MICROALGAE TO ENERGY

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Abstract

In today's scenario, algae are widely regarded as a promising source of renewable energy, based on its high growth rates, high oil content and ability to grow on waste water. Microalgae, an autotrophic microorganism with rich nutrition and high photosynthetic utilization degree, which are widely living in the sea and land. Microalgae can be converted into bioenergy such as biogas, biodiesel, and bio oil. As a result, high lipid content, less cultivated land use and short life time cycle are the typical advantages of microalgae as a potential substitute of fossil fuel. This paper, presents a general overview of algae, enumerating the differences between the families of algae and other vascular plants, and a review on the different cultivation methods.

The Soxhlet extraction of lipids from microalgae (Chlorella Vulgaris, Nannochloropsis sp., and Thalassiosira weissflogii), was carried out with several solvents (methanol, ethanol, isopropanol, acetone, and hexane), pure and mixtures, in order to optimize the extraction process. In the tested conditions methanol and the mixture of methanol acetone were the best solvents to extract microalgae oil.The extract liquid fractions were treated with activated carbon to remove the green pigment. Attempts to *in situ* algae oil transesterification were accomplished using acid (H_2SO_4) and base (NaOH and CaO) catalysts. The extend of extraction processes was assessed by infrared spectroscopy.

Keywords: renewable energy; microalgae; catalysts, lipid extraction, catalysis; in situ transesterification

1. Introduction

The petroleum reserves of today were simply a legacy of phytoplankton that grew over hundreds of millions of years ago, which were subjected to suitable conditions such as high pressure, temperature, anoxic conditions, and suitable formations and traps. The Present-day descendants of these sources of fossil energy, microalgae, still possess this unique ability to produce the same energy rich compounds that made their ancestors important to the development seen in our modern society. The tantalizing possibility that chemical engineers and energy technologist can still explore the ability of microorganisms that undergo photosynthesis has gained much interest recently amongst the scientific community. (Jonathan B. Shurin, 2016)

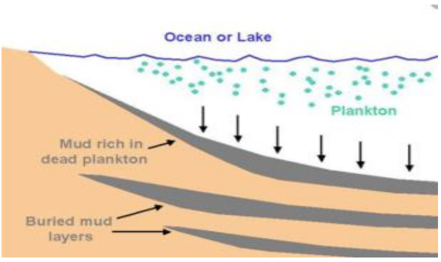


Figure 1:Process of oil formation from phytoplanktons millons of years ago.

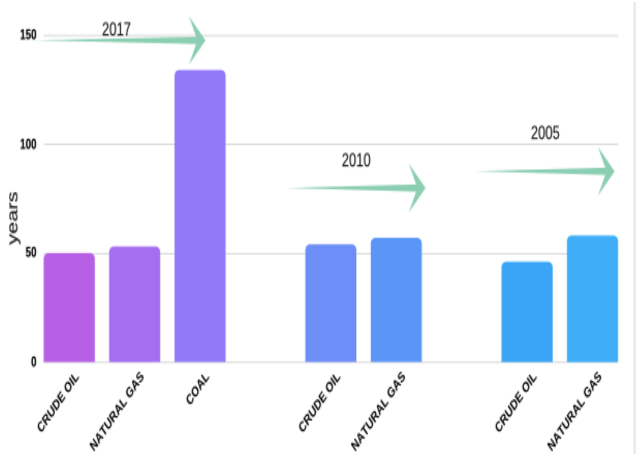


Figure 2:End of fossils fuel based on proven reserves for year 2005, 2010, 2017(BP Statistical Review of World Energy).

From the angle of renewability, dirty fuels like coal, oil, and gas are quite good and easy sources of energy and burning them to meet the societal energy demand is also a mature technology. However, this is plagued with a major problem: fossil fuel resources are finite and not renewable. Biomass, on the other hand, grows and is renewable. Accordingly with data from BP Statistical Review of World Energy, 2018,shows that the proven reserves are currently: Coal - 1,139 billion tonnes, Natural Gas ,-187 trillion cubic meters, and Crude Oil - 1,707 billion barrels, and based on this data matching with current consumption, the remaining life for coal would be 134 years, 53 years for Natural Gas, and 50 years for Crude oil, so in short, the proven reserves would soon be out by the years 2169, 2068 for coal and natural gas, respectively, and 2066 for Crude Oil.

AIM AND OBJECTIVES

The goal of this paper is to investigate the feasibility of obtaining biofuel from 3rd generation biomass, the factors affecting the technical and economic feasibility of obtaining a cost-effective energy (biofuel) from Microalgae, and the factors hindering the commercial viability.

This dissertation was carried out in the context of the project New processes for fuel production for road transportation (PTDC/EMS-ENE/4865/2014).

MICROALGAE

Microscopic algae, also called microphytes, are simply unicellular organisms which are ubiquitous, their presence could be seen in any kind of water varying from freshwater to marine systems depending on the species primarily in pigment composition, biochemical constituents and life cycle, size which could vary from a few micrometres (μm) to a few hundred micrometres. (M.P. Schenk et, al., 2008)

TYPES OF MICROALGAE

In their r esearch, Deng & Li, 2009, observed that microalgae can be found in a large range of places where light and water are present including ocean, lake, soils, ice, and rivers and that Microalgae can be divided into categories depending on their pigmentation, biological structure and metabolism

SIZE CLASSIFICATION

Microalgae are small organisms, which can be divided into 4 size categories as the microplankton (20 to 1000 µm), the nanoplankton (2 to 100 µm), the ultraplankton (0.5 to 15 µm) and the picoplancton (0.2 to 2 µm) (Gopinathan, 2004). Their small size allows them to do an effective photosynthesis, converting light energy with CO2 dissolved in water to produce lipids, carbon hydrates, proteins, etc. (Callieri & Stockner, 2002)

TAXONOMIC GROUPS

There are 4 main taxonomic groups that microalgae can be classified into which are:

- diatoms (Bacillariophyceae),
- green algae (Chlorophyceae),
- cyanobacteria or blue green algae (Cyanophyceaes) and
- golden algae (Chrysophyceae).

However, 6 other groups of microalgae exists, which includes the yellow-green (Xanthophyceae), golden algae (Chrysophyceae), red algae (Rhodophyceae), brown algae (Phaeophyceae), dinoflagellates (Dinophyceae), Prasinophyceae, and Eustigmatophyceae (Williams, 2010).

However, unlike the other groups of microalgae, which have lower lipid content and productivity compared with green algae or diatoms, Botryococcus sp., Dunaliella sp. and Chlorella sp. are examples of green algae taxonomic group that are reported to be the most promising species of microalgae for biodiesel production (Garofalo, 2010).

Table 1: Four most important microalgae groups in terms of abundance (https://core.ac.uk/download/pdf/41803397.pdf)

Microalgae	**Known species**	**Storage material**	**Habitat**
Green Algae	8 000	Starch and TAGs	Freshwater
Blue green algae	2 000	Starch and TAGs	Different habitats
Golden Algae	1 000	TAGs and carbohydrates	Freshwater
Diatoms	100 000	Carbohydrates and TAGs	Oceans, fresh and brackish water

In comparison to higher plants, microalgae do not have roots, stems, or leaves, but they have higher photosynthetic efficiency than plants or trees. Therefore, microalgae biomass cultivation will help in reducing concentration of CO_2 in the atmosphere at a faster rate than other land-based crops, especially when microalgae are cultivated under optimized environment conditions (Chisti, 2008).

Microalgae have received a lot of attention because they grow quiet fast, adapt to their environment easily, and their unique ability to concentrate useful chemicals and capture nutrients in an economical way.

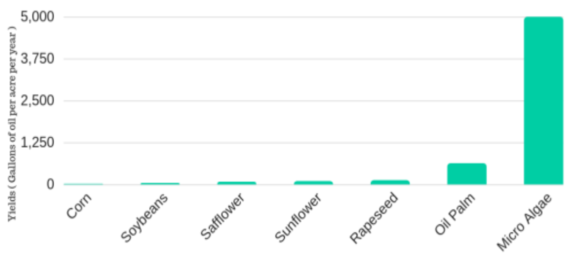


Figure 3:Yield of Oil per acre per year of Numerous Feedstocks. (Hanna, 1999)

They constitute the most fundamental positions in aquatic ecosystems, and therefore form the basis of food chains. The total biomass they represent is large enough to influence global climate systems. Estimates suggest that some 800,000 species of microalgae exist, yet of these only 50,000 have been documented (Mata TM, 2010).

2. Biofuels Production From Microalgae

Apart from its biofuel production capabilities, Microalgae can be utilized as sources of many products including chemicals (vitamins, pigments, antioxidants), oils (omega-3 fatty acids), protein, animal feed (for larval bivalves), and biomass for the production of ethanol and methane (Jiaxin Chen, 2018).

Biodiesel production from Microbial oil (MA) is significantly gaining interests due to the following reasons listed below: (Jiaxin Chen, 2018)

- rapid growth rate, usually two weeks from inoculation to harvesting,
- high lipids content as compared to other crops,
- problems on utilization of petrodiesel (depleting nature of proven reserves of fossil fuels),
- increase in the price of vegetable-based biodiesel and its increasing competition with food,
- the possibility of using non-arable land for MA cultivation.

Though there is a continuous effort to increase its lipid content and productivity, and one of the solution proffered is the use of genetic engineering (GE) technologies, there is still a controversy between science and environment about the risk posed by.

MA that are not cultivated for non-consumptive purposes present less risk when exposed to humans, but the effect on the environment is not yet resolved. GE technologies could help increase lipid content, pathogen resistance attributes, and high value of co-products (Ana F. Ferreira, 2016).

Nonetheless, algae biofuel conversion methods, such as transesterification, fermentation, and hydro-treatment, are more complex and economically expensive when compared to fossil-derived fuels and even biofuels from other feedstocks (Suganya T, 2016).

USED MATERIALS

The lipid extraction, transesterification, insitu-transesterification, and Purification of the microalgae species was carried out with the aid of the soxhlet extractor, density scale, petri-dishes, heaters, vacuum separator, filter paper, stop watch, and round bottom conical flasks, silica, activated carbon using various analytical reagents, on Chlorella vulgaris, Nannnochlorpsis oceania, and the 25g of Thalassiosira spp supplied by Algae for future in Lisbon.

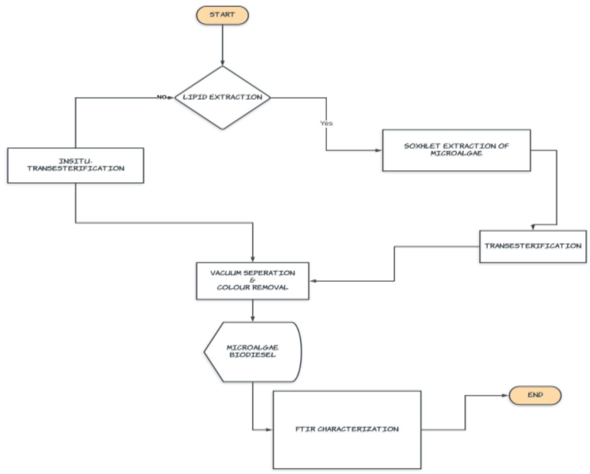


Figure 4:Flowchart for the Project work

For the extraction of the lipids from Microalgae, the effectiveness of various reagent was experimented either by using only a single solvent or by mixing the solvents in various proportions, the procedure below was followed;

- Firstly, the weight of the thimble is measure after drying for few second in the dryer;
- Then a known weight of the MA is dried, measured and transferred into the thimble which is made of cellulose,
- After which the thimble is placed in the soxhlet extractor and, connected to water source for the condenser to cool the vapour,
- A known volume of the reagent is placed in the conical flask, and after double checking all is set, Temperature is set to a little above the boiling point of the reagent(s) in the flask, then 3 hours was set for extraction,
- After extraction, the thimble is dried in the over oven, and measured to compare to the initial weight before extraction,
- Based on the current weight the lipid extracted is calculated using a program in Matlab, after which the extracted lipids content was calculated,

Figure 5:The stages of Microalgae Lipids extraction

3 TRANSESTERIFICATION PROCESS

The two methods of insitu-transesterification and extract-transesterification were conducted on the three species of MA, the ratio of methanol to biomass ranged from 5:1 to 40:1, with changing temperature, time, varying different catalyst type, and finally alcohol content in the process, basically using methanol and ethanol.

After extraction of the Lipids from the dry biomass, the extracted liquid was divided into two for transesterification, using methanol in excess with the aid of acidic/basic catalyst with the resulting fluid characterized with FTIR.

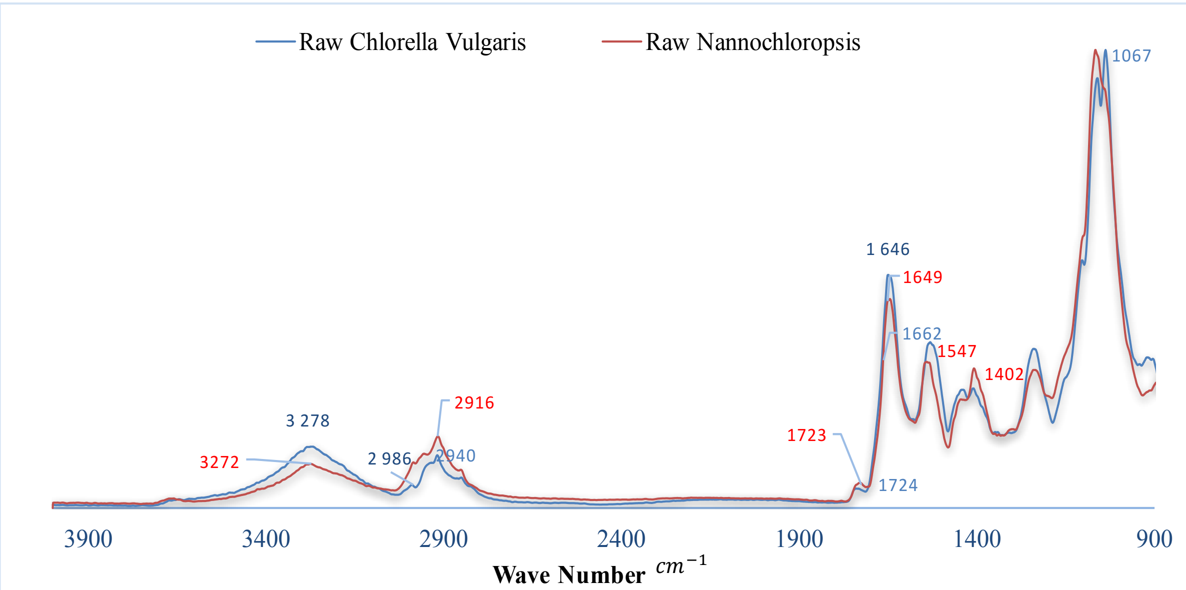
For insitu-transesterification the procedure are as follows;

- A methanol of 60-80ml is measure into the round bottom flask, with or without a co-solvent which was acetone for proper extraction of the lipids,
- Then the acid or basic catalyst is introduced into the flash, and it is stirred for 30 mins, after which the biomass is introduced and heated to around 65 degrees.
- Then the mixture is separated with a vacuum pump through filtration
- The resulting fluid is thereby characterized and decolourized with activated carbon
- The residue is dried and weighted to see how much extraction was carried out.

Figure 6: Methanogenesis of Microalgae

3. Results

The FTIR spectrum shows the way the macromolecular pool is distributed. There are



three main regions that relate to macromolecular pools, according to the lipid band (around 1740 cm−1), the amide I and amide II bands representing proteins (around 1660 and around 1540 cm−1) and the carbohydrate region (1200 – 900 cm−1).

The spectra of fresh samples of Chlorella vulgaris, and Nannochlorpsis spp. were characterized as shown in the figure 33 with each peak assigned a functional group, and the peak value of Nannochloropsis spp. in bracket.

The spectra belonging to protein are characterized by two strong features at 1646(1649) cm-1 for amide I, and 1545(1547) cm-1 for (amide II). These bands were due primarily, to C=O stretching vibration and a combination of N-H bending and C-N stretching vibrations in amide complexes, respectively. (Sigee et al., 2002)

Lipid spectra were characterized by two sets of strong vibrations, the C-H at 2916 cm-1, and the C=O mode of the side chain from ester carbonyl group at 1742 cm-1, carbohydrate absorption bands due to C-O-C of polysaccharides at 1146 cm-1,1067 cm-1, 1049 cm-1 respectively.

4.2 EFFECT OF SOLVENTS IN LIPID EXTRACTION

The extraction of samples with various solvents in time intervals ranging from 1 to 3 hours, resulted in the FTIR spectrum which are to be discussed.

Figure 7:FTIR of Thalassiora extract with methanol, acetone and propanol (E8)

The spectra above is from the liquid extract from soxhlet extraction with 40 ml of methanol, 140ml of acetone, and 20ml of propanol for 3 hours using 2.5g of Thalassiora spp. samples supplied by Algae for future in Lisbon. Qualitatively, the Peak 3355 is due to the (N-H) stretching present in the chlorophyll of the microalgae removed by the solvents, Lipid spectra were characterized by two sets of strong vibrations, the C-H at 2973 cm-1 and the C=O mode of the side chain from ester carbonyl group at 1710 cm-1, carbohydrate absorption bands due to C-O-C of polysaccharides between the region 1200-900 respectively.

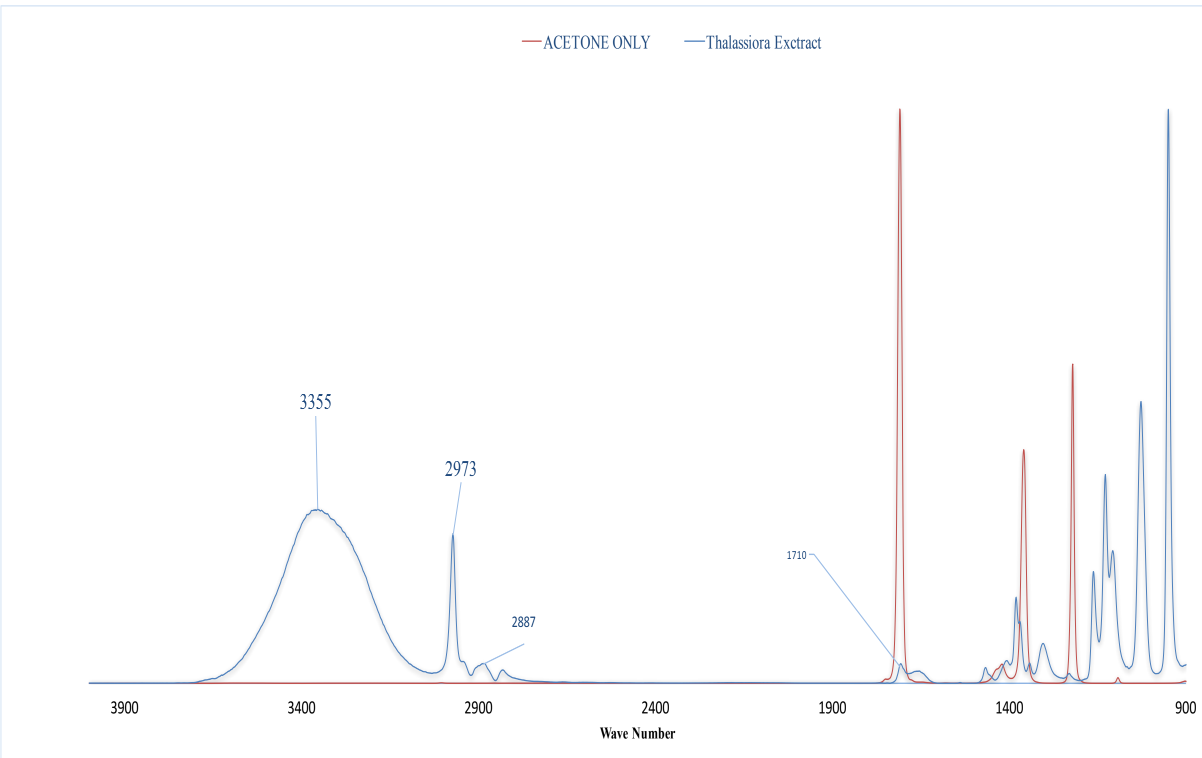


Figure 8: Thalassiosira sp. after chemical extraction on the left and after supercritical Co2 on the right

DECOLOZIATION OF THE BIODIESEL

The microalgae biodiesel produced from acid catalysis was quite darker, compared to the Biodiesel from basic catalysis which maintained the original green colour of the pigments contained in the microalgae sample. To meet the standard colour of colourless to yellow, activated charcoal of 0.3 g was added, and the mixture allowed to react for around 20 mins which after, the method of filtration was used to separate the mixture.

A change of colour was obvious and, the activated charcoal retrieved was seen to be still active for reuse.

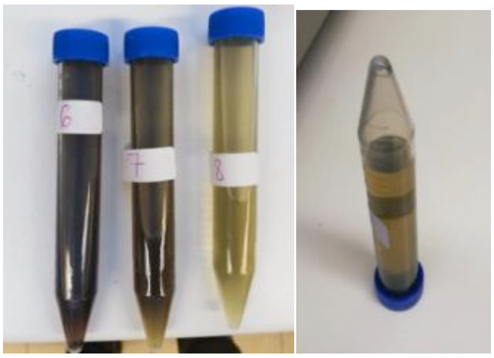


Figure 9a: Sample T6B, T7B, and T8B after reaction with activated carbon

CONCLUSIONS

One of the aim of this research project was to choose the best solvent or combination of solvents to extract lipids from microalgae efficiently, using the samples from Nannochloropsis spp., Thalassiosira spp., and Chlorella vulgaris. From the results, it shows that eithe the combination of methanol & acetone or the use of methanol alone is a good solvent for the lipid extractions from microalgae.

Currently, esterification and transesterification are the most commonly applied technology in the production of biofuel. For the paper, Insitu-transesterifcation as method of production of biodiesel, was used because it is becoming rather attaractive and highly effiecient in terms of bio-fuel production.The main draw-back of this process is that it consumes lots of solvents, water and it is highly energy intensive (about 30ml/seconds).

Biodiesel is a non-toxic, renewable, biodegradable, and more environmental friendly fuel which appears to be an alternative fuel to petro-diesel, but in the future other thermochemical methods, like hydrothermal liquefaction and pyrolysis would be needed to transform the residue left after making biodiesel into other combustible products.

Although, the industrial scale of production of biofuels from microalgae is at its early stage, it still represents a sustainable solution for transportation fuel that could serve as a replacement to the petro-diesel, since there is a possibility to produce microalgal biodiesel to satisfy the fast-paced rise in the energy demand within the restraints of land and water resources.

The biorefinery approach of biodiesel can lead to a more economical viable fuel which could replace petroleum based fuels or compete with other renewable energy technologies such as wind, solar, geothermal and other forms . Microalgae biodiesel is not yet economically viable despite the high potential in terms of productivity and sustainability. Most algae based biofuel concepts still require significant investment in research and development to make the process really become commercially viable.

The possibility of Microalgal farming should be incorporated with flue gas CO_2 mitigation and wastewater treatment to reduce the operating cost, thereby ensuring a cost-effective farming

Microalgae have the ability of decarbonization of flue gases as proven by the cultivation of these organisms to utilize the nitrogen and phosphorus as nutrients from waste water sources as a form of wastewater bioremediation.

Moreover, microalgal biodiesel can reduce the emission of NOx. Microalgae produce valuable co-products or byproducts such as H_2, ethanol, biopolymers, proteins, cosmetic products, carbohydrates, fertilizer, animal feed, biomass residue etc.

Microalgae cultivation does not require fertilizer, herbicides and pesticides, also from the combustion point of view the heating value of Microalgal biodiesel is more than that of other terrestrial plants, which is around 41MJ/kg as compared to the 37MJ/kg of soybeans or rapeseed.

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