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Fuelling Future Using Microalgae Technology: A Review Paper

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Abstract — Energy makes the world go round. According to the statistical energy report by some oil companies' fossil fuels meet approximately 88% of the world's energy need. The need for energy and thus fossil fuel is going to increase with increase in world population. With the estimated increase in population it is unsustainable to depend on the fossil fuel for further energy demand, owing to depleting world fuel reserves and GHG emission. This review paper focuses mainly on the alternative for fossil fuels, the Biofuels. Biofuels can offer several opportunities to increase income sources, provide sources for supplying fuel, to increase the employment opportunities in villages, to reduce GHG emissions into atmosphere and increasing the security of energy supply. This paper spots light on the biofuels currently under development and will be a major contributor towards fuelling the future. The first generation biofuels obtained from plants like corn, sugarcane, sugar beet etc. faces challenges like high land and water demand, low productivity, disturbing biodiversity and puts strain on the world market as these are consumed by people. So we have second generation biofuels derived from lignocellulosic forest and agricultural residue, non-food crop feedstock but they also have less productivity and require more land.

Therefore from the present knowledge and technology available the third generation biofuel especially from micro algae are of great importance. They can be easily cultivated, can live in harsh conditions, requires less water, can grow in waste water, their productivity is significantly higher, helps in sequestering carbon from environment etc. Microalgae are photosynthetic microorganisms and require light, sugars, CO2, N, P, and K for living that can produce lipids, proteins and carbohydrates in large amounts in less time and then can be processed to give biofuels and various valuable products. The selection of microalgae strain, the various methods of cultivating like Open pond or Closed system like photo bioreactor and techniques for harvesting of microalgae like flocculation, centrifugation, biomass filtration, ultrasonic aggregation, sedimentation etc. were studied. The extraction and purification of lipids were also studied. As a part of review, various algal biofuel conversion techniques which can be classified as thermal conversion and biochemical conversion were studied.

Some of the synergistic approaches like combining biofuel production with waste water treatment and carbon sequestering were observed. The concept of photosynthetic efficiency (PE) is also studied from which it is found microalgae have comparatively high PE and also high potential to increase PE and productivity making it most efficient biomass resource for biofuel production. Hence the further study should be carried out on increasing efficiency, scaling the process including integration of various technologies like wind, solar, tidal etc.

Keywords: bioenergy, biofuels, cO2 sequestration, microalgae, sustainability, third generation biofuels.

I. INTRODUCTION

Energy makes the world go round. Energy plays an important role in development of Nation and is obtained from conventional fuels mainly fossil fuels. In 2008 the annual world primary energy consumption was estimated to be 11,295 million tonnes of oil equivalent (mtoe). Contribution of the conventional fossil fuels to be 88% of the total primary energy consumption, with oil (35% share), coal (29%) and natural gas (24%) as the major fuels, while nuclear energy and hydroelectricity accounted for 5% and 6% of the total primary energy consumption, respectively [1]. In 2014, the annual world primary energy consumption was estimated to be 12928 million tonnes of oil equivalent (mtoe) [2] with the share of fossil fuel about 86% of the primary energy consumption i.e. an approximate increase of 1179 mtoe of fossil fuel consumption in five years. But the world reserves of fossil fuels are limited and may get exhausted with increase in consumption rate. Moreover, burning these fossil fuels for generating energy, releases the greenhouse gases like methane, carbon dioxide and nitrous oxide into the atmosphere. With the development of the emerging economies like China and India the energy consumption is expected to increase and the thus the emission of GHG into the atmosphere [3]. Therefore, it is the need of the hour to find an alternative to fossil fuels which is sustainable, environment friendly, renewable and cost effective. Biofuels can offer several opportunities to increase income sources, provide sources for supplying fuel, to increase the employment opportunities in villages, to reduce GHG emissions into atmosphere and increasing the security of energy supply [4]. Biofuels are typically classified as First generation, Second generation and Third generation biofuels. The paper focuses on the Third generation biofuels, mainly biofuels form microalgae covering selection of microalgae strain, the various methods of cultivation like open pond cultivation or closed system cultivation using photo bioreactor, harvesting of microalgae using various techniques like flocculation, centrifugation, biomass filtration, ultrasonic aggregation, sedimentation etc. The extraction and purification of lipids were also studied. Algal biofuel conversion techniques which are generally classified as thermal conversion and biochemical conversion were also briefly reviewed.

II. BIOFUELS

A. Brief About Biofuels

Biofuels are the fuels in any of the solid, liquid and gaseous form obtained from the biomass or bio waste and hence are also called the agrofuels. They can also be defined as the fuel whose energy is obtained through a process of biological carbon fixation. The various biofuels are ethanol, methanol, biodiesel, biobutanol etc.

Biofuels are classified as First generation, Second generation and Third generation biofuels depending upon the feedstock source. The feedstock for first generation biofuels comprise of corn, sugar cane, wheat, rapeseed oil etc. The technologies for the production of First generation biofuels are largely reported in the literature and are being practiced on commercial scale globally in many countries. It is estimated that the production and consumption of the liquid biofuels will increase in future [5], but it is difficult to meet the energy demand in transportation sector, with use of biofuels, due to following limitations: competition with food and fibre production, use of arable land, regionally constrained market structures, lack of well managed agricultural practices in emerging economies, high water and fertiliser requirements, and a need for conservation of bio-diversity [6]. The first generation biofuel sources are stable diets of many countries and hence the question whether to use these sources to feed the population or to generate fuels from them is hotly debated. Currently, about 1% (14 million hectares) of the world's available arable land is used for the production of biofuels, providing 1% of global transport fuels [4]. Hence, increasing the share of biofuel to near 100% is impractical due to its impact on the world's food supply and the large land requirements [7]. Hence the Second Generation Biofuels came into the picture.

The sources of second generation biofuels are non-food crops and oils obtained from the lignocellulosic matter like forest and agricultural residue, switch grass, wood, Jatropha seeds, cotton stalks etc. However, the technology for conversion in the most part has not reached the scales to meet the commercial scales [8]. For the biofuel to be economically viable it should be competitive with conventional fossil fuels; should require low to no additional land use; should enable air quality improvement i.e. by CO2 sequestration, and; should require less water requirement.

However, Third generation biofuels especially produced from microalgae have advantages over the previous biofuels generations [9] and has potential to fuel our future demand.

B. Biofuels from Microalgae

Microalgae are prokaryotic or eukaryotic photosynthetic microorganisms that can grow rapidly and live in harsh conditions due to their unicellular or simple multicellular structure Examples of prokaryotic microorganisms are Cyanobacteria (Cyanophyceae) and eukaryotic microalgae are green algae (Chlorophyta) and diatoms (Bacillariophyta) [10, 11]. The importance of microalgae in production of biofuels and its advantages over other fuels has been reported in many research papers. Microalgae are easy to grow, they can grow in harsh conditions, requires unaerable and little land to grow, it requires very less amount of water and can also be cultivated using water non potable for humans. Moreover they can grow almost anywhere, require sunlight and some simple nutrients. The growth rates can be accelerated by the addition of specific nutrients and sufficient aeration [15-17]. As microalgae takes in CO2 form atmosphere and nitrogen, phosphorous, potassium form soil or waste water for their living they are beneficial in applications of carbon sequestration and waste water treatment. Moreover the fuels extracted from the microalgae are environment friendly e.g. Algae biodiesel contains no sulphur and performs very similar to the conventional diesel.

C. Microalgae Need of the Hour for Producing Biofuel

The following are the advantages of using microalgae as source for biofuels productions:

Being simple in structure biofuels can sustain in any environment. It requires only sunlight, carbon dioxide, water and nutrients like N, P and K. Many strains of microalgae can be cultivated all year round. The biodiesel production from microalgae is 12000 l ha^{-1} in open ponds while that from rapeseed is 1190 l ha^{-1} [18]. Micro algae can be cultivated on non-arable land with very less amount of water. Thus preventing the land use change, deforestation, biodiversity change and requirement of heavy quantity of water. The microalgae can survive in very harsh conditions and in saline environment. They can be grown in waste water like that of sewage water. In many parts of the world and in India, micro algae is considered as non-food crop unlike corn, wheat, sugar cane and hence puts no strain on food market. Microalgae can grow very rapidly and have very high oil content (20-50%) of the dry weight of biomass; their exponential growth rates can double their biomass in periods as short as 3.5 hours [13, 19, 20]. It is reported in [13] that 1 kg of algal biomass consumes approximately 1.83 kg of CO2 which makes it beneficial in sequestering carbon from atmosphere. Microalgae can also be used for waste water treatment by removal of nitrogen and phosphorous compounds [29]. Apart from biofuels, microalgae can give other valuable derivatives having numerous applications in area like cosmetics, pharmaceuticals, nutrition, aquaculture etc. Micro algae yield for biodiesel production is shown in table [1]. It can be seen that the biodiesel productivity for microalgae is significantly higher than other competing feedstock.

Table I. Comparison of Microalgae With Other Biodiesel Feedstocks [4]

Plant source	**Seed oil content (% oil by wt. in biomass)**	**Oil yield (L oil/ha year)**	**Land use (m^2 year/kg biodiesel)**	**Biodiesel productivity (kg biodiesel/ha year)**
Corn/maize (Zea mays L)	44	172	66	152
Hemp (Cannabis sativa L)	33	363	31	321
Soybean (Glycine max L)	18	636	18	562
Jatropha	28	741	15	656
Canola/Rapeseed	41	974	12	862
Sunflower	40	1070	11	946
Castor	48	1307	9	1156
Palm oil	36	5366	2	4747
Microalgae (low oil content)	30	58700	0.2	51927
Microalgae (medium oil content)	50	97800	0.1	86515
Microalgae (high oil content)	70	136900	0.1	121104

III. BIOFUEL PRODUCTION FROM MICROALGAE

The typical process for the biofuel production from microalgae is shown in Fig. 1.The key process steps are selection of microalgae strain and site, cultivation, harvesting, biomass processing, extraction of oils and lipids and finally converting these into biofuels.

First the microalgae strain and the site for cultivation is selected based on the environmental conditions, the lipid content needed, biomass productivity etc. Then the algal biomass is cultivated using appropriate cultivating method i.e. open pond, raceway pond or photo bioreactor. The cultivated mass is then harvested using suitable technique e.g. flotation, sedimentation etc. This harvested biomass is then given suitable treatment like dewatering, thickening, filtering, drying for removing water and to concentrate the biomass before taking it to extraction. The oil and lipids are extracted from the biomass and these oils/lipids are sent for conversion processes. The conversion of biofuel is done either by thermal conversion or biochemical conversion based on the technically viable process or the end product required. Each block in the value chain stages are explained in detail in the further studies.

A. Microalgae Strain and Site Selection:

The microalgae strain and the site for cultivation is selected based on the environmental conditions, the lipid content needed, biomass productivity etc.

According to Maxwell et al. [22] following criteria need to be considered while selecting the site for cultivation:

1. Land topography
2. Water supply
3. Water demand and salinity
4. Easy access to nutrients
5. Easy carbon supply sources
6. Climatic and environmental conditions
7. Temperature and evaporation

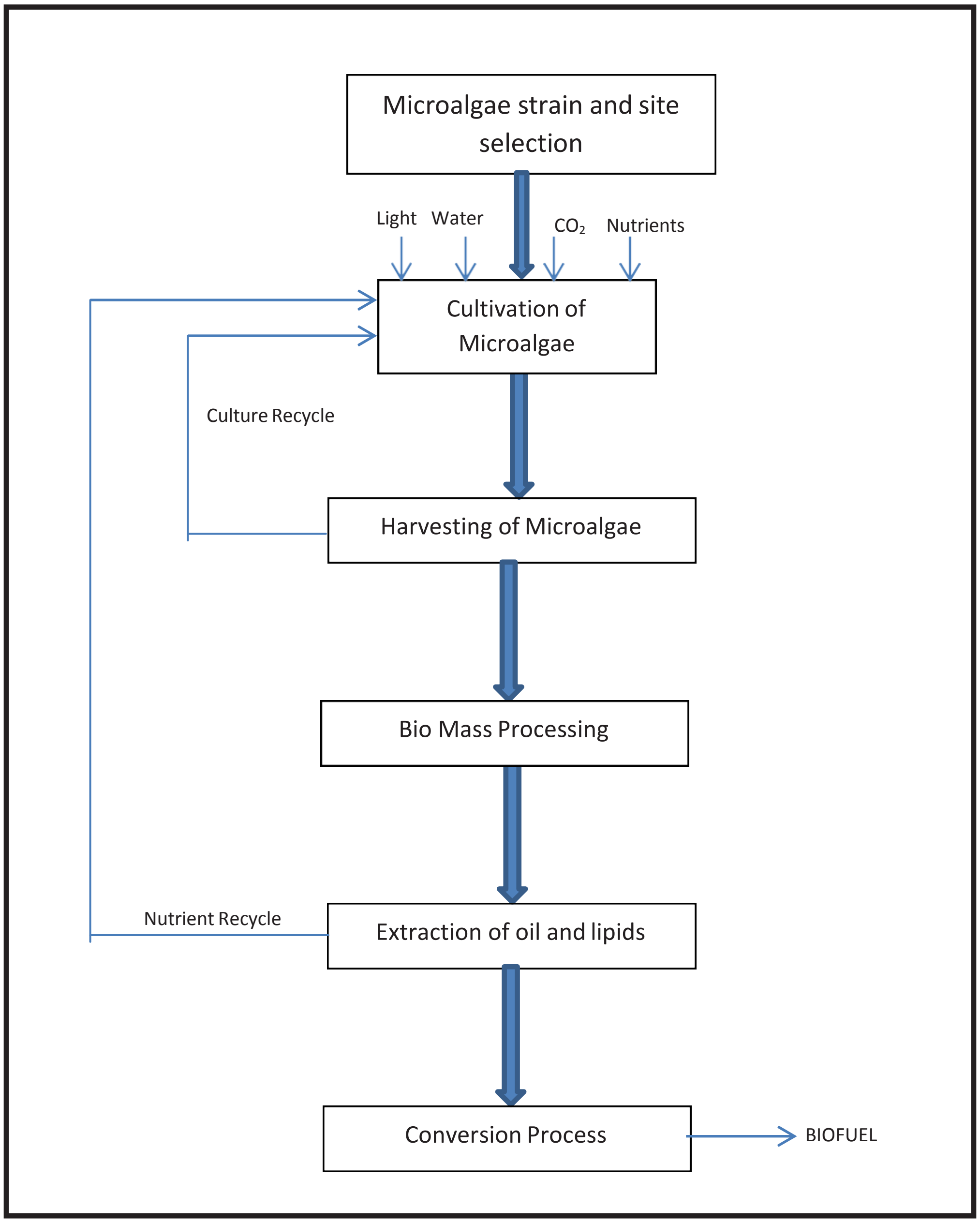

Fig. 1. Process Block Diagram for Biofuel Production From Microalgae

As the microalgae need to survive wide and harsh range of environmental conditions like high and low temperature, scarcity of water, salinity algal samples can be obtained from harsh environments like thermal spring or industrial waste water [4]. Some of the important factors to be considered while selecting algae strain are growing rate (total mass of biomass accumulated per unit time per unit volume), lipid content, resistance to environmental conditions, nutrients available, ease of biomass separation and also depends on the final product required [4]. Thus an extensive research and experimentation is required to select the perfect strain. For the research and experimentation the algae species can be obtained from the universities or from one thriving in environment. Although the process of species selection is time consuming and costs a lot, selecting right species for the production has some advantages.

B. Microalgae Cultivation

Cultivation is one of the most important processing steps in the biofuel production using microalgae. It not only decides the yield but also the cost of biofuel. Currently lot of research is being focused on the algae cultivation unit as it is important unit in biofuel production and determines the economic viability of the process. Microalgae may assume many types of metabolism namely autotrophic, heterotrophic, mixotrophic, and photoheterotrophic. De Pauw N et al. [24]

have defined above terms in detail. Phototrophic organisms grow photoautotrophically i.e. by using only sunlight as the source of energy to convert solar energy to chemical energy by photosynthetic reaction. Some grow heterotrophically i.e. by consuming organic compounds containing carbon. Mixotrophically growing organisms perform photosynthesis as the main energy source through both organic compounds and carbon dioxide. The algae species need only water, air, nutrients and most importantly sunlight for their growth. The equilibrium between operational parameters like temperature, light intensity, nutrients, pH and by-product removal plays an important role in cultivation of algae. Hence these parameters should be controlled carefully for obtaining good culture. Moreover care should be taken that the culture does not get contaminated. As per De Pauw et al. [24] experience has shown that infection is the indication of bad culture.

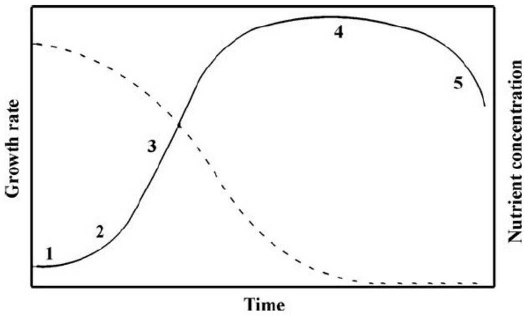

Fig. 2. Algae Growth Rate Vs. Time In Batch Culture (Solid Line) And Nutrients Concentration (Dashed Line) [4]

1. Lag phase
2. Exponential growth phase
3. Linear growth Phase
4. Stationary growth phase
5. Death Phase

The growth rate, the biomass generated and the overall cost of the biofuel production depends on the type of culture and cultivation process adopted. Microalgae can be cultivated in either open or closed system. The cultivation in the open system is usually done in an open pond. The open pond can be characterized as raceway pond and can be circular in shape, inclined and unmixed ponds [25]. While the cultivation in a closed system can be conducted in photobioreactor, which can be further categorized into many types including tubular, vertical, flat-plate, annular, fermenter-type and internally illuminated photo bioreactor [25]. Open pond production systems are generally open to the atmosphere and can be natural or artificial. They are made from closed loop circular as shown in Fig. 3 generally between 0.2 to 0.5 m deep [20]. The ponds are usually shallow, had if they been deep the sunlight would not have entered deep into the pond and the algae deep inside won't get light of required intensity. More over shadowing effect may occur i.e. the algae floating on surface may cast shadow on the algae below it by blocking the sun's rays. The raceway ponds are usually most commonly used for open cultivation. The raceway pond system was described in [20] as follows:

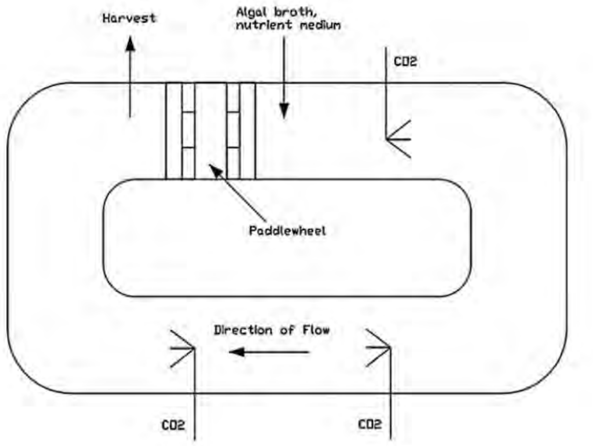

Fig. 3. Plan View Of Raceway Pond [20]

They are generally built in concrete, however compacted earth-lined pond with white plastic are also used sometimes. The algal broth and nutrients are introduced in front of the paddle wheel as shown in fig.3. It is then circulated in the loop up to the harvest point. Co2 is usually obtained from the atmosphere or submerged aerator may be installed as shown in fig. 3

The closed photobioreactor system is chosen to overcome the problems associated with the open systems. They include the tubular, flat and column structure. The comparative advantages and disadvantages are given in table 2. PBR consists of an array of straight glass or plastic tubes as shown in fig. 4 [20, 30, 62]. The tubular array can capture sunlight. They can be aligned either horizontally as reported in [20, 27], vertically as reported in [20, 28], inclined as reported in [20, 29] or as a helix as reported in [20, 30]. The algae cultures are recirculated with mechanical pump or airlift system. The airlift system allows CO2 and O2 to be exchanged between liquid and aeration gas [31]. Open and closed systems have comparative advantages and disadvantages as given in table 3.

The approach of cultivation can account to about 25% of the recoverable energy yield [32]. By manipulating the conditions inside the culture like dissolved oxygen, the nitrogen concentration, the nutrients content, the amount of light etc. the cultures with high yields can be obtained. A two stage culture was reported in [32], in this culture process the amount of nutrient and the conditions inside culture were manipulated in terms of concentration and time to obtain high cell number along with the cell lipid content. In this two stage process, the aim of the first stage is to increase the number of cells in the culture and in the second stage the cell formation is stopped and the focus remains on to increase the lipid content in the cells generated in the first stage. The effect of dissolved oxygen, the carbon dioxide, light conditions, nitrogen content, nitrogen source and the climatic conditions on the culture is reported in detail in [32].

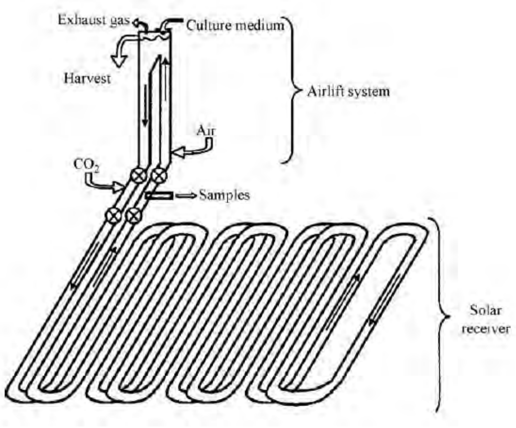

Fig. 4. Schematic of Horizontal PBR [20]

Table II. Advantages and Disadvantages of Open Pond and Photobioreactor [20]

Type of cultivation system	**Advantages**	**Disadvantages**
Raceway pond	Relatively cheaper than other systems and are easy to clean. No requirement of agricultural land non- agricultural land. Easy to maintain. Less energy required on the input side	Low biomass productivity Land occupied is high Limited to a few strains of algae Poor mixing, light and CO2 utilization Culture may get contaminated easily.
Tubular photobioreactor	Large surface area exposed to light Relatively cheaper Better biomass productivities	Some degree of wall growth Fouling affects the operation Large land space occupied
Flat plate photobioreactor	Biomass productivities are relatively higher. Sterilization of the system is easy. Low O2 build-up. Large surface area exposed to light. High degree of light penetration.	It is difficult to scale up Controlling the temperature in system is challenging Wall growth affects performance
Column photobioreactor	Design is compact. Low energy consumption. Mass Transfer effects are high. Good mixing. Sterilization is easy.	Small illumination area Expensive High shear stresses Designing and construction is difficult

Table III. The Advantages and Disadvantages (Comparison) of the Open and Closed System [4]

Culture systems for microalgae	**Closed systems (PBRs)**	**Open systems (Ponds)**
Controlling Contamination	Easy	Difficult
Risk of Contamination	Reduced	High
Sterility	Achievable	None
Process control	Easy	Difficult
Species control	Easy	Difficult
Mixing	Uniform	Very poor
Operation regime	Batch or semi-continuous	Batch or semi-continuous
Requirement of space	A matter of productivity	PBRs~ Ponds
Area/volume ratio	High (20-200 m^{-1})	Low (5-10 m^{-1})
Population (algal cell) density	High	Low
Investment	High	Low

Culture systems for microalgae	Closed systems (PBRs)	Open systems (Ponds)
Operating cost	High	Low
Capital/operating costs ponds	Ponds 3-10 times lower cost	PBRs > Ponds
Light utilization efficiency	High	Poor
Controlling temperature	More uniform temperature	Difficult
Productivity	3-5 times more productive	Low
Water losses	Depends upon cooling design	PBRs~ Ponds
Hydrodynamic stress on algae	Low-high	Very low
Evaporation of growth medium	Low	High
Gas transfer control	High	Low
CO2 losses	Depends on pH, alkalinity, etc.	PBRs~ Ponds
O2 inhibition	Greater problems in PBRs	PBRs > Ponds
Biomass concentration	3-5 times in PBRs	PBRs > Ponds
Scaling up	Difficult	Difficult

C) Harvesting The Culture

According to Borodyanski G et al. [33], harvesting process is energy intensive and thus very costly. The total cost for harvesting accounts for around 25% of the total cost of production of algae biofuel. The major cost intensive components are Electricity cost, costs of reagents and the cost for the maintenance of the separation equipment. The small size of the microalgae cells makes it difficult to harvest, making it costly. As reported in Danquah MK et al. [34] an ideal harvesting process should effectively remove the majority of strains and should also aid in achieving high concentrations of the biomass. Moreover the energy required should be low, easy to maintain and thus operating cost must be low. A solid liquid separation step is needed to harvest the algae biomass. Low cell densities, low light intensity and small size make the harvesting a difficult task. Choice of harvesting method depends on the cell density, the number of cells, final product required etc. As the biomass further needs to be treated to obtain valuable products and biofuel care must be taken that the biomass is not getting contaminated, many times the culture is recycled back to the cultivation tanks hence should be taken care of. The strain selection is also an important factor during harvesting the biomass, since certain species can be easily harvested due some properties unique to that species. For example, the cyanobacterium Spirulina’s long spiral shape (20–100 mm long) aids in natural, cost- efficient and energy efficient micro screening method [20, 36]. Generally microalgae harvesting is a two stage process [20]:

1. Bulk Harvesting: In which the biomass is separated from the bulk. The solid concentration after bulk harvesting is 2-7%. The concentration factor of this bulk harvesting method is 100 to 800 times. The methods in bulk harvesting are flocculation, floatation and gravity sedimentation. These are generally less energy intensive steps.
2. Thickening: It is more energy intensive and is used to increase the slurry concentration after bulk separation. The techniques employed are centrifugation, ultrasonic aggregation, filtering etc. In many literatures this step is often represented as dewatering step.

For removing very large amounts of water, two to more steps are necessary. Currently harvesting techniques involve mechanical, biological, chemical and to some extent electrical methods. New biological approaches can also be used to cut down the cost. Physical methods are the most reliable. The most commonly used to harvest microalgae biomass [37, 38].

a. Screening: Screening is employed to pre-process the microalgae culture. Micro strainer and vibrating screens can be used for the screening of the biomass. The efficiency of this operation depends on the size of the mesh and the size of the cells to be removed. In rotary drum, the drum is covered with a straining fabric. Continuous backwashing is required [39]. Although the process is simple and low investment is required, its efficiency in recovering bacterial-sized microalgae is very low and further processing is required [35].

b. Flocculation and Ultrasonic aggregation: This operation increases the effective size of the particle. Flocculation is generally employed before various other harvesting methods. Microalgae are negative in charge and hence this charge prevents the natural aggregation of the cells. Flocculants are added to remove the negative charge over the cells. Multivalent cationic and cationic polymers are added to neutralize the charge on the microalgae [20]. Flocculation can be induced by following ways:

    i. Bridging: It occurs when polymers or colloids attaches to the surface of two particles. A bridge gets formed between them due to this attachment.

    ii. Sweep Flocculation: It occurs usually when large particles get entrapped in massive mineral precipitation.

    iii. Electrostatic patch (or patching): The charged particle attaches to another charged particle with opposite charge, thus reversing that charge and creating a patch which connects with opposite charged patches.

Care should be taken that the flocculants do not harm or contaminate the biomass. Multivalent metal salts like ferric chloride (FeCl3) and aluminium sulphate are suitable [20]. Ultrasonic aggregation can also be used to harvest the biomass. An acoustically induced aggregation which is then coupled with the sedimentation operation can be used for the separation of biomass. In [40], Bosma et al successfully optimized the aggregation efficiency and concentration factor. The main advantages of ultrasonic harvesting are that it can be operated continuously without inducing shear stress on the biomass, which could destroy potentially valuable metabolites, and it is a non-fouling technique.

c. Floatation: Floatation can also be defined as– inverted sedimentation; here gas bubbles are fed to the broth which provides the lifting force that is needed for particle transport and separation [35]. As this method is capturing the microalgae in the micro bubbles there is no need to add the chemicals as in chemical flocculation. Many times some of the algae species float naturally on the water surface and thus are removed from the surface. This process is generally not viable technically.

d. Filtration: Filtration is the process in which water is removed from the biomass. It is usually employed after coagulation/ flocculation. Its application requires the maintenance of a pressure drop across the system to force fluid flow through a membrane. In this process, microalgae deposits on the filtration membrane and then tends to grow thicker as the process proceeds, increasing the resistance and decreasing the filtration flux at a constant pressure drop [35]. Filtration is only sustainable for harvesting microalgae having long length or those forming large colonies [35]. For harvesting relatively larger microalgae i.e. greater than 70 mm such as Spirulina, conventional filtration process is most appropriate. But this conventional filtration cannot be used to harvest algae species tending bacterial dimensions less than 30mm e.g. Scenedesmus and Chlorella [41, 20]. For recovery of such smaller algae cells, membrane microfiltration and ultra-filtration are technically viable alternatives to conventional filtration [42].Considering the cost for membrane replacement and pumping greater than 20m^3 per day, centrifugation techniques may be a more economic method for harvesting the biomass [43].

e. Centrifugation: Centrifugation is the most preferred method to harvest microalgae for laboratory study. This is because this technique does not required additional chemicals; however, this method requires more electrical energy compared to flocculation [32]. In large-scale harvesting processes, centrifugation provided good recovery and thickened the slurry, but the currently available equipment for centrifugation processes is too expensive. This hinders the application of this technique for commercial purposes. Concentrating the biomass could improve the centrifugation efficiency [32, 44]. However, to concentrate microalgae to 30% of dry particles requires approximately 1 MJ/kg of energy, which results in additional costs [32, 45]. In contrast, the direct filtration process harvests microalgae biomass directly by using a microbial membrane which only allows algal cells to pass through. This technique appears to be the cheapest technique to harvest microalgae. However, this technique requires backwashing to maintain the efficiency of the membrane filter and is time-consuming.

The above techniques can be used in combination for effective harvesting. Ex. Fig 5 shows the Combination of flocculation and filtration [32]. As seen in fig. 5 the biomass is cultivated either in PBR or open pond. The cultivated biomass is then collected in reservoir and then fed to mixer where the flocculants are added and mixed thoroughly. The alga cells gets aggregated which are then separated in the flotation column. The overflow from the column is filtered and dried to remove water and concentrate the biomass. Table 4 gives advantages and limitation of various microalgae harvesting processes.

C. Biomass Processing

The harvested biomass slurry is highly perishable and needs to be treated before, to increase its life. Dehydration processes are required to extend the viability of the harvested biomass depending upon the further product obtained from it. The dehydration processes include drying using solar energy i.e. sun drying, spray drying, drum drying, fluidised bed drying, freeze drying and Refractance Window^{TM} [20, 46]. Sun drying is cheapest method, but requires large drying surfaces and large drying time.

E. Extraction of Oils and Biofuels

Extraction processes are required to extract the oil from the algal cells that is then sent to conversion operation for converting it into biofuel or other agricultural products [32]. This extracted oil contains about (> 21.1 MJ/kg) of heating value [47]. The microalgae oil can be extracted either mechanically or chemically. Expeller presses, electromechanical methods, ultrasonic extraction and soxhlet extractors are some of the important Mechanical extraction methods [32]. Generally solvents like hexane and alcohols are required for extracting oil by physical processes. The oil from the microalgae can be extracted using solvents but the disadvantage is that further separation of solvent from the extracted oil is required. Cell disruption is required to extract oil from microalgae. The cell wall properties like the wall strength plays important role in extraction. Cell disruption methods that have been used successfully [48] include high- pressure homogenisers, autoclaving, and addition of hydrochloric acid, sodium hydroxide, or alkaline lysis. Some of the other techniques like using super critical solvents, ultrasonic extraction and using microwave are also reported in literature. The supercritical fluid extraction technique has the highest extraction efficiency compared to other techniques [32]. Los Angeles based Biofuel Company, OriginOil, combined ultrasound and electromagnetic pulse induction to extract the oil. The process involved breaking of the cell walls CO2 was added to the algae solution, which lowers the pH, and separates the biomass from the oil [49].

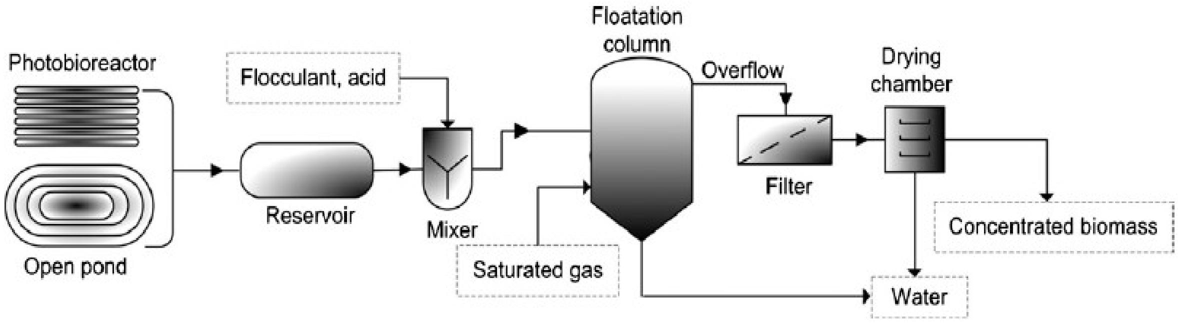

Fig. 5. The Harvesting Of Microalgae Based On The Flocculation And Filtration Technique [32]

Table II. Advantages and Disadvantages of Various Harvesting Processes

Harvesting method	Advantages	Disadvantages
Chemical coagulation/ flocculation	• Method is simple • Fast • Less to no energy needed	• It is an expensive method due to chemical requirements. • Toxic biomass • Recycling of culture medium is limited
Auto and bio-flocculation	• Inexpensive • Allows culture medium recycling • Non-toxic to biomass	• Changes in cellular composition • The algae may get contaminate.
Gravity sedimentation	• Easy, simple method • Relatively cheaper • No energy required	• Takes lot of time • Possibility of biomass deterioration • Low concentration of the algal cake
Flotation	• Good for large scale application • Lower in cost • Low space required • Short Operation times	• Chemical flocculants required
Electrical based processes	• Applicable to a wide variety of micro-algal species • No additional chemical flocculants required	• Poorly disseminated • High energetic and equipment costs
Filtration	• High recovery efficiencies • Allows the separation of shear sensitive species	• The possibility of fouling/ clogging increases operational costs • Membranes should be regularly cleaned • Membrane replacement and pumping represent the major associated costs
Centrifugation	• Fast operation • High recovery efficiencies	• Costly • Energy Intensive method • Appropriate only for high valued products • high shear forces may damage the cells.

E. Conversion to Biofuel

The oils and lipids extracted from the algal biomass can now be converted to the desired final product by employing various conversion technologies. The various available viable conversion options for converting the extracted oil to the required end products like the liquid and gaseous fuels are shown in figure. The conversion technique to be used depends on the types and sources of biomass, quantity of biomass, conversion option, desired form of energy, desired end product and the economic considerations [20]. The conversion techniques can be broadly classified as Thermochemical conversion and biochemical conversion.

In thermochemical conversion, the organic components in biomass are thermally decomposed to yield fuel products [50]. The different processes in thermochemical conversion are gasification, thermochemical liquefaction, pyrolysis, direct combustion.

In gasification, the biomass is partially oxidised into mixture of combustible gases. Gasification takes place at very high temperatures of the range 800-1000^0 C. In this process the biomass reacts with the oxygen and water from steam to generate mixture of CO, H2, N, CH4 and CO also known as syngas [51]. In [20, 52] partially oxidised Spirulina at temperature ranging from 850 to 1000^0 C, and determined the gas composition required to generate theoretical yield of methanol. They estimated that algae biomass gasification at 1000^0 C produced the highest theoretical yield of 0.64 g methanol from 1 g of biomass. The process of gasification is sparsely reported in literature and more research is still to be done [20]. Thermochemical liquefaction involves conversion of wet algal biomass into liquid fuel [53]. Thermochemical conversion is high pressure and low temperature process and needs catalyst in the presence of hydrogen to obtain bio-oil. Moreover it requires complex and expensive reactors for processing. It has ability to convert the wet biomass to the desired product. Pyrolysis is the process of conversion of biomass to biofuel at high temperature but in absence of air. The temperature range of this operation is 350-700° C [54].

Flash pyrolysis is another sub type of pyrolysis which works at moderate temperatures (500^0 C) and has short vapour residence time (about 1 s) [55]. It has high biomass-to liquid conversion ratio (95.5%) that can be achieved [56]. Compared to other technologies, pyrolysis is widely reported in literature. Direct combustion is the process where the biomass is burnt in the presence of air. The disadvantages of this process is pre-treatment of the biomass is must to remove water, chop the biomass and for grinding it to make suitable for combustion. Moreover the energy produced has no viable option for storage and need to be consumed immediately. It is normally used to produce electricity.

The biochemical conversion processes are anaerobic digestion, fermentation and photo biological hydrogen production. In anaerobic digestion the biomass is converted to biogas which consists of methane and carbon dioxide. The process involves breakdown of the organic matter to produce energy. It can process biomass with high moisture content. Alcoholic fermentation is the conversion process in which the Sugary, starchy or cellulosic biomass is converted into ethanol [20]. The biomass is broken down and the starch in it is converted to fermentable sugars. These sugars are then mixed with water and yeast at controlled warm temperatures in large tanks called fermenters. The yeast consumes this sugar and converts it into ethanol. The process is similar to obtaining ethanol form sugarcane. Purification is required to remove water and impurities in the dilute ethanol stream in order to obtain concentrated ethanol. The concentrated ethanol (95% volume for one distillation) is drawn as distillate in the liquid form. This then can be blended with gasoline, which fuels our cars.

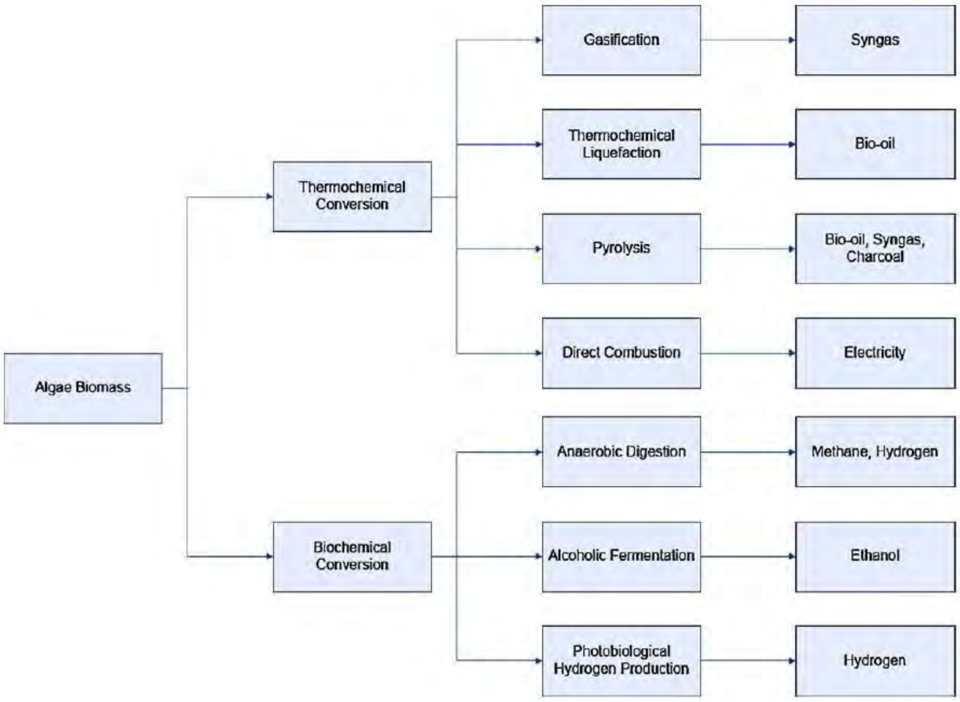

Fig. 6. Potential algal biomass conversion processes

IV. CO PROCESSES WHILE MICROALGAE BIOFUEL PRODUCTION

A. Carbon Sequestration

Microalgae require water, sun light and carbon dioxide for survival. Microalgae suffice its carbon dioxide requirement by capturing CO2 from atmosphere. Hence microalgae can be used to capture the CO2 from air. Microalgae can capture CO2 from sources like atmospheric CO2, CO2 emission from power plants and industrial processes, and CO2 from soluble carbonate. The mass transfer effects play major role in capturing carbon dioxide. The low content of carbon dioxide in atmosphere limits the CO2 capture making the process infeasible. In contrast to the above, CO2 concentration is high in the flue gas emitted from the power plants. This aids in achieving better recovery of CO2 [59]. Thus microalgae can help to reduce CO2 from flue gases but the flue gases contains other contaminants like SOx and NOx which may contaminate the culture and impede the microalgae growth. Moreover the flue gases are normally at high temperature and need to be cooled.

B. Wastewater Treatment

Industrial waste water contains organic contaminants along with chemicals, heavy metals and pathogens. The waste water is also good source of nitrogen and phosphorous. Microalgae require source of water and nutrients like N, P and K for their growth. Hence if waste water is used in cultivating microalgae the can consume these nutrients there by treating waste water while producing biofuels as a source of energy for industrial usage. Therefore biofuel production in conjunction with waste water would be a possible commercial application.

V. ENERGY EFFECIENCY FOR BIOFUEL PRODUCTION USING MICROALGAE

The concept of photosynthetic efficiency is given in detail in [57]. The impact of photosynthetic efficiency on microalgae biofuel production is reported in [20]. Photosynthetic Efficiency (PE) is the fraction of light energy that is fixed as chemical energy during their growth. Photosynthetic active radiation in the range of 400 to 700 nm, which constitute of only 42% of total energy from light spectrum, is captured [20]. This captured energy is then used to produce carbohydrates by consuming CO2 and water molecules as shown below

$$6CO_2 + 12H_2O + \text{photons} \rightarrow C_6H_{12}O_6 + 6O_2 + 6H_2$$

In [20], it is reported that the theoretical maximum PE for green type plants in bright sunlight is 13%. The factors like photo saturation, photorespiration and poor light absorption significantly reduce this PE to 1% to 2% for green plants. Microalgae have high PE due to their very simple structure than the other plants.

Raphael Slade et al. [60] have done a systematic review on microalgae cultivation for biofuel production with respect to cost, energy, environmental impacts and future prospects. The production systems were compared in terms of net energy ratio (sum of energy used for microalgae production divided by energy contained by dry biomass) for microalgae production. The technique of normalization was used for comparison of various microalgae cultivation processes for biofuel production. A positive energy balance would require technological advances and highly optimised systems.

VI. CONCLUSION

Third generation biofuel technology based on Microalgae would be the need of the hour due to obvious advantages over first and second generation biofuel with respect to land usage, photosynthetic efficiency as well as food and energy security. Microalgae strain selection coupled with selection of proper cultivation and harvesting step is critical from energy and cost efficiency point of view. Technological advancements are required for further improvements in energy efficiency and productivity to make them cost competitive with respect to fossil fuels. Co-Processing techniques for waste water treatment and carbon sequestration with biofuel production would help achieve good techno-commercial balance. Apart from biofuels other co products can be recovered and can be sold to reduce the cost of biofuels from microalgae.

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