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Conference report

Photosynthetic bioenergy utilizing CO_2: an approach on flue gases utilization for third generation biofuels

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ABSTRACT

One of the most important industrial activities related to the greenhouse gases emissions is the cement manufacturing process, which produces large amounts of carbon dioxide (CO_2). Only in 2010, 8% of CO_2 global emissions were due to cement industry. In this work, the use of CO_2 released by the cement sector is described as potential gas for microalgae culture since their biofixation efficiency is higher than terrestrial plants. Therefore, transformation of polluting gas fluxes into new and valuable products is feasible. In addition, bulk applications such as wastewater treatment and biofuels production can be coupled. Finally, microalgae biomass can be also used for the production of valuable compounds such as pigments, food supplements for both humans and animals, and fertilizers. In this review, flue gas emissions coupled to microalgae cultures are described. In addition, since microalgae can produce energy, the biorefinery concept is also reviewed.

1. 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) have also attracted many researchers to find solutions for this problem. Currently transportation and energy sectors are the major anthropogenic sources responsible for most of GHG emissions. Oceans absorb approximately one-third of the CO_2 emitted each year by human activities. However, the increment in these CO_2 levels at the atmosphere increases the amount of CO_2 dissolved in oceans, turning the water pH gradually to more acidic. This decrease of pH may cause the quick loss of coral reefs and marine ecosystem biodiversity with huge implications in ocean life and consequently in earth life (Ormerod et al., 2002; The Royal Society, 2005).

In addition, there are many concerns based on the reduction of crude oil reserves and difficulties in their extraction and processing, leading to a cost increase. This situation is particularly severe in the transportation sector, where there are no current relevant alternatives for fossil fuel demand. These problems are closely connected with economic development, prosperity, life quality, global stability, and therefore, require the establishment of long term strategies. In 1997, several countries around the world established targets for CO_2 reduction in order to meet the sustainability goals agreed under the Kyoto Protocol (Kyoto Protocol, 1997). The target was a 5% reduction in GHG emissions against 1990 levels. Later, a second commitment period signed by member nations at the climate change convention held in Copenhagen (2012), agreed to provide about US $100 billion for greenhouse mitigation by 2020 (Kintisch, 2010). Finally, a new target of, at least, 18% of GHG reduction by 2020 was established. This new international commitment promotes the development of new alternatives for reduction of GHG emissions, such as biofuels.

The term biofuel is referred to a solid, liquid or gaseous fuel that is predominantly produced from biorenewable feedstocks (Demirbas, 2009). The most common renewable liquid transportation fuels are bioethanol and biodiesel. These biofuels can replace gasoline and diesel respectively, in today cars with little or none modifications of vehicle engines. Biofuels can be classified based on their production technologies and feedstock: first generation biofuels (FGBs), second generation biofuels (SGBs), third generation biofuels (TGBs), and fourth generation biofuels (FoGBs)

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(Demirbas, 2011). FGBs are produced from sugar, starch, vegetable oils or animal fats, while SGBs are made from non-food crops, like wheat straw, corn and wood. Fuels produced from algae, also called algal oils, are classified as TGBs. Finally, FoGBs include crops that are genetically engineered to consume more CO_2 from the atmosphere than the amount of CO_2 that will be produced during their combustion as biofuels. Moreover, some fourth generation technology pathways include: pyrolysis, gasification, upgrading, solar-to-fuel, and genetic manipulation of organisms to secrete hydrocarbons. In addition, fourth generation technologies are based in the conversion of vegetal oil and biodiesel into biogasoline, using more advanced technology (Demirbas, 2011).

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 while increasing the security of energy supply. Biofuels are mainly produced from biomass or renewable energy sources and contribute to lower combustion emissions than fossil fuels per equivalent power output. Specifically, 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. In addition, the extensive plantation, the pressure for land use change and the increase of cultivated fields may lead to land competition and biodiversity loss, due to the cutting of existing forests and the utilization of ecological important areas. Furthermore to become a more viable alternative fuel, biodiesel must compete economically with diesel. Nowadays, the final cost of biodiesel mainly depends on the feedstock's price, that accounts 60–75% of the total cost of biodiesel (Lardon et al., 2009). In contrast, microalgae TGBs, contribute to a reduction in land requirements due to their higher energy yields per hectare as well to their non-requirement of agricultural land (Demirbas and Demirbas, 2010). Therefore, this article describes the potential use of microalgae as sustainable source for renewable fuels.

2. Literature framework

Microalgae are photosynthetic microorganisms capable to fixate CO_2 from the atmosphere. Therefore represent a big opportunity to overcome the global warming problem caused by the CO_2 emitted from anthropogenic activities. In this article, literature related to CO_2 emissions, producers, and capture technologies were consulted. In addition, since biofuel production from microalgae represents an alternative to overcome countries' energy security, literature describing biofuels production process and technologies were cited. Finally, advantages and drawbacks of this technologies are stated.

3. Carbon dioxide emissions

3.1. The cement industry

One of the most important industrial activities related to GHG is the cement industry that produces huge amount of carbon dioxide (CO_2). Including related combustion emissions, the cement industry accounts globally about 8% of global CO_2 emissions, leading to about 33.0 billion tons of CO_2 emissions for 2010. As well, global consumption of coal and natural gas is responsible for about 40% and 20% of total CO_2 emissions respectively (PBL, 2011).

According to CEMEX (2011), this Mexican Company produce 25.4 million metric tons of CO_2 per 95.6 million metric tons of cement. Assuming a CO_2 fraction of 20% in the gas flux (Ho et al., 2011), around 101.6 million metric tons of another gas mixture including SO_x, NO_x and particulated solid material are delivered to the atmosphere. However, GHG emissions from cement manufacturing are plant-specific and depend on the fuel mix, energy consumption, plant technology, among others factors. Currently, the two main GHG emission sources are the calcination/pyro-processing, generating 50% or more of total GHG emissions, and the fuel burning pyro-processing, which requires large quantities of fuels. Depending on the raw materials and the production process, a cement plant consumes fuel at a rate between 3200 and 5500 MJ/ton of clinker, in which 91% is fossil origin fuel. For this reason, industries and researchers should focus on the reduction of GHG emissions by developing alternative technologies to use the CO_2 delivered from current production processes, such as cement facilities.

3.2. CO_2 mitigation strategy

According to Yang et al. (2008) there are three options to reduce total CO_2 emission into the atmosphere: (1) reducing energy intensity use, (2) reducing carbon intensity use, and (3) enhancing the sequestration of CO_2. The first option requires efficient use of energy; the second one refers to the use of non-fossil fuels and the third option involves technologies to capture and reuse the CO_2.

Carbon sequestration can be defined as the capture and secure storage of carbon that would otherwise be emitted to, or remain in the atmosphere (Herzog and Golomb, 2004). According to Herzog and Golomb (2004), CO_2 capture processes from power production include three general categories. The first category refers to *flue gas separation* based on chemical absorption using monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA) (Yang et al., 2008). However, this process is only feasible when the CO_2 captured is used as a commercial commodity, so the absorption process, although expensive, is profitable because of the price of the commercial CO_2. The reaction of aqueous ammonia with an oxidize flue gas (converting SO_2 and NO to SO_3 and NO_2, respectively) in a wet scrubber has also been used for flue gas separation (Maroto-Valer et al., 2005). Once absorption process is concluded, ammonium regeneration requires heat input to thermally decompose ammonium bicarbonate and ammonium carbonate. Maroto-Valer et al. (2005) estimated that this process saves energy up to 60 percent compared to MEA process and the major by-products from this process include ammonium sulfate, ammonium nitrate, and ammonium bicarbonate. Ammonium sulfate and ammonium nitrate are well-known fertilizers, and the ammonium bicarbonate can be thermally decomposed to recycle ammonium. Also, for flue gas separation other alternatives have been described by Yang et al. (2008) as dual-alkali absorption (by sodium chloride), activated carbon, lithium compounds and membrane separation (polymeric, inorganic, carbon, alumina, silica and zeolite materials). The second category refers to *Oxyfuel combustion* in power plants by burning the fossil fuel with pure or enriched oxygen. In such a way, the flue gas will contain mostly CO_2 and H_2O. Of course, oxygen must be separated from nitrogen in the air. Although the air separation unit alone may consume about 15% of a power plant's electric output, the gaseous nitrogen, argon, and other minor ingredients of air are marketable by-products. Finally, *precombustion separation* refers to CO_2 capture before combustion and is usually applied in integrated coal gasification combined cycle. This process includes coal's gasification to produce a synthesis gas composed of CO and H_2. The CO reacts with water (water–gas shift reaction) to produce CO_2 and H_2, capturing the CO_2, and sending the H_2 to a turbine to produce electricity. Now

hydrogen is the primary fuel sent to the gas turbine or to other hydrogen fuel cells equipment.

However, in this article a fourth and natural carbon sequestration process is described: the *biological CO_2 fixation*. This process is currently achieved through the photosynthesis of all terrestrial plants and a tremendous number of photosynthetic microorganisms (Ho et al., 2011). However, plants are expected to contribute only with a 3–6% reduction of global CO_2 emissions (Skjånes et al., 2007). Therefore, since 50 years ago, researches have focus in the evaluation of microalgae and cyanobacteria (Acién Fernández et al., 2012) since they can grow much more faster than terrestrial plants, and their CO_2-fixation efficiency compared with higher plants is about 10–50 times higher (Costa et al., 2000). Also, 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).

Microalgae are photosynthetic microorganisms with simple growing requirements (light, sugars, CO_2, nitrogen, phosphorous, potassium) that can produce lipids in large amounts over short periods of time (Demirbas, 2011). Thus, microalgae and cyanobacteria biomass can also be used as feedstock for a variety of biofuels (De Morais and Costa, 2007; Ho et al., 2011). Furthermore, four applications are achieved by using microalgae biomass production as a CO_2 reduction strategy: i) production of biofuels, ii) enhancement of the economic yield of the carbon capture and storage through production of commodities or by-products from flue gases, iii) utilization of bacteria-microalgae consortiums to reduce the energy required for aeration in wastewater treatment plants and iv) utilization of microalgae to reduce the total CO_2 emissions released by wastewater treatment plants (Acién Fernández et al., 2012).

Microalgae can typically be used to capture CO_2 from three different sources: (1) atmospheric CO_2, (2) CO_2 emission from power plants and industrial processes, and (3) CO_2 from soluble carbonate (Brennan and Owende, 2010; Wang et al., 2008). 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. However, the potential yield from the atmosphere is limited by low CO_2 concentration in air (around 360 ppm) (Brennan and Owende, 2010; Stepan et al., 2002; Wang et al., 2008). 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). Since microalgae CO_2-fixation involves photoautotrophic growth of cells, CO_2 fixation capability of specific species should positively correlate with their cell growth rate and light utilization efficiency (Jacob-Lopes et al., 2009a,b). However, microalgae photosynthesis efficiency declines with increasing temperature, since CO_2 solubility is significantly reduced (Pulz, 2001). Some other obstacles in flue gases utilization are related to its low pressure and consequent power requirement for supply it into the system, as well as the possible addition of dust or heavy metals to the system (Acién Fernández et al., 2012).

Typically, industrial exhaust gases contain 10–20% CO_2 (Ho et al., 2011), as well as small amounts of SO_x and NO_x. Some strains are not inhibited by CO_2 with <50 ppm SO_x, but can be inhibited when NO_x is also present (Ho et al., 2011; Lee et al., 2002; Negoro et al., 1991). The elimination of SO_x from the flue gas can be performed using a chemical desulfurization system. However, NO_x removal is more difficult due to its lower solubility in the liquid phase. Tables 1 and 2 show some microalgae species tolerant to high-temperatures, high CO_2 concentrations and toxic compounds such as NO_x and SO_x (Ho et al., 2011). The selection of suitable microalgae strains for CO_2 mitigation has significant effect on efficacy and cost competitiveness of the bio-mitigation process. The desirable attributes of the microalgae strain include high growth and CO_2 utilization rates, high tolerance of trace constituents of flue gases such as SO_x and NOx, production of valuable products and co-products (biodiesel and biomass for solid fuels), simplicity in harvesting associated with spontaneous settling or bio-flocculation characteristics, high water temperature tolerance (to minimize cost of cooling exhaust flue gases), and possible coupling with wastewater treatment (Brennan and Owende, 2010).

Table 1
Comparison of the growth characteristics and CO_2 fixation performance of microalgae 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
Nannochloropsis sp.	15	25	0/50	300	564
Chlorella sp.	50	35	60/20	950	1790
Chlorella sp.	20	40	N.S.	700	1316
Chlorella sp.	50	25	N.S.	386	725
Chlorella sp.	15	25	0/60	1000	1880
Chlorella sp.	50	25	N.S.	500	940
Chlorogleopsis sp.	5	50	N.S.	40	20.45
Chlorococcum littorale	50	22	N.S.	44	82

N.S. – not specified.

4. Microalgae growth, culture system and harvesting

4.1. Cell growth and biomass production

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 microalgae production should attempt to replicate and enhance the optimum natural growth conditions.

Microalgae growth takes place by photoautotrophic or heterotrophic production. However some algae strains can combine autotrophic photosynthesis and heterotrophic assimilation of organic compounds in a mixotrophic process (Brennan and Owende, 2010; Perez-Garcia et al., 2011). In such a way, Mata et al. (2010) and Chojnacka and Marquez-Rocha (2004) described the growth conditions for some organisms, including microalgae:

- Photoautotrophic: use of light as a sole energy source (autotrophic photosynthesis) that is converted to chemical energy through photosynthetic reactions.
- Heterotrophic: utilization of only organic compounds as carbon and energy source (e.g. glucose, acetate, and glycerol).
- Mixotrophic: photosynthesis is performed as the main energy source; however, both organic compounds and CO_2 are essential. Also, amphitrophy means that organisms are able to live either autotrophically or heterotrophically, depending on the concentration of organic compounds and light intensity available.
- Photoheterotrophic: also known as photoorganotrophic, photoassimilation, or photometabolism, describes the metabolism in which light is required to use organic compounds as carbon source.

Microalgae can grow either in open ponds or closed systems, called photobioreactors. Table 3 shows a comparison between open and closed bioreactors (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. Moreover, the contamination by predators is an important drawback of this cultivation system as well as

Table 2
Comparison of the growth rate and CO_2 fixation ability of microalgae strains reported in the literature.

Microalgae species	CO_2 (%)	Specific growth rate (d^{-1})	Biomass productivity (mg L^{-1} d^{-1})	CO_2 consumption rate (mg L^{-1} d^{-1})	Operating strategies	Reactor type
Nannochloris sp.	15	N.S.	320	601	Batch	N.S.
Nannocholorpsis sp.	15	N.S.	270	508	Batch	N.S.
Phaeodactylum tricornutum	15	N.S.	150	282	Batch	N.S.
Chlorella sp.	20	5.76	700	1316	Batch	Tubular
Chlorococcum littorale	20	1.8	530	900	Batch	N.S.
Synechocystis aquatilis	N.S.	5.5	590	1500	Batch	N.S.
Botryococcus braunii	N.S.	0.5	900	1000	Batch	N.S.
Chlorella sp.	10	N.S.	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.S.	188	460.8	Batch	Bubble column
Chlorella vulgaris	10	N.S.	273	612	Batch	Bubble column
Microcystis aeruginosa	10	N.S.	220	520.8	Batch	Bubble column
Microcystis ichthyoblabe	10	N.S.	232	489.6	Batch	Bubble column
Chlorella vulgaris	0.8–1	N.S.	N.S.	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.S.	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.S.	335	700.2	Batch	Tubular
Aphanothece microscopic Nageli	15	N.S.	770	1440	Batch	Tubular
Aphanothece microscopic Nageli	15	N.S.	1250	5435	Batch	Bubble column
Anabaena sp.	Air	N.S.	N.S.	1450	Continuous	Bubble column
Scenedesmus sp.	10	N.S.	217.5	408.9	Batch	N.S.
Scenedesmus obliquus	10	1.19	292.5	549.9	Batch	N.S.

N.S. – not specified.

evaporation for solar exposure. Thus, high production rates in open ponds are achieved with algal strains resistant to severe culture environment conditions; for instance, *Dunaliella*, *Spirulina* and *Chlorella* sp. strains are cultivated in high salinity, alkalinity and nutrient restrictions (Harun et al., 2010; Lee, 2001).

Closed photobioreactors have attracted interest from researchers since contamination can be reduced allowing better control of cultivation conditions than the open systems; consequently, higher biomass productivities can be achieved (Grobbelaar, 2008; Harun et al., 2010). In addition, photobioreactors require less space, water lose by evaporation is lower and they possess higher efficiency capture of CO_2 from the atmosphere. However, cooling and heating systems are required to control the cultivation temperature (Pires et al., 2012). Photobioreactors commonly appear in three 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 an advantage of closed photobioreactors in comparison with open ponds (Pires et al., 2012).

Tubular design is more appropriated to the outdoor culture, having large illumination surface created by the disposition of the tubes. In addition, these reactors 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 configuration has the disadvantage of air pumping costs. Meanwhile, the flat-plate photobioreactors can achieve higher cell densities than the other bioreactors. Also, this type of bioreactors has lower power consumption, high mass transfer capacity, no dark zones and high photosynthetic efficiency (Pires et al., 2012).

Table 3
Comparison between microalgae production in open and closed bioreactors.

Factor	Open systems (raceway ponds)	Closed systems (photobioreactors)
Space required	High	Low
Area/volume ratio	Low (5–10 m^{-1})	High (20–200 m^{-1})
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 temperature control
Contamination control	Difficult	Easy
Capital investments	Low	High
Productivity	Low	3–5 times more productive
Hydrodynamic stress on algae	Very low	Low–high
Gas transfer control	Low	High

In photosynthetic cultures, the maximum utilization of microalgae for environmental uses is generally limited by light, which normally determines the productivity of autotrophic cultures (Ho et al., 2011). In addition, the amount of light energy received and stored by the cells has a direct relationship with the carbon fixation capacity, limiting the cell growth and biomass production. For this reason, it is necessary to enhance the light utilization efficiency that normally relies on increasing the surface area and shortening the light path and layer thickness of microalgae culture (Pulz, 2001). In addition, 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; Ho et al., 2011; Maeda et al., 1995).

4.2. Biomass harvesting

For microalgae biomass harvesting and processing, several technologies exist. According to Molina Grima et al. (2003) biomass can be harvested by centrifugation, filtration, gravity sedimentation or flocculation. It should be noticed that biomass recovery due to the small size of cells represents harvesting difficulties. In addition, culture broths are generally relatively diluted (0.5 kg/m^3). Therefore large volumes need to be handled to recover the biomass. Centrifuges can process large volumes relatively rapidly and the biomass can remain fully contained during recovery (Molina Grima et al., 2003). However the energetic input in this process yields high prices for the final product. In contrast, flocculation holds a lot of potential as a low-cost method for microalgae harvesting (Christenson and Sims, 2011; García-Pérez et al., 2014). Microalgal cells carry a negative charge that prevents aggregation of cells in suspension. Therefore the cell surface charge can be neutralized or reduced by adding flocculants such as multivalent cations or cationic polymers to the culture (Molina Grima et al., 2003). In addition, a pH increment in culture media induces autoflocculation, as result of precipitation of calcium and magnesium salts (García-Pérez et al., 2014). Finally, flocculants used should be inexpensive, nontoxic, and effective in low concentration. In addition, they should not have an effect in the further downstream processing (Molina Grima et al., 2003). In case of filtration, its recovery is satisfactory for relatively large microalgae such as *Spirulina platensis*, but fails to recover small algae species as *Scenedesmus*, *Dunaliella*, or *Chlorella*. Nevertheless, membrane microfiltration and ultrafiltration are possible alternatives to conventional filtration. However, membrane replacement and pumping are the major cost contributors to membrane filtration processes.

Once biomass is harvested, the algae slurry (5–15% dry solids) must be processed. Drying methods that have been used for microalgae include spray drying, drum drying, freeze-drying and sun drying (Molina Grima et al., 2003). Spray drying is the method of choice for high-value products, but it can cause significant deterioration of some algal components such as pigments. Freeze-drying, or lyophilization, has been widely used for drying microalgae in research laboratories; however, freeze-drying is too expensive for use in large-scale commercial recovery of microalgal products. Finally, dehydration or drying of the biomass is commonly used to extend the shelf-life of the biomass or to satisfy the requirements of the biomass processing. As example, in comparison with wet biomass, dry biomass allows higher extraction efficiency of intracellular metabolites such as oils (Molina Grima et al., 2003). Therefore, harvesting and downstream process should be adapted to algae species according to the cell size, the culture media concentration and the desired product.

5. Use of flue gas from cement industry

The cement industry is one of the major CO_2 producing sectors being responsible for about 8% of global emissions. It is reported a production of 193×10^6 metric tons of CO_2 by the cement industry, considering only member states of the European Union and Norway (2004) (Borkenstein et al., 2011). Hasanbeigi et al. (2012) reviewed 18 technologies for the reduction of CO_2 emissions by cement industry. They classified algal biomass utilization as an emerging technology in demo stage. Only a few studies regarding to flue gas usage from cement industry have been developed. Borkenstein et al. (2011) evaluated the air lift cultivation of *Chlorella emersonii* using flue gas derived from a cement plant. Pure CO_2 injection was used as a control and 5.5 L photobioreactors with controlled pH were used. After 30 days of cultivation, the flue gas had no visible adverse effects compared with the control reactors. The control essay (pure CO_2) resulted in a biomass yield of 2 g/L, CO_2 fixation of 3.25 g/L and growth rate of 0.1/day, meanwhile the flue gases reactors resulted in very similar parameters with 2.06 g/L in biomass yield, 3.38 g/L in CO_2 fixation and a growth rate of 0.13/day. Although there was no accumulation of flue gas residues in the culture media, the lead concentration in the microalgae biomass was three times higher with the flue gases. Therefore, lead accumulation and its effect on the downstream processing for biofuels production have to be investigated.

Lara-Gil et al. (2013) performed toxicity tests of a simulated cement industry flue gas in cultures of *Desmodesmus abundans* and *Scenedesmus* sp. The results suggest that nitrite and sulfite are not toxic for the tested microalgae at the maximum concentrations of 1067 ppm and 254 ppm, respectively, differing from bisulfate where concentrations above 39 ppm were toxic.

Studies related to flue gas from different industries can be considered useful despite of slight changes in flue gas composition. Chiu et al. (2011) performed studies with a thermophilic and CO_2-tolerant mutant strain of *Chlorella* sp. which was cultivated with flue gas, suggesting its use for biofuels production. When compared with the wild type strain, the mutant efficiently removed CO_2, NO and SO_2 from flue gas from a coke oven (used for steel production). Despite of slightly lower lipid content in the mutant *Chlorella*, the final biomass concentration was higher, compensating this deficiency. However, some studies have demonstrated that it's possible to increase the biomass and lipid production in microalgae by controlling the nitrogen source (Chandra et al., 2011).

Algal-bacteria consortium was cultivated in a 465 L high rate algal pond (HRAP) using diluted piggery wastewater and sparging filtered flue gas generated by combustion of natural gas (7% CO_2). Chemical oxygen demand (COD) and NH_4^+ were successfully removed, suggesting that flue gas sparging does not compromise wastewater treatment in HRAPs. However, pH lowering and nitrification were observed (De Godos et al., 2010).

Chlorella vulgaris was cultivated with flue gas originated from a municipal waste incinerator resulting in higher culture rates in comparison with the control culture supplied with a mixture of pure CO_2 and air. A slight accumulation of mercury was also observed when using the flue gas as a carbon source (Douskova et al., 2009).

Intermittent sparging and pH control by $CaCO_3$ addition demonstrated to be effective methods for the culture of *Scenedesmus dimorphus* with a simulated flue gas containing up to 20% CO_2, NO (500 ppm) and SO_2 (100 ppm) (Jiang et al., 2013). Initial optimization can be performed by a modeling approach, preventing poor biomass production or low CO_2 fixation rates when testing continuous flue gas sparging, like has been done previously with *Chlorella* sp. (He et al., 2012).

6. From CO_2 to biofuels production

Microalgae can serve as an alternative biofuel feedstock due to their rapid growth rate, greenhouse gas fixation ability and high lipid production capacity (Abanteriba et al., 2012). Moreover, the whole algal biomass or algae extracts can be converted into different fuel forms like biogas, liquid and gaseous transportation fuels as kerosene, ethanol, jet fuel, and biohydrogen through the implementation of processing technologies such as anaerobic digestion, pyrolysis, gasification, catalytic cracking, enzymatic or chemical transesterification. For biodiesel production, lipids transesterification is needed, while starch hydrolysis and fermentation is used to produce bioethanol (Demirbas and Demirbas, 2010; Singh and Olsen, 2011). However, these processes are complex, technologically challenging and economically expensive (Abanteriba et al., 2012).

Biofuels offer economic benefits, and in the right circumstances they can reduce emissions and make a small contribution to energy security (Singh and Olsen, 2011). In terms of greenhouse gases emissions, the CO_2 emitted from burning biofuel is assumed to be zero, as the carbon was taken out of the atmosphere when the algae biomass grew. Therefore, biofuels from microalgae do not add new carbon to the atmosphere (Abanteriba et al., 2012).

6.1. Biodiesel

Biodiesel is a biofuel that can directly replace petroleum-derived diesel without engine modifications, gaining a lot of attention due to its environmental and technological advantages. Table 4 lists some world companies that are using CO_2 capture technologies for biodiesel or co-products from algae cultures. In addition, other companies and research centers are working on microalgae culture and/or downstream process. These institutions are found in different countries including Spain, Israel, New Zealand, The Netherlands, Chile, Mexico, United Kingdom, Philippines, Switzerland, Japan, Spain, France, Finland, Thailand, India, Germany and Australia (Bart et al., 2010).

Lipids can be defined as any biological molecule which is soluble in an organic solvent. Membrane lipids 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 they expose their hydrophilic ends to the aqueous environment. Such molecules, in which one end (head) interacts with water and the other end (the tail) avoids it, are called amphipathic (Darnell 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). Acylglycerols consists of fatty acids ester-bonded to a glycerol backbone and are categorized according to its number of fatty acids as triacylglycerols (TAG), diacylglycerolds (DG), monoacylglycerols (MG). In contrast, FFAs are fatty acids bonded just to a hydrogen atom. Also, 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 as carotenes and chlorophylls (Halim et al., 2011).

Lipid production in microalgae mainly depends on the algae species, and it is affected by culture growth conditions, such as nutrients, salinity, light intensity, temperature, pH, and even, the association with other microorganisms. Nitrogen limitation is considered the most efficient strategy to increase the content of neutral lipids in algae, in particular formed by the triglyceride fatty acids with a high degree of saturation. However, this method produces a decrease in biomass productivity. In contrast, high light intensity and therefore high temperature, favor the accumulation of triglycerides substantially with high saturation profile. Meanwhile, low light intensities and temperature promote the synthesis of polyunsaturated fatty acids (PUFA) (Garibay-Hernández, 2009; Guschina and Harwood, 2006).

Various methods for lipid extraction from microalgae have been reported in literature, but the most common methods are mechanical extraction and liquid–liquid solvent extraction. Oil presses or expeller are common mechanic methods for extraction of oil from nuts and seeds. Therefore, same equipment and process would be appropriate for extraction of microalgae oil (Singh and Gu, 2010). Microalgae lipids have also been extracted with organic solvents. These include hexane, chloroform–methanol, ethanol, hexane–isopropanol or other polar/non polar solvent mixtures. During lipid extraction, the microalgal biomass is exposed to an eluting extraction solvent which extracts the lipids out of the cellular matrices (Halim et al., 2012).

Ryckebosch et al. (2011) described an optimized analytical procedure for lipid extraction from microalgae, in which chloroform–methanol 1:1 (%v/v) extract the highest lipid content and is thus the preferred solvent mixture for determination of total lipids. Once the cell debris is removed, more chloroform and water are added to induce biphasic partitioning. The lower organic phase (chloroform with some methanol) contains most of the lipids (both neutral and polar) while the upper aqueous phase (water with some methanol) constitutes most of the non-lipids (proteins and carbohydrates). In addition, it is noted that this method does not require the complete drying of microalgal biomass. This method was originally developed by Folch et al. (1951) for the isolation of total lipids from brain tissues. Chloroform, however, is highly toxic and its usage is undesirable. In comparison, hexane, a non-polar solvent commonly used in the comestible oil extraction process, is less toxic but with lower yield recoveries. Therefore the extraction process may be enhanced with a mixture of polar solvent, such as isopropanol (Halim et al., 2012).

Table 4
Global companies with CO_2 capture technology for algae culture.

Company	Region	Description
Seambiotic, Ashkelon, Israel.	Mediterranean	Produces algae for a variety of applications including health foods, fine chemicals and biofuels. Uses flue exit gases from the Israel Electric Company as source of CO_2.
A_2BE Carbon Capture, Boulder, Colorado.	USA	The companies develop carbon capture and recycle systems to use industrial CO_2 for algae culture follow by biomass gasification creating an integrated renewable fuel production system.
Algeneol Biofuels, Fort Meyers, Florida.	USA	Founded in 2006 based on algae culture 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	Founded 2006, intends to use microalgae to create a commercially viable biofuels. 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.

Currently, other technologies such as microwaves and ultrasound are coupled to solvent extraction enhancing the kinetics by the organic solvent through speedy disruption of the cellular structures. In the same way, supercritical fluid extraction (SFE) is an emerging green technology that has the potential to replace traditional organic solvent extraction. Crude lipids obtained from supercritical fluid extraction are free of extraction solvent. Therefore, no energy is needed for solvent removal. Supercritical carbon dioxide ($SCCO_2$) is the primary solvent used in the majority of supercritical fluid extractions. Its moderate critical pressure (72.9 atm) allows a reserved compression cost, while its low critical temperature (31.1 °C) enables successful extraction of thermally sensitive lipid fractions without degradation. Also, $SCCO_2$ facilitates a safe extraction due to its low toxicity, low flammability, and lack of reactivity. Furthermore, if the microalgal cells need to be cultivated at a coal-fired power station, the CO_2 required for supercritical conversion can be conveniently obtained from the scrubbed flue gas of the station (Halim et al., 2012).

For biodiesel production the relevant lipids from microalgae oil are the non-polar lipids TAG and FFA while acid, alkali or enzymatic catalysis (Fig. 1) can be used for the transesterification reaction of lipids with an alcohol (methanol, ethanol) to form Fatty Acid (M) Ethyl Esters (Chisti, 2007). The dosage of the methanol and the catalyst are controlled to avoid excess amounts of reagents, which reduce the quality of main product and increases the energy required to remove the excess of alcohol (Suali and Sarbatly, 2012). In case of an enzymatic catalysis, the excess of alcohol would be a large problem because inhibits the enzyme activity and thus decreases the catalytic activity (Maceiras et al., 2011). Lipid content and profile on microalgae depends mainly on culture conditions. However, total lipids in microalgae are usually from 20 to 50% of their dry weight. In addition, values in a range from 1 to 80% have also been reported (Brennan and Owende, 2010; Chisti, 2007; Demirbas, 2011; Ho et al., 2011; Mata et al., 2010). Finally, algae biodiesel contains no sulfur and performs as well as petroleum diesel, while reduces emissions of particulate matter, CO, hydrocarbons, and SO_x. However emissions of NO_x may be higher in some engine types (Mark Delucchi, 2003).

Lipids quantity and composition are key properties that determine biodiesel oxidative stability and performance properties. In order to produce a biodiesel with optimized properties, the following fatty acid profiles are desirable (Bart et al., 2010): (1) the lowest possible levels of saturated fatty acids (such as C16:0 and C18:0) to improve winter operability; (2) the highest possible levels of monounsaturated fatty acids (such as C18:1) for good stability and winter operability; and (3) the lowest possible levels of polyunsaturated fatty acids (such as C16:2 or C18:3) to increase oxidation stability. Since polyunsaturated fatty acids (PUFA) are susceptible to oxidation and saturated lipids increase cloud point and viscosity (Knothe, 2012), lipids with high amount of monounsaturated fatty acids (MUFAs) are preferable for biodiesel production (James et al., 2013). Nevertheless, environmental growth conditions determine the lipid quantity and composition (fatty acid profile) in the microorganism. Therefore, numerous studies based on the effect of culture conditions have been done in microalgae (Guschina and Harwood, 2006; James et al., 2013; Richmond, 2004; Van Wagenen et al., 2012; Yeesang and Cheirsilp, 2011).

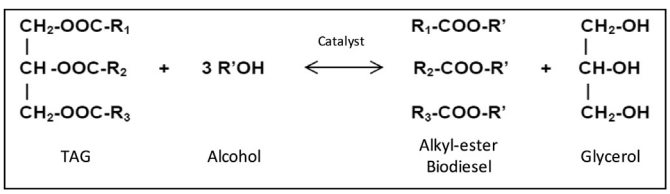

Fig. 1. Transesterification reaction for biodiesel production.

Richmond (2004) and Guschina and Harwood (2006), summarized the effect of culture growth conditions in some algae species. Nitrogen starvation increased total lipid content in *Ulva pertusa* (Floreto et al., 1993), *E. gracilis* (Regnault et al., 1995) and *Botryococcus* species (Yeesang and Cheirsilp, 2011). Moreover in contrast to the polar lipids of nitrogen-sufficient cells, neutral lipids in the form of triacylglycerols become the predominant components of lipids from nitrogen-depleted cells (Richmond, 2004). Phosphorous limitation usually causes the replacement of membrane phospholipids by non-phosphorus glycolipids representing and effective phosphate-conserving mechanism. However, Guschina et al., (2003) after algae growth with phosphorous limitation, concluded that the algae maintained their phosphoglyceride synthesis since there were significant endogenous phosphorus stores in the algae as revealed the X-ray electron microscopy probe. Light intensity in numerous studies with microalgae suggests that the cellular content of lipids and total polyunsaturated fatty acids (PUFA) are inversely related to light intensity. In addition, a decrease in growth temperature generally increases the degree of unsaturation of lipids in membrane systems. It seems that temperature, in a physiologically tolerant temperature range, may exert more significant effect on the relative cellular content of lipid classes rather than on total lipid content in the cells. The effect of carbon dioxide (CO_2) concentration has been studied in *Chlorella kessleri,* low-CO_2 cultures showed high contents of α-linolenate (Sato et al., 2003). In contrast, in *Chlamydomonas reinhardtii* mutant cia-3, a high content of PUFA was found in cultures with high CO_2 concentration. Finally, pH can also affect the lipid metabolism. Low pH stress in *Chlamydomonas* sp. increased the total lipid content compared with higher pH values (Tatsuzawa et al., 1996). However in *Chlorella* spp. alkaline pH resulted in triacylglycerides accumulation (Guckert and Cooksey, 1990).

6.2. Bioethanol

Fermentation is used commercially on a large scale in various countries to produce ethanol from sugar crops and starch crops (Demirbas, 2011). Bioethanol can be produced from several different lignocellulosic biomass feedstocks by hydrolysis process.

In this regard, algal biomass is gaining wide attention as an alternative renewable feedstock for the production of bioethanol (Singh and Olsen, 2011). Some microalgae are known to contain a large amount (>50% of the dry weight) of starch, cellulose and glycogen, which are raw materials for ethanol production. Also, the absolute or near absence of lignin makes the enzymatic hydrolysis of algal cellulose very simple. Furthermore, microalgae biomass waste with high starch/cellulose content after oil extraction can be hydrolyzed to produce sugary syrup for ethanol production (Fig. 2) and finally, algae can be harnessed as renewable source of biomass for ethanol production (Singh and Olsen, 2011).

According to Demirbas (2011) and Suali and Sarbatly (2012), the ethanol production by biomass fermentation includes: (a) *Pretreatment to release carbohydrates*, in which the starch can be extracted from the cells with mechanical tools (e.g., ultrasonic, explosive disintegration, mechanical shear, etc.) or by dissolution of cell walls using enzymes (Pandey et al., 2011). However, while the pretreatment improves the ethanol yield more than 33%, an increment of 30% energy requirement occurs. (b) *Fermentation of carbohydrates for ethanol production*. Although differences in carbohydrates composition of algae strains results in the utilization of many non-standard organisms for ethanol production, the most common organisms for bioethanol production are yeast as

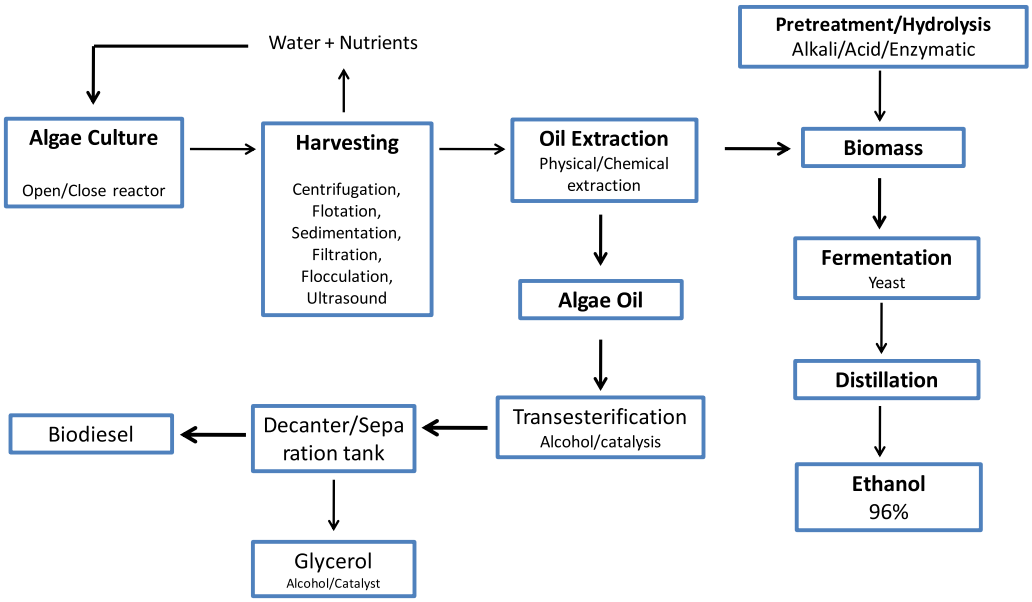

Fig. 2. Algae biofuels production approach. Biodiesel and bioethanol can be produced from microalgal biomass.

Saccharomyces cerevisiae (Yan et al., 2013). During ethanol production, four main reactions are involved. The first reaction is a glycolysis process, where one molecule of sugar, specifically glucose ($C_6H_{12}O_6$), is broken down into two pyruvate molecules ($CHCOCOO^-$). Then, glycolysis causes that two molecules of adenosine diphosphate (ADP) are reduced to two molecules of ATP and that two molecules of nicotinamide adenine dinucleotide (NAD^+) are reduced to two molecules of NADH. As well, this process produces water and hydrogen ions (H^+). The second step is the conversion of $CHCOCOO^-$ into acetaldehyde (CH_3CHO), catalyzed by pyruvate decarboxylase, which produces CO_2 and H^+. The third step is the conversion of the CH_3CHO produced in second step into ethanol ion ($C_2H_5O^-$) with the aid of the coenzyme NADH that was produced during the glycolysis process. Finally, the ethanol anion, which has similar properties to conventional ethanol, is protonated by hydrogen to produce ethanol (C_2H_5OH). In addition, during the fermentation process, CO_2 is produced as a side product. (c) *Separation and purification of ethanol*, in which the ethanol is drained from the tank and pumped to a holding tank to be fed to a distillation unit.

7. Economics and life cycle assessment for algal biofuels

Life Cycle Assessment (LCA) is a compilation and evaluation of the inputs, outputs and the potential environmental impacts of a product system throughout its life cycle (Pfromm et al., 2011). LCA based on biofuels has been done with no profitable results due to the economic and environmental impact. Particularly in microalgae biofuels, LCA debate focusses on life-cycle impacts of large-scale production, especially the impact on water usage, energy inputs, inorganic salts, phosphorous and nitrogen fertilizers (mainly produced from natural gas), methanol utilization for transesterification and glycerol production as co-product.

In Sander and Murthy (2010) work, centrifugation and press filtration for harvesting and solar and natural gas drying for dewatering were evaluated for energy consumption. The results showed that centrifuge utilization requires mayor energy and that natural gas drying of algae biomass comprises 69% of the entire energy input into the process. Quinn et al. (2013) work focused on three of the main process steps to produce biofuel from microalgae: microalgae biomass production, lipid extraction and the end-use of lipid extracted algae in four LCA scenarios. It was concluded that higher lipid content is desirable as it reduces equipment cost and footprint proportionately. In addition, the integration of an anaerobic digester positively impacts the net energy ratio of the microalgae-to-biofuel system. Finally, wet extraction process and recycle of lipid extracted algae should be practiced to reduce energy use.

In order to contribute to the reduction of energy consumption of algae biofuel process, different practices have been proposed. When microalgae are grown in seawater or wastewater, this biodiesel production may consume much less potable water than conventional feedstock-based biodiesel production. In addition, other alternatives are (1) production of ethanol from algae starch after oil extraction, (2) usage of glycerol and residual biomass for energy conversion, (3) water recycling once biomass was harvested, (4) cell wall disruption pretreatment by enzymatic lysis to enhance oil extraction, (5) pH adjustment with biological flocculants to aid harvesting and (6) use of solar heat for drying (Lardon et al., 2009; Pfromm et al., 2011; Yang et al., 2011).

Acién et al. (2012) developed an economic analysis for microalgae production and CO_2 fixation costs. The analysis considered a raceway pond with a volume/surface ratio depth of 0.2 m^3/m^2 and continuous operation with power consumption for mixing of 2 W/m^3. Also, an energy consumption of 0.1 kW/m^3 was assumed for the harvesting. The analysis considered six scenarios from pessimistic to optimistic. The pessimistic included costs of raw materials (CO_2, water and fertilizers) and a non-optimized process that requires 4 kg CO_2/kg biomass with a yield of 20 g/m^2-day; the optimistic excluded raw material costs due to the utilization of flue gases and wastewater, while consumes 2 kg CO_2/kg biomass and has a maximal theoretical yield of 60 g/m^2-day. The resulting production costs were 0.86 eur/kg for the pessimistic scenario and 0.14 eur/kg in the optimistic one. Finally, the cost of CO_2 fixation in the last scenario resulted in half of the total cost (0.07 eur/kg). However, CO_2 fixation is not the most expensive process in algae cultures.

Producing algae biodiesel requires large-scale cultivation and harvesting system with the challenging of reducing the cost per unit area (Mata et al., 2010). Specifically, harvesting contributes to 20–30% of total biomass producing cost due to the energy

consumption for dewatering. Therefore, research and improvements in this stage are necessary. Zeng et al. (2011) described an assessment of energy generation and CO_2 fixation ability of microalgae biodiesel production system. A 1000 m^2 microalgae cultivating area (0.5 m depth) with growth rate 30 g/m^2day, 30% microalgae lipid content, and harvesting, extraction and transesterification efficiencies of 90%, will generate 11,000 kg biomass, 3300 kg biodiesel per year and a net CO_2 fixation of 7000 kg. Therefore 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. Based on this results, biofuels from microalgae are more profitable than biofuels from cellulosic biomass because of the energy generation, CO_2 fixation capacity and higher growth rates (Mani and Sokhansanj, 2006; Shinners et al., 2007). However, due to the dilute nature of harvested microalgae culture, much more research work should be focus to enhance cultivation, energy-efficient dewatering and lipid extraction techniques (Zeng et al., 2011). As it was mentioned, an interesting approach for microalgae bulk harvesting is the high pH induced flocculation, a non-expensive and non-toxic separation method (Vandamme et al., 2012).

Pate et al. (2011) analyzed CO_2, water, sunlight, nutrients and land use, to estimate the optimal land area in the USA for algae autotrophic culture. The results showed that 10 billion gallons of biodiesel per year (15% of total US diesel fuel demand) can be successfully commercialized with dominant productivity in 19 states, making a significant contribution to US energy demand. In addition, it is known that 1.6–2 g of CO_2 would produce 1 g of algae biomass (Scotia Capital Inc, 2010). Moreover, the CO_2 delivered by cement companies is around 25.4 million metric ton per year. Therefore, coupling 70% of this effluent (17.8 million metric ton) to an algae culture, could produce around 8.89 million metric ton of algae biomass. Moreover, if algae biomass contains 20% of lipids, and reaction efficiencies of 90% are achieved during the transesterification reaction, 1.6 million metric ton of biodiesel would be produced.

8. Other applications and products from microalgae

Microalgae can also serve for other purposes besides biofuels production. Some possibilities are currently being considered (Mata et al., 2010). These include the wastewater treatment by removal of ammonia, nitrate and phosphate by utilization of these water contaminants as nutrients (Wang et al., 2008) and the utilization of algae biomass after oil extraction to be processed into ethanol, methane, livestock feed or used as organic fertilizer due to its high N:P ratio, or simply burned for energy cogeneration as electricity and heat (Wang et al., 2008). In addition, combined with their ability to grow under harsh conditions, and their reduced requirements for nutrients, they can be grown in areas unsuitable for agricultural purposes independently of the seasonal weather changes, thus there is not competing for arable land use, and wastewaters as the culture medium can be used, not requiring the use of freshwater (Mata et al., 2010). Finally, 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 lipids, polyunsaturated fatty acids, oils, sugars, pigments, antioxidants, high-value bioactive compounds, and other fine chemicals and biomass (Li et al., 2008a,b; Raja et al., 2008).

8.1. Biorefinery concept

Demirbas and Demirbas (2010) described biorefinery as a facility that integrates biomass conversion process and equipment to produce fuels, power, and value-added chemicals from biomass. The biorefinery concept (Fig. 3) is analogous to today's crude oil refinery, which produces multiple fuels and products from petroleum. 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 convert all kinds of biomass (all organic residues, energy crops, and aquatic biomass) into numerous products (fuels, chemicals, power and heat, materials, and food). Algae can easily be part of this concept because each strain produces certain amount of lipids, carbohydrates or proteins which biomass can be used in different process.

Microalgae currently produced are mainly used for human or animal consumption. In consequence, the price is high (10–300 eur/kg, with 250 eur/kg for aquaculture and human consumption) and the market's small (10–50 kt/year). If a significant contribution to CO_2 reduction is intended, the microalgae market must be enlarged. Reliable markets are the energy or commodity sectors, where the biomass price is much lower (0.01–0.5 eur/kg), however the entry of microalgae to this sector can only be possible if the production costs are lowered (Acién Fernández et al., 2012).

8.2. Wastewater treatment

A new potential of algae is now studied for wastewater treatment, since they provide a pathway for the removal of chemical and organic contaminants, heavy metals and pathogens from wastewater, while the algae biomass produced can be consequently used for biofuels production (Brennan and Owende, 2010). Hazardous or toxic compounds processing is also possible by microalgae, since they produce the oxygen required by bacteria to biodegrade pollutants such as polycyclic aromatic hydrocarbons (PAHs), phenolics and organic solvents (Brennan and Owende, 2010; Muñoz and Guieysse, 2006). Therefore, photosynthetic oxygen from microalgae production reduces the need for external mechanical aeration. Different studies have tested microalgae strains with diverse wastewater effluents. 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+}) in the wastewater. However, biosorption properties of microalgae depended strongly on cultivation conditions. Mainly photoautrophic species show greater biosorption characteristics (Brennan and Owende, 2010).

According to the wastewater characteristics (suspended solids, pH, biodegradability), different algae strains should be chosen. As example Chen et al. (2012) treated animal wastewater for nutrient removal with *Chlorella* sp., Lim et al. (2010) used *C. vulgaris* for bioremediation of textile wastewater, Mezzomo et al. (2010) cultivate *S. platensis* for biological treatment of swine wastewater and Mata et al. (2012) treated brewery effluent by *Scenedesmus obliquus*. All results showed that good removal efficiencies (60–80%) are achieved.

8.3. Pigments, lipids and others compounds

The marked trend and growing interest of consumers in new natural and healthy products instead of synthetic forms has forced food industry to develop novel products with functional ingredients. Currently, the importance of marine algae as a source of these functional ingredients has been well recognized due to their valuable healthy and positive effects since algae are 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 strain, various high-value chemical compounds may be extracted such as pigments, antioxidants, β-carotenes, polysaccharides, triglycerides, fatty acids, and vitamins (Table 5), which are largely used as bulk commodities in

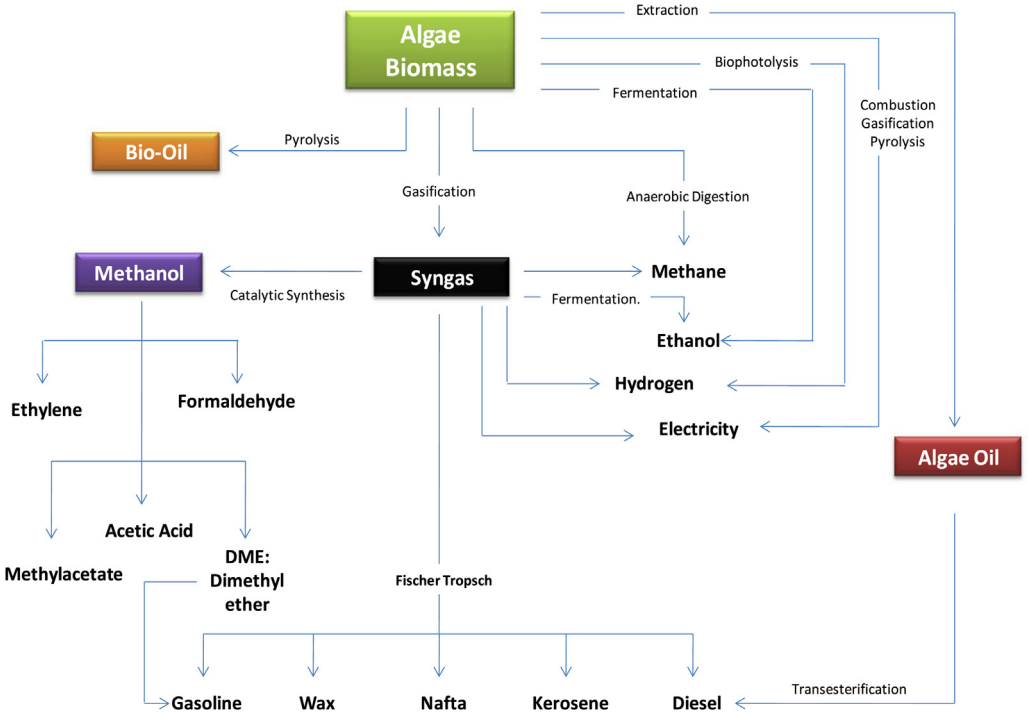

Fig. 3. Algae biorefinery concept.
(Adapted from Oilgae (2010)).

different industrial sectors (pharmaceuticals, cosmetics, nutraceuticals). Also, algal hydrocolloids, alginate, agar, and carrageenans produced from seaweeds (especially macroalgae) are largely used as viscosity modifying agents in foods and pharmaceuticals (Barrow and Shahidi, 2007).

In terms of protein, *Spirulina* and *Chlorella* are the most popular for human consumption. Specifically, *S. platensis* has been used as food source since the ancient civilizations in Asia and Mexico (Lago Texcoco during the Aztec civilization). In addition, currently is highly consumed as a vegetarian protein source.

In terms of fatty acids, currently the production of PUFA by marine and freshwater microalgae is subject of intensive research and commercial attention (Sijtsma and de Swaaf, 2004; Wen and Chen, 2003). Fish oil is the major source for the commercial production of these fatty acids but, since there is an increasing demand of 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 food quality consumed. However, some species of freshwater and marine algae contain large amounts of PUFAs and are widely used for aquaculture operations. The recent use of microalgae for eicosapentaenoic acid (EPA) production has gained attention on algae biotechnology research (Chen et al., 2007). Different studies have shown that 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, antiangiogenic, and neuroprotective activities (Guedes et al., 2011; Pangestuti and Kim, 2011). The three basic classes of NPs found in marine algae are chlorophylls, carotenoids, and phycobiliproteins. Chlorophylls are greenish lipid-soluble NPs which contain a porphyrin ring and are found in all algae, higher plants and cyanobacteria. Carotenoids are linear polyenes that function as

Table 5
Microalgae species of high value compounds extraction and applications.

Species	Product	Application areas
Spirulina platensis	Phycocyanin, γ-Linolenic acid, biomass protein	Health food, cosmetics
Chlorella vulgaris	Biomass, Pigments	Health food, food supplement
Dunaliella salina	Carotenoids, β-carotene	Health food, food supplement, feed
Haematococcus pluvialis	Carotenoids, astaxanthin, canthaxanthin, lutein	Health food, pharmaceuticals, feed additives
Porphyridium cruentum	Arachidonic acid, polysaccharides	Pharmaceuticals, cosmetics, nutrition
Isochrysis galbana	Fatty acids	Animal nutrition
Phaeodactylum tricornutum	Lipids, Eicosapentaenoic acid, fatty acids	Nutrition, fuel production
Lyngbya majuscula	Immune modulators	Pharmaceuticals, nutrition
Cryptecodinium cohnii	Docosahexaenoic acid	Pharmaceuticals, nutrition
Nannochloropsis gaditana, *Nannochloropsis* sp.	Eicosapentaenoic acid	Pharmaceuticals, nutrition
Schizochytrium sp.	Docosahexaenoic acid	Pharmaceuticals, nutrition
Scenedesmus almeriensis	Lutein, β-Carotene	Pharmaceuticals, nutrition, cosmetics
Chlorococcum sp.	Carotenoids, Astaxanthin	Pharmaceuticals, nutrition, cosmetics

(Sources: Guedes et al. (2011), Pulz and Gross (2004), Spolaore et al. (2006)).

light energy harvesters and antioxidants that inactivate reactive oxygen species (ROS) formed by exposure to light and air (Ioannou and Roussis, 2009). Also, carotenoids are considered to be accessory pigments since they increase the light-harvesting properties of algae, passing light excitation to chlorophyll production (Larkum and Kühl, 2005). Carotenoids can also be classified into two types, carotenes, which are unsaturated hydrocarbons, and xanthophylls, which present one or more functional groups containing oxygen. Finally, phycobiliproteins are water soluble fluorescent proteins used as accessory or antenna pigments for photosynthetic light collection absorbing energy in portions of the visible spectrum at 450–650 nm (Batista et al., 2006). Moreover, the three major categories of phycobiliproteins are phycocyanins, allophycocyanins and phycoerythrins. Phycoerythrins are the most abundant phycobiliproteins found in many red algae species. However, phycobiliproteins are the principal photoreceptor for photosynthesis in cyanobacteria, red algae, and cryptomonads. In many algae, phycobiliproteins are arranged in subcellular structures called phycobilisomes, which allow the pigments to be arranged geometrically in a manner which helps to optimize the capture of light and transfer of energy. Additionally, the colors of the phycobiliproteins arise from the presence of covalently attached prosthetic groups named bilins (Glazer, 1994).

It is important to notice that singular pigments are found in different algae strains and that environmental culture conditions will determine this pigments differentiation. For example pigment extractions of *Nannochloropsis gaditana* have shown *Chlorophyll a* and carotenoids (β-Carotene, Zeaxanthin and Violaxanthin) as present components in this microalgae (Ryckebosch et al., 2013), while other *Spirulina* and *Porphyridium* may contain phycocyanin and phycoerythrin respectively (Forján Lozano et al., 2007; Guedes et al., 2011).

9. Conclusions and future perspectives

This review describes the undeniable potential application of microalgae as an emerging technology to contribute significantly in the reduction of the GHG emitted to the atmosphere by the cement industry. In addition, microalgae lipids can be transformed into biodiesel to be used in the transport sector. However, design concepts, flue gas composition, temperature, microalgae culture and species must be evaluated for this application. Another approach includes a concept where microalgae can also be used for wastewater treatment and chemistry applications, complementing a biorefinery plant. However, since some studies have shown that microalgae cultured using flue gas from cement industry can accumulate heavy metals, final composition must be evaluated before considering commercial application of the produced biomass. Finally, it is expected that this review and perspective contributions have shown the starting point for research focused on integral management that can render cement industry to an environmental compatibility with energy production to achieve local and global sustainable goals.

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