Design and Planning of Biofuels Produced from Algae

Master Thesis
Department of Chemical Engineering, Lund University
2024-05-30

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Abstract

This thesis investigates the profitability of converting microalgae into biofuel using hydrothermal liquefaction the goal is to produce 100 000 tons of bio-oil each year. It explores various microalgae species and cultivation methods, identifying Chlorella vulgaris with a rotating attached biofilter as the optimal choice due to its high biomass concentration, eliminating the need for dewatering and expensive harvesting processes. The study includes a detailed simulation in Aspen Plus with an integrated process with HTL operating at 200 bar and 320 degrees celsius and hydrogen treatment operating at 15 bars and 350 degrees celsius. The simulation also incorporates components such as heat exchangers and separation units. The study also goes in briefly about the components needed to make the process work such as a hydrogen plant, wastewater treatment and a burner for gas. Cost analysis is conducted in Excel and evaluates both operational and capital expenses.

The Aspen simulations indicate a bio-oil yield of 60%. Post-hydroprocessing and hydrocracking, the bio-oil composition includes 77% diesel, 15% naphtha, and 8% gas. The analysis estimates a capital payback period of 49 years under standard conditions. A theoretical optimal scenario was made adjusting key parameters to their theoretical maxima, reducing the payback period to 5 years. The conclusion for the process is that the algae cultivation is expensive to build to make it profitable.

1 Introduction

Fossil fuels have long powered our world, but their finite nature and environmental consequences necessitate a reevaluation. For centuries, coal, oil, and natural gas have fueled our progress: coal ignited the Industrial Revolution, oil revolutionized transportation, and natural gas powered homes and industries. However, beneath their transformative contributions lies a complex reality. Fossil fuels are finite resources, extracted from ancient organic matter. As we continue to extract them, their reserves diminish, raising concerns about long-term availability. Moreover, burning fossil fuels releases greenhouse gases (GHGs), significantly contributing to global warming. As developing nations raise living standards, energy demand surges, creating a delicate balance between progress and environmental responsibility.

The oil industry reshaped the world by providing fuel for vehicles, but this progress came at a cost. Widespread fossil fuel use intensified GHG emissions, affecting climate and ecosystems. Developing countries aspire to industrialize, yet striking a balance between progress and environmental stewardship remains crucial.

Biofuel has emerged as a promising alternative to fossil fuels, aiming to reduce GHG emissions and provide a renewable energy source. Biofuel is obtained by chemically processing biomass from various sources. The first generation of biofuel (G1) comes from oil-bearing seeds and edible crops, but it faces the problem of competing with food resources for human consumption. The second generation of biofuel (G2) offers a great alternative, as it uses biomass from non-food resources, often by-products of the food processing industry. The third generation of biofuels (G3) introduces algae as a biomass source with significant potential. Algae are particularly exciting due to their ability to produce a large amount of biomass quickly and their high lipid content, which can be used as a source of oil.

This article will explore the use of different microalgae species for biofuel production. Each species has different pros and cons that can affect the final product, with varying ratios of lipids, carbohydrates, and CO_2 proteins resulting in different bio-oil yields. Different cultivation methods will be compared and evaluated to maximize growth and reduce expenses, including both direct and operational costs. The next step is the hydrothermal liquefaction (HTL) process, which will convert algal biomass into biocrude oil. This process will be simulated using Aspen software, with data collected from various sources to enhance understanding. All products from the HTL process will be further analyzed in the simulation. Aspen Plus is also used to simulate the hydrogen treatment on the resulting biocrude from HTL to upgrade the biocrude into usable products.

1.1 Aim

This thesis will explore the process of cultivating and then converting microalgae into biofuel by using hydrothermal liquefaction. The main goal of the article is to evaluate the possible profit or loss when constructing and operating the named process from scratch and producing 100,000 ton bio-oil each year. To achieve this goal several smaller goals need to be achieved in order to achieve the main goal. Firstly choosing a good microalgae for bio-oil production. Secondly choosing a cultivation that can handle the workload and not be too expensive both to build and operate. Thirdly simulating a HTL process and a hydroprocess to know the bio yield and products forming. Lastly evaluate the HTL process for any addons necessary to make the process run smoothly.

1.2 Disposition

The thesis explores the process of converting algae into biofuel and what is needed to make it work. The thesis goes through different cultivation methods and what cultivation is the most optimal for the process. The thesis also goes over HTL and biocrude upgrading with simulation over the reactions that occur. Finally an economic overview of the whole process from cultivation to finalized products.

2 Background

 The background goes through the needed information and data to begin the project to design and optimize the process to convert algae to biofuel.

2.1 Biofuels

Biofuels are categorized into generations, each with distinct characteristics. The first generation includes both liquid and gaseous fuels like biodiesel, vegetable oil, bio-ethers, and bio-alcohol. These fuels are derived from oil-bearing seeds and edible crops such as starch, sugarcane, animal fats, sunflower, rapeseed, and palm. The complex triglyceride molecules, composed of three fatty acid units linked to an ester molecule, make each oil unique. These triglycerides can be converted into biofuels through techniques such as transesterification, anaerobic decomposition, fermentation, and pyrolysis.(1)

The second generation of biofuels provides a more sustainable alternative as it uses non-food biomass. This biomass often comes from by-products of the food processing industry and wood factories, including dry wood and stalks of corn and wheat.

The third generation of biofuels introduces algae as a key component, ranging from microalgae to macroalgae. Algae processing extends beyond biofuel production, contributing to the nutritional industry, bioplastics, pharmaceuticals, special chemical manufacturing, and organic fertilizer production. Algae have unique properties such as carbon dioxide absorption, higher biomass production per square meter compared to traditional food crops, adaptability to saltwater environments, and high lipid content. These characteristics make algae a versatile solution in the biofuel industry. Algae's ability to absorb CO_2 provides significant environmental benefits by helping reduce the greenhouse effect. Additionally, their efficient biomass production per unit area and adaptability to saltwater conditions enhance the economic viability of algae-based biofuel production. These attributes, combined with their potential for diverse applications in various industries, highlight the importance of algae in shaping the future of sustainable bioenergy.(1)

2.2 Algae

Algae are a diverse group of photosynthetic microorganisms, including both microalgae and macroalgae. As a biofuel, algae have emerged as a focal point in the pursuit of sustainable and renewable energy. Microalgae, characterized by their unicellular or simple multicellular nature, exhibit remarkable growth rates under varying environmental conditions, underscoring their potential as an efficient biomass resource for biofuel production. Although macroalgae, or seaweed, are less commonly used for biofuel, they are still researched for their carbohydrate content, which can be fermented into bioethanol.

Microalgae's inherent ability for rapid growth, coupled with their reproductive capabilities, makes them an attractive candidate for biomass production. Their adaptability to diverse aquatic environments further enhances their potential as a sustainable and versatile feedstock for biofuel production. One notable feature of algae is their capacity to absorb carbon dioxide during photosynthesis, contributing to the mitigation of greenhouse gas emissions. Additionally, the relatively small land footprint required for algae cultivation compared to traditional crops makes them an environmentally favorable option for biofuel production.(1)

A pivotal factor in the viability of algae for biofuel production is their high lipid content. Many microalgae species accumulate substantial amounts of lipids, particularly triacylglycerols (TAGs), which can be transformed into biodiesel. The diversity in lipid composition among different algae species provides a rich landscape for researchers to select and genetically engineer strains with optimal lipid profiles for enhanced biofuel production. Algal lipids serve as a valuable feedstock for biodiesel production, utilizing methodologies similar to the conversion of vegetable oils. Moreover, carbohydrates present in algae are harnessed for the production of bioethanol and biobutanol, expanding the range of biofuels derived from these microorganisms.(1)

Microalgae's large surface-to-volume ratio allows them to capture significant amounts of nutrients, enhancing their growth. Their exceptional growth rate is due to their ability to capture solar energy more efficiently than terrestrial plants. Growing in water also facilitates efficient access to water, CO_2, and nutrients, enabling them to produce more biomass per unit of land compared to other oil-producing plants. Per hectare, algae are projected to produce between 58,700 and 136,900 liters of oil per year, depending on the type of algae and production method. This yield is about 10-20 times higher than that of the best oil-producing crop, such as palm, which produces approximately 5,950 liters per year and hectare.(5)

2.2.1 Algae growth

Various methodologies exist for cultivating algae, ranging from economical and rudimentary approaches to sophisticated and costly techniques. The principal in converting algae into biofuel lies in the operational and capital expenses associated with algae cultivation. Successful algae cultivation necessitates adequate exposure to light, dissolved carbon dioxide, and essential nutrients, predominantly phosphorus and nitrogen. Additionally, measures must be undertaken to ensure the cultivation environment remains uncontaminated, requiring thorough water purification prior to usage. Maintaining regulated pH levels is imperative for optimizing algae growth, as deviations can lead to the collapse of cell walls, resulting in the release of crucial biomass, such as lipids, into the water and complicating the harvesting process. The recommended pH range for cultivation is 8.2-8.7, as this range helps maintain cellular integrity and metabolic efficiency. Supplementing carbon dioxide into the medium proves instrumental in achieving the desired pH values. Illumination methods encompass natural sunlight or artificial sources such as fluorescent lamps, with optimal radiation falling within the ranges of 380-500 nm for blue light and 600-700 nm for red light, which are most effective for photosynthesis. While the illumination period can extend up to 16-18 hours. Algae growth is significantly influenced by the patterns of light they are exposed to. Research has shown that algae often grow faster when subjected to alternating dark and light cycles compared to continuous light exposure. This phenomenon can be explained through several key factors. First, photosynthetic efficiency plays a crucial role. During the light cycles, algae perform photosynthesis, converting light energy into chemical energy in the form of ATP and NADPH. These products are then used in the Calvin cycle, or dark reactions, to fix carbon dioxide into organic molecules such as glucose. The dark periods allow the algae to effectively process the energy captured during the light phase, optimizing overall photosynthesis and growth.(22)

Photoinhibition is another critical factor. Continuous exposure to light can damage the photosynthetic apparatus due to overexposure, reducing the efficiency of photosynthesis. Alternating dark periods provide time for the photosystems to repair and recover, maintaining higher productivity levels over time .
Moreover, algae need a balanced approach to energy production and utilization. Continuous light can cause an imbalance, where the energy produced is not effectively utilized, leading to metabolic stress. Dark periods offer time for cellular processes like respiration and growth to occur without the immediate input of light energy, ensuring a balanced metabolic state. Nutrient uptake also benefits from dark periods. During these times, algae can focus on absorbing and assimilating nutrients without the competing energy demands of photosynthesis. This ensures that essential nutrients are available when the light cycle resumes, enhancing overall growth rates. (22)

Temperature control is crucial, with the optimal range for algae growth typically falling between 10-25 degrees Celsius. Elevated temperatures beyond 35 degrees Celsius are detrimental to algae survivability.(1).

Nitrogen is an essential nutrient for algal growth because it is needed to produce amino acids and proteins. It is usually taken up in inorganic forms such as NO2- or NH4+, with NH4+ being the most prevalent

form in most waste streams and potentially the most preferred source of nitrogen because it requires less energy for microalgae to absorb. However, when adding ammonium to the cultivation solution, there is an equilibrium with ammonia, which is toxic to microalgae above a concentration of about 2 mM. This can be controlled by regulating pH or a calculated supply of nitrogen. Some strains of microalgae have the ability to assimilate organic nitrogen molecules, the most common one being urea.

Phosphorus can mainly only be taken up by microalgae in the form of orthophosphates, while other inorganic or organic forms of phosphorus generally need to be mineralized and converted to orthophosphates first. Phosphorus is vital for energy transfer and genetic material synthesis in algae, impacting overall growth and productivity.

Two distinct algae culture characteristics are delineated based on growth methods: batch culture and continuous flow culture. In batch culture, algal cells initiate growth with an abundance of resources, following a sigmoidal growth curve. The depletion of the growth medium poses a threat to the culture, although this can be mitigated by the incremental addition of small volumes of fresh medium.(1)

A turbidostat is a type of continuous culture system used to grow microorganisms, including algae, at a constant cell density. In a turbidostat, the culture's turbidity, which correlates with cell density, is continuously monitored and maintained at a preset level. When the cell density exceeds this level, fresh nutrient medium is automatically added to the culture vessel, and an equal volume of culture is removed. This process ensures that the algae are always in the exponential phase of growth, where they are most productive. The key advantage of a turbidostat is its ability to maintain optimal growth conditions by keeping the cell density constant, thus preventing nutrient depletion and waste accumulation that could inhibit growth. This system is particularly useful for studying the effects of various environmental conditions on algal growth and for producing large quantities of biomass under steady-state conditions. A chemostat is another type of continuous culture system used to grow algae and other microorganisms. In a chemostat, the growth rate of the algae is controlled by the rate at which fresh medium is supplied to the culture vessel. The dilution rate, which is the rate of fresh medium addition divided by the culture volume, determines the growth rate of the algae. The nutrient concentration in the incoming medium is usually limited to control the cell density and prevent overgrowth. Unlike turbidostat, a chemostat maintains a constant nutrient supply and waste removal rate, which allows the culture to achieve a steady state where the growth rate of the algae equals the dilution rate. This system is ideal for studying the relationship between nutrient concentration, growth rate, and cellular physiology. (1)

The imperative for a hydrothermal liquefaction process is to attain a biomass concentration of 200 g/L. HTL converts wet biomass into biocrude oil under high temperature and pressure, mimicking the natural geological processes that produce fossil fuels. Many cultivation systems necessitate multiple dewatering steps to achieve this elevated biomass concentration, often leading to a misleading estimation of the operational and capital costs associated with a cultivation system. (2)

Distinctive strategies exist to influence lipid growth in algae by manipulating their nutrient access during the growth phase. Initiating growth with a sufficient nitrogen supply and subsequently subjecting the cultivation to nitrogen deprivation stimulates increased cell production. Upon nitrogen deprivation, the cells redirect their resources towards enhanced production of carbohydrates and lipids. A similar dynamic is observed in relation to salinity, where escalating salt levels induce a reduction in metabolism, thereby augmenting the production of lipids and carbohydrates in the algae. These manipulations are applied in controlled environments to maximize lipid yield, which is crucial for efficient biofuel prod.(1)

2.2.2 Open pond system

The most prevalent cultivation method for algae is the open pond system, which is designed to emulate algae growth in natural lake environments. These ponds are typically about one foot deep and can be expanded in area as needed to optimize sunlight exposure. However, the open pond system faces challenges such as insufficient agitation and limited sunlight penetration, leading to suboptimal mass and heat transfer. To address these issues, open raceway pond (ORP) systems are often used. ORP systems incorporate a closed-loop recirculation system with paddles that enhance mixing and facilitate the circulation of carbon dioxide, improving overall growth conditions.(1)

Despite its cost-effectiveness in terms of construction and operation, the open pond system has significant drawbacks. It is highly susceptible to contamination from external sources, such as other microorganisms, and is vulnerable to weather-related disruptions that can affect growth rates and productivity.

A crucial but often overlooked aspect of operational costs in open pond systems is the dewatering process and harvesting. The costliness of this process is due to the typically low biomass concentration achieved in these systems, which is generally below 0.5 g/L. This is a significant shortfall compared to the minimum biomass concentration of 200 g/L required for efficient HTL processes. HTL processes convert wet biomass into biocrude oil, necessitating a high initial biomass concentration to be economically viable. Consequently, the low concentration in open pond systems leads to the need to use flocculation before harvesting to be able to harvest. After harvesting the algae need several dewatering steps to concentrate the biomass sufficiently for HTL. (4)

2.2.3 Photobioreactors

The photobioreactor (PBR) stands out as a closed reactor system, presenting a compelling alternative to open pond systems (OPS) due to its notable advantages in terms of enhanced productivity and the

production of high-quality algae. However, it is imperative to acknowledge that both capital and operational costs associated with PBRs are considerably higher. Researchers have developed various iterations of PBRs, including tubular, bubble, plate, horizontal, foil, and porous configurations. The predominant PBR variant employs tubular solar arrays, which maximize exposure to sunlight and enhance photosynthetic efficiency. (1)

A key strength of PBRs lies in their capacity to exert precise control over the growth environment. This includes meticulous regulation of temperature, illumination strength, and duration, the imposition of optimal light and dark cycles, pH balance, and effective contamination management. PBRs offer the capability to introduce carbon dioxide into the water through controlled pumping and agitate the water to improve mass transfer, ensuring that nutrients and gases are evenly distributed throughout the culture.

These controlled conditions enable PBRs to achieve higher productivity and produce algae with consistent quality, which is crucial for biofuel production and other high-value applications. Despite these advantages, it is noteworthy that photobioreactors typically yield a cell density of approximately 6 g/L, which is higher than that of open pond systems but still presents a challenge in terms of achieving the biomass concentration needed for downstream processes such as hydrothermal liquefaction. (1, 4)

2.2.4 Biofilm cultivation

The Rotating Attached Biofilm (RAB) algae cultivation system represents an innovative approach where cells thrive while attached to the surface of a supporting medium. This system involves the placement of a rotating cylinder-shaped biofilm within a rectangular pond. When the algae grow on the biofilm, the harvested mass has a significantly elevated biomass concentration of approximately 200 g/L. Remarkably, this obviates the necessity for any dewatering processes that are often a costly part of the process. In direct comparison to Open Raceway Pond (ORP) systems, the RAB system demonstrates a remarkable enhancement in productivity, achieving up to a 700% increase under identical growth conditions. (2, 4)

The average growth rate of the RAB system is reported to be 40 g/m^2 day, highlighting its efficiency in biomass production. (2, 4)

The rotation of the cylinder in the RAB system induces dark and light cycles, optimizing growth by enhancing photosynthetic activity and mitigating photoinhibition. Additionally, the reduced water volume in the RAB system is advantageous, contributing to heightened mass-transfer efficiency for carbon dioxide and essential nutrients such as nitrogen and phosphorus. Furthermore, the RAB system exhibits a reduced reliance on antibiotics and pesticides due to the inherent resilience of biofilms to contamination.

This multifaceted approach positions the RAB system as a promising and efficient methodology for algae cultivation. (2, 4)

2.2.5 Harvesting And dewatering

In algae cultivation, harvesting typically represents 20-30% of operational costs due to the low concentration of algae, which often necessitates flocculation . However, the Rotating Attached Biofilm (RAB) system offers a simpler and cheaper alternative. The harvesting process involves scraping biomass from the biofilm using a scraper blade. The blade traverses the entire cylinder, moving from one end to the other while the cylinder rotates continuously. This operation, lasting two hours, consumes 120 kWh per day and is conducted daily after sunset, achieving a harvesting efficiency of 90%. The residual biomass on the biofilm serves as a valuable inoculum for subsequent cultivation cycles. The RAB system attains a notable biomass concentration of 200 g/L, eliminating the need for costly dewatering processes before employing Hydrothermal Liquefaction. (4)

2.3 HTL

Hydrothermal Liquefaction is a thermochemical process used to convert microalgae biomass into valuable bio-oil. This process operates in an aqueous environment at medium temperatures (280-370°C) and high pressures (10-25 MPa), conditions that facilitate the breakdown of complex organic materials. During HTL, the entire microalgae biomass is utilized, including proteins, carbohydrates, and lipids, resulting in the production of bio-oil, an aqueous solution containing polar organic compounds, a gaseous phase, and a solid residue.(7)

One of the key advantages of HTL is its comprehensive use of microalgae components, which differentiates it from other biofuel production methods that primarily focus on lipids. This holistic utilization enhances the overall efficiency and yield of the process. The bio-oil produced can be further refined into various fuels, while the aqueous phase, rich in organic compounds, can serve multiple purposes.(7)

Heat recovery is a critical aspect of HTL, significantly enhancing its energy efficiency. This is typically achieved through a heat exchanger, which recovers heat from the aqueous phase and bio-oil. The recovered heat can be reused within the HTL process, reducing the overall energy requirement. Additionally, the gaseous phase produced during HTL can be utilized in an auxiliary burner to provide supplemental heat energy, further improving the sustainability of the process.(2)

Nutrient recycling is another important feature of HTL. The nutrient-rich aqueous phase contains significant amounts of nitrogen and phosphorus, essential for the growth of microalgae. These nutrients can be recovered and reused, reducing the need for external fertilizers and enhancing the economic viability of the process. Phosphorus can be extracted from the residual solid phase through acid extraction. This involves mixing the solid residue with sulfuric acid and stirring for approximately two hours, which dissolves the phosphorus, allowing it to be separated and reused. Similarly, the aqueous phase can be diluted with water to facilitate the recovery of nitrogen.(2)

Recent advancements in HTL technology have focused on optimizing these recovery and recycling processes to improve overall efficiency and sustainability. Research is ongoing to develop more efficient heat exchangers, enhance nutrient recovery techniques, and find better uses for the gaseous by-products. As these technologies advance, HTL could play a pivotal role in sustainable biofuel production, offering a more complete and efficient use of microalgae biomass.

2.3.1 Reaction pathway for HTL

The reactions for algae in a HTL process occur between 200-320 degrees celsius. Different Algae will respond differently to temperature and pressure. Looking at Chlorella pyrenoidosa (CP) and Spirulina platensis (SP) from (11). shows the yields over an HTL process at different temperatures for algae CP and SP. Generally, the biocrude yield increases as the temperature rises from 200 degrees to 300 degrees, then decreases, which applies to both algae types. The opposite can be observed for the aqueous phase yield, which decreases with increasing temperature for both algae. The solid residue decreases with increasing temperature, which is expected due to thermal decomposition occurring more rapidly and extensively. As expected, the gas yield also increases with higher temperature. Overall, similar trends are achieved for the two different algae, but there are small differences. The different results are because the unique chemical structure each algae possesses. Looking at the graph there are some similarities, the solid residue decreases for both cases with the temperature and the gas production increases with temperature. Both algaes have the lowest aqueous fraction at 280 degrees celsius. The highest bio-oil yield for CP is at 280 deg C with a yield of around 45% and at 300 deg C for SP with a similar yield to CP.

During a GC-MS analysis the chromatograms for the bio-crude oil samples showed components created at different temperatures. shows that fatty acid derivatives were the dominant chemical composition for both algaes. The fatty acid gets reduced with higher temperatures up to 280 deg C while the amides increases and then reverse from 280 deg C to 320 deg C. The long-chained hydrocarbon is a product from the fatty acids during decarboxylation during hydrolysis of the lipids during the reaction. The cyclic oxygenates increases for both CP and SP with temperature, a similar trend can be seen for N&O-heterocylic compounds in the bio-crude oil. This can be explained with higher temperatures may promote

recombination and repolymerisation of the reaction intermediates. Esters, ketones and alcohols decreases with increasing temperature.

Hydrothermal liquefaction is a thermochemical conversion process used to transform algal biomass into valuable biocrude oil, gases, and aqueous phase products. This process involves subjecting the biomass to high temperatures and pressures in the presence of water, leading to a series of complex chemical reactions. These reactions work synergistically to break down the biomass and convert it into different products. The primary reactions occurring during HTL include hydrolysis, depolymerization, decarboxylation, dehydration, hydrogenation, repolymerization, cracking, and reformation. One of the initial reactions in HTL is hydrolysis, where water molecules break down larger molecules into smaller ones. For example, lipids in algal biomass are hydrolyzed into fatty acids and glycerol, proteins into amino acids, and carbohydrates into simple sugars. This reaction is facilitated by the high temperature and pressure conditions of HTL, making the complex biomass components more accessible for further conversion. Following hydrolysis, depolymerization breaks down complex polymers such as proteins, polysaccharides, and lipids into simpler monomers. For instance, polysaccharides are converted into monosaccharides, and proteins are reduced to peptides and amino acids. Depolymerization ensures that the large biopolymers are sufficiently fragmented to undergo further chemical transformations. Decarboxylation is another critical reaction in HTL, involving the removal of carboxyl groups from molecules, resulting in the release of carbon dioxide. This reaction is particularly significant in the conversion of fatty acids and amino acids, reducing their molecular weight and transforming them into hydrocarbons and gases. In addition, dehydration reactions remove water molecules from organic compounds, leading to the formation of double bonds and the production of alkenes and aromatics. Dehydration helps in reducing the oxygen content of the bio-oil, which is essential for improving its quality and stability. Hydrogenation involves the addition of hydrogen to organic molecules, saturating double bonds and further reducing the oxygen content. This reaction plays a crucial role in upgrading the bio-oil by converting alkenes to alkanes and enhancing its overall quality. During HTL, repolymerization can also occur, where smaller molecules recombine to form larger, more complex structures. This process can lead to the formation of heavier bio-oil fractions and char. While repolymerization might seem counterproductive, it is a natural consequence of the dynamic HTL environment, contributing to the overall complexity of the resulting products. Cracking reactions, on the other hand, break larger hydrocarbon molecules into smaller ones, producing lighter hydrocarbons and gases. This reaction is essential for converting the heavy bio-oil fractions into more valuable lighter fractions, enhancing the yield of desirable products. Finally, reformation reactions, including water-gas shift reactions, produce hydrogen and other gases. These reactions contribute to the overall gas yield in HTL and play a significant role in the thermochemical conversion process. Research studies have demonstrated the effects of these reactions in HTL. For example (23) showed that higher temperatures in HTL lead to increased conversion of biomass into liquid and gaseous products, with a corresponding decrease in solid residues. Similarly, (24) reviewed the various sub- and supercritical water technologies used in thermochemical biofuel production, highlighting the importance of these reactions in the overall process.
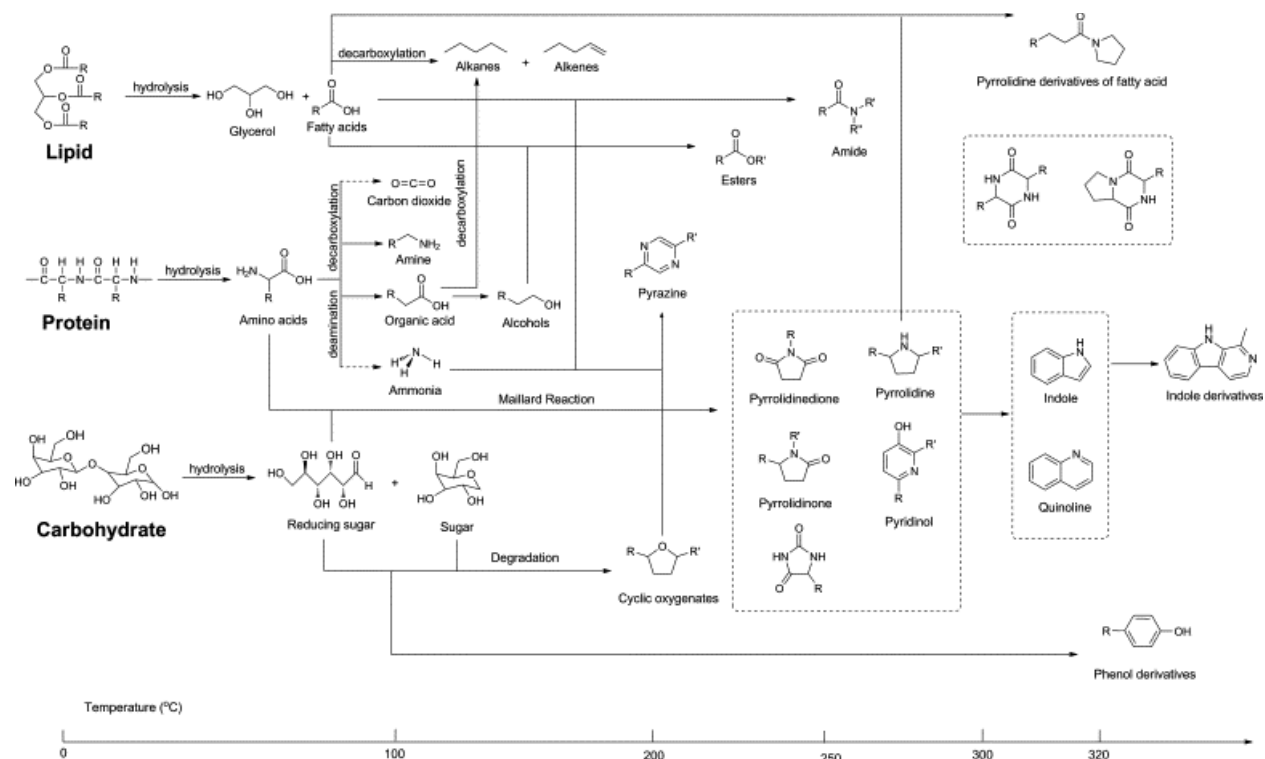
Fig 1. General reaction network of HTL on microalgae (11).

In the temperatures between 0-100 deg C protein is hydrolyzed to produce amino acids and some fatty acids. Lipid is hydrolyzed to produce glycerol and fatty acids with long carbon chains and carbohydrates is hydrolyzed to produce reduced sugars and non-reduced sugars. Between 100-200 deg C amino acids, fatty acids and sugars will undergo further decomposition. Amino compounds are produced by decarboxylation of the amino acids. Some amino acids will produce carboxylic acids and ammonia during deamination which removes the nitrogen from the algae. Some alkenes and alkanes are produced from long-chain fatty acids from decarboxylation during hydrolysis of lipids and amino acids. Above 200 deg C the hydroxyl groups in the long-chained fatty acids are replaced by ammonia from deamination of amino acids to produce aliphatic amine compounds. Some of the fatty acids will react to the alcohols from reduced amino acids to produce esters. N&O-heterocylic compounds are produced by maillard reaction between the amino acids and reduced sugars.

Lipids reaction

The lipids in microalgae are non-polar compounds with the form of triacylglycerols (TAGs). During HTL TAGs are hydrolyzed into fractions namely glycerol and fatty acids. Glycerol can then be hydrothermally decomposed to produce aldehydes or alcohols. The degradation of glycerol in super critical water are mainly methanol, ethanol, acrolein, allyl alcohol, formaldehyde, propionaldehyde, acetaldehyde and gas products.
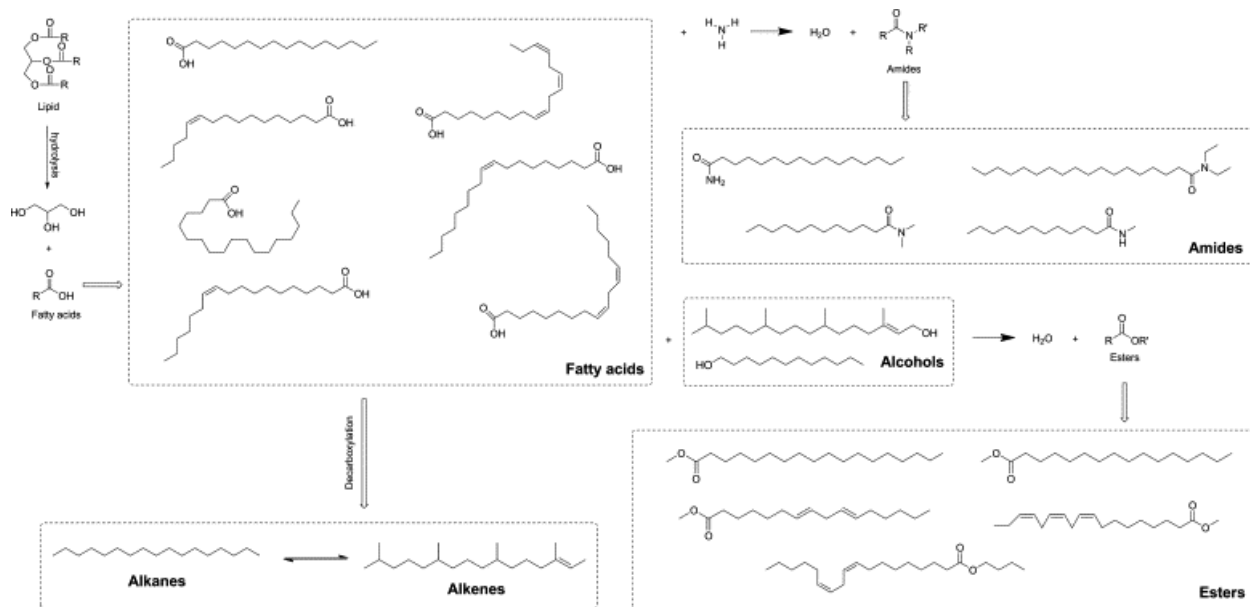
Fig 2. predicted pathway for lipids in HTL

2.3.2 Catalysts used in the hydrothermal liquefaction process

It is possible to use various catalysts in the HTL process to facilitate the conversion of microalgae biomass into bio-oil. The catalyst used for algae liquefaction in HTL can be classified into homogenous (water soluble) and heterogeneous (non-water soluble) The absence of a catalyst significantly diminishes the yield of bio-oil. The catalyst selection depends on the specific objectives of the bio-oil, which may influence factors such as yield, required temperature, pressure, and more. The hot water may be the factor that enhances the solubility of less-soluble organic compounds and the availability of ions (H+ and OH-), which are crucial for initiating and catalyzing the intermediate reactions of interest, such as hydride transfer, nucleophilic addition, versus cleavage and cracking. When supercritical water is used in the process, radical species are commonly generated, which results in the production of gaseous reactions. Regardless of whether super critical water is utilized or not, the rapid depolymerization of the polymeric compounds in the algae biomass occurs during the initial stages of the reactions. The polymerization or degradation process is contingent upon the species involved. According to certain literature, it has been suggested that the rapid degradation of carbohydrates does not result in the production of oil, but rather produces oxygenates such as aldehydes and ketones. However, these derivatives may undergo further conversion into hydrocarbons, including aliphatics and aromatics, especially in the presence of selective catalyst systems. The lipids in the biomass usually degrade into triglyceride derivatives and, consequently, glycerol. The fatty acid constituents possess a distinct resistance to degradation and, consequently, can undergo decarboxylation to yield hydrocarbons. The protein compounds known as polymeric derivatives of amino acids coupled with peptide linkages. They are susceptible to rapid hydrolysis under hydrothermal conditions, resulting in the production of amino acid monomers that then transform into

nitrogenous compounds in the final bio-crude oil. During the upgrading process, they also produce ammonia and nitrogenous gases. (6)

2.3.2.1 Homogenous catalysts

The soluble catalysts, also referred to as homogenous catalysts, are catalyst systems that exist in the same phase as the reactants. The most common forms of such catalysts are minerals and organic acids, their corresponding salts, metallic cations of transition elements (Zn^{2+} and Co^{3+}), and alkali compounds. Their function is to facilitate the cleavage of C-C bonds within the algae biomass, thereby enhancing the hydrolysis process and enhancing the dehydration process. After the HTL, these processes are responsible for the production of oxygenates, hydrocarbons, gasses, and solid residues. However, some studies suggest that homogenous catalysts are not suitable for producing hydrocarbons suitable for gasoline, diesel, and jet fuels. (6)

2.3.2.2 Heterogeneous catalysts

Heterogeneous catalysts can be used to mitigate the problems encountered with homogeneous catalysts. The heterogeneous catalyst, which is composed of solids, exists in a distinct phase with the reaction media. Their primary advantages are the ability to separate the phases at the end of the process and the possibility of reusing the catalyst after several cycles. Catalysis involves the adsorption-desorption of reactant species over the catalyst surfaces. This will initiate the intermediate stage of the reaction with sequential elementary steps. The catalyst should promote rapid bond cleavages, facilitate bio-oil production, and produce fuel-range hydrocarbons. catalysts used for heterogeneous processes are usually metals (Pd and Pt supported over carbon), zeolites, and SiO_2 and Al_2O_3.

The use of Chorella vulgaris sp and nannochloropisocculta sp as algae in reference (6) yielded 36% and 34% respectively. Using the catalyst, the active metals were despatched onto the alumina support via an incipient impregnation method involving 20 percent metal loading, except for Co, which was only 6 percent. The process of algal valorization was then carried out at a temperature of 350 degrees Celsius, employing a catalyst-water ratio of 1:9 for a duration of 1 hour. The ratio of Pt/Al_2O_3 and $CoMo/Al_2O_3$ was 39%, while the ratio of Ni/Al_2O_3 was 30%. For the nannochloropisocculta, all the catalysts decreased the yield of bio-oil. Upon conducting a chromatographic analysis of the bio-oil, it was observed that paraffinic and aromatic hydrocarbons were present subsequent to the incorporation of the catalyst. This was attributed to the elevated frequency of C-C and C-O cleavages, which result in their susceptibility to deoxygenation of oxygenates. A catalyst utilizing Ni/REHY (zeolite) was employed, resulting in the production of a bio-oil of. (6)

Several other studies have demonstrated that the incorporation of Pd/C and $CoMo/Al_2O_3$ catalyst can enhance the bio-oil yield from a non-catalytic process of 35% to 57% and 55%, respectively. Without a catalyst, the reaction mainly produced oxygenates.

Table 1. Effect of different heterogeneous catalyst during HTL (6)

Catalyst system	Algae species	HTL conditions	Bio-oil Yield	Bio-oil product
Non-catalytic	Nannochloropsis sp.	350 °C, 1 h, 0.384 g of catalyst, 95% water volume.	35	Mainly oxygenates.
Pd/C	Nannochloropsis sp.	350 °C, 1 h, 0.384 g of catalyst, 95% water volume.	57	Mainly C_{15} to C_{18}, 20%.
Pt/C	Nannochloropsis sp.	350 °C, 1 h, 0.384 g of catalyst, 95% water volume.	49	Mainly C_{15} to C_{18}
Ru/C	Nannochloropsis sp.	350 °C, 1 h, 0.384 g of catalyst, 95% water volume	50	Mainly C_{15} to C_{18}.
Ni/SiO$_2$-Al$_2$O$_3$	Nannochloropsis sp.	350 °C, 1 h, 0.384 g of catalyst, 95% water volume.	50	Mainly C_{15} to C_{18}.
CoMo/Al$_2$O$_3$	Nannochloropsis sp.	350 °C, 1 h, 0.384 g of catalyst, 95% water volume.	55	Mainly C_{15} to C_{18}.
Mainly C_{15} to C_{18}.	C. pyrenoidosa	7 g algae, 70 ml water, 0.35 g catalyst, 300 °C, 20 min	52	C_6 to C_{16}, > 20%

Sodium carbonate (Na_2CO_3) serves as a cost-effective catalyst, doubling the conversion to bio-oil and boasting an impressive 80% chemical recovery. Zeolites, with their cracking capabilities, can also act as catalysts, reducing molecular weight and enhancing bio-oil quality. However, given the inherent hydrocracking step in the process, zeolite catalysts may not be imperative.

(8) Used dry powdered S. platensis and tested HTL with three different catalysts Na_2CO_3, NiO and $Ca_3(PO_4)_2$. The experiment was done at 300-350 degrees celsius for 30-60 minutes with a ranging biomass concentration of 10-20%. The amount of catalyst used was based on 5% of the biomass weight. The reactor reached pressure up to 20.6MPa and was continuously stirred using a impeller at 300 rpm.

The results concluded that both NiO and $Ca_3(PO_4)_2$ favored gas formation and decreased the bio-oil yield while the Na_2CO_3 increased the bio-oil yield. (8)

Table 2. Comparing HTL with Na2CO3 with no catalyst for different temperatures and time. (8)

T(Celcius)	t(min)	Yield of biocrude oil (wt%)	Yield of biocrude oil (wt%)
		Non-catalytic	Catalytic
300	30	31.3±0.95	37.5±1.12
300	60	32.7±1.12	40.3±2.25
350	30	34.5±0.77	42.3±1.23
350	60	39.9±2.45	51.6±2.30

Table shows the impact of using a catalyst to increase the bio-oil yield but also the importance of increasing the time and temperature for better results. However that can be misleading due to the addition of operational costs when increasing the temperature and the operating time.

2.5 Biofuel upgrading

Hydrothermal liquefaction of algae is a promising method for converting algal biomass into biocrude oil. However, HTL biocrude typically contains high levels of oxygen, nitrogen, sulfur, and other impurities. To transform this biocrude into a high-quality, stable biofuel suitable for use as a drop-in replacement for conventional petroleum fuels, a refining process known as hydrotreatment is essential.

2.5.1 Hydrotreatment

Hydrotreatment, also referred to as hydroprocessing, is a catalytic process that improves the quality of HTL biocrude by removing impurities and enhancing its properties. The necessity of hydrotreatment arises from the need to reduce the oxygen content in biocrude, which contains significant amounts of oxygen in the form of alcohols, acids, esters, and phenolic compounds. High oxygen content leads to poor

fuel stability, high acidity, and lower energy density. By reducing the oxygen content, hydrotreatment improves the fuel's stability and calorific value.

Additionally, hydrotreatment removes nitrogen and sulfur, which are present in the biocrude due to the accumulation of these elements in the algal biomass. These heteroatoms need to be eliminated to prevent the formation of nitrogen oxides (NOx) and sulfur oxides (SOx) during combustion, as these emissions are harmful pollutants. Furthermore, hydrotreatment enhances the overall fuel properties of biocrude by increasing its hydrogen content, reducing viscosity, and improving distillation characteristics, making it more comparable to conventional fossil fuels. The process also stabilizes the biocrude by removing reactive components that could lead to polymerization and other reactions during storage and transportation.

The hydrotreatment process involves treating the biocrude with hydrogen at elevated temperatures and pressures in the presence of a catalyst. The primary reactions occurring during hydrotreatment include hydrodeoxygenation (HDO), hydrodenitrogenation (HDN), and hydrodesulfurization (HDS). Hydrodeoxygenation removes oxygen from organic compounds as water, converting oxygen-containing compounds into hydrocarbons and water. Hydrodenitrogenation removes nitrogen from organic compounds as ammonia, breaking C-N bonds and hydrogenating the resulting fragments to form hydrocarbons and ammonia. Hydrodesulfurization removes sulfur from organic compounds as hydrogen sulfide, breaking C-S bonds and hydrogenating the resulting fragments to produce hydrocarbons and hydrogen sulfide. (23)

The hydrotreatment process typically begins with pre-treatment, where the biocrude is filtered to remove solids and heavy residues that might deactivate the catalyst. The biocrude is then heated to the required reaction temperature and mixed with hydrogen gas. This mixture is passed over a catalyst in a reactor vessel under high pressure and temperature. Common catalysts used include sulfided cobalt-molybdenum (Co-Mo) and nickel-molybdenum (Ni-Mo) supported on alumina. The reaction products are subsequently separated into gaseous, liquid, and solid phases. The upgraded biocrude is collected as the liquid phase, while gases such as hydrogen sulfide and ammonia are removed. (23)

Hydrotreatment of HTL biocrude offers several significant benefits. It produces a high-quality, stable biofuel with properties similar to conventional petroleum fuels. By reducing the levels of nitrogen and sulfur, it minimizes the emissions of harmful pollutants such as NOx and SOx. The upgraded biofuel is compatible with existing fuel infrastructure and engines, requiring no modifications. Additionally, by improving the quality and stability of the biocrude, hydrotreatment enhances its market value and commercial viability.

In summary, hydrotreatment is a crucial step in upgrading biocrude derived from HTL of algae. It significantly improves fuel quality by removing oxygen, nitrogen, and sulfur, stabilizing the biocrude, and enhancing its overall properties. Through hydrodeoxygenation, hydrodenitrogenation, and hydrodesulfurization, the process produces a high-quality, stable biofuel that can serve as a sustainable alternative to conventional fossil fuels.

2.5.2 Hydrocracking

Hydrocracking is a subsequent refining process that follows hydrotreatment to further upgrade biocrude derived from hydrothermal liquefaction of algae. While hydrotreatment primarily focuses on removing impurities such as oxygen, nitrogen, and sulfur to stabilize the biocrude, hydrocracking is essential for breaking down larger, heavier hydrocarbon molecules into smaller, more valuable fractions suitable for use as transportation fuels. This process significantly enhances the quality and commercial viability of the final biofuel product.

Hydrocracking is necessary to further improve the properties of HTL biocrude by converting heavy, high-molecular-weight hydrocarbons into lighter products such as gasoline, diesel, and jet fuel. The biocrude produced from HTL, even after hydrotreatment, still contains a range of complex hydrocarbons that may not meet the specifications for conventional fuels. Hydrocracking helps achieve the desired fuel characteristics by improving fuel quality, increasing the yield of desirable products, and enhancing the stability and compatibility of the biofuel with existing fuel infrastructure.

Hydrocracking is a catalytic process that occurs at high temperatures, typically between 350-450°C, and high pressures, ranging from 70-200 bar, in the presence of hydrogen. The process involves two main steps: cracking of heavy hydrocarbons and hydrogenation of the resulting fragments. In the cracking step, long-chain hydrocarbons in the treated biocrude are broken down into shorter-chain hydrocarbons. This is facilitated by the use of bifunctional catalysts, which possess both acidic and hydrogenation-active sites. The acidic sites promote the cracking reactions, while the hydrogenation sites stabilize the resulting fragments. The smaller hydrocarbon fragments produced during cracking are then hydrogenated to saturate any remaining double bonds, preventing the formation of undesirable compounds and enhancing the stability of the final product.

The hydrocracking process involves several stages to ensure efficient conversion and separation of the desired products. The hydrotreated biocrude is first preheated and mixed with hydrogen before being fed into the hydrocracking reactor. Inside the reactor, the mixture is exposed to high temperatures and pressures in the presence of a bifunctional catalyst. Common catalysts used in hydrocracking include platinum or palladium supported on zeolites or other acidic materials. The reaction products are subsequently separated into gaseous, liquid, and solid phases. The hydrogen is recycled back to the reactor, while the liquid products are further refined to obtain specific fuel fractions such as gasoline, diesel, and jet fuel.

Hydrocracking offers several significant benefits in the upgrading of HTL biocrude. The process produces high-quality, stable fuels with properties comparable to conventional petroleum-derived fuels. It maximizes the yield of valuable liquid fuels, enhancing the economic viability of the biofuel production process. The flexibility of hydrocracking allows for the adjustment of the process to produce different ratios of gasoline, diesel, and jet fuel, depending on market demand and feedstock characteristics.

Additionally, the resulting biofuels are compatible with existing fuel distribution and consumption infrastructure, facilitating their adoption and use.

3 Method

This chapter will go over the chosen algae species and choice of cultivation backed by facts and advantages. Furthermore goes into the building of the process simulation in a aspen plus which is a simulation program often used in chemical engineering to simulate different processes in this thesis it is mainly focused on the design of the HTL and hydrotreater.

There are several assumptions needed to make this evaluation of the process and the cost of the process. Firstly the scaling, the cultivation is designed for a small amount of harvest by increasing the amount of algae yield each day some problems occur that will not be taken into account. Such problems are additional piping due to a larger land mass also requires more transport of nutrients and such. The cost of building more of something does not always scale 1:1 however in this thesis scaling is made 1:1 in some cases due to lack of time.

Second assumption is the HTL process, as it has not been laboratory tested the simulation and other studies is the only results that has been taken into account. Thus the resulted yield and what is produced can differ in reality.

3.1 Comparing different cultivation methods

To choose the right cultivation process for the process table 1 is introduced looking at three different cultivation methods, OPS, PBR and RAB. The table goes over seven different criteria capital cost, operational cost, harvesting cost, growth control, biomass concentration, growth per square meter and seasonal, ranking each category from 1-5 where 1 is the best score then ending with a total score. This way of evaluating the different methods has its flaws, mainly it is evaluated by literature data from a few sources to make this table more reliable. Each category needs to be evaluated further and more sources need to be looked at. However as a representation it works to choose the optimal cultivation method.

Table 1 displays the strengths of different algae cultivation methods. Starting with cost, the open pond system (OPS) is by far the cheapest alternative (1), followed by the Rotating Attached Biofilm (RAB) system (3), and then the Photobioreactor (PBR) (5). This is because constructing a pond is very inexpensive and does not require much maintenance. The PBR requires a tank, lights, and a stirrer, while the RAB system involves multiple inexpensive ponds and a rotating cylinder with a polymer growth film. Harvesting algae in OPS (4) is challenging due to the large area and small particle size thus flocculation is needed to harvest. In contrast, PBRs (2) have a controlled environment where harvesting is integrated into

the system and requires minimal additional effort. The RAB system (2) uses scraper blades, which are both time and cost-efficient.

Growth control in OPS (5) is difficult because it is open and can easily be contaminated with bacteria and other algae, making the process unpredictable. PBRs (1), being extremely controlled environments, can maintain specific algae strains and ensure consistent product outcomes. The RAB system (2) is less controlled than PBRs but offers some protection from contamination through the cultivation film, and additional measures such as water filtration and greenhouse cultivation improve control further.

In terms of biomass concentration, OPS achieves around 0.5 g/L, PBRs achieve 2-6 g/L, and RAB systems achieve approximately 200 g/L, significantly reducing the need for dewatering before proceeding to the next step. OPS (4) requires a large area to be effective, and the concentration yielded per square meter is low. PBR systems(1), often built vertically, yield high growth per square meter. RAB (2) has great growth compared to area used however it does not compare to PBR it can be built vertically. Seasonal growth is limited for OPS due to exposure to environmental and seasonal changes, while PBRs, housed in reactors, are not affected by weather except for potential heating or cooling needs. RAB systems, especially when augmented with greenhouses, have a longer growing season.

The RAB system scores the highest in this comparison, making it the clear winner, although the importance of each point has not been precisely weighted.

Table 3. Overlooking three different cultivation methods with a score 1-5 for each category with the lowest number being the best.

Cultivation method	OPS	PBR	RAB
Capital cost	1	5	3
Operational cost	2	4	3
Harvesting cost	4	2	2
Growth control	5	1	2
Biomass concentration	5	4	1
Growth per square meter	4	1	2
seasonal	5	1	3
Total score	25	18	16

The chosen cultivation system will be a Rotating Attached Biofilm (RAB) system with additional features. Specific size and measurements will be calculated in subsequent stages; however, preliminary figures are derived from existing research. The cultivation process involves placing rotating cylinders with

biofilm in rectangular-shaped pools, each measuring 200 meters in length, 1 meter in width, and 0.2 meters in depth. A total of 100 similar ponds will be employed, with each cylinder rotating around its axis at a constant rate driven by an electric motor, consuming 1440 kWh per day. The use of multiple smaller ponds reduces contamination risks and facilitates easier refilling and harvesting. To enhance environmental control, the ponds are covered with six greenhouses, regulating temperature during colder seasons and minimizing contamination and weather-related damages. Each pond accommodates 30.3 cubic meters of water, and blowers introduce flue gas to enhance carbon dioxide levels.

The chosen microalgae strain is Freshwater Chlorella vulgaris, which has a lipid content of approximately 45%. This lipid content is achieved by subjecting the microalgae to iron-increasing and nitrogen-limiting conditions during a steady phase. Despite the growth limitation induced by nitrogen deficiency, the microalgae exhibits a growth rate of approximately 20 g/m^2 per day. The carbon source for the microalgae is derived from CO_2, introduced with flue gas comprising 15% CO_2. The daily CO_2 requirement is 9220.43 kg, facilitated by blowers with an energy consumption of 720 kWh per day. The blowers also keep the water flowing to maximize the mass transfer of nutrients and CO_2 to the algae.

Both nitrogen and phosphorus are vital for growth, and fertilizers, urea, and diammonium hydrogen phosphate, are used to provide these nutrients. Due to ammonia volatilization and phosphorus precipitation, the efficiency for nitrogen and phosphorus is 0.9 and 0.95, respectively. Nutrient recycling is implemented by reusing the residual aqueous and solid phases from the Hydrothermal Liquefaction process, with recovery rates set at 90% for nitrogen and 30% for phosphorus, resulting in daily quantities of 193.53 kg and 86.523 kg, respectively.

Considering water evaporation and losses during harvesting in biofilm cultivation, an approximate daily loss of 260 cubic meters is noted. This lost water is replenished from treated tap water using coagulation, decantation, filtration, and disinfection processes, consuming 332 kWh per day, along with an additional 13 kWh per day for pumping purposes.

3.1.1 Algae cultivation

The goal is to produce 100,000 tons of bio oil each year, necessitating careful calculations of the required area, as well as capital and operational costs. These calculations will be done in Excel to provide an easy overview and facilitate quick adjustments of variables. The chosen cultivation method is RAB, which aims to achieve a dry algae biomass production rate of 40 g/m² per day, with a theoretical maximum of 120-150 g/m² per day. (16)

Each pond will be 200 meters long and 1 meter wide, covering an area of 200 m². Above each pond, a cylinder equipped with a rotator and balancer will be installed to ensure continuous rotation. This rotation facilitates the dark and light cycles essential for algae growth, aids in nutrient uptake from the water, and prevents the algae from drying out. The ponds will be housed within a greenhouse measuring 205 meters

in length and 150 meters in width, totaling an area of 30,750 m². This number is taken from (16). However to reach desired goal of producing 100,000 ton bio-oil per year the cultivation needs to be scaled up to an appropriate size.

Blowers will provide water circulation and inject carbon dioxide, enhancing algae growth. The selected biomass growth rate is 0.04 kg/m² per day.

Table 4. Table from excel that overview the area needed to produce a certain amount of algae.

Algae cultivation		
	value	prefix
Amount of bio-oil per year in ton	100000	ton/year
Amount of dry algae produced in ton each year:	166666.6667	ton/year
amount of dry algae per day:	555555.5556	kg/day
Rotating pond length:	200	m
Rotating pond width:	1	m
Rotating pond area:	200	m2
Growth in dry algae:	0.04	kg/m2*d
pond growth:	8	kg/pond*d
harvesting effeciency	90	%
Amount of ponds:	77160.49383	
Minimum ponds:	77161	
Amount of greenhouses	772	
Area of greenhouse	30750	m2
Added area for roads etc	20	%
Area needed	28486800	m2
Hectare	2849	ha
Number of öland	5.377196459	%
Number of fotball fields	4070	
OPS		
conc	0.00371	kg/m2 day
area	179694519.3	m2
	17970	ha
number of öland	33.91653927	%
number of fotball fields	25672	
RAB	6.307476307	

To produce 100,000 ton bio oil each year some assumptions need to be made, firstly looking at the aspen simulation the bio-oil yield is around 60%. The biomass is then calculated by dividing the bio-oil by 0.6. The algae produced per day is calculated by divide the amount of algae produced per year by 365 which is a bit unrealistic especially depending on where the algae farm is located. So a more realistic scenario would be to only harvest 300 days per year therefore dividing the produced algae per year by 300, this

results in a minimum of 555 ton of algae per day needs to be harvested. Each pond have an area of 200 m^2 and each pond produce 4 kg per day with a harvesting efficiency of 90% the number of ponds is then calculated by dividing the required algae per day by the pond growth times the harvesting efficiency. When it is rounded up the result is 46297 ponds, each greenhouse fits 100 ponds and requires an area of 150m x 205m. To make it more realistic 20% i added for roads and such in between the greenhouses this number could be an underestimate.

Table 5. Showing the cultivation energy needs for the different components

Energy calculations		
	value	prefix
Electric rotating motor:	0.1	kW
operating time	24	h
energy needed	185186.4	kWh/d
Blower:	0.05	kW
operating time	12	h
energy needed	92593.2	kWh/d
Harvesting scraper:	0.1	kW
Operating time:	2	h
Energy needed:	15432.2	kWh/d
water pump	0.088	kWh/m3
water pump energy	2874.96	kWh/d
water filtration and uv	0.11	kWh/m3
filtration and uv energy	3593.7	kWh/d
Total energy	300	MWh/d
Water needed		
water loss per pond:	0.4234	m3/pond
Total water loss	32670	m3/d

Each electric motor has an effect of 0.1 kW and works continuously during the whole day to prevent the biofilm and remaining algae from drying up. The energy needed is calculated by multiplying by the amount of ponds as each pond requires one electric motor. Blowers' energy needs are calculated the same way except each pond requires 2 blowers. For the water pump energy the water loss needs to be calculated first with each pond losing 0.4234 m^3/pond per day due to evaporation and the water the algae absorbs. Multiplying the loss with the amount of ponds needed result in a total loss of 65,400 m^3/d. The water pump energy and filtration and uv energy is then calculated by multiplying the total water loss. The total energy is the acquired by summarizing the total energy for each components resulting in 600 MWh/d.

Table 6. Added components both nutrients and carbondioxide

added components	value	prefix
	value	prefix
NH4NO3	0.32255	kg/pond
total NH4NO3	25	ton/d
NH4NO3 recovery	90	%
NH4NO3 total	2.5	ton/day
P2O5	0.1442166667	kg/pond
total P2O5	12	ton/d
P2O5 recovery	30	%
P2O5 total	8.4	ton/day
CO2	2.16	kg/kg biomass
total CO2	1200	TON CO2/day

Both ammonium nitrate and Phosphorus pentoxide are used as nutrients for the algae growth. Ammonium nitrate is used to introduce a nitrogen source and phosphorus pentoxide is used as a phosphorus source for the algae. The total ammonium nitrate is calculated by multiplying the kg/pond with the amount of ponds same calculation for the phosphorus pentoxide. The amount of carbon dioxide is depending on the amount of algae produced and results in 1200 ton per day. There are several options for nutrients for both the nitrogen and phosphorus sources but stated earlier for applying the same growth as source (13) the best option is to keep the nutrients the same.

Important note the scaling of the cultivation is linear in the calculations but in reality the large scale of the cultivation requires a lot of transporting to each greenhouse with water, nutrients and carbondioxide. The transportation of algae to the HTL process is also required with a small scale cultivation these transportation is negligible compared to everything else.

3.2 Aspen

The Chorella vulgaris will be selected as the algae for the simulation. The whole process schema can be seen in figure x in appendix.

The algae can not be found in the conventional library so it must be put in as a non-coventional solids as well as ash. The method chosen is Soave-Redlich-Kwong (SRK) and the stream class chosen is MIXCINC these properties are chosen from (17). Because the algae is a non-conventional material, density needs to be calculated by using the property method DCOALIGT and enthalpy is calculated using HCOALGEN. Using these approximation method requires PROXANAL, ULTANAL and SULFANAL to be filled in to calculate the values for density and enthalpy. Which is done in the algaestream in the NC solid tab.

The ULTANALand PROXANAL table are taken from source X. SULFANAL is calculated from the sulfur source from the ULTANAL table with calculation 1,2 and 3.

1. Pyritic = 0,45 * sulfur
2. Sulfate = 0,1 * sulfur
3. Organic = 0.45 * sulfur

Table 7. ULTANAL table for chorells vulgaris

ELEMENT	VALUE
ASH	8,7
CARBON	47,4
HYDROGEN	6,5
NITROGEN	8,8
CHLORINE	0
SULFUR	0,8
OXYGEN	27,8

Table 8. PROXANAL table for chorells vulgaris

ELEMENT	VALUE
MOISTURE	80
FC	18,4
VM	72,9
ASH	8,7

Table 9. SULFANAL table for chorells vulgaris

ELEMENT	VALUE
PYRITIC	0,36
SULFATE	0,08
ORGANIC	0,36

A pump is then placed to increase the pressure to 20 MPa which is the preferred pressure for the HTL process. After the pump the stream goes into a heat exchanger as the cold stream and the warm stream coming from the HTL reactor. The stream then continues to a heater to reach the optimal temperature of 320 degrees celcius. After the heater the stream goes into a Ryield reactor to break up the biomass into components instead. The yield has to be calculated from the ULTANAL table 7 using equation 1 to 7.

1. YIELD H = (1 -Xmoisture)*XH*mFeed = (1-0.8)*0.065*100 kg / 100

2. YIELD O = (1 -Xmoisture)*XO*mFeed = (1-0.8)*0.278*100 kg / 100

3. YIELD N = (1 -Xmoisture)*XN*mFeed = (1-0.8)*0.088*100 kg / 100

4. YIELD S = (1 -Xmoisture)*XS*mFeed = (1-0.8)*0.008*100 kg/ 100

5. YIELD C = (1 -Xmoisture)*XC*mFeed = (1-0.8)*0.474*100kg / 100

6. YIELD ASH = (1 -Xmoisture)*XASH*mFeed = (1-0.8)*0.087*100 kg/ 100

7. YIELD H2O= Xmoisture*mFeed = 0.8*100 kg/ 100

Table 10. Yield specification in the Ryield

Component	Basis Yield
C	0,0948
O	0,0556
N	0,0176
H	0,013
H2O	0,8
ASH	0,0174
S	0,0016

After the Ryield the stream continues into a STOIC reactor to produce the bio-oil, water phase and gas phase. This reaction was first done in a RGIBBS reactor that minimizes the Gibbs free energy without an attached reaction set or as a reactor using equilibrium reactions. However several problems occurred with the RGIBBS reactor, the first one was the equilibrium reactions that caused some molecules to be favored even though they should not. This occurred because the RYIELD divided the biomass into components and not molecules. RYIELD could have divided the biomass into the infinite amount of components of algae biomass possess but the amount of different molecules is hard to portray efficient and true. But one could make a case for selecting a few molecules that represent the protein, carbohydrates and lipids however that same effect would occur with some molecules would becomes dominant in the RGIBBS reactor due to the similar structure some posses. The other problem that occurred with using a RGIBBS with a RYIELD was that the RYEILD could not divide the components into pure elements. This meant that nitrogen became nitrogen gas which will not react at all as it should because in reality it is a bound into the biomass. This resulted in that no nitrogen components would form in the RGIBBS reactor. Therefore A STOIC reactor was chosen Where the yield number for the bio-oil components was taken from PNNL source. The problem with the stoic reactor is that the results are already set and is not affected by the temperature and pressure. This posses as a screwed reality not yielding the true results. However due to problem phasing RGIBBS it was the most reliable and closest to reality solution that worked.

The stream then continues to the heat exchanger to provide heat to the incoming algae stream. Then proceed to a valve to release the pressure down to 1 atm.

Separation is done in three steps, firstly a screen to remove the solids, secondly distillation tower to get rid of the gases present in the stream followed by a decant to separate the water from the bio-oil.

The stream then continues into a mixer with a second stream containing hydrogen gas for the hydroprocess. Then it goes into a pump to to reach the desired pressure for hydroprocessing at 100 bar followed by a heater to reach 400 degrees celsius.

The stream then goes into the hydroprocess which is a RGIBBS reactor. This reactor produce gas, diesel, nafta and heavy oil that require further hydrocracking to convert into more gas, diesel and nafta. No separation has been done in aspen but by calculating the amount of different

4 Results

This chapter will go over the results yielded from chapter 3 methods, including a economic overview.

4.1 Cost cultivation

Some costs are not the true value from a supplier but are estimations made because the item/product it is not in market.

Table 11. Shows the capital cost to build all the greenhouse.

Cultivation items	units	cost per unit	Cost mil$
Water filtration	354	500	0.177
UV	39	4000	0.156
Pumps	3088	125	0.386
Pipes pvc	168,682	1	0.168682
Greenhouse	772	661980.7756	512
rotating cylinders	77,200	500	38.6
ponds	77,200	5677.383112	439
blowers	154,400	200	30.88
rotating motors	77,200	50	3.86
water cleaning			0.887682

By far the building of the ponds and the greenhouses requires the most money, the greenhouse price is calculated from (18) with 2$ per square foot making it 21.5 $ per square meter this is also the lowest estimation so the number could be higher. The pond price was calculated by calculating the volume of the ponds with the concrete wall width taken into account and subtracting it by the volume of the pond. Then multiply the volume with concrete cost from(19) .

To get the total capital cost the same calculations as in the process cost are made. Adding all the values from table 11 we get the TIC then the TDC must be calculated followed by the indirect cost to get the total.

Electric bill prices comes from (20) and a prices in sweden.

Table 12. Operational cost for the cultivation

Added components	Cost	
NH4NO3	450	$/ton
NH4NO3 amount	2.5	ton/day
NH4NO3 cost	1125	$/day
P2O5	1400	$/ton
P2O5 amount	8.4	ton/day
P2O5 cost	11760	$/day
electrical	300	MWh/d
electrical cost	83.8116	$/MWh
electrical cost	25144	$/day
total	38029	$/day

Table 12 display the cost to operate the cultivation including nutrients and electrical costs. The most expensive are the electrical bill followed by the phosphor nutrient and lastly the nitrogen nutrient. The phosphor is more expensive and require more input each day due to worse recirculation of phosphor.

4.2 Results process

The HTL yielded a 60% bio-oil yield with various compounds listed in appendix at images x and x.

Table 13. HTL products streams yielded from aspen plus simulations.

HTL products streams	Yield wt%
Water phase	86.5% (92% water)
Biocrude	12.5% (60% yield from algae)
Gas	1%

Table 14. Display the percentages of the 100,000 bio oil each year and in the far left the total weight in ton.

amount of bio-oil	100,000		total in ton
amount of disel	70.5	70500	77166
nafta	12.3	12300	15330
gas	7.1	7100	7504
hydrocracker	10.1	10100	
hydrocracker-disel	66	6666	
hydrocracker nafta	30	3030	
hydrocracker gas	4	404	

Table 14 shows the yield after the hydrotreatment simulated in aspen plus as well as the hypothetical hydrocracking yield calculated from (14)

4.3 Cost process

The cost for the process include everything after the cultivation to the final product for example HTL, hydrotreater, hydrogenplant, CHG wastewater treatment, hydrocracker and all the parts to integrate the process. The calculations for the cost is taken from PNNL source, however to calculate for the difference in flow and size. The process in this thesis has a flow of 44% of the PNNL flow to calculate a approximate capital cost.

8. TCIB = TCIA*(CB/CA)E

TCIA = total cost of investment of project A ($)
TCIB = total cost of investment of project B - estimated ($)
CA = capacity of project A (t/y)
CB = capacity of project V (t/y)
E = scaling exponent = 0.7 (this exponent may change depending on the type of project or industry).

The cost for the process also includes parts that have not been simulated in aspen but should be part of the HTL process to make it complete, mainly a CHG wastewater treatment, heavy oil hydrocracking and a hydrogen plant.

Table 15. Shows each part that is used for the complete HTL process everything is in MUSD (million us dollars)

HTL Process	PNNL purchased (14)		my process purchased
HTL	85.9		48.67182371
CHG wasterwater treatment	81.4		46.12207742
HTL hydrotreating	24.7		13.99527411
Heavy oil hydrocracking	5.7		3.22967864
Balance of plant	10.4		5.892746992
hydrogen plant	28.6		16.20505423
Total installed cost (TIC)	236.7		134.1166551

Using equation 8 the cost is lower, TIC is then used to calculate other parts of the building process that is not visible at first hand table 15 shows this.

Table 16. Display of additional costs to build a process.MUSD (million us dollars)

Buildings (1% of TIC)	2.367		1.341166551
Site development (9% of TIC)	21.303		12.07049896
Additional pipping (4.5% of TIC)	9.6		5.439458762
Total direct cost (TDC)	269.97		152.9677794
			0
Indirect cost			0
Prorated expenses (10% TDC)	26.997		15.29677794
Home office and construction fees (20% TDC)	53.994		30.59355587
Field expenses (10% TDC)	26.997		15.29677794
Project contingency (10% TDC)	26.997		15.29677794
Startup and permits (5% TDC)	13.4985		7.648388968
Total Indirect	148.4835		84.13227865
			0
Fixed Capital investment	418.4535		237.100058

The additional costs are crucial to get a more realistic number as the capital cost. The building cost site development and additional pipping is all correlated to the total installed cost (TIC). The indirect costs are correlated to the total direct cost (TDC) and are needed to construct a process.

Table 17. Operational costs for the HTL process. MUSD (million us dollars)

Operational cost			0
Hydrotreater catalyst	1.02		0.5779424934
CHG catalyst	7.21		4.085260174
Hydrocracking catalyst	0.02		0.01133220575
Hydrogenplants catalyst	0.24		0.135986469
Natural gas	6.64		3.76229231
electricity	2.97		1.682832554
water makeup	0.09		0.05099492589
total	18.19		10.30664113

Table 17 Shows the cost to run the process year around with the highest cost being the CHG catalyst to clean the water phase after the HTL from hydrocarbons and other unwanted carbon molecules. Natural gas is the second largest operational cost to provide to the hydrogen plant to produce hydrogen to be able to upgrade the bio-oil into finished product both in the hydrotreater as well as the hydrocracker. Lastly is the electricity to run the whole process the other cost are negligible.

Table 18. Workers needed for the operate the process. MUSD (million us dollars)

Position title	number	total cost
Plant manager (1)	1	0.15
Plant Engineer (1)	1	0.07
Maintenance Super (1)	1	0.06
Lab manager (1)	1	0.06
Shift supervisor (5)	5	0.24
Lab technician (4)	4	0.16
Maintenance Tech (7)	7	0.28
Shift Operators (25)	25	1.2
Yard Employees (4)	4	0.11
Clerks & Secretaries (1)	1	0.04
Subtotal		2.36
Overhead & maintenance	90% of labor and supervision	2.124
Maintenance capital	3% TIC	7.101
insurance and taxes	0.7% FCI	2.9291745

4.3 Final result

The final result displays the outcome of the whole process from growing the algae to the final product in the form of diesel and nafta.

Table 19. Display the operational cost.

OPERATIONAL COST PER YEAR	MUSD	USD / M²	USD / Kilo
Operational cultivation	11.4	0.40	0.11
Operational process	10.2	0.36	0.10
Total Operational Cost	21.6	0.76	0.22

Table 19 Show the total operational cost for both the cultivation and the HTL process in million us dollars and also display the total operational cost per year. The cultivation cost is the most expensive due to a lot of electrical cost and not being able to recover enough phosphor. Table 19 also goes over the cost for each square meter used and how much each kg of biocrude cost to produce.

Table 20. Display the total revenue from both nafta and diesel.

SALES ASSUMPTIONS	Market Street Price in USD (tonnes)	Market Street Price in USD (kilo)
Disel	1,400	1.4
Nafta	650	0.7
PRODUCTION PER DAY	Annual production (tonnes)	Daily production[tonnes]
Disel	77,166	214
Nafta	15,330	43

Table 20 display what products the process can sell each year and for what price is the market prices.

Table 21. Shows the capital cost for cultivation, process, the total capital cost and years to payback the capital cost.

INVESTMENT ASSUMPTIONS	MUSD	USD / M^2	USD / kg
Capital cultivation	3,638	127.7	36.38
Capital process	237	8.3	2.37
Total Capital Investment	3,876	136.0	38.76

Table 21 shows the capital investments needed to build the cultivation and the process. Cultivation stands for almost 95% of the total capital investment which is extremely high. It also makes the price på square meter used and kg of biocrude extremely expensive.

Table 22. Yearly income and break even price.

INCOME STATEMENT	MUSD / YEAR
Sales Disel	108.0
Sales Nafta	10.0
Total Income	118.0
Direct and Operational Cost	-21.6
Gross Margin	96.4
Yearly "annunity" cost	-275.0
Result	-178.6
Break-even bulk tonne price	$3,206.13

Table 22 shows that with the market price for nafta and diesel the yearly results is in the negative with -178.6 MUSD this results is mostly due to the yearly annuity cost from paying back the extremely high capital investment. The interest rate is at 5% and the plant life is at 25 years. Break even price is then calculated to not lose money each year and it is around 3200 dollars per ton which is more than 2 times the market price for diesel and 5 times the amount of nafta which is not reasonable at the current state.

4.4 Theoretical optimal maxima for economic overview

Theoretical optimal maxima for economic overview is made to see if variables change for the better within a reasonable amount, what results can be yielded and is that result a possibility in the future.

In the dream scenario the first variable to change is the growth from 0.04 kg/m^2*d to 0.12 kg/m^2*d which is the theoretical maximum. Next change is to up the amount of recovered phosphorus from 30% to 90% which is possible with extracting the phosphorus from the solid phase from HTL. Then reducing the cost

to build ponds and greenhouses to 20% of their original cost. Lastly increase the amount of bio-oil yield from the HTL from 60% to 80%

Table 23. Display the capital cost for the best case scenario as well as displaying the years to pay back the capital cost.

Capital cultivation	236.098542	mil $
Capital process	237.100058	mil $
capital total	473.1986	mil $
Years to pay back	5.199984616	

By implementing the changes the years to pay back are reduced down to 5.2 years which is a much more reasonable amount of time.

First variable to change is the growth increasing it to the maximum growth of 0.12 kg/m^2*d from 0.04 kg/m^2*d. This change have huge impact on the whole system reducing the capital cost from 3640 million $ to 1220 million $ reducing the cost to a third of its original cost. One observation can be made that the growth is almost 1:1 with the capital cost. The operational cost goes from 28200 $/day to 12700 $/day, the change is not quite as large as the capital cost this is because only the electrical prices changes due to less equipment needed, however the nutrients stay the same and only needs to be more concentrated.

The next variable to change within reason is the amount of nutrients than can be recovered, the nitrogen nutrient is already at 90% and can not be recovered any further. Phosphorus however is only at 30% and with extracting of the solid phase from the HTL the recovery could go up to 90%. Lastly reducing the cost to construct the ponds and greenhouse to 20% of the original cost.

With all theses best case scenario changes the capital cost for the cultivation goes down to 320 million $ and the operational cost is down to 9400 $/day resulting in a revenue of 90 million $ per year. THe amount of years to pay back the capital cost goes from 87 to 6 years.

4 Discussion

The discussion will be divided into several parts first discussing the cultivation process both the procedure and the cost to operate and build it. Followed by the HTL process doing the same thing as the cultivation and lastly putting them together and summarize.

4.1 Discussion cultivation process

Looking at the yielded results reveals some glaring problems due to the chosen cultivation process. Firstly the amount of space needed is one of the positives only taking into consideration that OPS take up 6.3 times more space than the RAB. However a deeper comparison needs to be made not only looking at the utilized area but also cost including capital and operational. Same comparison should be made with PBR aswell to get a better picture of the most lucrative cultivation method.

The energy required to operate the cultivation is heavily depended on the blowers to provide CO_2, rotating motors and the harvesting scrapers. This problem mainly comes down to a scaling problem, the sources that was mimicked had smaller scale cultivation while this process needed to produce more than 100 times the amount. This caused the small prices to add up and become a problem, by converting each cylinder to a larger conveyor belt with a biofilm would reduce the amount of rotating motors to larger one which could be more effective. Furthermore reduce the amount of blowers by replacing them for larger more effective ones to still provide the same amount of flue gas and provide circulation in the water. The amount of scarper would also be reduced to one for each conveyor belt however the harvesting time would most likely increase. This solution merits further investigation to address the scaling issues in such cultivation.

Comparing the energy requirements further would be interesting because dewatering is a huge part of OPS and PBR, but without further investigation a higher biomass from the RAB may be insignificant compared to the drawbacks when it comes to cost. Comparing the harvesting further for OPS and PBR would also be interesting as it usually stands for 20-30% of the operating costs.

The cost for nutrients to operate the process is about 34% and most of that cost comes from the phosphorus nutrient cost. Even though more nitrogen is needed, about 90% of the nitrogen used can be recycled from the water phase from HTL and only about 30% can be recycled for phosphor. This could be a larger percentage if the solid phase could extract the phosphor in a better, less expensive way. However in this article the recycling of nutrients is not looked upon enough to make any assumption other than what other studies have shown, thus more research is needed.

As 1200 tons of CO2 are required per day, a process that produces a substantial amount of CO2 or carbon capture should be nearby. It is also possible to gather CO2 from the CHG wastewater treatment and other parts of the plant however that may come with unwanted substances, but more research is needed to evaluate the feasibility of this operation. Water requirements may also pose a problem, as the ponds lose approximately 10,891 m³ per day. However, about 15% of this water should be recycled after CHG wastewater treatment.

4.1.1 Discussion cultivation cost

The main issue with this process is the capital cost of cultivation, particularly the expenses related to the greenhouse and ponds. As outlined in Section 3.1.1, one solution involves converting the cylinders to a conveyor belt system, which would significantly reduce pond costs because fewer large ponds are cheaper than numerous smaller ones. Another option is removing the greenhouse, but this presents challenges. First, contamination would likely increase despite the natural resistance of the biofilm. Second, leaves and other debris could get stuck on the biofilm, inhibiting growth. Third, blowers would be less effective due to wind, impacting flue gas injection and carbon dioxide absorption efficiency. Lastly, without the temperature stability provided by a greenhouse, cultivation could not operate as many days annually, and the equipment's lifespan could be affected by environmental conditions.

Ponds and greenhouses represent over 90% of the costs, so smaller expenses are negligible by comparison. In terms of operational costs, 66% is attributed to electricity, with 62% of the electrical bill stemming from the rotating cylinders. As rotating motors are essential, costs cannot be cut unless the conveyor belt solution is implemented to reduce the number of motors and, consequently, the electrical expenses. Approximately 30% of the electricity cost comes from blowers; a possible solution is using larger blowers solely for flue gas, though an alternative stirring mechanism would be required.

The remaining operational costs involve nutrient addition for growth. While the nutrient amount should not be altered to maintain growth, better nutrient recycling could reduce costs. Nitrogen, which is water-soluble and present in the water phase from HTL, can be recycled up to 90% after CHG wastewater treatment. However, phosphorus nutrients pose a challenge, as only 30% can be recycled through the water stream. Most phosphorus ends up in the solid phase and requires extensive extraction, necessitating further research to determine its feasibility.

The method for calculating total and indirect costs is based on Source (15), but scaling from cultivation to process construction should be reconsidered, as some expenses may vary. Potential green environment government funding for promising biofuel projects could be factored into the techno-economic analysis, but should not solely determine the payback period or break-even price. Such funding can also help lower loan interest rates, further reducing break-even costs. Bulk purchasing might lower some prices, but the exact reduction is uncertain and likely requires supplier input.

4.2.1 Discussion on the whole process

There is renewed interest in producing liquid fuels from algae through catalytic hydrothermal liquefaction, which can yield bio-oil suitable for diesel, gasoline, and jet engines. An alternative is upgrading bio-oil after liquefaction which is done in the selected process. The bio-oil yield depends on the algae species and catalyst used. Homogeneous catalysts like carbonates and hydroxides have been tested, but their inefficiency and non-recyclability limit their use.

Heterogeneous catalysts, such as zeolites, SiO_2, Al_2O_3, and supported metals, have shown promise in algae upgrading. CoMo-based catalysts have also been studied, with bio-oil yields of 20–60%, indicating room for efficiency improvement. Potential enhancements include replacing Co or Mo with Ni, Ru, or Pd, using acidic supports like SO_4/ZrO_2, and adjusting zeolite properties and metal loadings. Further research is needed to fully understand the process chemistry for optimal catalyst design.

As stated in the thesis catalytic hydrothermal liquefaction is not efficient and sustainable to use therefore will the HTL not use any catalyst.

4.2.2 Discussion on the whole process cost

The cost of the process is primarily derived from the PNNL source, using equation 8 for scaling to the appropriate level. However, this may pose scaling issues, considering that the PNNL source is from 2013. An inflation rate should be added to make the cost estimates more accurate. In examining the Total Installed Cost (TIC), the HTL and the CHG wastewater treatment are the most expensive components. While reducing or eliminating HTL costs is not feasible, CHG is not essential for production. An alternative method to clean water from hydrocarbons, without removing valuable nitrogen nutrients, could reduce the capital cost. However, further research is required to make any decisions.

Regarding operational costs, the CHG catalyst is once again the most expensive component, highlighting the importance of finding a replacement for CHG in water treatment. The next highest operational cost is the natural gas used for the hydrogen plant. One potential cost-reduction strategy is to extract methane gas from the gas produced in the HTL process to use as natural gas. However, this process may be costly, and burning methane for energy could be more profitable.

4.3 Final discussion

The process is currently not profitable enough to justify building and suggests waiting for further scientific research before pursuing bio-oil from algae. Even in the optimal scenario, the payback period remains too long, and the break-even price is far above market value. To make this process viable, it is crucial to reduce the cost of algae cultivation. This can be achieved through methods such as increasing production

per square meter or finding cheaper cultivation techniques. Additionally, further advancements in genetic engineering and biotechnology could significantly enhance algae strains, potentially increasing biomass yield and oil content, thus making the overall process more economically feasible. The issue does not arise from the HTL process itself; even if the industrial segment of the process were made more cost-effective and efficient, the primary challenge lies in improving cultivation methods.

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Appendix

H2	0,000166418
N2	0,0138325
H2O	0,8
CO2	0
O2	0,0413894
BIOMASS	0
ASH	0,0174
C	0,00956695
S	0,00110871
CO	0
SO2	0
AMMON-01	0,000458052
METHA-01	3,46684e-05
ETHAN-01	4,20737e-05
METHA-03	6,72505e-05
ETHAN-02	0,000399653
ACETO-01	0,00050385
FORMI-01	0,00399313
ACETI-01	0,00156288
GLYCE-01	0,00079893
3-HYD-01	0,00123751

Image x. First part of the mass fractions from HTL

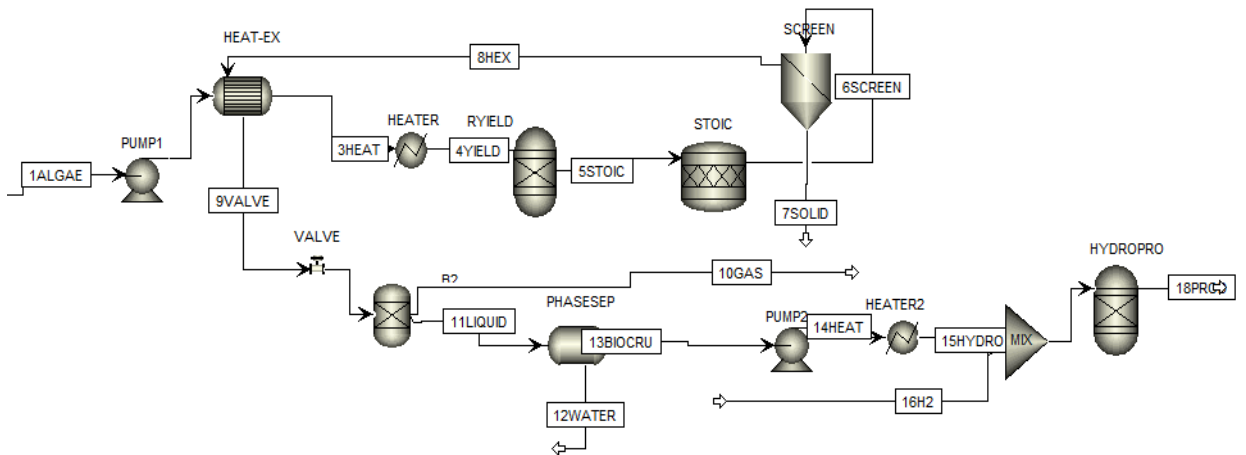|	
3-HYD-01	0,00123751
1-ETH-01	0,00455297
N-MET-01	0,00176501
ETHYL-01	0,00138152
P-CRE-01	0,00281437
P-ETH-01	0,00317942
INDOL-01	0,00304887
7-MET-01	0,00227595
MYRIS-01	0,00394527
PALMI-01	0,019946
OCTAD-01	0,00983748
METHY-01	0,018632
N-HEX-01	0,0133473
ETHYL-02	0,00269379
NAPHT-01	0,00406586
CHOLE-01	0,00359732
DI-N--01	0,0123548

Image x. Second part of the mass fractions from HTL.

Image x. Simulation of the whole process in aspen