Investigation of cold water marine macroalgae potential for bio-refinery integrated hydrothermal liquefaction

- A process residue study -

Master's Thesis

Lukas Jasiūnas

Aalborg University
Department of Energy Technology

Department of Energy Technology
Aalborg University
http://www.et.aau.dk

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Lukas Jasiūnas

Supervisor(s):
Lasse A. Rosendahl
Thomas H. Pedersen

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Abstract:

The study focuses on investigating the potential of cold water brown macroalgae as a suitable biomass feedstock for biocrude production via supercritical hydrothermal liquefaction (HTL). The work undertook an integration-oriented approach: a bio-refinery concept with demineralisation and high added value product extraction steps prior to residue valorisation in the form of HTL biocrude had been envisioned. The project scope included leaching (water, citric acid and utilising the acidic aqueous byproduct from a continuous HTL setup), alginate extraction via sulphuric acid and sodium carbonate bathing and fucoidan extraction using calcium chloride. Demineralisation was done to identify whether the inorganics (up to 33 wt.% on dry basis) present in the feedstock are in any way beneficial for effective conversion. The produced 6 sets of biocrudes were characterised by elemental (CHNS) and thermogravimetric (TGA) analysis. Similarly, in order to obtain complete mass balances, all by-products (solid, aqueous and gaseous) were quantified and analysed. A biofuel precursor of acceptable yields and quality was sought. Such a product is also defined by low heteroatom concentrations and high energy recovery (ER). Short HTL (i.e. reaction time of 10 min instead of the baseline 15 min) and the extent of leaching residue neutralisation were also evaluated as a method to improve processing economics and ease potential integration.

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Preface

This work is the Master's thesis written by Lukas Jasiūnas for obtaining the Master of Science (MSc) degree in Thermal Energy and Process Engineering, with a specialisation in Hydrothermal Liquefaction, from Aalborg University located in Aalborg, Denmark. The work was carried out in the Biolab facilities on main campus. I had the perfect opportunity to combine newly found passion for studying the nuances of HTL with my never ending plight to work towards efficient yet sustainable practices and facilities.

I would like to express my gratitude to my supervisors, Thomas H. Pedersen and Lasse A. Rosendahl, who were enthusiastic and supportive along the way. Not to mention the mighty lab team: Anne, thanks for taking care of us; Federica, thanks for helping out when it was most needed and Luca, thanks for all the crazy hours in front of the evaporator. It will be missed.

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Lukas Jasiūnas
ljasiu14@student.aau.dk

Summary

The study focuses on investigating the potential of cold water brown macroalgae as a suitable biomass feedstock for biocrude production via supercritical hydrothermal liquefaction (HTL). Two macroalgae genera were chosen: *Fucus vesiculosus* and *Saccharina latissima*. The work undertook an integration-oriented approach: a biorefinery concept with demineralisation and high added value product extraction steps prior to residue valorisation in the form of HTL biocrude had been envisioned. A process scheme that is novel within the academic field of HTL.

The project scope included fresh *F. vesiculosus* demineralisation via water, citric acid and the acidic aqueous byproduct as the three tested leaching agents. Furthermore, alginate extraction via sulphuric acid and sodium carbonate bathing and fucoidan extraction using calcium chloride were performed with both *F. vesiculosus* and *S. latissima*. Demineralisation was done to identify whether the inorganics (up to 33 wt.% on dry basis) present in the feedstock are in any way beneficial for effective conversion.

The produced 6 sets of biocrudes were characterised by elemental (CHNS) and thermogravimetric (TGA) analysis. Similarly, in order to obtain complete mass balances, all by-products (solid, aqueous and gaseous) were quantified and analysed. A biofuel precursor of acceptable yields and quality was sought. Such a product is also defined by low heteroatom concentrations and high energy recovery (ER).

Short HTL (i.e. reaction time of 10 min instead of the baseline 15 min) and the extent of leaching residue neutralisation were also evaluated as a method to improve processing economics and ease potential integration.

5 hypotheses were expressed in the beginning, all of which were at least partially confirmed by the end of the work.

Abbreviations

CHNS - elemental carbon, hydrogen, nitrogen and sulphur analysis

DAF - Dry and Ash Free basis

ER - Energy Recovery

FFN - Fresh Fucus vesiculosus, non-rinsed

FFR - Fresh Fucus vesiculosus, rinsed

FSR - Fucus vesiculosus, summer harvest, rinsed

GHG - Green house gases

HHV - Higher Heating Value

HTL - Hydrothermal Liquefaction

IEA - International Energy Agency

NIMS - Non-indigenous marine species

SAR - Saccharina latissima, autumn harvest, rinsed

SSR - Saccharina latissima, spring harvest, rinsed

TGA - thermogravimetric analysis

WS - Water solubles

HTL runs:

Run 1 - raw FFR as feedstock

Run 2 - citric acid leached FFR as feedstock

Run 3 - fucoidan residues as feedstock

Run 4 - alginate residues as feedstock

Run 5 - neutralised citric acid leached FFR as feedstock

Run 6 - 10 min retention time, raw FFR as feedstock

1 Introduction

1.1 Global issues and the need for biorefineries

As time goes, more and more academics acknowledge the dangers of and step up to fight anthropogenic green house gas (GHG) emissions. One of the largest consumers of unsustainable energy resources is the transportation sector. Figure 1.1 shows two road emission development scenarios. The above line indicates that if humankind would stop generating more CO_2, it would be possible to maintain an invariant statistics. But for how long? The proposed 2°C scenario, presented by IEA, includes a drastic cut in transportation generated GHG emissions in order to approach a sustainable level of energy use.

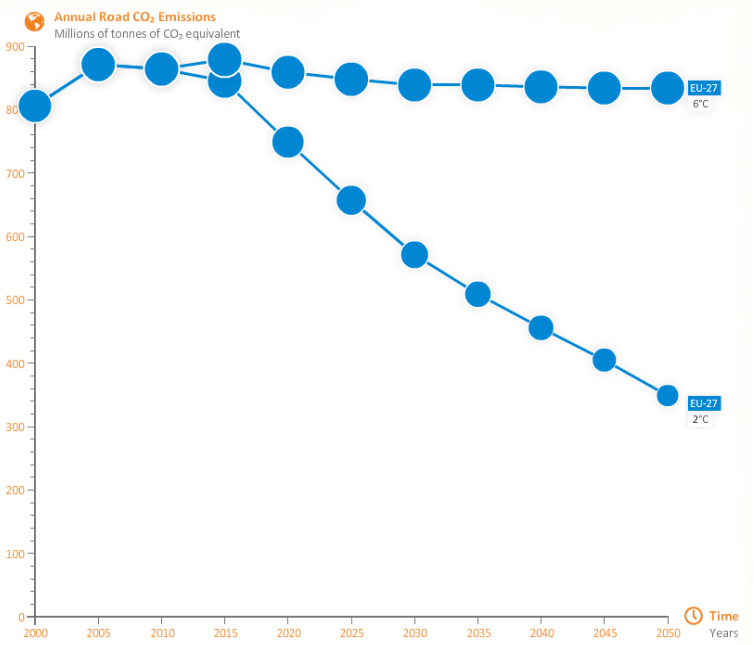


Figure 1.1: Transport CO2 emission predictions: same tendency (above) and the 2°C scenario [1].

It is clear that the transportation sector is on a verge of change. There are

many contending technologies that aim to collectively replace the use of fossil fuels. Hydrogen, electricity, electrofuels - all are developing quickly. However, it is the assumption of many that an intermediary fuel is necessary in order not to collapse the widespread and well developed infrastructure. Biofuels are an option for fulfilling this exact demand. A combination of sustainable cultivation and well planed integration might make biomass, the precursor of several types of fuels, a major player in future energetics. Its global abundance, short life cycles promise a more sustainable and carbon dioxide free world.

However, biomass has received its fair share of criticism over the years. 1st generation, crop based biofuels such as biodiesel and bioethanol are facing more and more controversy due to the unavoidable need for land usage change and competition with land grown food crops. 2nd generation feedstocks are always welcome, especially as it usually comes at a lower price. However, problems with low initial quality and recalcitrance are slowing things down for biomass. Not to mention that advanced, 3rd generation feedstocks are still at their infancy based on algae and other less competitive energy crops. Efficient utilisation of 2nd and 3rd generation feedstocks is vital for the future success of sustainable bio-market.

The study aims to investigate how one largely available biomass, marine macroalgae, could enter this world-saving challenge. As table 1.1 simply shows, the competition for growing marine biomass is virtually non existent, especially when comparing it to land based feedstocks. The lack of competing crops is vital for biomass farming as the biological mechanism of carbon sequestration is one that requires huge growth areas and exposure solar radiation. Much research is necessary, though, to bring a new biomass up to speed and right into the world of competitive energetics. Technology needs to be developed for everything from macroalgae growing to harvesting and even on land or offshore converting and refining. However the fact that we must look into possibilities that offer a chance of sustainable production. It is a logical step to look into marine biomass resources for bio-energy and bio-product production.

Table 1.1: Both terrestrial and marine biomass types currently utilised for energy production

Terrestrial	vs.	Marine
Algae		Algae
Crops		
Lignocelluloses		
Waste streams		

1.2 What is marine macroalgae?

Macroalgae, also known as seaweed, are large multicellular algae species. All seaweed can be classified into three groups: brown (Phaeophyta), green (Chlorophyta) and red algae (Rhodophyta). These benthic (i.e. seabed dwelling) organisms grow near coastal areas, typically not lower than 50 meters below sea level. Here, their environment is virtually invariant in terms of water temperature and salinity [2]. However, seasonal solar irradiance variations have significant effects on the growth rates and chemical composition of the macroalgae.

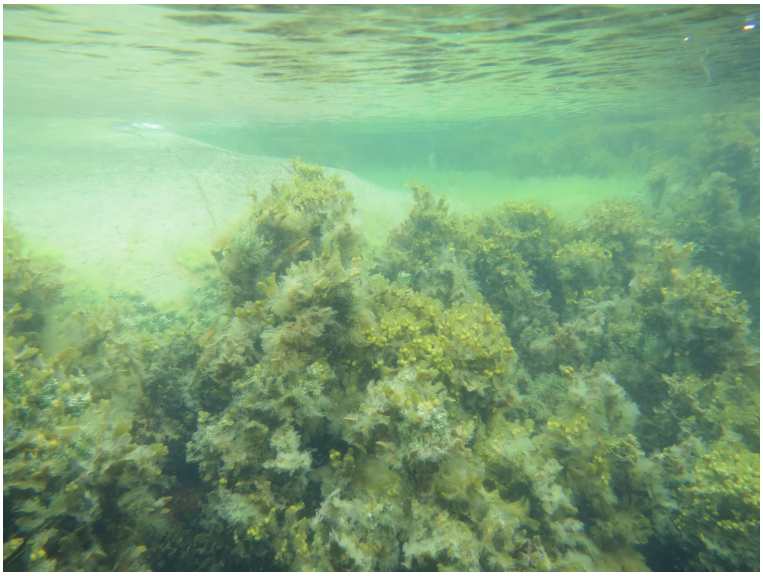


Figure 1.2: Wild F. vesiculosus growing along the Swedish coastline. Picture source: `http://balticseaweed.com/2014/02/07/the-underwater-map-shows-the-way/`

Similarly to terrestrial biomass, macroalgae utilise light as their energy source. Seawater, on the other hand, is the growth medium, where the organisms capture dissolved CO_2 and nutrients throughout their life cycle. The potential value of marine algal biomass is increased due to its CO_2 and fertilizer bioremediation capacity [3]. One more similarity to abundant terrestrial plants is that seaweeds perform a number of ecosystem services such as nursing wildlife, cycling nutrients and reducing coastal erosion.

Growth and harvesting of macroalgae

Studies show that wild brown algae (e.g. Saccharina, Undaria, Sargassum, and Ecklonia) exhibit growth rates of 3.3-11.3 *kg dry weight / m^2 per year* [2]. Such high biomass productivity sums up to a harvest potential of 2-10 *dry tons / ha per year* in Denmark alone [4].

Despite the fact that seaweed harvesting/cultivation is yet to be widely practised in Europe, technology transfer from the experienced Asian farming nations start to bear fruit in know-how via macroalgae growing tests and trials across Europe. Off the coast of Scotland, Saccharina latissima (the sugar kelp) has already been harvested at 15 *dry tonnes / ha per year*. Already at this stage, the prevailing conclusion is that careful species and growing site configuration leads to increased areal productivity [5].

Despite similar temperature requirements (i.e. 10-15 °C), brown macroagae differ from their green and red counterparts in terms of solar irradiance needs. 30 μmol/m^2/s is sufficient for normal growth compared to 88.5 μmol / m^2 / s for green and 25-75 μmol / m^2 / s for red marcroalgae [5]. This shows promise that *Phaeophyceae* might be most suitable for multi annual harvesting in the Northern hemisphere. Here, harvesting several times throughout the year is seen as a viable option for avoiding the otherwise more complicated and costly issue of fresh biomass storage and stockpiling. Furthermore, when comparing relative plant growth rates, brown macroalgae come on top once again with 7-16 %/day, compared to 8.04 %/day and 1-3.5 %/day as exhibited by green and red algae, respectively [5].

All in all, brown macroalgae are shown to have a maximum energy yield (over 45 %) over a growing period. A value significantly greater than the yields of most terrestrial biomass (e.g. energy crops: 30–35 % lignocelluloses: 20–25 %). All thanks to their high productivity rates. [5]

Chemical composition of macroalgae

Chemical analyses carried out globally show that macroalgae samples differ significantly in composition. Variations are apparent across habitats, seasons and species. Seasonal differences in *Phaeophyceae* are expressed via storage carbohydrate (i.e. laminaran and mannitol) accumulation and subsequent release throughout the lighter and darker seasons, respectively [2]. High variation is also noticed in terms of ash content [6, 4]. In early spring, brown macroalgae are usually high in alginate, ash and protein but analyses show low carbohydrate concentrations [7]. As soon as the algae start to receive more light, their photosynthetic activity surges, leading to an increased sugar production. Correspondingly, the relative amounts of ash, alginate and proteins plummet [7].

Table 1.2 is given as a quantification of the previously described compositional variations. The data is based on literature figures describing Saccharina spp. As the results indicate, *Saccharina spp.* are chemically dominated by inorganics and polysaccharides. Removal of nitrogen containing proteins and the sulphated fucoidan is preferred as far as high quality HTL biocrude production is concerned. Having HTL feedstock prepared in such a way (i.e. with heteroatoms coincidentally selectively removed) seems more reasonable than reaction shifting towards a

pure hydrocarbon product in spite of the initial biomass composition.

1.2.1 Macroalgae products and current utilisation

Despite their abundance and previously discussed high productivity, macroalgae are an under-utilized biomass resource. Statistics illustrate that just around 1 % of the total available macroalgae is currently utilized by humans [10]. Out of this biomass, brown macroalgae are the most utilised - the first industrially cultivated algae worldwide [10]. Most significantly exploited uses include a share in the vast Asian food market and phycocolloid extraction. These carbohydrate polymers are used for their water absorptive and gelling properties. Most notably, alginates are extracted from brown algae. Meanwhile carrageenan and agar are green and red seaweed extractives, respectively [2].

Besides phycocolloids, brown algae contain fucoidan, a sulphated polysaccharide, that is highly viscous once extracted. Macroalgae are believed to make use of fucoidan in order to avoid drying out when exposed to air. Despite its uses in many industries (e.g. in dietary supplementation, nutraceuticals and cosmetics), research must be carried out in order to tame the fucan's aging and acid/base induced instabilities, and truly commercialise the product [11].

Throughout recent years, the plight to utilise sustainable plant-based protein sources for human consumption has also taken off. Macroalgae are among the potential new biomass resources for effective high quality protein extraction [12].

Marine algae as a biofuel feedstock

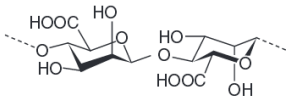
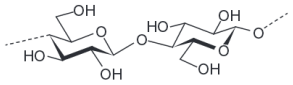
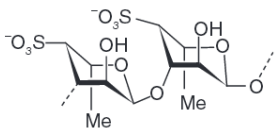
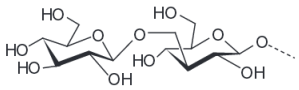
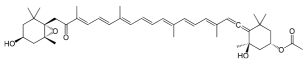
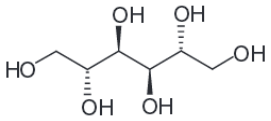
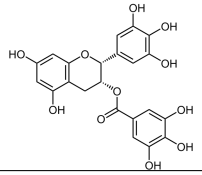
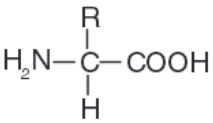
Researchers worldwide have carried out numerous studies on various energy production technologies, using macroalgae as the input feedstock. As Figure 1.3 shows, these can be grouped into two major types: biochemical and thermochemical conversion. Direct combustion is excluded as an option due to the raw macroalgae containing high amounts of low melting temperature alkali metals. Otherwise, the pathway depends on the demanded output fuel. With the exception of solid fuel, the feedstock has shown potential for multiphase fuel production.

Starting from left to right:

- Anaerobic digestion: besides that, studies have already been carried out on post alginate extraction anaerobic digestion [13]. The extraction residues are shown to typically be recalcitrant to microbial fermentation [5].

- Bioethanol production: despite the fact that mannitol and laminarin polysaccharides are relatively inexpensive to extract, macroalgae conversion to bioethanol is a subject still under research. Mainly due to the fact that conventional sugar fermenting organisms are not capable of digesting alginate compo-

Table 1.2: Saccharina spp. composition based on literature for referential purposes

Compound	**[wt. %, dry basis]**	**Structure**	**Source**
Alginate	23 to 34.5		[5]
Ash	Up to 50	Alkali ions, metals	[7]
Cellulose	10 to 15		[8]
Fucoidan	5 to 8.8		[5]
Laminaran	1 to 20		[9]
Lipids	Up to 5		[5]
Mannitol	10 to 25		[2]
Polyphenols	Up to 14		[2]
Protein	3 to 23		[2] ,[5]

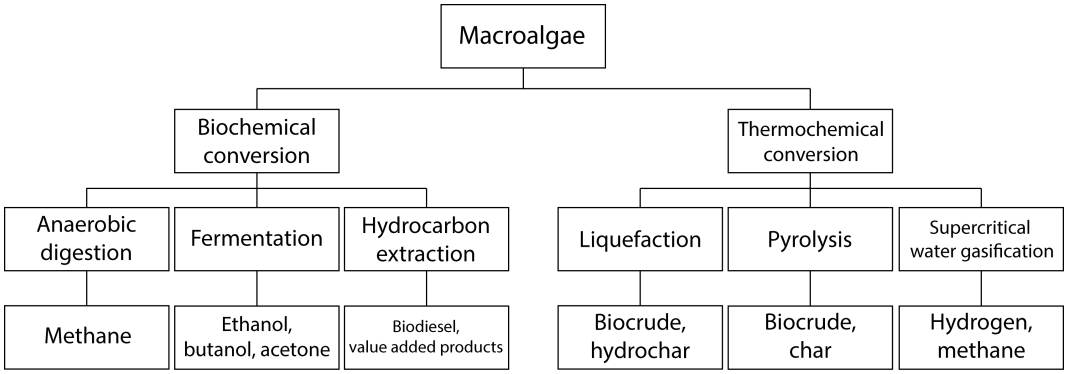


Figure 1.3: Fuel production pathways using macroalgae as feedstock [10].

nents, hence a search for economically viable enzymes and correspondingly superior processing conditions is ongoing [5].

- Due to low lipid content (less than 5%) exhibited by brown and red macrolgae, biodiesel production is an unlikely, yet technically plausible, conversion path for this type of marine biomass [10].

- HTL: When compared to conventional liquefaction feedstock (i.e. lignocelluloses), macroalgae feature a distinct advantage of not having recalcitrant lignin in their structure. This potentially should lead to lower costs in the form of less severe pretreatment as depolymerisation of lignin will not be a necessary processing step [14]. However, according to Biller et al., biocrude productivity via HTL follows a path of lipids > protein > carbohydrates, which leads to lower yields when compared to high lipid/protein feedstocks (e.g. microalgae) [15].

- Pyrolysis: similarly to HTL, macroalgae bring the advantage of lignin absence. However, an expensive drying step will be necessary to render the wet biomass suitable for biocrude production via pyrolysis.

- Supercritical water gasification: Besides HTL, catalytic supercritical water gasification (SCWG) is another technology capable of converting wet biomass into fuel. Macroalgae gasification was shown to be feasible for producing a methane-rich biogas. However, initial studies show that salt separation is necessary in order to remove sulphur prior to gasification and minimise catalyst poisoning, which in turn yields non-converted carbon in the aqueous phase [3].

Environmental concerns

Depending on seaweed harvesting strategy (i.e. from wild beds or cultured farm sites), energetic utilisation would compete directly with macroalgae usage as a food and phycocolloid source. Similarly to terrestrial biomass harvesting, fears are expressed that seaweed overexploitation, even at the intensity it is carried out currently, may result in irreversible damage to the local ecosystems in terms of multi-species habitat destruction [7].

Besides over-harvesting, introducing new macroalgae species into ecosystems might lead to biotic homogenisation (ecosystem assimilation via species' invasion and consequential extinction of other species) worldwide. Not to mention other anthropogenic disturbances such introductions may invoke (e.g. climate change enhancement, coastal pollution, etc.). Macroalgae should be considered as a highly potent non-indigenous marine species (NIMS). Their macroscopic dimensions and quick growth rates can alter the function and structure of a given ecosystem by monopolizing growth area, developing into ecosystem alternators, changing pre-established food chains. Finally, there is a risk of spreading beyond their designed growth site via biological dispersal [16].

1.3 Biofuel production via hydrothermal liquefaction

When compared to anaerobic digestion, hydrothermal liquefaction (HTL), commonly performed at reaction times in the order of several to tens of minutes, is capable of fast biofuel production [10].

Despite high levels of inorganics, alkali metals present in macroalgae are hypothesized to have a catalytic effect on the conversion. HTL of biomass is commonly carried out in alkaline media to reduce formation of solids and promote repolymerisation into liquid compounds. Partially confirmed by Anastasakis et al., where the researchers reached highest biocrude yields without using an external catalyst [17]

When discussing the by-products of HTL processing, effective utilisation methods will always be favoured instead of disposal. The solid residues (often referred to as char or hydrochar) were shown to exhibit potential in the field of water treatment. For example, the char can be magnetically activated and used as an adsorbent to enhance and make full use of its high surface area and porosity. Hence secondary thermochemical processing (i.e. pyrolysis) of the dry by-product can be utilised to produce pollutant removal capable materials [10]. The aqueous stream is studied as a microalgae growth medium or feedstock for supercritical water gasification or aqueous phase ketonization. The produced CO_2 can potentially be utilised for enhanced algae growth or in electrofuel producing concepts. Whereas the trace amounts of H_2 could alleviate the otherwise cost intensive biocrude up-

grading process.

Previous studies show that HTL biocrude often exhibits a high energy density equivalent to at least 70 % of that of fossil crude [18]. In case of macroalgae as feedstock, the lower energy content is a result of heteroatoms present in the biocrude. Nitrogen and sulphur originate from the proteins and sulphated carbohydrates, respectively, whereas oxygen is in all major polysaccharides. The higher nitrogen and sulphur content in algal biomass is shown to directly result in *more contaminated* biocrudes compared to lignocellulose derived alternatives [23].

Evidence of physical degradation of stainless steel reactors was already shown in previous work with micro scale supercritical HTL. The author studied the liquefaction of spent mushroom compost - an agricultural waste product. A more severe extent of degradation is expected to take place when converting halide containing macroalgae due to enhanced corrosion [18].

1.4 Novelty and study objectives

Even though macroalgae have been used as a feedstock for HTL in many studies throughout the recent years [18, 19, 20], according to the author, liquefaction of post alginate and fucoidan extraction residues has yet to be performed. However, such feedstock was already studied for energetic utilisation, using other conversion technologies such as anaerobic digestion [13], pyrolysis [21] and hydrothermal carbonisation [22].

The fact that HTL is capable of processing non-algae derived low value wet material, for example sewage sludge and manure, brings merit to a positive outcome of this study [23]. Here, the focus is set on utilising a residual material stream that is generated by macroalgae factories, which could potentially become modern bio-refineries producing both high value products and HTL biocrude at high capacities.

The outline shown in figure 1.4 summarises the study plan. The aim is to show alginate and fucoidan extraction residues can indeed be converted to high quality biocrude for further upgrading and integration in the present liquid fuel infrastructure. Furthermore, the effects of raw macroalgae demineralisation are investigated as despite the extraction of high value organics, the post-processed algae are hypothesized to still contain high amounts of ash. Focus is set testing whether extensive neutralisation of leaching residues is necessary and if shorter reaction times could benefit HTL of low quality algal feedstock.

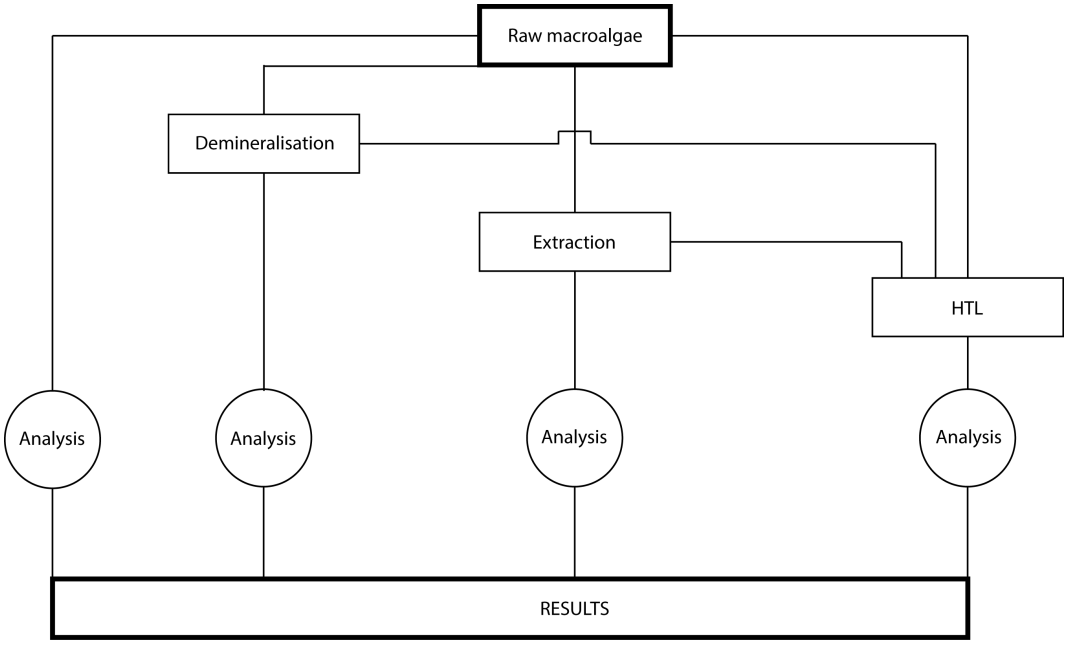


Figure 1.4: Experimental outline

2 Macroalgae samples

2.1 Acquired material

Multi seasonal samples of two brown macroalgae genera, *Fucus vesiculosus* and *Saccharina latissima*, were acquired for the experimental part of the study. Specifically these two algae were chosen due to their wide establishment in the geographical area of immediate interest (i.e. the Baltic sea). In some parts of western Baltic sea, *F. vesiculosus* is in fact the only large, canopy-forming brown macroalgae. They grow along rocky coasts, in low depths [24]. Similarly, *S. latissima* are also abundant in the Baltic region.

2.1.1 Macroalgae composition

Macroalgae sample composition is represented via proximate, ultimate analysis, protein content estimation, moisture content determination and higher heating value measurements.

Proximate and ultimate analyses:

Thermogravimetric analysis (TGA) was performed in an inert atmosphere (purged with nitrogen) using a PerkinElmer STA6000 TG/DSC analyser. Samples of 4-7 mg were heated to 950 °C at a temperature ramp rate of 10 °C / min. The nitrogen flow rate was set to 20 ml/min throughout the entire procedure.

In figure 2.1, moisture content, volatile matter and fixed carbon are defined as the mass loss between ambient and 120 °C, 120 °C and 575 °C and the difference between the mass at 575 °C and the previously determined ash content, respectively.

CHNS analysis was carried out on a Vario Macro Cube simultaneous CHNS analyser from Elementar. Here, samples of 70-80 mg were analysed in triplicates. Table 2.1 summarises the results of both proximate and ultimate analysis.

Here, seasonal composition variability among *F. vesiculosus* and *S. latissima* samples is confirmed not only in terms of ash content but also volatile matter. Macroalgae harvested in the warm season (i.e. the summer FSR and autumn SAR)

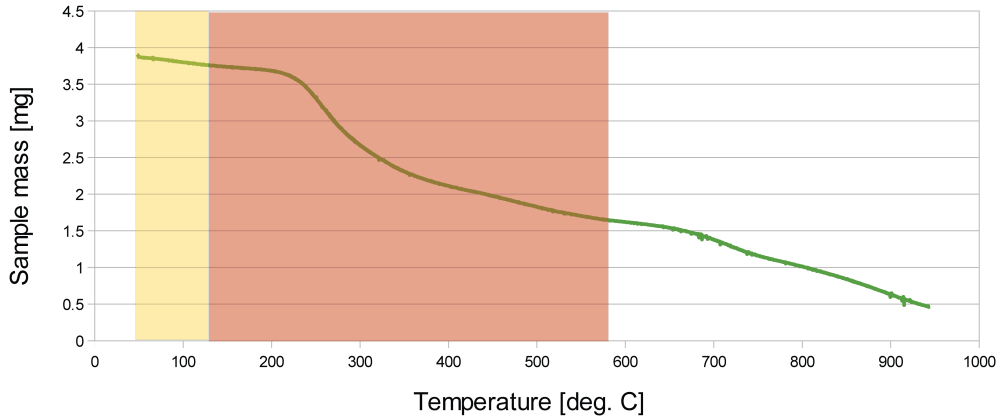


Figure 2.1: FFN mass loss curve during TGA, moisture and volatile matter determination zones are highlighted.

exhibit lower ash and higher volatile contents. In terms of elemental differences, the biggest seasonal deviation occurs in the form of nitrogen which is more abundant in cold season harvests. However, these differences in nitrogen concentration are hypothesized to be brought on by the well known consumption of energy storing carbohydrates throughout during winter. A fact that is confirmed by slight increases in elemental carbon and hydrogen.

Cross strain comparison reveals that *F. vesiculosus* ash content is nearly season independent, although twice as high as that of the low yielding SAR. However, if proven to be compatible with effective HTL, the ash invariability show promise for multi-seasonal harvesting.

Interestingly, rinsing the fresh macroalgae with deionised water led to an ash reduction of $\sim$5 wt. % in FFN. Furthermore, elemental analysis suggests that some fucoidan could be washed out as the sulphur content is slightly reduced.

A nitrogen-to-protein conversion factor of 5 was used in order to estimate the amount of proteins present in the acquired macroalgae samples [25]. The values ranged from 2.8 wt. % and 4.85 wt. % in warm season harvests to 15.7 wt. % and 11.65 wt. % in cold season samples in rinsed *F. vesiculosus* and *S. latissima*, respectively.

Moisture content

In house moisture analysis (KERN MLS, sample sizes 0.66 $\pm$0.06g) showed that the freshly harvested F. vesiculosus algae contain 77.42 $\pm$0.46 wt. % moisture. The results are based on a multi-sample analysis where three data points closest to the statistical average are used. However, the observed extreme points were at 76.95

Table 2.1: Proximate and ultimate analyses of the five different macroalgae

	FFR	FFN	FSR	SAR	SSR
Proximate analysis [wt. %, dry basis]					
Volatiles	54.16	57.5	61.1	70.93	56.76
Fixed carbon[a]	20.23	11.73	11.92	15.85	9
Ash	22.42	27.39	21.83	10.89	32.65
Ultimate analysis [wt. %, dry basis]					
C	36.90	36.74	38.13	38.86	34.26
H	6.06	5.71	6.42	6.82	5.49
N	3.14	3.26	0.56	0.97	2.33
S	1.12	1.66	1.44	0.26	0.56
O[a]	30.36	25.24	31.62	42.20	24.71
[a] - calculated by difference					

wt. % and 80.74 wt. %.

Knowing that effective HTL of high-ash macroalgae can be carried out at total solid loadings of ∼20 wt. % [20], an as received moisture content of 75-80 wt. % could potentially lead to direct conversion of fresh macroalgae. Although more research is necessary, especially in order to evaluate whether wet particle reduction would be a necessary pretreatment step.

Determining calorific values:

Higher heating values (HHVs) of the dried and milled macroalgae samples were measured in triplicates using an IKA C2000 basic bomb calorimeter. The samples were combusted in a steel vessel in a pressurised oxygen environment. The temperature rise of a known volume of water determined the heat of combustion.

Table 2.2: HHV measurements of the five macroalgae samples

Algae	**Harvest**	**Water rinsed?**	**Report reference**	**HHV [MJ/kg]**
S.latissima	Spring	Rinsed	SSR	12.79 ± 0.03
F.vesiculosus	Winter	-	FFN	14.34 ± 0.01
F.vesiculosus	Summer	Rinsed	FSR	14.79 ± 0.17
F.vesiculosus	Winter	Rinsed	FFR	14.95 ± 0.01
S.latissima	Autumn	Rinsed	SAR	15.51 ± 0.25

3 Demineralisation

Despite its advantages, macroalgae tend to contain high amounts of inorganics, as is the case in this study - the chosen sample, FFR contains 22.42 wt. % of ash. High amounts of inorganics in the initial feedstock raise the risk of encountering poor quality (i.e. containing low melting temperature metals) and low biocrude yields. Researchers have already attempted macroalgae de-ashing. It is shown that acidic demineralisation is an effective method [26].

3.1 Experimental setup

Initial screening tests were carried out on *Laminaria digitata* brown macroalgae. Ash removal efficiencies of 5 different leaching agents (deionised water, acetic, citric, hydrochloric and sulphuric acids) were measured. A combination of significant ash removal and relatively water-lean neutralisation procedure led to the decision that citric acid performed the best.

Following up on the results from the above study, a weak citric acid ($C_6H_8O_7$) solution was chosen as the first leaching agent. Naturally, demineralisation with deionised water was also carried out in order to establish baseline results. Finally, with a view to investigate an alternative means to utilise one of the by-product streams of continuous HTL, the aqueous phase was used as the third leaching agent. Its acidic nature gives merit to investigate the de-ashing potential and thus valorise the otherwise challenging by-product. The raw aqueous product was a sample previously collected at the local semi-continuous HTL plant with a view to represent a real-life synergistic opportunity. The sample was slightly acidic with a pH level below 5.5 [27].

Figure 3.1 depicts all process steps included in the acid leaching treatment. Three samples were processed in each solution. The extent of secondary rinsing (i.e. 1, 4, 5 and 8 washing steps) was varied.

The raw macroalgae (FFR for this set of experiments) was pre-rinsed with cold water in order to remove any unbound inorganics (Step I in figure 3.1). Figure 3.2 shows that besides minuscule sand particles, various crustaceans are still present on the harvested biomass. This shall be taken into account when dealing with large

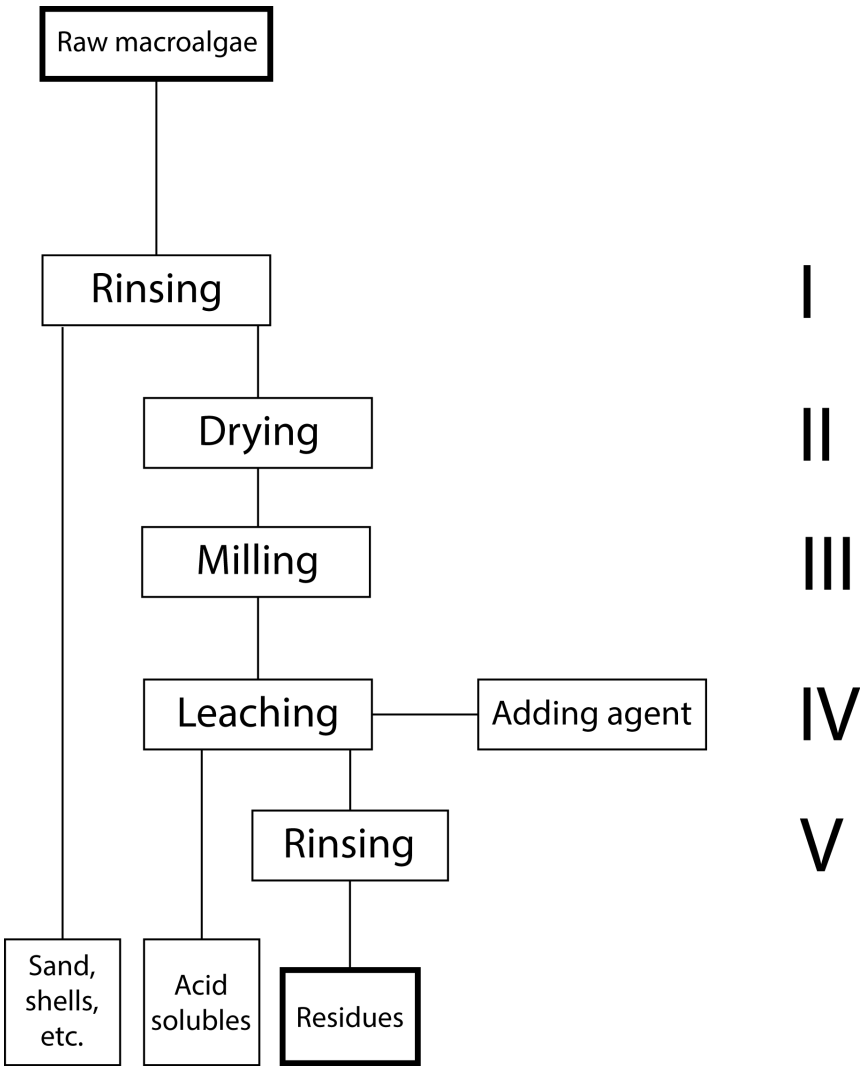


Figure 3.1: Acid demineralisation scheme

scale continuous operation in order to avoid processing inorganics unnecessarily and reducing the risk of fouling and reactor/filter plugging. Not to mention the direct effect macroalgae harvesting has on the local fauna and, possibly, even entire ecosystems.

Figure 3.2: Life on fresh F. vesiculosus

3.1.1 Water leaching

In order to set up a baseline, water was used as a leaching agent. This was done to identify to what extent water plays a role in the extraction of macroalgae inorganics. It is vital to compare a pure water treatment to the other dilute acidic solutions.

3.1.2 Citric acid leaching

After the initial rinsing, the biomass is dried and milled (FOSS *Cyclotec*^{TM} 1093, particle size: $\leq$200 μm, steps II and III in the schematics). In the case of citric acid leaching, the now dry and powdered macroalgae are mixed in a 1 wt. % $C_6H_8O_7$ solution (12.5 g acid solution / g macroalgae). The leaching process takes place overnight (18 hours of continuous stirring at 1000 rpm and at room temperature). As mentioned before, the procedure was adapted and modified from the performed screening tests on *L. digitata*. However, instead of a leaching time of 4 hours, in this study the samples were leached overnight (a corresponding duration of 19 hours) this was done in order to confirm that despite the weak

acidity of the leaching agent, a longer retention time might compensate and increase demineralisation efficiency. This was confirmed by an ash removal of 47.15 wt. % compared to the initial 27.21 %. After leaching, the mixture is centrifuged (for 5 minutes at 4000 rpm) in order to remove the leachate. Then, the neutralization/rinsing procedure takes place (step V). Neutralization is a part of the study in order to process a non-acidic feedstock. It is done as alkaline processing media were found to suppress char formation from carbohydrates [27]. De-ionised water is added to the residues (12.5 *g water / g initial macroalgae*) and stirred manually. Subsequent centrifugation is utilised for separation. Different numbers of the coupled rinsing-separating steps were enforced in order to set up for analysis of HTL of post-demineralisation macroalgae. The focus here is to determine whether a great neutralization extent is truly necessary for efficient HTL of acid leached macroalgae. The experimental design included drying (at least for 18 hours at 105 °C) the residues after 1, 4 and 8 rinsing repetitions (i.e. simulated water consumption ranging from 12.5 to 100 *g / g of dry initial macroalgae*). Ultimately aiming to dismiss the need for water-intensive post-treatment. The pH levels were measured initially, after the leaching period and after each rinsing step (WTW pH 3210 meter, accuracy of $\pm$0.2 pH points).

3.1.3 *HTL water* leaching

As pointed out in the beginning of the section, the aqueous HTL effluent (referred to as "HTL water" from now on) was used as an alternative leaching agent. This is done to simulate a scenario where an internal mass stream is preferentially utilised instead of an externally supplied material. Here, as in the case of citric acid treatment, figure 3.1 can also be used as a processing reference.

However, several differences between the two methods must be clarified. Only $\approx$ 50 ml of HTL water was available for the needs of this project. In order to accommodate for the required leaching medium, the available 50 ml were diluted with de-ionised water to reach a total volume of 300 ml. This being said, it is worthwhile to note that the pH of the solution did not change significantly, stabilising at pH 5.6 prior to mixing.

The same acid solution-to-biomass ratio of 12.5 and the leaching conditions were kept.

3.2 Results and discussion

This section will highlight the discussions that arose throughout the study and summarise the findings. Observations related to residue pH, the effectiveness of the three leaching methods and how they relate to subsequent HTL are presented.

3.2.1 Leaching residue pH levels

As figure 3.3 shows, all demineralisation runs (i.e. water, citric acid and *HTL water* washing) would require post processing neutralisation, should that prove to be necessary for effective macroalgae conversion.

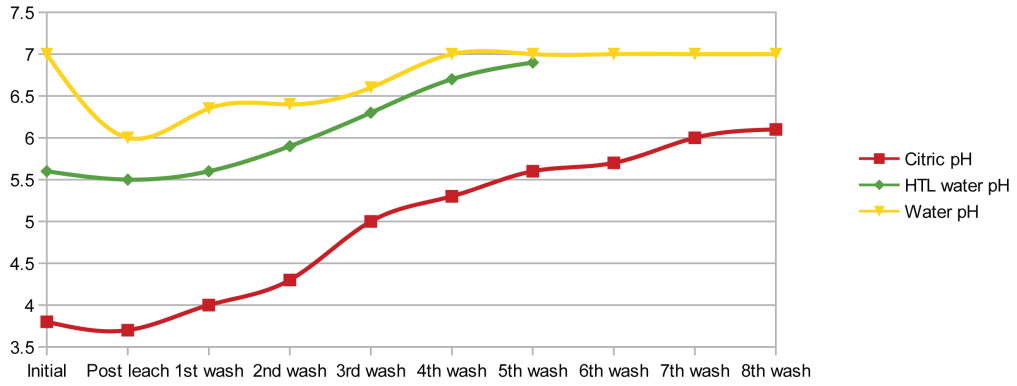


Figure 3.3: Change in pH throughout the leaching procedure. Here, *initial* describes the feedstock and demineralisation agent mixture, whereas *post leach* - pH measured right after the leaching procedure

Naturally, after the water leaching step, macroalgae residues reached a pH level of 6 - same as measured on the fresh *F. vesiculosus*. Presumably caused by the inorganics present in the marine macroalgae. However, it did take 4 washing steps (i.e. 50 *g water / g initial macroalgae*) to reach a steady pH 7 reading.

In the case of *HTL water* leaching, 5 washing steps brought the pH up to 6.9, compared to the initial pH of 5.6. This indicates that if the leaching agent is shown to perform well in terms of ash reduction, there would be no need for strong, dedicated acid solutions. However, further studies are necessary in order to show the full neutralisation extent required post non-diluted *HTL water* demineralisation.

Finally, the addition of 1% citric acid lead to pH 3.8, the lowest initial pH level throughout the study. Furthermore, a mere pH 6.1 was reached after 8 washing steps (i.e. 100 *g water / g initial macroalgae*). This indicates an alarmingly high water consumption related to washing out the last acid residues or, alternatively, a need for an external alkaline agent. The latter could only be justified by high ash reduction and subsequent HTL performance, or if the addition of an alkaline catalyst would be synergistically beneficial.

However, yet another aspect to take into account is the fact that, as shown in figure 3.4, each washing step comes at a cost. Organic matter is also lost throughout the neutralisation process. Although more advanced techniques, such as reactive solvent citric acid extraction, might be able to reduce the water demand [28]. In this

study, water washing was investigated as the cheap and widely available method. In the end, it is crucial to investigate whether neutralisation is at all necessary and if so, to what extent.

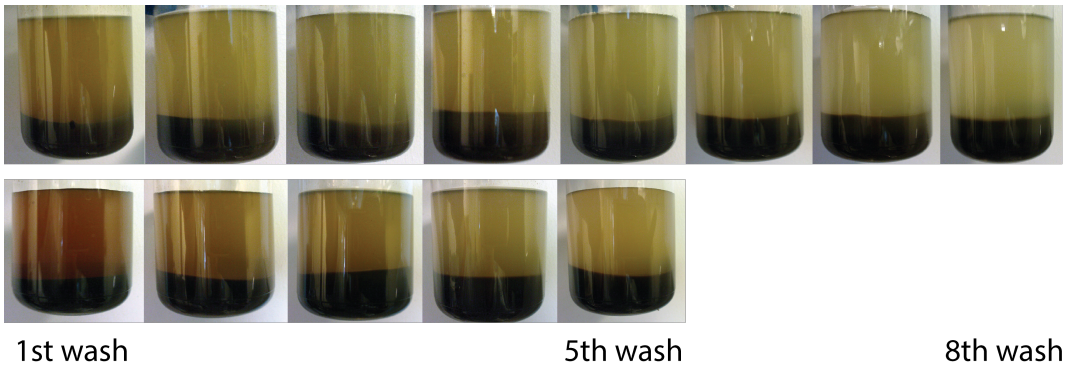


Figure 3.4: Filtrate colour change throughout neutralisation steps of citric acid (above) and *HTL water* (below) leached FFR. Pictures taken post washing steps 1 through 8 (or 5) from left to right.

3.2.2 Water leaching

The first and most significant finding is that dry feedstock grinding combined with water leaching does indeed lead to a reduced ash content. As shown in table 3.1, a reduction of over 30 % was reached, followed by further decreases in inorganics throughout subsequent "neutralisation" steps. The final ash content, measured after first reaching pH 7 (i.e. after washing step 4), of 13.71 wt. % resulted in an overall ash reduction of 38.85 %. Besides that, the final baseline measurement (i.e. ash content after 8 H_2O washes) shows that there is no statistically significant change in inorganics post neutralisation.

3.2.3 *HTL water* leaching

In terms of ash reduction, *HTL water* performed worse than deionised water, resulting in 16.17 and 14.89 wt. % ash prior to and post neutralisation, respectively. The 2.51 wt. % of ash present in the leachate are thought to be the reason for why the agent's acidic effect was impaired. The ash is hypothesized to consist mainly, if not entirely, of the used catalyst, potassium carbonate which in turn will only add to the suspected high concentration of potassium salts in the marine feedstock. Interestingly, neutralisation did not decrease the ash content notably, as was the case in water leaching as well. Here a further reduction of just 1.28 wt. % was recorded, compared to the 1.9 wt. % drop in the case of pure water treatment. Judging solely based on ash reduction capacity, diluted *HTL water* leaching is slightly inferior with a maximal demineralisation capacity of 33.59 %.

Table 3.1: Comparison of how the three leaching agents and subsequent neutralisation steps influence the final ash content of the FFR residue. Untreated FFR was determined to contain 22.42 wt. % ash.

Leaching	**No. of H_2O washes**	**Ash [wt. %]**
Water	1	15.28 ±0.20
Water	4	13.71 ±0.33
Water	8	13.38 ±0.36
HTL water	1	16.17 ±0.91
HTL water	4	15.06 ±0.96
HTL water	5	14.89 ±0.59
Citric	1	14.53 ±0.42
Citric	4	13.36 ±1.36
Citric	8	11.85 ±0.37

3.2.4 Citric acid leaching

Finally, citric acid treatment showed highest ash removal performance with *F. vesiculosus*. The initially reached 14.53 wt. % were further reduced down to 11.85 wt. % after 8 washing steps, resulting in ash reductions of 35.19 % and 47.15 %, respectively. It is understandable that such results are brought on by the combined effects of both acid and water leaching. In terms of ash removal, 1 % citric acid leaching is comparable to but slightly superior to extensive water leaching.

3.2.5 Discussion

In order to properly compare the three investigated methods and discuss their performance, another dimension of comparing the leaching residues was included - HHV determination. When studying figure 3.5, it is clear that all leaching agents lead to a higher quality energetic feedstock. And although the differences are minor, the claim that citric acid treatment performs best, is confirmed with a highest HHV of 16.16 MJ/kg compared to the initial 14.95 MJ/kg of raw FFR. Based on this data, it would seem that extensive water washing is not beneficial as post neutralisation washes indicate lower HHV. The study explains this behaviour by claiming that in all cases, full demineralisation extents are reached prior to neutralising. Whereas subsequent water washes are more effective at removing organics.

The above can also be argued by elemental analysis of the residues. In the case of citric acid leaching, when comparing residues post 1 and 8 H_2O washes, despite a drop in inorganics of 2.68 wt. % - the fractions of elemental carbon and hydrogen increased just by 1.69 % and 0.19 %, respectively. Therefore, it is clear that

macroalgae lose organics through subsequent water washing. The author would like to point out that changes in nitrogen fraction were negligible (below 0.1 wt. %), whereas no conclusions could be drawn from sulphur content measurements.

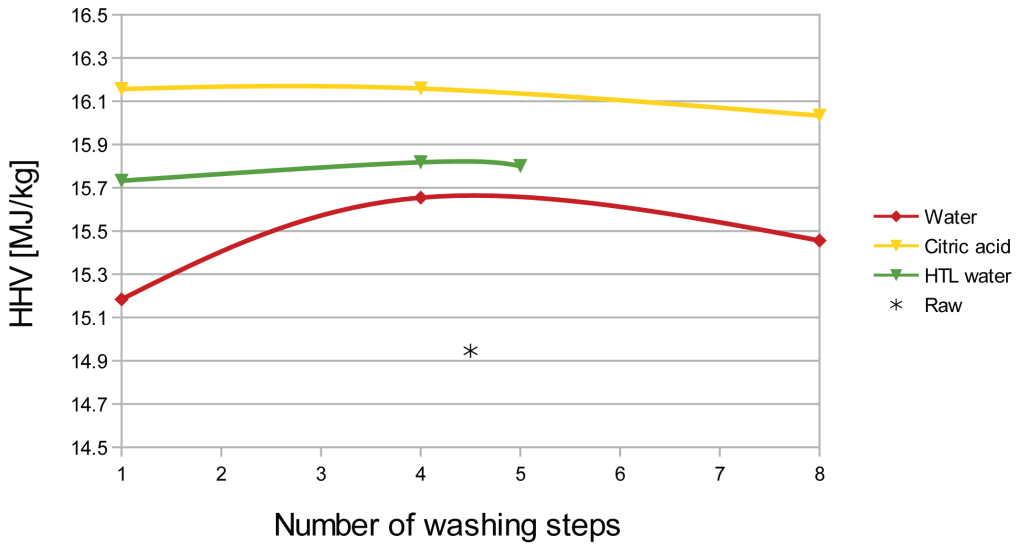


Figure 3.5: HHV development throughout the neutralisation procedure of the three tested demineralisation methods. Higher heating value of untreated FFR is given as a reference.

Finally, comparing the generated amounts of post leaching residues of each treatment (visualised in figure 3.6) may shed even more light on the matter. As it turns out, the three treatments lead to slightly different quantities of residues initially - 61.75 wt. %, 65.15 wt.% and 68.66 wt. % with citric acid, *HTL water* and water leaching, respectively. This correlates well with the determined demineralisation effectiveness of the agents. Simply put, the more inorganics are removed, the less residue remains. Interestingly, no matter what leaching method was performed initially, the washing steps rendered the residues nearly identical by weight. This shows that neutralisation and subsequent washing is leaching agent independent in terms of residue generation.

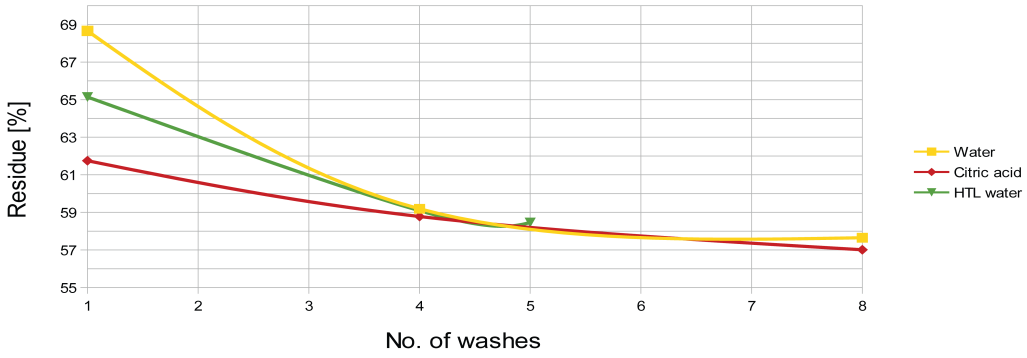


Figure 3.6: Leaching residue development throughout subsequent water washing steps.

4 Added value product extraction

4.1 Experimental setup

Experiments were setup in order to simulate alginate and fucoidan extraction from FFR and SAR macroalgae. These two variations were chosen in order to study the less advantageous scenario, where marine biomass harvests from the cold season are utilised. In the case of fucoidan potential, this was confirmed by the fact that elemental sulphur content is lower in FFR and SAR at 1.12 wt. % and 0.26 wt. %, respectfully, than it is in corresponding summer and spring harvested samples.

4.1.1 Alginate extraction

Figure 4.1 shows the experimental flow of the performed alginate removal procedures (adapted from [29]). Three samples (sample size: 5 g) of each FFR and SAR were processed.

Firstly, the rinsed macroalgae are dried and milled (FOSS *Cyclotec*^{TM} 1093, particle size: $\leq$200 μm). Then, the powder is mixed in a 0.5M H_2SO_4 solution (13.58 g solution / g algae) and stored overnight (minimum 21 h) in a dark cabinet (step III). Then, the mixture was centrifuged (5 min at 4000 rpm) and the liquid solution was removed. An intermediary washing step (13.58 g H_2O / g initial algae) with subsequent centrifugation (4000 rpm, 5 min) was performed to remove any residual H_2SO_4. A 4 % Na_2CO_3 solution (19.95 g Na_2CO_3 solution / g initial algae) was added to the residues. The mixture was stirred magnetically (800 rpm) for 2 hours (all represented by step IV in the schematics). After soaking, the mixture was once again centrifuged to separate the solubles. A washing step (19.95 g water / g initial algae, mix, centrifuge, drain) took place next (the final V step). All of the above process steps were carried out at room temperature.

Finally, the residues were carefully removed from the centrifuge bottles and placed in an induction oven to dry for at least 18 hours at 105°C.

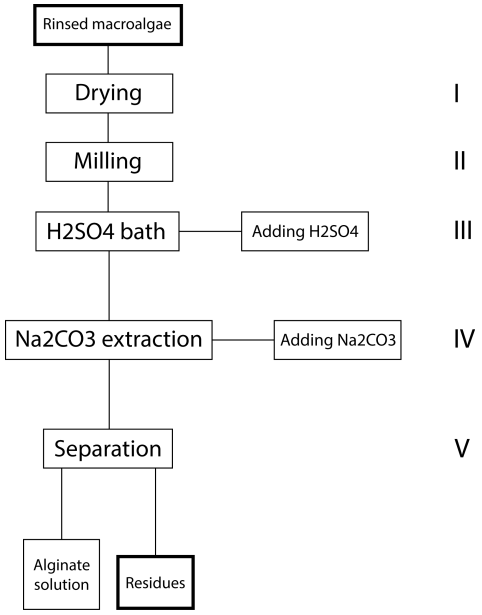


Figure 4.1: Alginate extraction procedure

4.1.2 Fucoidan extraction

Figure 4.2 illustrates the employed simulative fucoidan extraction procedure (adapted from [21]). Three samples (sample size: 5 g) from each FFR and SAR have been analysed in order to confirm the data and check how the method performs with two algae strains.

The water rinsed macroalgae were processed mechanically via drying and milling (shown by processing steps I and II). Subsequently fucoidan was extracted in a $CaCl_2$ solution (step III). The extraction was finished throughout two steps: samples were exposed to two 20 min long magnetic stirring (1000 rpm) sessions in 1 wt. % $CaCl_2$ solutions (16.67 g solution / g algae). After each stirring, the mixtures were centrifuged at 4000 rpm for 5 min in a SIGMA 6-16S centrifuge and the separated liquid was removed. A similar procedure followed the two extraction-separation steps: the residues were mixed with water (16.67 g water / g initial algae) and centrifuged once more in order to remove any remaining calcium chloride (step IV). All steps were carried out at room temperature. Finally, the residues were oven dried at 105°C for a minimum of 18 hours, cooled in a desiccator, weighed and stored in air tight containers until further processing.

4.2 Results and discussion

Outcomes of the two extraction routes are presented in this section. Special focus is set on the amounts of generated residues, their elemental composition and

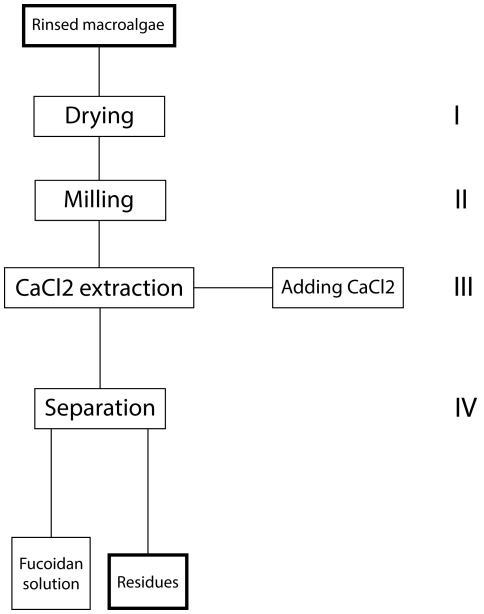


Figure 4.2: Fucoidan extraction procedure

decreases in inorganics that can be classified as extraction losses. Finally, the discussion is extended to HHV development post extraction.

4.2.1 Alginate extraction residues

An experimental summary is presented in table 4.1. The important finding here is that despite the high extent of extraction, shown by dramatic weight reductions in both FFR and SAR, the two macroalgae lead to significantly different amounts of residues. Post extraction residues obtained from FFR added up to 41.88 wt. % of the initial feedstock mass, whereas the procedure proved to perform more severely on SAR, leaving just 11.18 wt. % of insoluble solids behind. This could be explained by the fact that the autumn harvested SAR still have more alginate, whereas the *F. vesiculosus*, harvested in late winter, were consuming their energy stocks throughout the cold season, when solar irradiance is at its lowest.

Table 4.1: Alginate extraction summary

Algae	Sample [g]	H2SO4 [g]	H2O rinse [g]	Na2CO3 [g]	H2O rinse [g]	Residue [wt. %]
FFR	5.03 ±0.05	68.26 ±3.30	68.73 ±0.53	100.25 ±0.26	100.68 ±0.30	41.88 ±0.16
SAR	5.01 ±0.02	68.07 ±0.94	68.33 ±0.15	100.3 ±0.22	100.33 ±0.19	11.18 ±0.42

This is further confirmed by reported measurements of winter *F.vesiculosus* and autumn *S. latissima* - the latter is shown to contain more than double the amount of alginate [30, 8]. However, the possibility that structural differences among the

two macroalgae genera add to such results cannot be ruled out.

4.2.2 Fucoidan extraction residues

The experimental results from the two fucoidan extraction runs are presented in table 4.2. Despite the fact that the experiments were performed with minimal procedural variations, the results exhibit the same trend - as it was in the case of alginate removal, post fucoidan extraction residues from FFR vary significantly from SAR in terms of residual mass. FFR and SAR residues corresponded to 68.17 % and 28.99 % of the initial biomass, respectively. Once again, the autumn harvested *S. latissima*, were affected much more by the chemical extraction process.

Table 4.2: Fucoidan extraction summary

Algae	**Sample [g]**	**1^{st} CaCl2 [g]**	**2^{nd} CaCl2 [g]**	**H2O [g]**	**Residue [%]**
FFR	5.03 ±0.04	84.73 ±1.10	83.82 ±0.46	82.94 ±0.35	68.17 ±0.33
SAR	5.04 ±0.03	83.70 ±0.33	85.38 ±0.63	83.45 ±0.45	28.99 ±0.10

Physical differences in both isolated fucoidan solutions and the produced residues can be clearly seen in figure 4.3. Here, FFR derivatives appear characteristically darker.

Figure 4.3: Extracted fucoidan solution and post-fucoidan extraction residues from FFR (left samples) and SAR (right samples)

4.2.3 Extraction losses

Elemental analysis of the residues was carried out in order to evaluate the effect alginate and fucoidan extraction has on the elemental quantities of heteroatoms, specifically nitrogen and sulphur, present in the biomass. In the case of FFR, elemental nitrogen was decreased by fucoidan extraction (1.84 wt. % compared to the initial 3.14 wt.%) but remained unchanged after alginate extraction. A similar

tendency of higher nitrogen fraction in post alginate residues compared to post fucoidan residues was shown in SAR samples. However, with this biomass, the nitrogen content increased with both treatments: 1.97 wt. % and 4.08 wt. % compared to the initial 0.97 wt. % post fucoidan and alginate, respectively. Sulphur removal via fucoidan extraction gave mixed results as well: a logically decreased fraction of 0.37 wt. % (compared to the initial 1.12 %) in FFR and an insignificantly higher content of 0.43 wt. % (initial 0.26 wt. %) in SAR. The development in elemental sulphur indicates that the fucoidan extraction procedure is not highly effective.

Ash development is yet another characteristic of the residues that was studied. Table 4.3 summarises the measured values. When looking into FFR solely, fucoidan extraction did not influence the final ash content significantly. On the other hand, residues generated by alginate extraction exhibit a significantly higher amount of inorganics. In the case of SAR, both fucoidan and alginate extraction procedures rendered the residues higher in inorganics with ash contents of 16.72 wt. % and 39.86 wt. %, respectively. Once again, alginate pretreatment resulted in a dramatic increase in ash.

Both fucoidan and alginate extractives from FFR were ashed in order to compare the de-ashing performance of the two procedures. Both sets of extractives showed similarly low amounts of dissolved inorganics. This confirmn the extraction methods, especially alginate removal, selectively dissolve organics and virtually no inorganics are lost.

Table 4.3: Ash removal throughout added value product extraction. Ash content of raw FFR: 22.42 wt. %, raw SAR: 10.89 wt. %

Sample	**Extraction**	**Ash [wt. %]**	**Ash colour**
FFR	Fucoidan	20.46 $\pm$1.26	Light
FFR	Alginate	46.09 $\pm$1.12	Dark
FFR Fucoidan solution		1.71 $\pm$0.71	Light
FFR Alginate solution		2.43 $\pm$0.36	Dark
SAR	Fucoidan	16.72 $\pm$0.12	Light
SAR	Alginate	39.86 $\pm$0.72	Dark

As figure 4.4 indicates, the produced ash samples differed in colour, namely light post fucoidan and dark - post alginate extraction. This served as a solid basis for further ash analysis in order to identify how this visual difference corresponds compositionally.

Unsurprisingly, the inorganics present in fucoidan and alginate residues are dominated by calcium and sodium, respectively. The increased concentrations of

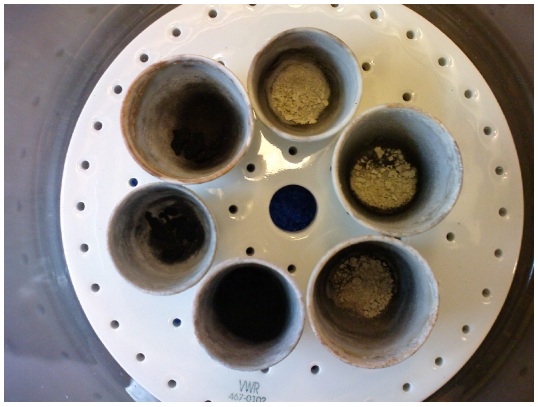


Figure 4.4: Difference in ash colour after fucoidan (light colour ash) and alginate (dark ash) extraction

these elements are caused by the fact that a single post extraction washing step does not remove all traces of $CaCl_2$ and Na_2CO_3. The high amounts of calcium are the reason for the unusually light colouration of fucoidan residues. However, ash composition of raw FFR, also listed in table 4.4, shows a clear alkali and alkali earth metal dominance to begin with. Potassium, sodium, calcium and magnesium are the most abundant inorganics.

Similarly for both procedures, potassium, magnesium, manganese are extracted to a great extent. Meanwhile, concentrations of heavier metals: aluminium, copper, nickel and zinc remain nearly invariant. Notable differences occur with the migration of iron, strontium and phosphorous - in all cases alginate extraction seem to remove more of these elements. The addition of H_2SO_4 is the suspected culprit as the strong acid is commonly used as an effective demineralisation agent [31].

Table 4.4: ICP ash analysis of raw FFR, fucoidan and alginate residues. Metal concentrations above 0.1 mg/g are reported.

	Metal concentration [mg/g]											
Sample	**Al**	**Ca**	**Cu**	**Fe**	**K**	**Mg**	**Mn**	**Na**	**Ni**	**P**	**Sr**	**Zn**
Raw FFR	0.85 ±0.3	42.83 ±0.1	0.13 ±0.01	1.93 ±0.1	104.90 ±2.7	30.65 ±1.9	0.48 ±0.02	49.03 ±3.1	0.73 ±0.1	10.35 ±0.7	4.05 ±0.3	0.19 ±0.01
Post Fucoidan	3.70 ±0.3	253.53 ±5.8	0.21 ±0.01	4.04 ±0.1	13.34 ±1.5	2.96 ±0.1	0.13 ±0.01	6.48 ±0.1	0.97 ±0.01	4.51 ±0.04	3.58 ±0.1	0.26 ±0.01
Post Alginate	5.01 ±0.1	8.33 ±0.4	0.11 ±0.01	0.36 ±0.02	3.20 ±3.2	1.10 ±0.1	- -	95.76 ±8.0	0.58 ±0.1	1.03 ±0.1	0.32 ±0.03	0.05 ±0.01

4.2.4 Discussion

Higher heating values of the produced residues were measured and compared to the initial feedstocks. The results are visualised in figure 4.5. With FFR, both extraction procedures led to higher HHV values, whereas only SAR fucoidan residues showed a decreased HHV.

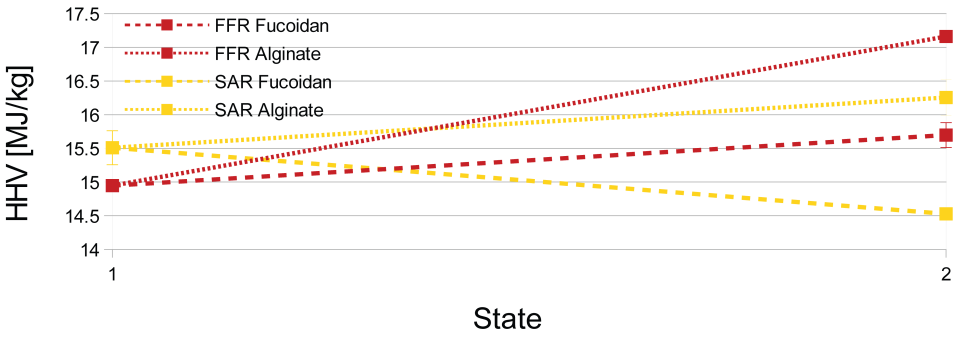


Figure 4.5: Raw (State 1) and post-extraction (State 2) HHVs of FFR and SAR macroalgae

5 Hydrothermal liquefaction

5.1 Experimental setup

6 separate HTL runs were carried out throughout this study. The experiment list can be seen in table 5.1. Here, the main focus is set on HTL of treated macroalgae, namely de-ashed, post fucoidan and alginate extraction. Additionally, effects of post de-ashing neutralisation and a shorter retention time are analysed.

Table 5.1: HTL experiment overview

Reference	Algae	Pretreatment	HTL conditions	Hypothesis/argument
Run 1	FFR	Raw	Normal	Baseline
Run 2		De-ashed		Demineralisation improves yields
Run 3		Fucoidan extraction		Effective HTL with fucoidan residues
Run 4		Alginate extraction		Effective HTL with alginate residues
Run 5		De-ashed and neutral		Post de-ashing neutralisation is not necessary
Run 6		Raw	Short	High quality biocrude at shorter reaction times

All experiments were carried out in stainless steel (grade 316) 12ml micro reactors. Feedstock mass loadings of 20 % ($\pm$2 %) were used, and all reactions were carried out at 400°C ($\pm$5 °C).

Upon feedstock slurry preparation, the specific macroalgae powder was combined with distilled water to form the predefined mixture. A total of 5 g ($\pm$0.1 g) of slurry was then loaded into the reactors. Nitrogen gas was used to simultaneously leak test (80 bar) and purge the reactors to evacuate atmospheric oxygen. Hereafter, two reactors and thermocouples were mechanically coupled to an agitator providing mechanical mixing of the reagents inside the reactors while being processed. The two reactors were then submerged into a preheated, fluidised sand bath and held for 15 minutes of retention time. The retention time is defined as the time that passes between the moment when the reactors have reached the preset temperature of 400 °C ($\pm$5 °C) and the instance of manually submerging the reactors into the cool ($\sim$20 °C) water bath. After quenching in water for a minimum of half an hour, the separation procedure begins.

5.1.1 HTL product separation procedures

As shown in figure 5.1. Firstly, the gaseous products were weighed, sampled and vented via top mounted valves (step I).

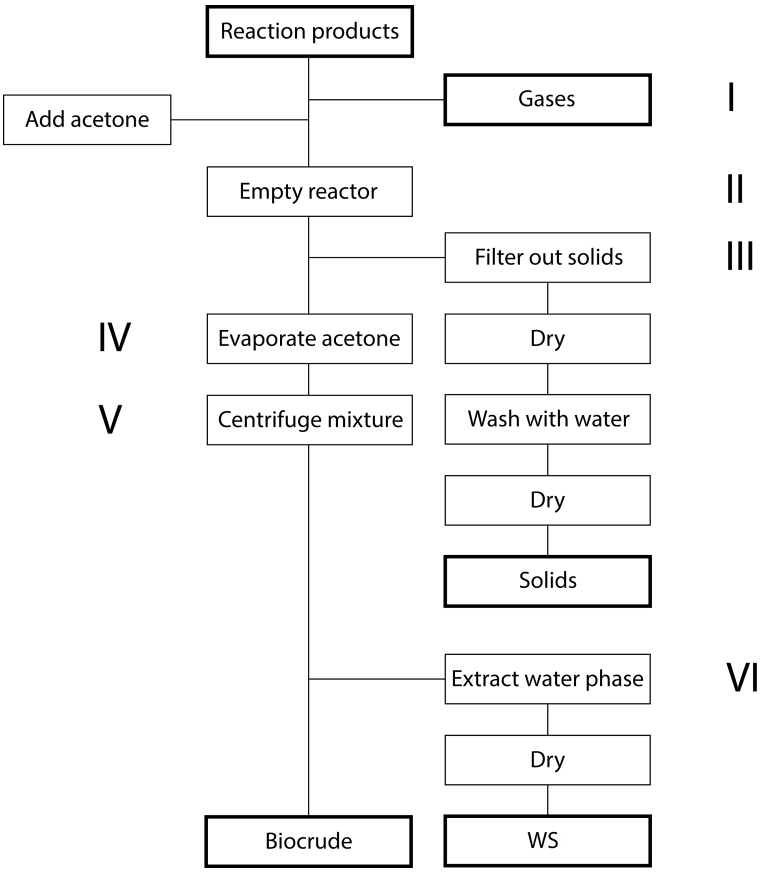


Figure 5.1: HTL product separation procedure

The remaining products consisted of solid residues, biocrude and an aqueous phase. The reactors were washed with acetone in order to remove all biocrude traces from the reactor (step II). The liquid phase was then separated from the char by vacuum assisted mechanical filtration (VWR, particle retention: 5-13 μm, step III). The solids present on the filter were then dried overnight at 105°C and re-filtered with 250 ml of distilled water. The remaining solid residues were dried once again, weighed and defined as the water and acetone insoluble solids. Acetone was then evaporated from the homogeneous liquid fraction and the biocrude fraction was manually extracted after centrifuge-aided phase separation (steps IV and V). The higher density extracts were defined as biocrude, whereas the aqueous by product was collected, dried, weighed and denoted as water solubles (step VI) The yield of WS will increase after adding the weight of the solids that indeed

were soluble in water.

Figure 5.2 shows an overview of all analysis procedures involved in HTL product characterisation. From left to right, post reaction gases are weighed, adjusted for initial nitrogen addition and analysed via GC analysis. The aqueous products were weighed prior to and after in order to show the extent of experimental error due to water losses during acetone evaporation. The produced biocrudes are weighed, then their proximate analysis is done via TGA and the water contents are measured via Karl Fischer titration, respectively. Finally, the produced solids are weighed, washed with water, dried, reweighed and ashed. This procedure is done in order to determine the acetone and water insoluble solids correctly and looking into how much inorganics are present in the by-product.

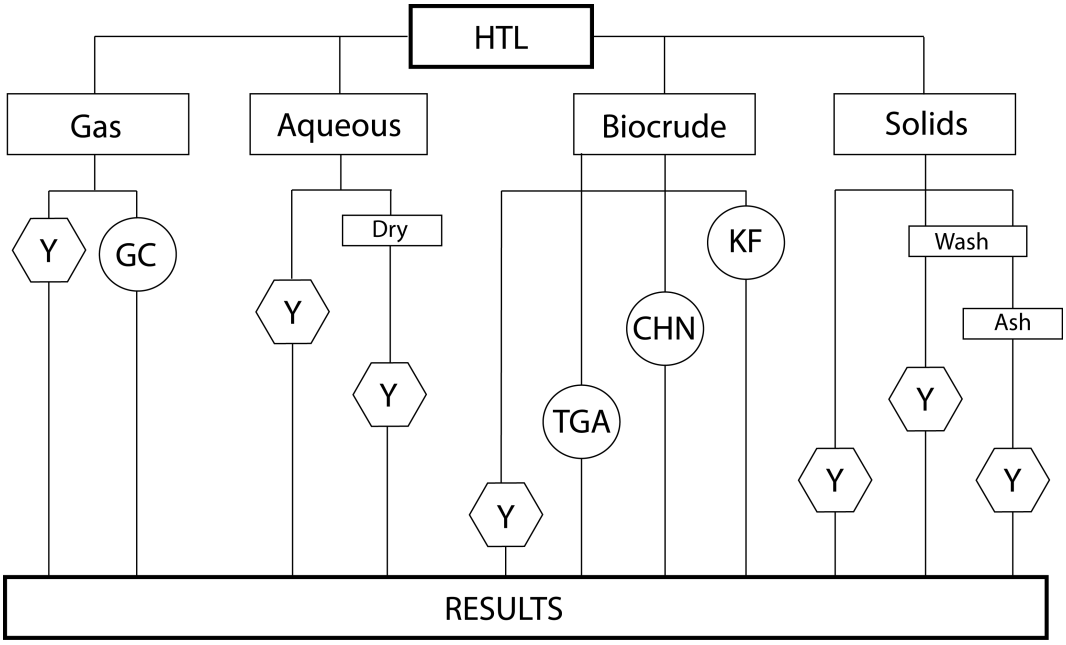


Figure 5.2: Post-HTL analytical procedure, here "Y" - yield measurement, "GC" - gas chromatography, "KF" - Karl Fischer titration, "CHN" - ultimate analysis, "TGA" - thermogravimetric analysis, "dry", "wash", "ash" - corresponding analogue steps.

5.2 Calculation methods

The section describes all calculative methods that were used for determining both product/by-product yields and quality parameters such as biocrude HHV, H/C_eff and O/C.

5.2.1 Yield calculations

Both biocrude and gas yields were calculated on a dry and ash-free (DAF) basis according to equations 5.1 and 5.2. Similarly, yields of solids were calculated on a dry basis, as shown by equation 5.3.

$$Yield_{biocrude} = \frac{Mass\,of\,biocrude}{Mass\,of\,dry,\,ash\,free\,feedstock} \quad [\%] \tag{5.1}$$

$$Yield_{gas} = \frac{Mass\,of\,gases}{Mass\,of\,dry,\,ash\,free\,feedstock} \quad [\%] \tag{5.2}$$

$$Yield_{solids} = \frac{Mass\,of\,washed\,solids}{Mass\,of\,dry feedstock} \quad [\%] \tag{5.3}$$

Finally, the yield of water solubles (WS) was also determined on dry feedstock basis, by adding the weighed WSs and the amount of solids washed out with water (equation 5.4). This procedure was adapted in order to better represent the generated amount of WSs. Previously utilised methods of presenting the data as *process water + WSs* were shown to be inconsistent (i.e. variations in mass up to 25 % among single run triplicate data). Such differences are believed to be caused by the non-automated evaporation step - depending on the duration of this step, more or less process water is lost. However, this does not impair the results of the study as preserving process water was never among the objectives. Furthermore, presenting dry WS data instead is more reliable.

$$Yield_{WS} = \frac{Mass\,of\,WS + mass\,lost\,during\,water\,washing\,of\,solids}{Mass\,of\,dry feedstock} \quad [\%] \tag{5.4}$$

5.2.2 Biocrude quality indicators

Higher heating value estimation

Due to the inability of measuring the HHVs of the produced HTL biocrudes directly (i.e. micro reactors do not yield sufficient amounts), the study resorted to elemental HHV estimation. In order to represent the biocrude in a comparable

manner, several HHV estimation formulas were tested against laboratory measurements or raw macroalgae, demineralisation and added value product extraction residues. Table 5.2 shows the full list of cross-checked formulas.

Table 5.2: HHV correlations tested in this study

Authors (year)	**HHV formulas [MJ/kg, on dry basis]**
Dulong (1880)	$0.33829 * C + 1.44277 * H + 0.0942 * S - 0.18036 * O$
IGT (1978)	$0.3417 * C + 1.3221 * H + 0.1232 * S - 0.1198(O + N) - 0.0153 * Ash$
Grabosky and Bain (1981)	$0.328 * C + 1.4306 * H - 0.0237 * N + 0.0929 * S - (1 - Ash/100)(40.11 * H/C) + 0.3466$
Buckley (1991)	$0.3491 * C + 1.1783 * H + 0.1005 * S - 0.1034 * O - 0.0151 * N - 0.0211 * Ash$
Channiwala and Parikh (2002)	$0.3491 * C + 1.1783 * H + 0.1005 * S - 0.1034 * O - 0.0151 * N - 0.0211 * Ash$
Friedl et al. (2005)	$0.00355 * C^2 - 0.232 * C - 2.230 * H + 0.0512 * C * H + 0.131 * N + 20.6$
Sheng and Azevedo (2005)	$-1.3675 + 0.3137 * C + 0.7009 * H - 0.0318 * O$
Yin (2010)	$0.2949 * C + 0.825 * H$

The correlation derived by *Friedl et al* (equation 5.5) was shown to give most accurate results - 13 out of 15 values were within 5 % of the experimental measurements. Meanwhile, the last two (the HTL non-participating raw SSR and post fucoidan SAR) were best represented by *Sheng and Azevedo's* solution (results were within 5%). The formula by *Friedl et al* shall be used throughout the project to estimate biocrude HHVs.

$$HHV = 0.00355 * C^2 - 0.232 * C - 2.230 * H + 0.0512 * C * H + 0.131 * N + 20.6 \ [MJ/kg] \tag{5.5}$$

Hydrogen-to-carbon and oxygen-to-carbon ratios

Hydrogen-to-carbon and oxygen-to-carbon ratios on an elemental basis were calculated for each of the produced biocrudes. Such quality parameters allow for direct comparison with biocrudes produced from other biomass sources, different HTL conditions and even fossil fuels. In literature, yet another ratio, the *effective hydrogen-to-carbon* ratio, is often presented in order to compensate for any water present in the produced biocrude. Contrary to such an approach, the study included measuring the total water content by Karl Fischer titration and subtracting the results both from biocrude yields and elemental composition.

5.2.3 Energy recovery calculation

Energy recovered in the form of produced biocrudes was calculated as well in order compare the energetics of each HTL run, additionally to biocrude yield and quality. The recovered ratio is calculated on dry feedstock basis by equation 5.6.

$$ER = \frac{Mass\,of\,biocrude * estimated\,HHV}{Mass\,of\,dry\,feedstock * measured\,HHV} * 100\% \quad [\%] \tag{5.6}$$

5.3 Results and discussion

All HTL related results are presented in this section. Starting with product yields and biocrude quality, the overview continues with composition analysis of the produced solids and gases. Finally, the chapter ends with a discussion.

5.3.1 HTL yields

Biocrude yields varied between 15.22 wt. % and 28.21 wt. % on DAF basis. As shown in figure 5.3, short HTL (run 6) and HTL of neutralised citric acid leaching residues (run 5) performed the worst in terms of biocrude yields. Meanwhile, the baseline run with untreated FFR resulted in a yield of 19.36 wt. %. Finally, all three remaining biomass treatments (i.e. citric acid leaching, fucoidan and alginate extraction) led to increased biocrude yields. Alginate extraction residue conversion produced the most biocrude on DAF basis, 28.21 wt. %.

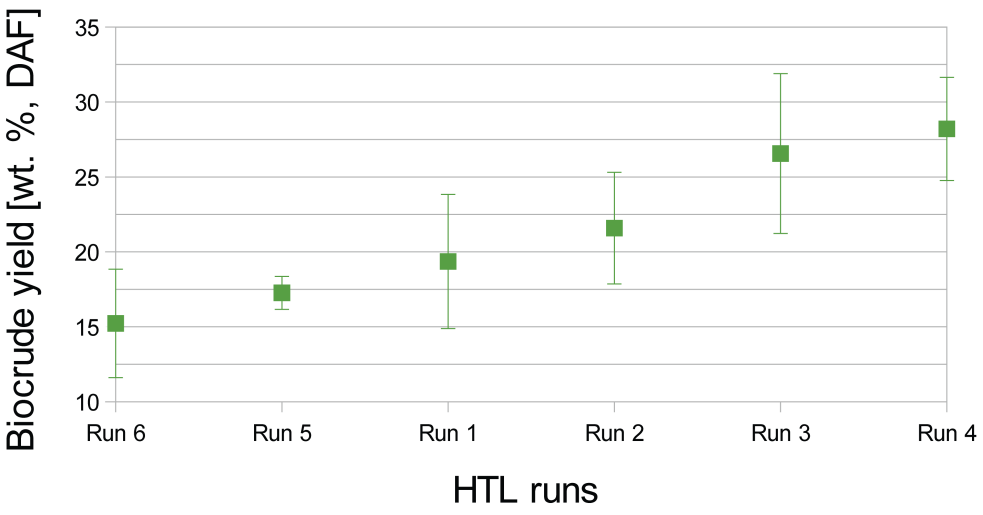


Figure 5.3: HTL biocrude yields. Expressed on DAF basis.

Next, it is interesting to look at the four phase HTL products in terms of measured mass yields. As pointed out before, based on 1 g of dry feedstock, runs 2,3 and 4 resulted in significantly higher biocrude yields (figure 5.4).

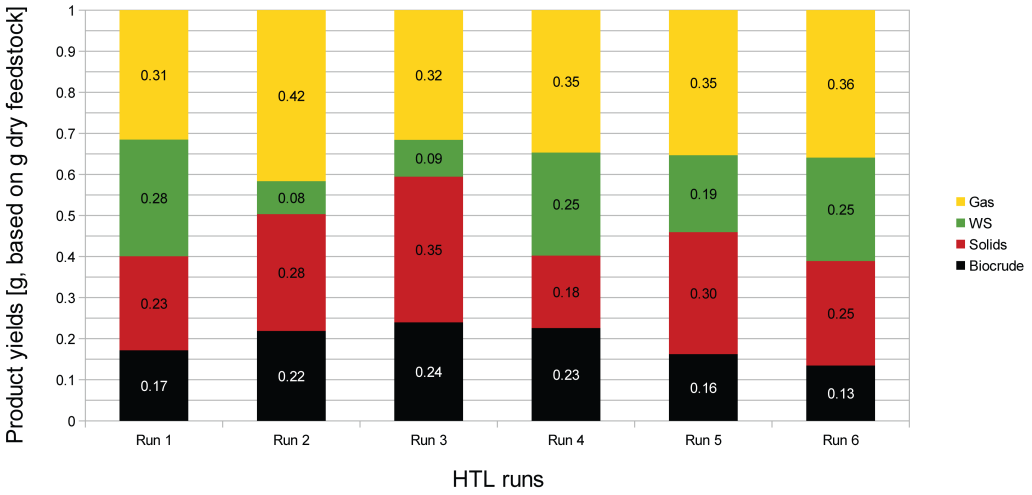


Figure 5.4: HTL product yields

On the other hand, runs 2, 3 and 5 led to highest production of solids. Fucoidan extraction residues performed the worst (0.35 g of solids), whereas alginate residues generated the least amount of solids (0.18 g). The difference is significant and definitely worth to consider.

Runs 2 and 3 led to significantly lower amounts of WS, 0.08 g and 0.09 g, respectively. In comparison, the overall average of produced WS was 0.19 g, with run 1 generating the most, 0.28 g WS.

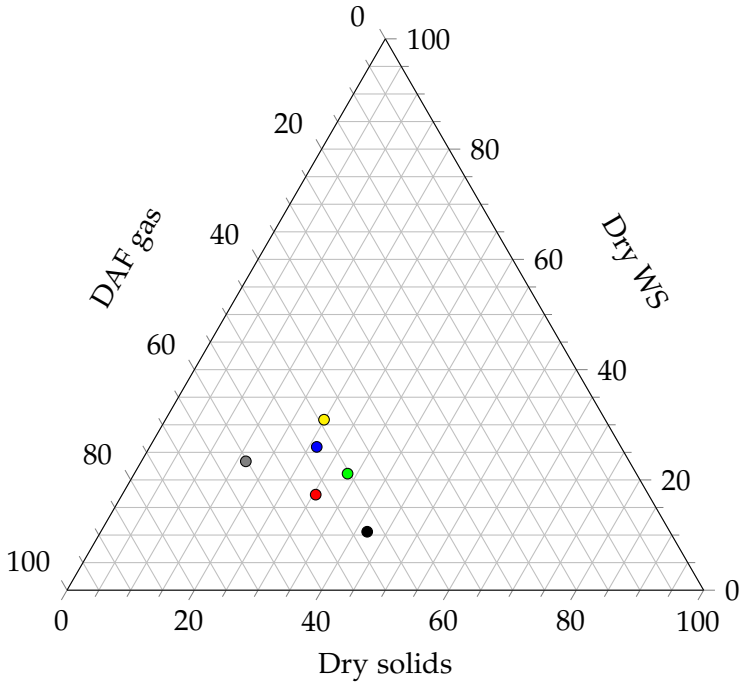
Gas yields were rather consistent throughout the experimental procedure with the exception of run 2, the citric acid leaching residues led to the highest amount of produced gases, 0.42 g, compared to the average of 0.35 g.

The produced by-products were scaled with respect to each other in order to represent proportional yields and plotted on figure 5.5. Here the aim was to see whether it is possible to determine some kind of biocrude tendencies based on by-product yield distribution. In general, it seems that the worse performing runs (i.e. 1, 5 and 6) exhibit a slight tendency to form more WS and less gases. Whereas there is no correlation in terms of solids, as all three high biocrude yielding runs are spread out within the range of 16.40 to 41.85 %, while the worse performing runs average out at 28.21 %.

5.3.2 Biocrude quality

Besides identifying the high biocrude yielding parameters, it is crucial to establish how the different HTL runs perform in terms of produced biocrude quality. This is first and foremost assessed by elemental H/C and O/C ratios. The results are

Figure 5.5: Relative HTL by-product distribution: run 1 (●), run 2 (●), run 3 (●), run 4 (●), run 5 (●) and run 6 (●)



presented in a Van Krevelen diagram (figure 5.6). Here, the aim of maximising hydrogen content and minimising oxygen is highlighted. Runs 5 and 6 seem to perform the best with high H/Cs of ∼1.54 and low O/C ratios between 0.05 and 0.08. However, as shown by the characterisation of fossil crude, upgrading via deoxygenation is necessary even for the best performing biocrudes. Runs 2, 3 and 4 also produced biocrudes of good quality. As indicated by the oxygen rich product of baseline run 1, it is clear that all pretreatments/conditions (i.e. demineralisation, added value product extraction and even short retention) lead to superior biocrudes.

Elemental analysis of the produced biocrudes is presented in table 5.3.

Proximate analysis of the produced biocrudes did not show significant differences in volatile matter and fixed carbon which averaged at 83.32 ±2.30 wt. % and 16.68 wt. % respectively. The high amount of volatiles is promising for further refining as only the volatile compounds can be distilled into lighter hydrocarbons such as diesel, jet fuel and gasoline.

5.3.3 Neutralisation and short HTL study cases

A direct comparison between runs 2, 5 and 1, 6 is necessary in order to discuss whether either an extensive water neutralisation or a shorter retention time of 10

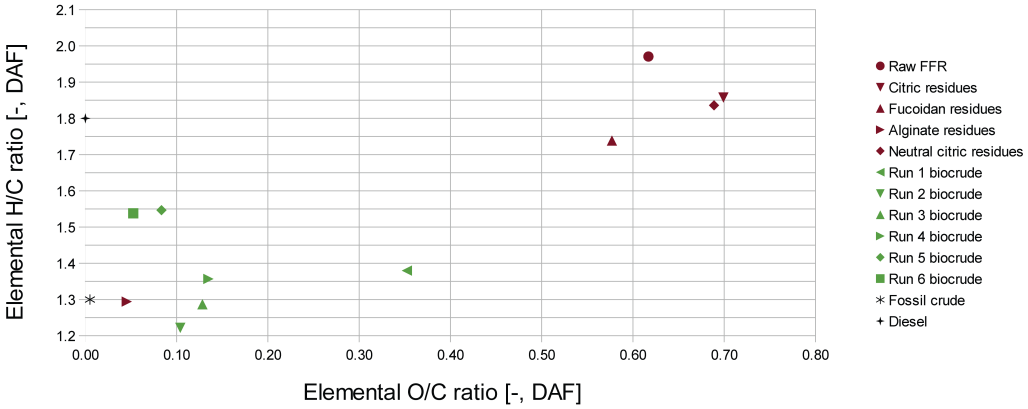


Figure 5.6: Van Krevelen diagram characterising the initial algal feedstocks and the produced HTL biocrudes in terms of elemental H/C and O/C ratios. Fossil crude and diesel are shown for reference.

Table 5.3: Elemental analysis of the produced HTL biocrudes

	C [wt. %]	H [wt. %]	N [wt. %]	S [wt. %]	O [wt. %]
Run 1	60.23	6.93	3.08	1.47	28.29
Run 2	77.96	7.94	2.75	0.54	10.81
Run 3	75.52	8.10	2.97	0.49	12.92
Run 4	74.63	8.44	3.02	0.51	13.41
Run 5	78.09	10.06	3.17	n.m.	8.68
Run 6	79.85	10.23	4.33	n.m.	5.58
n.m. - not measured					

min benefits the biocrude yields and quality.

In terms of biocrude yield (figure 5.3), both neutralised residues and short retention led to very low results, with run 5 performing slightly better. It is rather difficult to define a tendency based on by-product distribution. Leached biomass runs exchanged gas and WS production, with the neutralised residues generating a higher amount of gases. On the contrary, short HTL produced proportionally less gas (5.5).

Coming back to figure 5.6, run 1 biocrude retained an alarmingly high amount of oxygen. Based on a significantly lower O/C ratio and a slight increase in H/C, a shorter retention is definitely the superior condition from this point of view. Meanwhile things are slightly less obvious with neutralised leaching residues - the O/C ratio remained nearly identical. Nonetheless, the H/C improved by more than 20 %.

5.3.4 HTL by-product composition

Characterisation of the solid and gaseous by-products was extended to ash analysis and gas chromatography. Biocrude ash content is neglected in this study as parallel work with supercritical micro-batch HTL of another brown macroalgae, Laminaria digitata, has shown that biocrude ash concentrations do not exceed 1 wt. %.

Solids

The chemical composition analysis of the produced solids was limited to defining how much residual organics are present. As shown in 5.7, with one exception, residual organics did not vary much throughout the 6 HTL runs, averaging at 70.87 wt. %. However, run 3 (fucoidan residues) varied significantly, comprising of just 52.54 wt. % organics. Going back to figure 5.4, since the gas yield of run 3 was average and the amount of produced WS significantly lower than in other runs, the fact that such a high fraction of solids was produced leads to think that more inorganics ended up in the solid phase by-product stream and thus reduced the apparent concentration of solid organics.

Based on the revealed content of inorganics, an ash migration scheme is proposed. Figure 5.8 illustrates the case of run 1. According to an assumption that inorganics are significantly present just in two of the by-products, namely the solids and WS, leads to potentially more than 50 % ash among the water solubles. Ash content both in the feedstock and HTL solids was measured, whereas the missing amount is assigned to WS, where the percentage is simply calculated based on the total yield of WS. This raises doubt in the potential of utilising the aqueous HTL product for direct water phase recirculation as effectively done with lignocellulosic feedstocks [27], or leaching.

Ash analysis of run 1 solids (table 5.4) revealed that with the exception of

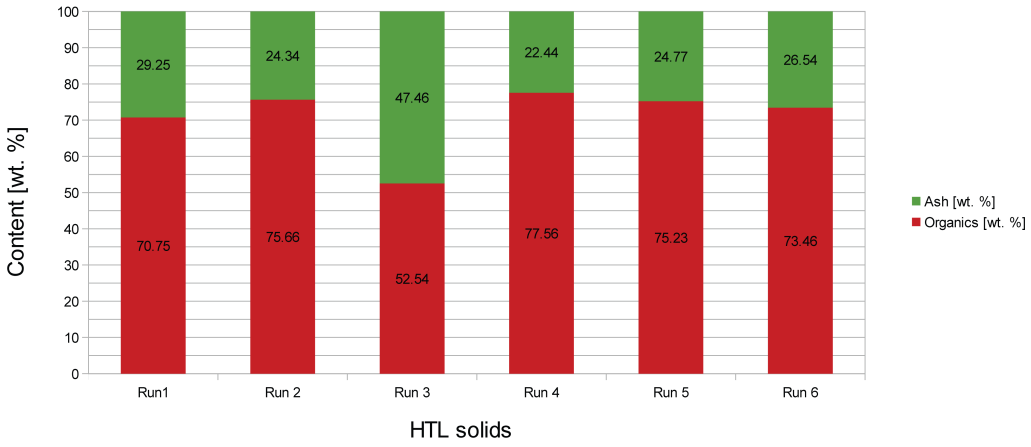


Figure 5.7: Inorganics and organics present in HTL solids

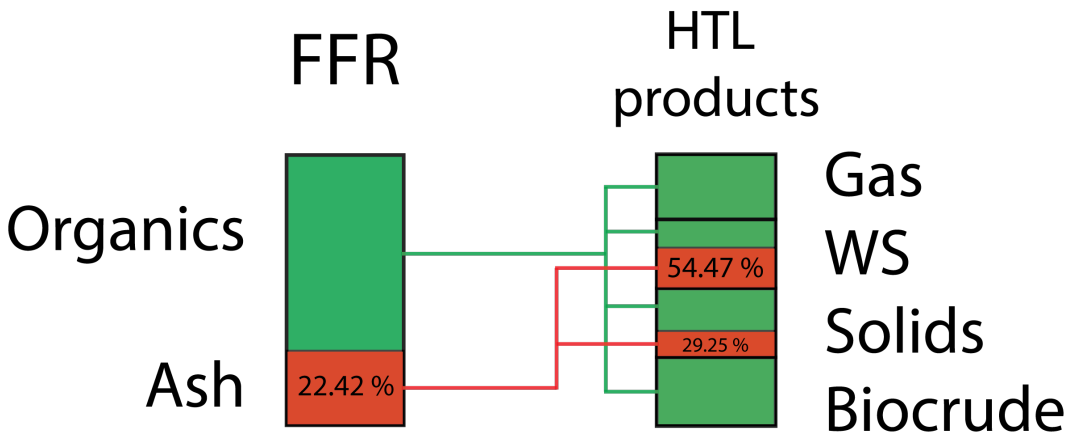


Figure 5.8: Proposed ash migration scheme in HTL run 1.

potassium and sodium, all measured metal concentrations increased comparing to raw FFR. This is expected as potassium and sodium salts (e.g. KI, KCl, NaCl, Na_2CO_3, etc) are highly soluble in water and hence are believed to be washed out throughout the product separation procedure. Meanwhile, fears of reactor degradation are confirmed by the fact that concentration levels of stainless steel originating metals (i.e. chromium, iron, manganese, nickel and titanium) increased or, in the case of chromium and titanium, appeared.

Gases

Similarly to product yields, gas analysis shows that all HTL runs produce gases of similar composition. The only major deviations were gaseous by-products of runs 3 and 4. As seen in figure 5.9, run 3 gases contained a significantly higher amount of CO, whereas run 4 in turn produced more H_2. Besides that, all produced gases were dominated by CO_2 (minimum of 84.61 vol. % and up to 91.61 vol. %) and contained traces of CO, H_2 and CH_4, indicating that the majority of oxygen is removed via decarboxylation and decarbonylation reactions.

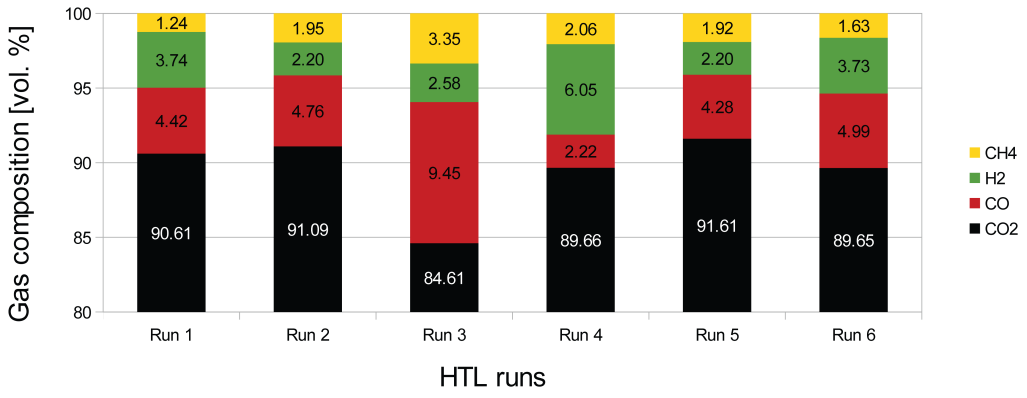


Figure 5.9: HTL gas composition

5.3.5 Discussion

The presence of water soluble solids among the solids post filtration and the energy recovery potential of the experimental HTL runs are to be discussed in greater detail.

Water soluble solids

An additional water washing step was introduced post filtration in order to check whether there were any water solubles that were precipitated by the used acetone.

Table 5.4: ICP ash analysis of raw FFR and run 1 solids. Metal concentrations above 0.1 mg/g are reported.

	Metal concentration [mg/g]														
Sample	**Al**	**Ba**	**Ca**	**Cr**	**Cu**	**Fe**	**K**	**Mg**	**Mn**	**Na**	**Ni**	**P**	**Sr**	**Ti**	**Zn**
Raw FFR	0.85 ±0.3	0.03 ±0.1	42.83 ±0.1	- -	0.13 ±0.1	1.93 ±0.1	104.9 ±2.7	30.65 ±1.9	0.48 ±0.1	49.03 ±3.0	0.73 ±0.1	10.35 ±0.7	4.05 0.3	- -	0.19 ±0.1
Run 1 solids	3.27 ±0.3	0.31 ±0.1	144.93 ±2.0	0.31 ±0.1	0.54 ±0.1	9.05 ±0.3	8.23 ±0.3	83.38 ±0.2	1.7 ±0.1	9.02 ±0.5	3.75 ±0.1	37.97 ±0.4	12.78 ±0.4	0.18 ±0.1	1.1 ±0.1

The mere fact that a solvent was used in order to clean the reactors and separate the products might impair the reliability of the results. The gravimetrically separable biocrude is easily isolated without the use of external solvents in continuous HTL facilities [27].

The performed washing step revealed mass losses ranging from 7.96 % to 54.15 % in the case of run 4 and 3 solids, respectively. Here, the use of sulphuric acid during alginate extraction is hypothesized to have rendered the biomass residues recalcitrant to subsequent water treatments (i.e. low mass loss) due to the acid's structural destructiveness and demineralisation effectiveness. During the screening tests with *L. digitata*, sulphuric acid leaching was shown to break down crystalline macroalgae structures. Interestingly, mass losses across runs 1,6 and 2,5 remained virtually invariant at 37 wt. % and 22 wt. %, showing that neither extensive water neutralisation, nor halving the retention time influence the amount of WS that get precipitated during acetone filtration. All in all, it is obvious that without extra washing, reported amounts of produced solids risk to be neither acetone and water insoluble, nor representative for real-life in-line filtered HTL facilities.

Energy recovery in HTL biocrudes

HHVs of the biocrudes were estimated in order to calculate the energy recovery associated with the produced biocrudes. The results varied from as low as 25.82 MJ/kg in the case of run 1, up to 42.34 MJ/kg and 44.30 MJ/kg for run 5 and 6 biocrudes, respectively. The latter values are well within the range of conventional fossil crudes.

In terms of HTL processing and energy efficiency, energy recovery in the main fuel product, namely the biocrude, is essential to evaluate the potential feasibility of the specific conditions or feedstock. Figure 5.10 shows that runs 2, 3 and 4 perform the best with alginate residue HTL biocrude resulting in a ER of 53.02 %. On the other end of the spectrum, run 1 (i.e. raw FFR, baseline HTL conditions) exhibited an ER of just 26.04 % whereas biocrudes from runs 5 and 6 contained $\sim$30 % of the initial feedstock energy.

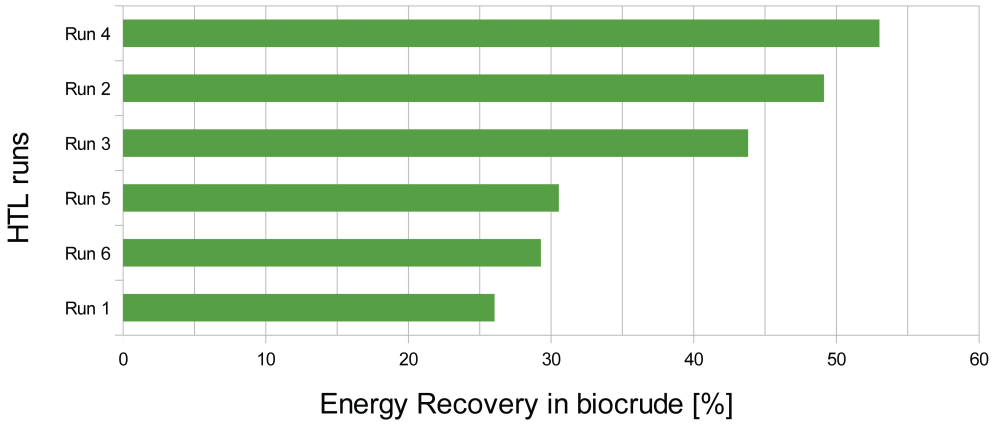


Figure 5.10: Energy recovery in HTL biocrude

6 Conclusions

The conclusions, as is the entire structure of the project are arranged in a way that the three main aspects of the study: demineralisation, added value product extraction and hydrothermal liquefaction of macroalgal biomass are presented in separate sections.

6.1 Demineralisation

All three demineralisation methods led to reduced amounts of ash and consequently higher HHVs. Whereas the residual amounts levelled out already at mild neutralisation (washing step 4). *HTL water* solution performed the worst, presumably due to the presence of potassium carbonate. Citric acid leaching with neutralisation resulted in the least ash, corresponding to an ash removal efficiency of 47.15 %. Meanwhile, extensive water leaching (with 8 "neutralisation" steps) performed as well as citric acid leaching with mild neutralisation. Whereas the full extent of water leaching led to an ash reduction efficiency of 38.85 %.

Extensive water leaching could be considered a viable alternative for acid demineralisation. However, HTL of water washed FFR is necessary to confirm this claim and compare the two methods thoroughly.

Should feedstock neutralisation be necessary, citric acid leaching showed most resistance: 8 water washing steps were necessary to neutralise the biomass. Adjusting the pH by adding a base is not a good alternative as studies show that in HTL of macroalgae, additional alkali metals impair the process performance. Acid recovery is an appealing prospect that should be investigated specifically for HTL.

6.2 Added value product extraction

Both alginate and fucoidan extractions led to highly different residual masses for the two tested macroalgae, in the two cases FFR proved to be the more resistant. However, alginate extraction with both macroalgae led to residues with high ash concentrations, speculatively due to the use of sulphuric acid in the extraction process, which is known for its high extraction and structural decomposition potential.

In all cases except for fucoidan extraction from SAR, the residues had higher HHVs than the initial biomass samples.

6.3 Hydrothermal liquefaction

Fucoidan and alginate extraction residues led to the highest biocrude yields, at 26.56 wt. % and 28.21 wt. %, respectively, as shown in table 6.1. Meanwhile, short retention and neutralised leaching residues resulted in the lowest yields. In terms of H/C and O/C ratios, on the other hand, the latter two performed the best, whereas raw FFR biocrude exhibited a significantly higher O/C ratio of 0.35. In terms of H/C, citric leaching and fucoidan extraction residues performed the worst. Nitrogen content was rather invariant and high with slight deviations in acid leached residues with the lowest nitrogen content of 2.6 wt. %, and short retention FFR - the highest nitrogen content of 4.08 wt. %.

Table 6.1: Yield and quality summary of the produced biocrudes. Data presented in weight % is calculated on DAF basis.

	Biocrude yield [wt. %]	H/C [wt/ %]	O/C [wt. %]	N [wt. %]	ER [%]	HHV [MJ/kg]
Run 1	19.36	1.38	0.35	2.99	26.04	25.82
Run 2	21.59	1.22	0.1	2.6	49.14	42.34
Run 3	26.56	1.29	0.13	2.78	43.81	36.88
Run 4	28.21	1.36	0.14	2.94	53.02	44.3
Run 5	17.26	1.55	0.08	3.04	30.54	36.97
Run 6	15.22	1.54	0.05	4.08	29.28	38.44

Despite slightly different tendencies in terms of biocrude yield, citric acid leaching and alginate extraction residue biocrudes exhibited the highest HHVs and ER.

Surprisingly, raw FFR biocrude production underperformed with an average yield and low ER. Otherwise, all initial hypotheses were confirmed:

- Run 2 - Demineralisation led to a slightly higher HTL biocrude yield
- Run 3 - HTL of fucoidan extraction residues resulted in a relatively high biocrude ER
- Run 4 - HTL of alginate extraction residues led to a high biocrude ER
- Run 5 - Despite great quality in terms of H/C and O/C, neutralisation is not advised as it led to significantly lower yields and ER
- Run 6 - Despite high quality in terms of H/C, O/C and HHV, the produced biocrude contained a higher amount of N

6.4 Future work

The author suggests including protein extraction residues as a feedstock. Besides that, the discussion on macroalgae demineralisation could use results from HTL of water and *HTL water* leached algal biomass for in depth comparison.

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A Appendix A name

Here is the first appendix