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Biofuel Production from Algae

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A B S T R A C T

Biofuels are the most awaited research and the algal biofuels are the most promising alternative discovered. A microalga represents "Green Gold mines" for generating energy and is also eco-friendly. Algal strains like *Chlamydomonas, Chlorella, Scedesmus, Botryococcus braunii* produce biofuels. Potential of the flue gas and the wastewater of a sugar factory with carbon dioxide mitigation to support microalgae growth for biofuel and bio-fertilizer production are also studied. Algal biofuels as third generation feedstock is suitable for biodiesel and bioethanol productions. The concentration of carbon dioxide in the atmosphere increases due to various anthropogenic interventions and microalgae captures this carbon source and it is used as a source to produce lipids for the generation of biofuel and therefore it helps in decrease global warming impacts.The current research on the third-generation biofuels is the best alternative bio resource that avoids the disadvantages of first- and second-generation biofuels. According to life science analysis, microalgae biofuel is identified as one of the major renewable energy sources for sustainable development.

Keywords: Algal biomass, *Spirulinamaxima*, Global carbon cycle, Nano additive, microalgae.

1. Introduction

The current fossil fuel reserve doesn't meet the increasing demands. This leads to the quest for renewable sources such as biofuels. Microalgae are microorganisms that swiftly replicate through photosynthesis, absorbing light in the presence of nutrients and CO_2.Microalgae improves the air quality by absorbing atmospheric CO_2 and utilities minimal water (Wang et al., 2008). The algal strain is selected for biofuel production based on oil content, production yield, downstream processing and also on adaptability towards high oxygen concentration, temperature variations and water chemistry. The microalgae require minimal input for metabolic process-namely sunlight, CO_2 and water, with few required mineral nutrients and they are not dependent on seasons. The CO_2 incorporated as lipids in microalgae can be used as biofuel (Ramanan et al.,2009). Hybrid systems (combination of both open and closed system), can be used to achieve high biomass productivity. The biofuels derived from microalgae includes biodiesel, biogas, hydrocarbons, hydrogen, biosyngas, ethanol.

1.1.PRODUCTION OF MICROALGAE BIOMASS AND BIOFUEL

Microalgae biomass and biofuel production has two major phases:

1) Upstream process

2) downstream process

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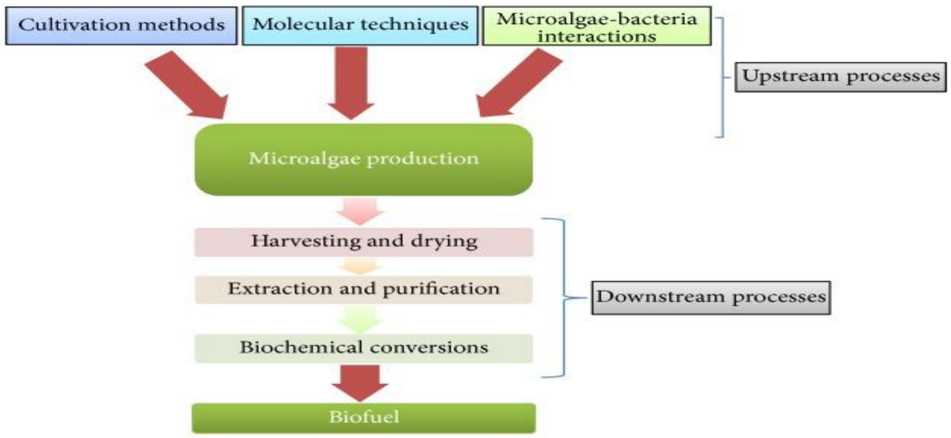

Fig 1: Methods involved in production of biofuel from algae

1) Upstream Processes

The upstream phase maximizes biomass quality and quantity. Production of microalgae biomass is done by three different types of culture systems batch, semi-batch, and continuous systems. Microalgae can be cultivated by phototrophic, heterotrophic, mixotrophic, or photoheterotrophic methods (Wang et al.., 2014) cultivation methods. Among these, only phototrophic cultivation is for large scale microalgae biomass production (Borowitzka et al.,1999).

i) Phototrophic Cultivation: Microalgae are cultivated in open ponds and closed Photobioreactors (PBRs have high photosynthetic efficiency and growth rates (Chisti et al.,2017).

ii) Heterotrophic Cultivation: In heterotrophic cultivation, microalgae utilize organic carbon. The advantages are the good control on cultivation procedure, elimination of light, and low cost of biomass harvesting. Contamination from other organisms is a problem due to the presence of organic substrate like glucose (Chen et al.,1996).

iii) Mixotrophic Cultivation: Most of the microalgae utilize both the autotrophic and heterotrophic pathways, indicating that they are able to photosynthesize and utilize organic material (Zhang et al.,1999). Microalgae which exhibit mixotrophic metabolism are *spirulina platensis* (cyanobacteria) and *Chlamydomonas reinhardtii* (Chen et al.,1996).

2) Downstream Processes

i) Harvesting and drying of microalgae biomass: After attaining sufficient biomass, the microalgae cells are separated from water and prepared for downstream processing. Generally, one or more solid-liquid separation steps are required for microalgae biomass separation (Wang et al.,2008) (Harith et al.,2009) (Harith et al.,2010).

ii)Extraction and Purification of Lipids from Microalgae Biomass: The most important aspects to be considered for selection of appropriate oil extraction process are the cost, efficiency, toxicity, and ease of handling. Supercritical carbon dioxide and osmotic shock are not commercially viable methods due to high operation costs (Awasthia et al., 2011).

iii) Microalgae Biomass Conversion Technologies: Microalgae biomass conversion technologies are classified into different types such as biochemical conversion, thermochemical conversion, chemical reaction, and direct combustion (Pena et al., 2008).

1.2 MICROALGAE CULTIVATION AND CROP SYSTEM

Two main means of microalgae cultivation have been developed (Laamanen et al.., 2019). In Open systems, the culture is exposed to the atmosphere (basins). Closed systems are where cultures have little or no direct contact with the atmosphere (photobioreactors) (Aitken et al.., 2019). The choice of the production system depends on the degree of control necessary for the production of the desired product and its value. At the industrial level, microalgae are often grown in ponds.

Open systems

It has been predominantly used for the industrial culture of microalgae. Open systems are easier and cheaper to build and operate. They are energy efficient and have easy maintenance and cleaning (Brennan et al..,2019). For these reasons, they are still considered to be viable crop systems, despite their low productivity. Open systems usually use only natural light. However, microalgae in these culture systems are subjected to daily and seasonal variations in temperature and light intensity. Crop conditions are poorly controllable, contamination problems and large losses of water by evaporation are observed in this type of culture system.

Closed systems

Photobioreactors are reactors made from transparent materials. Their design is based on the illuminated surface, the efficiency of the mixture and the control of the culture parameters (temperature, carbon dioxide and oxygen content, pH. Closed systems have been designed to alleviate the problems of the basin (Brennan et al..,2019). They offer a closed culture environment, they protect the culture from direct contamination, allow better control of the conditions of cultures: the temperature is controlled effectively, the access to the light is increased, the evaporation of the culture medium is minimized, the supply of CO2 is facilitated and its losses are limited. The photobioreactor allows the removal of oxygen produced by photosynthesis. Therefore, fragile microalgae can be cultivated. The design of photobioreactors should be optimized for each species of microalgae, relative to its physiological characteristics and growth characteristics. In addition, photobioreactors remain very expensive to produce and operate.

2. SCOPE OF ALGAE AS THIRD GENERATION BIOFUELS

To avoid the disadvantages of first- and second-generation biofuels, advance development in algal biomass for production of third generation biofuels (mainly biodiesel, bioethanol, biogas, biohydrogen, bio-oil and syngas productions) was developed. Algae has low content of lignin and hemi-cellulose so it results in increased hydrolysis and fermentation efficiency. The main purpose for selecting algae is because of its short harvesting cycle (Chisti, 2007; Schenk et al., 2008). The methods involved includeBiochemical conversion, Thermochemical conversion, or chemical conversion.

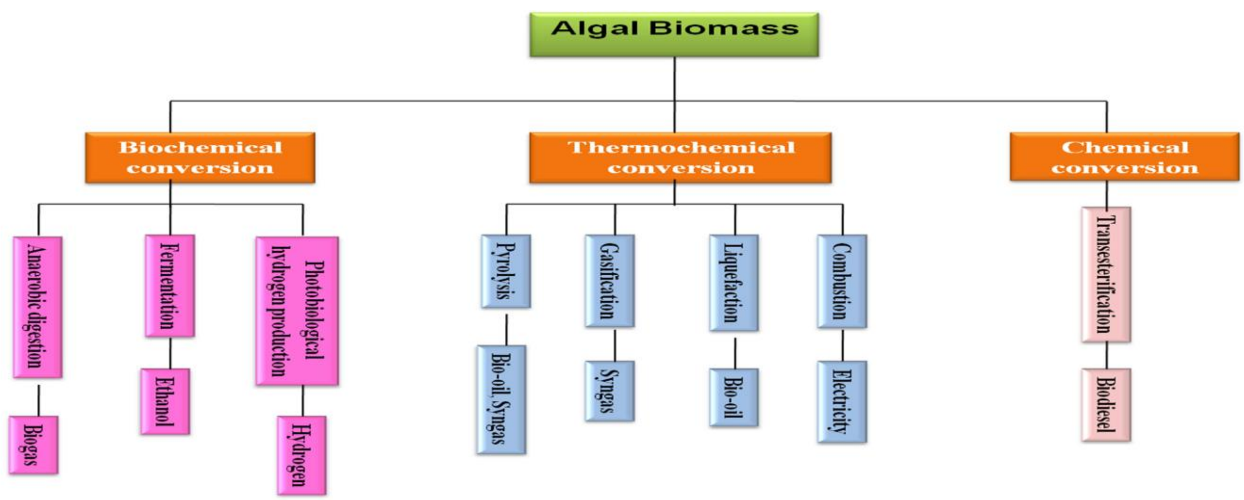

Fig 2.Algal biomass

1) Chemical conversion (Biodiesel) The species of microalgae- *Kirchneriella lunaris, Ankistrodesmus fusiformis, Chlamydocapsa bacillus*, and *Ankistrodesmus falcatus* has high levels of polyunsaturated FAME, are mostly preferred for the production of biodiesel (Nascimento et al., 2013). About 5,000–15,000 gal of biodiesel can be produced from algal biomass per acre per year (Spolaore et al., 2006; Chisti, 2007).

2)Bio-chemical conversion: Low lignin and hemicelluloses content in algae in the algal biomass have been considered more suitable for the bioethanol production (Chen et al., 2013). Recently, attempts have been made through the fermentation process. There are different micro and macroalgae such as *Chlorococcum sp., PrymnesiumparvumGelidium sp.*, which have been used for the bioethanol production (Eshaq et al., 2011; Rajkumar et al., 2014). Fermentation of various species of algae like *Scenedesmus*, *Spirulina*, *Euglena*, and *Ulva* for biogas production has been done (Samson et al., 1986; Yen et al., 2007; Ras et al., 2011; Zhong et al., 2012; Saqib et al., 2013). Factors that limit the biogas production includes requirement of larger land area, infrastructure, and heat for the digesters (Collet et al., 2011; Jones et al., 2012). Biohydrogen can be produced through different processes like biophotolysis and photo fermentation (Shaishav et al., 2013). *Gelidium amansii* (red alga) is found to be the potential source of biomass for the production of biohydrogen through anaerobic fermentation (Park et al.,2011).

3) Thermochemical Conversion Bio-oil is formed in the liquid phase from algal biomass. Bio-oil from pyrolysis of algae (*Nannochloropsis* sp.) at 300°C after lipid extraction, which composed of 50wt% acetone, 30wt% methyl ethyl ketones, and 19wt% aromatics such as pyrazine and pyrrolewas done (Porphy et al.,2012). High temperatures (800–1000°C), converts biomass into the combustible gas mixture through partial oxidation process, called syngas or producer gas.

3. BIODIESEL PRODUCTION FROM MICROALGAE

The first- and second-generation biodiesel research are in saturated level but third generation i.e., biodiesel from algae research is in promising stage (Demirbas, 2009). Biodiesel from algae is renewable, biodegradable, nontoxic, and potential as a green alternative fuel for CI engine (Mata et al., 2010). For the experiment Spirulina maxima was collected from the local area at Dhaka, Bangladesh. A quantity of 1 L crude oil was poured into a flask heated at 55°C. An appropriate volume of methanol and the sulfuric acid mixture was heated at 55°C in a separate flux and then poured into algal oil. To observe the AV of the mixture and yield, methanol to oil ratio, catalyst concentration, reaction temperature, reaction time, stirring speed were varied at different conditions. A typical acid catalyst esterification was carried out. The optimum condition for next step was fixed up according to the lowest AV values of the yield. Then, the mixture was kept in a distinct funnel. The upper layer which contains biodiesel was separated. Catalyst, alcohol, impurities etc. were removed from bottom layer esterified oil was used for transesterification. The next step is transesterification. The esterified oil was poured into the glass reactor and heated at 55°C. In separate flasks, the catalyst KOH was dissolved in methanol at various concentration and molar ratio. Then methanolic KOH was heated to 55°C and mixed with the esterified oil. A typical base catalyst transesterification was carried out (Huang et al., 2010). The mixture was allowed to settle down. The upper phase contained biodiesel was collected and lower phase containing glycerol was discarded.

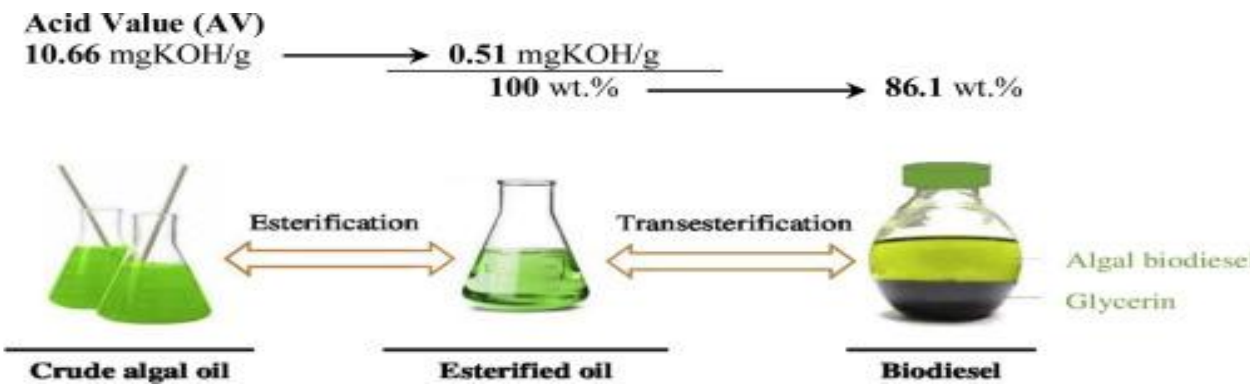

Fig 3.Esterification and transesterification reactions

Then the yield of biodiesel (% w/w) is calculated for different conditions by using the following Eq. (3)

$$\text{Yield of biodiesel (\%)} = \frac{\text{Weight of the biodiesel produced(g)*100\%}}{\text{Weight of the algal oil sample used(g)}}$$

Biodiesel produced were analysed by GC-MS analyser, to analyse the free fatty acids of the biofuels. FTIR analysis was done to find out functional group. The physicochemical analysis were carried out according to the standards, as follows: kinematic viscosity at 40°C, cetanenumber, acid value, iodine value, flash point, Flash point and carbon residue. For the transesterification reactions the maximum biodiesel yield (65%) was achieved at molar ratio of 9:1 for 30 min of reaction time. The maximum biodiesel yield (75%) was obtained at catalyst concentration of 0.75 wt% after 20 min of reaction time. The maximum biodiesel yield (80.13%) was obtained for the temperature of 65°C at around 25 min of reaction time. The maximum biodiesel yield (86.1%) was obtained for the string speed 600 rpm after 20 min of reaction time (Suganya et al.,2013). The biodiesel was then characterized by GC-MS (model- GC–MS-QP 2010, Shimadzu) analyser and it had higher concentration of unsaturated fatty acid (linoleic, linolenic acids) and lower concentration of saturated fatty acids (myristic, stearic acids). Then the FTIR analysis was done the biodiesel and the functional groups were characterised.

Components	Structure	Column B (*t*)
Palmitic acid	C16:0	40.20
Palmitoleic	C16:1	9.18
Stearic	C18:0	1.18
Oleic	C18:1	5.43
Linolecic	C18:2	17.87
Linolenic	C18:3	18.34
Others	-	7.46

4. LASTEST DEVELOPMENT IN MICROALGAE -BIOFUEL PRODUCTION WITH NANO-ADDITIVES

The main objective was to delineate the synergistic impact of microalgal biofuel integrated with nano-additive applications. Numerous nano-additives such as nano-fibers, nano-particles, nano-tubes, nano-sheets, nano-droplets, and other nano-structures' applications have been used to facilitate microalgae growth to biofuel utilization. Prospects of solid nano-additives and nano-fluid applications in the future on microalgae production, biomass conversion to biofuels and enhancement of biofuel combustion for revolutionary advancement in biofuel technology. This study highlighted the potential biofuels from microalgae and recounted suitability of potential microalgae with an integrated design generating value-added co-products.

Nano-particles' incorporation with microalgae cultivation e.g., cell suspension, cell separation, and cell harvesting, biofuel conversion technologies, and biofuel application have amplified the overall yield in every stage (Safarik et al.., 2019). According to the studies, a very small amount of colloidal hydrous iron(III) oxide particles boosted almost 100% microalgae cell suspension; magnetic particles incorporated with aluminum sulfate were very effective for cell separation from the mixed culture Anabaena and Aphanizomenon, silver nano-particle application on Chlamydomonas reinhardtii and Cyanothece microalgae harvesting increased 30% higher biomass productivity; and calcium-oxide nano-particles escalated the large-scale biodiesel conversion yield up to 91% via catalytic transesterification.(Kim et al.., 2019).

5. LIMITATIONS OF BIOFUEL PRODUCTION FROM ALGAE

Cost effective technological strategies suggested to develop microalgae biofuel production are development of biorefinery or coproduct strategy, designing high photosynthesis efficiency photobioreactors, development of cost-effective technologies, development of genetic engineering technology understanding the symbiotic interactions between microalgae and bacteria that may affect the biomass and lipid production in microalgae.

6. WORLD MARKET FOR BIOFUEL PRODUCTION

Large scale commercial production of microalgae began in Japan in early 1960s by culturing chlorella as food additive. By 2004, the microalgae industry produced 7000 tonnes of dry matter per annum (Wang et al.,2008). Biofuel production in the world has increased recently in the production of bioethanol from sugar crops and cereals. United states and Brazil remained the top most bioethanol producers in the world. Currently, the European Union countries have a small share (6%) in the global biofuel production Europe, biodiesel production occupies the top position (79.55%).

7. CONCLUSION

Microalgae utilization for biofuel production is undoubtedly desirable all over the world. Though this approach is energy-efficient and environment-friendly, experts are still looking for an innovation that can boost the microalgae-biofuel yield. Hence, this emphasized on the synergistic effect of nano-additive-enhanced microalgal biofuel for mercantile approach and fuel-yield extension. It is worthwhile to say that microalgal biofuel production is thought to help stabilize the concentration of carbon dioxide in the atmosphere and decrease global warming impacts. Now a days, biodiesel became an acceptable alternative and microalgae have been experimented as potential feedstock for biofuel in current era and a prominent innovation such as in Spirulina. In this investigation of Spirulina maxima, a two-step process was employed for biodiesel production. First step, esterification was accomplished to reduce the AV and second step, alkaline transesterification was performed for maximizing biodiesel yield (86.1%). In spite of the many advantages, microalgae biofuels also have some disadvantages such as low biomass production and small cell size that makes the harvesting process costly. These limitations could be overcome by designing advanced photobioreactors and developing low- cost technologies for biomass harvesting, drying and oil extraction. In addition, application of genetic engineering technology in the manipulation of microalgae metabolic pathways is also an efficient strategy to improve biomass and biofuel production. Genetic engineering technology plays an important role in the production of valuable products. Therefore, further research in the development of upstream and downstream technologies will benefit the commercial production of biofuels from microalgae.

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