Isaac Plant

Potential for Hydrothermal Liquefaction from Cultivated Macroalgae

WC: 3200

Introduction

Liquid fuels are likely to remain a significant portion of the transportation for the foreseeable future due to the need for air transportation and shipping. At the moment, these fuels are fossil fuel based and carbon intensive. One potential route to replace liquid fossil fuels is through the use of biofuels. Up to this point, terrestrial biomass has been viewed as the most promising source for conversion to biofuels. Switchgrass, in particular, has been a leading contender for agriculture development due to its hardiness and fast growth (Wei-Dong, 2011). However, as Figure 1 demonstrates, demand for jet fuel is expected to rise and by 2040 will require use of 40 to 60% of all excess land that the DOE views as viable for biofuel production (EIA, 2013). Considering that jet fuel makes up only a small portion of current liquid fuel use (and of intractable liquid fuel use) other resources need to be developed. In the case that biomass is pursued as a primary source for liquid fuel, sources that grow in areas not currently considered arable are needed. While biomass from waste streams and wood based materials are both possibilities, they suffer from various disadvantages (diversity of source for the former and carbon content over the long run for the latter) that are not discussed in detail here.

Macroalgae cultivation, on the other hand, may be able to provide significant amounts of biomass that can be grown in underutilized areas (Konda, 2015).

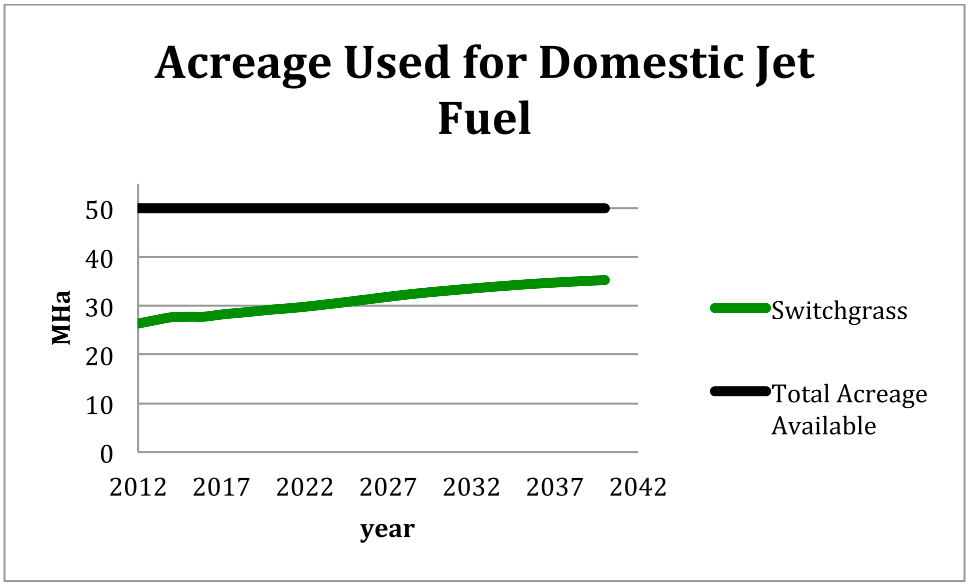

Figure 1. Comparison of estimated available acreage for biofuel to acreage need for switchgrass to supply all US jet fuel demand.

Common methods of biomass conversion to liquid fuels, such as pyrolysis and gasification, require dry feedstock (JA, 2016). However, harvested macroalgae has moisture content of 80-90% water compared to the relatively low moisture content of terrestrial biomass after harvesting (such as switchgrass at 18%). The high water content of macroalgae means that they often require more energy than is contained in the macroalgae to be dried to 18%, as can be seen in Figure 2.

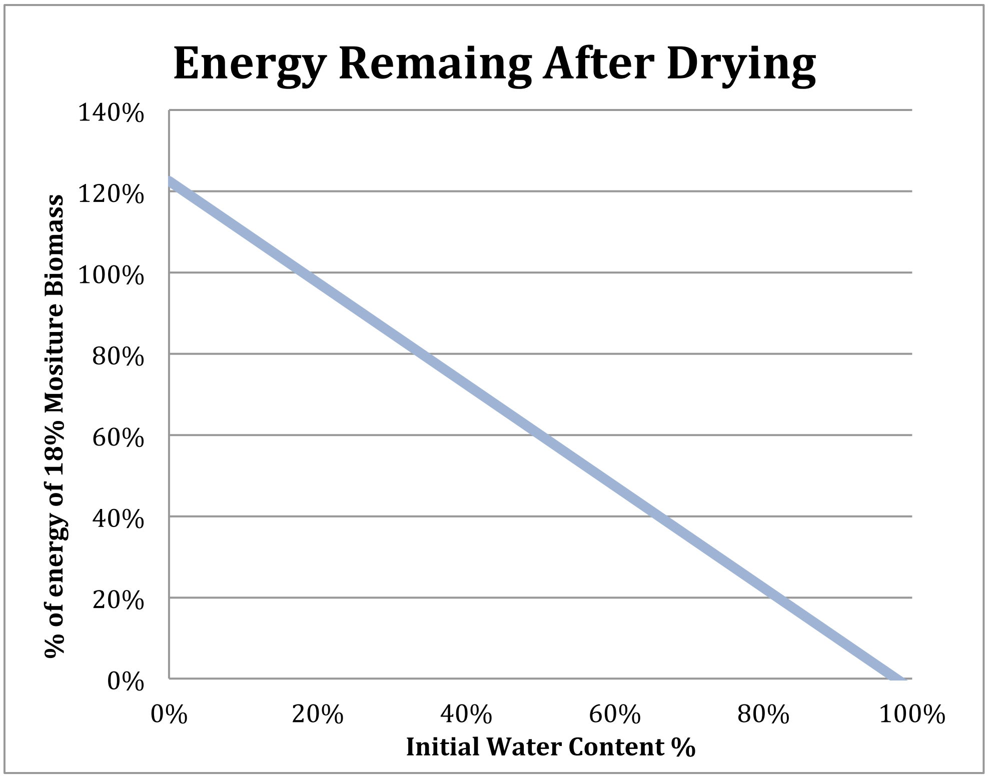

Figure 2. Comparison of energy remaining after drying biomass to 18% relative to initial moisture content.

Hydrothermal liquefaction is the leading contender for conversion of wet biomass into liquid fuel, and I will spend the rest of the paper examining the maturity of this technology for conversion of macroalgae to liquid fuel on a large scale. This paper deals with macroalgae culture and hydrothermal liquefaction as tandem technologies, since any pilot projects will likely be closely linked. Further work is needed to determine the energy and economics of these technologies if developed separately on a large scale.

Hydrothermal Liquefaction

Hydrothermal liquefaction (HTL) is a method to convert essentially any biomass to a mixture of biocrude, biochar, gas, and water-soluble compounds. HTL occurs at moderate temperatures (350 C) and high pressures (20 MPa), in the subcritical phase of water (Douglas, 2015). The subcritical phase of water has distinct properties from that of standard condition water and of supercritical water. From a reaction standpoint, the most important of these are increased solubility of hydrophobic compounds, increased viscosity, and an increased dissociation constant resulting in higher concentrations of hydronium and hydroxide (Sohail, 2011). Typically, biomass is diluted in a range of 1:10-1:15 dry mass to water and is maintained in reaction conditions for various amounts of time depending on the biomass. HTL produces a range of products that is highly dependent on the composition of biomass as well as the presence of any catalysts. New catalysts are not an area of significant new research, but varying the exact feedstock and catalyst composition can have significant effects. Generally, alkaline solutions are used for HTL of wet biomass as this reduces acid related polymerization (Milledge, 2014).

HTL from Macroalgae

Any biomass and water mixture can be used as reactants for HTL, but the relative lipid, sugar, protein, fatty acid mixture of the biomass will greatly effect the reactions that occur during HTL. Macroalgae are composed as described in Table 1. Macroalgae is notable for its significant ash component, which is a result of salt sequestration by the organism. The ash is found in the biochar and aqueous fraction of HTL and the salts do appear to have an affect on the HTL reactions. Optimization for particular salt varieties is unlikely, however, considering that optimization is necessary based on changes in biomass feedstock and this will account for changes in salt (Milledge, 2014).

Products of Hydrothermal Liquefaction

HTL produces a product known as biocrude, which is similar in composition to crude oil, biochar, which is the solid residue with ash components and limited amounts of carbon, an aqueous fraction, containing dissolved carbon and salts, and gas, which is primarily methane and carbon dioxide. Biocrude can be used as a direct replacement for crude oil, but its high oxygen and nitrogen content make thermal upgrading a necessity for widespread use. The biocrude produced from algae has variable elemental composition depending on its sources material, but generally has a HHV of around 30 kJ/kg. A general HTL setup is shown below in Figure 3.

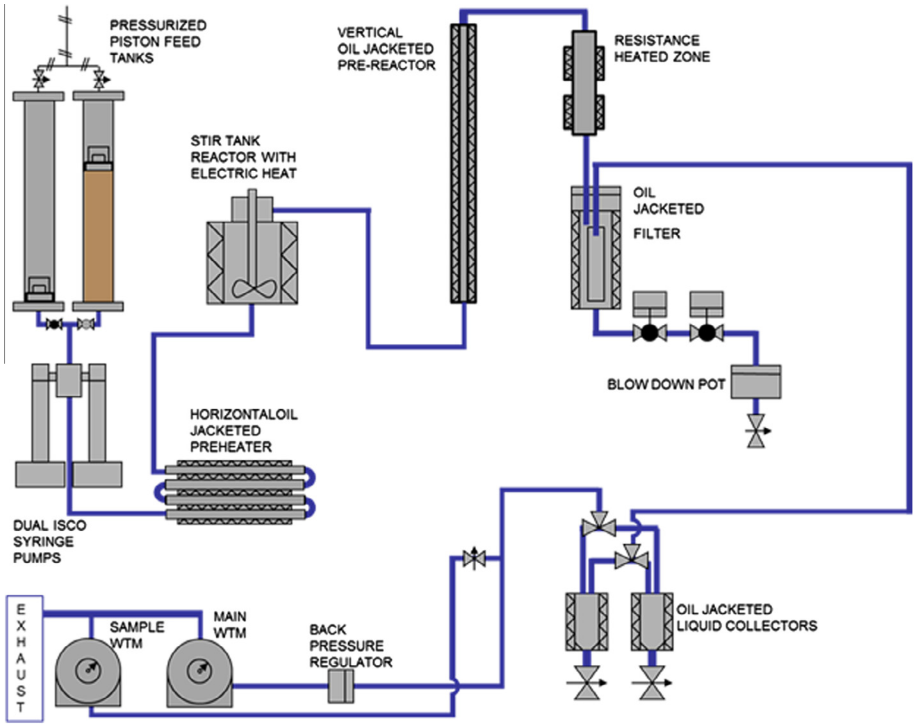

Figure 3. HTL set up (Daniels, 2014).

HTL Aqueous Fraction

A significant portion of total carbon can be found in the aqueous fraction (AF), 15% by one measurement, as well as significant amounts of salts, nitrogen, phosphate and sulfate (Xiaowe, 2016). Depending on the proposed HTL set up, two viable options are present: using the fraction as a growth media for bacterial culture or hydrothermal gasification to convert the remaining dissolved carbon into a mixture of methane and carbon dioxide. Limited work has been done on using the AF for bacterial cultural, however heterotrophic growth (i.e. bacteria consuming the organic compounds) has been shown to survive on dilutions of the AF. AF is appealing for this use since it can be produced in large volumes and is sterile. This set up, depending on the needs of the plant, could be used to produce high value chemicals (such as pharmaceuticals) that could provide a substantial economic buffer to a macroalgae-HTL system. Alternatively, hydrothermal gasification can convert essentially all of the dissolved carbon in the AF to gas. Hydrothermal gasification is a similar technology to HTL, except that it uses higher temperature, super critical, water to shift the reaction products towards gases. By volume, about 60% of the produced gas is methane, 30% is CO2, and 5% is ammonia.

HTL Biochar

Unlike biocrude, biochar has a low HHV, ranging from 10-18 kJ/kg, and accounts for about 6% of total carbon content of macroalgae (Appendix). As such, further upgrading of the material appears unlikely. While analyses vary based on the analytical technique, biochar generally is reported to have high nitrogen, phosphate, and sulfur content. These two features make biochar a good candidate for use as either fertilizer or as carbon sequestration. Sequestration of solid biochar would either allow for a carbon negative fuel or offset other fuel use, however neither of these have been accounted for in current carbon flow models.

Upgrading of Biocrude

HTL has low specificity and tends to incorporate significant portions of oxygen and nitrogen. Hydrodeoxygenation and hydrodenitrification (referred to here as Hydrothermal Treatment) are the most common methods to upgrade HTL biocrude to a usable fuel mix (Zhu, 2015). These are catalytic processes, similar to sulfur scrubbing from petroleum, that use molecular hydrogen to reduce carbon molecules, thereby decreasing their oxygen and nitrogen content. Hydrogen is generated onsite, usually from methane, adding potentially both extra equipment as well as feedstock requirements. HT reduces both the oxygen and nitrogen content to below 1%, and upon severe treatment to essentially zero. The product from HT can be integrated directly in to the crude pipeline, either being used as such or fractionated into gasoline, diesel, and jet fuel among other products. Alternatively, the heavy nitrogen content in HTL biocrude results from proteins in the biomass, and it is an alternative route is to fractionate biomass before HTL to separate out the proteins, although this is a more appealing route for microalgae where lipids can be separated out and processed in a more precise process than HTL. Analysis of the methane content of the AF indicates it is high enough to provide the needed hydrogen for upgrading of the biocrude (see Appendix, Sheet:Hydrogen Content). In the later analysis I will assume increased energy use for gasification of the AF but have omitted the inclusion of natural gas as a hydrogen precursor.

Laboratory Scale HTL

Laboratory scale HTL is performed in bulk reactors; that is all of the reactants are placed in a closed container that is then heated and pressurized. Bulk reaction setups are resistant to scale up since it requires reactors that are directly proportional in size to biomass being converted. For scale up to be it is necessary to be able to perform HTL in a continuous flow reactor (Douglas, 2015). Two forms of continuous flow reactors are viable for HTL, continuous stirred-tank reactor and plug flow reactor. Pilot scale studies have demonstrated continuous stirred-tank reactors with good results. However, plug flow reactors are preferable as they reduce moving parts, which can significantly reduce maintenance costs, and they can be more easily scaled. Further, plug flow reactors generally demonstrate significantly better product homogeneity and conversion on large scales, while tank reactors are equilibrium limited in conversion. The price and reliability difference is difficult to compare these two reactors without doing large-scale pilot experiments, and the results used here are based on continuous stirred-tank reactor.

<u>Algae Fuel Source</u>

Algae are divided into microalgae and macroalgae. Microalgae are microscopic organisms commonly observed as floating "tides" and have been explored extensively for the production of biodiesel (Sate-of-the-art, 2016). Microalgae is converted to biodiesel through extraction of lipids by fractionation and then conversion of the lipids to biodiesel through transesterfication. While promising, this process requires growing the microalgae in open ponds, and collecting the organisms so they are dense enough to process, which require significant amounts of land and water as well as energy. Further only the lipids are used for fuel production, resulting in much of the biomass being wasted. Overall, the return on energy investment is debated, but may in fact be negative (Bim, 2016). Macroalgae, however, may avoid these problems.

Macroalgae is commonly referred to as seaweed and grows naturally in many coastal areas and inland waterways around the world. The vast majority of macroalgae is grown as food, either for specialty products like alginate or for diets in parts of asia. Recently, as the development of microalgae into commercially viable biodesiel has stalled and fears have resurfaced about the current food supply system, the cultivation of macroalgae has begun to attract more mainstream interest. While unlikely to replace a substantial portion of our diet, macroalgae may be able to positively contribute to our liquid fuel needs.

Macroalgae is comprised of many distinct species, but as a whole they differ from microalgae in that they have lower lipid content, making them unsuitable for fractionation and transesterfication. Further, harvested macroalgae have significantly higher moisture content than terrestrial plants. Growth is highly variable between species and locations. However, the medium-scale culture of macroalgae is routine and high growth rates can be achieved. Some recent work has been done to map out the areas in the United States that would be amenable to large-scale cultivation, shown below in Figure 4. While the reality of large scale aquaculture is debatable, the possibility makes it an important option to consider.

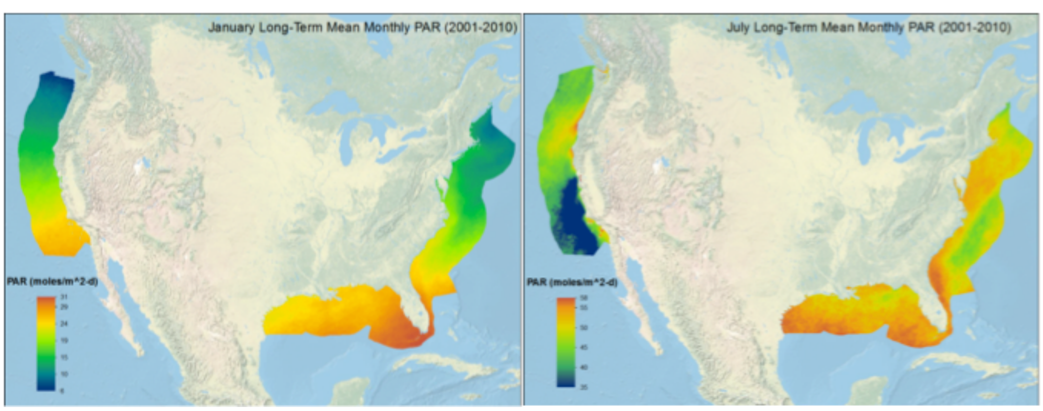

Figure 4. Potential for microalgae growth (Resiladi, 2014)

Growing Seaweed for HTL

Seaweed cultivation, as with most modern agriculture, requires significant capital investment (Bim, 2016). This period makes certain species of seaweed very expensive ($3000 per ton) particularly relative to terrestrial plants that can sell for as little as $75 tonne (discussed later). As LCOE evaluation later will show, this is a significant bottleneck to large-scale use of macroalgae for biofuels.

Algae Processing for HTL

Macroalgae is cultivated by ships and then transported a short distance to shore. At the dock, the algae is generally moved off the ships by a conveyor belt and transported to an attritor, which grinds it. Grinding the seaweed has two functions: first, it allows the liquefied seaweed to be transported by pipeline to the final processing facility, which is more efficient than, by conveyor belt or rail. Second, hydrothermal liquefaction requires a semi-homogenous input, which ground algae can provide. This processing is more similar to wet terrestrial plants (clover, fresh grasses) than it is for microalgae, with microalgae requiring significant energy input for harvesting and dewatering (Liu, 2016). The grinding of seaweed has been reported in the literature and calculations per kg are made in the appendix and energy use is discussed below. After grinding, the macroalgae slurry is pumped to the HTL plant and into the reaction vessel. Systems currently in use are capable of pumping macroalgae slurry, notably those used for wood pulp movement during paper production (Douglas, 2016). The calculation for the energy use of a common pump is in the appendix. The calculation works under the assumption that the power used to pump is proportional to the amount pumped, which likely falls apart under longer distances. However, that is beyond the scope of this report.

Results

HTL of macroalgae to produce bioefuels is still under active development and in the absence of pilot studies addressing specific concerns many questions will remain unanswered. However, estimates of the energy, carbon, and cost balance from cultivation to biofuel can be made for this technology, which in turn suggests important future questions. To control for data presentation over different studies, I standardized all values relative to kilogram of wet feedstock. This is particularly important for comparison between different feedstock, since while initial feedstock will have very different moisture content, the wet feedstock that is fed into HTL is standard. In these cases HT biocrude is compared to diesel as recent studies have shown them to be most similar.

Cost

Both algal culture and HTL requires significant capital outlays, as described above, but current literature on macroalgal cultivation suggest truly astonishing capital requirements. Currently, per liter biofuel produced from macroalgae, capital cost for cultivation dominates the per liter biofuel capital costs of HTL systems, as shown in Figure 5. A significant portion of this is likely due to the small scale of current macroalgae cultivation relative to other industrial and agriculture activities. The data shown for capital outlay for macroalgae cultivation is based off of data for a

100 tonne/yr operation, while the data for the HTL comes from a model for a 13000 tonne/day plant (Bim, 2016, Douglas, 2015). However, even if scale of operation decreased the capital cost for cultivation by 80%, the cost outlay for cultivation would still be larger than the entire HTL system. Interestingly, this is much closer to the total cost of cultivation of kale, which also sells for about the same price as macroalgae (discussed below).

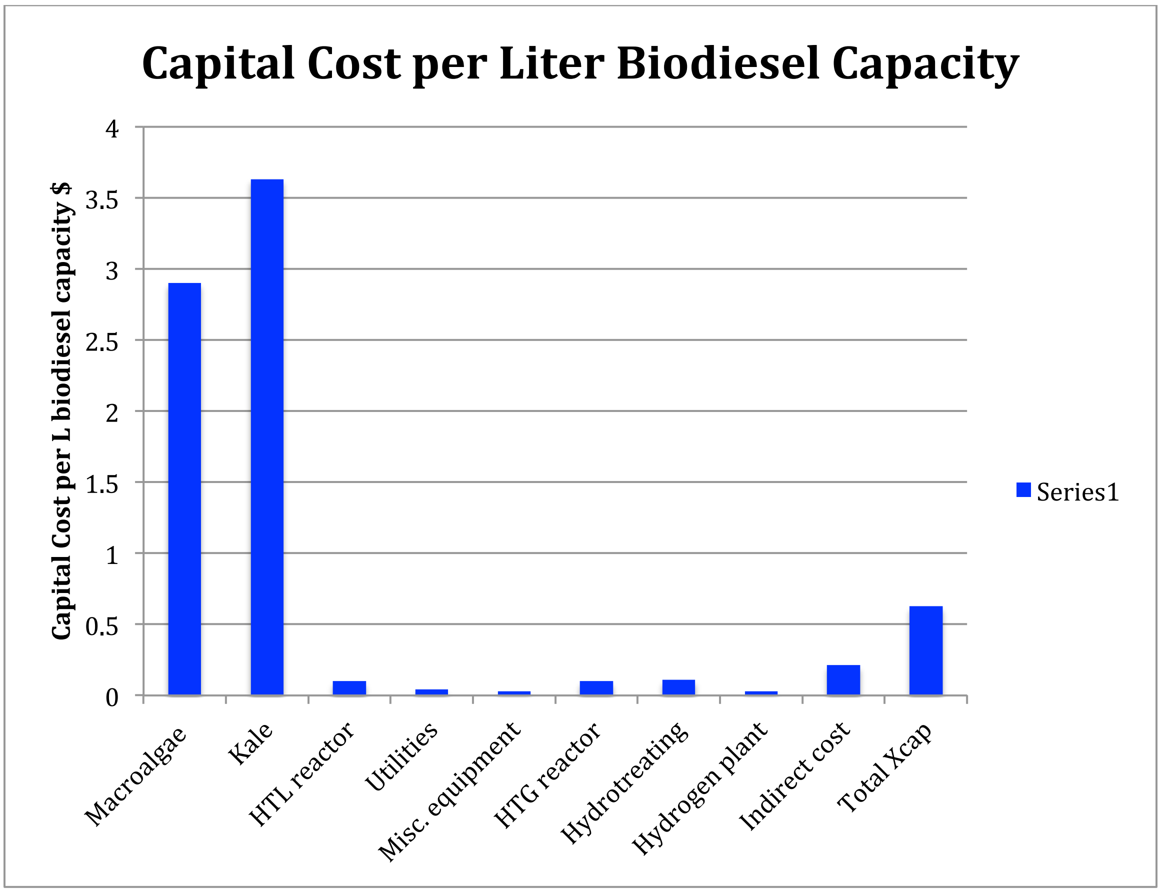

Figure 5. Capital cost of components of HTL system, plus for macroalgae and Kale

Energy

HTL is method for upgrading energy, which can be seen by the loss of total energy between the feedstock and the final products (either biocrude or HT biocrude) in Figure 6. It is important to note the significant gain in energy that occurs between the biocrude and HT biocrude. This is a result of the reduction by hydrogen gas. In previous studies the HT has been modeled by hydrogen (or natural gas to produce hydrogen) would be introduced into the system to reduce the biocrude (Douglas, 2015, Liu, 2016). That increases the energy density of the HT biocrude, but it reduces the net energy. Due to the analysis done in earlier that demonstrated sufficient hydrogen to perform HT, we can avoid modeling that loss. Finally, all of the pre-culture through pumping processes do take energy, but they are relatively small and therefore not visible in the figure (see the Appendix for details).

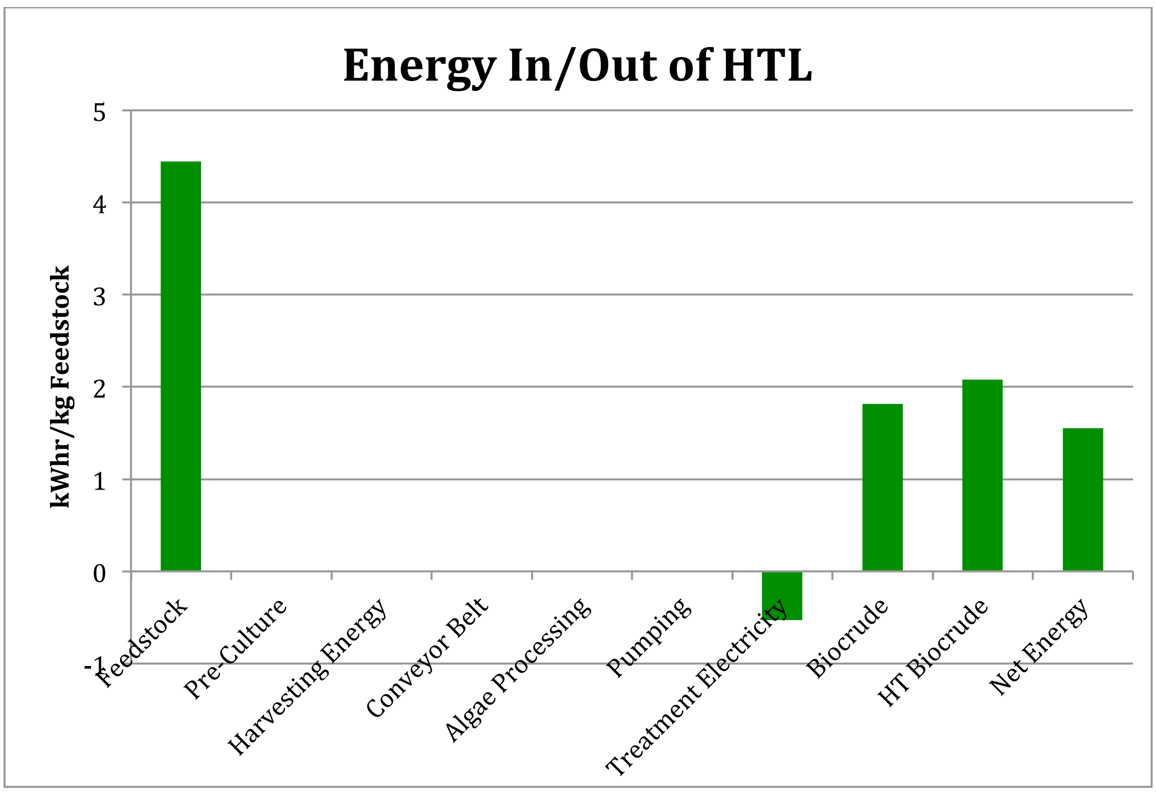

Figure 6. Energy investment in HTL processing of macroalgae.

Levelized Cost of Energy

As mentioned earlier, the cost of macroalgae is exceptionally high and this is shown in Figure 7. Clearly, it is not possible to develop a commercially viable biofuel from a biomass that sells for more than the fuel itself.

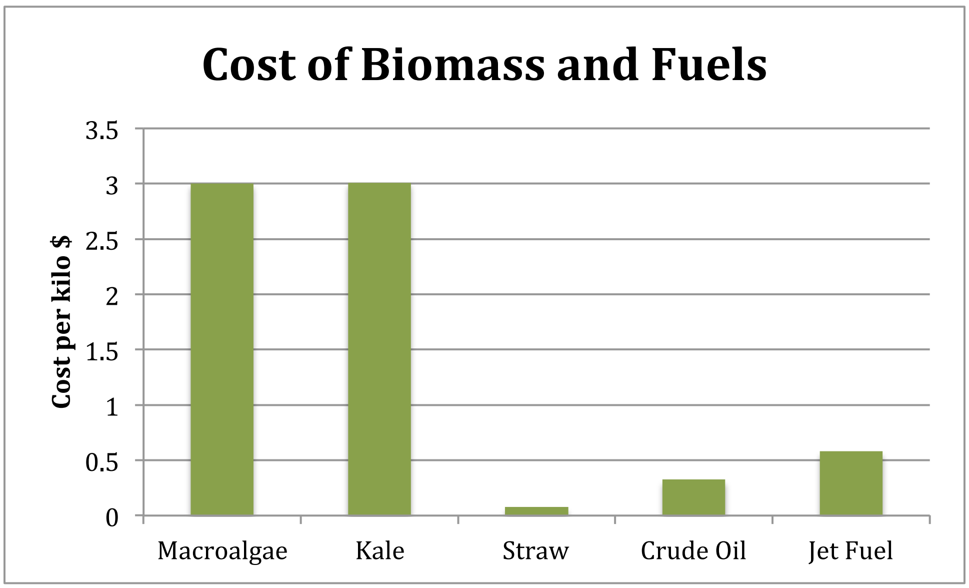

Figure 7. Cost per kilogram of relevant materials.

In Figure 8 the levelized cost of energy (LCOE) is plotted for a range of feedstock price per kg. Importantly, if macroalgae cost $0.075/kg as hay does, then it would be possible to break even relative to conventional diesel.

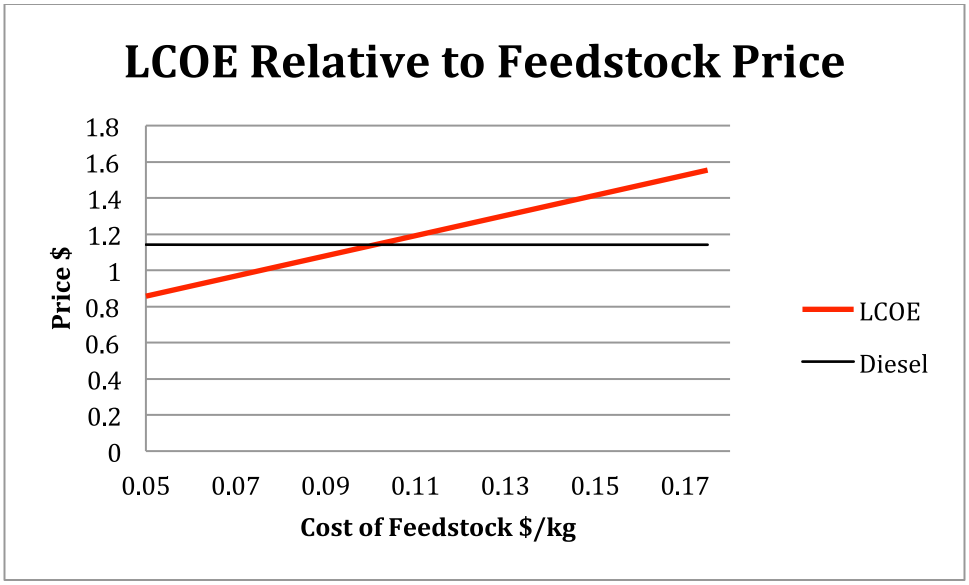

Figure 8. LCOE of HTL biofuel relative to feedstock cost.

Carbon

The carbon production of this technology mirrors the energy usage of the processing steps, as the production of macroalgae does not require any fixed carbon input. All of the processing steps can be fueled by electricity, and are assumed to be, except for harvesting of the algae, which must be done by boat (and assumed to be diesel powered). Carbon intensity is based off of CA ARB listings. As expected, the vast majority of carbon production comes from electricity input (Figure 9) which is as expected based on the energy inputs shown earlier. Overall, the biodiesel is a significant reduction in carbon production over conventional diesel, and would have zero carbon production if the electricity is generated with renewables.

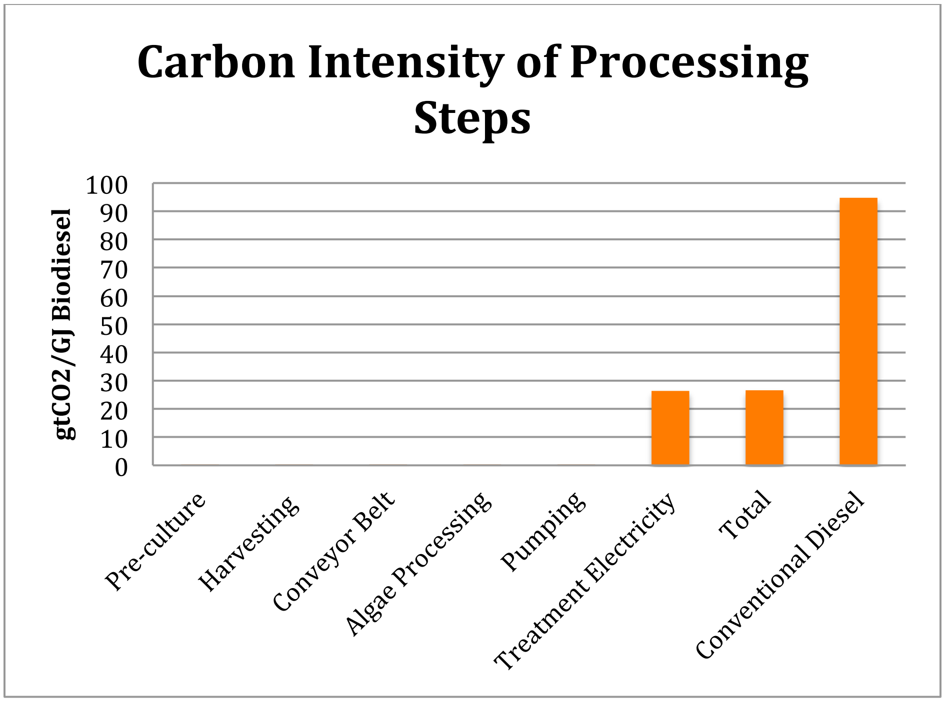

Figure 9. Carbon intensity of processing steps per GJ of biofuel produced compared to conventional diesel.

Analysis of HTL for other biomass has demonstrated a higher LCOE than equivalent conventional fuel (Douglas, 2014). However, as Figure 8 and Figure 6 suggest, if macroalgae can be produced at costs equivalent to terrestrial biomass then HTL with HT is an appealing technology. Finally, an advantage of performing algal HTL that has not been discussed is that the byproducts are environmentally neutral (Liu, 2014). As such, processing plants can be located relatively close to areas where macroalgae is being grown without fear of contaminating either the growth environment or coastline features

Conclusion

Previous work on hydrothermal liquefaction has focused on either anaylsis of bench top processes or theoretical analysis of larger scale set ups designed to process terrestrial biomass. In this analysis I have demonstrated that HTL with HT is an appealing approach to creating biofuels from macroalgae and that if only capital costs from HTL and HT are considered, it is commercially feasible. This is particularly true when the AF is gasified and used directly to create hydrogen for HT of the biocrude, a previously unreported finding. The elephant in the room, however, is the extremely high price of macroalgae. Based on the energy used to process and pre-culture the macroalgae, there is no immediate argument for the necessity of this price point and it may come down if large scale cultivation is pursued. It is recommended that further studies are done to asses how much US coastline is available for macroalgae aquaculture and the potential for econmices of scale to reduce the price. Until the price comes down, HTL from macroalgae seems commercially unviable and mostly of academic interest. It does not make sense to produce biofuels from the kale of the sea.

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