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Denitrogentaion of Algal Biocrude

The future of the world is based on the production of oil, coal, and natural gas. In the world today, cars are ran on oil, electricity is produced by coal and heating is often supplied by natural gas. However, the abundance of these fossil fuels is quite scarce at the current consumption rate. As projected by Ecotricity[1] the world's oil abundance, based on known reserves, will be exhausted by 2052. The world uses about 11 billion tons of oil per year[1], and is only projected to increase per year. With the increasing need of oil to produce gasoline, diesel, kerosene, etc. it is imperative for the world to find a new source of renewable, high yield, and energy packed fuel to power the world in to the future. One promising fuel that may replace oil is algal biofuel, which is produced from algae and converted into a liquid biofuel. With the feedstock for the fuel being algae there a few associated perks: renewable, easy to produce, and less emissions to produce[2]. The issue at hand with algae biofuel production is how to begin to make an algae biofuel to replace a fuel that has been perfected for the past 150 years. To create a replacement requires time to research to find the starting materials, beginning processes, scaling up processes, and improving upon processes.

The first aspect of researching algae biofuels is what algae to start with. There are many different species of algae that have varying compositions. The most important aspects of fuels is the abundance of carbon-hydrogen chains that can release a lot of energy via combustion. The importance of having an energy rich fuel is to replace gasoline which has an extremely high energy content. The higher heating value of gasoline is 46.4MJ/kg[4]. However in biofuels, the amount of protein present in the sample effects the energy content of the fuel. Proteins by character have many amino acids present, which entails Nitrogen in the biofuel. Certain elements present in the biofuels reduces the energy content of the fuel, like Nitrogen, Oxygen and Sulfur. While bomb calorimetry is the most accurate in determining the heat value of the fuel, the use of the Dulong's equation can also be utilized. The Dulong's equation uses the elemental percent of Carbon, Oxygen, Nitrogen, Sulfur, and Hydrogen to calculate the higher heating value(HHV).

$$HHV=0.335(CC)+1.423(HC)-0.154(OC)-0.145(NC)$$

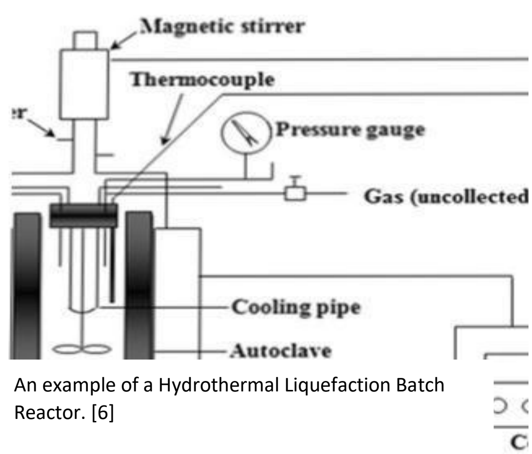
The Dulong's Equation for higher heating value. CC,HC,OC, and NC are the weight composition of Carbon, Hydrogen, Oxygen and Nitrogen respectively. Answer in MJ/kg. [4]

As shown in the above equation the presence of Oxygen and Nitrogen reduces the HHV of the fuel. This would make biofuel less energy dense and less useful as a transportation fuel similar to gasoline. The presence of Sulfur in alga is also extremely low, which allows for negligible calculation in the above equation. For this reason the choice of the feedstock is important in creating an efficient algal biofuel, below is some data on various types of algae and their specific compositions. However, processes to extract nitrogen play in an important role in creating algal biofuel. Another important aspect in the removal of Nitrogen from algae is the formation of noxious gasses when combusted. To reduce these problems Nitrogen removal from biocrude has been made a priority.

Strain	Protein	Carbohydrates	Lipids	Nucleic acid
Scenedesmus obliquus	50-56	10-17	12-14	3-6
Scenedesmus quadricauda	47	-	1.9	-
Scenedesmus dimorphus	8-18	21-52	16-40	-
Chlamydomonas rheinhardii	48	17	21	-
Chlorella vulgaris	51-58	12-17	14-22	4-5
Chlorella pyrenoidosa	57	26	2	-
Spirogyra sp.	6-20	33-64	11-21	-
Dunaliella bioculata	49	4	8	-
Dunaliella salina	57	32	6	-
Euglena gracilis	39-61	14-18	14-20	-
Prymnesium parvum	28-45	25-33	22-38	1-2
Tetraselmis maculata	52	15	3	-
Porphyridium cruentum	28-39	40-57	9-14	-
Spirulina platensis	46-63	8-14	4--9	2-5
Spirulina maxima	60-71	13-16	6-7	3-4.5
Synechoccus sp.	63	15	11	5
Anabaena cylindrica	43-56	25-30	4-7	-

Data on the percent composition of different species of algae. [3]

Once the alga is chosen the next step is to process the alga into crude. While there a few processes to convert algae into oil, the two most common are extraction with a solvent, and hydrothermal liquefaction[5]. Both processes require cultivation of algae in a proper medium. The best medium is salt water, with sun exposure and nutrients in the water[5]. Algae can be produced rather easily in most conditions. Then the algae must be harvested and prepared for the various process. Extraction of the energy rich compounds in alga require first to dry the algae which requires a lot of energy and time. Then the dried algae is extracted with an organic solvent like hexane to extract certain parts of the algae to create specific types of fuel. For example extracted triglycerides in algae can be reacted with methanol to produce biodiesel[5]. While this process has been extensively used, the second type of processing may pose greater future success. Hydrothermal liquefaction(HTL) begins with wet algae, and does not require drying. The wet algae is then subjected to either batch or continuous process at extremely high pressure and high pressure. Normally the process is held at upwards of 350 degrees centigrade and pressures of 21,000 KPa(3000psi). These conditions convert the algae into liquid biocruude, water and solid biochar. Phases are separated into biocrude, water and biochar[5]. Research in this experiment will be focused on biocrude product. Due to the ease of creating biocrude from HTL the process will be adopted in this lab for all testing of biocrude. In this lab most biocrude is produced at 350 degrees centigrade about 2000psi in a batch reactor with a residence time of 1 hour. Despite the ease of



An example of a Hydrothermal Liquefaction Batch Reactor. [6]

the process and ability for lab to create biocrude, impurities like Nitrogen and Oxygen from alga composition, limits usability. Further processes are used to remove Nitrogen and Oxygen.

Removal of Oxygen, Nitrogen and Sulfur has historically been a key process in the petroleum manufacturing sector. The reason to remove these impurities in crude oil is that organic nitrogen and sulfur compounds are environmentally harmful and reduce further catalytic reactions[7]. The most notorious removal method for impurities in crude oil is Hydrodenitrogenation(HDN) and Hydrodesulfurization(HDS). HDN and HDS are carried out concurrently with Hydrogen gas, in the presence of a transitional metal catalyst and temperatures above 300 degrees centigrade[7]. Normally the catalyst is a mixture of Cobalt and Molybdenum. However, researchers are always attempting to use different metals like Platinum, Palladium Cadmium and Rhenium[7]. Processing of algal biocrude is modeled after crude oil and shows similar mechanism for impurity removal. Various experiments have been carried out by researchers in upgrading of biocrude HDN. In one experiment a group of researchers found that denitrogenation of biocrude with Pt/C catalyst was not as effective as Pt/C catalyst with high pressure Hydrogen atmosphere in Nitrogen removal. The former had 3.68% residual Nitrogen content, while the latter had 1.50% residual Nitrogen[8]. Another group reported HTL obtained, HDN upgraded biocrude with only 1.69% Nitrogen content and a HHV of 43.4MJ/kg [8]. Both studies show excellent results in Nitrogen removal of algal biocrude obtained from HTL via HDN. However, HDN is extremely costly to utilize in production of biofuels. First, the cost of metallic catalysts is very expensive. For example the price for pure Pt is about $29.90 per gram, for Pd about $32.40 per gram while Rhenium is about $2.80 per gram[9]. In lab purposes make these expenses manageable, however scaling up processes would entail much larger quantities at the same price which would make the procedure much less feasible. Not only these catalysts but the need for high pressure Hydrogen atmosphere would also be extremely costly due to supplying enough Hydrogen, and safe guarding from combustion of Hydrogen gas. For the sake of replacing commercial fuels with biofuel from algae; price of production and energy content must be comparable to that of crude oil based fuels.

The alternative that has gained some tread in denitrogenation of algal biocrude obtained from HTL is through adsorption. Adsorption is the process by which molecules of liquids or gasses adhere to a thin layer of solids or to liquids they are in contact in[10]. Adsorption is a mechanism of impurity removal that can be significantly more cost effective than HDN, and only requires running a stream through a specific medium. The medium will adsorb certain aspects of the stream and release the rest. A downside of adsorption is that a specific adsorbent, or contact medium, must be chosen for certain scenarios. A few example of adsorption mediums are silica gel, activated carbon, zeolite, activated red mud and biochar. While current research on the use of adsorbents for denitrogenation of algal biocrudes is limited, other field have been utilizing adsorption already. One example is pollutant removal from wastewater using adsorption. Research was carried out in the effectiveness of biochar on the adsorption of various pollutants present in livestock wastewater. The researchers found that not only biochar but various other adsorbents could remove Quinolone(antibiotics) at 45.88mg/g of bamboo biochar created from pyrolysis[11]. For heavy metals the that biochars created from microalge, trees, wheat, and pecan skin could remove many toxic metals. The results showed a removal of Hg of 13mg/g adsorbent, for Pb about 18mg/g adosrbent and for Mo 78.5mg/g adsorbent[11]. The importance of this study is that adsorption has been shown to remove pollutants effectively in other fields. The most related study observes the removal nitrate from water via adsorption with activated carbon and clintophile[12]. In every respect, pH of nitrate solution, dosage of adsorbents, temperature and contact time activated carbon showed a higher nitrate removal than clintophile.[12] The peak removal of nitrate from synthetic wastewater of 100mg/L nitrate ions, was at 60mL solution, 4 grams activated carbon, 20 degrees centigrade, 60min contact time and pH of 6.5. The nitrate removal efficiency of the activated carbon was 62.61% and the highest for clintophile was 11.45%[12]. Another experiment that was completed was the understanding of nitrate and nitrite anion removal from wastewater using activated carbon from rice straw and compared to other published results[13].

Adsorbent	qo (mg/g)	Ref.
RS2/Na_2CO_3	8.2	This work
Bamboo powder charcoal	1.25	[29]
Commercial activated carbon	1.09	[29]
M. oleifera hull (anion exchanger)	11.78	[30]
Lauan sawdust (anion exchanger)	8.68	[30]
Coconut husk	7.44	[30]
Persimmon tealeaf (anion exchanger)	5.58	[30]
Pine bark (anion exchanger)	4.34	[30]
Rice hull (anion exchanger)	6.2	[30]
Sugarcane bagasse (anion exchanger)	3.72	[30]
Chinese tealeaf (anion exchanger)	2.48	[30]
Surfactant-modified zeolite (100% HDTMA loading)	3.97	[30]
Surfactant-modified zeolite (150% HDTMA loading)	6.63	[30]
Surfactant-modified zeolite (200% HDTMA loading)	5.64	[30]

Comparison of the monolayer adsorption of Nitrate anios capacities of various Activated Carbon samples[13]

These two experiments show that activated carbon shows the best potential in Nitrate anion adsorption. However the choice between which adsorbent to use is still quite difficult to determine until ultimately experimenting. The best method to start with would be adsorption of the algal biocrude instead of synthetic nitrate solutions on the best adsorbents listed above. This would require various analytical tools to determine chemical makeup before and after adsorption, as well as yield, and HHV of the upgraded fuels. From here, conditions can be manipulated based on which new adsorbents can also be tested like red mud, which is a toxic by-product of aluminum production, silica gel and perhaps biochar. Similar to the previous experiments, conditions of reaction could also be modified like temperature, residence time, dosage, and pH. After this stage, determining the best adsorbent based on Nitrogen and Oxygen removal, cost, and versatility of process. Perhaps certain adsorbents might be better for different algal feed stocks which will also contribute to experimentation. Once the bulk of experimenting with conditions has been determined scaling up the processes will begin. The goal of the project is to create a system that can eventually be used commercially, therefor research would need to be conducted on scaling the best processes up for future use. There are many pathways the denitrogenation of algal biocrudes obtained from HTL by adsorption can go, but the research should prove beneficial to HDN.

Links and Name of Files Used

1. https://www.ecotricity.co.uk/our-green-energy/energy-independence/the-end-of-fossil-fuels
2. https://link.springer.com/content/pdf/10.1007%2Fs12209-017-0051-4.pdf
3. http://www.oilgae.com/algae/comp/comp.html
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9. https://apps.catalysts.basf.com/apps/eibprices/mp/defaultmain.aspx
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11. biochar on wastewater.pdf
12. Evaluation of Nitrate Removal.pdf
13. Removal Of Nitrate and Nitrite Anions