**Reviewing Ethanol Liquefaction of pretreated natural microalgae in producing algal biofuel**

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**Algae has shown great promise as a possible leader in reducing CO2 emissions through biodiesel production. It is able to fix nitrogen, phosphorus, and heavy metals. Algae has a short growth cycle, low requirements for growth condition, and the ability to cultivate on non-arable land. New methods are beginning to use all product of algae biomass to generate a higher quality of biofuel. Conversion discussed in this article includes a pretreatment of raw microalgae by Soxhelt extraction of lipids or hydrothermal treatment for extraction of saccharides and proteins, and liquefaction of raw and pretreated samples in sub/supercritical ethanol. The composition of biocrude from the raw algae was complex, the biocrude from lipid extracted algae had poor quality, and the extraction of saccharides and proteins by hydrothermal pretreatment simplified the composition, reduced the nitrogen content, and improved the higher heating value for biocrude. That being said, algal biofuels are not ready to compete in the oil and gas industry, but proves that the algae research is heading in the right direction.**

**Introduction**

It is apparent that relying on fossil fuel energy is not a sustainable solution for our energy needs. Therefore, there is a relatively new research initiative aiming at developing new energy resources that do not require carbon emissions. Biofuel is a fuel derived directly from living matter. It can be used as a replacement for fossil fuels like coal and petroleum. It is produced through contemporary processes from biomass.

Biomass has shown great promise as alternate energy resource for reducing CO2 emission. Unfortunately, first generation biofuels (biofuels derived from terrestrial crops) have caused water shortages and contributed to deforestation. Second generation biofuels (biofuels derived from lignocellulosic agriculture and forest residues) have issues with competing land, but address the previous issues with first generation biofuels. Today, vegetable and plant oils are used as replacement for petroleum diesel. *Microcystis, Cyclotella, Cryptomonas,* and *Scenedesmus,* are all-natural algae that are easily and cheaply grown, have short growth cycles, and have the ability to fix nitrogen, phosphorus, and heavy metals from polluted waters. Hence, making algae biomass a great option for generating biofuel. Unfortunately, a low-cost process has not been found that results in a high-quality yield of algae. Different pretreatments and solvents are constantly being tested in this field to create a sustainable solution.

Extractive-transesterification is usually used when processing algae to produce biodiesel. This means lipids are extracted from dry algae using organic solvents. It is then converted to fatty acid alkyl esters by catalytic transesterification. Because algae has a multi-layered cell wall, more energy is needed for the extraction process. The harder it is for the solvent to penetrate the cell, the more energy the process requires. The saccharides and proteins that are extracted are also not used.

**Recent Progress**

New research and new methods are beginning to use all products from the algae biomass. For example, a thermochemical conversion method that uses the entire algae has been tested. This includes performing under supercritical liquefaction which produces higher yield of oil and higher energy density, but also contains higher amounts of oxygen and nitrogen. The presence of oxygen and nitrogen results in bad fuel quality. The goal is to convert either lipids, saccharides, and proteins, without degrading the other two choices. Fractional pyrolysis of microalgae was conducted via lipid saccharide extraction previously. Although there was a higher yield of bio-oil, the composition was simplified after the extraction of lipid. Meaning pre-treating the algae by extracting lipid can improve oil quality.

Methanol has been used in the past due to its low cost, but it is not a sustainable solution. Ethanol has been used to replace the solvent as a more renewable solution in the liquefaction process. In the study “Production of high-quality biofuel via ethanol liquefaction of pretreated natural microalgae”, a non-catalytic, two step novel method for converting microalgae is used. The algae is gathered from water blooms from Taihu Lake, and is pretreated by extraction of either lipid, proteins, or saccharides. The result was used as feedstock for the ethanol liquefaction process. This produced high quality algal biomass.

 The lipid extraction was performed using a Soxhelt apparatus. A Soxhlet extractor allows for unmonitored and unmanaged operation while efficiently recycling a small amount of solvent to dissolve a larger amount of material. After the extract was cooled, it was mixed with water and transferred into a centrifuge tube. The lipids were recovered through rotary evaporation. The extraction of saccharide and proteins were performed using an autoclave and the extraction was then stirred and cooled. The solid residue was filtrated from the liquid and dried in an oven. An autoclave reactor was used for the ethanol liquefaction experiment. Algae was mixed with ethanol and then added to the reactor. The reactor was cooled with water and the mixture was collected and washed with ethanol and oven dried.

Several solvents were tested for the lipid extraction pretreatment and methanol gave the highest yield at 5.4% wt%. A mix of two solvents were eventually used. The yield of biocrude was 57.3wt% with temperature increasing to 260 degrees Celsius. The results also suggested that degradation of raw algae generated gaseous products. The extraction of lipids made the biocrude and liquid products yields lower but overall, it yielded the conversion of algae and the production of gaseous products. The compounds in biocrude were analyzed by a gas chromatography mass spectrometry (GC-MS) and then classified into different groups. Only a fatty acids and a few fatty acid ethyl esters were detected and it was determined that the fatty acids were not esterified completely at lower temperatures. The decomposition of proteins resulted in gaseous products from the liquefaction of raw algae. The Soxhelt extraction did not extract the lipids fully as fatty acids still remained in the algae after the extraction, but hydrocarbons were not found after the extraction. Lipid extraction at low temperatures was helped by dissolution or conversion of proteins to small nitrogenous molecules. The saccharide extraction process made the components in biocrude simple and purer with esters.

**Discussion**

The extraction process did not fully extract all the lipids, while the hydrothermal treatment could extract most of saccharides and some proteins. The biocrude from lipid extracted algae had poor quality. The composition of the pretreatment algae was complex containing N-containing compounds, esters, fatty acids, and more. This resulted in a low higher heating value (HHV) that went down after the conversion of proteins was facilitated after lipid extraction, but the HHV increased in the liquefaction of the enzyme SPEA. There was a large portion of extracted solution from SPEA which can be used in conversions and as animal feed. The degradation of proteins was facilitated from the poor quality from the extracted algae. The composition was also simplified by the extraction of saccharides and part of proteins by the hydrothermal pretreatment. This improved the higher heating value for the biocrude.

Although the results from the composition and extraction of the saccharide and part of proteins were positive results, the process would still not be a viable solution to fit the standards in the energy sector. Algae has potential to be a valuable biofuel, but as of right now, more research needs to be done for it to be found in everyday gas stations. The results show that we are on the right track to finding an efficient way to break down algae.

By finding a new way to produce algae biofuels, we could reduce the amount of carbon dioxide emissions produced by fossil fuels. This would help fight the main problem-climate change. Shifting weather patterns are causing to threaten our food production and rising sea levels are increasing the risk of catastrophic flooding. Renewable energy is a step in the right direction in fixing the earth and its atmosphere.

**References**

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