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Production of Bio diesel from Algae

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ABSTRACT

In today's world, the majority of the energy needed is derived from burning fossil fuels. The negative impact due to fossil fuels is heavy on the environment. The appropriate infrastructure to replace fossil fuels with more renewable and environmentally sound energy sources still being many decades away, biofuels seem like the best alternative. Biofuels emit the same amount of CO2 as regular fossil fuels, but the crops that produce biofuels consume a lot of that CO2 while growing such that the net CO2 is often negligible or zero. Algae biofuels have been found to be Carbon positive, meaning that they consume more CO2 while growing than they emit while burning. In the present review we study the feasibility of producing biodiesel from algae.

Keywords— *Biodiesel, Algae, Biofuel, Environment, Carbon positive*

1. INTRODUCTION

The production of biodiesel from microalgae consists of extracting lipid bodies that contain large amounts of triacyl glycerides (TAG) and can be further refined into biodiesel via transesterification. The first step in making biofuels is harvesting the algae biomass. After the harvesting of the biomass is completed, the next step is the extraction of lipids. By definition, lipid extraction from wet algal biomass consists of disrupting/damaging the algal cell walls in the solution in which the microalgae were cultivated in. After the cell walls have been disrupted, lipids from the algae are then separated from the rest of the constituents by a host of methods but the methods most often used include the use of organic solvents.

After the lipids are extracted, the next and final step in the synthesis of biodiesel is transesterification of the lipids. Biodiesel is produced by transesterification of these extracted lipids with an alcohol, such as methanol or ethanol, on an alkaline, acid or enzyme catalyst, and it is composed of a mixture with at least 96 wt% of fatty acid methyl or ethyl esters (FAME or FAEE).

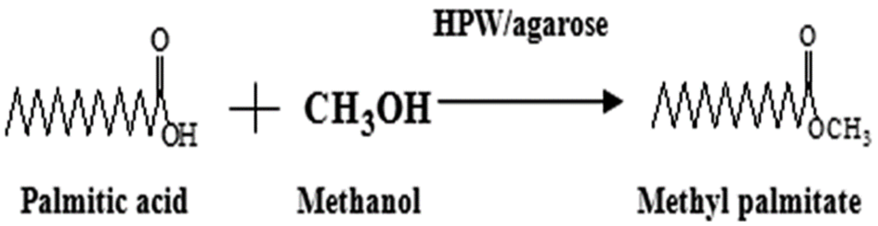

Fig. 1: The above image shows the transesterification process for palmitic acid. A similar reaction occurs for all other free fatty acids during transesterification

1.1 Process Flow Diagram

Figure 2 gives the process flow diagram.

2. HARVESTING (DEWATERING AND CENTIFUGATION)

Prior to the application of separation devices, flocculation can be used in order to ease the following dewatering steps. Diverse mineral salts (e.g., aluminium sulphate, ferric chloride) or organic polymers (chitosan) can serve as flocculants. However, addition of chemicals is expensive, can interfere with extraction, or is even regarded as harmful to the environment. Auto flocculation, for example, by stopping aeration with the effect of a pH shift, might avoid these detriments. The success depends on the presence of polysaccharides or specific proteins on the cell surface and is therefore strain and process dependent.

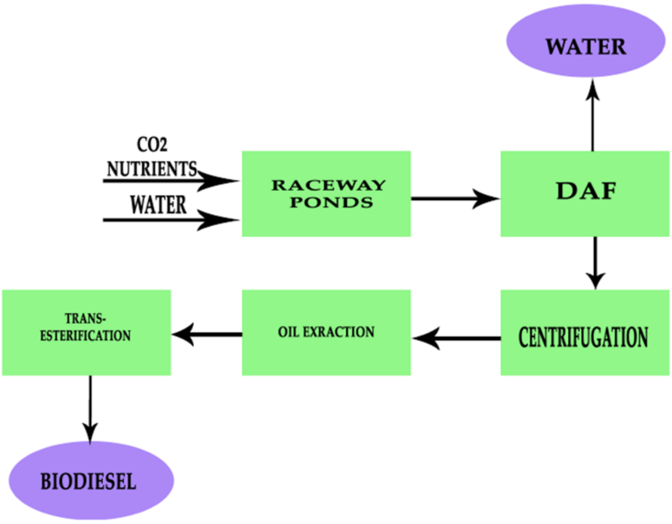

Fig. 2: Process flow diagram

Harvesting of the biomass comprises of separation and dewatering of the algae cells. Dewatering in this context means removal of the intercellular medium to an extent of about 90% resulting in a pasty pumpable product, while the intracellular water (>80%) keeps unchanged. Harvesting can be done in principle by filtration or centrifugation. However, microalgal suspensions exhibit for the moment low solid concentration of less than, for example, 1 $g \cdot L^{-1}$ and a low added value with respect to biofuels. This fact leads to changes in operation of classical approaches towards lower energy consumption and also triggered the design of new separation devices.

Filtration is the classical method in bio separation. Harvesting in open ponds is sometimes still done using manual sieves. Press filtration is the standard operation procedure in sludge dewatering. Basic problems are the compressible filter cakes with low specific permeability and high maintenance demand. The process development to overcome these problems goes in two different directions. One is the application of shear forces tangential to the filtration membrane with the effect of shear forces to prevent the formation of a filter cake. The other one is belt filtration with continuous cake removal and belt drying by pressing.

Centrifugation is regarded as the most effective separation method for large scale operations. Disk stack separators and also newly designed centrifugal devices especially for microalgae are operated at, for example, 3,000–4,000 g to reduce cell damage and claim efficiencies even below 1 kWh/m^3.

3. EXTRACTION

Bligh and Dyer is a procedure for the extraction and separation of lipids from microalgae using chloroform/methanol/water and also for the analysis of extracted lipids. Lipids from microorganisms' matrices such as microalgae are hydrophobic molecules which are soluble in many organic solvents. They can be divided according to the polarity of their head groups: neutral lipids (acylglycerols, free fatty acids, sterols, sterols esters, waxes and hydrophobic pigments) which are synthetized by the cells to store energy, and polar lipids (phospholipids, glycolipids, polysaccharides and proteins) which are the matrix of the cellular membrane.

Methanol, chloroform and water are added to the sample in a two-step extraction and, after phase separation, lipids are quantified in the chloroform phase. The compounds with a known amount of water are dissolved in this binary system and are then separated by transition from the monophasic system to the biphasic system induced by the addition of water: the final composition is located inside the miscibility gap. The partition of compounds between the WR (water rich phase) and the OR (organic rich phase) phases can be estimated in a first approximation by Hansen's solubility parameters as a roughly quantitative description of "like dissolves like"; the proteins and sugars are preferably partitioned into the WR layer and lipids into the OR layer. The adding of potassium chloride in the separation step can modify the distribution of lipids between the two phases. This phenomenon is supposed to be due to cations generated by the salts (KCl) which decreased the dissociation of lipids by a mass action effect, which, therefore, shift lipids to the OR phase, keeping salts in the WR phase. It can be also considered as a typical salting-out effect.

4. TRANSESTERIFICATION

After the lipids are extracted, the next and final step in the synthesis of biodiesel is transesterification of the lipids. Biodiesel is produced by transesterification of these extracted lipids with an alcohol, such as methanol or ethanol, on an alkaline, acid or enzyme catalyst, and it is composed of a mixture with at least 96 wt.% of fatty acid methyl or ethyl esters (FAME or FAEE).

Biomass with low residual water content is prerequisite for the typical transesterification with a homogenous base catalyst as the remaining water leads to undesirable saponification reactions. Soap formation also occurs in consequence of a high content of free fatty acids found in some algae and is to be prevented because saponification impairs the subsequent separation process and leads to partial consumption of the catalyst. Although base catalysis is favoured due to faster reaction kinetics and requirement of lower reaction temperatures saponification can be avoided when acid catalysts are used instead of alkaline ones, acid or base catalysts necessitate an additional neutralization process step. However, further attempts aim at replacing homogenous with heterogeneous catalysts. The latter reduce complexity of the process, cost, and the use of hazardous chemicals because separation and recovery of the catalyst as well as neutralization are dispensable.

To increase efficiency of the extraction process previous cell disruption can be taken into account in order to enhance solvent access to the storage lipids. The higher content of algal polyunsaturated fatty acids may induce adverse side reactions during transesterification. However, some of these fatty acids, for example, eicosapentaenoic acid (C20:5), attain higher prices on the healthcare, nutrition, or other markets. Therefore, gentle transesterification conditions and an additional separation step of products could improve profitability of the overall process.

5. MASS BALANCE

5.1 Open Pond

For the sake of our mass balance, we will consider our open pond to be 250 m^3 and 1m in depth. On average, this pond will be able to grow 90-175 kg of algae. For our consideration, we took 120 kg algae to be the weight of algae grown.

Now the total mass of the pond will be 250 kg of water and the 120 kg of biomass grown. That will be:

$$250 + 120 \text{ kg} = 370\text{kg}$$

Our basis for the mass balance would be 100 kg of total solution which will contain 32.43 kg algae and 67.57 kg water.
Basis:

100 kg solution = 32.43 kg algae biomass
67.57 kg water

This 100 kg solution is taken from the pond and then it is pumped to the dewatering and harvesting station.

5.2 Dewatering and Harvesting

After our solution passes through the DAF and the centrifuge, the product stream has 90% solids in it and 10% water and the by-product stream has 90% water and 10% of solids in it. Product stream Contents:

$$0.9 * 32.43 = 29.189 \text{ (Algae Biomass)}$$
$$0.1 * 67.57 = 6.757 \text{ (Water)}$$

$$\text{Product stream} = 29.189 + 6.757 = 35.946 \text{ kg}$$

5.3 Extraction

Add water and 0.87 kg KCl to the product stream to make the entire solution 100 kg
The ratio for Bligh and Dyer is 1.8:2:2 for Water solution: Chloroform: Methanol
Therefore is 100 kg water solution being 1.8 parts, 2 parts Chloroform and Methanol comes out to 111 kg

Reagents:
100 kg water and biomass solution
111 kg Chloroform
111 kg Methanol

We consider the lipid content in the algae to be 24% dry weight

$$\text{Lipid content} = 0.24 * 29.183 = 7 \text{ kg}$$

Once the procedure is complete, 60% of all lipids are in the chloroform layer which is the layer from which we get our lipids.

$$\text{Lipids extracted} = 0.6 * 7 = 4.2 \text{ kg}$$

The Chloroform is separated from the lipids by means of Buchner funnel and we get 99% lipids from the separation.

$$\text{Final Extract of lipids} = 4.158 \text{ kg}$$

The by-products are the solution of Methanol = 111 kg, Water = 67kg, KCl = 0.87 kg, Algae biomass residue = 28.23 kg.

5.4 Transterification

The lipids extracted majorly contain non-polar lipids. These contain various actual lipid molecules having different Molecular weights. These molecules are either free fatty acids, Tri, Di or Mono-acyl glycerides. The stoichiometry for the transesterification will be either 1:1,1:2,1:3 parts of Acyl glycerides: Methanol respectively. We assume the average and consider 1:2 parts for the mass balance.

To get the average Molecular weights of the lipids, we consider the lipids in our experiment Palmitic acid and Stearic acid and we average their molecular weights to get the weight that we have considered.

$$\text{Avg. weight of lipids considered} = (284.48 + 256.43)/2 = 265 \text{ g/mol}$$

Considering 2 parts of Methanol being used

$$\text{Methanol used} = 64 \text{ g/mol}$$

The reaction will give products:

$$\text{FAME} = 237\text{g/mol}$$
$$\text{Glycerol (By-product)} = 92 \text{ g.}$$

Now our,
Lipids are 4.158 kg which comes out to 15.6905 mol.

So for 4.158 kg lipids we have the reaction.
Reactants:
Lipids = 4.158 kg
Methanol = 1.004 kg

Products:
FAME = 3.718 kg
Glycerol = 1.4445 kg

Total amount of FAME Obtained = 3.718 kg
FAME in the end makes up our biodiesel

6. ENERGY UTILISATION

6.1 Open Pond

We will continue with the same assumptions as we did for our mass balance, and the same basis at each stage for our energy utilization. Let us consider the energy required to cultivate 120 kg of algae biomass in our open pond. The water inside the pond needs constant mixing to ensure even growth of all algae cells in the pond. A paddlewheel is used for mixing of the water; a large commercial paddlewheel will need approximately 0.0208 $kWh/m^2.d$ of energy. Thus for our pond of 250 m^3, we will need approximately 250 * 0.0208 = 5.2 kWh/d. Accounting for the growth lag of the algae cells, to get a fully grown batch of algae cells it would require somewhere around 25 days. We also need to supply a constant steady flow of CO_2 throughout the growth period of our algae. We considered that CO_2 in the form of flue gas from nearby industries will be used and will be introduced into the pond by a pump. Let us consider the distance between the flue gas origin and our pond is short and that it would take approximately 2 kg of CO_2 for 1 kg algae biomass to grow till full growth. So, we need 240 kg of CO_2.

The energy required to pump CO_2 will be approximately 5.55 kWh.

Total energy required for mixing = 5.2 * 25 = 130 kWh.
Total energy to pump CO_2 = 5.55 kWh.

6.2 Harvesting/Dewatering

We take a 100 kg solution from the open pond for our basis here. Now the Dissolved Air Flotation (DAF) machine requires approximately 0.8 kWh/kg (Per kg of biomass), and the centrifuge machine requires approximately 1.85 kWh/kg (Per kg of biomass). In our 100 kg solution we have 32.43 kg biomass. Thus, the calculation becomes,

Total energy required by DAF machine = 0.8 * 32.43 = 26 kWh
Total energy required by Centrifuge machine = 1.85 * 32.43 = 60 kWh

6.3 Extraction

Now we have the basis of 29.189 kg biomass. The only energy required for the extraction of lipids will be for the mixing and the separation of the reagents. This will require approximately 20.45 kWh.
Total energy required for extraction = 20.45 kWh

6.4 Transesterification

Here we have 4.185 kgs of lipids as our basis. In our consideration, the transesterification phase of our process would not require any energy. Finally, we get our FAME that is going to be separated from the by-product glycerol by using a separating funnel or other gravity utilizing separation methods. Finally, we get 3.718 kg FAME.

Total energy required to 100 kg solution to turn into 3.718 kg
FAME = Total energy required for mixing + Total energy to pump CO_2 + Total energy required by DAF machine + Total energy required by Centrifuge machine + Total energy required for extraction
= 130 + 5.55 + 26 + 60 + 20.45
= 242 kWh
Total energy required = 242 kWh.

7. COST ESTIMATION

Open Pond

1. Nutrients - Rs. 220.56
2. Flocculants - Rs. 245.09
3. Waste disposal - Rs. 245.09

Total = Rs. 710.74

Extraction

1. Methanol - Cost of 1 kg methanol = Rs. 18, Cost of 111kg = Rs. 1998
2. Chloroform - Cost of 1kg = Rs. 38, Cost of 111kg = Rs. 4218
3. KCl - Cost of 1 kg = Rs. 20, Cost of 0.87 kg = Rs. 17.4

Total = Rs. 6233

Transesterification

1. Methanol - 18 x 1.07 = Rs. 19.26
2. KCl (catalyst) - 1

Power used = 242kWh

Cost of 1kWh = Rs. 15
Total Power Cost = Rs. 3630
Total cost estimated for production = Rs. 10645.98

8. CONCLUSION

The pitfalls of cultivating algae artificially for synthesis of biofuels are very evident. The capital costs are huge and very specific environmental conditions are required to be able to successfully we find from our basis of consideration in this project that, making biofuels from algae will only be feasible if we have very large volume yields from our algae cultivation and if the recycling of the reagents for the extraction is efficient. However, at the current time it is not feasible due to the high economical costs.

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