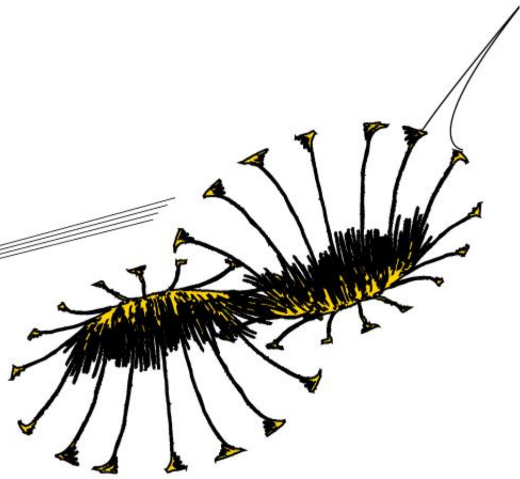
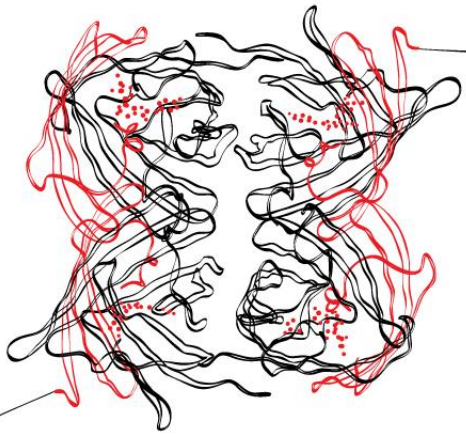
ENERGY FROM THE SEA

Hydrothermal liquefaction of algae





Internship report
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Period: August – November 2014
Location: Trondheim, Norway

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SINTEF

This experimental research (August – November 2014) is done in commission of SINTEF Energy Research, located in Trondheim (Norway). It is done by Jina Charissa Bhagwandas, author of this report, for the completion of her internship (20 European Credits) of the study Mechanical Engineering with as specialization Thermal Engineering at the University of Twente, located in Enschede (Netherlands).

Jina Bhagwandas
February 2015

List of abbreviations

FD	Freeze-dried
HTL	Hydrothermal Liquefaction
OD	Oven-dried
P	Pressure
T	Temperature
S	Smoothie

Abstract

Cultivated brown macro-algae harvested in the summer of 2014 in Trondheim Bay, *Laminaria saccharina,* were converted into bio-crude by hydrothermal liquefaction in a batch reactor. The influence of the different type of storage conditions [smoothie, freeze and oven-dried powder] and the different reaction temperatures [200, 300, 350 °C] was assessed. The general conclusion that can be drawn is that the oil yields of all the experiments were extremely low. The product yields of the freeze and oven-dried powder as feedstock were more or less the same, while the yields of the smoothie as feedstock were not as expected. The explanation for this is that probably the smoothie was still not homogenous enough compared to the freeze and oven-dried powder.

The product yields of the freeze and oven-dried powder were the highest for the experiments with a reaction temperature of 300 °C.

The low heating rate of the batch reactor, losses during processing, influence of the errors in the balance which were higher than normal due to the relatively small quantities of oil, making use of a separation method that still can be improved, a batch of *Lamminaria Saccharina* with a low content of carbohydrates and the possibility of a hydrothermal carbonization process instead of the actual hydrothermal liquefaction process are all statements which could have caused the extremely oil yields in general.

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Introduction

Today's world relies heavily on fossil fuels. These types of fossil fuels are finite resources that will eventually dwindle, too expensive or too environmentally damaging to retrieve. In contrast, the many types of renewable energy resources such as wind, solar, biomass etc. are constantly replenished and will never run out. At the moment there is a lot of research about how to convert these renewable energy resources into electricity, heat or (bio-)oil. For the production of biofuels and bio-chemicals there are mainly two different conversion processes, namely; biological and thermochemical conversion (1). Thermochemical conversion is a chemical reforming process of biomass in a heated and usually pressurized oxygen deprived enclosure, where long-chain organic compounds break into short-chain components. Some thermochemical conversion processes are combustion, gasification, pyrolysis and hydrothermal liquefaction (HTL) (2).

This research is about the conversion of a specific kind of biomass. Productivity, scalability and a continuous feedstock supply are the key factors in the selection of a biomass feedstock (3). The specific kind of biomass that is used for this research is a type of algae called *Laminaria Saccharina*. This is a brown macro-alga which was harvested in Trondheim bay. It has a high carbohydrate content and contains large amounts of mannitol [14 % of dry weight] and laminarin [16 % of dry weight] (4). These values of mannitol and laminarin are typical quantities of cultivated *Laminaria Saccharina* harvested by Agrimer Algues Marines in an area covering hundred kilometres of shore, including the Ouessant archipelago, heart of the Mer d'Iroise (5).

Laminaria Saccharina is also called 'sugar kelp'. It can grow in a broad range of environments and does not require fresh water and arable land for cultivation thereby avoiding the highly contentious food versus fuel debate (3). According to these facts algae seems like an interesting feedstock. Since an alga is a high-moisture biomass, hydrothermal liquefaction is a promising technology for conversion of this type of biomass into biofuels and chemicals.

At the moment cultivated macro-algae cannot be delivered as a continuous feedstock supply. It is only harvested maximum twice a year. This means that this type of algae needs to get stored. There are various types of storage conditions for wet biomasses.

The objective of this experimental research is to determine the influence of the various storage conditions and different reaction temperatures on the final hydrothermal liquefaction product properties.

With the given research objectives the following tasks are identified:

- Understanding the process by:
    - Literature review of Hydrothermal Liquefaction.
    - Literature review of the specific type of alga: *Laminaria Saccharina.*
- Experimental Research;
    - Customize the reactor setup.
    - Feedstock preparation.
    - Performance of the experiment.
    - Collect and separate the HTL products.

- Process and analyze the results of the experimental research.
- Draw conclusions and suggest recommendations for further research.

1 Hydrothermal liquefaction of biomass

Hydrothermal liquefaction (HTL) is a direct liquefaction process where biomass is converted into liquid oil with the presence of a solvent (in most cases water) at moderate temperatures of 200-350 °C and high pressures of 100-250 bar (1).

1.1 The elements on which the final HTL product relies on

Hydrothermal decomposition of biomass leads to the formation of various compounds depending upon the composition and physical properties of the biomass feedstock and solvent, process conditions and the presence of catalyst. The products of HTL can be classified in to four different categories (1):

- Oil phase (also called bio-oil or bio-crude).
- Aqueous solution of organic components.
- CO_2-rich gas phase.
- Solid char.

1.1.1 Composition and physical properties of the biomass feedstock and solvent

The process parameters and properties are summarized in Table 1-1.

Table 1-1. Relevant hydrothermal liquefaction process parameters adapted from (1).

Property class	Parameter
Biomass properties	Type of biomass feedstock and composition of main organic constituents Proximate analysis (moisture, ash, volatiles, fix-carbon) and ultimate analysis Particle size and distribution Density Porosity
Solvent properties	Chemical composition: water, alcohols Density Dielectric constant Ionic product Solubility Diffusivity Heat capacity Thermal conductivity Dynamic viscosity Surface tension

1.1.1.1 Biomass feedstock

The reaction pathways for hydrothermal liquefaction of biomass depend on the components of the biomass. Each type of biomass has its own specific composition. The main biomass components are (6):

- Carbohydrates.

- Lignin.
- Protein.
- Lipids.

The degradation products of these components in sub-critical water differ significantly for each specific type of biomass; however the basic reaction mechanisms for HTL remain the same. The basic reaction mechanisms can be described as (1) (6):

- Depolymerization of the biomass.
- Decomposition of biomass monomers by cleavage, dehydration, decarboxylisation and deammination.
- Recombination of reactive fragments.

1.1.1.2 Solvent

Previous research has shown that in general, under similar temperature conditions, oil yields increased when using water as solvent compared to alcohols and acetone (7) (8) (9) (10) (11). From the phase diagram of water, see Figure 1-1, it can be seen that at moderate temperatures of 200-350 °C and high pressures of 100-250 bar water is in liquid state and has the properties of near-supercritical (sub-critical) water. Sub-critical water is used as a solvent, reactant and catalyst for biomass conversion (1) (6). It has a low viscosity and high solubility of organic substances. These two properties make sub-critical water an excellent medium for fast, homogenous and efficient reactions (6). Furthermore sub-critical water has a relative high density and dissociation constant. The combination of these two properties favors the ionic reaction (6). Sub-critical water as a reactant and catalyst transforms the molecules through a cascade of reactions that leads to oil. By adding H^+ to open carbon bonds the water causes organic material to disintegrate and reform into fragments that then transform into hydrocarbons (2). The acidic and basic nature of hot water drives this cascade.

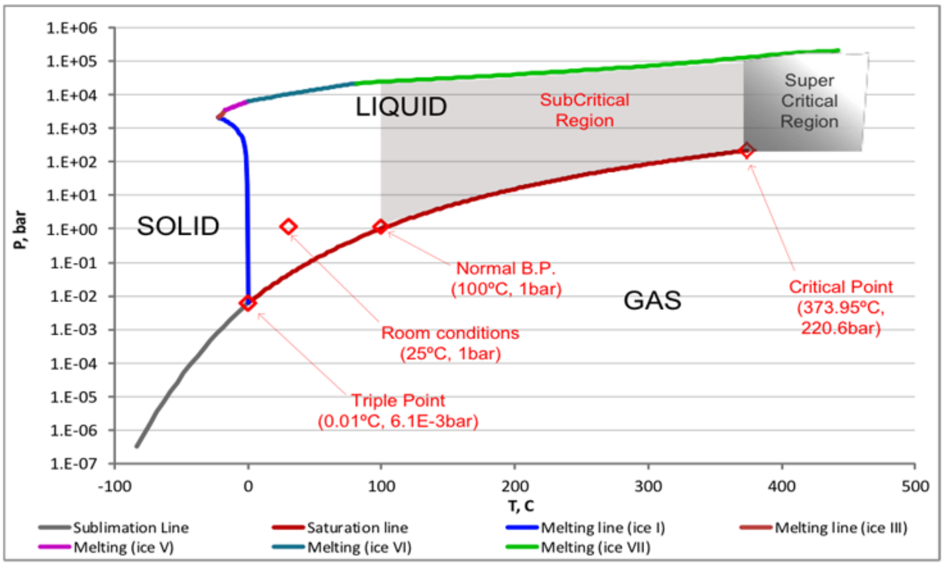


Figure 1-1. The phase diagram of water adapted from Clemson University Restoration Institute (12).

1.1.2 Process conditions

The parameters such as temperature, residence time, solvent to biomass ratio, heating rate, and pressure are important for the quality of the end product (13).

1.1.2.1 Temperature

At low temperatures biomass liquefaction is endothermic and exothermic at high temperatures (13). The optimum temperature for maximum oil yield is sequential since the properties of water changes rapidly under near critical conditions (1). At the beginning increasing temperatures triggers the bio-oil yield, but after reaching a certain peak for the oil-yield a further increase in temperature reduce the production of oil from biomass. The explanation for this behavior is as a result of two mechanisms that become dominant at high temperatures. The two mechanisms are:

- The secondary decompositions and Bourdard gas reactions become active at high temperatures which lead to the formation of gases (14).
- The recombination of free radical reactions leads to the char formation due to their high concentrations (13).

1.1.2.2 Residence time

There has been a lot of previous research about the effect of residence times on hydrothermal liquefaction of biomass. Anastasakis and Ross (4) observed that a 15-min holding time at one specific temperature was sufficient for the seaweed to form oily-compounds, giving the highest bio-oil yield. A higher residence time resulted in a decrease of the bio-oil yield. Similar results were obtained by Qu et al. (15), where a residence time of 10-min produced the highest oil yield from the HTL of a woody biomass and by Yin et al. (16) during the HTL of cattle manure. From these results there can be concluded that longer residence times after the biomass conversion to liquid oil reaches its maximum promote re-polymerization of the newly formed products (1). The gaseous yield increases with an increasing residence time. However, according to Boocock and Sherman (17), longer residence times suppressed the bio-oil yield except for very high biomass to water ratios.

1.1.2.3 Solvent to biomass ratio

There are many researches done about the effect of the solvent to biomass ratio water or solvent density on hydrothermal liquefaction product yields. The solvent to biomass ratio is considered as a key parameter, because it acts as both a hydrogen donor and as a solvent for hydrolyzing the high molecular weight carbohydrates present in biomass (4). Increasing the solvent to biomass ratio leads to higher production of bio-oil (1), possibly due to enhanced extraction by denser solvent medium. Wang et. al. (18) observed that high solvent to mass ratios reduced the amount of solid residues. Apart from residues reduction, high amounts of solvents also decreased gas yields.

1.1.2.4 Heating rate

According to previous research done by Quang et. al. (19), the effects of heating rate on the products yield are very strong. It has been confirmed with experimental research that higher heating rates during HTL of biomass enhanced significantly the bio-oil yield. There are some possible explanations for this, although the chemistry behind this effect is not yet fully understood. The possible explanations are summed up below, adapted from Quang et.al. (19);

- Rapid heating accelerates the degradation reactions of biomass materials.
- Rapid heating reduces unwanted side reactions and promotes reactions forming more bio-oil.
- Rapid heating accelerates the breaking of biomass cell and thus eases the releasing of cell contents into the hydrothermal media for subsequent reactions.
- Rapid heating minimizes the char formation and/or the re-polymerization.

1.1.2.5 Pressure

The pressure has low to negative effect on the yield of liquid oils in supercritical medium. The main purpose of pressure is to have one single phase during liquefaction. This single phase liquefaction is necessary to avoid large enthalpy inputs required for phase change of solvents (13). Once the conditions for HTL are achieved, the pressure has a negligible role in enhancing the oil yield (13).

1.1.3 Effect of catalyst

Hydroxides, carbonates, bicarbonates and formates of the alkali metal are used as catalysts during hydrothermal liquefaction in general. Anastasakis and Ross (4) investigated the influence of a catalyst on the hydrothermal liquefaction of *Laminaria saccharina*. They used potassium hydroxide (KOH) as a typical catalyst to investigate this effect. An increased catalyst dosage resulted in a decrease in the bio-crude yield. It can be concluded that KOH reduces the formation of bio-crude and favors the solubility of organics in the aqueous phase.

1.2 Advantages and disadvantages of HTL

The major processing differences that separate HTL from other thermo chemical conversion processes are that it occurs at elevated pressures and that it is performed on wet biomass, using water as a critical reactant in the decomposition process (11).

1.2.1 Advantages of HTL

For wet biomasses HTL is a promising method, because there is no drying of wet biomasses required. This means that energy losses associated with drying can be avoided. HTL delivers a high-energy bio-crude that is lower in oxygen and moisture content compared to pyrolysis bio-crude (2).

1.2.2 Disadvantages of HTL

Corrosion in the subcritical water environment is a critical issue. In particular acidic and oxidizing conditions can cause rapid corrosion, and this can be even more severe at subcritical conditions than at supercritical conditions, due to the relatively dense and polar character of subcritical water. Main forms of corrosion are pitting corrosion, general corrosion, intercrystalline corrosion and stress corrosion cracking.

Another disadvantage is salt deposition in the reactor if the amount of minerals in the feedstock is very high. This could lead to reactor clogging (1).

1.3 Previous research on HTL of *Laminaria saccharina*

Anastasakis and Ross (4) have done experimental research about the influence of reaction conditions on the liquefaction behavior of *Laminaria saccharina*. Their batch came from the Barnacarry Bay in Scotland during the spring of 2008. They investigated the influences of the reactor loading, reaction time and temperature by making use of a batch autoclave with a heating rate of 25 °C/min. The experiments were performed for a range of different biomass/water ratios (5-20%), residence times (15-120 min) and temperatures (250-370°C). They found that a biomass/ratio of 1/10 and a 15-min residence time at a temperature of 350 °C was sufficient enough for the seaweed to form oily compounds, giving the highest bio-crude yield. Increasing the residence time resulted in a decrease of the bio-crude yield, indicating re-polymerization or re-condensation of the newly formed compounds. Increasing the temperature resulted in an increase in bio-crude yield and a corresponding decrease in the residue fraction. In their investigation, the maximum bio-crude yield was 19.3 % at 350 °C (4).

Quang-Vu Bach et. al. (19) experimentally studied HTL of *Laminaria saccharina,* harvested in Trondheim bay, by a high-throughput screening technique using sealed quartz capillary reactors. They achieved very high heating rates with these reactors, which resulted in much higher bio-oil yields than the bio-oil yields from Anastasakis and Ross (4). They made use of three different heating rates, namely; high heating rate [585°C/min], middle heating rate [321°C/min] and a lower heating rate [146°C/min]. The other process conditions [a residence time of 15 minutes, a temperature of 350 °C and a biomass/water ratio of 1/10] were adapted from Anastasakis and Ross (4). The results of Quang-Vu Bach et. al. experimental research can be found in Figure 1-2. They concluded that heating rates have a big influence on the oil yields. The higher the heating rates, the higher the bio-oil yield was achieved.

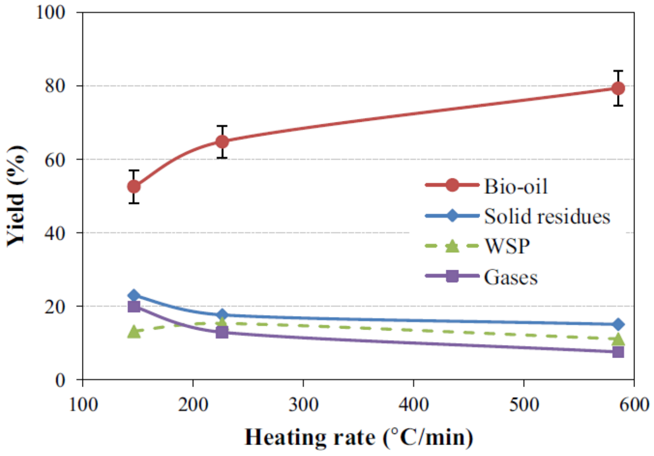


Figure 1-2. The effect of heating rate on the products yield (T = 350°C; residence time = 15min; biomass/water ratio = 1/10) by Quang Vu Bach et. al. (19).

2 Experimental research

The influence of the various storage conditions (smoothie, freeze-dried and oven-dried powder) on the end hydrothermal liquefaction product properties was investigated. Furthermore there was also investigated what influence the reaction temperature had on the end hydrothermal product properties while holding all the other parameters constant. In order to keep the water in the subcritical phase the pressure needed to be increased with an increasing temperature, see Figure 1-1 for the water phase diagram. Three different temperatures were applied, 200 °C, 300 °C and 350 °C for each feedstock (form). This means that there were nine experiments in total. Several repetitions were performed for each of the experiments, from which the average values were calculated and reported as the experimental results. The experimental matrix can be seen in Table 2-1. The experiments were carried out in a batch reactor by the author of this report.

Table 2-1: Experimental matrix.

Feedstock	**T = 200 °C**	**T = 300 °C**	**T = 350 °C**
Smoothie	Experiment 1A	Experiment 1B	Experiment 1C
Freeze-dried powder	Experiment 2A	Experiment 2B	Experiment 2C
Oven-dried powder	Experiment 3A	Experiment 3B	Experiment 3C

The Number corresponds to the feedstock.
The Letter corresponds to the temperature.

2.1 Feedstock preparation

Laminaria Saccharina, a brown macro-alga harvest in Trondheim Bay, was the used feedstock for all experiments but in different forms.

Three different forms of *Laminaria Saccharina* were applied. The different forms of *Laminaria Saccharina* that were applied are as follows:

- Smoothie: smoothie made out of fresh *Laminaria Saccharina* followed by freezing at a temperature of −45 °C and melting before making use of it.
- Freeze-dried powder: *Laminaria Saccharina* was freeze-dried, ground to a mean particle size of <500 μm and stored in air-tight bags.
- Oven dried [T=105°C] powder: *Laminaria Saccharina* was oven-dried for 48 hours, ground to a mean particle size of <500 μm and stored in air-tight bags.

The analysis of the cultivated and wild seaweed harvested in Trondheim Bay is given in Table 2-2. For this experimental research there was only made use of cultivated seaweed (batch 1).

Table 2-2. Analysis of cultivated seaweed harvested in Trondheim Bay.

	Batch 1 (cultivated)
Harvesting date	11-06-2014
Dry weight [% of ww]	12,9
Laminarin (as glucose) [% of dw]	0,2
Mannitol [% of dw]	3,8

The moisture content of batch 1 was determined by subtracting 100% minus the divided weight after oven drying the fresh algae at a temperature of 105°C for 24 hours and the weight before this process. The ash content was determined with thermo-gravimetric analysis at a temperature of 500°C for 4 hours. The proximate analysis can be found in Table 2-3.

Table 2-3. Proximate analysis of *Laminaria Saccharina*.

	Smoothie	**Freeze-dried powder**	**Oven-dried powder**
Proximate (wt.%)			
Ash content	49	49	49
Moisture content	89	89	89

The hydrothermal liquefaction of cultivated *Laminaria saccharina* was performed in a batch reactor without the addition of a catalyst. Several repetitions were performed for each of the experiments, from which the average values were calculated and reported as the experimental results. The results, discussions and conclusions are all based on the weight of the end HTL products since the biochemical and ultimate analysis of the smoothie, freeze and oven-dried powder performed by the MS laboratory of SINTEF Materials and Chemistry were not available yet when the report was submitted.

2.2 Experimental setup and procedure

The experiments were performed in a 250 ml Parr reactor model 4651 batch reactor. Furthermore, the experiment setup consisted of a bench-top ceramic heater, 4923EE, and a temperature controller, Parr reactor controller 4838. The system was connected with a nitrogen bottle for purging and pressurizing the reactor prior to each specific experiment. After complementation of the reaction, the reactor was cooled down by putting the batch reactor in a bucket filled with ice-cubes. Figure 2-1 shows a schematic drawing of the setup.

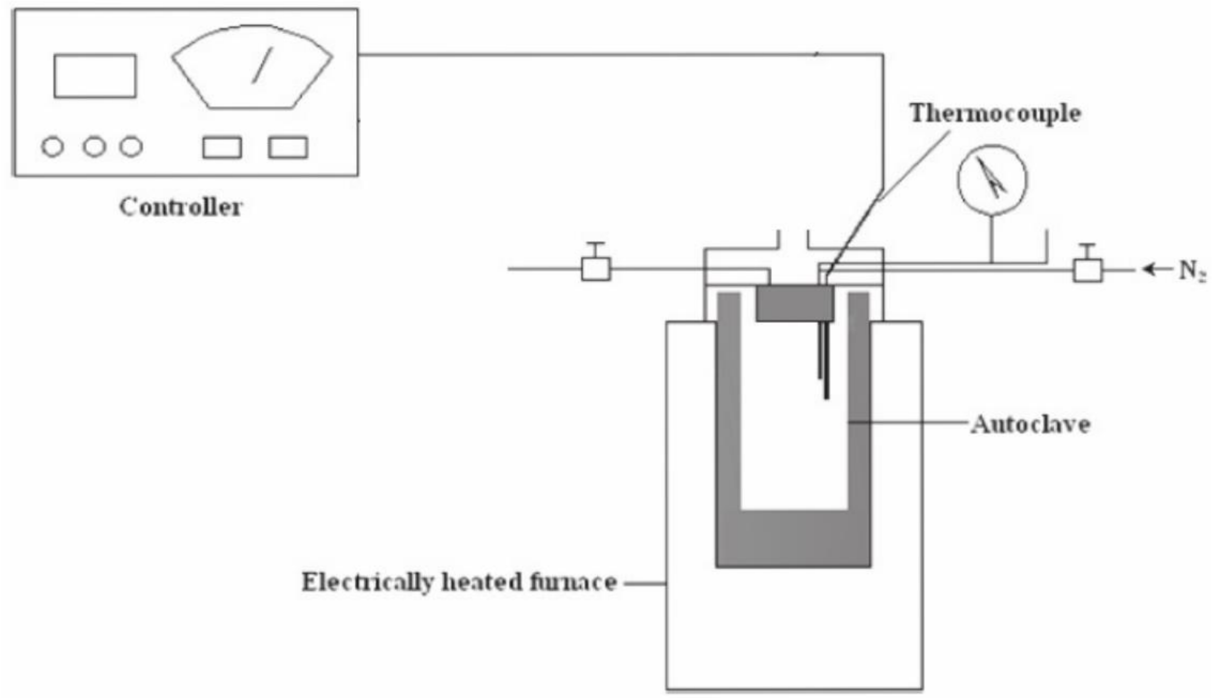


Figure 2-1. Schematic drawing of the setup.

Table 2-4 shows the process conditions of the experiments for the three different temperatures carried out in the batch reactor.

In a typical experiment with the smoothie as feedstock, the reactor was charged with 100 gram of smoothie. The reactants were heated at the desired temperature (200°C, 300°C or 350) for 60 minutes. A long residence time was used in order to match the long heating up times.

In a typical experiment with the freeze-dried and oven-dried powder as feedstock, the reactor was charged with 11 gram of powder and 89 gram of distillated water. The reactants were heated at the desired temperature (200°C, 300°C or 350 °C) for 60 minutes. The ratio of water to biomass ratio is based on the moisture content of *Laminaria Saccharina* which is 89%. Actually the water that was evaporated during the drying process of *Laminaria Saccharina* was added back.

Table 2-4. Process conditions of the experiments (see experiment matrix, Table 2-1).

Process conditions			
Temperature [°C]	200	300	350
Heating rate [°C / min]	4,2	3,2	2,7
Pressure [bar]	70	250	300
Residence time [min]	60	60	60

2.3 Product collection and separation

Once the reactor was cooled down, the gases produced by the reaction were immediately vented inside a fume hood followed by disassembly of the reactor. The reaction mixture (minus the gas product) was suction filtered over a filter paper. The solid residue was oven dried at a temperature of 105°C for 24 hours to afford a dry solid fraction (bio-char). The solid residue was measured before and after oven drying to calculate how much water was evaporated during the drying process.

The liquid products (oily phase and the water soluble products phase) were diluted with an appropriate amount of dichloromethane in a separation funnel to separate these two phases from each other. After several minutes two layers were formed;

- A hydrophilic or aqueous phase (containing water soluble products) on the top.
- A hydrophobic phase (bio-oil dissolved in dichloromethane) on the bottom.

The hydrophilic and hydrophobic phases were measured after approximately 20 hours after the separation process to make sure that all the dichloromethane was evaporated.

The product yields were calculated with equation 3-1, adapted from (3), where $Y_{product}$ is the bio-crude, bio-char and water soluble products yield in wt.% on a dry weight. $W_{product}$ is the mass of the specific product and $W_{feedstock}$ is the mass of the used feedstock for that specific experiment.

$$Y_{product} = \left(\frac{W_{product}}{W_{feedstock}}\right).100\% \qquad 2\text{-}1$$

The elemental compositions of the phases (oil, aqueous and solid) were analyzed externally, by the MS laboratory of SINTEF Materials and Chemistry. The results were not available when the report was submitted.

2.3.1 Improved separation method

During the experiments it is concluded that the separation method can be improved.
To show that there is a difference there is made use of a different separation method as the one described in paragraph 2.3.

The difference in the improved separation method was that the reaction mixture (-gasses) were diluted with an appropriate amount of dichloromethane instead of only the liquid products. The purpose of this was to include the products (bio-oil) which might be there in the solid residues. The rest of the method was ditto as the one described in paragraph 2.3. The disadvantage of this method was that there was a lot of ice forming during filtration which resulted in a clogged funnel. The reason for this ice forming was because of the fast evaporation of the dichloromethane in combination with the suction pump. The clogged funnel leaded into a lot of losses during this filtration process.

3 Results

During hydrothermal liquefaction of brown macro-algae, the starting material was converted to bio-crude, bio-char, water soluble products and gasses. The presented results, discussions and conclusions are all based on the weight of the end HTL products.

Figure 3-1, Figure 3-3 and Figure 3-5 present the product yields of the end HTL products on wet basis with smoothie, freeze-dried and oven-dried powder as feedstock, respectively. Figure 3-2, Figure 3-4 and Figure 3-6 present the oil yield on dry-ash free basis with smoothie, freeze-dried and oven-dried powder as feedstock, respectively. The observations listed below are based on these graphs.

General:

- Extremely low oil yields in general.
- The oil yields from the freeze-dried powder [0,077-0,124-0,093 %] and the oven-dried powder [0,084-0,126-0,08 %] are more or less equal.
- Solid residues are higher at 200 °C for all the feedstocks which results in also the highest amount of evaporated water.

Smoothie:

- Results are not as expected.
    - The experiment at 200 °C gives the best oil yield.

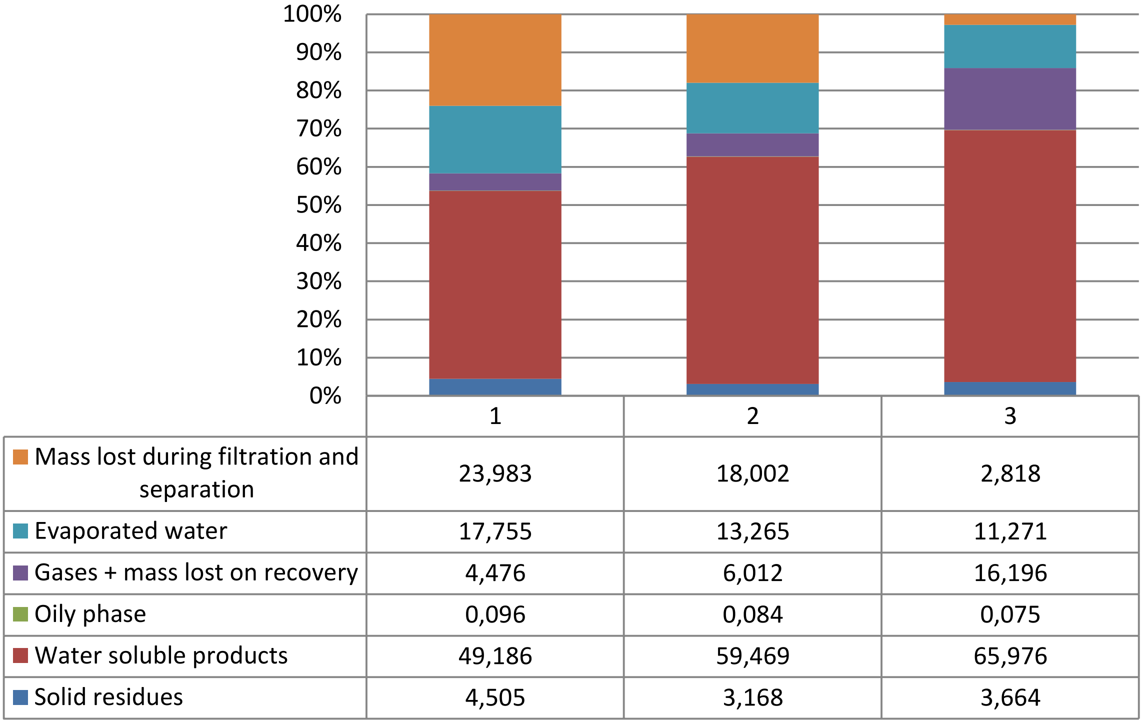
Freeze dried powder:

- The experiment at 300 °C gives the best oil yield

Oven dried powder:

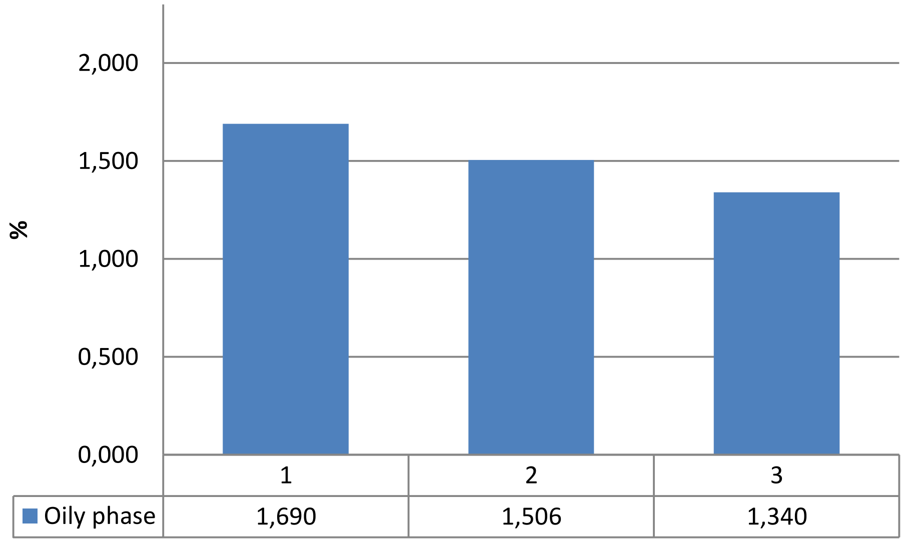
- The experiment at 300 °C gives the best oil yield.

Smoothie



	1	2	3
🟧 Mass lost during filtration and separation	23,983	18,002	2,818
🟦 Evaporated water	17,755	13,265	11,271
🟪 Gases + mass lost on recovery	4,476	6,012	16,196
🟩 Oily phase	0,096	0,084	0,075
🟥 Water soluble products	49,186	59,469	65,976
🟦 Solid residues	4,505	3,168	3,664

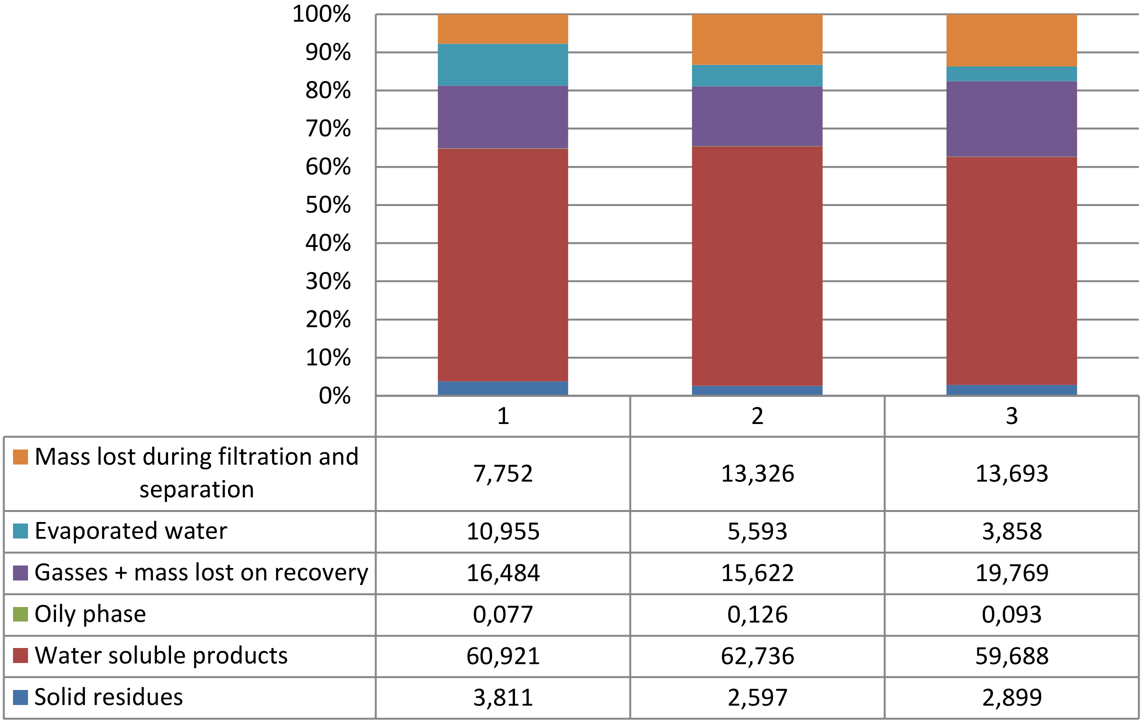
Figure 3-1: Product yields of the end HTL products on wet basis with smoothie as feedstock. [1 = 200 °C; 2 = 300°C, 3 = 350°C]



	1	2	3
🟦 Oily phase	1,690	1,506	1,340

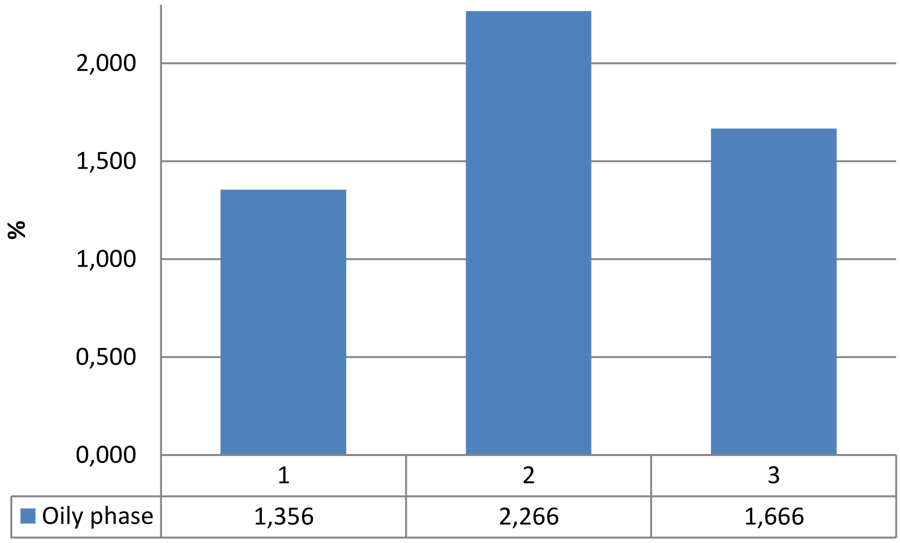
Figure 3-2: Oil yield on dry-ash free basis with smoothie as feedstock. [1 = 200 °C; 2 = 300°C, 3 = 350°C]

Freeze-dried powder



	1	2	3
🟧 Mass lost during filtration and separation	7,752	13,326	13,693
🟦 Evaporated water	10,955	5,593	3,858
🟪 Gasses + mass lost on recovery	16,484	15,622	19,769
🟩 Oily phase	0,077	0,126	0,093
🟥 Water soluble products	60,921	62,736	59,688
🟦 Solid residues	3,811	2,597	2,899

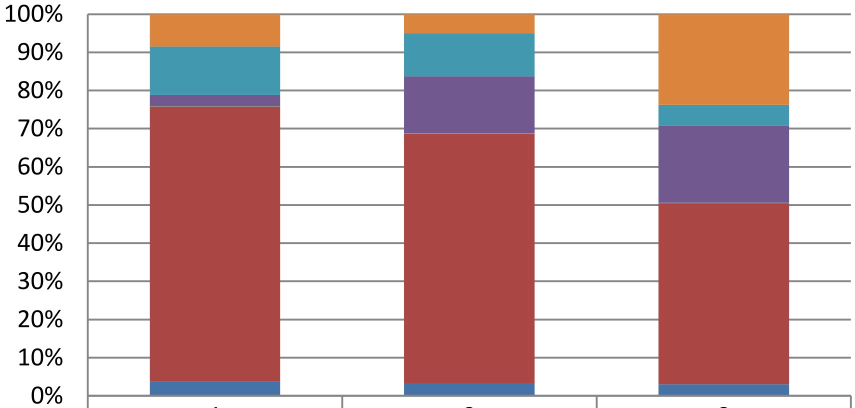
Figure 3-3: Product yields of the end HTL products on wet basis with freeze-dried powder as feedstock. [1 = 200 °C; 2 = 300°C, 3 = 350°C]



	1	2	3
🟦 Oily phase	1,356	2,266	1,666

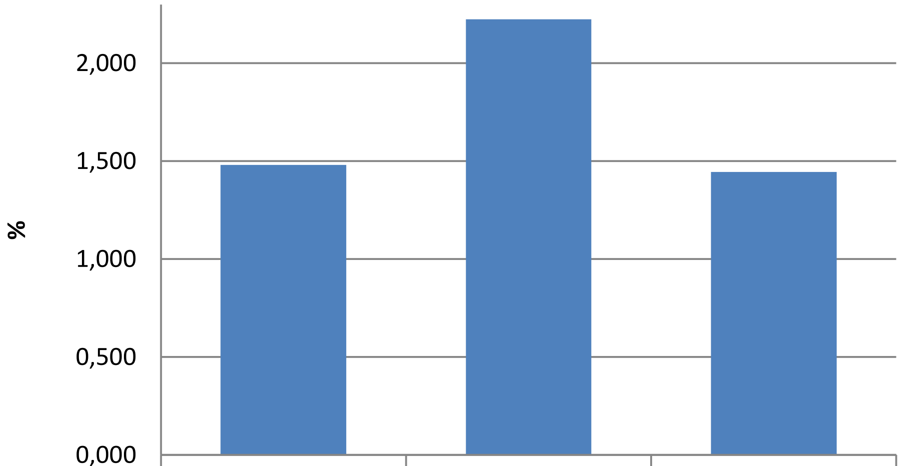
Figure 3-4: Oil yield on dry-ash free basis with freeze-dried powder as feedstock. [1 = 200 °C; 2 = 300°C, 3 = 350°C]

Oven-dried powder



	1	2	3
🟧 Mass lost during filtration and separation	8,519	5,050	23,726
🟦 Evaporated water	12,669	11,279	5,499
🟪 Gasses + mass lost on recovery	3,008	14,924	20,175
🟩 Oily phase	0,084	0,124	0,081
🟥 Water soluble products	71,935	65,276	47,512
🟦 Solid residues	3,785	3,348	3,007

Figure 3-5: Product yields of the end HTL products on wet basis with oven-dried powder as feedstock. [1 = 200 °C; 2 = 300°C, 3 = 350°C]



	1	2	3
🟦 Oily phase	1,480	2,223	1,445

Figure 3-6: Oil yield on dry-ash free basis with oven-dried powder as feedstock. [1 = 200 °C; 2 = 300°C, 3 = 350°C]

3.1 Improved separation method

To prove that this separation method indeed gives higher oil yields some experiments were done for every type of feedstock. A reaction temperature of 300 °C was used, because the oil yields were the highest at this temperature. There was a lot of loss during these experiments and there were no repetitions due to time lack. This means that the results presented in

Figure 3-7 are not 100% reliable. These experiments were done to show that oil yields are indeed higher with an improved separation method.

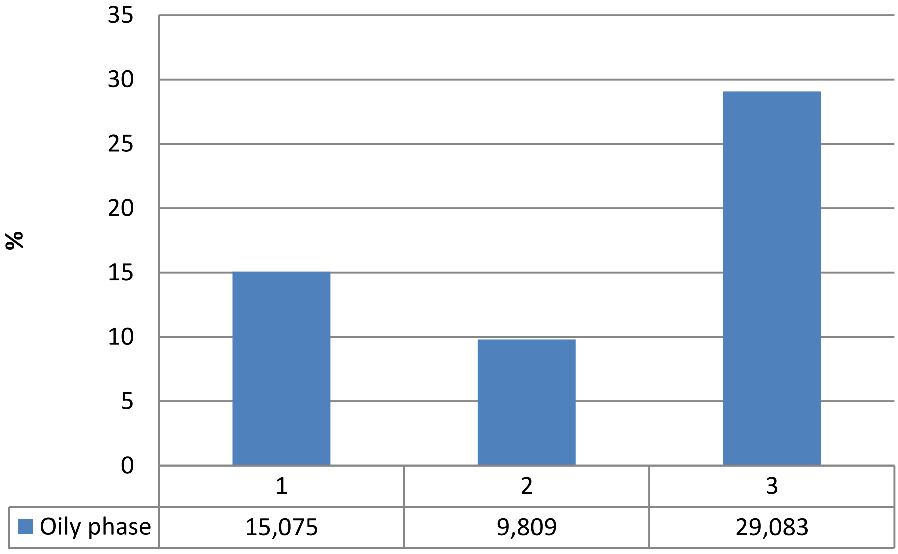


Figure 3-7: Oil yield on ash-dry free basis with the improved separation method, T = 300℃ [1 = Smoothie; 2 = freeze-dried powder; 3 = oven dried powder]

4 Discussions

It has been demonstrated that the use of a batch reactor for HTL of algae resulted in extremely oil yields in general. This can be explained by several facts. The low heating rate of the batch reactor, losses during processing, influence of the errors in the balance which were higher than normal due to the relatively small quantities of oil, making use of a separation method that still can be improved, a batch of *Lamminaria Saccharina* with a low content of carbohydrates and the possibility of a hydrothermal carbonization process instead of the actual hydrothermal liquefaction process are all statements which could have caused the extremely oil yields in general. Below there has been elaborated on each statement.

Heating rate

The heating rate of the batch reactor was extremely low [2,7 ; 3,2 ; 4,2 °C / min]. According to previous research done by Quang-Vu Bach et. al. (19) the heating rate of the reactor has a big influence on the oil yields. High heating rates increase the oil yield drastically. Their results are presented in section 1.3. Their experimental research showed that the higher the heating rates, the higher the bio-oil yield. With the results of previous research the conclusion can be drawn that the low oil yields can be explained by the extremely low heating rates of the used batch reactor. Although the chemistry behind the fact that high heating rates increase the oil yield drastically is not yet fully understood, there are some possible explanations which are as follows (19):

- Rapid heating accelerates the degradation reactions of biomass materials (20) (21).
- Rapid heating reduces unwanted side reactions and promotes reactions forming more bio-oil (22).
- Rapid heating accelerates the breaking of biomass cell and thus eases the releasing of cell contents into the hydrothermal media for subsequent reactions (20).
- Rapid heating minimizes the char formation and/or the re-polymerization (23).

For future research it is advisable to make use of much higher heating rates than used for this experimental research. Continuous flow reaction systems equipped with static mixing mechanisms can achieve high heating rates (19). These reaction systems are also suitable for upscaling, keeping in mind that solid residues may cause clogging problems.

Losses during processing

According to the results of all the experiments it is clear that there were a lot of losses during processing. The bio-crude that is formed can become trapped on the walls of the reactor, resulting in losses. Also, according to Anastasakis and Ross (4), during the evaporation of the dichloromethane phase, many light volatiles are lost. The filters and the funnels used for the separation of the products contributed to additional losses.

Errors in balance

The influence of the errors in the balance was higher than normal due to the relatively small quantities of oil.

Improved separation method

The yield of the aqueous products were simply calculated by the difference of feedstock and the total mass collected from gaseous products and solid residues due to the limitation of products recovery methods. Products separation procedure is important for HTL of algae because high efficient products recovery is an important insurance for further application of HTL. Definitions used in HTL products, especially the bio-crude oil products, need to be clarified based on the separation, solvent and extraction procedure.

It was clear that the improved separation method indeed gave higher oil yields.

A batch with a low content of laminaran and mannitol

The cultivated seaweed used during these experiments was harvested during the summer of 2014. According to Anastasakis et. al. (4), usually *Lamminaria Saccharina* has high laminarin and mannitol contents. Compared to usually batches, see Table 4-1 for the comparison, this batch 1 contained less laminarin and mannitol. This is also one of the reasons why the oil yields were lower than expected. Anastasakis et. al. and Quang-Vu Bach et. al. found higher oil yields. They probably made use of seaweed with higher carbohydrates content.

Table 4-1. Comparison of batch 1 and *Lamminaria Saccharina* of Agrimer

	Batch 1 (cultivated)	***L.S* of Agrimer**
Harvesting date	11-06-2014	-
Dry weight [% of ww]	12,9	10-20
Laminarin (as glucose) [% of dw]	0,2	16,0
Mannitol [% of dw]	3,8	14,0

Hydrothermal carbonization

Due to the relatively high solid residues there can be concluded that all of the experiments were hydrothermal carbonization instead of hydrothermal liquefaction. This is caused by the low heating rates of the batch reactor. There can be concluded again that the heating rate of the reactor is a very important parameter.

Smoothie

The first experiments were with the non-stirred smoothie as feedstock. The oil yields, which are not presented in the report, were lower than the oil yields of the experiments with the stirred by human power smoothie as feedstock. The experiments with the non-stirred smoothie as feedstock were considered as unsuccessful. Though, an important conclusion could be drawn from these results. The conclusion was that the effect of stirring is noticeable in the end results. During storage some parts of the alga-smoothie sank down, that is why it is important to make it fully homogenous before making use of it.

Although the smoothie was stirred by human power before making use of it the results were not as expected. The oil yields for the experiment with a temperature of 200°C were higher than the oil yields of the experiments with a temperature of 300 and 350 °C. The explanation for this is that the smoothie was still not homogenous enough compared to the freeze and oven-dried powder, because it is stirred by human power.

The smoothie as feedstock can be quite difficult to handle since during storage some parts of the alga-smoothie sank down. It is important to make it fully homogeneous to obtain reliable results.

Freeze and oven-dried powder

The results of the freeze and oven-dried powder were more or less the same, as expected. The highest oil yield was at a temperature of 300°C. Previous research of Javaid Akhtar, and Nor Aishah Saidina Amin (13) has proved that at the beginning increasing temperatures triggers the bio-oil yield, but after reaching a certain peak for the oil-yield a further increase in temperature reduce the production of oil from biomass. The explanation for this behavior is as a result of two mechanisms that become dominant at high temperatures. The two mechanisms are:

- The secondary decompositions and Bourdard gas reactions become active at high temperatures which lead to the formation of gases (14).
- The recombination of free radical reactions leads to the char formation due to their high concentrations (13).

The results of this experimental research support this theory. For all the three different type of feedstocks the highest oil yield was reached when a temperature of 300 °C was applied.

4.1 Product utilization

Since the oil yields were so low it is important that the other formed products during this process have some industrial use in order to have some profit from this hydrothermal liquefaction conversion of algae process. The other formed products are:

- Solid residues
- Water soluble products
- Gasses

All products (minus the gasses) have been sent for the proximate, biochemical and ultimate analysis to the MS laboratory of SINTEF Materials and Chemistry. Since the results were not available yet when the report is submitted the analysis of this paragraph is based on literature research.

4.1.1 Bio-oil

The majority of compounds of bio-oil are dichloromethane soluble (24). The bio-oil yield was obtained by weighing the solvent extracted material after evaporation of the solvent. It was difficult to clearly separate the solvent and products with lower boiling point. According to Vardon et. al. bio-oil is a complex mixture with a large number of compounds and a broad distribution of molecular weight (25). In general, major compounds identified by Gas Chromatography– Mass Spectrometry(GC–MS) consist of cyclic nitrogenates (e.g., pyrolle, indole, pyrazine, and pyrimidine compounds),cyclic oxygenates (e.g.,phenols and phenol derivatives with aliphatic side-chains), and cyclic nitrogen and oxygen compounds(e.g., pyrrolidinedione, piperidinedione, and pyrrolizinedione compounds) (25).

To produce hydrocarbon fuels from the bio-oil extracted from algae via HTL, the bio-oil needs to be upgraded through catalytic HTL primarily to remove oxygen and nitrogen (24).

4.1.2 Aqueous products

Aqueous products are generated in the HTL processes, because water is involved in the conversion process. The utilization of the HTL aqueous products plays an essential role on the overall effectiveness. According to ChunyanTian et. al. the main constituents of HTL aqueous include $NH4^+$, $PO4^{3-}$and metallic ions, such as K^+, Na^+ and Mg^{2+} (24).

4.1.3 Solid residue

According to CunyanTian et.al. solid residue is normally ash, rich in inorganics. It consists of inorganics and remaining organic matter (24). The yield of solid residue highly depends on ash content in the feedstock.

5 Conclusions and recommendations

Hydrothermal liquefaction experiments of a brown macro alga, called sugar kelp, were carried out in a batch reactor. The heating rate of the batch reactor was extremely low which may have been lead to hydrothermal carbonization instead of hydrothermal liquefaction. The general conclusion that can be drawn is that the oil yields of all the experiments were extremely low.

The first goal of this experimental research was to determine whether the various storage conditions had any influence on the end HTL product properties. *Laminaria Saccharina* was the used feedstock in three different forms, namely; smoothie, freeze and oven-dried powder. The results of this research were that the product yields of the freeze and oven-dried powder were more or less the same. The product yields of the smoothie differed from the product yields of the freeze and oven dried powder. Since there is no control over the homogeneity of the smoothie, the freeze and oven-dried powder are better forms to handle and to work with for the hydrothermal liquefaction of algae.

The second goal of this experimental research was to determine which temperature gives the best oil yield. Three different reaction temperatures were used, namely: 200°C, 300°C and 350 °C. The results of this research showed that the temperature of 300 °C resulted in the highest oil yield. It is preferable to use 300 °C for hydrothermal liquefaction of algae for any form.

Higher bio-oil yields of the process would be possible to achieve by making some improvements during the process. The most important parameter to improve is the heating rate. To reach higher oil yields it is important to do experiments in a reactor that can achieve higher heating rates, for example a continuous reactor equipped with static mixing mechanisms (19).

For further experimental research it is also import to vary the residence time in order to search for the optimum residence time. The relatively long residence time of 60 minutes was chosen in order to match the long heating up times of the batch reactor. Previous research of Anastasakis and Ross (4) has shown that 15 minutes were sufficient enough for the seaweed to form oily compounds, giving the highest bio-crude yield. A higher residence time resulted in a decrease of the bio-oil yield.

Another important statement to mention is that this batch of cultivated seaweed (batch 1) had an extremely low laminarin and mannitol content compared to the usual contents of laminarin and mannitol found in this type of alga, see Table 4-1 for the exact numbers of the content of laminarin and mannitol. *Laminaria Saccharina* is commonly known as 'sugar kelp', because of its high carbohydrate content. Usually it contains large amounts of mannitol and laminarin. It is recommended to repeat these experiments with a different batch where the laminarin and mannitol contents are higher than the contents of batch 1.

As already mentioned in chapter 4, definitions used in HTL products, especially the bio-crude oil products need to be clarified based on the separation, solvent and extraction procedure. This is why it is so important to make use of a correct/advanced separation method. As can be seen in chapter 4, a slightly different separation method can indeed increase the oil yield. This was proved by doing an experiment for each feedstock. It is recommended to do research on the optimal separation method for these kind of experiments since this have a big influence on the end result.

Since the oil yields were so low the viability of a full scale plant for HTL of algae might be possible only if there are also valuable products in the other phases such as the water soluble products and the gas phase.

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