Photosynthetic Bioenergy Utilizing CO_2 from a Mexican Cement-Manufacturing Facility: A review

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Abstract.

One of the most important industrial activities related to Green House Gases (GHG) emissions is the cement making industry that produce large amount of carbon dioxide (CO_2), approximately 15 million tons of CO_2, 2008. GHG emissions from cement manufacturing depend on the fuel mix, energy consumption, plant technology, and other variables, and are plant-specific. In this study evaluated the use of CO_2 produced by the cement manufacture process as a potential application of microalgae culture and establish the important relationships of nutrient composition, biodiesel production and scale up parameters using different strains of cyanobacteria that can growth base on a flue gases diet. This promising technology is based on the biological capture of CO_2 using microalgae and cyanobacteria. These microorganisms can fix CO_2 using solar energy with efficiency ten times greater than terrestrial plants. The biomass produced can also be used for high value co-products as cosmetics, human health, human and animal food, fertilizers and biofuels. This review describes the situation caused from anthropogenic activities and a sustainable solution for CO_2 capture. In 2011 cement companies have produced 25.4 million metric tons of CO_2 per 95.6 million metric tons of cement. Therefore, transform the gas fluxes that are polluting the atmosphere into new and valuable products is possible. These are positive reasons for large and global companies to invest in the new and alternative technologies.

Key Words

Microalgae, Lipids, CO_2 biofixation, GHG emissions, Cement Companies.

Introduction.

Current excessive demand for energy, fossil fuel depletion, increases in oil prices and environmental constraints have forced countries to investigate renewable energy alternatives to replace traditional energy sources. The global energy crisis and countries political pressure to reduce the greenhouse gases (GHG) attracting many researchers to find solutions for this problem. Transportation and energy sectors are the major anthropogenic sources responsible in for most of GHG emissions. For example Agriculture is the third largest anthropogenic source of GHG emissions. GHG contributes not only to global warming (GW) but also to other impacts on the environment and human life. Oceans absorb approximately one-third of the CO_2 emitted each year by human activities and as its levels increase in the atmosphere, the amount dissolved in oceans will also increase turning the water pH gradually to more acidic. This pH decrease may cause the quick loss of coral reefs and of marine ecosystem biodiversity with huge implications in ocean life and consequently in earth life (Ormerod, 2002; The Royal Society, 2005). On the other hand there are concerns the reduction of crude oil reserves and difficulties in their extraction and

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processing, leading to an increase of its cost (PEMEX, 2009[a,b]). This situation is particularly acute in the transportation sector where currently there are no relevant alternatives to fossil fuels. This problem intimately connected with economic development and prosperity, quality of life, global stability, and require from all countries to establish long term strategies. For example, many countries and regions around the world established targets for CO_2 reduction in order to meet the sustainability goals agreed under the Kyoto Protocol, 1998. Finally, nations at the climate change convention held n Copenhagen in 2012 agreed to provide about US $100 billion for greenhouse mitigation by 2020 (Kintisch, 2010). Presently many options are being studied and implemented in practice, with different degrees of success, and in different phases of study and implementation.

Biofuels production is expected to offer new opportunities to diversify income and fuel supply sources, to promote employment in rural areas, to develop long term replacement of fossil fuels, and to reduce GHG emissions, boosting the use of renewable fuels on transport and increasing the security of energy supply. The most common biofuels are biodiesel and bio-ethanol, which can replace diesel and gasoline, respectively, in today cars with little or none modifications of vehicle engines. They are mainly produced from biomass or renewable energy sources and contribute to lower combustion emissions than fossil fuels per equivalent power output. Biodiesel is produced from vegetable oils (edible or non-edible) or animal fats. Since vegetable oils may also be used for human consumption, it can lead to an increase in price of food-grade oils, causing the cost of biodiesel to increase and preventing its usage. The potential market for biodiesel far surpasses the availability of plant oils not designated for other markets. The extensive plantation and pressure for land use change and increase of cultivated fields may lead to land competition and biodiversity loss, due to the cutting of existing forests and the utilization of ecological importance areas. To become a more viable alternative fuel and to survive in the market, biodiesel must compete economically with diesel.

The end cost of biodiesel mainly depends on the price of the feedstocks that accounts for 60–75% of the total cost of biodiesel fuel. Thus transition to third generation biofuels, such as microalgae, can also contribute to a reduction in land requirements due to their presumed higher energy yields per hectare as well as to their non-requirement of agricultural land. As petroleum supplies diminish in the world, the United States becomes increasingly dependent upon foreign sources of crude oil. The United States currently imports approximately two-thirds of its petroleum and more than 60% of this petroleum is used for transportation fuels. Thus, the U.S. the Energy Independence and Security Act (EISA) was enacted in response to concerns about global energy security and supply. The Act contains provisions designed to increase the availability of renewable energy that decreases greenhouse gas (GHG) emissions while at the same time also establishing an aggressive Renewable Fuels Standard (RFS) (EPA, 2009). This new fuels standard mandates the production of 36 billion gallons of renewable fuels by 2022 of which at least 21 billion gallons must be third biofuels.

From the renewable energy products, biofuels derived from algae, particularly microalgae, have the potential to help the U.S. meet the new RFS while at the same time moving the nation ever closer to energy independence. The cultivation of algae at a commercial scale could provide sufficient fuel feedstock to meet the transportation fuels needs of the entire United States. However, despite their huge potential, the state of technology for producing algal biofuels is regarded by many in the field to be in its infancy. There is a general consensus that a considerable amount of research, development, and demonstration (RD&D) needs to be carried out to provide the fundamental understanding and scale-up technologies required before algal-based fuels can be produced sustainably and economically enough to be cost-competitive with petroleum-based fuels. Similar concerns about the energy and GW interested to the Mexican Government and set a program to develop biodiesel form algae. Mexico is a country highly dependent on its oilfields, therefore it a priority issues on the government agenda. In Mexico, the Mexican government has announced its “Manhattan Project” with an initial goal of producing 1 percent of its jet fuel from algae by 2015.

One of the most important industrial activities related to GHG is the cement industry that produce huge amount of carbon dioxide (approximately 15 millon tons of CO_2, 2008), and one of the most important cement companies of the world is CEMEX (CEMEX, 2009), reaching 95.6 million metric tons of cement production in 2011 **(Table 1)**.GHG emissions from cement manufacturing depend on the fuel mix, energy consumption, plant technology, and other variables, and are plant-specific. The two main GHG emission sources are the calcination/pyro-processing, which is generally the largest source of GHG emissions which can generate 50 percent or more of total cement manufacturing GHG emissions and during the fuel burning in pyro-processing which requires large quantities of fuels. Depending on the raw materials and the actual production process, a cement plant consumes fuel at a rate between 3,200 and 5,500 megajoules per tonne (MJ/t) of clinker, in which 91 % is fossil origin fuel (GHG Protocol, 2009).

For this reason, a major objective of the project is investigating ways to produce biodiesel base on the carbon dioxide produced with the flue gases form the cement furnaces. This project is of key importance to resolve an important piece of the challenges associated with commercial-scale algal biofuel production base on a GHG that is the principal responsible of the GW. The consortium of Arizona State University (U.S.) and Instituto Tecnologico de Estudios Superiores de Monterrey (Mexico), two important universities for its countries joint forces to help CEMEX to find new opportunities to reduce the GHG emissions and produce biodiesel to contribute to the U.S. and Mexico´s agenda to ensure GW mitigation and fuels for the transport to ensure sustainability.

Table 1: CEMEX World production rate (CEMEX annual report 2011)

Country	**Cement Production Capacity (millions metric tons/year)**
Mexico	29.3
United States	17.1
Northern Europe[1]	11.9
Mediterranean[2]	18.8
South, Central America and the Caribbean[3]	12.8
Asia[4]	5.7
Total	**95.6**

[1] Includes operations in Austria, Czech Republic, Finland, France, Germany, Hungary, Ireland, Latvia, Lithuania, Norway,Poland, Sweden, and the United Kingdom.

[2] Includes operations in Croatia, Egypt, Israel, Spain, and the United Arab Emirates.

[3] Includes operations in Argentina, Colombia, Costa Rica, Dominican Republic, Guatemala, Nicaragua, Panama, Puerto Rico, as well as other operations in the Caribbean region.

[4] Includes operations in Bangladesh, China, Malaysia, the Philippines, and Thailand

According to CEMEX Annual Report 2011, they increased the utilization of alternative fuels (biomass, refuse-derived fuels and tires) to 25% of cement plants’ total. Based on this performance, they have established a new 2015 target of a 35% substitution rate for alternative fuels. The Company also has reduced the CO_2 emissions per ton of cement by more than 23% from 1990 levels; this is equivalent to 7.6 million metric tons of CO_2 emissions annually, which means that by 2011 they have produced 25.4 million metric tons of CO_2 per 95.6 million metric tons of cement. If we assume an amount of 20% of CO_2 in industrial gas flux (Shih-Hsin et al., 2010), an amount of 101.6 million metric tons of another gas mixture that include SO_x and NO_x are delivered to the atmosphere. For these reasons, develop a process coupled that mitigates these emissions is necessary.

CO_2 Mitigation Strategy

Biological CO_2 fixation is currently achieved through the photosynthesis of all terrestrial plants and a tremendous number of photosynthetic microorganism (Shih-Hsin et al., 2010). However, plants are expected to contribute only a 3-6% reduction in global CO_2 emissions (Skjanes et al., 2007). However, microalgae and cyanobacteria can grow much faster than terrestrial plants, and ther CO_2-fixation efficiency is about 10-50 times better (Costa et al., 2000). In natural solar energy, the photosynthesis of most microalgae is saturated at about 30% of total solar radiation, in the range of 1700-2000 $\mu E\ m^{-1}\ s^{-1}$ (Pulz, 2001). The biomass of microalgae and cyanobacteria could also be used as the feed stock for a variety of biofuels, pharmaceuticals, cosmetics and nutritious foods, representing additional benefits from de microalgal CO_2 reduction process (De Morais and Costa, 2007; Shih-Hsin et al., 2010). A combination of CO_2 fixation, biofuel production and wastewater treatment may thus provide a very promising alternative to curren CO_2 mitigacion strategies,Wang et al., 2008; Shih-Hsin et al., 2010.

Microalgae can typically be used to capture CO_2 from three different sources: atmospheric CO_2, CO_2 emission from power plants and industrial processes, and CO_2 from soluble carbonate (Wang and Wu, 2008; Brennan and Owende, 2009). Capture of atmospheric CO_2 is probably the most basic method to sink carbon, and relies on the mass transfer from the air to the microalgae in their aquatic growth environments during photosynthesis (Wang and Wu, 2008; Brennan and Owende, 2009). However, the potential yield from the atmosphere is limited by low CO_2 concentration in air (360 ppm) which makes it economically infeasible (Stepan et al, 2002; Brennan and Owende, 2009). In contrast, 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% (Bilanovic et al., 2009; Brennan and Owende, 2009), and adaptability of this process for both photobioreactor and raceway pond systems for microalgae production.

Since microalgal 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 (Jacob-lopes et al $2009_{a,b}$). Moreover, microalgal photosynthesis efficiency declines with increasing temperature, since CO_2 solubility is significantly reduced (Pulz, 2001). 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 (Shih-Hsin et al., 2010). The amount of light energy received and stored by the cells has a direct relationship with the carbon fixation capacity, allowing the ability for cell growth and biomass production. Reason why is necessary enhancing the light utilization efficiency, normally this relies on increasing the surface area and shortening the light path and layer thickness (Pulz, 2001).

Species that grow well under the natural day-night cycle are suitable for large scale outdoor cultivation systems (Stewart and Hessami, 2005), and strains that can directly use the CO_2 in power-plant flue gas are preferred (Benemann, 1993, Maeda et al., 1995, Shih-Hsin et al., 2010). Industrial exhaust gases contain 10-20% CO_2 (Shih-Hsin et al., 2010). Some strains are not inhibited by CO_2 with <50 ppm SO_x, but can be inhibited by CO_2 when NO_x is also present (Lee et al., 2002; Negoro et al., 1991; Shih-Hsin et al., 2010). **Table 2** and **Table 3**, list microalgae species that are tolerant to high-temperatures, high CO_2 concentrations and toxic compounds such as NO_x and SO_x and some strains that have considerable CO_2 fixation ability respectively (Shih-Hsin et al., 2010). The selection of suitable microalgae strains for CO_2 biomitigation has significant effect on efficacy and cost competitiveness of the bio-mitigation process. The desirable attributes for high CO_2 fixation include: high growth and CO_2 utilization rates; high tolerance of trace constituents of flue gases such as SO_x and NOx; possibility for valuable by-products and co-products, e.g. biodiesel and biomass for solid fuels; ease of harvesting associated with spontaneous settling or bio-flocculation characteristics; high water temperature tolerance to minimize cost of cooling exhaust flue gases; be able to use the strain in conjunction with wastewater treatment (Brennan and Owende, 2009).

Table 2

Comparison of the growth characteristics and CO_2 fixation performance of microalgal strains under different CO_2 concentrations, temperature and NO_x/SO_x contents.

Microalgae Specie	**CO_2 (%)**	**Temperature (°C)**	**NO_x/SO_x (mg L^{-1})**	**Biomass productivity (mg $L^{-1}d^{-1}$)**	**CO_2 Consumption rate (mg $L^{-1}d^{-1}$)**
Nannochloris sp.	15	25	0/50	350	658
Nannochoropsis sp.	15	25	0/50	300	564
Chlorella sp.	50	35	60/20	950	1790
Chlorella sp.	20	40	N.D	700	1316
Chlorella sp.	50	25	N.D	386	725
Chlorella sp.	15	25	0/60	1000	1880
Chlorella sp.	50	25	N.D	500	940
Chlorogleopsis sp.	5	50	N.D	40	20.45
Chlorocuccum littorale	50	22	N.D	44	82

Microalgal Culture

Under natural growth conditions phototrophic algae absorb sunlight, and assimilate carbon dioxide from the air and nutrients from the aquatic habitats. Therefore, as far as possible, artificial production should attempt to replicate and enhance the optimum natural growth conditions. Photoautotrophic production is autotrophic photosynthesis; heterotrophic production requires organic substances (e.g. glucose, acetate, glycerol) to stimulate growth, while some algae strains can combine autotrophic photosynthesis and heterotrophic assimilation of organic compounds in a mixotrophic process (Brennan and Owende, 2009; Perez-García et al., 2010). Mata et al., 2009 based on Chojnacka and Marquez-Rocha, 2004 described the grow conditions for some organisms including algae:

- Photoautotrophically, i.e. using light as a sole energy source that is converted to chemical energy through photosynthetic reactions.
- Heterotrophically, i.e. utilizing only organic compounds as carbon and energy source.
- Mixotrophically, i.e. performing photosynthesis as the main energy source, though both organic compounds and CO2 are essential. Amphitrophy, subtype of mixotrophy, means that organisms are able to live either autotrophically or heterotrophically, depending on the concentration of organic compounds and light intensity available.

- Photoheterotrophycally, also known as photoorganitrophy, photoassimilation, photometabolism, describes the metabolism in which light is required to use organic compounds as carbon source. The photoheterotrophic and mixotrophic metabolisms are not well distinguished, in particular they can be defined according to a difference of the energy source required to perform growth and specific metabolite production.

Table 3
Comparison of the growth rate and CO_2 fixation ability of microalgal strains reported in the literature.

Microalgal species	CO_2 (%)	Specific growth rate (d^{-1})	Biomass productivity ($mgL^{-1}d^{-1}$)	CO_2 consumption rate ($mgL^{-1}d^{-1}$)	Operating strategies	Reactor type
Nannochloris sp.	15	N.D.	320	601	Batch	N.A.
Nannocholorpsis sp.	15	N.D.	270	508	Batch	N.A.
Phaeodactylum tricornutum	15	N.D.	150	282	Batch	N.A.
Chlorella sp.	20	5.76	700	1316	Batch	Tubular
Chloracoccum littorale	20	1.8	530	900	Batch	N.A.
Synechocystis aquatulis	N.A.	5.5	590	1500	Batch	N.A.
Botryococcus braunii	N.A.	0.5	900	1000	Batch	N.A.
Chlorella sp.	10	N.D.	940	1767	Batch	Bubble column
Chlorella vulgaris	Air	0.4	40	75	Batch	Tubular
Chlorella emersonii	Air	0.38	41	77	Batch	Tubular
Scenedesmus sp.	10	N.D.	188	460.8	Batch	Bubble column
Chlorella vulgaris	10	N.D.	273	612	Batch	Bubble column
Microcystis aeruginosa	10	N.D.	220	520.8	Batch	Bubble column
Microcystis ichthyoblabe	10	N.D.	232	489.6	Batch	Bubble column
Chlorella vulgaris	0.8-1	N.D.	N.D.	6240 (max)	Batch	Membrane
Euglena gracilis	10	0.96	153	382	Batch	Tubular
Chlorella kessleri	6	0.27	87	164	Batch	Tubular
Scenedesmus obliquus	6	0.26	85	160	Batch	Tubular
Spirulina sp.	6	0.44	200	376	Serial	Tubular
Scenedesmus obliquus	12	0.22	140	263	Serial	Tubular
Spirulina sp.	6	0.42	210	394	Batch	Tubular
Scenedesmus obliquus	6	0.22	105	198	Batch	Tubular
Chlorella kessleri	6	0.38	65	122	Batch	Tubular
Chlorella vulgaris	0.09	N.D.	150	3450 (max)	Batch	Membrane
Chlorella sp.	2	0.492	171	857	Batch	Bubble column
Chlorella sp.	10	0.252	381.8	717.8	Batch	Air lift
Chlorella sp.	10	0.11	610	1147	Semi-batch	Air lift
Chlorella sp.	5	N.D.	335	700.2	Batch	Tubular
Aphanothece microscopic Nageli	15	N.D.	770	1440	Batch	Tubular
Aphanothece microscopic Nageli	15	N.D.	1250	5435	Batch	Bubble column
Anabaena sp.	Air	N.D.	N.D.	1450	Continuous	Bubble

						column
Scenedesmus sp.	10	N.D.	217.5	408.9	Batch	N.A.
Scenedesmus obliquus	10	1.19	292.5	549.9	Batch	N.A.

Microalgae can grow either in open ponds or closed systems named photobioreactors, **Table 4** makes a comparison between the open and closed bioreactors concerning the production of microalgae (Pires et al., 2012). 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 sp*. are cultivated in high salinity, alkalinity and nutrition, respectively (Haron et al., 2010; Lee, 2001). Closed photobioreactors have attracted much interest by researchers, because, as contamination can be reduced, they allow better control of cultivation conditions than in open systems; consequently, higher biomass productivities can be reached (Haron et al., 2010; Grobbelaar , 2009). Photobioreactors require less space; they lose less water by evaporation and CO_2 to the atmosphere. However, cooling and heating systems are required to control the cultivation temperature (Pires et al., 2012). Photobioreactors appear in different configurations: vertical column reactors (bubble columns or air-lift); tubular reactors; and flat-plate reactors. The air-lift reactors have great potential for industrial processes, due to low level and homogeneous distribution of hydrodynamic shear (Vunjak-Novakovic et al., 2005) which constitutes a disadvantage of closed photobioreactors to open ponds. The medium circulates in a cyclic pattern through channels built for this purpose (Pires et al., 2012). Tubular design is more appropriated to the outdoor culture, having large illumination surface created by the disposition of the tubes; they can be configured in vertical, horizontal or inclined planes (Pires et al., 2012). The vertical tubular reactors increase the contact time between the gaseous and liquid phases, increasing the CO_2 mass transfer (Stewart and Hessami, 2005). However, this disposition has the disadvantage of air pumping costs. On the other hand, the flat-plate photobioreactors can achieve higher cell densities than the other bioreactors (in more than an order of magnitude). Additionally, this type of bioreactors has lower power consumption; high mass transfer capacity; no dark zones; and high photosynthetic efficiency (Pires et al., 2012).

Table 4
Comparison between microalgae production in open and closed bioreactors.

Factor	**Open systems (raceway ponds)**	**Closed systems (photobioreactors)**
Space required	High	Low
Evaporation	High	No evaporation
Water loss	Very High	Low
CO_2-loss	High	Low
Temperature	Highly Variable	Required cooling
Weather dependence	High	Low
Process control	Difficult	Easy
Shear	Low	High
Cleaning	None	Required
Algal species	Restricted	Flexible
Biomass quality	Variable	Reproducible
Population density	Low	High
Harvesting efficiency	Low	High
Harvesting cost	High	Lower
Light utilization efficiency	Poor	Good
Most costly parameters	Mixing	Oxygen and temperatura control
Energy requirement (W)	4000	1800

Capital investments	Low	High

Biodiesel from algae

Biodiesel, a biofuel that can directly replace petroleum-derived diesel without engine modifications, has gained a lot of attention due to its environmental and technological advantages. Algae have been used as food since ancient times, and they have had applications in aquaculture, wastewater treatment, chemicals and pharmaceutical production and energy bioconversion processes. Algae fuel, it is considered TGB (Third Generation Biofuel), due to the fact that this technology emerged after bio-alcohol and bio-diesel fuels (Dermibas and Dermibas, 2010). In **Table 5**, are listed some world companies that are using CO_2 capture technologies for biodiesel or co-products from algae culture.

Lipids can be defined as any biological molecule which is soluble in an organic solvent. Membrane lipids do contain long chained fatty acyl groups, but these are linked, usually by an ester bond, to small highly hydrophilic groups. Consequently, membrane lipids orient themselves in membranes so as to expose their hydrophilic ends to the aqueous environment. Such molecules, in wich one end (head) interact with water and the other end (the tail) avoids it, are called amphipathic (Darnel et al., 1986). Most lipids contain fatty acids and can generally be classified into two categories based on the polarity of the molecular head group: (1) neutral lipids which comprise acylglycerols and free fatty acids (FFA) and (2) polar lipids (amphipathic lipids) which can be further sub-categorized into phospholipids (PL) and glycolipids (GL). Acylglycerol consists of fatty acids ester-bonded to a glycerol backbone and is categorized according to its number of fatty acids: triacylglycerols (TAG), diacylglycerolds (DG), monoacylglycerols (MG). FFA is a fatty acid bonded to a hydrogen atom. It is known that there are also some types of neutral lipids that do not contain fatty acids, such as hydrocarbons (HC), sterols (ST), ketones (K) and pigments (carotenes and chlorophylls) Halim et al., 2011.

For biodiesel production the relevant lipids from microalgae oil are the non polar lipids TAG and FFA. Acid/alkali catalysis (Fig. 1) for the (trans)esterification with an alcohol (methanol, ethanol) is used to form Fatty Acid (M)Ethyl Esters. Lipid content and distribution in microalgae depends heavily on culture conditions. Total lipids in microalgae are usually from 20 to 50% of their dry weight but values have been reported in a range from 1 to 80% (Garibay et al., 2009).

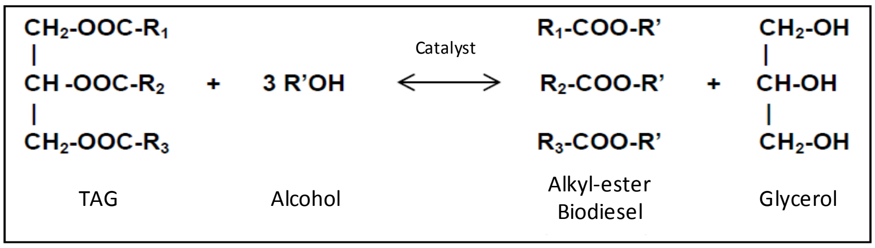

Fig. 1: Transesterification Reaction for Biodiesel Production.

Microalgae can provide feedstock for several different types of renewable fuels such as biodiesel, methane, hydrogen, ethanol, among others. Algae biodiesel contains no sulfur and performs as well as petroleum diesel, while reducing emissions of particulate matter, CO, hydrocarbons, and SO_x. However emissions of NO_x may be higher in some engine types (Delucchi MA, 2003).

The utilization of microalgae for biofuels production can also serve other purposes. Some possibilities currently being considered are listed below (Mata et al., 2009).

- Removal of CO_2 from industrial flue gases by algae bio-fixation (Wang et al., 2008), reducing the GHG emissions of a company or process while producing biodiesel (Directive 2003/30/EC, 2003).
- Wastewater treatment by removal of NH_4^+, NO^3 PO^4, making algae to grow using these water contaminants as nutrients (Wang et al., 2008).
- After oil extraction the resulting algae biomass can be processed into ethanol, methane, livestock feed, used as organic fertilizer due to its high N:P ratio, or simply burned for energy cogeneration (electricity and heat) (Wang et al., 2008).
- Combined with their ability to grow under harsher conditions, and their reduced needs for nutrients, they can be grown in areas unsuitable for agricultural purposes independently of the seasonal weather changes, thus not competing for arable land use, and can use wastewaters as the culture medium, not requiring the use of freshwater (Mata et al., 2009).
- Depending on the microalgae species other compounds may also be extracted, with valuable applications in different industrial sectors, including a large range of fine chemicals and bulk products, such as fats, polyunsaturated fatty acids, oil, natural dyes, sugars, pigments, antioxidants, high-value bioactive compounds, and other fine chemicals and biomass (Li et al., 2008a; Li et al., 2008b; Raja et al., 2008).

Table 5
Global Companies with CO_2 capture technology for algae culture.

Company	Region	Description
Seambiotic, Ashkelon, Israel.	Mediterranean	Founded in 2003, produces algae for a variety of applications including health foods, fine chemicals and biofuels. Working with the Israel Electric Company (IEC) using IEC's smokestack for a source of CO_2.
A_2BE Carbon Capture, Boulder Colorado.	USA	The companies build carbon capture and recycle (CCR) systems that take advantage of Algae's capacity to profitably recycle industrial CO_2. An advanced combined energy conversion system combines algal CO_2 capture technology with biomass gasification and thus creates an integrated renewable fuel production system.
GreenFuel Technologies, Cambridge, Massachusetts.	USA	Builds algal biofactory systems which use recycled CO_2 to feed the algae. The developed system can capture up to 80% of the CO_2 emitted from a power plant during the day when sunlight is available.
Algeneol Biofuels, Fort Meyers, Florida.	USA	The company founded in 2006 to develop industrial-scale algaculture systems to make ethanol from algae on desert land using seawater and CO_2. Patented a technology with blue-green algae, cyanobacteria that are N_2 fixing which reduces their fertilizer costs.
Solix Biofuels, Fort Collins, Colorado.	USA	Company founded in April 2006, intends to use microalgae to create a commercially viable biofuel that will play a vital role in solving climate change and petroleum scarcity without completing the global food supply.

	Proposed to build its first large-scale facility at the nearby New Belgian Brewery, where CO_2 produced during beer production would be used to feed the algae.

Zeng et al., 2011, relates that a 1000 m^2 microalgae cultivating area (0.5 m depth) with growth rate 30 g/m^2 d, whit 30% microalgae lipid content, and harvesting, extraction and transesterification efficiencies 90%, will generate 11,000 Kg biomass, 3300 Kg biodiesel per year and a net CO_2 fixation of 7000 kg. Hence the average biodiesel productivity is 3.3 kg/m^2 per year allowing a net CO_2 fixation capacity of 7 kg/m^2 per year. Considering energy generation combined with CO_2 fixation capacity, as well as growth rate, biofuels from microalgal biomass are much more preferable compared to biofuels generated from cellulosic or microbial biomass (Shinners et al., 2007; Mani et al., 2006). However, due to the dilute nature of harvested microalgal culture, much more research work on cultivation, energy-efficient dewatering and lipid extraction techniques should be focus (Zeng et al., 2011).

Biorefinery Concept

Dermibas and Dermibas, 2010, described biorefinery as a facility that integrates biomass conversion processes and equipment to produce fuels, power, and value-added chemicals from biomass. The biorefinery concept **(Fig. 2)** is analogous to today's crude oil refinery, which produces multiple fuels and products from petroleum.

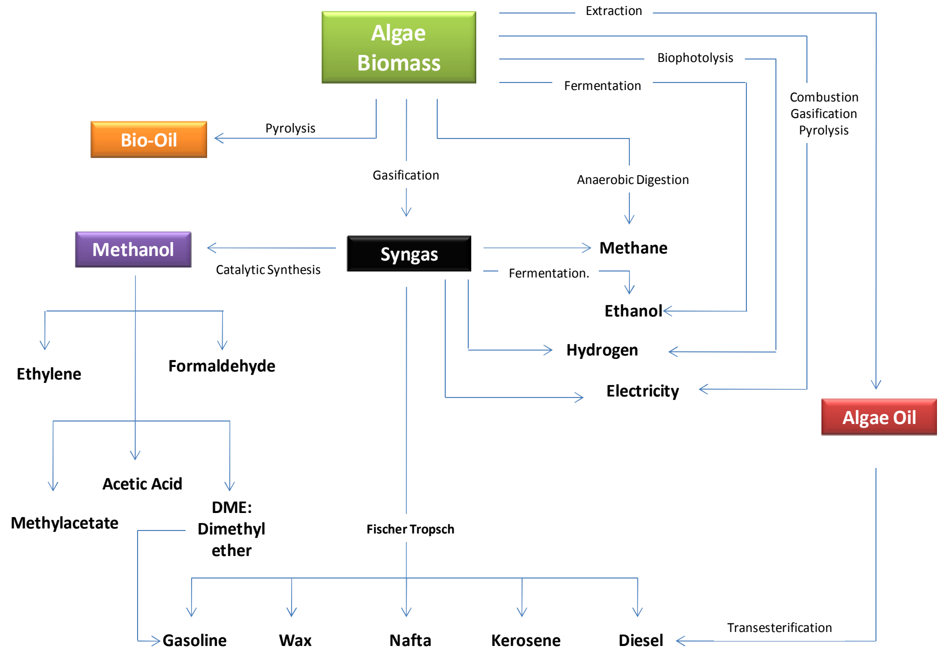

Fig. 2: Algae Biorefinery Concept.

Biorefinery refers to the conversion of biomass feedstock into a host of valuable chemicals and energy with minimal waste and emissions. In a broad definition, biorefineries process all kinds of biomass (all organic residues, energy crops, and aquatic biomass) into numerous products (fuels, chemicals, power and heat, materials, and food and feed). Algae can easily be part of this concept because each species produces certain amount of lipids, carbohydrates or proteins which biomass can be used in different process.

Waste Water Treatment

A new potential of algae has been study recently for waste water because they provide a pathway for the removal of chemical and organic contaminants, heavy metals and pathogens from wastewater while producing biomass for biofuel production (Brennan and Owende, 2009). For processing of hazardous or toxic compounds, it is possible to use microalgae to generate the oxygen required by bacteria to biodegrade pollutants such as polycyclic aromatic hydrocarbons (PAHs), phenolics and organic solvents (Muñoz R and Guieysse B, 2006; Brennan and Owende, 2009). Photosynthetic oxygen from microalgae production reduces or eliminates the need for external mechanical aeration. Chojnacka et al., 2005, found that *Spirulina sp.* acted as a biosorbent, thus was able to absorb heavy metal ions (Cr^{3+}, Cd^{2+}, and Cu^{2+}). Biosorption properties of microalgae depended strongly on cultivation conditions with photoautrophic species showing greater biosorption characteristics (Brennan and Owende, 2009). Algea species must be study according to the growth conditions and characteristics for each waste water effluent. Different authors have include some microalgae species for water treatment has Chen et al.,2011, that treated animal waste for nutrient removal with *Chlorella sp*, Lim et al., 2010 used *Chlorella vulgaris* for bioremediation of textile waste water, Mezzomo et al., 2010 cultivate *Spirulina platensis* for biological treatment of swine wastewater and Mata el al., 2011 treated brewery effluent by *Scenedesmus obliquus* with good results.

Other Applications and products from Microalgae

The marked trend and growing interest of consumers in new natural and healthy products in food industry instead of synthetic forms has forced to develop novel products with functional ingredients. The importance of marine algae as a source of functional ingredients has been well recognized due to their valuable healthy and positive effects. Therefore, research of novel ingredients with biological activities from marine algae have attracted a great deal of attention for been a source of polyunsaturated fatty acids (PUFA), polysaccharides, natural pigments (NPs), essential minerals, vitamins, enzymes, and bioactive peptides (Pangestuti and Kim, 2011).

Depending on the microalgae species various high-value chemical compounds may be extracted such as pigments, antioxidants, β-carotenes, polysaccharides, triglycerides, fatty acids, vitamins, and biomass, which are largely used as bulkcommodities in different industrial sectors (e.g. pharmaceuticals, cosmetics, nutraceuticals, functional foods, biofuels). Also, algalhydrocolloids alginate, agar, and carrageenan are produced from seaweeds (especially macroalgae) and largely used as viscositymodifying agents in foods and pharmaceuticals (Barrow and Shahidi, 2008).

Currently, the production of PUFA by marine and freshwater microalgae is subject of intensive research and increasing commercial attention (Wen and Chen, 2003; Sijtsma and Swaaf, 2004). Fish oil is a major source for the commercial production of these fatty acids but, since there is an increasing demand for purified PUFAs, some alternative sources are being sought. Moreover, the quality of fish oil depends on fish species, season/climate, geographical location of catching sites and the quality of food consumed. Some species of freshwater and marine algae contain large amounts of high-quality PUFAs and are widely used at the moment to produce PUFAs for aquaculture operations. The recent use of microalgae for eicosapentaenoic acid (EPA) production has gained attention on algae biotechnology research (Cheng et al., 2007). Different studies have shown that eicosapentaenoic acid (EPA, 20:5) is essential for the regulation of some biological functions as prevention factor of arrhythmia, atherosclerosis, cardiovascular diseases and cancer. Pulz and Gross, 2004.

Among functional ingredients identified from marine algae, NPs have received particular attention. These NPs besides their role in photosynthetic and pigmentation effects, exhibit various biological activities such as antioxidant, anticancer, anti-inflammatory, anti-obesity, anti-angiogenic, and neuroprotective activities. Therefore, various NPs isolated from marine algae have attracted much attention in the fields of food, cosmetic, and pharmacology (Pangestuti and Kim, 2011; Guedes et al., 2011). Three basic classes of NPs found in marine algae are chlorophylls, carotenoids, and phycobiliproteins. Carotenoids are linear polyenes that function as light energy harvesters and antioxidants that inactivate reactive oxygen species (ROS) formed by exposure to light and air (Ioannou and Roussis, 2009). Carotenoids are considered to be accessory pigments since they increase the light-harvesting properties of algae by passing on light excitation to chlorophyll (Larkum and Kühl, 2005), they can also be classified into two types: carotenes, which are unsaturated hydrocarbons, and xanthophylls, which present one or more functional groups containing oxygen. Pigment extractions of *Nannochloropsis gaditana* have shown Chlorophyll a and carotenoides as β-Carotene, Zeaxanthin and Violaxanthin as present components in this microalgae species. Forjan et al., 2007; Guedes et al., 2011.

Conclusions:

Anthropogenic activities estimated as fossil fuels combustion and industry process has increase the CO_2 concentration in the atmosphere on a non sustainable level that put at risk the human safe and biodiversity, for this reason is necessary reduce these emissions and search alternative sources of energy. Cement Companies are responsible of high amount of CO_2 delivered to the atmosphere while microalgae have shown higher CO_2 capture than higher plants, therefore design a process coupled with flue gasses exhaust of cement chimneys and microalgae culture can be developed. Additionally, microalgae produce lipids that can be transformed in biodiesel to be used in the transport sector. Design concepts, microalgae culture and species must be evaluated for this application at the same time parameters of flue gas composition and temperature. Microalgae can also be used for waste water treatment and chemistry applications complementing a biorefinery plant.

In 2015 CEMEX establish a target of 35% reduction of fossil fuels for alternative fuels. In 2011 they have produced 25.4 million metric tons of CO_2 per 95.6 million metric tons of cement. In theory 25.4 million of tons of CO_2 can be fixed with microalgae and produce approximately 50 million tons of biomass. Thus, with a 20% tranesterificable fats that can transform into 10 million tons of biodiesel. This action is in agreement to the 2015 CEMEX plan. Therefore, transform the gas fluxes that are polluting the atmosphere into new and valuable products is possible. Furthermore microalgae growth in controlled culture conditions can produce high quality biomass for human consumption or pharmaceutical treatment. These are positive reasons for large and global companies to invest in the new and alternative technologies.

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