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Biofuels from Algae

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1. Introduction

1.1. Current sources of biofuels

The United States, as well as numerous other countries throughout the world, is seeing a rapid rise in the amount of power and fuel required to maintain the current and future lifestyles of its citizens. With the rapid increase in global consumerism and travel seen over the recent decades due to improvements in technology and the increase in international interactions, the demand for fuel is rapidly growing, as can be seen in Figure 1. Due to the worldwide demand for fuel, which currently is primarily fossil-derived, supplies are being strained and costs are rapidly rising. In order to satiate this rapid increase in demand and stem the shrinking supply, new alternative sources of fuel must be brought to the market that can be used to replace standard petroleum based fuels.

Currently, there are several sources of alternative fuels that can be used to replace or supplement traditional petroleum based fuels. Some of these sources include alternative fossil-derived sources such as coal, natural gas, and hydrogen derived from hydrocracking, while other sources come from more renewable sources such as biomass. Biomass has several advantages when it comes to fuels in that there are numerous sources such as terrestrially grown starch based or cellulosic material, waste derived material, or aquatic and marine based organisms, each of which has unique components and characteristics useful for fuel production.

Due to the structural variability of the various types of biomass available, a wide range of technologies can be used to convert the organic molecules into a useable form of fuel. As food substrates (such as carbon dioxide in autotrophic organisms or sugars in heterotrophic organisms) are metabolized, a range of cellular components are assembled to perform numerous duties to keep organisms alive and reproducing. Starches and celluloses are assembled from carbohydrates to provide rigid structural support in many woody biomasses as

well as acting as a sugar storage method for quick conversion to a food source in times of famine. Proteins and amino acids are the building blocks of DNA structures and additional biomass. Lipids provide a highly energy dense storage system while also serving as a transport mechanism for several nutrients vital to metabolic activity. However, when broken down to the most basic levels, these organic compounds all contain energy which can be extracted through several methods. Table 1 shows a breakdown of some common algal biomass cellular components.

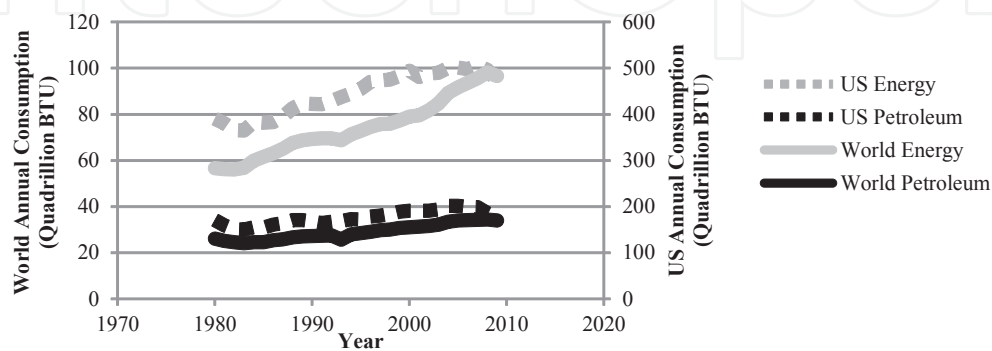


Figure 1. Annual Consumption of Total Energy and Petroleum in the United States and the World [1]

Species	Protein (%)	Carbohydrate (%)	Lipid (%)
<i>Ankistrodesmus</i>	36	24	31
<i>Nitzschia</i>	36	14	22
<i>Chlorella</i>	55	24	21
<i>C. protothecoides</i>	38	52	11
<i>C. emersonii</i>	32	41	29
<i>C. vulgaris</i>	29	51	18

Table 1. Variations in the chemical composition of selected algal species [2, 3]

Sources of biofuel currently being produced range in production rate from the laboratory scale through full scale implementation. Technologies to break down starches and cellulosic materials into sugars for subsequent conversion to bioalcohols has been extensively developed and scaled to produce billions of gallons per year to add into petroleum derived gasoline. Other structural components such as lipids have a high energy content to them and have characteristics that closely mimic petroleum diesel and kerosene, and thus, only require simple chemical reaction (i.e., transesterification) for use as a biofuel, and have been developed up to a quasi-large scale of volumetric output that can be seen in some regional market places, as well as in home production for personal use.

1.2. Aquatic biomass

In order to produce the vast amounts of fuel needed by the United States, and the rest of the world, there will be a demand for massive quantities of biomass to be grown. This could be problematic when using terrestrial biomass, since in most cases, growing plants would require a switch from using land for food sources to energy sources. An alternative source of biomass, however, is available in the form of aquatic and marine species of biomass such as kelps, algae, and other types of water borne plants or bacteria. Aquatic and marine biomass (excluding bacteria) are typically plant-like in that they are autotrophic organisms that contain photosynthetic pigmentation, can utilize inorganic carbon for biomass development, and express molecular oxygen as a byproduct. However, these organisms do not suffer from the inherent liability of requiring fertile soil to grow, minimizing competition with the food supply chain. Also, as microscopic organisms, they do not require abundance of land to develop root systems and large floral brush in order to absorb sunlight and nutrients, and therefore, a much more effective utilization of space. With rapid growth rates that can typically double in concentration in less than a day, it is possible to have daily harvests, creating a steady and abundant supply of biomass for harvesting. As such, marine and aquatic biomass can be a useful alternative source of biomass that can be used to produce a wide range of biofuels for commercial use, while avoiding several of the more common pitfalls associated with more traditional sources of terrestrial biomass, and thus, will be the biomass focus of discussion for the remainder of this article.

Primarily, growth of algae for the production of oils and energy conversion has focused on microalgae, including species of diatoms and cyanobacteria (as opposed to macroalgae, such as seaweed), although some bacterial species (such as *Clostridium sp.*) have been demonstrated for production of biologically derived hydrogen and methane [4]. To date, there have been numerous studies of algae and other water based biomass in order to identify strong candidates for biomass accumulation rates as well as lipid content for production of biodiesel. Some strains are summarized for these characteristics in Table 2. There is also a wealth of microbial biomass resources available as a by-product of industrial activities such as sewage treatment, brewing industries and food processing that could provide biomass or nutrients for further microbial biomass growth [5, 6]. With this concept, it is feasible to use algae as a means for tertiary wastewater treatment in order to utilize trace nutrients such as phosphorous- and nitrogen-containing compounds, or can be used at industrial processes as a way to absorb carbon dioxide by entraining algal cultures to gaseous exhaust streams.

Growth of aquatic and marine biomass is not without challenges though. Maximum growth rates of the microorganisms typically occur under very specific conditions, and any variance on these conditions can cause substantial delays in biomass development. Also, open pond algal systems (which are common for algae production due to their ease of construction and inexpense) are susceptible to contamination from various airborne microorganisms that can decrease overall productivity. And of prime concern, is the ability to separate algae from water, which due to their very dilute nature, can be expensive and inefficient. Several methods are used to do this, such as flocculation with chemicals (such as hydroxides or alum) or

electric fields, filtration, centrifugation, or thermal drying, but each of these methods is not without bulky equipment, expensive materials, or long processing times.

2. Lipids and biodiesel

The diesel engine, created by Rudolph Diesel in 1893 as an alternative to steam engines, has seen a marked rise in use over the past decades as newer engines coming to market have become such cleaner combustors. Since the engines are so efficient, they are ideal for use in heavy transport such as rail and ship, but as technology and advances in fuel make the engine emissions cleaner, more and more small engine vehicles are coming to market in light trucks and passenger cars in the US and Europe as well as the rest of the world.

Species	Biomass Productivity (g/L/D)	Growth Rate (d ⁻¹)	Biomass Conc. (g/L)	Lipid Content (% by dry weight)	Reference
<i>Chlorella luteorividis</i>		0.55		28.5	[7]
<i>Chlorella protothecides</i>		1.32		31.2	[7]
<i>Chlorella regularis</i>		3		44.4	[7]
<i>Chlorella vulgaris</i>	1.9		1.9	53	[8]
<i>Scenedesmus bijuga</i>		6.1		35.2	[7]
<i>Scenedesmus dimorphus</i>		5.9		43.1	[7]
<i>Scenedesmus obliquus</i>		5.4		42.6	[7]
<i>Dunaliella salina</i>	0.3			35	[9]
<i>Spirulina platensis</i>	0.1				[9]
<i>Tetraselmus chui</i>	1			23.5	[10]
<i>Botryococcus braunii</i>	10.8			25-75	[11]
<i>Nannochloropsis sp</i>	72			31-68	[11]
<i>Nannochloropsis oculata</i>	2.4			22.8	[10]
<i>Phaeodactylum tricornutum</i>		0.003		2.5	[12]

Table 2. Productivity of Selected Algal Species

Diesel engines have the ability to run on various sources of fuel. Originally the engine was tested using pure peanut oil and vegetable oil, though today, the engine is commonly run on fossil fuel based diesel fuel, a type of kerosene. To reduce the amount of petroleum based diesel being used in today’s market several alternative types of fuel have been introduced that are compatible with these engines. Among the alternatives, generally seen are the lipid based straight vegetable oils and the modified biodiesels. Straight vegetable oil will burn

without problem in diesel engines; however, preheating of the fuel is required in order to reduce viscosity to pumpable levels. Biodiesel fuels, which are generally from the same source of lipids as straight vegetable oils or algal oils, are a much better suited fuel because they match several of the same characteristics as modern diesel fuel, and thus, require little to no engine modifications or fuel pretreatment modifications.

2.1. Sources of lipids

Lipids are a general set of cellular components that are grouped together by the common trait that they are soluble in non-polar solvents. Throughout living organisms, there are several sources of lipids that play various roles in biochemical processes including energy storage and water insoluble nutrient transport across cell membranes that include neutral lipids, phospholipids, steroids, waxes, and carotenoids. Since lipids have a generally low oxygen and high carbon and hydrogen content, they are very energy dense molecules. This characteristic, along with their natural abundance and similarities with petroleum based fuels, make them ready targets for processing and use as a blend or replacement to traditional fuels.

Neutral lipids (commonly referred to as “fats”), which are widely regarded as one of the most common sources of lipids, and which has the highest potential for use as an alternative fuel, can be found in various forms throughout different organisms, and will be the primary topic of focus for this discussion. Most marine and aquatic biomass can store lipids within the cell that can range from a small fraction to upwards of 80% of the cellular weight. Due to this trait, research and production scale operations have been centered on utilizing aquatic biomass for lipid production and conversion to fuel with the remaining cellular components being recycled for mineral content or discarded.

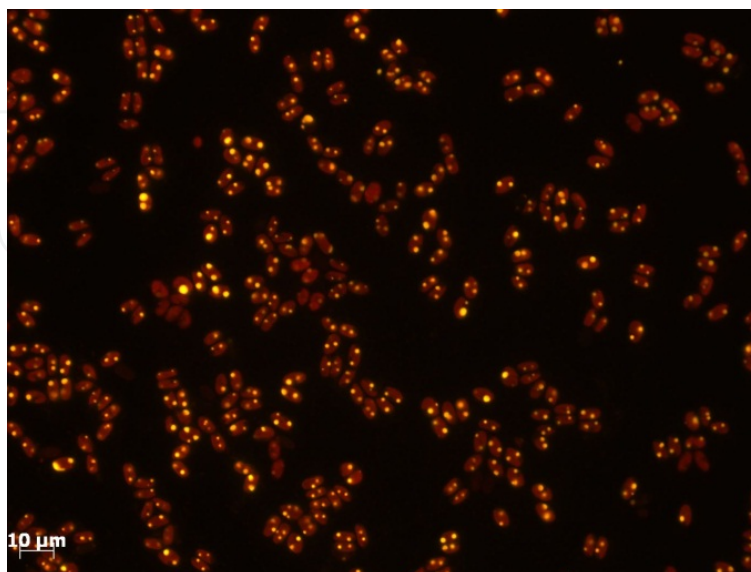
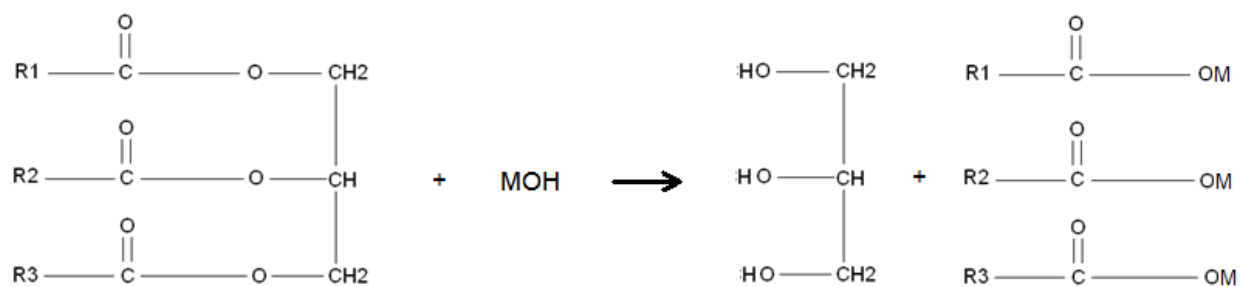


Figure 2. Nile Red Fluorescence Image of *Nitzschia* sp.



Scheme 1. Transesterification reaction schematic

Figure 2 shows an example of a marine diatom *Nitzschia sp.* stained with Nile Red fluorescence stain (red color shows chlorophyll and yellow shows lipid fluorescence).

Neutral lipids consist of a glycerol molecule (a three carbon alcohol) and one to three fatty acids (referred to as mono-, di-, or tri- acylglycerols depending on number of fatty acids present) with the fatty acids being various carbon chain lengths and having various levels of unsaturation (unsaturated, mono-unsaturated, poly-unsaturated, etc.). Fatty tissues in animals serve as both an energy storage mechanism as well as a means of insulation against temperature extremes. Algae primarily store fats in the cell membrane to serve as an energy storage medium as well as a nutrient transport system to shuttle metabolites into and out of the cell. Several studies have been conducted to attempt to identify the distribution of fatty acids in algae and other aquatic biomass [13-15].

2.2. Ideal lipid characteristics for biodiesel

Biodiesel is produced primarily through the transesterification reaction of triglycerides and alcohol usually in the presence of a metal catalyst and can be visualized by the chemical reaction equation found in Scheme 1. where “R” groups are functional carbon chains varying in length and level of saturation and “M” is a metal, usually referring to sodium or potassium. The resultant glycerol that is produced is generally treated as a by-product and either sold for commodities use or burned to provide heating if necessary. This process is dependent on water content and pH, which dictates pre-processing demands in order to minimize the formation of soaps and maximize the production of wanted fatty acid ester compounds.

During this reaction the fatty acids tails are removed from the glycerol backbone leaving a glycerol molecule and one to three fatty acid esters (almost always either ethyl or methyl alcohol yielding a methyl or ethyl ester). These fatty acid methyl esters (FAME) or ethyl esters (FAEE) will vary in characteristics as a fuel based on carbon chain length as well as degree of unsaturation and location of unsaturated bonds. Some of the characteristics of biodiesel that are affected by fatty acid chemistry are viscosity, cloud point, and freezing point, among other factors important to engine performance. In general, there are several trade-offs that must be made with regards to saturation of fatty acids, branching of the fatty acid

chain, and the carbon chain length, as each will have positive and negative attributes affecting fuel performance.

As the length of the molecule increases, the cetane number, and thus the heat of combustion, increases, this in turn decreases NO_x emissions. However, as the length of the fatty acid chain increases, the resultant biodiesel has increased viscosity leading to a pre-heating requirement. Also, as fatty acids become more branched there is a benefit of the gel point (the temperature at which the fuel becomes gel-like and has complications flowing through fuel lines) decreasing. The negative to higher branching is that the cetane number will decrease due to a more difficult combustion. As saturation of the fatty acid chain increases, there is a decrease in NO_x emissions and an improvement in fuel stability. As saturation increases, there is an increase in melting point and viscosity, both undesirable traits in a fuel.

Since there are so many trade-offs in the production of biodiesel, it is very difficult, if not impossible, to pick one ideal source of fatty acid for conversion to fuel. The multitude of climates across the globe will necessitate various traits in fuel such as the gel point, melting/freezing point, and oxidative stability. This leads to the argument of localized production of specific biomass sources that can be tailored to produce the types of lipids most suited to fuel that specific region, which will keep transportation costs down, as well as provide for the local economy. In following this method, there will be ample biomass produced to meet the specific needs of each climate, reducing environmental stresses that can occur due to overproduction for large scale purposes.

2.3. Enhancement of lipid production

Due to the various conditions that microorganisms grow and the constant flux of nutrients that can persist in nature, there are numerous types of lipids found that can change in concentration as the local environments evolve through typical ebbs and flows of materials. In response to these changes, microorganisms will change their cellular structures (i.e., lipid accumulation) by storing energy in various forms in order to utilize existing nutrients and energy to prepare for leaner conditions that may occur. In practical terms, this concept can be leveraged in order to produce high concentrations of intracellular lipids in marine and aquatic biomass in order to maximize the amount of lipids that can be harvested. Several studies have been conducted to determine what conditions affect the lipid composition and concentration of microorganisms. The more common techniques applied to increase the production of lipids from algae have through genetic manipulation [16], where genetic markers are manipulated that allow for increased lipid production to occur in the cell under normal conditions, by alteration of the cultivation conditions [17, 18], or by addition and manipulation of nutrients and chemicals added to the media [19]. By utilizing methods such as these, algal lipids can be increased by a substantial amount without increasing the footprint of required reactor space, nor greatly increasing the amount of time between harvests.

3. Synthetic fuels from biomass

3.1. Synthetic fuels

Unlike biofuels, which transform biological molecules into petroleum substitutes, synthetic fuels take a raw biological material, and through chemical processing, create compounds identical to petroleum fuel. This has a very distinct advantage over common biofuels in that there are no compatibility issues between the traditional fuels nor is there a need for any engine or fuel line modifications required. Synthetic fuels are usually made by utilizing a complex biological molecule and through thermal processing, break down the material into simple chemical building blocks (i.e., methane, carbon monoxide, hydrogen, etc.) and reform them into target chemicals. There are limitations with synthetic fuels production, especially when pertaining to production from aquatic and marine biomass where the water content is naturally higher than 99% by weight in its natural state, since initial breaking down of the products is usually through thermal processing that require dry or near dry conditions. However, since algae and aquatic biomass has such diverse characteristics and high cellular energy density, there is benefit for using either algae where the lipids have been extracted or whole algal cells as feedstock for these thermal synthetic fuel processes and thus can be considered as an option for production of synthetic fuels.

3.2. Methods for synthetic fuel production

There are three common methods for producing molecular precursors for synthetic fuels from biomass, and several variants of each method, dependent on the specific feedstock characteristic. These three methods are gasification, pyrolysis, and liquefaction. Pyrolysis and liquefaction will both produce a form of bio-oil that can be processed along with petroleum oil stocks and made into useful fuel products, while gasification will produce gaseous products such as carbon monoxide, methane, and hydrogen (commonly called syngas or synthesis gas in this process), and can be further refined directly to produce specific fuel molecules.

3.3. Gasification

Gasification is a process in which carbonaceous materials are exposed to heat and a sub-stoichiometric concentration of air to produce partially oxidized gaseous products that still have a high heating value with relatively lower concentrations of carbon dioxide due to limited oxygen [20]. Syngas can be catalytically reformed into a liquid fuel through the Fischer-Tropsch process, which converts carbon monoxide and hydrogen into long-chain hydrocarbons. By-products of the process include ash (formed from alkali-metal promoters present in the original reaction), char and tars that are created due to inefficiencies in mixing and heat distribution. This can be problematic when using water based biomass as the feedstock, since there will either be very high costs (in both energy and cost) to dry, or numerous unwanted products formed through side reactions. Three main types of gasification reactor are commonly used in industry: fixed bed, fluidized bed and moving bed. Each process has in-

herent advantages and drawbacks based on the complexity of the reactors, operating costs and product quality for use in the combustion of biomass. A more in-depth discussion of the design criteria and problems associated with using biomass as a fuel source for gasification reactors can be found in recent review articles [20, 21].

3.4. Liquefaction

Liquefaction is a process of converting biomass into a bio-oil in the presence of a solvent—usually water, an alcohol, or acetone—and a catalyst [22]. Liquefaction operates at milder temperatures than gasification, but requires higher pressures. Liquefaction can be indirect, wherein biomass is converted into gas and thence into liquid, or direct, in which biomass is converted directly into liquid fuel [23]. Bio-oils produced in direct liquefaction processes usually produce heavy oils with high heating values and value-added chemicals as by-products. Direct liquefaction also produces relatively little char compared to other thermochemical processes that do not utilize solvents. In addition, liquefaction has the advantage that the method is not hindered by the water content of the biomass, giving credence to utilizing this method for water based biomass. The use of water as a solvent can significantly reduce operating costs, and recent studies with sub- and super-critical water have demonstrated increased process productivity by overcoming heat-transfer limitations [24, 25]. Operating parameters and feed quality significantly influence the overall quality of the oil produced by these processes. A recent review presented an exhaustive comparison of the operational variables that affect the liquefaction of biomass and concluded that a well-defined temperature range is the most influential parameter for optimizing bio-oil yield and biomass conversion [22]. Similarly, catalyst choice can alter the heating value of the final liquefaction product and reduce the quantity of solid residue [25].

3.5. Pyrolysis

Pyrolysis is a process in which organic matter is exposed to heat and pressure in the absence of oxygen. The primary components of this process are syngas molecules like those found in gasification, as well as bio-oils and charred solid residues [26]. Pyrolysis methods are defined by the rate of heating, which directly affects the residence time of the reaction [27]. In slow pyrolysis, for example, the material is exposed to reactor conditions for five minutes; in fast pyrolysis, residence time is reduced to one to two minutes and in flash pyrolysis to less than five seconds. The residence time of the pyrolysis reaction greatly influences the composition of oils, gases and chars that are formed [28-30]. Several studies have been performed to identify the effect of operational variables— reactor conditions and variations in feedstock material —on the quality of the pyrolysis oils, gases, and chars [27, 30]. The oils typically produced during pyrolysis reactions are high in moisture content, and corrosive due to low pH. Pyrolysis of biomass is typically constrained by the high water content of the raw material, and current pyrolysis methods for biomass conversion have not reached the stage of commercial development. Ongoing research, however, aims at maximizing energy potential from biomass and optimizing conversion methods to achieve commercialization at marketable levels [31, 32].

4. Ethanol

Several species of cyanobacteria, including *Chlamydomonas reinhardtii*, *Oscillatoria limosa*, *Microcystis* PCC7806, *Cyanothece* PCC7822, *Microcystis aeruginosa* PCC7806 and *Spirulina platensis* produce ethanol via an intracellular photosynthetic process. After selecting strains for ethanol, salt and pH tolerance, ethanol production can be enhanced through genetic modification [33]. These strains are long-lived and can be grown in closed photobioreactors to produce an ethanol containing algae slurry. This process for ethanol production from algae is currently being demonstrated by Algenol Biofuels [34-36]. The cyanobacteria are grown in flexible-film, polyethylene-based closed photobioreactors containing seawater or brackish water as medium. Industrial (or other waste) CO₂ is sparged into the bags to enhance growth of the microorganisms. Nutrients (primarily nitrogen and phosphorus) are supplied to sustain growth. At maturity, the microorganisms produce ethanol. The ethanol in the liquid phase will maintain an equilibrium with the ethanol-water in the vapor phase. The ethanol-water in vapor phase condenses along the walls of headspace which is collected by gravity for ethanol recovery. Algenol aims to produce 56,000 L of ethanol per hectare per year using 430 polyethylene bags established over a one hectare footprint each containing 4500 L of culture medium with a cyanobacteria concentration of 0.5 g/L. Unlike other algae derived biofuel processes, the algae are retained in the bags while the ethanol water condensate is removed for ethanol recovery. It is expected that the photobioreactors will be emptied once a year to replace the seawater, growth media and cyanobacteria.

The ethanol concentration in the algal cultures is expected to range between 0.5 and 5 % (w/w) depending on the ethanol tolerance levels of the strain and that of the condensate between 0.5 and 2% [36]. Since the maximum ethanol concentration is expected to be only 2 %, conventional distillation for ethanol recovery will not be energy efficient. A vapor compression steam stripping (VCSS) process is being developed to concentrate the ethanol to 5-30 % (w/w) range. VCSS is a highly heat integrated process that offers the potential for energy efficient separation even at low ethanol concentrations. This is then followed by a vapor compression distillation process to concentrate ethanol to an azeotropic 94% concentration. Life cycle energy requirements and greenhouse gas emissions for the process are dependent on the ethanol content of the condensate from the photobioreactors. Detailed analysis using process simulation software have shown that net life cycle energy consumption (excluding photosynthesis) is 0.55 down to 0.2 MJ/MJ_{ethanol} and net life cycle greenhouse gas emissions is 29.8 down to 12.3 g CO₂e/MJ_{ethanol} for ethanol concentrations ranging from 0.5 to 5% by weight [36]. Compared to gasoline these values represent a 67% and 87% reduction in the carbon footprint on an energy equivalent basis [36].

One of the technological challenges for this approach appears to be developing genetically engineered cyanobacterial strains that can tolerate high concentrations of ethanol. The ethanol concentration in the growth medium will affect the vapor phase ethanol content which in turn will affect the content of the condensate recovered from the photobioreactor. There is a dramatic increase in energy consumption in a conventional distillation process as ethanol

content decreases below 7.5% (by volume). Energy required almost doubles when ethanol content decreases from 12% down to 5% (by volume).

Another challenge would be the economical disposal of spent algal cultures. Sterilization and inactivation of large volumes of biomass can involve extremely energy intensive unit operations like heating, or expensive processes like ultra violet treatment or chlorination.

5. Anaerobic digestion

Biogasification (or anaerobic digestion) is a biochemical process that converts organic matter to biogas (a mixture of methane, 50-70%, and balance carbon dioxide) under anaerobic conditions. Biogas can be used as a replacement for natural gas or it can be converted to electricity. The process is mediated by a mixed, undefined culture of microorganisms at near ambient conditions. Several terrestrial biomass feedstocks (agricultural residues, urban organic wastes, animal wastes and biofuel crops) have been anaerobically digested and commercial scale digesters exist for the biogasification of such feedstocks.

Anaerobic digestion offers several advantages over other biofuel production processes like ethanol fermentation or thermochemical conversion. The microbial consortia in an anaerobic digester are able to naturally secrete hydrolytic enzymes for the solubilization of macromolecules like carbohydrates, proteins and fats. Therefore, unlike in ethanol fermentation process there is no need to incorporate a pretreatment step to solubilize the macromolecules prior to fermentation. In addition, since the process is mediated by a mixed undefined culture, issues of maintaining inoculum (or culture) purity does not arise. Being a microbial process, there is no need to dewater the feedstock prior to processing unlike in thermochemical conversion where the feedstock is dried, to improve net energy yield. This is advantageous when it comes to processing aquatic biomass as these can be processed without dewatering. The anaerobic digestion process will also mineralize organic nitrogen and phosphorous, and these nutrients can be recycled for algae growth [37].

The process primarily takes place in four steps. A mixed undefined culture of microorganisms mediates hydrolysis, fermentation, acetogenesis and methanogenesis of the organic substrates as shown in Figure 3. During hydrolysis, the complex organic compounds are broken down into simpler, soluble compounds like sugars, amino acids and fatty acids. These soluble compounds are fermented to a mixture of volatile organic acids (VOA). The higher chain VOAs like propionic, butyric, and valeric acids are then converted to acetic acid in the acetogenesis step. Acetic acid is converted to methane during methanogenesis. Hydrogen and carbon dioxide are also liberated during fermentation and acetogenesis. A different group of methanogens converts hydrogen and carbon dioxide to methane. This mixed microbial culture thrives in the pH range of 6-8. Digestion can be performed either at mesophilic conditions (30 - 38°C) or thermophilic conditions (49 - 57°C).

Aquatic biomass – macrophytes [38], micro and macro algae, have all been tested as feedstock for biogasification. Microalgae have proportions of proteins (6–52%), lipids (7–23%)

and carbohydrates (5–23%) that are strongly dependent on the species and environmental conditions [39–41]. Compared with terrestrial plants microalgae have a higher proportion of proteins, which is characterized by a low carbon to nitrogen (C/N) ratio. The average C/N for freshwater microalgae is around 10.2 while it is 36 for terrestrial plants [40]. Usually the digestion of terrestrial plants is limited by nitrogen availability; however for microalgae this situation does not arise. Besides carbon, nitrogen and phosphorus, which are major components in microalgae composition, oligo nutrients such as iron, cobalt, zinc are also found [42]. These characteristics of microalgae make it a good feedstock for anaerobic digestion.

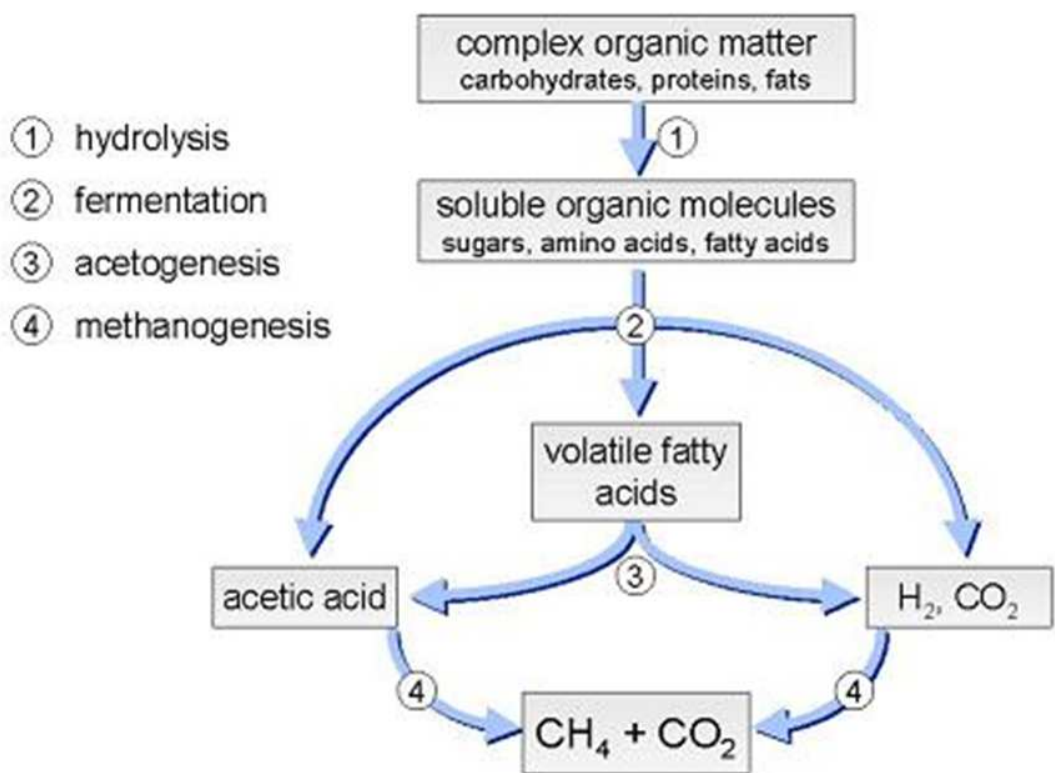


Figure 3. Pathways for mineralization of organic matter to biogas in an anaerobic digestion process

Previous studies have shown that macro algae like *Ulva lactuca*, *Gracillaria vermiculophylla*, *Saccharina latissima* etc. can be anaerobically digested producing methane at yields ranging from 0.1–0.3 L CH_4 /g volatile solids (VS) [43]. Methane yields of microalgae like *Spirulina platensis* (fresh water), and *Scenedesmus* spp. and *Chlorella* spp. (fresh water) ranged between 0.2 and 0.3 L CH_4 /g VS [44, 45] when these were codigested with other feedstocks like dairy manure and waste paper sludge, whereas other microalgae like *Tetraselmis* sp (marine), *Chlorella vulgaris* (fresh water), *Scenedesmus obliquus* (fresh water) and *Phaeodactylum tricornutum* (fresh water) produced an average methane yield ranging from 0.17 to 0.28 L CH_4 /g VS [45–47] when digested as sole feedstock. Table 3 summarizes microalgae digestion studies reported in the literature. The Table also lists the methane yield of cellulose powder as a benchmark to compare the methane potentials of microalgae feedstocks. Depending on the

type of microalgae, the methane potentials range from 5 to 78% of methane potential of cellulose. Choice of microalgae has an impact on the methane yield.

More recently when *Nannochloropsis oculata* was biogasified [48] in laboratory scale digesters at thermophilic temperature, the methane yield obtained was 0.20 L at STP/g VS. *N. oculata* was chosen because it can be grown easily in brackish or seawater, has a satisfactory growth rate and can tolerate a wide range of pH (7-10) and temperature (17 – 27° C). *N. oculata* is not rich in lipids but contains predominantly cellulose and other carbohydrates, which makes it a good feedstock for anaerobic digestion instead of biodiesel production. On a % (w/w dry matter) basis, the composition of *N. oculata* is: 7.8% carbohydrate, 35% protein and 18% lipid. Rest of the components are amino acids, fatty acids, omega-3, unsaturated alcohols, ascorbic acid [49]. About 88% of the carbohydrate is polysaccharide. Of the polysaccharides, 68.2% is glucose, and the rest are fucose, galactose, mannose, rhamnose, ribose and xylose.

Based on *N. oculata* growth observed in the pilot raceways and the methane yield from digestion of this alga, an analysis was carried out to estimate energy production and land requirements. Currently the algae harvesting rate from the raceways are 9.64 g ash free dry weight (afdw)/m²/d. Note that afdw (ash free dry weight) is the same as volatile solids content. An often cited study for algae growth has yielded a much higher productivity of 50 g afdw/m²/d for *Platylomonas* sp [50]. The algae biomass yield obtained in this study was only about 20% of the productivity potentially attainable. Optimization of growth conditions for *N. oculata* may improve its productivity. Using the methane yield value of 204 L/kg VS for anaerobic digestion of *N. oculata*, the annual energy output from a facility that grows the algae and subsequently digests it would be 27 MJ/m²/year. The area occupied (or footprint) of the digester(s) would be far less than the land area required for growing the algae. If the methane produced from this facility is converted to electricity, the electrical energy output would be 2.25 kWh_e/m²/year assuming that the efficiency of converting thermal energy to electrical energy is 30%. The household electrical energy and natural gas consumption in the US for the year 2010 was 11,496 kWh/year and 2070 m³/year respectively. If the algae biogasification facility were to supply the entire electrical energy requirements for a household, the land area required would be 5108 m² (1.26 acres). If in addition, the facility were to supply the natural gas needs, then an additional 2900 m² (0.77 acres) would be needed. In other words ~2 acres of land could supply all the energy needs of a household in US. If the algae productivities were improved then land requirement could be further reduced. At 50 g afdw/m²/d algae productivity, the land requirement would only be about 0.4 acres.

Despite useful methane production potential from biogasification and the ability to process dilute algal slurries in a digester, there are challenges to be overcome to commercialize this approach for producing bioenergy from microalgae. One bottleneck is that some feedstock characteristics can adversely affect anaerobic digestion. Unlike defined cultures used for production of biofuels like ethanol or butanol, the microbial consortia in an anaerobic digester is capable of secreting extracellular enzymes to hydrolyze and solubilize macromolecules like cellulose, hemicellulose, proteins and fats. This characteristic has enabled several terrestrial biomass feedstocks like sugarbeets, sugarbeet tailings, napier grass, sorghum and aquatic biomass like water hyacinth and giant kelp to be successfully digested using practi-

cal retention times. However, degradability of feedstocks containing high fraction of lignin (for example sugarcane bagasse, switchgrass, miscanthus and woody biomass like pine, eucalyptus) is poor in an anaerobic digester. The refractoriness of these feedstocks has been attributed to low moisture, crystalline nature of the cellulose, and complex association of the component carbohydrates within lignin [51]. As seen from Table 3, the digestibility of microalgae varies. Species with no cell wall or cell encapsulation composed of proteins like *Chlorella vulgaris* and *Phaeodactylum tricornutum*, has a higher yield of methane. *Dunaliella tertiolecta* has very low methane yield of 0.018 L/kg VS due to the presence of a cell wall consisting of cellulose fibers distributed within an organic matrix. So depending on the type of microalgae used it may be necessary to carry out some form of pretreatment of algae to improve methane yield and rate of methane production. The type of pretreatment may depend on algae type.

Strain	Source	Pretreatment	Digester operating conditions	Methane Yield L/kg VS	Reference
<i>Chlorella vulgaris</i> *	Fresh	None	No co-digestion Digestion at 30±5° C	0.22	[47]
<i>Tetraselmis</i> sp.	Marine	None	No co-digestion Digestion at 35°C	0.25	[46]
<i>Scendesmus obliquus</i>	Fresh	None	Hybrid flow through at 33±2°C and 54±2°C	0.17	[48]
<i>Phaeodactylum tricornutum</i>	Marine	None	Hybrid flow through at 33±2°C and 54±2°C	0.28	[48]
<i>Dunaliella tertiolecta</i> *	Marine	None	Serum bottle at 37°C	0.018	[47]

*Sample dried and then frozen at -24°C

Table 3. Summary of microalgae anaerobic digestion studies

6. Conclusion

Aqueous and marine biomass can be processed into a variety of sources of energy. Due to the extreme dilution in water, non-thermal processes such as anaerobic digestion, fermentation to bioalcohols, and lipid extraction are logical and useful methods to utilize key components of microorganisms to produce biofuels for the replacement or supplementing of traditional fossil fuels. However, thermal methods such as gasification of wet biomass may play a role in producing specialty fuels such as jet fuel that require a specific ratio of higher hydrocarbons that would prove otherwise difficult to manufacture, even given the requirement of intense drying.

In order for biofuels sourced from aqueous and marine biomass to secure a market share in the world, research and development needs to further nature's ability to produce higher concentrations of biomass with targeted characteristics and reduced footprints, while better utilizing available nutrients. This will allow for an ample supply of biomass to be produced without competition with the human food chain, that can be used renewably produce fuel that can power the world's mobile fleet.

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