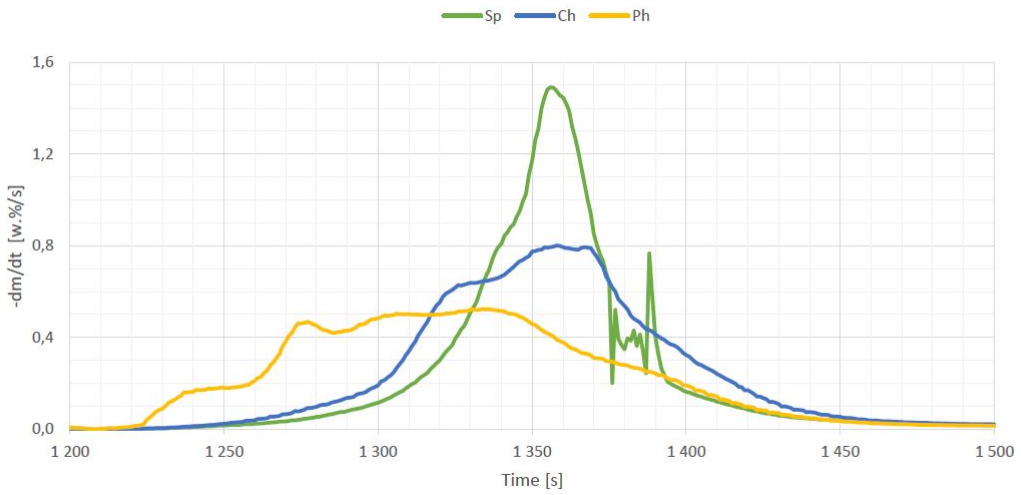

Figure A.1.11: DTG, in the time span of 1200-1500 seconds.

When oxygen is introduced into the test chamber of the TGA instrument, the sample starts to burn thus creating the small bump in figure A.1.10, shown as an enlarged picture in figure A.1.12.

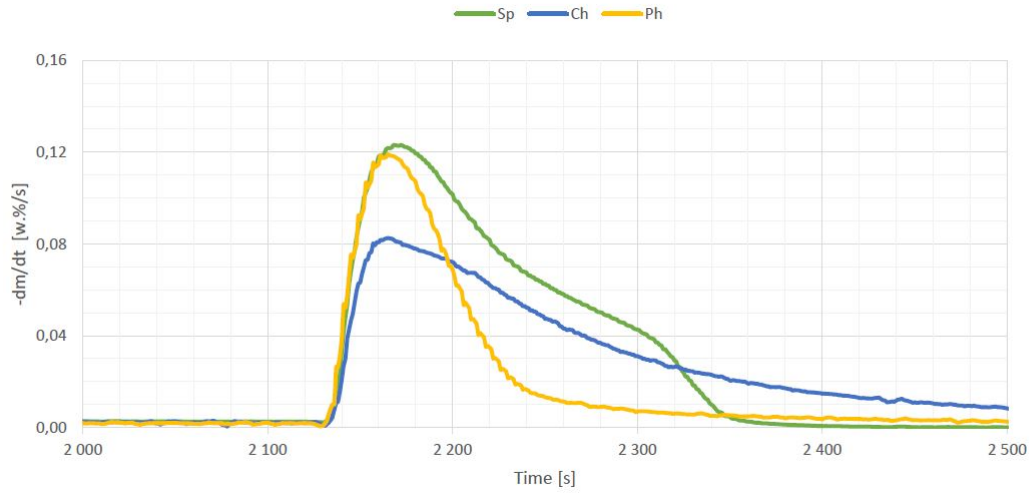

Figure A.1.12: DTG, in the time span of 2000-2500 seconds.

Figure A.1.13 shows the DTG curve versus the temperature. From the figure the main peaks of the decomposition step is seen. Main peak occurs at 370°C and some roughness in the graph at around 400-420°C, for *S. platensis*. Decomposition of *C. vulgaris* shows first a peak at 320°C, then a main peak around 370-390°C. For *P. tricornutum* a small peak occurs at 180°C, then a second peak at 230°C and the largest at 335°C.

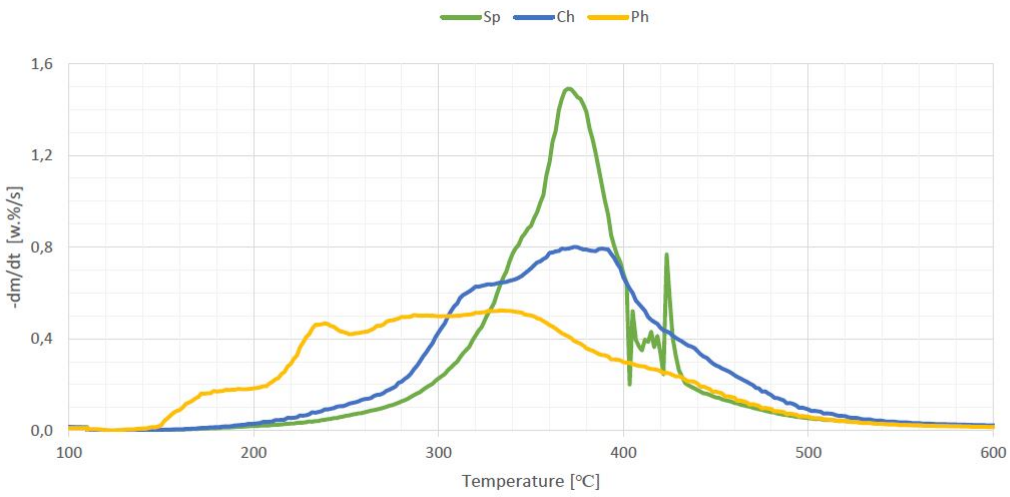

Figure A.1.13: DTG graph, in the temperature range 100-600°C.

Appendix B

Microalgae Literature

In this appendix information on properties of microalgae HTL from literature is presented. This was done to discover, and keep track of important information for this study.

B.1 Hydrothermal Liquefaction of Microalgae

In table B.1.1, conditions for microalgae HTL found in literature is listed. Three main species based on the algae used in analysis, is presented. The *Spirulinaplatensis* algae slurry was used in a batch reactor with the initial pressure of 2 MPa before heating [52], the pressure at 350 $°C$ was not specified.

The higher heating value of biocrude from HTL of algae is shown in table B.1.2. Calculations used in determining the HHV may vary for the values reported.

Table B.1.2: HHV of algae HTL biocrude.

Algae	HHV (MJ/kg)	Ref.
Chlorella	33.8	[9]
Chlorella vulgaris	35.0	[11]
Spirulina	32.0	[9]
Spirulina	35.8	[12]
Spirulina platensis	35.27	[52]
Nannocholorpsis gaditana	37.2	[11]
Phaeodactylum tricornutum	35.9	[11]
Phaeodactylum tricornutum	37.4	[74]

Composition of protein, carbohydrates and lipids for the *P. tricornutum* alga is presented in table B.1.3. The ash content of *Phaeodactylum tricornutum* reported as 24.6 wt.% from [11].

Table B.1.1: HTL experiments of algae. (Mark ^{A} and ^{B} heat rate of 5° C/min until 350° C, then 1° C/min until 400° C [76]).

Algae	Feed wt.%	Temperature °C	Pressure	Residence time [min]	Biocrude yield	Reactor type	Catalyst	Ref.
Chlorella	10	350	206 bar	1.4-5.8	~40 wt.%	cont.	-	[33]
Chlorella	10	350	250 bar	3	41.7 wt.%	cont.	-	[9]
Chlorella sp.	25	220	35 MPa	90	82.9 wt.%	batch		[75]
Chlorella	20	348	2930 psia	27	38 wt.%	cont.	-	[10]
Spirulina	20	300	10-12 MPa	30	32.6 wt.%	batch	-	[34]
Spirulina	20	300	10-12 MPa	30	31 wt.%	batch	-	[12]
S. platensis	20	350	2 MPa (initial)	60	39.9 wt.%	batch	-	[52]
P. tricornutum	7	375	25-27 MPa	5	54.3 wt.%	batch	-	[11]
P. tricornutum	20	350-400^{A}	20 MPa	>100^{B}	31 wt.%	batch	-	[76]
P. tricornutum	-	350	-	15	39 wt.%	batch	-	[74]

Table B.1.3: Protein, carbohydrate and lipid content of *P. tricornutum* alga.

	Protein wt.%	Carbohydrate wt.%	Lipids wt.%	Ref.
P. tricornutum	36	26	18	[7]
P. tricornutum	37.5	-	21.9	[11]

The major components of the products from HTL of algae, is important for the selection of components used in computer simulation. A list of studies found in literature containing the major components determined by GCMS is presented in table B.1.4.

Table B.1.4: Major components determined by GC/MS.

Algae	Table.	Specifications	Ref.
Nannochloropsis sp.	6	-	[32]
Aurantiochytrium sp.	4	-	[65]
Chlorella, *Spirulina*	4	-	[51]
Several sp.	4	Name	[50]
Spirulina	3	Name/Area%/RT	[34]
Chlorella, *Nannochloropsis*	5	Name/Area%/RT	[75]
Chlorella, *Nannochloropsis*	C-1	Name/wt.%/comp./CAS	[10]

In table B.1.5 the HTL yield distribution from several experiments is listed. The gas phase of *Spirulina* was determined by difference, of total recovery [12]. A HTL process simulation by Zhu et al. [35], uses HTL yield distribution from experimental work. The percentages are 51.2 biocrude, 4.34 gas, 42.84 aqueous and 1.62 solid waste.

Gas phase products from HTL contain several gases. Usually with a large fraction of the total being CO_2. Table B.1.6 shows some of the gasses that occur.
The N_2 content of the *Spirulina platensis* in table B.1.6, is caused by the use of excess N_2 in the reactor during HTL [52].

Table B.1.6: Gas phase products.

Algae	Gases	Ref.
Nannochlororpsis sp., *Chlorella* sp.	CO_2, CO, CH_4 and N_2	[75]
Spirulina platensis	N_2, H_2, CH_4, CO and CO_2	[52]

The crude oil products from HTL of algae contain hundreds of compounds in a complex mixture. Depending on the algae species and process conditions the complex mixture vary, thus only the major components are usually identified in different studies. Table B.1.7 and B.1.8, is a list of components from several HTL studies. In the

Table B.1.5: HTL yield distribution. The HTL of *Chorella vulgaris*$_1$ and *Chorella vulgaris*$_2$ were conducted in the same study at different temperatures, respectively 375 °*C* and 250 °*C* [11]. Algae species marked $_1$, $_2$ and $_3$, values may be higher or lower than a total of 100% due to the calculations used in [11]. ($_a$ The gas phase of *Phaeodactylum tricornutum* is assumed to be 5% [76]).

Algae	Biocrude %	Aqueous organic %	Gas %	Solids %	Ref.
Chlorella	38	59 (+ash)	1	2	[10]
Chorella vulgaris$_1$	55.3	16.8	22.4	3.9	[11]
Chorella vulgaris$_2$	33.0	29.9	10.8	27.0	[11]
Nannochloropsis	56	39 (+ash)	5	1	[10]
Spirulina	31	23	35	11	[12]
Scenedesmus	45	17	30	7	[12]
Phaeodactylum tricornutum$_3$	54.3	12.6	27.5	6.7	[11]
Phaeodactylum tricornutum	31	64	5$_a$	-	[76]
Nannochlororpsis sp., *Chlorella* sp.	45.4-62.7	13.2-37.9	2.0-6.6	12.1-25.4	[75]

third column (A), components in the biocrude from *Chlorella* and *Nannochloropsis* chosen for Aspen Plus by [10, Table C-1]. Column four (B) contain the major components in the biocrude from HTL of *Chlorella* sp. algae, detected by GC-MS [75, Table 4]. Fifth column (C), component of crude from HTL of *Spirulina* identified by GC-MS [34, Table 3]. In the sixth column (D), the major components from HTL of *C.vulgaris*, *Spirulina*, using catalyst of alkali and organic acids [51, Table 4].

Table B.1.7: Components in biocrude from HTL.

Formula	Designation	A	B	C	D
C6H11NO	1-ethyl-2-pyrrolidinone	X			
C5H9NS	N-methylthiopyrrolidone	X			
C8H10	Ethylbenzene	X			
C7H8O	Phenol, 4-methyl (p-Cresol)	X		X	X
C8H10O	Phenol, 4-ethyl-	X		X	
C8H7N	Indole	X		X	
C9H9N	1H-Indole, 7-methyl-	X			
C14H29NO	Myristamide (C14 amide)	X			
C16H33NO	Palmitamide (C16 mide)	X			
C18H37NO	Stearamide (C18 amide)	X			
C16H30NO	Palmitoleic acid (C16:1FA)	X			
C16H32O2	Palmitic acid (Hexadecanoic acid)	X	X		X
C18H34O2	Oleic acid	X			
C10H8	Naphthalene	X			
C27H46O	Fused rings (cholesterol)	X			
C18H16N2	Aromatic amines	X			
C30H50O4	1,2-benzenedicarboxylic acid)	X			
C8H15NO	1,2,3-Trimethylpiperidin-4-one		X		
C10H22	3-Ethyl-3-methylheptane		X		
C9H17NO	4-Piperidinone, 2,2,6,6-tetramethyl-		X		
C6H12	Cyclohexane		X		
C9H20	2,3,4-Trimethylhexane		X		
C15H32	2,6,11-Trimethyldodecane		X		
C9H40	Octadecane, 5-methyl-		X		
C20H42	n-Eicosane		X		
C16H48O8Si8	Cyclooctasiloxane, hexadecamethyl-		X		
C26H54	Octadecane,3-ethyl-5-(2-ethylbutyl)-		X		
C14H28O2	Tetradecanoic acid		X		
C15H26O	6-epi-shyobunol		X		
H18O7Si8	Octasiloxane		X		
-	1,8-dimethyl-8,9-epoxy-4-isopropyl-		X		
C18H54O9Si9	Octadeamethyl-cyclononasiloxane		X		
C8H6O2	Phenylglyoxal			X	
C6H6O	Phenol			X	X
C13H18	Naphthalene, 1,2,3,4-tetrahydro-1,1,6-trimethyl-			X	

Table B.1.8: Components in biocrude from HTL (continues).

Formula	Designation	A	B	C	D
C7H11NO2	2,5-Pyrrolidinedione, 1-propyl			X	
C11H18O3	1,5-Dioxaspiro[5.5]undecan-9-one, 3,3-dimethyl-			X	
C10H11N	Benzonitrile, 2,4,6-trimethyl-			X	
C10H23NO	Hydroxylamine, O-decyl-			X	
C15H32O	1-Dodecanol, 3,7,11-trimethyl-			X	X
C13H26	5-Tridecene, (Z)-			X	
C8H17N	1, Butylpyrrolidine				X
C10H21N	1, Pentyl piperidine				X
C2H5NO	Acetamide				X
C8H10O	Phenylethyl alcohol				X
C5H7NO2	Piperidine-2,5-dione				X
-	n-Methyl butylacetamide				X
C8H10O	4, Ethyl phenol				X
C15H30	1, Pentadecene				X
C8H15NO	1, Butyl 2-pyrrolidinone				X
-	Hydroxyl ethyl succinimide				X
C9H9N	1, Methyl indole				X
C17H36	Heptadecane				X
-	2, Phenylethyl acetamide				X
-	Hexadecane tetramethyl				X
-	1,3 Heptadecyn-1-ol				X
-	Piperidine derivative				X
C20H40O	Phytol				X
-	Indole Derivative				X
C16H33NO	Hexadecanamide				X
-	Unknown aliphatic amide				X
-	Fatty acid derivative				X
-	Stearic acid derivative				X

Appendix C

Aspen Plus Model

In this appendix, the properties and flowsheet used in the Aspen Plus simulation model is described.

C.1 Aspen Plus Properties

In the tables below components and properties, for the Aspen Plus simulation model are shown. Main operation conditions are entered in Aspen Plus as values shown. The yield of components is added as percentages calculated in Excel sheets, based on values from tables below. Acronyms was used for simplification, and are presented in table C.1.1.

Table C.1.1: Acronyms used in Aspen model for the three species of algae.

Algae species	Acronym
Chorella vulgaris	CH
Spirulina platensis	SP
Phaeodactylum tricornutum	PH

Algae biomass is added in Aspen model as non-conventional components, defined by the proximate and ultimate analysis as shown in table C.1.2. In the Aspen model a moisture content of 7.5 % was used for PH, this was done to simplify calculations in proximate analysis since the result from proximate was 83.2 % moisture. The value used is approximate the percentage moisture of the dried *Phaeodactylumtricornutum* algae slurry, from TGA. Ash and oxygen content in table C.1.2 differs from those presented in the result section of algae analysis. The reason is that the ash content from TGA was used in calculation of oxygen. Only small differences are seen in the ash content, and should not be of major concern.

Table C.1.2: Component attribute in Aspen Plus model. (^{A} dried PH algae).

		CH	SP	PH
Proximate:	%MC	5.5	5.7	7.5^A
	%VCM	82.4	79.6	77.9
	%Ash	5.4	8	15.8
	%FC	12.2	12.4	6.3
Ultimate:	Carbon %	51	48.5	44.2
	Hydrogen %	7	6.8	6.9
	Nitrogen %	9.5	11.2	7.4
	Ash %	6.6	7	13.4
	Oxygen %	25.9	26.5	28.1

The conditions, feed and yields of each algae species used in modeling the HTL process in Aspen Plus is shown in table C.1.3. Initial pressure, temperature and slurry feed rate is chosen to be equal for all three species algae. The component weight percentage of PH was modified to make a total value of 100 %. The yield weight percentage of CH in table C.1.3 was reported on a dry, ash free algae [10]. Feed solids was 20 wt.% ash included, and 18.7 wt.% ash free basis. Yield of SP algae calculated as a percentage biomass dry, including ash [12]. Yield of PH algae was on dry, ash free biomass[11].

Table C.1.3: Operation conditions and initial specifications for Aspen model.

	CH	SP	PH
Initial pressure	101.4 kPa	101.4 kPa	101.4 kPa
Initial temperature	$15°C$	$15°C$	$15°C$
Slurry feed rate	300 kg/hr	300 kg/hr	300 kg/hr
Operating conditions			
Pressure	20.2 MPa	12 MPa	27 MPa
Temperature	$348°C$	$300°C$	$375°C$
Solid content feed	18.7 wt.%	20 wt.%	7 wt.%
Water content feed	81.3 wt.%	80 wt.%	93 wt.%
Yield:	wt.% (dry, ash free)	wt.% (dry)	wt.% (dry, ash free)
Biocrude	38	31	54
Aqueous organics	59	23	12
Gases	1	35	27
Solids	2	11	7
Reference study	[10]	[12]	[11]
Experiment reactor	continuous	batch	batch

Components in the biocrude and aqueous phase organics used in the Aspen model, are show in table C.1.4 and C.1.5. This list of components used by Jones at al.

[10, Table C-1], does not represent the components and percentages in the actual HTL products. They are chosen to match the key properties of the products, using conventional type components from Aspen Plus database. In column 3, 4, 5, table C.1.4 and C.1.5, components in biocrude and aqueous phase represent the total of each phase. In column 3, 4, 5, the wt.% of each component on the yield values in table C.1.3 are presented.

Table C.1.4: Biocrude components used in Aspen model.

Biocrude component	Name	CH	SP	PH
1-ethyl-2-pyrrolidinone	1E2PYDIN	2.58%	2.11%	3.67%
N-methylthiopyrrolidone	C5H9NS	0.39%	0.32%	0.55%
Ethylbenzene	ETHYLBEN	0.97%	0.79%	1.38%
Phenol, 4-methyl	4M-PHYNO	1.94%	1.58%	2.75%
Phenol, 4-ethyl-	4EPHYNOL	1.94%	1.58%	2.75%
Indole	INDOLE	1.94%	1.58%	2.75%
1H-Indole, 7-methyl-	7MINDOLE	1.29%	1.05%	1.83%
Myristamide (C14 amide)	C14AMIDE	1.29%	1.05%	1.83%
Palmitamide (C16 mide)	C16AMIDE	5.80%	4.73%	8.25%
Stearamide (C18 amide)	C18AMIDE	2.58%	2.11%	3.67%
Palmitoleic acid (C16:1FA)	C16:1FA	5.15%	4.2%	7.33%
Palmitic acid (Hexadecanoic acid)	C16:0FA	3.86%	3.16%	5.5%
Oleic acid	C18FACID	0.65%	0.53%	0.92%
Naphthalene	NAPHATH	1.94%	1.58%	2.75%
Fused rings (cholesterol)	CHOLESOL	0.64%	0.53%	0.92%
Aromatic amines	AROAMINE	3.08%	2.52%	4.4%
1,2-benzenedicarboxylic acid	C30DICAD	1.93%	1.58%	2.75%

Table C.1.5: Aqueous phase organic components used in Aspen model.

Aqueous phase organics	Name	CH	SP	PH
Methanol	METHANOL	8.63%	3.36%	1.75%
Ethanol	ETHANOL	1.73%	0.67%	0.35%
Acetone	ACETONE	1.73%	0.67%	0.35%
Formic acid	FORMACID	17.24%	6.74%	3.51%
Acetic acid	ACEACID	5.18%	2.02%	1.05%
Glycerol	GLYCEROL	1.73%	0.67%	0.35%
Carbon dioxide	CO2	11.72%	4.57%	2.39%
Ammonia	NH3	5.35%	2.08%	1.09%
3-pyridinol	3-PYRDOL	2.59%	1.01%	0.53%
1-ethyl-2-pyrrolidinone	1E2PYDIN	1.1%	0.43%	0.22%
N-methylthiopyrrolidone	C5H9NS	2%	0.78%	0.41%

The solid phase products from the HTL process as used in Aspen model are shown in table C.1.6. Ash and char as wt.% of the yield, added as non-conventional components in Aspen model. In term of simplification these components were both defined

as 100 % ash in PROXANAL and ULTANAL, this was due to no reference study found for the composition of the ash and char.

Table C.1.6: Components in the solid phase.

	CH	SP	PH
Ash %	1	5.5	3.5
Char %	1	5.5	3.5

Gas phase components used in Aspen model is shown in table C.1.7. The percentage of CO_2 and H_2 of CH from [75], CO_2 of SP from [9].

Table C.1.7: Gas phase components on a wt.% of the yield.

	CH	SP	PH
CO_2 %	0.86	33.25	23.49
CO %	0.04	0.7	0.41
CH_4 %	0.04	0.35	1.01
N_2 %	0.04	0.35	1.01
H_2 %	0.02	0.35	0.41

The heating value from the three main reference studies used in the modeling of the HTL processes for the three species algae, are presented in table C.1.8. Higher heating value of *Spirulina platensis* and *Phaeodactylum tricornutum*, from [12] and[11]. *Chorella vulgaris* calculated based on elemental analysis results from [10].

Table C.1.8: Biocrude higher heating value.

Biocrude	HHV (MJ/kg)
Chorella vulgaris	38.67
Spirulina platensis	35.8
Phaeodactylum tricornutum	35.9

C.2 Aspen Plus Model

The two main flowsheets used in the simulation is shown in the figure C.2.1 and C.2.2.

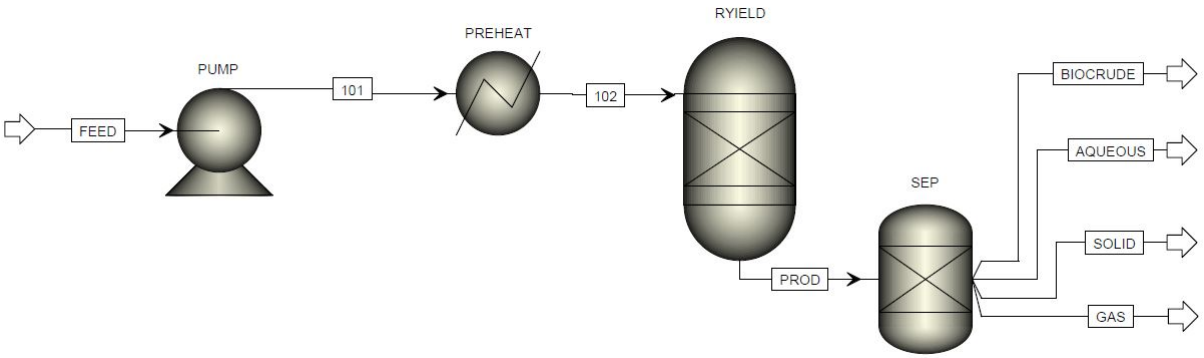

Figure C.2.1: Flowsheet 1, of the algae HTL process.

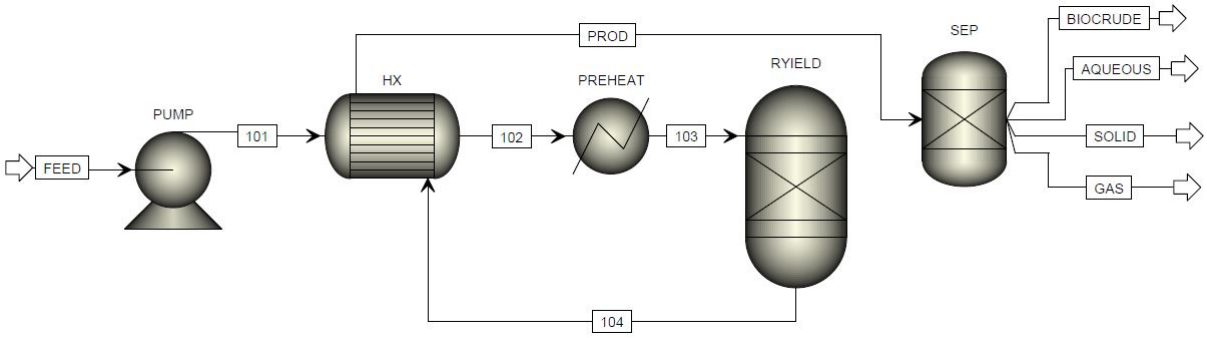

Figure C.2.2: Flowsheet 2, of the algae HTL process.

The heat exchanger implemented in plant 2, has a heat transfer area of 2 m^2. Using an overall heat transfer coefficient of $850 W/m^2K$. A sensitivity analysis was performed for the heat exchanger. By increasing the area, the outlet temperature of stream 102 increased, while the temperature of the product stream decreased. Thus, the heater duty decreases.