Comparison of two analytical techniques to produce a viable biocrude fuel from Macroalgae

Introduction

Fossil fuels are currently the most widely used fuel source, and are known to be pollutants that are harmful to the environment. Fossil fuels, when burned, release carbon dioxide into the atmosphere adding to the greenhouse gases and the overall warming of the earth. In addition to being harmful pollutants, fossil fuels are not renewable in the lifetime of humans. According to Carbon Dioxide Information Analysis of the U. S. Department of energy, the global output of carbon into the atmosphere in 2014 was 9.8 billion metric tons. In recent years, there has been a push towards renewable fuels. The first push in biofuels is to use first generation biofuels. First generation biofuels are commonly made from vegetable oils and corn sugars, and they usually produce biodiesel, corn ethanol, or sugar alcohol as the fuel source. They have the advantage of being economical and more environmentally friendly, but the disadvantage of being in competition with food supplies and often needing to be mixed with conventional fuels to be used. Now with advances in technology, the industry has started to turn to second generation biofuels. Second generation biofuels are manufactured from biomass usually using chemical processes.[10]

Biomass is the burnable fuel derived from plant and or animal materials. Biomass can be converted into a biocrude fuel, which can serve as a sustainable alternative to unsustainable, harmful fossil fuels. Some advantages to using the techniques that yield second generation biofuels are: the use of plant mass that does not compete with food stock, like grasses and invasive species, and they are also more environmentally friendly. Second generation biofuels also take advantage of the entire plant and not just the alcohols and sugars as in first generation biofuels.[11] It is important to note that the biofuels will still release carbon dioxide into the atmosphere just as the fossil fuels do. Biofuels are environmentally friendly, because the source of the fuel is the plants which have to ability to remove the carbon dioxide form the air. The release of carbon dioxide is counterbalanced by the carbon dioxide that the plant is able to remove from the air which means these methods do not necessarily add to the overall amount of greenhouse gases.[11]

Our proposed research involves finding a second generation biofuel replacement to fossil fuels through the isolation of biomass from macroalgae, specifically *Sargassum muticum* and *S. horneri*. *Sargassum muticum* and *S. horneri* were chosen due to their classification as an invasive species of macroalgae in San Diego, and their relationship to another invasive type of macroalgae, *Sargassum patens*. An experiment from 2012 by the Li, D lab used *S. patens*, which is in the same family as *S. muticum* and *S. horneri*, to produce a biocrude to be used as a fuel.[14] The highest biocrude yield for *S. patens* was by hydrothermal liquefaction, and the high heat value (HHV) analysis was found to be 27.1 MJ/kg which was increased due to increased amounts of carbon and hydrogen after hydrothermal liquefaction.[9] Although a similar hydrothermal liquefaction procedure to the Li study will be used, issues that were not addressed in the Li study such as: an evaluation of side-by-side analysis of two methods (hydropyrolysis and hydrothermal liquefaction) to increase the efficiency of extracting a biocrude fuel, a comparison of the types of local, invasive macroalgae will be addressed, and the procedure will be expanded upon to provide a more efficient method of extracting the biocrude fuel from the macroalgae.

The biomass from *Sargassum muticum* and *S. horneri* can be converted to a biocrude derivative using hydropyrolysis and hydrothermal liquefaction. Hydropyrolysis of a biomass to create a biocrude fuel is the thermal decomposition which takes place when organic compounds are heated to high temperatures in the presence of water. Hydrothermal liquefaction of a biomass to create a biocrude fuel is the thermal depolymerization process used to convert wet biomass into a bio-oil/bio-crude under moderate temperature and high pressure.[11] This research will provide a new, greener type of biofuel, through green chemical techniques of hydropyrolysis and hydrothermal liquefaction, that can be marketed. While the use of a second generation biofuel like macroalgae reduces our carbon footprint and reliability on unsustainable fossil fuels, the possible environmental impacts associated with growing and harvesting the macroalgae cannot be ignored. Even though *S. muticum* and *S. horneri* are classified as an invasive species in San Diego, there are still species of organisms that rely on the macroalgae fields that grow to survive. In addition to the possible destruction of marine habitats through the harvesting of *S. muticum* and *S. horneri*, the growth of *S. muticum* and *S. horneri* fields could disrupt marine habitats by introducing these invasive species to previously non-invaded areas. If successful, the proposed research will provide a new, greener type of biofuel that can be marketed at a reasonable, or even lower price. With the success of creating the new biofuel we will also be helping the local environment by removing invasive species and bringing the local marine habitats back to a more natural state.

Proposed Research:

Planned Experiments or Theoretical Investigations:

The species of kelp, *Sargassum muticum* and *S. horneri*, will be investigated as potential sources for biofuels. Both of these species are local invasive species in San Diego. There is evidence that *Sargassum* family can produce possible biofuels.[9] The two methods that will be employed on the two species are hydropyrolysis and hydrothermal liquefaction. These processes will be able to create the biofuels that will be analyzed for the ability to be a viable biofuel.

The harvesting of the kelp for initial testing is estimated to take a month to identify and locate the two species and contact to marine environmentalist groups. Once the kelp is able to be continuously harvested from a stable environment, it should not take more than 4-6 months before this experiment is running at a rate that can be used in practice.

Objectives and Tasks:

The main objective is to compare the viability of *Sargassum muticum* and *S. horneri* as biofuel precursors, while determining the appropriate method to accomplish the highest energy output per kilogram. The first task is to create the algae feedstock, also known as biomass. Next, the methods of hydrothermal liquefaction and hydropyrolysis will be conducted on each of the macroalgae species, performed in triplicate. For the results, the yield, and the higher heating value will be measured via bomb calorimeter.

Before employing the use of hydrothermal liquefaction or hydropyrolysis, the investigated macroalgae must first be converted to biomass. To create the sample biomass, the invasive macroalgae *Sargassum muticum* and *S. horneri* will be collected from the Pacific Ocean off the coast of San Diego via a diver. While these species are invasive, coordination with marine environmentalist groups will allow for the identification of safe harvesting regions. The macroalgae species will each be dried outside for a week before being pulverized by a plant disintegrator, and will be stored in a desiccator until use in either hydrothermal liquefaction or hydropyrolysis.

Hydrothermal liquefaction is a documented method use to depolymerize biomass into bio-oil.[11] Using a modified cylindrical reactor as outlined by other documented reports, hydrothermal liquefaction will be employed at 3MPa and (320-380°C) under an inert atmosphere (via N_2 gas).[9] After the liquefaction process has completed, chloroform ($CHCl_3$) and water (150mL for 25 grams of biomass) will be used as extraction solvents with 5% Na_2CO_3 by weight as a catalyst. The gas boiled off will be recondensed for later characterization. The organic layer (chloroform soluble) will contain the potential biofuel.To extract the potential biofuel from the chloroform, a rotary evaporator will be ran at 40°C to remove the chloroform solvent. The resulting product of each kelp species will be saved for later characterization. The solid waste will be dried in a vacuum oven; the water soluble layer will be ran through the rotary evaporator at 60°C for 16 hours. These portions will also be saved for later characterization.

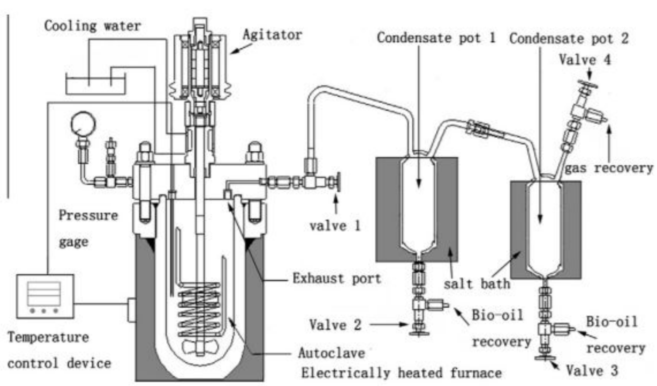

Figure 1. Experimental apparatus for hydrothermal liquefaction. Li, Demao, et al. “Preparation and characteristics of bio-Oil from the marine brown alga Sargassum patens C. Agardh.”

The second process for the isolation of biofuel from biomass is hydropyrolysis. An autoclave with an internal volume of 20mL will be used with 0.2g of Mo_2C as a catalyst. Dry macroalgae (~2.0g) was loaded into the reactor which was then sealed; the air within the sealed reactor will be replaced with H_2 at high pressure (~4-6MPa). The reactor will be heated within a salt bath to 120°C before a quench and the addition of 10mL of dicholoromethane as outlined in documented research[16]. The dichloromethane solvent can then be evaporated off of the bio-oil using a rotary evaporator at 40°C. The biofuel product will be subjected to analytical methods.

Figure 2. Hydropyrolysis apparatus and conditions. Chang, Zhoufan, Peigao Duan, and Yuping Xu. "Catalytic hydropyrolysis of microalgae: influence of operating variables on the formation and composition of bio-oil."

To evaluate each biofuel, the yield and the higher heating value (HHV) will be compared among the four main biofuels (one for each macroalgae and the respective process) according to documented methods.[13, 16] Yield provides the physical efficiency by mass, whereas the HHV provides the efficiency by energy. The yield as weight percent will be calculated for each biofuel and the resulting byproducts. These byproducts will include the solid residue, recondensed gas runoff, and the separated liquid of each process. GC-MS will identify the components of the resulting biofuels according to National Institute of Standards and Technology (NIST).[9] Elemental analysis will be used to calculate an expected HHV from the mass percentage of each element compared to ash.[5] A bomb calorimeter will be used to determine the higher heating value (or HHV, measured here in MJ/kg) after the post-combustion products return to room temperature (25ºC). To conclude the viability of *Sargassum muticum* and *S. horneri*, the yield and higher heating values will be reported in table format with four entries with denoted processes next to the species name.

Possible Outcome:

The outcome for this proposed experiment is an easily accessible biomass that can be turned into biofuel. Since these processes use invasive species for the biomass, there would be minimal impact on the environment, and the cost of this would remain low since the process itself is not that expensive. Beyond the scope of this experiment, should both methods and macroalgaes prove to not serve as viable sources of biofuel, there are other invasive macroalgaes in San Diego whose capacity to yield biofuels is unknown at this time.[14] The creation of this biofuel can help reduce the use of fossil fuels in our country, since the biofuel will outcompete fossil fuel sales in California-$3/gallon as of 27 November 2017 - by providing a cheaper fuel source that has the added benefit of being more environmentally friendly as well.[4] This will have a large positive impact on our environment, and since the species that will be used is invasive and relatively easy to obtain, there would be no real negative impact on the environment.

References

1. Bach, Quang-Vu, et al. "Fast hydrothermal liquefaction of a Norwegian macro-Alga: Screening tests." *Algal Research*, vol. 6, no. B, Oct. 2014, pp. 271–276. *ScienceDirect*, doi:10.1016/j.algal.2015.11.003.
2. Bazilchuk, Nancy. *Renewable Energy World*, 22 Oct. 2014, www.renewableenergyworld.com/articles/2014/10/turning-humble-seaweed-to-biofuel.html.
3. Black, Brenna A., et al. "Aqueous Stream Characterization from Biomass Fast Pyrolysis and Catalytic Fast Pyrolysis." *ACS Sustainable Chemistry & Engineering*, vol. 4, no. 12, May 2016, pp. 6815–6827., doi:10.1021/acssuschemeng.6b01766.
4. *California Gasoline and Diesel Retail Prices*, U.S. Energy Information Administration, 27 Nov. 2017, www.eia.gov/dnav/pet/pet_pri_gnd_dcus_sca_w.htm.
5. Channiwala, S. A., and P. P. Parikh. "A unified correlation for estimating HHV of solid, liquid and gaseous fuels." Fuel 81.8 (2002): 1051-1063.
6. Choi, Joonhyuk, et al. "Production of brown algae pyrolysis oils for liquid biofuels depending on the chemical pretreatment methods." *Energy Conversion and Management* 86 (2014): 371-378.
7. Ditomaso, Joseph M., et al. "Biofuel vs Bioinvasion: Seeding Policy Priorities." *Environmental Science & Technology*, vol. 44, no. 18, 2010, pp. 6906–6910., doi:10.1021/es100640y.
8. Dorminey , Bruce. "From the Sea to the Pump: Is Kelp a Viable Biofuel?" *Renewable Energy World*, 14 June 2013, www.renewableenergyworld.com/articles/2013/06/from-the-beach-to-the-pump-is-kelp-a-viable-biofuel.html
9. Li, Demao, et al. "Preparation and characteristics of bio-Oil from the marine brown alga Sargassum patens C. Agardh." *Bioresource Technology*, vol. 104, 2012, pp. 737–742., doi:10.1016/j.biortech.2011.11.011.

10. Rather, M. A., et al. “Catalytic hydrothermal carbonization of invasive macrophyte Hornwort (Ceratophyllum demersum) for production of hydrochar: a potential biofuel.” International Journal of Environmental Science and Technology, vol. 14, no. 6, 31 Dec. 2016, pp. 1243–1252. Springer.Link , DOI: 10.1007/s13762-016-1227-5.
11. Naik, S.n., et al. “Production of first and second generation biofuels: A comprehensive review.” *Renewable and Sustainable Energy Reviews*, vol. 14, no. 2, 2010, pp. 578–597., doi:10.1016/j.rser.2009.10.003.
12. Oak Ridge National Laboratory. “Annual Global Fossil-Fuel Carbon Emissions - Graphics.” *Carbon Dioxide Information Analysis Center*, 3 Mar. 2017, cdiac.ess-dive.lbl.gov/trends/emis/glo_2014.html.
13. Singh, Navneet R., et al. “Estimation of Liquid Fuel Yields from Biomass.” *Environmental Science & Technology*, vol. 44, no. 13, 2010, pp. 5298–5305., doi:10.1021/es100316z.
14. Smith, Jennifer. “Invasive Seaweed on the San Diego Coast” UCSD.edu. Scripps Institution of Oceanography, UC San Diego. Web. 7 Nov. 2017.
15. Vadlamani, Agasteswar, et al. “Cultivation of Microalgae at Extreme Alkaline pH Conditions: A Novel Approach for Biofuel Production.” *ACS Sustainable Chemistry & Engineering*, vol. 5, no. 8, 2017, pp. 7284–7294., doi:10.1021/acssuschemeng.7b01534.
16. Chang, Zhoufan, Peigao Duan, and Yuping Xu. "Catalytic hydropyrolysis of microalgae: influence of operating variables on the formation and composition of bio-oil." Bioresource technology 184 (2015): 349-354.