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Biosequestration of industrial off-gas CO_2 for enhanced lipid productivity in open microalgae cultivation systems

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ABSTRACT

Utilizing industrial off-gas CO_2 in open system photosynthetic microalgae cultivation is a biological means to mitigate greenhouse gas emissions. The captured CO_2 can also enhance production of microalgal lipids for conversion into biodiesel. However, environmental stressors such as temperature, pH, luminosity, salinity, metal toxicity, nutrient availability, and shear stress can impact the CO_2 fixation process and lipid biosynthesis.

We discuss the mechanisms of carbon fixation and lipid synthesis in microalgal cells, commercial microalgae cultivation systems, and the limitations and potentials of utilizing industrial off-gases. The influences of operational and environmental factors on CO_2 sequestration rates and lipid production, as well as manipulative approaches for enhanced lipid production are also reviewed.

1. Introduction

Sustainability is a primary principle in natural resource management that involves operational efficiency, minimization of environmental impact and socio-economic considerations [1]. Concerns about the lack of fossil fuels, variations in crude oil prices, greenhouse gas emissions and accelerated global warming show that continued reliance on fossil fuel energy resources is unsustainable.

Global warming and climate change are generally accepted as the consequence of increased greenhouse gas emissions. The temperature of the earth has increased by 0.85 °C from 1880 to 2012, of which 0.6 °C occurred in the past 30 years [2]. It is further anticipated that the global temperature will rise to 5.8 °C by 2100 [3]. The outcomes are expected to include melting polar ice and increased sea levels, changes in weather patterns leading to droughts and floods [3], increased ocean acidity, species extinction and unbalanced biodiversity [4–6]. Moreover, climate change has a negative impact on societal influencers including health, food and clean water security, economic growth, and cost of living [7]. These issues have led to a worldwide interest in anthropogenic CO_2 capture and mitigation methods, not least, due to the introduction of legislation restricting or capping industrial emissions [8–10].

Common CO_2 management methods include carbon capture and storage (CCS) through geo-sequestration and ocean-sequestration [11–13], enhanced oil and gas recovery (EOR and EGR) [14–16], enhanced coal bed methane recovery (ECBM) [17–19], chemical methods (adsorption and absorption) [10,20,21], physical methods (cryogenic distillation or membrane filtration) [22–25] and biological mitigation methods [26,27] (through terrestrial plants, macro and microalgae, microbes and biochar) [28–31].

However, the above existing methods do have disadvantages. For CCS these include high transportation costs and the possibility of reservoir leakage being released back to the atmosphere or oceans, which in turn could lead to ocean acidification [8,32–34]. Chemical methods involving CO_2 separation from industrial off-gas by using solvents can suffer from evaporative losses, high energy requirements for solvent recycling and corrosion, leading to high operational costs [35–37]. Solid adsorbents such as alumina or zeolites that chemically adsorb CO_2 in active sites [10,38,39] can lose efficiency very quickly with high temperatures, meaning that they are not suitable for many industrial off-gas streams [2,40–42].

Cryogenic distillation, a physical method of carbon capture, is extremely energy intensive and is not considered economical for industrial practices [2,43,44]. Membrane technology can be used to filter industrial off gases with a very high CO_2 concentration. However, they foul easily causing large pressure drops [45–47]. Challenges of the EOR and EGR mitigation methods include high energy requirement for injecting pressurized CO_2 in the enhanced oil and gas recovery methods, and leakage into the water aquifer [15,48].

All of these mitigation methods are based on using the CO_2 after separating it from the off-gas stream. Biological mitigation using microalgae can, however, capture CO_2 without the need to separate it

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from the off-gas. Microalgae in fresh and saline water use CO_2 as a carbon source and convert it into organic carbon for producing cellular compounds such as lipids, proteins, and carbohydrates. The resulting biomass can be used as a feedstock for food, fuel, animal feed and value-added products [6,49–51]. Microalgae are also about 50 times more efficient at sequestering CO_2 than terrestrial plants due to faster growth rates [52,53].

Microalgae, unicellular, filamentous or colonial, are simple in structure and energy is directed via photosynthesis into growth and reproduction without establishing or maintaining complex tissues and organs [52,54]. In general, microalgae offer the prospect of high biomass yields without requiring any arable land and also have the potential to be cultivated in off-shore containment. Moreover, some microalgal species grow well in saline and wastewater, making them a more promising feedstock than terrestrial crops that rely on a supply of fresh water [9,55,56].

The first mono-algal cultures, *Chlorella vulgaris,* were obtained by Beijernick (1890) and developed for studying plant physiology by Warburg in the early 1900's. Mass culture of microalgae began to be a focus of research after 1948 at Stanford (USA), Essen (Germany) and Tokyo (Japan) [57].

Large-scale commercial production of microalgae started in Japan with *Chlorella* in the 1960's, followed by *Spirulina* in Mexico and Thailand in the 1970's. Forty-six of the worlds large-scale factories were producing greater than 12,000 kg of microalgae per year by 1980 [58]. As a source of β-carotene, *Dunaliella salina* was the third microalgae plant established in Australia in 1986 [59]. The commercial production of cyanobacteria (blue-green algae) started in India at about the same time. These plants were soon followed by other countries such as the USA and Israel [57]. It should be noted that microalgae production plants around the world have been established in year-round warm climate areas, as opposed to regions such as North America and Northern Europe.

More recently, there has been significant interest in extracting lipids from microalgae and transesterifying them into biodiesel [60,61]. Most species of microalgae have a dry weight lipid content of 20–50% [61,62], whereas terrestrial crops (e.g., soy, canola, palm, corn or jatropha) have a lipid content of less than 5% [63,64].

Despite many studies conducted on biological anthropogenic CO_2 mitigation through microalgae cultivation, there is a lack of reviews on large-scale cultivating facilities focusing on biodiesel production (Fig. 1). Therefore, the objective of this review is to address that lack by summarizing the limitations, potentials, and impacts of operational and environmental factors on CO_2 biosequestration and lipid production suitable for conversion to biodiesel.

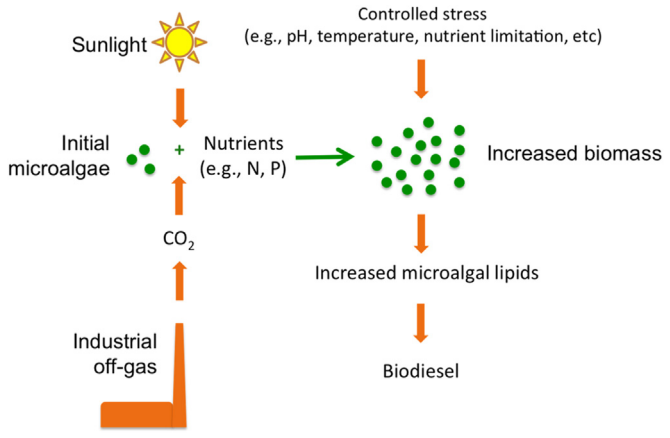

Fig. 1. Schematic diagram of the biological CO_2 mitigation and biodiesel production.

2. CO_2 sequestration in microalgae

Biological carbon sequestration using microalgae has been more recently considered as a method to mitigate anthropogenic CO_2 through photosynthesis, whilst producing value added products. Sequestration of CO_2 in microalgae occurs in two steps: a carbon concentrating mechanism and a photosynthesis process.

2.1. Carbon concentrating mechanism

In microalgae, Ribulose 1,5-bisphosphate carboxylase/oxygenase (RuBisCO) is the main enzyme involved in catalyzing CO_2 fixation through the reductive pentose phosphate pathway [65,66]. The first product of carbon fixation, 3-phosphoglyceric acid (3-PGA), is converted into essential elements of cells such as carbohydrates, lipids, and amino acids [67,68].

Poor performance of RuBisCO due to low affinity for CO_2, tendency to react with O_2 and low turnover rate results in energy consuming photorespiration, and a low CO_2 fixation rate [69,70]. Low diffusivity of CO_2 in water is also a limiting factor in RuBisCO enzymatic activity. Dissolved inorganic carbon in water can exist at equilibrium in forms of CO_2, H_2CO_3, HCO_3^- and CO_3^{2-}, but only HCO_3^- and CO_2 are considered as substrates for RuBisCO [66].

Bicarbonate (HCO_3^-) can be consumed by microalgae directly by cation exchange and active transport or indirectly through catalytic conversion into CO_2 and OH^- [71]. Enzymatic conversion of dissolved inorganic HCO_3^- into CO_2 is aided by carbonic anhydrase enzymes (CA). There are three types of carbonic anhydrase: (i) Periplasmic Carbonic anhydrase (pCA) for keeping a balance between CO_2 and HCO_3^- and continuously supplying CO_2 to cells; (ii) Cytosolic Carbonic Anhydrase (cyCA) for accelerating the transport of CO_2 and HCO_3^- from the plasma membrane to chloroplasts and (iii) chloroplast carbonic anhydrase (chCA) as the inorganic carbon transport system located on the chloroplast envelope that delivers HCO_3^- to the stroma [72].

The process of increasing the CO_2 level at the RuBisCO active sites is known as the CO_2 concentrating mechanism (CCM), which increases CO_2 fixation and photosynthetic rates and inhibits photorespiration [73]. However, the CO_2 concentrating mechanism was not detected in golden-brown algae, likely limiting the distribution of these algae to niches with adequate CO_2 availability [69,74]. RuBisCO has been observed in major algal species in one or more crystal-like proteinaceous structures within plastids called pyrenoids [66,75]. Despite an unclear functionality of pyrenoids, Moroney and Ynalvez [76] proposed that pyrenoids might play an important role in carbon concentrating mechanisms by separating RuBisCO from the CA in the stroma of the chloroplast [69].

2.2. Photosynthesis process

In the process of photosynthesis, photoautotrophic microalgae use light energy in the active radiation range (400–700 nm) to convert CO_2 into glucose while releasing oxygen. This can be empirically presented as follows:

$$6H_2O + 6CO_2 \rightarrow C_6H_{12}O_6 + 6O_2 \quad (1)$$

This process occurs in two light dependent and light independent stages. First, in the light dependent stage, microalgal cells absorb and store light energy. Antenna complexes and carotenoids transfer the light energy to the photochemical reaction centers of P700 and P680 (part of photosystem I and II) on the thylakoid membrane of the chloroplast [77]. Molecules of ADP and $NADP^+$ are converted into energy carrying molecules of ATP and NADPH through an electron transport chain. When excited electrons move to electron acceptors, the reaction center remains in an oxidized state [73]. Molecular oxygen is the product of this stage.

In the light independent stage, absorbed CO_2 along with ATP and