Joel Collett

03/27/17

Chem 8069

Liquid Biofuel Production Using Hydrothermal Liquefaction of Algae

Abstract

Human society, especially transportation, requires energy-dense fuels to operate. The limited source of fossil fuels and their potential negative environmental effects mean that alternative fuel sources should be found. When using plant matter as the basis for a fuel, much of the energy required for generation is supplied from the sun via photosynthesis, and the carbon is supplied via its removal from the atmosphere as CO_2. Currently, the highest yielding source of lipids used for biofuel is algae, and one promising technology for conversion of the algae into a product similar to mineral crude oil is Hydrothermal Liquefaction (HTL).

Introduction

The inevitable exhaustion of fossil fuels means that alternative fuels must be sought for transportation and other applications where high energy density is desirable. Potential fuel sources should be renewable, meaning that they will not be used up in time. One attractive option for a renewable fuel source is plant biomass. When plants undergo photosynthesis they use energy from the sun to reduce CO_2 from the air into potentially useful chemicals. Since the energy available from the sun is much higher than our needs, the amount of fuel which can be produced is limited only by available land, nutrients, and the chosen plant's efficiency in producing molecules suitable for fuel use.

One of the major drawbacks of fossil fuel use is that it is taking carbon which has been stored underground for millions of years in the form of hydrocarbons, oxidizing it, and releasing it as CO_2 into the atmosphere, driving global warming. The advantage of fuels generated from biomass is that their carbon source *is* CO_2, meaning that burning them will not produce a net increase in the atmospheric CO_2 concentration. Products which are created from the biomass which are not used as fuel can be viewed as a carbon sink, actually resulting in a net reduction in the atmospheric CO_2 concentration.

Another potential benefit to the use of biofuels is political/social. Currently, much of the world is dependent on oil and natural gas fuels which are generated in politically unstable and war torn areas. Biofuels could be generated in any country that has the land and climate appropriate for the growth of plants.

Selection of a biomass source is dependent on the type of fuel desired. Plants produce a number of compounds which are valuable as fuel precursors including: sugars, starches, cellulose and lignin, and lipids (triglycerides). Lipids can be converted into a biocrude which has similar properties and energy density as mineral crude oil, and can be further processed to yield a biodiesel fuel. The remaining compounds are appropriate to be converted to lower alcohols via yeast or other microbe fermentation. Fermentation has been used to produce ethanol and methanol as fuels but suffers from several drawbacks:

1) High sugar and starch producing plants are used as food sources; growing them for fuel means they affect the economy of the food market, potentially raising food prices.
2) The non-food sources such as cellulose and lignin fermentation require pre-treatment, usually with enzymes, to break down the polymers to simple sugars, increasing the energy cost associated with the final product.
3) Yeast fermentation does not efficiently utilize its carbon source. The overall reaction for glucose to ethanol is: $C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2$. From this it can be seen that a third of the carbon is returned to the atmosphere as CO_2.

4) Small alcohols have a lower energy density than biodiesel mixtures.

To avoid these drawbacks it is desirable to utilize non-food bio sources which are high in lipids for the creation of fuels similar to mineral oils. This strategy comes with the added benefit of requiring minimum infrastructure change to be effectively used [1].

There are a number of plants which produce high amounts of lipids. Soy beans, rape seed, sunflower, various nuts, oil palms, etc. Most of these compete with the food economy, however, and the high yielding oil palm only grows in areas where much of the world's rainforests are located, and deforestation is another ecological concern. The highest lipid yielding organisms are algae (this includes both plants and the cyanobacteria Spirulina)[1]. Furthermore, algae does not compete with food markets, can be grown in ponds on land not suitable for agriculture, and can potentially utilize waste water as a growth medium and nutrient source. In addition, algae ponds can be enriched in CO_2 via the direct application of power plant flue gas [1].

Discussion

Where algae differ most from other bio sources is growing medium and water content. Finding ways to cultivate and harvest algae in high yields is a problem which until recently has not been considered. Algae's high water content (80-90 wt%) also provides challenges when generating fuels. Typical fuel production methods from other bio sources are pyrolysis, torrefaction and gasification. These methods all employ high temperatures in the absence of oxygen to produce various fuel product fractions from bio sources. These three processes all require the bio mass to be mostly dry, however, and thus are more suited to sources such as wood and grain stems which start with a lower water content [2]. Removing large amounts of water from algae is energetically unfavorable, so a process which can be run in the presence of water is advantageous. One such process is Hydrothermal Liquefaction (HTL).

HTL is an algae to fuel conversion process which utilizes catalysts, high temperatures (280-370 °C), and high pressures (10-25 MPa) [2]. At these temperatures and pressures water is just below its critical point, and the solubility of hydrophobic compounds increases. The subcritical water is crucial, as water above the critical point tends to favor radical reactions which result in production of smaller molecules and gasses [2]. The HTL process results in the production of a liquid biocrude oil phase, as well as various gases, aqueous soluble byproducts, and some insoluble solids. The quality of oil produced is similar to that of crude mineral oil and is suitable to be refined using already available technologies. One benefit of HTL treatment over simple lipid extraction strategies (oil pressing or solvent extraction) is that it is capable of converting other non-useful molecules into the oil fraction.

Lipids mostly in the form of triglycerides are hydrolyzed from their glycerol backbone under HTL conditions. The resulting fragments can combine to form longer hydrocarbon chains or esterify with short chain alcohols to create fatty acid esters, which are the traditional makeup of biodiesel. These molecules create a hydrophobic liquid phase in the reactor [2].

Proteins quickly hydrolyze into amino acids which are further decarboxylated to produce small amines and carbonic acid. The amines can further deaminate to produce ammonia which is soluble in the aqueous phase, and polymerize/ring close to form larger nitrogen containing hydrocarbons which are soluble in the oil phase [2].

Much of the carbohydrate content of the algae is converted to polar organic acids and alcohols which are soluble in the liquid phase. Some larger oxygen containing molecules may also be formed which are soluble in the oil phase [2].

Catalysts utilized are generally water soluble bases such as KOH or Na_2CO_3. The use of heterogeneous metal catalysts has been investigated with mixed success. To date, it seems that little work has been done with homogeneous organometallic catalysts [2].

On average, in test cases, the process results in a weight distribution (as a % of total algal organic mass) as follows: 39% biocrude oil suitable for refinement to various fuel fractions, 47% aqueous soluble byproducts (ammonia, phosphates, lower alcohols, organic acids), 6.5% “char” insoluble high carbon solids, 7.5% gas, mostly CO_2 and H_2. This distribution is an average of a number of literature values which was used for an economic analysis of process design [3]. Individual oil yields of up to 82% have been realized in continuous flow bench scale tests [5].

An idealized plant utilizing HTL technology could function as follows [3]:

1. Algae would be grown in ponds utilizing residential waste water as the primary nutrient source.
2. Extra growth medium water would be removed until solids were >20 wt%.
3. The bio slurry would be treated with HTL conditions for up to an hour.
4. The gas phase would be separated and the hydrogen recovered for oil refinery use, the CO_2 would be returned to the algae ponds.
5. The oil phase would be distilled into fuel fractions using traditional refinery techniques.
6. Since the water phase would contain much of the nitrogen, phosphorous, and trace minerals required for algae growth it would have the organic acids and alcohols removed and recycled as growth medium for the ponds.
7. The solids would be burned in a power plant to provide some of the electricity for the pumps and heating, and the resulting CO_2 flue gas would also be sent to the ponds.

There are challenges to industrial operation of the above process. Firstly, pumping a high solids slurry at the pressures used in HTL is not currently practiced in other industries [4]. Second, the economics of the process as a whole are highly dependent on the recycling of nutrients from the aqueous layer back to the algae growth medium to limit fertilizer costs [3]. This has the potential to be realized via an additional, similar technology known as Catalytic Hydrothermal Gasification (CHG) which could be used to convert many of the organics in the aqueous phase into useful fuel gases while leaving the ammonia and phosphates for nutrients [4]. Similarly, waste water as a source of nutrients is highly desirable, but introduces the added variable of a potentially non-uniform initial growth matrix [2]. Also of concern is the amount of nitrogen in the biocrude. The HTL process converts proteins into oil soluble molecules which increase the NO_x emissions for a burned fuel. Removing the excess nitrogen is an added cost for the process [3].

The HTL process, while a viable way to create biocrude suitable for refinement, is not yet an economically feasible venture. Increases in efficiency need to be realized before this technology will be able to compete with fossil fuels. A lifecycle analysis study found that a gallon of diesel produced with algae feedstock would cost around $10/gal before treatment of water waste streams were taken into account. When NO_x removal of flue gas and wastewater treatment were taken into account this number increased to $18.65 [3]. The price of mineral-sourced diesel fluctuates with the oil market but averages around $3/gal. Clearly, methods to recycle waste water, reduce nitrogen content, and increase the overall efficiency are needed.

Conclusions

The HTL process for creation of biocrude from algae is a potentially valuable technology which could lead to the economically feasible production of oil in the near future. The advantages are: reduction in greenhouse gas emissions, production of a fuel compatible with current transportation technology, and a renewable, energy dense, fuel source.

References

[1] Voloshin, R. A.; Rodionova, M.; Zharmukhamedov, S.; Veziroglu, T; Allakhverdiev, S. Review: Biofuel production from plant and algal biomass. *J. Of Hydrogen Energy* **2016**, *41*, 17257-17273.

[2] Barreiro, D. L.; Prins, W.; Ronsse, F.; Brilman, W. Hydrothermal liquefaction (HTL) of microalgae for biofuel production: State of the art review and future prospects. *Biomass Bioenergy* **2013,** *53*, 113-127.

[3] Mu, D.; Ruan, R.; Addy, M.; Mack, S.; Chen, P.; Zhou, Y. Life cycle assessment and nutrient analysis of various processing pathways in algal biofuel production. *Bioresource Technology* **2017,** *230*, 33-42.

[4] Elliot, D.C.; Biller, P.; Ross, A. B.; Schmidt, A. J.; Jones, S. B. Hydrothermal liquefaction of biomass: Developments from batch to continuous process. *Bioresource Technology*, **2015,** *178*, 147-156.

[5] Elliot, D. C.; Hart, T. R.; Schmidt, A. J.; Neuenschwander, G. G.; Rotness, L. J.; Olarte, M. V.; Zacher, K. O.; Allbrecht, K. O.; Hallen, R. T.; Holladay, J. E. Process development for hydrothermal liquefaction of algae feedstocks in a continuous flow reactor. *Algal Research* **2013,** *2*, 445-454.