

RESEARCH ARTICLE

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The Operation Parameters of Hydrothermal Liquefaction (HTL) Of Algae into Bio-Oil: A Review

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ABSTRACT

Microalgae consists of lipid, protein and carbohydrate in many varieties of the strains. The conventional approach for making biofuels from microalgae has been to subject high-lipid strains to subsequently energy-intensive thermal drying, solvent extraction and transesterification to produce biodiesel. These steps are costly and require the use of organic solvents unhealthy to both humans and the environment. Moreover, lipid-rich strains are usually slow-growing microalgae, and generally lipid mass fraction varies between 20 and 50%. The extraction process of algae is not well defined. Extraction of oil from algae is very difficult as it has very high moisture content and the cell membrane of algae does not rupture easily like that of seed. Pressing, chemical solvent, supercritical fluid and ultrasonic are some of the methods that are being used for algae oil extraction. Hydrothermal liquefaction (HTL) appear to be a promising medium temperature and high pressure thermochemical conversion that process the whole microalgae biomass in order to produce a liquid energy carrier (biocrude oil). The high water content of microalgae makes them a good raw material for hydrothermal liquefaction in subcritical water. The process conditions usually used in the range from 250 to 375 °C, 10-20 MPa and microalgal mass fractions of 5 – 20% in the slurry feed, and shorter reaction time, which can be achieved while consuming only 12% of the energy needed for their complete dewatering. The bio-oil products have low oxygen and nitrogen content that have higher heating value (HHV).

KEY WORDS: algae, HTL, conversion, operating conditions, bio-oils

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I. INTRODUCTION

The world's demand for oil is expected to rise 60% from the current level by 2025.¹ In view of the interesting oil demand and the depleting oil reserves, development of innovative techniques for the production of biofuels from novel renewable biomass feedstock sources are gaining importance all over the world. Biomass, whether terrestrial or aquatic, is considered a renewable energy sources. Biomass can be converted by several processes to intermediate solid, liquid or gaseous. The aquatic biomass represents the strategy that is most ready to be executed on a large scale without any economic or environmental penalty.²

Algae have received a great deal of attention as a novel biomass sources for the generation of renewable energy. Microalgae are microscopic photosynthetic organisms that can be considered as versatile biological cell factories for renewable biofuel production, with higher photosynthetic efficiency, faster growth rates and higher area-specific yields than terrestrial biomass. They have simple growth needs (water, light, a carbon source and nutrients), and their main constituents are

proteins, carbohydrates and lipids. Macroalgae are generally fast growing and are able to reach sizes up to 60 m in length.³ Growth rates of macroalgae far exceed those of terrestrial plants. Brown algae biomass of the average productivity was approximately 3.3 to 11.3 kg dry weight m⁻² yr⁻¹, for non-cultured algae and up to 10 to 13.1 kg dry m⁻² over 7 month for cultured algae compared with 6.1 to 9.5 kg fresh weight m⁻² yr⁻¹ for sugar cane.⁴ Algae are both unicellular and multicellular autotrophic aquatic life forms.

The advantages of algae over terrestrial biomass feedstocks are: (i) algae have higher biomass productivity (40 – 60 dry ton/ha-yr)⁵, than other energy crops; (ii) they have a high carbon sequestration rate (1.8 kg of CO₂/kg of dry algae)⁶, resulting in the reduction of atmospheric CO₂ level; and (iii) they can be grown under conditions which are unsuitable for conventional crop production.⁷ Microalgae can be grown both in fresh water and marine environment, but macroalgae can grow only in marine environment.⁸

The common process operation used for algal-derived fuel production can be grouped into

four main areas: i) Cultivation, ii) harvesting, iii) Extraction, and iv) Conversion of oil into fuel . In the future successes of macroalgal-derived fuel will be dependent on achieving an optimised, energy efficient process in each of these four areas. Many processes for the manufacture of fuels from biomass, such as direct combustion, pyrolysis, gasification, and current commercial biodiesel production, require a dry feedstock and drying is required prior to energy extraction. The inclusion of a drying stage in macroalgae-to-fuels processes will have a significant impact on economic, since the water content of macroalgae (80 – 90%).⁹ Many processes for the manufacture of fuels from biomass, such as direct combustion, pyrolysis, gasification, and current commercial biodiesel production, require a dry feedstock and drying is required prior to energy extraction. The inclusion of a drying stage in macroalgae-to-fuels processes will have a significant impact on economic.

In the past, macroalgae applications mainly focused on their usage as food, animal feed, and bio-fertilizer, cosmetics and medicinal.¹⁰ Recently, algae have received a great deal of attention as a novel biomass source for the generation of renewable energy.¹¹ Conventional approach for making biofuel from algae used transerterification that requires dewatering and drying of wet algae and also used organic solvent for the extraction of lipids which makes it expensive.¹² Recently, studies on hydrothermal liquefaction of aquatic plants such as algae in particular has been increasing and gaining interest as the process is mostly suited for conversion of wet feedstock. Furthermore, in hydrothermal liquefaction of algae, not only the lipids but the whole algae is also used for producing bio-crude and

the total yield is higher than the original lipids in the algal biomass, this suggest that oils are produced from non-lipid component of the algal biomass as well.¹³

I.1 Macroalgae

Macroalgae constitute the most important component in the marine ecosystems that serve for the marine bioresources prevention by preventing eutropication and pollution.¹⁴ Macroalgae belong to the lower plants, in that they do not have roots, stems, and leaves. Instead, they are composed of a tallus (leaf-like) and sometimes a stem and a foot. Some species enclose gas-filled structures to help in buoyancy. They can grow very fast and in sizes of up to tens of meters in length.¹⁵ In their natural environment, macro-algae grow on rocky substrates and form stable, multilayered, perennial vegetation, capturing almost all available photons. Approximately 200 species macroalgae are used worldwide.

Macroalgae are mainly utilized for the production of food and extraction of hydrocolloids, and it is possible to produce ethanol from algae.¹⁶ Macroalgal biomass contains high amounts of carbohydrates at least 50%, which can be used in ethanol fuel production.¹⁷ Microalgae can provide several different kinds of renewable biofuel. These include methane produced by the anaerobic digestion of the algal biomass. Biodiesel is synthesized from the micro algal oil,¹⁸ and biohydrogen produced by a photobiological mechanism. Serious interest is also motivated by concern about global warming that is associated with the use of fossil fuels. The carbohydrate contents of some macroalgae are given in Table 1.

Table 1. Carbohydrate contents of Macroalgae¹⁹

Species	Group (or phylum)	Carbohydrate (%)
<i>Ulva</i>	Green algae	42.0
<i>Enteromorpha</i>	Green algae	64.9
<i>Monostroma</i>	Green algae	63.9
<i>Laminaria</i>	Brown algae	39.3
<i>Alaria</i>	Brown algae	39.8
<i>Sargassum</i>	Brown algae	33.0
<i>Padina</i>	Brown algae	31.6
<i>Porphyra</i>	Red algae	45.1
<i>Rhodymenia</i>	Red algae	44.6
<i>Gracilaria</i>	Red algae	61.75

Macroalgae have low amounts of lignin, they have significant amounts of sugars that could be used in the fermentation process for the production of bioethanol.¹⁷ From an economic point of view it is not viable to produce biofuels from macroalgae with the current technology, except if the production

process is combined with another, such as pollutant removal or the production of bio-based products.²⁰ Macroalgae as feedstock will add a new sector of this area for various commercial applications. Macroalgae have advantages above microalgae, as being easier to harvest, but they grow slower and have lower lipid

content than microalgae.

I.2 Microalgae

Microalgae are photosynthetic microorganism that are found in both marine and freshwater habitats. Microalgae have been classified based on various characteristics such as pigmentation, photosynthetic storage products, the arrangements of photosynthetic membranes, and other morphological features. At present, microalgae species are divided into four groups, namely diatoms (Bacillariophyceae), green algae (Chlorophyceae), blue green algae (Cyanophyceae), and golden algae (Chrysophyceae).¹

As heterotrophs, the algae rely on glucose or other utilizable carbon sources for carbon metabolisms and energy. The biomolecules such as carbohydrates, proteins, lipids, and nucleic acids are the common constituents in microalgae.²¹ Microalgae are not lignocellulosic in composition, and the chemistry is entirely different, involving proteins, lipids and carbohydrates.²²

Microalgae are an especially promising for advanced biofuels production for a number of compelling reasons, including high photosynthetic efficiency, higher area specific yield, possibility of a frequent harvest because of their rapid growth rate. They can also be cultivated in different climates, in saline water and on non-arable land so there is no competition with conventional cropland. Its cultivation can be coupled with wastewater bioremediation since they can also remove nitrogen, phosphorus and heavy metals.²³

Microalgae appear to be an attractive renewable energy source.²⁴ Many strains of microalgae are known to produce high quantities of lipids that can be converted into biodiesel.²⁵ Biofuel production using microalgal farming offers the following advantages:

- Increased efficiency or decrease in the cost. The production cycle does not directly affect the human food chain supply system, avoiding the food against fuel conflict.

Table 2. Oil content of microlagae²⁷

Feedstock	Oil content (% dry wt)
<i>Botryococcus braunii</i>	25 – 75
<i>Chlorella sp.</i>	28 – 32
<i>Chlorella vulgaris CCAP211/11b</i>	19.2
<i>Chlorococcum sp. UMACC112</i>	19.3
<i>Chaetoceros muelleri F&M</i>	33.6
<i>Chaetoceros calcitrans CS 178</i>	39.8
<i>Cryptothecodium cohnii</i>	20
<i>Cylindrotheca sp.</i>	16 – 37
<i>Dunaliella primolelecta</i>	23
<i>Isochrysis sp.</i>	25 – 33
<i>Monallanthus salina</i>	>20
<i>Nannochloris sp.</i>	20 – 35
<i>Nannochloropsis sp.</i>	31 – 68
<i>Neochloris oleoabundans</i>	35 – 54
<i>Nitzschia sp.</i>	45 – 47
<i>Phaeodactylum tricornutum</i>	20 – 30
<i>Pavlova lutheri CS182</i>	30.9
<i>Schizochytrium sp.</i>	50 – 77
<i>Scenedesmus sp. F&M-M19</i>	19.6
<i>Scenedesmus sp. DM</i>	21.1
<i>Skeletonema sp. CS252</i>	31.8
<i>Tetraselmis suecica</i>	15- 23

- Microalgae do not give any competition for land-based plants used for food production, fodder, and other value-added products.²⁶
- Microalgae can grow in fresh, brackish, or salt water environments or non-arable lands that are incompatible for growing other crops and conventional agriculture.²⁸
- The most common microalgae contain oil ranges

between 20 and 50% by dry weight of biomass, but superior productivities can be attained.²⁹

- Microalgae are able to produce various valuable supplementary products such as carbohydrates, proteins, biopolymers, and residual biomass, and these can be used for feed or fertilizer purposes.
- Considering of microalgae as an efficient cellular system for harvesting solar energy for

production of various organic compounds.³⁰

- Microalgae are able to fix carbon dioxide in the atmosphere, assisting the reduction of atmosphere carbon dioxide levels, which is recently considered a global crisis.
- Microalgal lipids are typically neutral lipids. Owing to their high degree of saturation and fast accumulation in the cellular system at various stages of microalgal growth. Oil content of microalgae as shown in Table 2.

In spite of the high productivity, biodiesel from microalgae still has not yet become economical, algal biodiesel has been priced higher than petroleum based diesel.³¹ In comparison oil yield to other crops as shown in table 3. In order to meet the economically feasible co-products with higher value should be produced such as lipid and protein. Extracting lipid and proteins from microalgae prior to HTL improve the economics of the process while at the same time reducing the nitrogen content of the biocrude oil.³²

Table 3. Feedstock oil yield²⁷

Crop	Oil yield (L/ha-Y)
Soybean	450
Camelina	560
Sunflower	955
Rapeseed	1,190
Jatropha	1,890
Oil Palm	5,950
Microalgae	3,800 – 50,800

II. HYDROTHERMAL LIQUEFACTION (HTL) OF ALGAE

The conventional approach for making biofuels from microalgae has been to subject high-lipid strains to subsequently energy-intensive thermal drying, solvent extraction and transesterification to produce biodiesel. These steps are costly and require the use of organic solvents unhealthy to both humans and the environment. Moreover, lipid-rich strains are usually slow-growing microorganisms, and generally lipid mass fraction varies between 20 and 50%.²⁷ The extraction process of algae is not well defined. Extraction of oil from algae is very difficult as it has very high moisture content and the cell membrane of algae does not rupture easily like that of seed.³³ Pressing, chemical solvent, supercritical fluid and ultrasonic are some of the methods that are being used for algae oil extraction.

In order to make microalgae an economically viable alternative for biodiesel production, the revenues from all their fractions need to be maximized. In this context, hydrothermal liquefaction appears to be a promising medium

temperature and high pressure thermochemical conversion that processes the whole microalgae biomass in order to produce a liquid energy carrier (biocrude oil). The high water content of microalgae makes them a good raw material for hydrothermal liquefaction in subcritical water. The process conditions reported in literature usually range from 250 to 375 °C, 10-20 MPa and microalgal mass fractions of 5 – 20% in the slurry feed, which can be achieved while consuming only 12% of the energy needed for their complete dewatering.³⁴

Liquefaction is a medium temperature and high pressure process where biomass is converted into a stable liquid hydrocarbon fuel (bio-oil) in the presence of a catalyst and hydrogen.³⁵ Hydrothermal liquefaction are used for processes where wet biomass is converted to bio-oil in sub- and supercritical solvents or pressurised aqueous pyrolysis.³⁶ But the bio-oil products are lower in oxygen and moisture content than from pyrolysis.³⁷ The ability of hydrothermal liquefaction to handle wet biomass makes it one of the most interesting methods of producing biofuel from algae.³⁸

In hydrothermal processing wet algae can be used to produce oils which can be upgraded and used.³⁹ Moreover this process not only proceeds oil from lipids, as in case of conventional lipid extraction method, but also from carbohydrate and proteins, thereby increasing the total oil production with respect to initial lipid percentage.⁴⁰ High throughput, high energy content, ability to use varied feedstock like waste and lignocellulosic waste, and no need of maintaining specialized microbial cultures or enzyme are some of the added advantages of this process.¹³

III. INFLUENCED OF THE OPERATION CONDITIONS

Bio-oil and other products from Hydrothermal Liquefaction (HTL) of biomass depends upon various operating parameters. The operating parameters include reaction temperature, pressure, reaction time, heating rate, biomass loading, catalysts, solvent, and type of solvent.^{41,42}

III.1 Reaction temperature

Temperature appears to be a critical parameter in the HTL process. Temperature was the most influential parameter upon the yield and properties of bio-oil. Therefore, temperature was selected as the first parameter rather than other variables to investigate its influence on the product distribution and the properties of bio-oil. Typical temperature operation lies on the sub- and supercritical conditions. Typical operating temperatures reported in literature are in the range of 250 – 375 °C.^{12,40,43} Increasing the

temperature leads increasing the bio-oil yield, and then decreases as the temperature further increased above 350 °C.⁴⁴ Increasing the temperature lead the decreases of the oxygen content and a consequently higher heating value (HHV).^{45,46} By surpassing the critical point of water, the biocrude yield starts to decline. Supercritical water enhances radical-induced cracking of biocrude molecules to form lighter, more volatile compounds that form gas, which is consistent with the higher gas yield at supercritical conditions.

At the subcritical range of temperatures, the yield of organics in the aqueous phases appears to decrease with an increase in temperature, indicating that higher temperatures promoted the conversion of intermediate water-soluble products. The gas increases with higher temperature, as well as the concentrations of CH₄ and C₂ hydrocarbons. The solid decreases with higher temperature.⁴⁰

Typical operating temperatures reported in the literature are in the range of 250 – 375 °C, in which bio-oil yield increases with increasing temperature, and then decreases as the temperature is further increased above 350 °C.^{44,45} As the temperature increases, the ionic product of water increases drastically near the critical point, and water in this conditions has ability to hydrolyze complex compounds catalyzed by the H⁺ and OH⁻ ions,⁴⁷ as a result these complex proteins, carbohydrates and lipid macromolecules undergo isomerization, defragmentation/ depolymerization and condensation reactions to form bio-oil. If the temperature goes above critical temperature, ionic product decreases and free radical reactions dominates.⁴⁴ The change in temperature not only exchanges the bio-oil yield but also affects its properties; increase in the temperature also leads to a decrease in oxygen content and consequently higher HHV.^{12,45}

Different studies have reported results of bio-oil as a function of temperature.^{43,44} Anastasakis⁴³ found that bio-oil yield obtained from liquefaction of *L.saccharina* was highest at 350 °C resulted 19.3 wt.%, and decreased as the temperature increased further to 384 °C, and resulted 17 – 18 wt.%. The gas yield increased and the char formation decreased as the temperature increased. Increase in temperature from 250 to 350 °C resulted in increase in carbon content in bio-oil (from 76.6 wt% to 82 wt %) and decrease in oxygen from 10.3 wt.% to 5.4 wt.% content in the bio-oil. Nitrogen content in the oil increased first and then decreased as the temperature increased further.

Alba⁴⁰ also reported that the bio-oil yield from *Desmodesmus sp.* Depended on the reaction temperature between the range of 175 – 450 °C, with the increase of temperature, the yield increased at first and decreased on further increase in temperature. The maximum oil yield 49 wt.% was obtained at 375

°C at 5 minutes reaction time and decreased thereafter. Higher temperature leads to rapid hydrolysis of protein into nitrogen compounds e.g. amines, amides, pyroles and indoles through series of decarboxylation and deamination reactions.^{39,48} The increasing concentration of N compounds in the biocrude is undesired and they pose serious challenges in refining operations.⁴²

III.2 Reaction time

The reaction time is defined as the period during which in the set temperature is maintained for HTL, not accounting for the heating and cooling periods. The effect of reaction time is closely linked to the temperature, to attain a high biocrude oil yield, higher temperatures require lower reaction times. In any case, the reaction time most frequently applied is 60 minutes. These may be an opportunity to optimize the reaction time and temperature in order to minimize the cost of the process, while Alba⁴⁰ attained 49.4% with only 5 min, and at 375 °C.

Normally, high temperature reaction require lower holding time to achieve higher conversion.⁴² In hydrothermal media, the heavier can convert into liquids, gases or residues as a result of secondary and tertiary reactions,⁴⁹ which may occur at higher residence time. Boocock⁵⁰ reported that longer residence times suppressed the bio-oil yield except for very high biomass to water ratios. Alba⁴⁰ observed with the use of sodium carbonate catalyst, there was negligible increase in bio-oil yield for the residence time range of 5 – 60 minutes at 300 °C, but there was significant increase in bio-oil yield at 200 °C. Anastasakis⁴³ reported that increasing the residence time resulted in a decrease of the bio-oil yield, the maximum bio-oil yield of 19.3 wt.% was obtained at 15 min residence time. Jena⁵⁰ observed the bio-oil yield to increase until 60 min and thereafter decreased with further increase in reaction time. Karagoz⁵¹ observed the decomposition products were not similar for longer and shorter residence times both for 180 °C and 250 °C.

Currently, research is mostly focused to enhanced biocrude yield at the shortest possible reaction time.^{53,52} The data obtained in this study confirms that biocrude yields can be produced at very short reaction times, which is economically more advantageous when operating at subcritical conditions. Alba⁴⁰ reported biocrude yield of 49 wt.% from *Desmodesmus sp.* treated at supercritical condition of 375 °C, and 5 min. Similarly various algal strain used by Barreiro⁵⁴ processed at 375 °C, 5 min recorded biocrude recovery biocrude yield of 45.6 – 58.1 wt.%. Faeth⁵³ reported a biocrude recovery of 66 wt.% from *Nannochloropsis sp* processed at 1 minute holding time and at supercritical temperature of 600 °C. The explanation

for higher biocrude yield at short time holding time could be due to the quick release of the intracellular content of the microalgae leading to very sharp decrease in solid residue and increase in high biocrude yield.⁴⁴

III.3 Heating rate

The effect of the heating rate on the biocrude yield remains still unclear. The results for *Nannochloropsis acculata* and *Chlorella vulgaris*, Biller^{39,55} show that no effect can be noticed by increasing the heating rate from 10 to 25 °C min⁻¹.

The heating rate also affects the biomass hydrolysis. For a continuous flow-type reactor, a high heating rate shortens the residence time of the biomass, resulted in a reduced degradation of the glucose product, therefor leading to a high production yield of glucose. Using low heating rate of 0.18 °C/s, the hydrolysis and decomposition reactions occurs in a heterogeneous phase conditions. These compounds probably decompose further to water-insoluble residues at high temperatures.

Using higher heating rates of 2.2 °C/s, the hydrolysis and decomposition reactions can occur in a homogeneous phase. Reactions mechanisms of cellulose under homogeneous and heterogeneous conditions are very different as evident by the formation of "glucose char" in the former or the formation of "cellulose char" in the later. Rapid heating rate avoids biopolymers depolymerize and start degrade before the right reaction temperature is reached. It was observed that cellulose hydrolysis rate in water at 25 Mpa increased tenfold between 240 and 310 °C.⁴⁸

III.4 Effect of Biomass Loading

Biomass loading expressed in precentage of the mass ratio of dry algae to feedstock. Many researchers⁴³⁻⁴⁵ have investigated the potential effect of biomass loading on hydrothermal liquefaction. High biomass to water ratios can suppress dissolution of biomass components and reaction rate due to the relative interactions among molecules of biomass and that of water becoming less influential.⁴⁹ According to Jena⁴⁵, Bio-oil yield from *Spirullina* increased from 32.5 wt.% to 39.9 wt.%, when the solids concentration increased from 10 wt.% to 20 wt.% and then remained constant with further increases to 50 wt.%. Valdez⁴⁴ observed of bio-oil yield from 36 to 46 wt.% of the *Nannochloropsis* concentration in the slurry increases from 5 to 35 wt.%.

With different species of algae might have behaved differently results during hydrothermal liquefaction. Anastasakis⁴³ observed that the bio-oil yield increased as the biomass to water ratio increased from 2/30 to 3/30 and had no influence when the ratio was further increased. In case of the

other effects like loading ratio and residence time for algaes biomass, some studies have been performed but there are not much literatures to fully understand the effect of those parameters and moreover it depends upon the type of algae strains.

The main biochemical composition of algae are carbohydrates, lipids, and proteins. These biochemical components undergoes decomposition/de-polymerization, degradation, re-polymerization to form products. According to Sasaki,⁵⁶ below super-critical region glucose degradation rate was higher than cellulose hydrolysis rate, but as the temperture approached and entered super-critical region cellulose hydrolysis rate proved to be higher than glucose degradation rate. The cellulose hydrolysis rate increased ten fold between 240 and 310 °C in water at 25 MPa, and also at 280 °C within 2 minutes, 100% cellulose conversion was achieved.⁵⁷

Lipids are naturally fats and oils. They are non-polar compounds with mainly aliphatic character,⁴⁸ which can undergo reactions that can convert them into ready substitutes for conventional hydrocarbons.¹³ Rapid hydrolysis of fatty acids were achieved in liquid water at temperature of 330 – 340 °C, for 10 – 15 minutes, giving 90 – 100 % yields of free fatty acids. Fatty acids have high thermal stability but it can be partly degraded at hydrothermal conditions to produce long chain hydrocarbons, which have excellent fuel properties.⁴⁸

Proteins are the major biomass components found in algae. Amino acids are the building block of protein come from algae. Conversion of protein into bio-oil under HTL conditions leads to high nitrogen content in the bio-oil which are undesirable as it produce NOx gases. Considering the stability, peptide bonds are more stable than glycosidic bonds and thus slow hydrolysis of protein is achieved at 250 °C.⁵⁸ According to Rogalinski,⁵⁹ the highest yield of amino acid from hydrolysis of bovine albumin (BSA) was obtained at 290 °C and 65 seconds, but the total yields were very low due to degradation of amino acids. There was complete decomposition of all amino acids at 330 °C and 200 seconds. Macroalgae have higher ash than microalgae, resulting in lower yields of biocrude oil,⁴³ it is indicated that microalgae could be more easily converted into biocrude oil than macroalgae.

III.5 Catalysts

There are many types of catalysts such as homogeneous and heterogeneous catalysts. Homogeneous catalysts employed for HTL are acids (H₂SO₄, HCl, and acetic acid), salts and alkalis (CaCO₃, Ca(OH)₂, HCOONa, and HCOOK⁶⁰; Na₂CO₃, NiO, Ca₃(PO₄)₂).⁶¹ The Acids and alkalis enhance the hydrolysis of algal biomass, while metal

ions favor the dehydration during HTL.⁶² The bio-oil increased for various catalysts in the order of $\text{Na}_2\text{CO}_3 > \text{CH}_3\text{COOH} > \text{KOH} > \text{HCOOH}$.⁶³

They appear to improve the liquefaction yields and decrease the solid residues. These catalysts cause a rise in pH, which inhibits the dehydration of biomass molecules and promotes decarboxylation. It is also believed that they enhance the water-gas shift reaction, favoring the formation of H_2 and CO_2 .⁶⁴ The H_2 gas may act as reducing agent, thus increasing the heating value of the oil.⁴⁸ They are concerns about the role that they play, as they appear to be consumed during the process, so they might be considered as reagents rather than catalysts.

Majority of the work has focused on homogeneous catalysis by acid, alkali or metal salts, because homogeneous catalysts are cheap, compared with heterogeneous catalysts. However, homogeneous catalysts have drawbacks of special requirement on HTL reactor material and being difficult to recycle.⁶¹ In comparison, heterogeneous catalysts have the advantages of reaction selectivity and post HTL separation is more easily.

Several heterogeneous catalysts have been reported in the literature: Pd, Pt or Ru supported on C; CoMo, Ni, Ni/SiO₂, Al₂O₃ and zeolite.¹³ Beside the advantages, they can present several drawbacks, such as sintering, dissolution, poisoning or interparticle diffusion limitations. Duan and Savage⁶⁵ tested six different heterogeneous catalysts, changing the headspace environment used during the reaction (inert with He or reducing with H₂). Ce/HZSM-5 was more superior than HZSM-5 as a liquefaction catalyst of *C.pyrenoidosa*.⁶⁶

Various kinds of biomass resources (i.e. algal, woody, lignin, rice husk) have used in the non-catalytic hydrothermal liquefaction. Non-catalytic hydrothermal liquefaction of algal biomass results in high bio-oil yields. Experimental conditions of some influential literature for non-catalytic hydrothermal liquefaction of biomass was summarized by Tekin.⁶⁷

The presence of heteroatoms such as N, O, and S in the algal biocrude posses major challenges for the downstream refining process to produce fuel products.^{40,55} Elliotts⁶⁸ recently reported that heteroatoms in biocrude could be removed or reduced by hydro-treatment in the presence of suitable catalysts. Catalysts for upgrading of bio-oil from algae used Ni-Ru/CeO₂,⁶⁹ NiMo/Al₂O₃ catalysts were promising to produce high yields in gasoline range.⁷⁰ Galadina⁷¹ also found that solid catalysts given for improving bio-oil quality.

III.6 Solvents

Hydrothermal liquefaction is a medium temperature and high pressure thermochemical

process during which biomass is broken down into fragments of small molecules in water. The light fragments, which are unstable and reactive, can then re-polymerize into oily compounds with various ranges of molecular weights.⁷² Many solvents have been used during this kind of treatment, such as water, ethanol, methanol, acetone and 1,4-dioxane. Among these used solvents, water is the most environmental friendly. Li⁷³ proposed that in the liquefaction of biomass into bio-oil fractions obtained in water have a lower carbon content and higher oxygen content, with lower heating value. To enhance the yield of liquid products with lower oxygen content, hence higher heating value, the used organic solvents have been adopted.⁷⁴⁻⁷⁶

Solvents have remarkable effect on the liquefaction reaction. Some articles reported that the liquefaction of biomass in the present of organic solvents were effectively lowers the viscosity of heavy oil derived from biomass liquefaction.⁷⁶ Although solvents have shown obvious reactive activity in many works, it is still unclear how solvents affect the biomass liquefaction process. Liquefaction of biomass with proper solvents is a process that can prospectively be integrated with optimized conditions to produce fuel and valuable chemicals.⁷⁷ The role of the solvent during treatment is usually to fragment the biomass and stabilise the fragmented products to ensure maximum production of bio-oil. The better solvent is at stabilising the fragments, the higher the oil yield and the lower the solid biochar fraction.⁵⁰ Jin⁷⁸ reported that hydrothermally liquefaction of microalgae in sub-and supercritical acetone, temperature range of 170 – 350 °C, time varies from 5 to 120 minutes. The highest biocrude yield of 60.1 wt% was achieved at 290 °C, the HHV values ranging from 28.7 to 37.1 MJ/kg.

III.7 Organic solvents

Water is very common solvent in hydrothermal liquefaction process for marine biomass.^{41,79,80} The properties of water has well known in sub- and supercritical conditions. In sub- and supercritical conditions the properties of water was change, either density, dielectric constant, ionic product and pkw.⁸¹ The water has two unique feature: one is a high ion product at elevated temperatures. This fact indicates that the water can act as an acid or base catalysts. Another feature is a low relative dielectric constant. It's indicating that the water can be used for extracting hydrophobic substances from natural resources. Water at sub-critical conditions becomes an effective solvent but is significantly less corrosive than other chemical solvents.⁸²

Many researchers used organic solvent for

microalgae conversion into bio-oil, such as acetone⁷⁸, ethanol⁸³. Zhang⁸³ reported that *Chlorella pyrenoidosa* was hydrothermally into bio-crude. The ethanol-water solution have the best performance with highest bio-crude yield of 57.3% and the lowest solid residue yield of 9.4%. Jin⁷⁸ liquefaction of microalgae in temperature varies 170 to 350 °C, acetone microalgae ratio 2/2.5 to 16/2.5, and time varied from 5 to 120 min. The highest bio-crude yields of 60.1% wt.% was achieved at 290 °C.

IV. CONVERSION IN HTL PROCESS

Degradation algae in the HTL process resulted solid residue, liquid water soluble and gaseous products. Biomass of algae has dry basis is solid pattern. The conversion was degradation of the solid into liquid and gaseous.

The complex organic materials in the form of biomass and biogenic waste is cracked and reduced into heavy oil and useful chemicals. Biomass consists of lignin, cellulose and hemicellulose in variety of composition. Algae consists of mostly lipid, protein and carbohydrate in variety of species.

Some of the complex chemical reactions that occur during liquefaction.⁸⁴ Those involved, (1) cracking and reduction of cellulose, hemicellulose, lignin, protein and lipid into smaller fragment; (2) hydrolysis of cellulose and hemicelluloses to glucose and other simple sugar; (3) hydrogenolysis in the presence of H₂; (4) reduction amino acids; (5) reformation reactions via dehydration and decarboxylation; (6) degradation of C-O and C-C bonds and (7) hydrogenation of functional groups. Reactive fragments reacts to each other to built bigger stable molecules that called bio-crude. Some fragment further degradation become gaseous such H₂, metan, CO₂ and CO.

The aims to screen parameters operation is to get higher yield bio-oil and good quality. Higher yield bio-oil can be derived high presentage of oil fraction, higher HHV value can be resulted by the bio-oil that have oxygen and nitrogen in lower contents.

V. CONCLUSIONS

Hydrotherm al liquefaction appears to be promising process that can proceed micoalgae into bio-oil. HTL can be compatible with current algae conversion technology. Algae residue after extraction of biodiesel, such residue or other high-value products can be further converted into biocrude oil via HTL. Thus constituting an example of biorefinery of whole algae. Algae have the ability to contribute to resolving the issues of energy and the environment. The process conditions used to process algae in the range of 250 to 375 °C, 10 – 20 Mpa and microalgal mass fraction of 5 – 20% in the slurry feed. The

residence time 5 – 120 minutes, and bio-oil yield about 45.6 – 58.1 wt.%. HTL of the halophytic microalga *Tetraselmis* sp. indicated that shorter reaction time and temperature below super-critical point would ideal to achieved maximum biocrude yield. HTL treatment with shorter reaction time has many advantages, which include reduction in capital costs and energy consumption. Shorter reaction time is excellent candidate to transform to continue process that closely to real scale up operations.

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