Analyzing Methods of Removing Chlorophyll in the Production of Biodiesel From Microalgae

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Introduction

Microalgae is an autotrophic organism taking its part in the new trend of biodiesel. Not only can it sufficiently replenish itself with insignificant nutrients, it performs great in reducing emissions and other environmental costly effects compared to naturally derived fuels such as coal, petroleum, and other fossil fuels. The reduced gaseous emissions is unquestionable to solving the challenges that become more prominent as time and human development advances; these challenges battling the environment include decreasing greenhouse gases, climate change, global warming. Other than reducing adverse symptoms, renewable energy can secure natural energy supply and reduce energy dependence in first and third world countries. Achieving renewable energy, specifically microalgae biodiesel is still in progress due to the lack of technology sufficient enough to retain the expenses required. Algae consist of various strains where the macronutrients of proteins, lipids, and carbohydrates vary. Synthesized biodiesel or more specifically, fatty acid methyl esters (FAME) is a product of transesterification, with reactants coming from algae lipids (triglycerol) and methanol. This process itself is relatively simple however the strenuous process of commercializing biodiesel from algae remains rather difficult. An important and vital factor that challenges algae to be commercialized is its oxidation stability. Chlorophyll being prominent in algae, when exposed to light or oxygen increases the formation of various degradation products. Here we evaluate the methods of removing chlorophyll and its effect on quality of biodiesel.

Methods

Growing Microalgae
Two samples of water, one gallon each was collected from Lake Boren (16.20 ac.) and from a canal in Newport Shores connecting to Lake Washington. Each sample was mixed with a gallon of distilled water in addition of 1 tbsp of Miracle-Gro® Water Soluble All Purpose Plant Food per week.

Collecting and Concentration
The sample was concentrated in two different methods. Water containing algae was put into a 1 L beaker and the water was set on a hotplate to evaporate a majority of the water. Both the unprocessed sample and the evaporated sample were put into test tubes to be centrifuged for 1-2 minutes. The process was repeated by removing the water from the centrifuged heterogeneous mixture, then adding more sample to increase the amount of concentrated microalgae.

Dissolving Microalgae
100 mL of Hexane was mixed for each gram of Microalgae and left for a week. The solution was processed through a distillation bulb to remove hexane from dissolved microalgae. Another sample was filtered through a Büchner Funnel and placed in a nitrogen evaporation chamber (N-Evap).

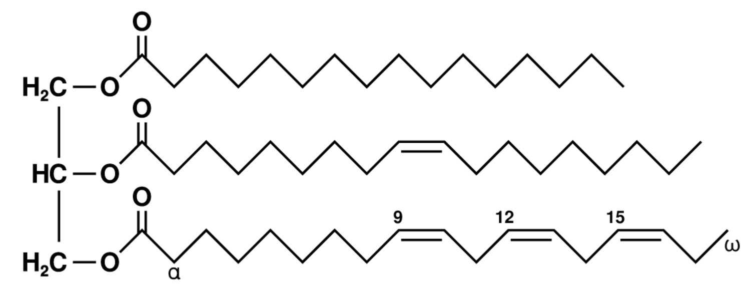
Saponification/Removing Chlorophyll
1% ethanol added to dried algae. Measured Sodium Hydroxide pellets and were dropped into the solution. Saturated chloride was added, along with hexane, 1:2:1 v/v/v solution to saturated sodium chloride to hexane used. Filtered solution using Büchner Funnel. Separated hexane using a separatory funnel then evaporating hexane by placing under the N-Evap.

Esterification
100 mL of methanol added to evaporated remains of sodium hydroxide and fatty acids.

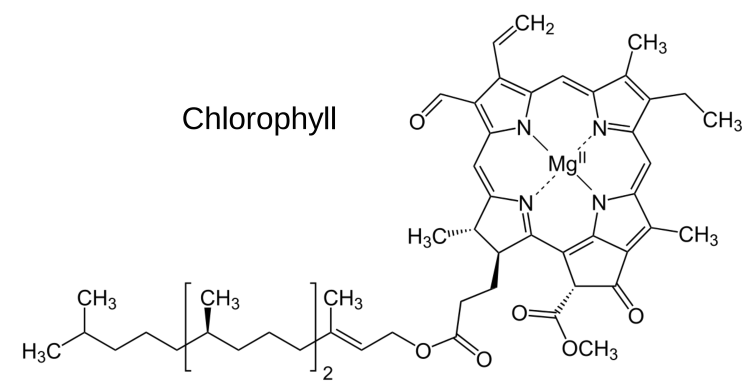
Discussion/Results

After separating and concentrating the microalgae, many challenges were faced in the goal of processing algae oil into biodiesel. In part of the transesterification process, it became apparent that doing so alongside the process of removing chlorophyll became rather cumbersome. Chlorophyll, which is the most abundant carotenoid, is a water insoluble/liposoluble magnesium-porphyrin compound. Being liposoluble, the compound is easily dissolvable in organic solvents such as chloroform, ethanol, acetone, and hexane. Dissolving the chlorophyll in hexane included dissolving lipids of the microalgae. Separation of the two byproducts was not tested, however the inclusion of lipid in hexane means the chance of significant loss. Both byproducts are liposoluble and water insoluble without excess treatment. These behavioral similarities challenge the separation of the two through organic solvent. The microalgae dissolved in hexane for multiple days, and was evaporated in the n-evap. After using the Büchner funnel, the solution was clear but colored with green pigment, an indication of chlorophyll.

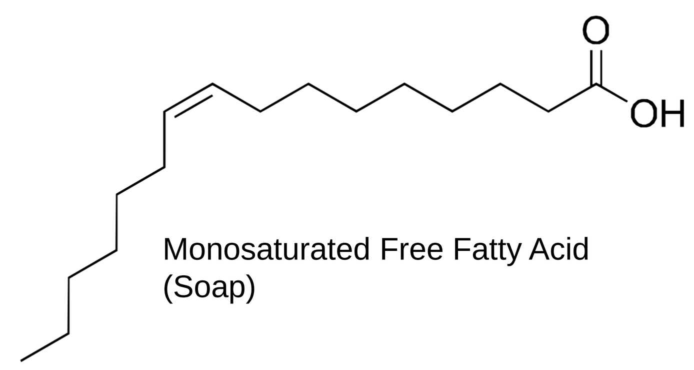
Furthermore, the presence of sodium hydroxide will saponify the chlorophyll, leading to the production of water-soluble chlorophyllin and phytol (C55H72O5N4Mg + 2NaOH = C34H30O5N4MgNa2 + 2CH3OH + C20H39OH) [4]. Alongside the addition of sodium hydroxide (NaOH), triglyceride or the algae fat will react with the hydroxide anion (OH-) breaking the ester bond of the triglyceride and turning it into a carboxylic functional group, resulting in free fatty acids. Without the presence of water, transesterification can occur with the presence of methanol (CH3OH), where the carboxylic functional group of the free fatty acid would be substituted, adding to the compound a methyl ester functional group, resulting in a more volatile and compatible fat for combustion, fatty acid methyl ester (FAME) as well as another byproduct, glycerol. However, the presence of water creates an unpredictable yield of FAME production. With the presence of water in the solution, H+ of H2O will also bind alongside CH3 from the methanol, leaving an uncertain amount of FFA and FAME. To limit the production of free fatty acids in water, saturated sodium chloride can be added to "salt out" the reaction. The addition of sodium chloride will dissociate into ions, causing an acid-base reaction where hydroxide (OH-) will react with the H+ from the carboxylic acid functional group of the free fatty acid, leaving its conjugate base, the carboxylate. The sodium chloride ions will surround what now is the carboxylate salt, leaving it as a precipitate. Testing various methods was not achieved however further data collection, testing, and analysis is required to compare and compete for efficient/high yield methods.



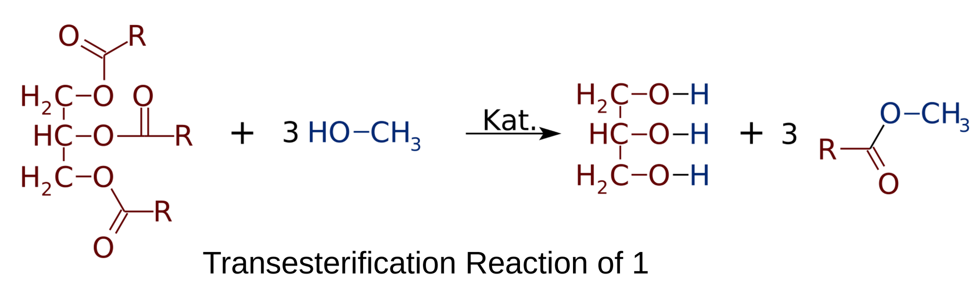
Example of a triglyceride



Chlorophyll



Monosaturated Free Fatty Acid (Soap)



Transesterification Reaction of 1 Triglycerol and 3 Methanol Turning Into Glycerol and 3 Fatty Acid Methyl Esters

Conclusion

Microalgae will most definitely play a role in the upcoming development of biodiesel. It's suitable for lab conditions however more experimentation and research is required to maximize the yield of fatty methyl esters, along while reducing the various products that assist oxidation. In the attempt to remove chlorophyll and quite simultaneously enact the transesterification process, both methods of saponification and organic solvent remains unfinished and unreported. Chlorophyll and other carotenoids will indefinitely decrease the efficiency of transesterification and quality of biodiesel, making the removal process a key component in commercialization. In terms of commercialization potential, a method of removing chlorophyll and experimenting for an efficient way to simply produce biodiesel requires more research. While the diminishing crisis of natural resources continues, further research on creating efficient biodiesel must persist to increase sustainable and renewable energy sources for the future.

Future Work

Limitation on time and sample amount led to a shortcoming of experimenting. Future work should be focused on collecting more data by testing different variations of methods. For the hexane extraction, a .45 micrometer filter should have been applied to examine further filtration of chlorophyll. The transesterification process of the hexane sample was not reported but remains important for further experimentation and a conclusion. For this research project, various methods of chlorophyll removal and transesterification should be experimented furthermore and tested for data to be analyzed.

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