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Pre-design of a system for CO₂ biological removal

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ABSTRACT

Global warming resulting from the emission of greenhouse gases, especially CO₂, has become a major concern in recent years. Therefore many technologies have been developed to treat CO₂. This project will be based on literature review for making a pre-design of a system for CO₂ biological removal. The technologies reviewed will be algae and other autotroph organisms. One of this technologies will be elected to apply this bibliographical data to a real waste treatment plant that emits CO₂.

The following is a project about the design and construction of a tubular photobioreactor to produce microalgae *Chlorella* KR-1. Using combustion gases from a fuel-oil boiler in Cementos Molins Industrial plant. The reactor was pre-design for the treatment of 1.5 m³ s⁻¹ of gas and contained a pre-treatment on scrubber for minimizing the nitrogen dioxides presented in the combustion gases. The final maximum biomass concentration of 0.9 g L⁻¹ was obtained. Finally, a proportional scale-up was carried out for a photobioreactor, which was fed with the total flow of gases from the boiler.

Key words: Combustion gas, microalgae, *Chlorella* KR-1, biofuels, photobioreactor, carbon dioxide.

1. Introduction

Over the past years, human activities have altered the global carbon cycle significantly. The altered carbon cycle is mainly caused by increased CO₂ emission to the atmosphere due to extensive burning of fossil fuels. With the rapid increase of the global population and the industrialization of more and more countries, the consumption of energy is explosively growing. Currently over 85% of the global energy demand is being supported by the burning of fossil fuels. The reasons for this skewed reliance on fossil fuels as our primary energy source is due to the inherent energy density, abundance, and the economic dependence of modern society on the acquisition and trade of these resources.

Fossil fuels will continue to play an important role in the foreseeable future, mainly in power generation and industrial manufacturing. The burning of these fossil fuels releases large amount of CO₂ to the atmosphere; this disturbs the carbon balance of our planet which has been steady over hundreds of millions of years. Global warming has been reached to an alarming level due to the change in global environment. Industries related to electricity generation, natural gas processing, cement, iron and steel manufacturing, combustion of municipal solid waste are the major contributors of atmospheric CO₂ because of their dependence on carbon sources like coal, oil, natural gas for fulfilling their energy demand. The increase of the CO₂ concentration in the atmosphere influences the balance of incoming and outgoing energy in the atmospheric system, leading to the raise of average surface temperature of earth (Packer, 2009). Thus, CO₂ has often been cited as the primary anthropogenic greenhouse gas as well as the leading culprit in climate change. Although there are many uncertainties, it is beyond all doubt that strategies to reduce CO₂ emissions are urgently required to minimize the effects of climate change.

This provides an opportunity for the development of microalgae-based CO₂ mitigation technology based on microalgae's capability of photosynthesis to carry out carbon fixation. Microalgae are able to grow at a much faster rate than most terrestrial plants, thereby having higher CO₂ fixation rates. Moreover, microalgae have been considered the most effective platform for CO₂ reutilization, as the microalgal biomass obtained by the consumption of CO₂ is a very useful feedstock for the production of biofuels and bio-based chemicals (Chen *et al.*, 2011).

2. Objectives

This project was based on a review of the bibliography on biological technologies for removing CO₂. With data collected, make a “pre-design” of a system for CO₂ removal in a real installation. The objectives of this project are:

- Review of organisms capable to transform CO₂
- Selection of a real installation to treat.
- Review of different systems for CO₂ biological removal.
- Selection on technology and organisms to use in the design.
- Pre-design of the treatment plant.

3. Selection of installation that produces CO₂

Energy, oil, steel and cement companies are responsible for an important part of CO₂ emissions in Spain. Carbon emissions of a country depend on fixed sectors (industrial and energy facilities) and diffuse sectors, which are the remaining emissions. The main responsible for emissions of carbon dioxide are those energy-based companies such as Endesa and Repsol. Following by those big cement companies, Cemex and Cementos Molins Industrial.

The chosen plant that produces CO₂ is Cementos Molins Industrial, because the data is publicly available on the website. This is dedicated to the production and sale of concrete and sand, special mortars, prefabricated concrete and cement and other byproducts. This last line of business is the main industrial activity: the manufacture and marketing of cements, both high alumina and Portland.

This activity is centred in Sant Vicenç dels Horts and Pallejà (Barcelona), where the manufacturing plants are. The production process begins with the extraction of different raw materials. Specifically, they are: sandstone, limestone and clay.

The material extracted at the quarries is transported to the factory by trucks and, along with other raw materials, is fed into the process of manufacturing Portland and high alumina cements. The manufactured material is transferred to storage silos for shipment, whether directly in trucks for bulk sale, or passing through the cement sack machine for shipment in sacks.

The production process requires a great deal of energy, both for the manufacturing process of products and for the auxiliary processes, like the extraction of material at the quarries, transport to the factory, crushing, conditioning, etc. The energy consumed has three main sources: coal, electricity and oil derivatives, which are what contributes most to the increased total energy consumption. The energy proceeding from coal (soft coal) is used mainly in the high alumina cement production process. The oil derivatives are used as fuel in the manufacture of Portland cement (oil coke and fuel), in the transport activities related to the process and for feeding the heating and hot water system in the offices (diesel). As regards electricity, consumption is concentrated in powering machinery, lighting offices and other services.

The manufacture of cement is a process that emits certain pollutants. These are sulfur dioxide, nitrogen oxides and carbon dioxide. In table 2, it shows the most significant concentration of pollutants from kilns. The CO₂ emitted into the atmosphere in the manufacture of cement has two main sources: firstly, the reaction of decarbonizing lime, responsible for the 50% of the emissions and, secondly, the combustion need to reach the high temperatures required to form clinker, which emits another 40%. The remaining 10% is generated by auxiliary activities and transport (Cementos Molins Industrial, S.A., 2007).

Table 2. Production parameters in Ciments Molins

Flue gases temperature	100 °C
NO_x concentration	175 ppm
SO_x concentration	5 ppm
CO₂ concentration (v/v)	20 %
CO₂ emission	2,500 kg / day
Total amount of gases	2·10 ⁹ m ³ / year

4. Bibliography review on biological technologies

The selection of appropriate microalgae species for microalgae cultivation, determines the success in CO₂ bioconversion for biomass production. According to the literature, the bibliographic results will be presented in table form, biomass production is the most significant indicator into CO₂ sequestration by microalgae cultivation (Cheah et al., 2014). The ideal algal species should have high sinking capacity, high tolerance to CO₂ concentration, toxic pollutants concentrations, temperature, nutrients limitation and pH effect. As shown in Table 1, the microalgae species *Scenedesmus*, *Botryococcus braunii*, *Chlorella* and *Synechocystis aquatilis* are the most promising species for carbon sequestration. *Chlorella* KR-1 was identified as the species which possesses higher biomass production. In Table 1, *Chlorella* sp., *Botryococcus braunii* sp. and *Synechocystis aquatilis* possess high biomass productivity.

Chiu et al. (2008) reported about *Chlorella* sp. can grow under 100% CO₂, although 10% CO₂ was sufficient to achieve the maximum growth rate. The optimal CO₂ concentration for most microalgal species is usually recommended to be 0.038–10%. Table 1 shows that the best CO₂ fixation rates were often obtained in closed reactor systems (e.g. bubble column, air lift column and tubular column). It should be noted that the high performance of *chlorella* KR-1 is obtained under different experimental conditions, such as light intensity, CO₂ concentration and photobioreactor design. This variation may affect the microalgal fixation efficiency and biomass productions. It can tolerate CO₂ only up to a certain level after which it becomes detrimental for the growth of the cells because of the two reasons. Firstly environmental stress induced by the higher CO₂ concentration which causes biological reduction in the capacity of algal cells for CO₂ sequestration. Secondly at higher CO₂ concentration, the culture pH decreases due to the formation of high amount of bicarbonate buffer (Sobczuk et al., 2000).

Table 1. Some microalgal species that have been studied for CO₂ removal.

Microalgal species	Maximum CO₂ % (v/v) tolerance	Specific growth rate (d⁻¹)	Biomass productivity (mg / (L d))	CO₂ consumption rate (mg / (L d))	Reactor type	Reference
<i>Chlorella</i> sp.	20	5.76	700.0	1,316	Tubular	Sakai et al. (1995)
<i>Chlorococcum littorale</i>	20	1.80	530.0	900.0	N.A	Kurano et al. (1995)
<i>Scenedesmus</i> sp.	10	N.D	188.0	460.8	Bubble column	Jin et al. (2006)
<i>Chlorella</i> NCTU-2	10	0.25	381.8	717.8	Air lift	Chiu et al. (2009)
<i>Synechocystis aquatilis</i>	N.A	5.50	590.0	1,500	N.A	Murakami and Ikenouchi (1997)
<i>Botryococcus braunii</i>	N.A	0.50	900.0	1,000	N.A	Murakami and Ikenouchi (1997)
<i>Chlorella</i> KR-1	10	N.D	940.0	1,767	Bubble column	Sung et al. (1999)
<i>Chlorella vulgaris</i>	10	N.D	273.0	612.0	Bubble column	Jin et al. (2006)

Microalgae species grow well in optimal pH ranges. *Chlorella* sp. can tolerate to pH below 4. Input gas usually contains high concentrations of NO_x and SO_2 , which reduce the pH of culture medium. Since microalgal CO_2 fixation involves photoautotrophic growth of cells, the CO_2 fixation capability of specific species should positively correlate with their cell growth rate and light utilization efficiency. The presence of SO_2 strongly inhibits microalgae growth. When the SO_2 concentration exceeds 100 ppm, it is almost impossible to grow most microalgae. Some microalgal species are able to grow with difficulty under conditions of high SO_2 concentration; however, they have a longer lag phase than in the absence of SO_2 . When the SO_2 concentration increases, the inhibition effect is increased, resulting in a sharp reduction in carbon fixation and biomass production, for instance, even *chlorella* KR-1, which is considered a high-performance microalgal species, could not survive under the conditions of 150 ppm SO_2 with 15% CO_2 (Lee et al., 2000).

The NO concentration usually has a two sided influence on the growth of microalgae. An extremely low concentration of NO may even be absorbed by the cultivation medium and transformed into NO_2 as the source of nitrogen nutrition for microalgae when using inorganic forms (Zhao and Su, 2014). However, this positive influence is quite limited: the increased NO concentration results in at least a decreased growth rate of microalgae for decreasing microalgae growth. Typically, SO_x and NO_x in flue gas can be treated separately by flue gas desulfurization and selective catalytic reduction processes, respectively, or simultaneously by the combined treatment systems before the treated gas stream enters a microalgae reactor (Zhao and Su, 2014).

As shown in Table 1, a few species could grow well and achieve high CO₂ fixation ability (500–1,800 mg L⁻¹ d⁻¹) under a relative high tolerance for temperature or CO₂ concentration. One should consider that some microalgae species are tolerant to relatively high temperatures (close to and greater than 30°C). Rahaman et al. (2011) reported about these types of microalgae can be cultivated in conjunction with the use of high temperature flue gases from industrial sites. These thermos tolerant strains may also simplify species control, as the optimum growth temperature of most microalgal species is in the range of 20–30°C. Low temperature of cultural medium is unfavorable for the enzyme activity of ribulose biphosphate carboxylase oxygenase, leading to reduction in photosynthesis rate. In contrast, high temperature inhibits microalgal metabolic rate and reduces the CO₂ solubility. Low CO₂ solubility causes photorespiration whereby the ribulose biphosphate carboxylase oxygenase enzyme will bind with O₂ rather than CO₂, in consequence this reduces carbon bioconversion rate by 20–30% (Zeng et al., 2011). For example, *Chlorella* sp., grow at temperatures of up to 42°C, and their tolerance to both high temperatures and high CO₂ content makes them potentially appropriate microbial cells for photobioreactors that are involved in CO₂ capture for flue gases.

Species that grow well under the natural day–night cycle are suitable for large scale outdoor cultivation systems and strains that can directly use the CO₂ in power plant flue gas are preferred (Stewart and Hessami, 2005). Industrial exhaust gases can contain 10–20% CO₂. Some strains are not inhibited by CO₂ with <50 ppm SO_x, but can be inhibited by CO₂ when NO_x is also present (Lee et al., 2002). As shown in Figure 1, this summarizes and compares the microalgal CO₂ sequestration abilities of algal isolates reported in the literature most with microalgal CO₂ consumption rates of 200–600 mg L⁻¹ d⁻¹; while some *Chlorella* sp. achieved CO₂ removal rates of 800–1,000 mg L⁻¹ d⁻¹, and could also remove sulfur dioxide, nitrogen oxides, and volatile organic compounds (Keffer and Kleinheinz, 2002). Application of such strains may minimize the cost of pre-treatment of flue gas. It should be noted that the performance of the microalgal strains mentioned above may be obtained based on different culture or experimental conditions, such as CO₂ concentration, temperature, cultural medium, light intensity, and the photobioreactor design.

The variation in those conditions may affect the CO₂ fixation efficiency of the strains. Hence, the information provided in Figure 1 is not a strict comparison of the performance among those strains, but rather a literature survey on what type of microalgal strains had been used to develop strategies for CO₂ emissions mitigation with a brief summary of the results under the specific culture and operation conditions for each microalgal strain (Keffer and Kleinheinz, 2002).

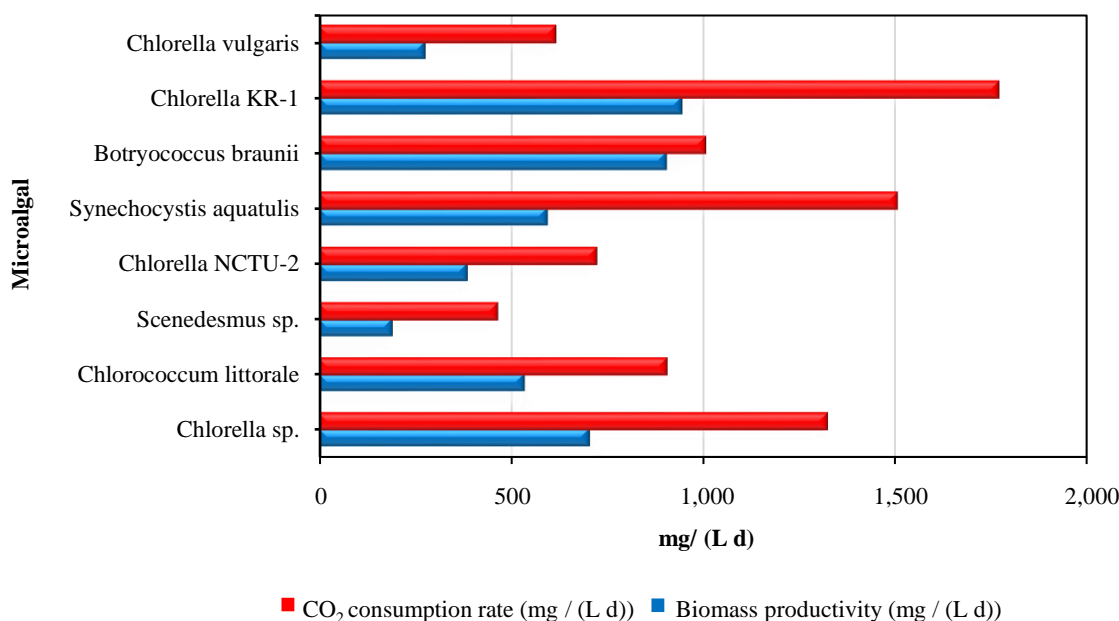


Figure 1. Analysis and comparison of microalgal CO₂ fixation ability.

Respect to the radiation, there are systems that work with artificial and natural light, then CO₂ removal rate and light intensity/periods are the major factors in photosynthetic carbon assimilation in plants and other photosynthetic organisms. In photosynthetic cultures, the maximum exploitation of microalgae for environmental uses is generally limited by light, a factor which normally determines the productivity of autotrophic cultures. Generally, the amount of light energy received and stored by the cells has a direct relationship with the carbon fixation capacity, consequently determines the productivity in the biomass and the cell growth rate. Therefore, enhancing the light utilization efficiency is substantial to obtain higher CO₂ fixation ability.

The general approach to achieve higher light utilization efficiency primarily relies on increasing the surface area and shortening the light path and layer thickness (Pulz, 2001). Most current photobioreactor design follows the principle of maintaining a high surface/volume ratio to bring more surface area (Posten, 2009). Saturation light intensity roughly varies from 140 to 210 $\mu\text{E m}^{-2} \text{s}^{-1}$ with a good estimation. For example, according to saturation light intensity of *Chlorella* sp. and *Scenedesmus* sp. are around 200 $\mu\text{E m}^{-2} \text{s}^{-1}$ (Hanagata et al., 1992). In outdoor condition, light availability is the dominant factor determining the productivity.

Generally, the light regimen itself is influenced by light intensity, light incident angle, surface area, cell density, and cell composition. Furthermore, the light regimen in an outdoor environment is also significantly influenced by geographic location, day period, and weather conditions. Therefore, designing the photobioreactors with high entering luminousness and high mixing efficiency is the key to promote the light utilization efficiency and microalgal cell growth. The closed system has certain advantages with regard to the maximum fixation of CO_2 , biomass productivity, great process control, and high photosynthetic efficiency, as well as with regard to obtaining no contaminated biomass for extracting biomolecules (Skjanes et al., 2007). The efficiency of CO_2 removal or fixation in a closed cultivation system depends on the microalgal species, CO_2 concentration, photobioreactor design and operating conditions (Chiu et al., 2009). In other words, the CO_2 removal efficiency and fixation depend on the species of microalgae due to the physiological conditions of algae, such as the potential for cell growth and CO_2 metabolism.

5. Selection of organism

Algae are eukaryotic organisms. Presence of chlorophyll and other pigments help in carrying out photosynthesis. The true roots, stems or leaves are absent. Algae can be multicellular or unicellular. Mostly they are photoautotrophic and carry on photosynthesis, some of these are chemo heterotrophic and obtain energy from chemical reactions as well as nutrients from organic matter. Microalgae can fix CO₂ using solar energy with efficiency ten times greater than terrestrial plants. Algae belong to a wide range of habitat like fresh water, marine water, in deep oceans and in rocky shores (Xin et al., 2011). Some microalgal species are discussed:

Chlorella species, some green algae are reported to easily grown at very high CO₂ concentration. It is very common to be used as carbon sequestration. It is found in fresh water, single cell organism containing chlorophyll a and b and has high photosynthetic efficiency to convert CO₂ to O₂ (Sobczuk et al., 2000).

Scenedesmus species is ubiquitous organism. *Scenedesmus* species is commonly found in fresh water lakes and rarely in brackish water. They belong to the family Scenedesmaceae, colonies of 2, 4 or 8 cells are arranged linearly or slightly in a zigzag manner. CO₂ biofixation and lipid production observed under different CO₂ levels (0.03% to 50% v/v) of *Scenedesmus obliquus* SJTU-3 and *Chlorella pyrenoidosa* SJTU-2 (Jeong et al., 2003).

Nannochloropsis species, CO₂ concentration affected biomass production and lipid accumulation of *Nannochloropsis oculata* NCTU-3 in semicontinuous culture. Lipid accumulation increased from logarithmic to stationary growth phase. *N. oculata* NCTU-3 with 2% CO₂ was cultured in a semicontinuous system with high cell density of inoculums in the system aerated with higher CO₂ concentration (5–15% CO₂) (Ota et al., 2009).

Chlorococcum species, Green alga *Chlorococcum littorale* (high CO₂ tolerance species) was investigated in the presence of inorganic carbon and nitrate at 295 K and a light intensity of 170 μmol-photon/m²/s. Bubbled CO₂ concentration was adjusted by mixing pure gas components of CO₂ and N₂ to avoid photorespiration and β-oxidation of fatty acids under O₂ atmospheric conditions. Fatty acid content was almost constant at CO₂ concentrations (5% to 50%) (Kurano et al., 1995).

Spirulina species is a small spiral coil shaped blue green algae. *Spirulina* species naturally grows in mineral rich water. *S. platensis* generally 80.40% biomass was produced at the 318.16mg/L/day CO₂ fixation rate. Higher productivity achieved with approximates 1% CO₂ added to *Arthrospira platensis* (Zhao and Su, 2014).

After the literature review, it is *Chlorella* KR-1 the strain that will be used for this final master work because it has been used in various industrial applications and found that a strain of fast growing microalgae capable of fixing CO₂ from combustion gases. It contains high amount of protein (51–58%), carbohydrate (12–17%) and lipid (14–22%) that could be used for various applications like health food, nutritional supplements, animal feed, biofuels, etc. Flue gas is inexpensive and rich source of CO₂, approximately 400 times more concentrated than atmospheric CO₂ and thus can be exploited for microalgal mediated CO₂ fixation (Cheah et al., 2015).

Literature also shows that *Chlorella* sp. can grow under 100% CO₂, although 10% CO₂ was sufficient to achieve the maximum growth rate. The cultural characteristics indicate that *Chlorella* KR-1 is a suitable strain for dense cultivation under CO₂ concentrations of industrial discharge gases. It has the major requirements for treating flue gases, tolerance to high concentrations of CO₂, high growth rate at high cell density, a broad range response to pH and temperature values, it may be used for large-scale cultivation to fix CO₂ directly from flue gas. In table 3, it shows that the *Chlorella* KR-1 grow at high temperatures and high concentrations of NO_x and SO_x.

Table 3. Temperature and input gas tolerance of some microalgal species.

Microalgal species	Maximum CO ₂ % (v/v) tolerance	Maximum temperature tolerance (°C)	NO _x /SO _x (mg L ⁻¹)	Reference
<i>Chlorella sp.</i>	20	40	N.D	Sakai et al. (1995)
<i>Chlorella</i> KR-1	50	25	N.D	Sung et al. (1999)
<i>Chlorella</i> KR-1	15	25	0/60	Lee et al. (2002)
<i>Chlorogleopsis sp.</i>	5	50	N.D	Ono and Cuello (2007)
<i>Chlorocuccum littorale</i>	50	22	N.D	Ota et al. (2009)
<i>Chlorella</i> T-1	50	35	60/20	Maeda et al. (1995)

Despite microalgae is efficient in CO₂ bioconversion with cultivation strategies like costly and energy required CO₂ bubbling, treated flue gas can become the potential CO₂ source for microalgal cultivation. The typical CO₂ concentration in flue gas is at 15% (v/v), which is approximately 400 times more concentrated if compared to atmospheric CO₂. This has resulted to the usage of flue gas for microalgae cultivation. *Chlorella* KR-1 was observed to be successfully fixing the actual flue gas discharged from boiler, without any treatment (Singh and Singh, 2014). This could be due to the characteristics of *Chlorella sp.* which has strong adaptability on high temperature and low pH of flue gas (Razzak et al., 2013).

Chlorella KR-1 species showed maximum growth at 10% CO₂ and good growth rate up to 50% CO₂ and no CO₂ fixation at 70% CO₂ concentration. *Chlorella* is also a popular food supplement which provides all essential amino acids. *Chlorella* KR-1 has good growth at 30% CO₂, with a wide range and temperatures up to 40 °C (Sung et al., 1999). Some investigator observed direct CO₂ fixation by *Chlorella* KR-1 which was successfully done using actual flue gases (SO_x and NO_x) from a liquefied natural gas or diesel fueled boiler and the results have indicated that *Chlorella* KR-1 may be applied for direct CO₂ fixation from actual flue gas (Lee et al., 2002). Flue gas in high temperature after the cooling and scrubber treatment is usually found to be suitable for cultivating thermos tolerant microalgae like *Chlorella* sp. T-1 and *Chlorella* KR-1. They were able to grow at temperature of 35 and 40 °C, respectively (Zhao and Su, 2014). *Chlorella* sp. can survive and grow in hot springs at temperature 42 °C with more than 40% (v/v) CO₂ (Razzak et al., 2013).

Therefore, after review the literature, the microalgal chosen is *Chlorella* KR-1, it was identified as the species which possesses higher biomass production, in Table 1 where it is shown that the microalgae chosen, has more biomass productivity and increased CO₂ consumption rate, could also remove sulfur dioxide, nitrogen oxides, and volatile organic compounds. The high performance of *Chlorella* KR-1 is obtained by different experimental conditions, such as light intensity, CO₂ concentration and photobioreactor design.

6. Selection of technology

Successful microalgae cultivation requires supply of adequate sunlight, CO₂ and nutrients. Comprehensive design of cultivation system is aimed to provide the optimal growth conditions for microalgal growth, thus maximizing the biomass production. The selection microalgal cultivation systems are still depending on these factors like: cost, CO₂ capture source, type of target products and the nutrient sources. The types of microalgae cultivation systems are summarized:

Open pond system is the most commonly applied for large scale microalgae cultivation due to its low cost and ease in operation and maintenance. It is commonly used for industrial application, to produce significant amount of products for commercial purposes at relatively low cost. The open pond is commonly designed as 0.25 m in width, with area of 0.2–0.5 ha for commercial purpose microalgal productions. Open pond system possesses high surface area per volume, allowing the high CO₂ mitigation. Additionally, if the nutrient sources used is wastewater, incorporated with CO₂ supplied from flue gas, the open pond system is usually applied. Nevertheless, open pond system suffered some drawbacks whereby it requires significant land area, the culture is subjected to high risk of contamination or predators and the evaporative water lost can be significant due to the open structure (Zhao and Su, 2014). Thus, some ponds are covered with transparent material to promote growing period of microalgae, prevent evaporation loss and facilitate CO₂ distribution.

Closed system (photobioreactors) have gained much interest by researchers due to better control of cultivation parameters and capability to satisfy carbon requirement. It was also evident that PBR cultivation has achieved high photosynthetic efficiency and biomass productions compared to open pond system. These advantages are even more important if the desired microalgae are used for pharmaceutical purposes or highly selective products applications (Fernandes et al., 2014). Photobioreactors are designed in configuration to maximize photosynthetic efficiency and CO₂ mass transfer efficiency; minimize cultivation dark zone and power consumption.

After the literature review, the cultivation systems are categorized into open and closed systems. The open systems are outdoor facilities consisting of ponds, lagoons, deep channels, shallow circulating units and others. In contrast, the closed systems are vessels or tubes with walls that are made of transparent materials and that are located in outdoors under sunlight irradiation or artificial irradiation.

Open systems of microalgal cultivation can be mainly divided into those that utilize natural and artificial freshwaters. With regard to the technical complexity, most open systems are much simpler than closed photobioreactor systems. Using outdoor open systems of microalgal cultivation for CO₂ mitigation, which is the closest to the natural environment, has received a growing amount of support recently (Jeong et al., 2003). However, outdoor systems are significantly limited with regard to cell growth due to several environmental issues, such as significant vapor losses, CO₂ diffusion to the atmosphere, varying temperatures and light utilization, as well as the threat of contamination and pollution (Carvalho et al., 2006). In comparison with open systems, closed photobioreactors are characterized via regulated and well controlled cultivation, with the additional benefits of low contamination risk, high CO₂ fixation efficiency, high metabolic flexibility, and controllable hydrodynamics (Grima et al., 1999). Such systems usually have a larger surface area (high surface/volume ratio) exposed to the light source to reduce the shadow effect, which is one of the main causes of the inhibition of microalgae in open systems.

The criteria for a good microalgal CO₂ fixation photobioreactors system are good mixing, gas transfer, and light distribution. Various closed photobioreactors are currently used for microalgae cultivation, including vertical column systems, plate type systems and tubular systems (Chiu et al., 2009). Vertical-column photobioreactors are compact, low cost, and easy to operate. Furthermore, they are very promising for large scale cultivation of algae. It was reported that bubble-column photobioreactors can attain a good mixing with low shear stress, low energy consumption, high potentials for scalability, easy to sterilize, readily tempered, good for immobilization of algae, reduced photo-inhibition and photo-oxidation. Although vertical bubble columns and airlift cylinders have a low surface/volume, they have substantially greater gas hold ups than horizontal reactors and a much more chaotic gas-liquid flow, and consequently can attain substantially increased radial movement of fluid that is necessary for improved light-dark cycling (Sánchez et al., 1999).

Literature also shows bubble column is widely used in the industries because of their simple construction and operation. These photobioreactors are usually consisting of cylindrical vessels in which gas is sparged into the liquid. The absence of moving parts and their suitable heat and mass transfer characteristics, along with their inexpensive operational costs from low energy input requirements, make them suitable for the mass production of microalgae. Mixing inside the photobioreactor is attained through the bubbles released at the sparger which coalesced immediately forming larger bubbles and rose rapidly along the axis of the columns, setting the entire liquid into circulation, with upward movement near the cylinder axis and downward movement near the walls.

Therefore, after review the literature, the photobioreactor chosen is bubble column reactor consists of vertical arranged cylindrical column made of transparent material. The introduction of gas takes place at the bottom of the column and causes a turbulent flow to allow optimal gas exchange. As shows in Figure 2, to obtain sufficient light for bubble column, the diameter should not exceed 0.2 m or light availability inside the photobioreactor will be severely reduced (Sánchez et al., 1999). In addition, the height of a single device is limited to about 4 m for structural reasons and to reduce mutual shading of reactors in a multicolumn facility that would be necessary for any commercial-scale operation (Sánchez et al., 1999).

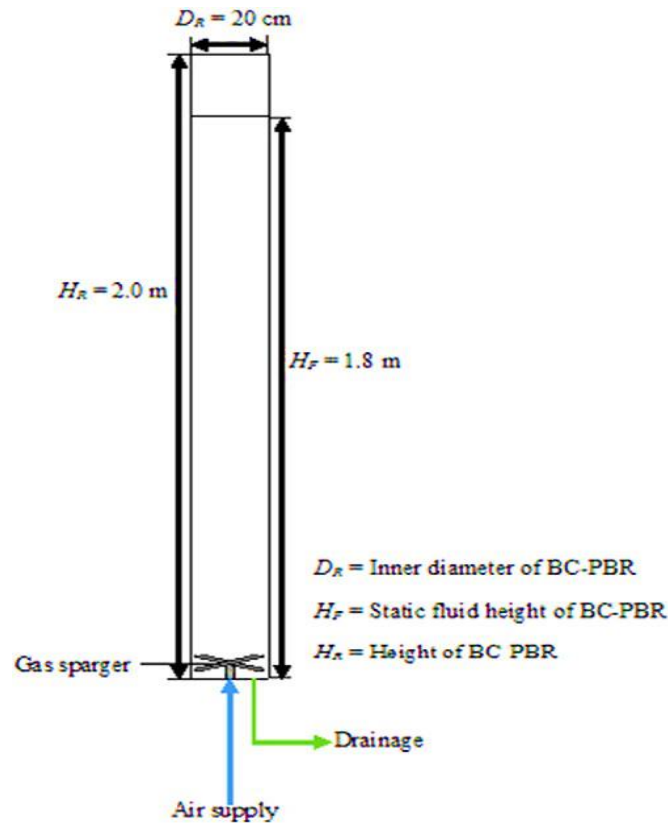


Figure 2. Schematic diagram for operating Bubble column photobioreactor (Khoo et al., 2016).

7. Pre-design system to remove CO₂

7.1. Relevant aspects

a) Growth medium

Chlorella KR-1, a highly CO₂ tolerant and fast growing microalga, isolated in Youngwol, Korea, was used in this project. The Detmer agar medium had the following composition in mg/L: Ca(NO₃)₂, 1000; KCl, 250; MgSO₄·7H₂O, 250; KH₂PO₄, 2.50; FeCl, 0.002. The plate was cultured for 2 weeks at 25°C. Illumination was provided by fluorescent light. Light intensity was about 50 μmol/m²/s. A modified M4N medium (Sung et al., 1998) was used to culture *Chlorella* KR-1 and had the following composition: (in mg/L); KNO₃ 5000; MgSO₄·7H₂O, 2500; KH₂PO₄, 1250; NaFeEDTA, 14; H₃BO₃, 2.86; MnSO₄·7H₂O, 2.5; ZnSO₄·7H₂O, 0.222; CuSO₄·5H₂O, 0.079; Na₂MoO₄, 0.021. The initial pH of the medium was 5.5.

b) Mixing

Mixing plays a major role in ensuring light intensity distribution, sufficient CO₂ transfer and maintaining uniform pH. In bubble column reactors, the longer time for the air to reside in the medium with smaller bubbles, more mass transfer is expected. Mixing is necessary to prevent algae sedimentation at the same time avoid the cell attachment to the reactor wall. Mixing also ensures that all cells are equally exposed to the light and nutrients and improves gas exchange between the cultural medium and the air. Mixing in bubble column reactor can be characterized by the axial dispersion coefficient, mixing time, circulation time and Bodenstein number.

c) Light penetration

Illumination inside the photobioreactor influences biomass composition, growth rate, and product formation. Microalgae need light within the photosynthetically active radiation to obtain energy by photosynthesis. The wavelength of the photosynthetically active radiation ranges from 400 to 700 nm, which is equal to visible light (Lopez and Rojas 2010). In dense culture, the gradient of light varies along the radius of the photobioreactor because of light attenuation. The attenuation of light intensity is dependent on its wavelength, cell concentration, geometry of photobioreactor and the penetration distance of light.

d) Gas injection

The introduction of CO₂ supply via bubbles into the photobioreactor should be strongly considered in the design. CO₂ injection refers to the process by which carbon dioxide is artificially introduced into the photobioreactor. Several studies have shown that aeration of carbon dioxide rich gas through a photobioreactor provides CO₂ to the algae and also aids in deoxygenating of the suspension and provides mixing to increase the cycle frequency thereby limiting light inhibition. However, from the economic point of view, a high aeration rate will lead to higher running costs, so that it is not recommended for the large-scale production of microalgae (Zhang et al., 2002). Therefore, as shown in Table 4, several studies have characterized the optimum concentration by carbon dioxide gas for microalgal production in the photobioreactor. Air enriched with 5% or 10% (v/v) CO₂ at gas input speed of 0.0456 m s⁻¹ (Zhang et al., 2002).

e) Gas mass transfer

It is analyzed from the carbon supply and transfer through CO₂. The transference mass of gas to liquid, is mainly studied with gas grip, which is the volume fraction of the gas phase in the gas-liquid dispersion, in Table 4 shows mass transfer of CO₂, as residence time of the gas in the liquid and combination with bubble size (Sánchez et al., 2000).

f) Carbon Supply

Carbon is the most important nutrient for cell growth; CO₂, H₂CO₃, HCO₃⁻, CO₃²⁻. Microalgae used as inorganic carbon synthesis of organic compounds in the middle autotrophic. Entire flow of carbon supplied is determined by the gas bubbling rate and CO₂ partial pressure; selecting the appropriate combination of these two variables is the key to prevent carbon limitation in cultivating microalgae (Sánchez et al., 2000).

g) CO₂ transfer

The incidence of chemical reactions between CO₂ and OH⁻, H₂O and NH₃ in the liquid phase can lead to increase rates of absorption of CO₂ by the cultural medium. Prediction and improvement of mass transfer of gas to liquid in the photobioreactor is often equivalent to the prediction and improvement coefficient overall mass transfer. The area between gas-liquid phases can be improved either increasing or decreasing gas grip predominant bubble size (Barbosa et al., 2003), but the gas is very fine bubbles, because of its long residence time in the fluid, equilibrate with the liquid and therefore contribute little to mass transfer. The fluid properties such as pressure, density, viscosity and ionic strengths affect gas grip and the coefficient of overall mass transfer.

h) Bubble size

The area between the phases and mass transfer coefficient showed opposite dependence with bubble size; consequently, the gas grip was more sensitive to diameter bubble mass coefficient. As seen above, the coefficient gas liquid mass transfer increases within a range of bubble size in columns bubbler and airlift reactors. Small bubbles (<2 mm diameter) are more harmful to the larger bubbles cells (10 mm diameter) (Carvalho et al., 2006). Therefore the size of bubble, the gas flow rate and the CO₂ pressure should be adjusted to specific requirements of each culture.

i) Oxygen Removal

High levels of oxygen are toxic to most organisms phototrophic and next to a high light intensity exposure can cause photo oxidative death in culture. The injection of gas from the bottom of photobioreactor favors mixing, supplies enough CO₂ and depending on the height of the photobioreactor, efficient removal is achieved oxygen dissolved in the medium (Barbosa et al., 2003), with the increase in the speed of the liquid, which is a function of the gas input, dissolved oxygen concentration in the medium decreases, improving biomass production, however high speed liquid causes damage and death cell.

Table 4. Some conditions in the photobioreactor

Microalgae	<i>Chlorella</i> KR-1
Average temperature of culture	35 °C
Surface/volume ratio	0.830 m ⁻¹
Light source	Halogen lamp 40W
Lighting period	Daylight 12h - 12h Darkness
Gas Input speed	0.045 m s ⁻¹
Flow rate	Bubble regime
Specific growth rate (μ)	8.447 · 10 ⁻³ h ⁻¹
Gas grip (ϵ)	7.503 · 10 ⁻³
Average residence time of the gas dispersion	0.150 s
Coefficient of overall mass transfer of CO₂	0.037 s ⁻¹

7.2. Pre-design

The photobioreactor for microalgal culture and CO₂ reduction is presented schematically in Figure 3. The characteristics, dimensions and operating ranges, such as periods and light intensity, temperature, pH and others, were defined in table 5, and then a culture height of 1 m, diameter photobioreactor of 10 cm, was chosen as the material for the glass container. The reactors were illuminated with halogen lamps of 40 W. The culture irradiated with a light intensity 200 $\mu\text{E} / \text{m}^2 / \text{s}$ (Lopez and Rojas 2010).

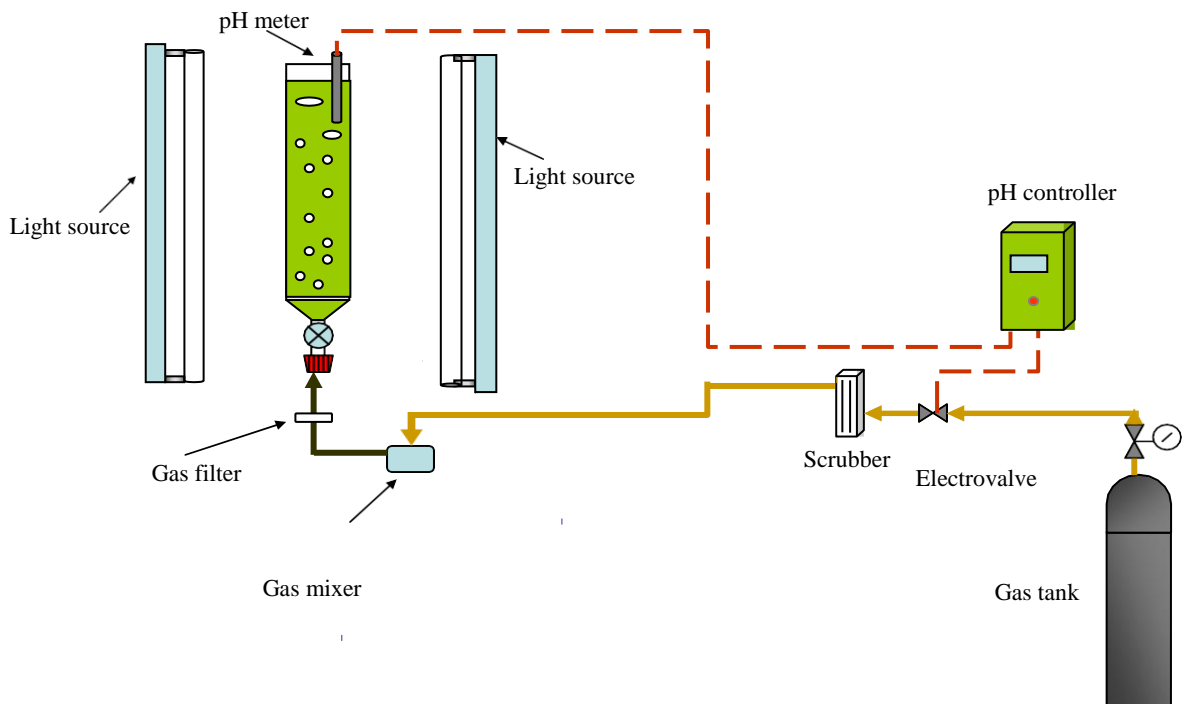


Figure 3. Schematic diagram of the photobioreactor for CO₂ removal

Figure 3, shows the schematic of the experimental setup and auxiliaries necessary for constant air bubbling, pH control and controlled delivery of CO₂. The air bubble was 0.4 L/min per liter of culture. CO₂ injection and regulation of pH were controlled, so that an increase in the set point pH detected, the valve that injects CO₂ into the air stream until the pH returns its value to the set point. The concentration of CO₂ in air is set to 20%. The cultures were lit with 12 hour photoperiod light and 12 hours of darkness. The temperature varies between 27 and 35° C, depending on the radiated light, due to the heat provided by the lamps. The pH was maintained at 8 during the culture (Martinez, 2012).

Technologies for NO_x removal include combustion control and post-combustion treatment. Combustion control aims to reduce the NO_x formation during combustion of fossil fuel. Post-combustion methods include selective non-catalytic reduction, selective catalytic reduction and scrubbing etc. Among these technologies, scrubbing methods are economically competitive and have advantage of controlling other acid gases and particulates at the same time (Yang et al., 1996). The tolerance of microalgae to NO_x depends on microalgal cell density, NO_x concentration NO_x gas flow rate and reactor type (Yoshihara et al., 1996). The Table 5, shows that the NO_x concentration is very high and would produce the inhibition *Chlorella* KR-1, then is performed a pretreatment for reduction. Microalgae requires NO_x is eliminated (Table 3).

Table 5. Starting values for Pre-design

Microalgae	<i>Chlorella</i> KR-1
Reactor type	Bubble column
Average temperature of culture	35 °C
Light source	Halogen lamp 40W
Amount of injected gases	$4,8 \cdot 10^{-4} \text{ m}^3 \text{ s}^{-1}$
Diameter	10 cm
Gas Input speed	0.045 m s^{-1}
Height	1.1 m
Flue gases temperature	100 °C
NO_x concentration	175 ppm
SO_x concentration	5 ppm
CO₂ concentration (v/v)	20 %
Total amount of gases	$1.5 \text{ m}^3 \text{ s}^{-1}$
Available space	200 m ²
CO₂ consumption rate	$1,767 \text{ mg L}^{-1} \text{ d}^{-1}$

Aqueous solutions of numerous oxidative absorbents such as hydrogen peroxide, organic tertiary hydro peroxides, sodium chlorite, KMnO₄ and chlorine dioxide have been investigated to determine their efficiency in the removal of NO_x (Deshwal et al., 2008).

Chlorine dioxide can clean up both NO_x and SO₂ simultaneously in a wide range of pH (Deshwal et al., 2008). Hence euchlorine will not only reduce the cost, also can solve the problem of pH adjustment. Therefore, aqueous euchlorine solution has been chosen for the combined removal of NO_x and SO₂ from the flue gas. Euchlorine oxidized NO into NO₂ completely and subsequently absorbed into the scrubbing solution in the form of nitrate. Simultaneous removal of SO₂ and NO. The input of SO₂ and NO concentrations were 500 and 350 ppm respectively, and were introduced by passing euchlorine gas into the scrubbing solution. A consistent and reproducible SO₂ and NO_x absorption efficiencies around 100% and 72% were observed at euchlorine feeding rates of 3.045 mmol/min. Furthermore, euchlorine proved a remarkably efficient oxidant as well as absorbent in a wide pH range of 3.5 to 8. The oxidizing as well as absorption ability of euchlorine was not affected by pH. The byproducts of the reaction in the combined removal of SO₂ and NO_x using euchlorine solution are sulphate, nitrate and chloride which are not hazardous materials, thus causing no secondary pollution (Deshwal et al., 2008).

Lee et al. (2011) reported about that maintaining the pH of the culturing media at an adequate value was quite important to enhancing the tolerances of the microalgae to SO_x and NO_x. Controlling the pH by adding an alkaline solution (NaOH), using a low flow rate of gas fed to the culture, and using a high concentration of inoculating cells were effective methods to prevent growth inhibition *Chlorella* KR-1,

As investigated in the literature, the starting values in Table 5 were used to calculate the number of modules that was necessary to have the data as gas combustion occurs in the plant. This value corresponded to 1.5 m³ s⁻¹ at normal temperature and pressure. Photobioreactor for amount of injected gases 4.8·10⁻⁴ m³ s⁻¹ at normal temperature and pressure is assumed. Since it supposed that the modules function and reproduce the results of the pilot photobioreactor, then 3,125 modules would be required under the experimental conditions, the area equivalent of 1,100 m², from the amount of photobioreactors and the surface it is estimated to need 250,000 W, representing 6,250 lamps. Furthermore, with respect to CO₂ used it is calculated one amount of biomass produced during the growth phase and the total volume of culture. Photobioreactor for possible would be expected that the fifth day of operation, 500 kg biomass would be produced to a final concentration of 0.9 grams per liter.

8. Conclusions

- *Chlorella* KR-1 was identified as the species which possesses higher biomass production. It should be noted that the high performance of *chlorella* KR-1 is obtained under different experimental conditions, such as light intensity, CO₂ concentration and photobioreactor design and showed maximum growth at 10% CO₂ and good growth rate up to 50% CO₂. Flue gas in high temperature after the cooling and scrubber treatment is usually found to be suitable for cultivating thermos tolerant microalgae.
- The chosen plant that produces CO₂ is Cementos Molins Industrial, because the data is publicly available on the website. The manufacture of cement is a process that emits certain pollutants. These are sulfur dioxide, nitrogen oxides and carbon dioxide.
- The best CO₂ fixation rates were often obtained in closed reactor systems (e.g. bubble column, air lift column and tubular column). Bubble column is widely used industrially because of their simple construction and operation. These photobioreactors are usually consisting of cylindrical vessels in which gas is sparged into the liquid.
- The reactor was pre-design for the treatment of 1.5 m³ s⁻¹ of gas and contained a pre-treatment on scrubber for minimizing the nitrogen dioxides presented in the combustion gases. The final maximum biomass concentration of 0.9 g L⁻¹ was obtained. Finally, a proportional scale-up was carried out for a photobioreactor, which was fed with the total flow of gases from the boiler.

9. Recommendations

- It is recommended to study on the ability of tolerance *Chlorella* KR-1 regarding the presence of other products of combustion such as NO_x and SO₂ and determine their influence as potential nutrients in the microalgal culture.
- It should be made related to the influence of light intensity and photoperiod in the culture system studies proposed in this project because they are parameters that affect both the microalgal growth and CO₂ sequestration.
- Experimentation *Chlorella* KR-1 in other photobioreactors that allow lesser degrees of hydrodynamic stress even in open ponds, because they are characterized by low turbulence.
- Make photobioreactors using sunlight as this use of artificial light which means energy savings and compare growth in both cases in order to establish differences and similarities.

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