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Photosynthetic bioenergy utilizing CO_2 from plant flue gas: an approach on microalgae based third generation biofuels production*

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***Abstract*— The interest in microalgae based CO2 removal and biofuels production has increased over the past few years. The conversion of CO2 into chemical and biofuels products without pollution via photosynthetic CO2 bio-fixation approach is a promising way to not only reduce CO2 emissions but also generate more economic value. It has great potential as renewable fuel sources because of rapid growth rate and the ability to store high-quality lipids and carbohydrates inside their cells for biofuels production. This article reviews the literature on microalgae that were cultivated using captured CO2, technologies related to the production of biofuels from microalgae and the possible commercialization of microalgae-based biofuels to demonstrate the potential of microalgae. In this respect, a number of relevant topics are addressed: the nature of microalgae, CO2 capture via microalgae; the techniques for microalgae cultivation, harvesting and pretreatment; and the techniques for lipid extraction and biofuel production. In this work, flue gas emissions coupled to microalgae cultures are described. In addition, since microalgae can produce energy, the biorefinery concept is also reviewed.**

Keywords— Microalgae, Biofuels, Biorefinery, CO2 removal, Carbon-negative technology.

I. Introduction

To reduce the effects caused by this environmental problem, several technologies were studied to capture CO2 from large emission source points: (i) absorption; (ii) adsorption; (iii) gas-separation membranes; and (iv) cryogenic distillation. Absorption of CO2 is effected using various chemical agents such as Monoethanolamine (MEA), solid adsorbents like activated carbon, or zeolite 5A. Membranes and cryogenic fractionation have also been employed for the removal of CO2. The chemical methods of CO2 separation are highly energy intensive and expensive. Conventional carbon capture technologies (largely using chemical methods) have a capture efficiency of 85–95%. It has been reported that 3.7 GJ of energy/tonne of CO2 absorbed is required during the regeneration of MEA, which corresponds to around 370 kg of extra CO2 (per t CO2 absorbed) emitted if this energy input comes from a fossil fuel such as coal. The resulting streams with high CO2 concentrations are transported and stored in geological formations. However, these methodologies, known as carbon capture and storage (CCS) technologies, are considered as short-term solutions, as there are still concerns about the environmental sustainability of these processes. Fig 1 shows the different types of conventional CO2 capture technologies [1,2].

However, a potential and promising biologic approach, microalgae-based CO2 fixation and energy/resource utilization, has received significant attention over the last two decades due to its techno-economic feasibility and environmental friendliness. In essentials, the microalgae essentially biologically fix and store CO2 via photosynthesis, which can convert water and CO2 into organic compounds without secondary pollution. Microalgal-CO2 fixation features potential advantages over other carbon capture and storage approaches, such as a wide distribution, high photosynthesis rate, good environmental adaptability and easy operability. Additionally, the microalgal biomass can be harvested after CO2 fixation to produce microalgal biofuel that can be utilized as a renewable or sustainable energy source (Fig. 2)

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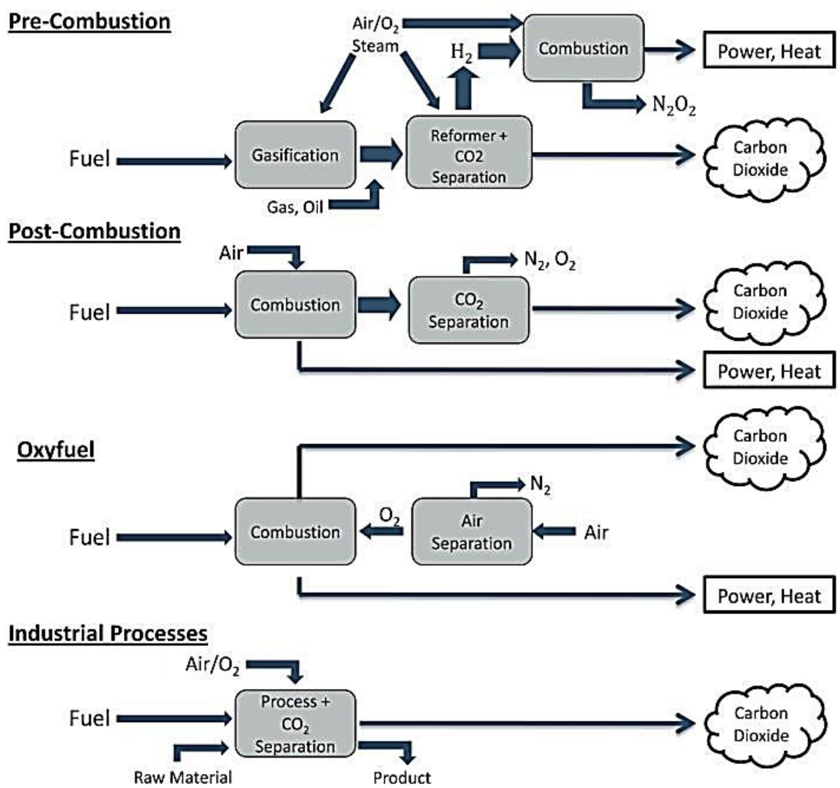

Fig.1. The four main technology concepts for CO_2 capture

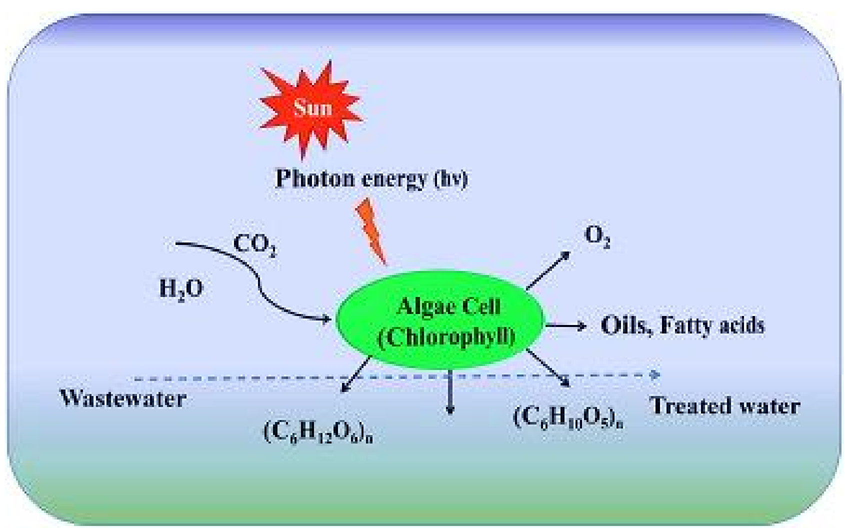

Fig 2. Microalgae species uses light energy (e.g. from the sun) to produce chemical energy by photosynthesis during natural growth cycle

II. BIOSYNTHESIS OF LIPID IN MICROALGAE

Microalgae are photosynthetic microorganisms with simple growing requirements (light, sugars, CO_2, nitrogen, phosphorous, potassium) that can produce lipids in large amounts over short periods of time. Microalgae transform the solar energy into the carbon storage products, leads to lipid accumulation, including TAG (triacylglycerols), which then can be transformed into biodiesel, bioethanol and biomethanol. Most microalgae species produce lipid, carotenoid, antioxidant, fatty acids, enzyme

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polymer, peptide, toxin, and sterols. A diverse range of microalgae species uses light energy (e.g. solar energy) to produces chemical energy by photosynthesis with the natural growth cycle of just few days (Fig.2).

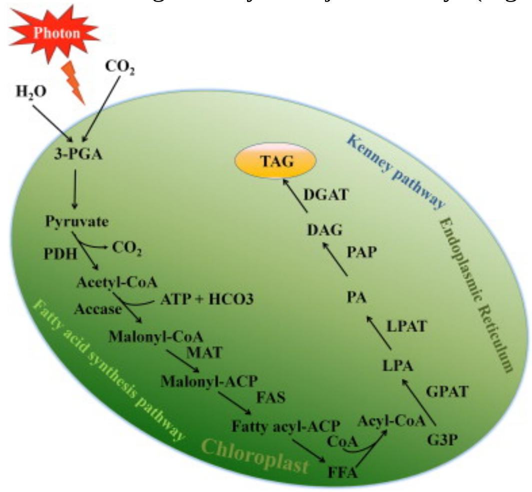

Fig. 3. Pathway of the synthesis of triacylglycerols (TAGs), as storage of lipid as chemical energy by microalgae**.**

III. BIOLOGICAL CO_2 FIXATION

A promising technology is the biological capture of CO_2 using microalgae. These microorganisms can fix CO_2 using solar energy with efficiency ten times greater than terrestrial plants. Moreover, the capture process using microalgae has the following advantages: (i) being an environmental sustainable method; (ii) using directly the solar energy; and (iii) co-producing high added value materials based on biomass, such as human food, animal feed mainly for aquaculture, cosmetics, medical drugs, fertilizers, biomolecules for specific applications and biofuels. Microalgae can typically be used to capture CO_2 from three different sources: (1) atmospheric CO_2, (2) CO_2 emission from power plants and industrial processes, and (3) CO_2 from soluble carbonate.

Furthermore, four applications are achieved by using microalgae biomass production as a CO2 reduction strategy: i) production of biofuels, ii) enhancement of the economic yield of the carbon capture and storage through production of commodities or by-products from flue gases, iii) utilization of bacteria-microalgae consortiums to reduce the energy required for aeration in wastewater treatment plants and iv) utilization of microalgae to reduce the total CO_2 emissions released by wastewater treatment plants.

IV. MICROALGAE REMOVAL OF CO_2 FROM INDUSTRIAL FLUE GAS

CO_2 capture from flue gas emissions from power plants that burn fossil fuels achieves better recovery due to the higher CO_2 concentration of up to 20%. Since microalgae CO_2-fixation involves photoautotrophic growth of cells, CO_2 fixation capability of specific species should positively correlate with their cell growth rate and light utilization efficiency (Fig.4). The advantages of using microalgae to capture CO_2 from coal combustion flue gas are:

1. High purity CO_2 gas is not required for algal culture. Flue gas containing varying amounts of CO_2 can be fed directly to the microalgal culture. This simplifies CO_2 separation from flue gas significantly;
2. Some combustion products such as NOx or SOx can be effectively used as nutrients for microalgae. This could potentially negate the use of flue gas scrubbing systems for power plants;
3. The microalgae could yield high value commercial products. The sale of these high value products could offset the capital and operating costs of the process; and
4. The envisioned process is a renewable cycle with minimal negative impacts on the environment

A. Power plant

Flue gases from coal power plants can be a potential CO_2 source for the production of micro-algal biomass. Micro-algae can utilize CO_2 with the help of solar energy, ten times more efficiently than terrestrial plants. Micro-algae can be grown in saline conditions or wastewater throughout the year. Flue gases are generally dominated by N_2 (72–74%), CO_2 (4.8–26.9%), H_2O (9–13.8%) and O_2 (0.7–15%). However, they also contain smaller quantities of NO (59–1500 mg/Nm^3), NO_2 (2–75 mg/Nm^3), SO2

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(20– 1400 mg/Nm$_3$), SO_3 (0–32 mg/Nm$_3$), CxYx (0.008–0.4%), CO (100– 11250 mg/Nm^3), particulate matter (2000–15000 mg/Nm$_3$) and heavy metals (2.2 mg/Nm$_3$). Typically flue gases are treated for the removal of particulate matter, heavy metals and NOx and SOx to comply with the regulations on effluent discharge and air quality.

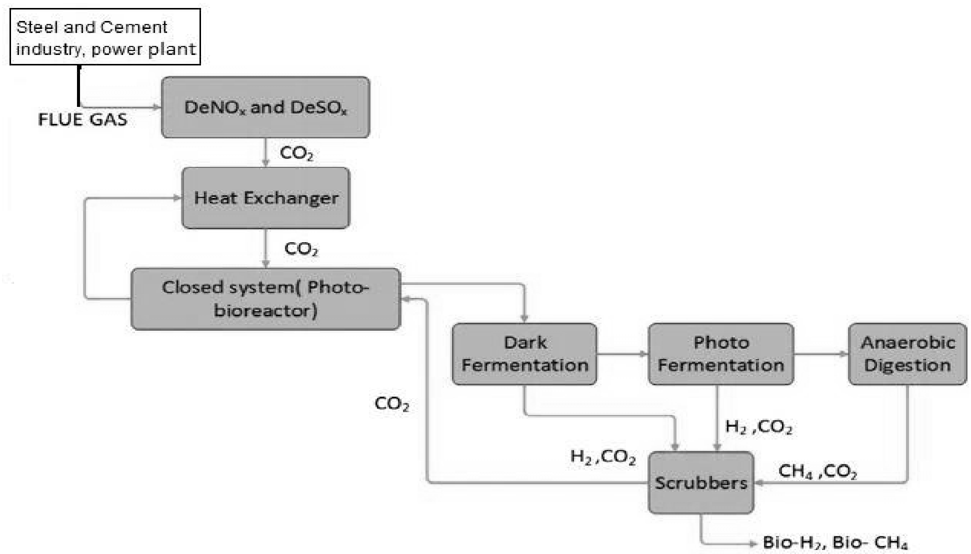

Fig.4. Microaglae CO_2 removal using industrial flue gases

B. Cement industry

The cement industry is one of the major CO_2 producing sectors being responsible for about 8% of global emissions. It is reported a production of 193 × 10^6 metric tons of CO_2 by the cement industry, considering only member states of the European Union and Norway (2004). Hasanbeigi et al.[24] reviewed 18 technologies for the reduction of CO_2 emissions by cement industry. They classified algal biomass utilization as an emerging technology in demo stage. Only a few studies regarding to flue gas usage from cement industry have been developed. Borkenstein et al. [25] evaluated the air lift cultivation of *Chlorella emersonii* using flue gas derived from a cement plant. Pure CO_2 injection was used as a control and 5.5 L photobioreactors with controlled pH were used. After 30 days of cultivation, the flue gas had no visible adverse effects compared with the control reactors. The control essay (pure CO_2) resulted in a biomass yield of 2 g/L, CO_2 fixation of 3.25 g/L and growth rate of 0.1/day, meanwhile the flue gases reactors resulted in very similar parameters with 2.06 g/L in biomass yield, 3.38 g/L in CO2 fixation and a growth rate of 0.13/day. Although there was no accumulation of flue gas residues in the culture media, the lead concentration in the microalgae biomass was three times higher with the flue gases. Therefore, lead accumulation and its effect on the downstream processing for biofuels production have to be investigated.

Lara-Gil et al. [26] performed toxicity tests of a simulated cement industry flue gas in cultures of *Desmodesmus abundans* and *Scenedesmus sp.* The results suggest that nitrite and sulfite are not toxic for the tested microalgae at the maximum concentrations of 1067 ppm and 254 ppm, respectively, differing from bisulfate where concentrations above 39 ppm were toxic. Studies related to flue gas from different industries can be considered useful despite of slight changes in flue gas composition.

V. MICROALGAE CULTIVATION TECHNOLOGY

Microalgae with the composition of $CH_{1.7}O_{0.4}N_{0.15}P_{0.0094}$ are simple photosynthetic organisms living in aquatic environments, where they can convert CO_2 and H_2O to biomass using sunlight. Factors influencing the microalgae growth include: abiotic factors, such as light intensity and quantity, temperature, O_2, CO_2, pH, salinity and nutrients (N, P, K, etc.); biotic factors, such as bacteria, fungi, viruses and competition for abiotic matters by other microalgae species; operational factors, such as mixing and stirring degree, width and depth, dilution rate, harvest frequency and addition of bicarbonate. The cultivation technologies being pursued to produce microalgae for biofuels generation mainly include open ponds, photobioreactors and fermenters.

A. Bioreactors

Microalgae can grow either in open ponds or closed systems (photobioreactors). Fig. 5 shows images of the most common bioreactor configurations. Table 1 makes a comparison between the open and closed bioreactors concerning the production of

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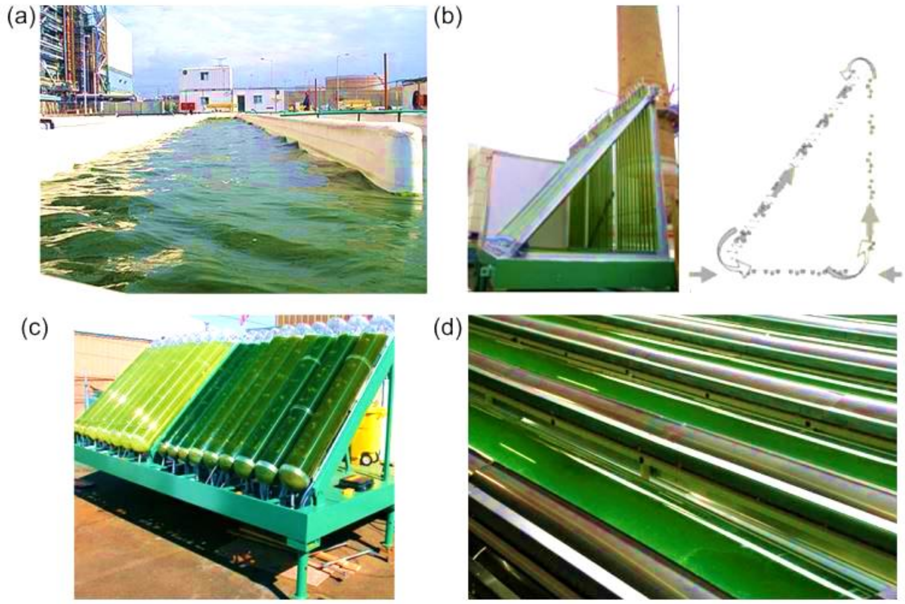

Fig.5. Reactor configurations for microalgal cultivation: (a) raceway pond; (b) air-lift reactor; (c) bubbl column reactor; and (d) horizontal tubular reactor. (a) From Seambiotic; (b) from Green Fuel Technologies – MIT, a courtesy from Vunjak-Novakovic et al.[27]; (c) from Green Fuel Technologies; and (d) from http://www.algaelink.com

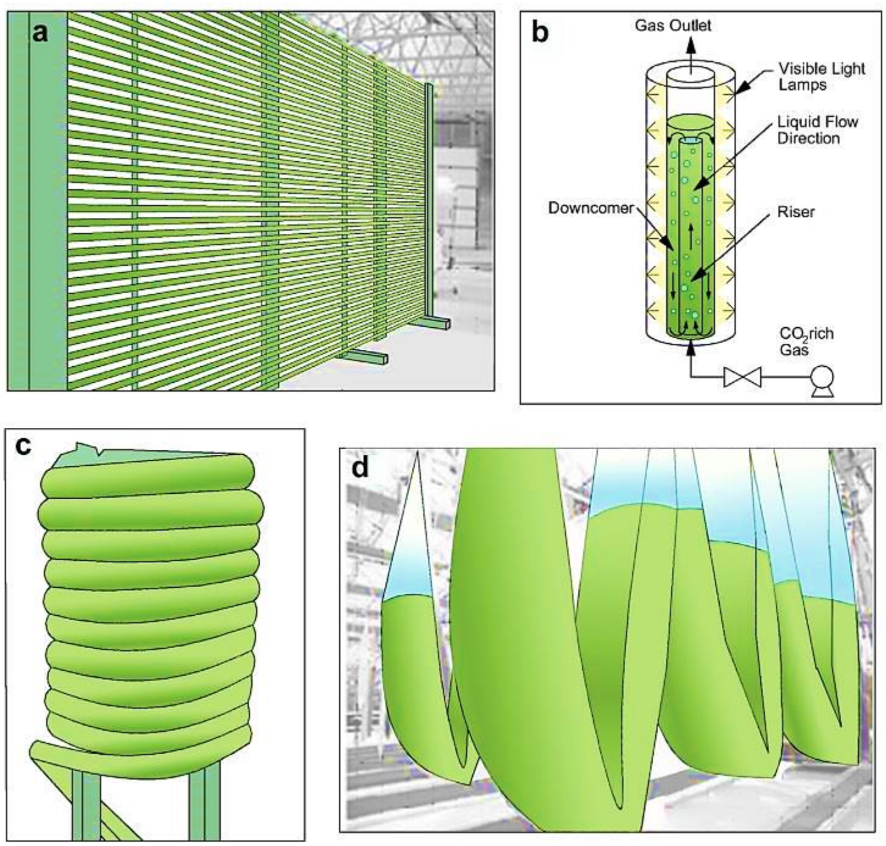

Fig. 6. Closed cultivation system: (a) horizontal tubular photobioreactor at Varion Aqua Solution Ltd., UK (b) Bubble column air-lift photobioreactor, BBSRC, UK. (c) Helical– tubular photobioreactor (d) Large-scale plastic bag photobioreactors [28].

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microalgae. The production in open ponds depends on the local climate due to the lack of control in this type of bioreactors. The contamination by predators is an important drawback of this cultivation system. Thus, high production rates in open ponds are achieved with algal strains resistant to severe culture environment; for instance, the *Dunaliella*, *Spirulina* and *Chlorella spp.* are cultivated in high salinity, alkalinity and nutrition, respectively. Besides the technological simplicity, the production in open systems is not cheap due to the downstream processing costs. In addition, contamination is another major problem of open systems with large-scale microalgal production. Unwanted algae, mold, fungi, yeast and bacteria are the common biological contaminants often found in these open systems.

VI. MICROALGAE HYBRID TECHNOLOGIES

A. Algal bio-refinery concept

The concept of biorefining is similar to the petroleum refineries in which multiple fuels and chemicals are derived using crude oil as the starting material. Similarly, biorefining is sustainable biomass processing to obtain energy, biofuels and high value products through processes and equipment for biomass transformation. A more specific and comprehensive definition of a biorefinery has been given by IEA Bioenergy Task 42 document which states, “the sustainable processing of biomass into a spectrum of marketable products and energy”. In a broad definition, biorefineries convert all kinds of biomass (all organic residues, energy crops, and aquatic biomass) into numerous products (fuels, chemicals, power and heat, materials, and food). Algae can easily be part of this concept because each strain produces certain amount of lipids, carbohydrates or proteins which biomass can be used in different process. The biorefinery concept has been identified as the most promising way to create a biomass-based industry. There are four main types of biorefineries: biosyngas-based refinery, pyrolysis-based refinery, hydrothermal upgrading-based refinery, and fermentation-based refinery. Biorefinery includes fractionation for separation of primary refinery products. The main goal of the biorefinery is to integrate the production of higher value chemicals and commodities, as well as fuels and energy, and to optimize the use of resources, maximize profitability and benefits and minimize wastes [33].

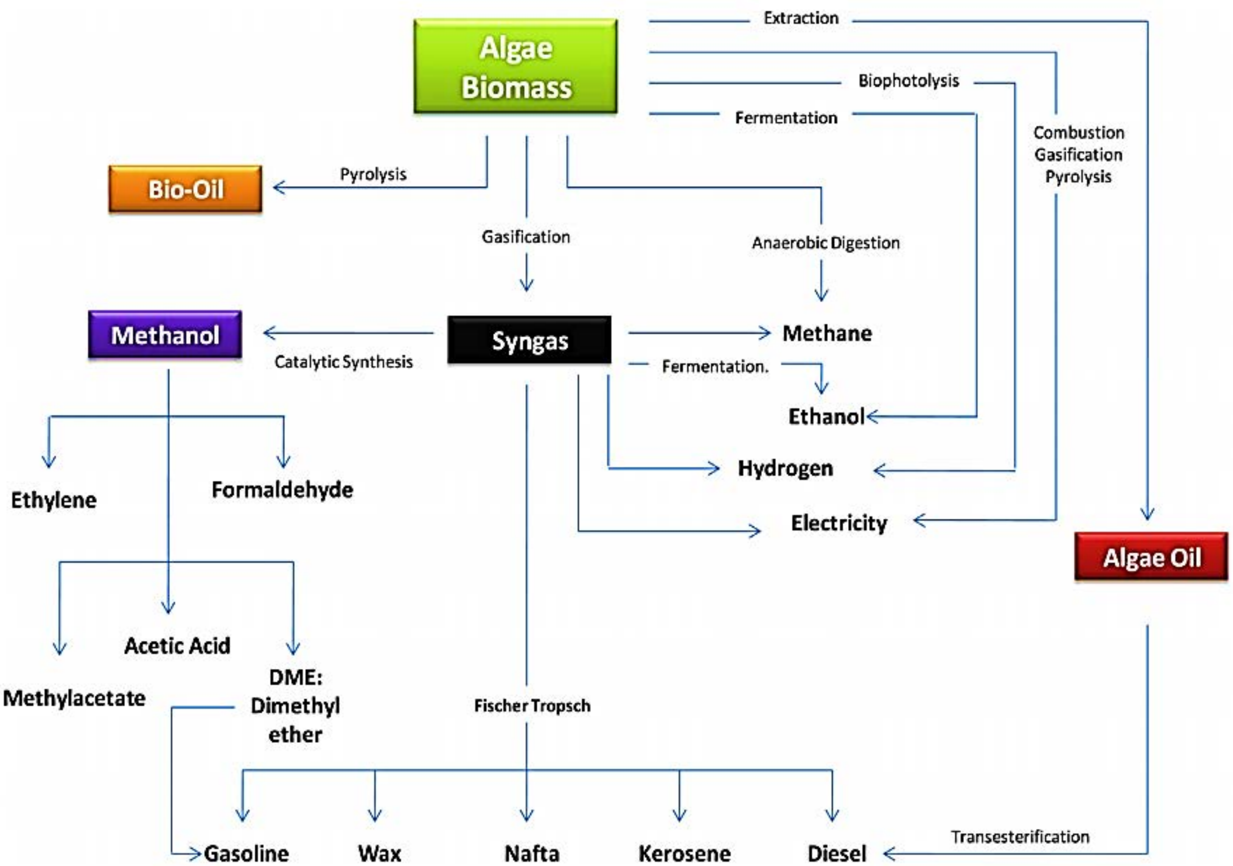

Fig.7. Algae biorefinery concept.

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Microalgae are considered to be futuristic raw material for establishing a biorefinery because of their potential to produce multiple products. A new biorefinery-based integrated industrial ecology encompasses the different value chain of products, co-products, and services from the biorefinery industries. Cross-feeding of products, co-products and power of the algal biofuel industry into the allied industries is desirable for improving resource management and minimization of the ecological footprint of the entire system. The biomass, after the oil has been extracted from it, can be used as animal feed, converted to fertilizer and for power generation. The power generated can then be put back to producing more biomass. The CO_2 released by the power generation plant can be used again for the production of algal biomass, thus reducing CO_2 in the atmosphere. Selected species of microalgae (freshwater algae, saltwater algae and cyanobacteria) were used as a substrate for fermentative biogas production in a combined biorefinery. Anaerobic fermentation has been considered as the final step in future microalgae based biorefinery concept [34].

B. Wastewater treatment

Photosynthetic microorganisms such as microalgae can use pollutants as nutrients (N, P and K) and grow in accordance with environmental conditions, such as light, temperature (generally 20-30 ^{0}C), pH (around 7.0), salinity, and CO_2 content. On the other hand ecofriendly pollutant removal is a major issue in current day research. Many researchers consider microalgae as green technological medium for pollutant removal from wastewater. Removal of organic and inorganic pollutants (NO_3^-, NO_2^-, NH_4^+, PO_4^{3-}, CO_2, Cd, Zn, Ni, Co, Mn, Cu, Cr, U, Hg(II), Cd(II), Pb(II), B, TBT (tributyltin), phenols and Azo compounds) from wastewater by different algae is shown in Table 1.

Table: 1 Removal of inorganic and organic pollutant from wastewater by different algae

Microalgae species	**Pollution control**
Anabaena, Oscilatoria, Spirulina, S. platensis	NO_3^-, NO_2^-, NH_4^+, PO_4^{3-}
Anabaena sp.	2,4,6-trinitrotoluene
Ankistrodesmus sp, *Scenedesmus sp, Microactinium sp, Pediastrum* sp,	CO_2
Chlamydomonas reinhardtii	Hg (II), Cd(II), Pb(II)
Chlorella sp.	Boron
Chlorella miniata	Tributyltin (TBT)
Chlorella vulgaris, Chlorella sp.	Tributyltin (TBT)
Chlorella vulgaris	Azo compounds
Chlorella vulgaris	NH_4^+, PO_4^{3-}
Chlorella spp.	P
Chlorella vulgaris	Cd, Zn,
Chlorella vulgaris, Scenedesmus rubescens	N and P
Chlorella salina	Co, Zn, Mn
Coelastrum proboscideum	Pb
Isochrysis galbana	NH_4^+
Ochromonas danica	phenols
Oedogonium hatei	Ni
Oedogonium sp, *Nostoc sp.*	Pb
Oscillatoria sp. *H1*	Cd(II)
Phormidium bigranulatum	Pb(II), Cu(II), Cd(II)
Phormidium laminosum	Cu(II), Fe(II), Ni(II), Zn(II)
Scenedesmus quadricauda	Cu(II), Zn(II), Ni(II)
Spirulina platensis	Cr(VI)
Streptomyces viridochromogenes, Chlorella regularis	U
Ulva lactuca	Pb (II), Cd (II)
Undaria pinnatifida	Ni, Cu

There are several reasons for the cultivation of microalgae in wastewater such as: (i) cost-effective treatment, (ii) low energy requirement, (iii) reduction in sludge formation, and (iv) production of algal biomass for biofuel production. Microalgae are efficient to remove different types of pollutants and toxic chemicals such as nitrogen, phosphorous, potassium, nitrite, silica, iron, magnesium and other chemicals from municipal and industrial wastewater. In addition, microalgae have high capacity to accumulate heavy metals (selenium, chromium, lead), metalloids (arsenic) and organic toxic compounds (hydrocarbons) to form microalgae biomass which subsequently can be used for biofuel production. The Chlorella spp. has diverse range of different pollutant compare to other microalgae. Other several algae such as *Ourococcus multisporus, Nitzschia cf. pusilla*,

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Chlamydomonas mexicana, S. *obliquus*, *C. vulgaris,* and *Micractinium reisseri* were efficient to remove nitrogen, phosphorus, and inorganic carbon. The highest achieved capacity *C. mexicana* for removal of nitrogen, phosphorus, and inorganic carbon were 62%, 28% and 29%, respectively. Simultaneously the lipid productivity and lipid content were reported 0.31±0.03 g/L and 33±3%, respectively. Using microalgae for combined renewable energy production along with efficient wastewater treatment systems at a low cost, offers an innovative promising direction for an integral approach to water and energy problems and climate change mitigation.

VII. CONCLUSIONS

Algae are the fastest growing organisms in the world. Microalgae are known for faster growth rates than terrestrial crops. Additionally, the microalgal biomass can be harvested after CO_2 fixation to produce microalgal biofuel that can be utilized as a renewable or sustainable energy source. The per unit area yield of oil from algae is estimated to be from 18,927 to 75,708 litters/per acre, per year; this is 7–31 times greater than terrestrial crops although there are claims of higher yields of up to 100,000 liters per hectare per year.

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