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Sub and Supercritical Fluid Technologies for the Production of Renewable (Bio) Transportation Fuels

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Additional information is available at the end of the chapter

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1. Introduction

1.1. Biofuels and feed stocks

The limitation on the availability of petroleum based fuels and environmental concerns have made humans look at alternative fuels such as biofuels, wind energy, solar energy, hydroelectric power, hydrogen, nuclear energy and so on. Among all these alternative energy sources, biofuels are one of the potential alternative energy sources that can fulfill a part of the current energy demand. The concept of biofuels dates back to the 19th century when researchers tried to use vegetable oil as a fuel for diesel engines. But the problems associated with the usage of oils directly as fuel and the availability of fossil fuels made the concept of vegetable oil fuels uneconomical. Due to rapid depletion of petroleum based fuels, ever increasing consumption of fuels in developing nations and environmental concerns led scientists and governments to develop fuels based on oils or lipids. These oils or lipids cannot be used directly as liquid fuels but can be processed and/or upgraded to be used as a blend or as a direct substitute for the regular fuel. Biodiesel, green diesel, bio-jet fuel or green jet fuel and green gasoline are examples of renewable transportation fuels. Vegetable and plant oils, animal fats, and waste cooking oil from food processing industries have been used as a primary feedstock for the production of renewable transportation fuels. Along with these sources, micro algae have also attained significant attention as a source of oil/lipids, due to high productivity of oil compared to plants in a given period of time and area [1]. Apart from the higher lipids, algal biomass is being used as a source for the production of proteins, amino acids and carbohydrates [2, 3]. Cultivation of algal biomass in waste water treatment plants which contribute to the cleaning of water and production of fuels. In spite of having more oil yield than plant crops, algae

feedstock has its own problems of processing the biomass such as harvesting, drying and extraction of oil to produce biofuels. Various processing technologies are available to produce these bio fuels from different feed stock materials. This chapter focuses on the production of biodiesel from oils/fats and wet algal biomass through supercritical alcohol transesterification, novel methods for extraction of oil/lipids from wet algal biomass, liquefaction of whole algal biomass through hydrothermal extraction and liquefaction (HT E&L) and catalytic hydrothermalolysis to produce regular hydrocarbon fuels from oils using supercritical water. Before discussing the biofuels production, the sub and super critical technologies will be discussed.

1.2. Sub and supercritical conditions

As shown in figure 1, the four phases of a pure material or compound can be observed at different temperature and pressure conditions. When a compound is heated above its boiling point and below its critical point under pressure, it is called a subcritical fluid and when a compound is heated above its critical point is called as supercritical fluid. The sub critical and supercritical fluids possess different physical-chemical properties compared to their properties at normal conditions. They are compressibility (like gases) due to reduced densities, increased polarity due to reduced dielectric constants and they have catalytic properties attained by variations in ion dissociation constants. Above the critical point the particular material obtains gas like densities, liquid like solvating properties and intermediate mass transfer kinetics [4]. By varying temperature and pressure, these enhanced capabilities of the sub and supercritical fluids are being used for environmentally benign selective separations, catalytic reactions for production or purification of various products. The commonly known supercritical fluids are water, CO_2 , ethanol, methanol, ethane, methane etc. In this chapter the utilization of water, methanol, and ethanol to produce various kinds of biofuels or fuel intermediates will be discussed.

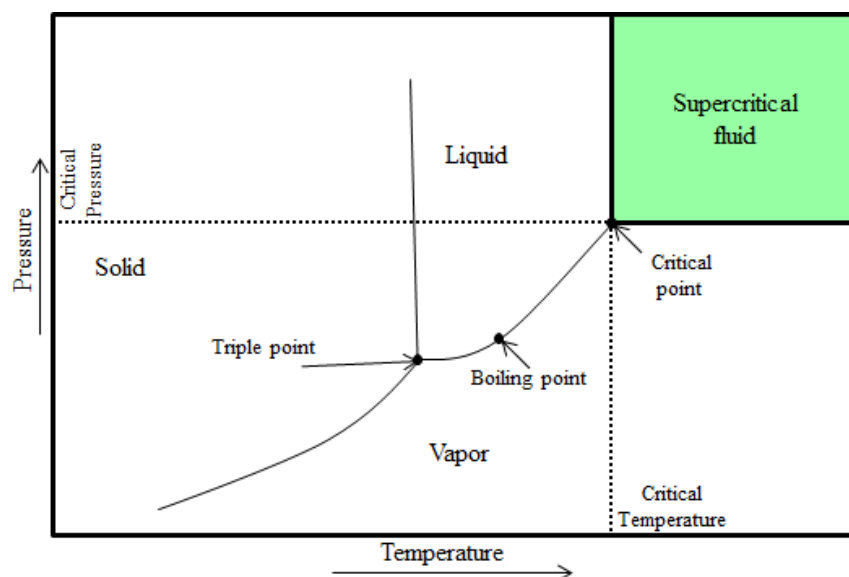


Figure 1. Phase diagram of a pure compound

2. Supercritical alcohol process for the production of biodiesel from oils/fats/lipids

Biodiesel is one of the first generation biofuel developed that is being used in present day transportation. Biodiesel is not a new source of alternative fuel, it has a long history. When Rudolph diesel invented the diesel engine, he also suggested that pure vegetable oils can be used as a fuel in those engines. Three decades later basic research has started to use modified vegetable oil as a fuel in the diesel engine. This modified vegetable oil can be called as biodiesel. It took almost a century after the invention of diesel engine to start extensive research on biodiesel and its use as a fuel. Biodiesel is a fuel derived from biomass such as vegetable oil, animal fat, algae or other renewable resources which consist of long chain alkyl esters. Biodiesel is a nontoxic, renewable, biodegradable, and eco-friendly fuel. Biodiesel produces lower emissions compared to that of regular petroleum based fuels. Biodiesel usage in the place of regular diesel fuel can reduce emissions such as SO_x, CO, particulate matter and hydrocarbons in the exhaust gas and it is better than regular diesel fuel in terms of sulfur content, flash point, aromatic content, and cetane number. Biodiesel does not contribute to a net rise in the level of carbon dioxide in the atmosphere and has the capability of minimizing the intensity of the greenhouse effect. Biodiesel is more promising fuel because of its renewability, energy security and the high energy content consistent with that of petroleum based fuels. Biodiesel can be used as a fuel blend or as a substitute and will have similar properties to that of regular diesel. Several countries around the world have made it mandatory to sell regular diesel fuel with a blend biodiesel and gasoline with a blend of ethanol in order of environmental concerns to address. The blend concentration varies and can be denoted by different notations such as B100 (pure biodiesel), B50 (50% biodiesel, 50% petroleum diesel), B20 (20% biodiesel, 80% petroleum diesel), B10, B5 etc.

There are different processes to make biodiesel from renewable feedstock. These include but are not limited to pyrolysis, micro emulsions, dilution, catalytic cracking, and transesterification. Pyrolysis is a thermo chemical process that decomposes organic material in the absence of oxygen. In this process, the biomass will be converted into bio oil which is similar to crude oil. This oil will be further converted to small chain hydrocarbons via hydro treating and hydrocracking and then used as transportation fuels. Micro emulsions are isotropic mixtures of oil, water and a surfactant; which can be blended with petroleum diesel fuels, solvents such as alcohols and can be used as transportation fuels. Other methods like dilution and catalytic cracking and transesterification can also be used for the production of biodiesel.

Among all these processes, transesterification is one of the most economic and to produce biodiesel simplest way. Transesterification or alcoholysis is a process in which the triglycerides present in the oils chemically react with alcohol to produce alkyl esters with or without the aid of a catalyst. Alcohols like methanol, ethanol, propanol, butanol and amyl alcohol can be used for transesterification. When the transesterification occurs in the presence of methanol, it is known as methanolysis and the esters formed are known as fatty acid methyl esters. Ethyl esters, propyl esters and butyl esters will be produced when their respective alcohols are used in the transesterification process. On an industrial scale, methanol a 'refinery residue' is the

primary alcohol used for the production of biodiesel. Ethanol is an agricultural product which is renewable, non-toxic, eco-friendly and can also be used for biodiesel synthesis. Figure 2 shows a simple mechanism of transesterification reaction with ethanol as alcohol.

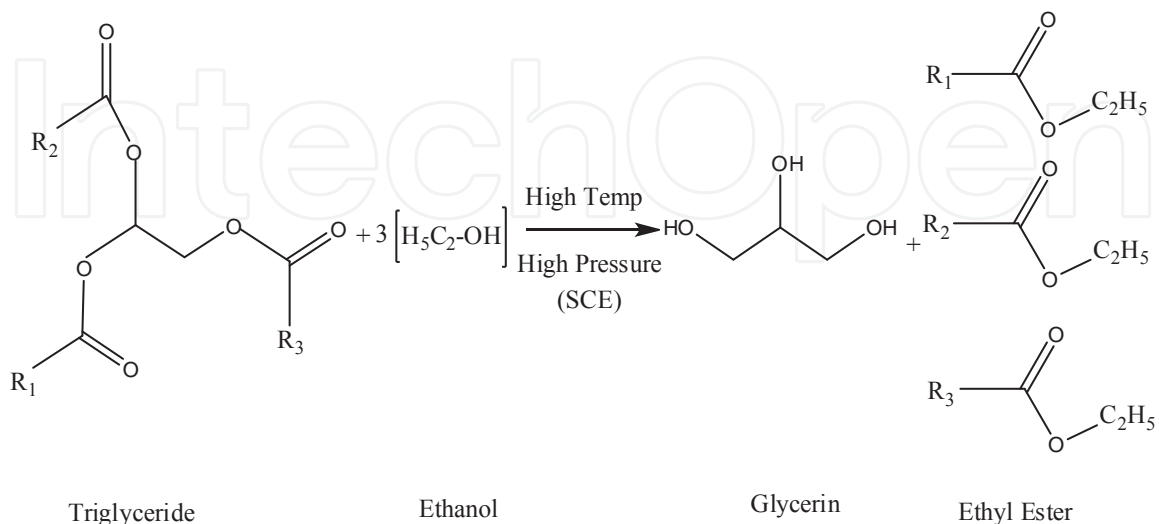


Figure 2. Transesterification reaction: R1, R2 and R3 are long chain hydrocarbons which may be same or different

Biodiesel can be produced by various transesterification methods using alkali, acid or enzyme catalysts or by advanced methods such as microwave irradiation and ultrasonic transesterification. The alkali process gives a high purity, high yield biodiesel in a short span of reaction time but is not suitable for oils with high free fatty acid (FFA) content, for these oils, acid esterification followed by alkali transesterification can be employed to reduce the high FFA content and to improve the biodiesel yield. However, the longer reaction time and low catalyst recovery are problems in this process. Enzyme catalytic transesterification requires longer reaction times. All the methods mentioned above have their limitation and challenges such as longer reaction time, lower reaction rate, and weak catalytic activity.

To overcome these limitations, non-catalytic transesterification can be implemented to produce biodiesel under supercritical alcohol conditions [5]. Under supercritical conditions, the intermolecular hydrogen bonding in the alcohol molecule will be significantly decreased. As a result, the polarity and dielectric constant of alcohol are reduced allowing it to act as a free monomer. Alcohol at supercritical conditions can solvate the triglycerides to form a single phase of oil/alcohol mixture and yield fatty acid alkyl ester and diglycerides. Diglyceride is further transesterified to form ethyl ester and monoglyceride, which in the last step is then converted into alkyl ester and glycerol. Vegetable oils which include edible oils such as palm oil, sunflower oil, rice bran oil, rapeseed oil and non-edible oils such as jatropha oil, paradise oil, and pongamia oil can be used in biodiesel production. Waste cooking oil, algae and animal fats such as lard, tallow, yellow grease are also potential feedstock in the production of biodiesel. Table 1 shows the fatty acid profiles of some common biodiesel feed stocks collected from literature from Balat et al., [6] and others. The fatty acid profiles of the same (particular) feed stocks may vary due to its cultivation conditions and extraction methods.

| Feed stock | C16:0 | C16:1 | C18:0 | C18:1 | C18:2 | C18:3 | others |
|---------------------------|-------|-------|-------|-------|-------|-------|--------|
| Sunflower oil | 6.4 | 0.1 | 2.9 | 17.7 | 72.9 | 0 | 0 |
| Palm oil | 42.6 | 0.3 | 4.4 | 40.5 | 10.1 | 0.2 | 1.1 |
| Soybean oil | 13.9 | 0.3 | 2.1 | 23.2 | 56.2 | 4.3 | 0 |
| Rapeseed oil | 3.5 | 0 | 0.9 | 64.1 | 223 | 8.2 | 0 |
| Tallow [7] | 26.2 | 1.9 | 33.67 | 30.1 | 0.7 | 0 | 0 |
| Lard [8] | 24.7 | 2.9 | 13.1 | 42.48 | 13.64 | 1.16 | 2 |
| Waste cooking oil [9] 6.8 | 0.4 | 3.7 | 22.8 | 65.2 | 0.1 | 0 | 0 |

Table 1. Fatty acid profiles of various biodiesel feed stocks

The catalytic transesterification processes requires a lower amount of alcohol (1:9 oil to alcohol ratio), and mild temperatures (60°C) for the production of biodiesel. Alkali catalysts like potassium hydroxide, sodium hydroxide, sodium methoxide, potassium methoxide and acid catalysts like hydrochloric acid, phosphoric acid, and sulfuric acid can be used as catalysts in catalytic transesterification but catalyst separation, free fatty acid and water interference in the reaction, glycerol separation, and energy intensive are disadvantages. The use of different feed stocks, different alcohols greatly vary the processing conditions; the complete conversion may not be achieved with such changes in the process, reaction times could reach hours or days and separation of product becomes much more challenging.

In a non-catalytic supercritical alcohol process, the transesterification of triglycerides and the alkyl esterification of fatty acids will occur simultaneously with a shorter reaction time and reduced the energy consumption due to the simplified separation and purification steps. This process does not require any pre-treatment of the feed stock regardless of its fatty acid composition and profile. In non-catalytic supercritical transesterification the oil to alcohol ration varies between 1:40-45 depending upon the feed stocks fatty acid profile, 290-350°C temperature, and reaction pressure above saturation pressure [5, 10]. Introduction of co-solvent into the reaction mixture decreases the critical point of alcohol, increases the mutual solubility of the oil and alcohol at lower reaction temperatures and accelerates the reaction rate under supercritical alcohol conditions [11]. Normally methanol and ethanol are being used as alcohol to produce biodiesel. But longer chain alcohols like 1-butanol, 1-propanol and 1-octanol could also be used to produce biodiesel. The critical conditions of these alcohols are presented in Table 2.

| Alcohol | Critical Temperature (°C) | Critical Pressure (bar) |
|------------|---------------------------|-------------------------|
| Methanol | 240 | 78.6 |
| Ethanol | 243 | 63.1 |
| 1-Propanol | 264 | 50.3 |
| 1-Butanol | 290 | 43.5 |
| 1-Ocatanol | 386 | 26.5 |

Table 2. Transesterification alcohols and their critical conditions

The major influencing factors on the yields of biodiesel are type of alcohol, reaction temperature, oil to alcohol ratio, reaction time and pressure. The critical temperatures increase with increase in chain length or molecular weight of the alcohol. At the same temperature, the acidity of longer chain alcohols tends to decrease resulting in slower reactivity or slightly more reaction time than the short chain alcohols. However the cold flow properties of the biodiesel produced with long chain alcohols are better than the biodiesel produced with short chain alcohols [12]. All these factors influence the selection of alcohol, as it affects both the economics and energetics of the process. The yield of biodiesel increases with the increase in reaction temperature above the critical conditions of the alcohols. Beyond the optimum temperature, the yield may start decreasing due to degradation of fatty acids at higher temperatures. Usually this also depends on the fatty acid profiles; as poly unsaturated fatty acids (PUFAs) are thermally unstable at higher temperatures. Feed stocks having more PUFAs may give higher yields at slightly lower temperatures than the feed stocks having less PUFAs [13]. The usual optimum reaction temperature ranges between 290-350°C, which also depending on the other reaction parameters.

| Feed stock | FAME | FAEE | FABE |
|----------------------------------|-----------------------|-----------------------|-----------------------|
| Camelina oil [15] | | | |
| Reaction temperature: 310°C | Yield: 91% | Yield: 85% | Yield: 84% |
| Oil to alcohol molar ratio: 1:40 | Reaction time:24 min. | Reaction time:28 min. | Reaction time:45 min. |
| Rapeseed oil [12] | | | |
| temperature: 300°C | Yield: 99% | Yield: 94% | Yield: 86% |
| Oil to alcohol molar ratio: 1:42 | Reaction time:15 min. | Reaction time:45 min. | Reaction time:45 min. |
| Rapeseed oil [12] | | | |
| temperature: 350°C | Yield: 94% | Yield: 94% | Yield: 89% |
| Oil to alcohol molar ratio: 1:42 | Reaction time:4 min. | Reaction time:10 min. | Reaction time:10 min. |

Table 3. Variation in the yields of biodiesel with different alcohols

As mentioned earlier the long chain alcohols need higher reaction temperatures to get higher yields of biodiesel than the short chain alcohols. The molar ratios of oil to alcohol vary for different feed stocks with different alcohols. This usually ranges between 1:40-45 at optimum reaction temperature. A lower amount of alcohol negatively affects the yields as the reverse transesterification reaction tries to go backwards. On the other hand more alcohol also reduces the yields by changing the critical point of the mixture to higher temperatures, where the optimum temperature of the reaction is not sufficient to perform the forward reaction. This also imposes another economic barrier as this extra alcohol requires more energy to heat, and will need to be recycled after separation process [14]. Supercritical alcohol processing is very

fast compared to conventional transesterification. The typical processing times of supercritical processes are 5-30 minutes depending upon the type of alcohol and reaction temperature. The reaction pressure also slightly increases the yield of biodiesel above its saturation pressure at a particular reaction temperature. But it is always a better option to use the lowest possible pressures; as high pressure demands more energy and capital investment. Variation in the yields of biodiesel and reaction times with respect to alcohol is shown in Table 3.

3. Supercritical water process for the production of green fuels from oils/fats/lipids

The catalytic hydrothermolysis (CH) is another process which produces regular hydrocarbon transportation fuels from oils or fats. The supercritical water performs the hydrolysis of vegetable oils to produce biocrude oil. This biocrude oil consists of a wide range of compounds such as straight chain, branched chain and cyclic hydrocarbons (alkanes, alkenes and aromatics etc.,) and their distribution varies depending upon the processing conditions and feed stock. An increase in temperature towards critical point the causes oils/fats become miscible with water around 300-330°C [16].

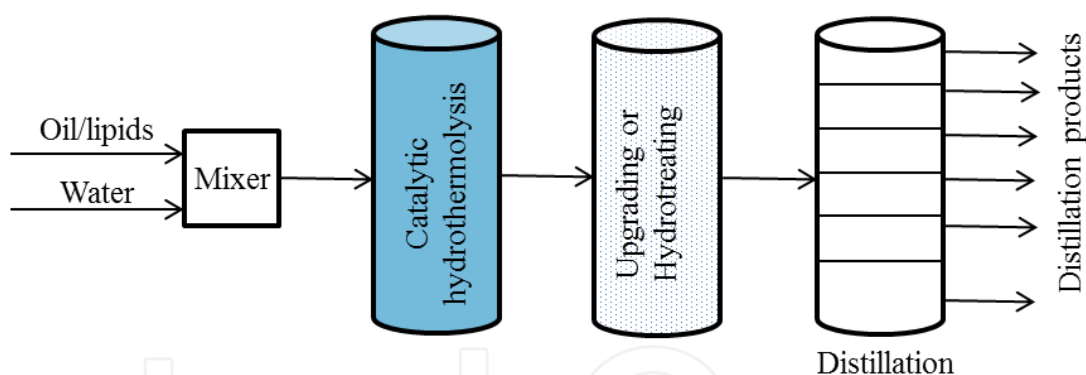


Figure 3. Catalytic hydrothermolysis process

During this process, triglycerides undergo hydrolysis reaction to form free fatty acids and glycerol. Compared to thermal cracking and pyrolysis, the formation of gaseous products will be reduced to the minimum in CH process. At higher temperatures, decarboxylation and cyclization reactions of fatty acids and glycerol produce alkanes, alkenes, carbon dioxide and water. The aqueous phase contains small amounts of smaller hydrocarbons and glycerol. Use of external catalyst such as KOH and NaOH enhances the production of alkanes. Use of metal oxide catalysts favors the production of alkenes. [17]. The biocrude oil produced during this process must be hydrotreated or reformed to meet commercial fuel standards. The upgrading process is discussed later in the chapter. Catalytic hydrothermolysis is performed to produce jet fuel and diesel range hydrocarbons. Oil and water are processed at 9:1 (vol. ratio) and

between 450-475°C. The resulting biocrude is then upgraded with commercial nickel catalyst to produce jet fuel and diesel range hydrocarbons [18]. The schematic of the CH process is shown in Figure 3. The hydrogen utilization during the CH process can be reduced compared to direct catalytic cracking of oils. The fatty acid profile of feed stock, water to oil ratio, rate of heating and reaction pressure determines the final product properties.

4. Supercritical alcohol process for the production of biodiesel from wet algal biomass

The utilization of vegetable oils to produce biodiesel has resulted in stress on domestic markets and often disrupted the production capacities to lower levels of the operating plants [19]. Other feed stocks like waste cooking oil and animal fats are not sufficient to meet commercial demands and to make biofuels at profitable scales. Researchers identified microalgae as an alternative crop to produce oils in larger volumes, with smaller areas of land and in shorter periods of time. The active research on algae has started in the 1970s due to the oil crisis. Microalgae are single cell plants which grow in most of the marine environments around the globe. They can be cultivated under autotrophic and heterotrophic conditions depending upon the species. Due to their faster photosynthesis they grow much faster and consume more CO₂ when compared to oil producing energy crops. Algae can be harvested in cycles of 6-14 days depending on the strategies and cultivating conditions.

Microalgae are being cultivated in open race way ponds and in closed photo bioreactors. Open raceway ponds are much cheaper to operate, but very hard to control the conditions within the pond. Open ponds are more vulnerable to the atmospheric conditions and other invading species which greatly affect both quantity and quality of algal biomass. On the other hand, photo bioreactors provide a very controlled environment which helps to produce biomass with better quality and quantity than open ponds. But operating costs of photo bioreactors are very high, prohibiting it for the use in biofuels production. Many research institutions and private corporations have developed the best suitable systems for their needs. After cultivation biomass can be harvested with techniques such as centrifugation, flocculation and hydro cyclones etc. The biomass content or water content in the biomass varies for different systems. The extraction of oil is the most energy intensive step in algal biofuels production. The drying step that occurs prior to the solvent extraction of oil consumes nearly 90MJ of energy which is nearly 85% of the total energy consumed to produce 1 kg of biodiesel. Techniques like Supercritical CO₂ extraction, pyrolysis and gasification also need dry biomass. Due to this these methods are also not suitable for the production of biofuels with algal biomass. Biodiesel could be produced directly from the algal biomass by using supercritical alcohol transesterification process.

The direct conversion of wet algal biomass into biodiesel is demonstrated with *Nannochloropsis sp.* with supercritical methanol and ethanol as conversion media without using catalyst. The FAMES and FAEEs can be produced with free fatty acids and triglycerides present in the algal biomass. As the temperature rises from normal room temperature to supercritical conditions,

the reduced dielectric constant provides enhanced extraction capabilities to the alcohols to open/break the cell walls and to extract lipids. The cells structure disintegrates into small particles at higher temperatures due to enormous pressure, providing complete conversion of lipids into biodiesel. After reaching the critical points of the alcohols, the transesterification reaction takes place. At higher pressures the cell structure will be destroyed and provides more access to the lipids for transesterification reaction. The cell structures of the biomass before and after conversion are presented in Figure 3. The algal cells containing large globules of lipids (indicated by arrows) along with other cellular organelles (Figure 3a) are completely destroyed and disintegrated (figure 3b) into a network of pieces [20].

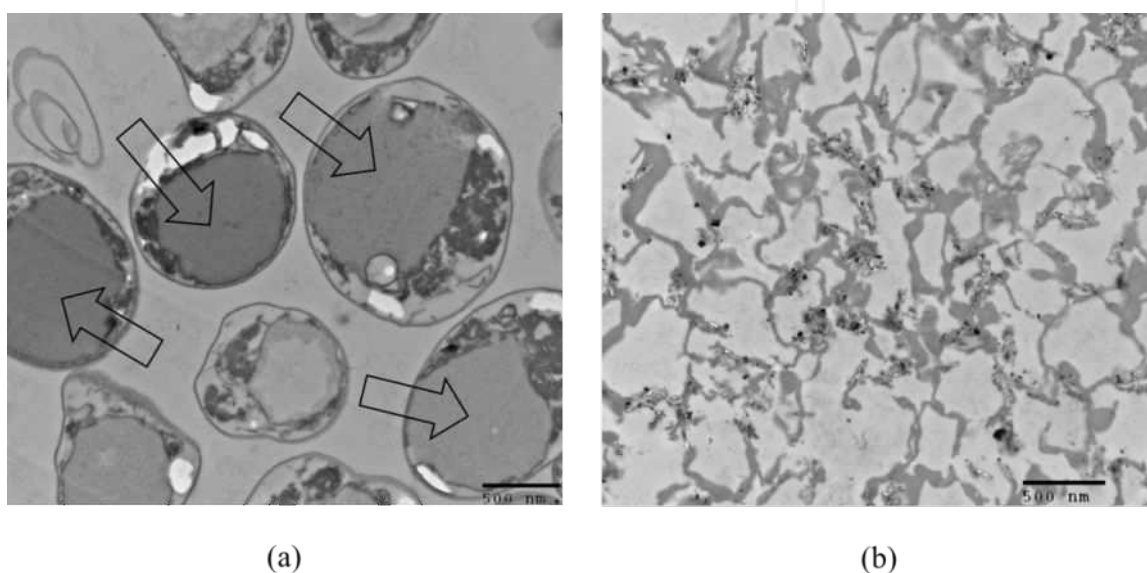


Figure 4. TEM images of algal cells before (a) and after (b) in supercritical ethanol conversion

The major influencing parameters of the direct conversion are reaction temperature, algae to alcohol ratio (wt.:vol.) and reaction time. The optimum reaction conditions for both methanol and ethanol are presented in Table 4. The algal biomass used in the experiments has 50% (supercritical methanol) and 52% (supercritical ethanol) of total lipids on ash free dry weight basis. As the temperature increases the extraction takes place below critical point, and transesterification starts from critical point. The maximum yields observed are 84% and 67% at 255°C and 265°C respectively. The short chain containing methanol has produced more biodiesel than ethanol similar to the vegetable oil transesterification. Same amount of alcohol may have been another reason for the lower yields with ethanol. When compared to the supercritical alcohol transesterification of vegetable oils and fats, the reaction temperatures of the direct conversion methods of algae are very low. This is due to the difference in fatty acid profile of algal biomass. The algal biomass used in these studies has more unsaturated (~40-45%) and polyunsaturated fatty acids (PUFAs) (~10%); which are thermally unstable and causes the reduction of biodiesel yields at higher temperatures. The decomposition of PUFAs was observed at higher temperatures above the optimum reaction temperature in both studies [21, 22].

| Algal biomass: | Yield (on the basis of total lipids) | Reaction temperature (°C) | Algae to alcohol ratio (wt./vol.) | Reaction time (min.) |
|----------------------------|--------------------------------------|---------------------------|-----------------------------------|----------------------|
| <i>Nannochloropsis sp.</i> | | | | |
| FAME (methanol)[22] | 84% | 255 | 1:9 | 25 |
| FAEE (ethanol)[21] | 67% | 265 | 1:9 | 20 |

Table 4. Reaction conditions for maximum yields of biodiesel with algal biomass

When compared to biodiesel production using vegetable oils by supercritical alcohol process, nearly 2-3 times more alcohol is needed for algal biomass conversion. More energy is required for the separation of the extra alcohol, making the process more energy intensive. The production of biodiesel directly from the wet algal biomass is possible; but supercritical processing of expensive feedstock like algae demands complex infrastructure and higher energy, making production of biofuels less profitable. During this process valuable byproducts like polyunsaturated fatty acid ethyl esters are lost in order to maintain the fuel properties.

5. Subcritical water processing of wet algal biomass to produce green fuels

Recently, many researchers have identified, and studied the importance of byproducts in the production of algal biofuels. Algae are being used to produce various kinds of natural products like protein, polyunsaturated fatty acids (PUFAs), vitamins, carbohydrates, and dietary fibers. Extraction and separation of these compounds is a key factor for the commercialization of algal biofuels [23, 24]. The recovery of these valuable products cannot be achieved using direct conversion methods due to severe processing conditions and degradation of these compounds. New novel methods called hydrothermal extraction and liquefaction (HT E&L) or subcritical water extraction or liquefaction can be used for the recovery of valuable products along with energy dense biocrude oil, and bio-char from wet algal biomass. Water attains these selective extraction and liquefaction properties due to increased temperature and pressure. The dielectric constant of water reduces slowly with increasing temperatures, which provides more solvating power to the water. This solvating power varies with the process parameters which include temperature, pressure, solids loading and extraction time. This technique has been used for many selective extraction applications such as bioactive components from *Haematococcus pluvialis* microalga[25], nutraceutical compounds from citrus pomaces[26], and oils from coriander seeds[27]. Typical extraction temperature will vary between 120-250°C, and changes along with pressure variation for a particular target compound. Another major advantage of this method is higher extraction efficiencies can be achieved when compared to conventional solvent extraction.

Similar to the above given examples, lipids from wet algal biomass can be extracted. In this process water present in the harvested algal biomass itself acts as the solvent; which also eliminates the drying step in the process and achieves maximum extraction of oil. This selective extraction of lipids is demonstrated with the wet algal biomass of *nannochloropsis salina*. The reaction temperature, solids (biomass) loading and reaction time are studied to extract the

maximal amount of lipids from the biomass. The RSM (response surface methodology) analysis of extraction results indicated that the increase in temperature causes increase in the yield of crude extract and lipids with in the crude extract up to 217°C. Due to increased solvating power or reduced dielectric constant; further rise in temperature caused a reduction in crude extract due to secondary reactions which caused redistribution of crude extract into other product fractions like the water phase or gas phase. The biomass loading is another crucial parameter which affects the extraction efficiency. The amount of crude extract is increased with more diluted biomass and a maximum is found to be at 5%; meaning less biomass loading provides more solvent for the extraction of target compounds. But at the same time the energy consumption should also be considered; more water in the biomass requires more energy to reach the target processing conditions. Due to this, optimum biomass loading was increased to 7.5%, which slightly affects the extraction efficiency. The reaction time was found to be very when compared large to solvent extraction techniques, and maximum extraction was achieved within 25 min. Through this subcritical water extraction method nearly 60-70% of the lipids present in the algal biomass can be extracted. Along with the lipids, the water fraction contains sugars, sugar alcohols, and PUFAs in algae oil which have commercial value in the pharmaceutical and food industry; Additionally the bio-char contains proteins (~45% by wt.) and 24.9 MJ/kg of energy making it another valuable byproduct [28]. The biodiesel produced with subcritical water extraction with thermal energy recovery (60%) and utilization of bio-char to produce biogas (methane) consumes only 28.23 MJ of energy for 1kg biodiesel [29]. The process can be used only for algal biomass which has more lipids and for the production of biodiesel. In order to produce biofuels from algal biomass having fewer lipids, higher hydrothermal processing conditions should be used.

Further increase in temperature of the hydrothermal extraction process, results in hydrothermal liquefaction due to the enhanced reaction capabilities of water. The density of water decreases as the temperature and pressure rise towards the critical point and drops drastically after the critical point; here water medium attains gas like densities and liquid like solvent properties. The ability of water in these conditions to provide H⁺ or OH⁻ ions (varying ion product (K_w) of water) is useful in performing acid or base catalyzed reactions without using external catalysts [30-32]. During the hydrothermal liquefaction, the macromolecules present in the biomass are subjected to hydrolysis, which degrades them into smaller molecules. During this process, the oxygen present in the biomass will be removed by dehydration in the form of water, and by decarboxylation in the form of carbon dioxide. During the liquefaction process energy dense biocrude oil, aqueous phase with water soluble compounds, bio-char and gaseous product will be produced [31, 33]. The subsequent intermediate reactions of the hydrolyzed or extracted compounds determine the yields of product fractions, which are influenced by processing conditions.

Numerous studies on hydrothermal liquefaction of algae are available in literature. Few examples of these studies are hydrothermal liquefaction of algal biomass *nannochloropsis sp.*, [34], *chaetomorpha linum*[35], *chlorella pyrenoidosa*[36], or *spirulina plantesis*[37]. The typical processing temperature used for hydrothermal liquefaction ranges between 250-370°C. The yields and properties of the products vary with reaction temperature. The yield of energy dense

biocrude oil increases with rise in temperature up to 350°C. Lower yields can be observed at lower temperatures due to a decrease in hydrolysis of the biochemical compounds and repolymerization. Above 350°C, hydrothermal gasification becomes more dominant and contributes to the production of more gaseous products rather than biocrude oil. The typical yields of biocrude oil yields range between 20-60% on the ash free dry weight basis (AFDW). As the temperature rises the water becomes more reactive than an extraction solvent due to its increased ion dissociation constant. The ion dissociation constant at 250°C is 1000 times greater than at the room temperature [38]. Because more protons and hydroxide ions present in these conditions hydrolysis becomes more active reaction. The hydrolysis reaction causes the degradation of basic chemical compounds, and when accompanied by reactions like repolymerization produces bio-crude oil. The yields differ with process conditions, and biochemical composition of the algal biomass. The contribution of lipids, proteins and carbohydrates to the yield of biocrude oil yield are in the order of lipids>proteins>carbohydrates [39]. The biocrude oil yields of commonly used algal biomass are presented in Table 5. The high heating value (H.H.V) of biocrude oil varies in the range of 32-39 MJ/kg. The reaction temperature greatly affects the quality of biocrude oil. At lower processing temperature, lipids contribute more to the yield of biocrude oil which contains more energy or higher H.H.V. At higher temperatures, due to the contribution of protein derived compounds and increased nitrogen in biocrude oil the H.H.Vs of biocrude oil reduce to lower levels. The variation reaction pressure beyond saturation has little to no effect on the product distribution in HTL of algae [36]. Even though most of the studies have used residence times between 20-120 minutes in batch (reactor) mode operation, 2-5 min. of reaction time is sufficient to get better biocrude oil yields in a continuous flow system [40].

| Algal Biomass | Biochemical composition | | | Reaction conditions Temperature, solids loading and Reaction time | Biocrude yield (% of AFDW) |
|------------------------------------|-------------------------|---------|---------------|---|-------------------------------|
| | Lipids | Protein | Carbohydrates | | |
| <i>Chlorella sp.</i> [40] | 4 | 60 | 25 | 350°C, 10% and 3 min. | 42 |
| <i>Chlorella sp.</i> [41] | 60 | 9 | 13 | 300°C, 20% and 90 min. | 66 |
| <i>Nannochloropsis sp.</i> [41] | 14 | 52.4 | 5 | 300°C, 15% and 60 min. | 48.4 |
| <i>Nannochloropsis salina</i> [42] | 12 | 37 | 33 | 310°C, 25% and 30 min. | 46 |
| <i>Spirulina platensis</i> [42] | 6 | 60 | 19 | 350°C, 25% and 30 min. | 38 |
| <i>Nannochloropsis sp.</i> [34] | 14 | 59 | 20 | 300°C, and 10 min. | 50 |
| <i>Nannochloropsis sp.</i> [43] | 28 | 52 | 12 | 350°C, 21% and 60 min. | 43 |
| <i>Spirulina platensis</i> [44] | 11 | 49 | 31 | 350°C, 20% and 60 min. | 39 |
| <i>Scenedesmus sp.</i> [45] | 13 | 56 | 25 | 300°C, 20% and 30 min. | 45 |
| <i>Spirulina sp.</i> [45] | 5 | 64 | 20 | 300°C, 20% and 30 min. | 31 |
| <i>Dunaliella tertiolecta</i> [46] | 20 | 63 | 15 | 340°C, and 5 min. | 41 |
| <i>Dunaliella tertiolecta</i> [47] | 22 | 24 | 46 | 300°C, 10% and 60 min. | 30 |
| <i>Chlorella sorokiniana</i> [47] | 4 | 30 | 54 | 300°C, 10% and 60 min. | 18 |

Table 5. Yields of biocrude oil produced with various strains of algal biomass

The other product fractions are bio-char, aqueous phase and gaseous fraction. The bio-char yield decreases with an increase in temperatures, as the metabolites of the biomass converts into other products. The range of bio-char yields can be found between 10-70% depending on the processing temperature and time. Bio-char produced at lower temperatures tend to have higher H.H.V due to hydrothermal carbonization. The H.H.V of bio-char can be around 18-22 MJ/kg at lower temperatures and reduces to 8-10 MJ/kg at higher processing temperatures above 300°C. Due to extraction or conversion of biochemical compounds present in the biomass at higher temperatures, H.H.Vs of the bio-char are reduced compared to the H.H.V of the original biomass and bio-char produced at lower temperatures [20].

The aqueous phase of the HTL is another valuable product fraction which contains essential nutrients ($\text{NH}_3\text{-N}$ and PO_4^{3-}), amino acids and carbohydrates depending on the processing temperature. The hydrolysis of proteins results in the formation of amino acids, and the deamination (further hydrolysis) of these amino acids produces the ammoniacal nitrogen. Usually the amount of ammoniacal nitrogen increases with an increase in temperature, because the amino acids decompose rapidly at higher temperatures. At the same time, the concentration of amino acids decreases due to rapid conversion with an increase in HTL temperatures. The other valuable nutrient phosphate behaves in a different way; the amount of phosphate in water phase decreases with an increase in temperature and deposits in the bio-char fraction. The concentrations of these nutrients can be as low as 400 ppm for $\text{NH}_3\text{-N}$, 6 ppm for PO_4^{3-} and as high as 6300 ppm for $\text{NH}_3\text{-N}$, 3000 ppm for PO_4^{3-} . However, these concentrations vary greatly with the biochemical composition of the biomass and the processing temperature [20, 48, 49]. Recycling these nutrients back to cultivation is a very crucial step as it can save of fresh on addition nutrient supply and reduce overall cost. Along with the nutrients, the aqueous phase also contains valuable carbohydrates including polysaccharides, monosaccharides, sugar alcohols, amino acids and glycerol. At milder temperatures most of the carbohydrates present in the algal biomass are extracted into the aqueous phase. With an increase in HTL temperature, these polysaccharides hydrolyze to yield simple sugars and derivative compounds. At higher processing temperatures these compounds start degrading or converting into other product fractions due to secondary and tertiary reactions. A Typical optimum point for the extraction of polysaccharides is around 160°C [50]. Similar to the extraction of lipids, polysaccharides from algal biomass can be extracted at lower temperatures, and the remaining biomass can be used to produce biocrude oil. The recoverable quantity of polysaccharides and biocrude oil depends on the original biochemical compositions of the biomass.

As mentioned earlier, separation and recovery of these valuable amino acids, nutrients, and carbohydrates is vital for the production of algal biofuels. This concept of algal bio refinery with sequential HTL (SEHTL) or hydrothermal extraction and liquefaction (HT E&L) is shown in Figure 4. The processing strategies for each strain of biomass vary as they possess different biochemical composition. The separation of these compounds provides a much needed economic life line and also improves the quality of biocrude oil. The removal of amino acids and nitrogen based compounds at lower temperatures reduces the quantity of nitrogen in the biocrude oil produced in the second step. When compared to cellulosic ethanol production,

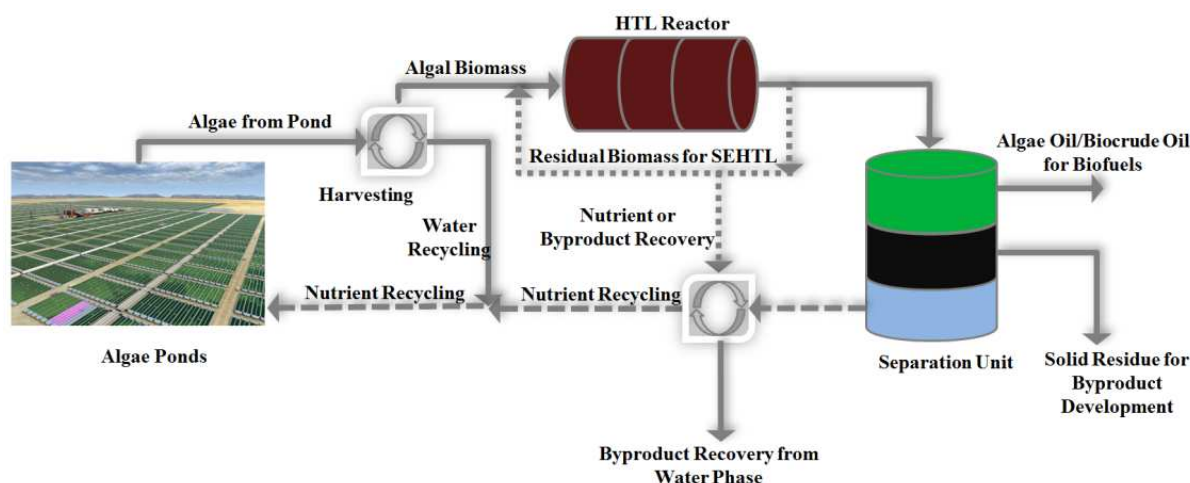


Figure 5. Algal biorefinery with HTL process

HTL of algal biomass has better energy return on investment (EROI) and lower emissions can be achieved [41].

The biocrude oil produced in the HTL process contains nitrogen (4-9 wt.%) and oxygen (2-7wt. %). The biocrude oil produced with oils/fats in the CH process is easy to upgrade compared to biocrude oils produced with algae due to the absence of nitrogenous compounds. Due to the presence of nitrogen and oxygen, processing the biocrude oil becomes slightly complex. Two strategies can be followed to produce hydrocarbon fuels from biocrude oil. The first one is, co-processing the biocrude in existing petroleum refineries by diluting the crude petroleum up to the permissible levels of nitrogen and oxygen. The second option is direct processing of biocrude oil with suitable catalysts. These catalysts include metal oxides of Ni, Co, Mo, Pt and W supported on γ -Al₂O₃, SiO₂, zeolites and carbon. Commercialization of these catalysts for processing biocrude oil may take some more time. More research and development is needed to optimize both the HTL of algal biomass and suitable catalysts for biocrude oils with varying properties. Compared to conventional jet fuel, the biojet fuel produced from algal biomass with HTL and upgrading can reduce life cycle greenhouse gas emissions by 76% [51].

6. Conclusions

The sub and supercritical processing methods seems promising for the production of renewable transportation fuels from various feed stocks. Supercritical alcohol processing provides much better path to produce biodiesel from cheap feed stocks such as animal fats and waste cooking oils. These feed stocks need very intensive pretreatments to produce biodiesel through catalytic transesterification. They can be directly processed using the supercritical alcohol method. At the same time the price of feed stock also plays a vital role to determining the sustainability of this process. Catalytic hydrothermolysis is being used by many corporate companies to demonstrate the possibility of producing high grade jet fuels and naval distillates. This technology is ready to deploy during certain critical political or environmental

scenarios. Hydrothermal extraction and liquefaction is acquiring more interest in the research domain due to its ability to produce a wide variety of products. HT E & L processes are identified as the best possible techniques for the production of biofuels from algal biofuels. The current research is more focused on cultivation and recovery of byproducts from algal biomass through sequential HTL. The algae biofuel research is still in the research and development stage and may take a couple of years to be commercialized.

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