Chapter 13
Biofuels from Microalgae: Photobioreactor Exhaust Gases in Oxycombustion Systems

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Abstract The aim of this chapter is to present a comprehensive overview of integrated bio-oxycombustion systems with photobioreactors. Divided into seven distinct topics, the chapter discusses issues related to fundamentals of oxycombustion, the operational implications for oxycombustion-enhanced performance, oxygen produced by photosynthesis, volatile organic compounds as energy source, photobioreactors design, the process integration in bio-oxycombustion systems, and the hurdles of bio-oxycombustion technology, summarizing a range of useful strategies directed to the sustainable development of industrial combustion systems.

Keywords Biological carbon capture and utilization · Microalgae Oxyfuel · Volatile organic compounds · Gaseous fuels · Process integration

1 Introduction

Carbon capture and storage or use (CCS/CCU) is recognized as one of the options to mitigate the increase of atmospheric carbon dioxide (CO_2) concentration (Koytsoumpa et al. 2017). However, through biological carbon capture and utilization (BCCU) as a concept of bioconversion of greenhouse gases (GHG) into value-added metabolic products, oxycombustion has gained considerable attention in recent years (Jajesniak et al. 2014).

Oxycombustion is a promising carbon capture technology due to its ability to reduce emissions by up to 90%, improving the energy efficiency of industrial combustion systems. However, the main barrier to be overcome from

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oxycombustion is the obtaining of a high-purity, low-cost oxygen supply, in order to save fuel and energy (Chen et al. 2012b).

In this context, photobioreactors could be the key to getting around this problem. This equipment can provide substantial oxygen (O_2) concentrations through water photolysis reactions during microalgae cultivation. In theory, it is possible to generate on average 0.73 kg of O_2 for every 1 kg of CO_2 bioconverted, demonstrating the production potential of this substance in photobioreactors (Jacob-Lopes et al. 2010, 2017).

In addition, these bioprocesses produce several volatile organic compounds (VOCs), which have considerable energy value, besides releasing, in the photobioreactor exhaust gases, substantial concentrations of unconverted CO_2, which could improve the thermal performance of combustion systems (Jacob-Lopes and Franco 2013).

Therefore, in order to satisfy the oxygen supply required in oxycombustion systems, a promising technological route has been developed through the integrated bio-oxycombustion process. This bioprocess refers to the simultaneous production of two metabolic bioproducts: O_2 and VOCs from the direct conversion of GHG. These compounds are released with photobioreactor exhaust gases, which can be subsequently integrated as oxidizers and gaseous fuels, respectively, in industrial combustion processes. Furthermore, the unconverted CO_2 can be potentially used as nitrogen diluent. With this in mind, the aim of this chapter is to present a comprehensive overview of integrated bio-oxycombustion systems with photobioreactors.

2   Fundamentals of the Oxycombustion

Carbon capture from large point source emitters is a fast-developing technology that can mitigate the impact of anthropogenic CO_2 production. Oxycombustion has proven to be a potential capture technology mainly due to its perceived superiority in relation to efficiency and simplicity (Olajire 2010). Several authors have provided comprehensive information about the different aspects of oxycombustion technology (Buhre et al. 2005; Wall et al. 2009; Toftegaard et al. 2010; Scheffknecht et al. 2011; Chen et al. 2012a, b; Yin and Yan 2016; Khalil et al. 2017; Gładysz et al. 2017).

In a conventional combustion system, air is used as the oxidizer, and the coming CO_2 from the flue gas is diluted by N_2 of air, resulting in a reduced CO_2 concentration per capture (about 15% v/v). In oxycombustion, a combination of practically pure oxygen (usually 95% v/v) and recycled flue gas is used as the oxidizer for burning the fuel. Such flue gas is composed mainly of CO_2 and H_2O, which is used to control the flame temperature in the burner and fill the volume removed N_2, ensuring that there is enough gas to carry heat through the system (Stanger et al. 2015). Carbon dioxide concentration in the flue gases increases by

approximately 17–70%, depending on the fuel used, and can then be captured, stored, or used (Buhre et al. 2005).

By determining the physical and chemical processes that the fuel experiences during oxycombustion, characteristics such as heat and mass transfer, temperature, stability and flame velocity, ignition, and pollutant formation are affected globally (Chen et al. 2012a, b). The main impacts are related to the differences in properties of CO_2, the diluent gas in oxycombustion, and N_2, the diluent in the combustion with air (Yin and Yan 2016). Table 1 shows the different physical properties and chemical effects of main gases resulting from oxycombustion (CO_2 and H_2O) and conventional combustion with air (N_2 and O_2), which induces substantial changes in combustion processes.

The total heat and mass transfer in a furnace include radiative and convective heat transfer and depend especially on the flame temperature and gas properties. Radiation is the principal mode of heat transfer in combustion processes, playing a dominant role in the furnace. The entire flame is considered to be a constant source of radiation, and its radiative energy release rate is improved when the emissivity (ε) is higher, that is, when the capacity of a substance to emit heat is greater. Thus, unlike diatomic molecules, such as N_2, triatomic molecules such as CO_2 and H_2O are radiating species and have higher partial pressures, and consequently, the absorptivity and emissivity of the flue gas substantially increase (Chen et al. 2012b).

As for convection, there is a greater contribution to heat exchange, which is influenced by flow velocity of gases, density, viscosity, thermal conductivity, and specific heat capacity, which are also functions of flame temperature. The rate of convective heat transfer coefficient in both oxycombustion and combustion with air can be expressed in terms of dimensionless numbers, such as the Reynolds and the Prandtl numbers, and by fluid thermal conductivity. Thus, the thermal conductivity of CO_2 is slightly higher than that of N_2, not significantly altering the heat transfer. However, the lower kinematic viscosity of CO_2 and its higher density, due to the higher molecular weight (44.09) when compared to N_2 (28.01), results in a larger Reynolds number and, therefore, a higher convective heat transfer coefficient (Yin and Yan 2016). In terms of specific heat capacity, it is observed that at 1000 °C, the N_2 presents a $C\rho$ of 34.18 kJ/k mol, whereas CO_2 has $C\rho$ 57.83 kJ/k mol, further highlighting the high heat transfer of these gases in oxycombustion conditions (Cengel 2003).

In relation to flame temperature, it is necessary to recirculate between 60 and 80% of the oxycombustion of gases into the furnace, aiming to moderate excess temperature due to the increase of oxygen concentration injected, and also to achieve a similar profile of heat transfer in relation to combustion with air. High O_2 concentrations increase the adiabatic flame temperature, which is the largest attained temperature in the combustion products without heat exchanging inside or outside the system, and this occurs due to lack of N_2 dilution. In this case, to moderate excess temperature, the proportion of recycled flue gas and the O_2 concentration to be injected must be adjusted in order to achieve the same flame temperature as in the combustion with air. On the other hand, if the recycled flue gas amount is higher, it will result in a lower average O_2 concentration for furnace

Table 1 Physical properties of the main gases diluents in oxycombustion and conventional combustion with air at 1 atm pressure and at 1000 °C (Griffiths and Barnard 1995; Cengel 2003)

Chemical compound	Chemical formula	Molecular weight [g/mol]	Density (ρ) [kg/m^3]	Specific heat capacity ($c\rho$) [kJ/mol K]	Thermal conductivity (k) [W/m K]	Thermal diffusivity (α) [m^2/s]	Emissivity and absorptivity	Kinematic viscosity (ν) [m^2/s]	Mass diffusivity[a] (m^2/s)	Prandtl number
Nitrogen	N≡N	28.01	0.24	34.18	0.082	9.83×10^{-3}	~0	2.00×10^{-4}	1.70×10^{-4}	0.70
Carbon dioxide	O=C=O	44.09	0.38	57.83	0.097	4.37×10^{-3}	>0	1.31×10^{-4}	1.30×10^{-4}	0.75
Water	H—O—H	18.01	0.16	45.67	0.136	1.89×10^{-3}	>0	3.2×10^{-4}	–	4.60
Oxygen	O=O	31.99	0.27	36.08	0.087	8.67×10^{-3}	~0	2.09×10^{-4}	–	0.63

[a]Mass diffusivity refers to the binary diffusion of O_2 in CO_2 and N_2

entry. In this case, flame temperature and gas temperature are lower. This way, low O_2 concentrations may result in lower stability and flame propagation velocity and, consequently, fuel may not burn completely. In parallel, there is a delay in the flame ignition in oxycombustion and this may vary according to the particle size of fuel and its properties, temperature, gas properties, heating rate, and aerodynamic impacts (Wall et al. 2009; Toftegaard et al. 2010).

Finally, the formation and emission of pollutants in oxycombustion should be considered. Due to the atmosphere rich in CO_2 and H_2O, extremely acidic gases such as SO_x and NO_x are formed, causing fouling and corrosion in the exhaust gas output device, which may affect combustion efficiency and damage the equipment. However, the emission is less intense due to pollutant reduction during flue gas recycling, lower formation of thermal NO by N_2 removal, and higher CO concentrations (Stanger and Wall 2011; Normann et al. 2009).

3   Operational Implications for Oxycombustion-Enhanced Performance

3.1   Oxygen Supply

Oxycombustion technology requires highly pure oxygen to function effectively. For this purpose, there are some technologies that separate oxygen from air, such as cryogenic air distillation, adsorption, absorption, and polymeric membranes. However, only the first option, which requires an air separation unit (ASU), presents maturity for large-scale application. The other options are in the early stages of research and development (R&D) and cannot be applied to the full-scale operations (Olajire 2010; Leung et al. 2014).

Conventionally, an ASU for oxycombustion should produce an oxygen stream with purity ranging from 95 to 99%. Energy consumption of separation increases as a function of oxygen purity. The purer the oxygen, the greater the amount of energy consumption involved in the separation process, directly influencing the composition of the gases formed, oxycombustion performance, as well as overall cost of the plant (Banaszkiewicz et al. 2014).

In terms of capacity, ASUs have been designed with design features to meet total oxygen production from 1000 tons (30,000 Nm^3/h) to 5500 tons (165,000 Nm^3/h). Today, the world's largest plant with an ASU for oxygen supply operates at a capacity of 4000 ton/d O_2 (Linde Group 2017). Therefore, assuming that, on a 500 MW oxycombustion power plant operating on an industrial scale, the oxygen supply should be around 10,000 ton/d (Higginbotham et al. 2011), 3 more ASU plants would necessarily have to operate simultaneously, or an ASU with greater capacity than the existing ones should be developed. At the same time, the expected energy consumption to separate 1 ton of oxygen from the air would be 150–200 kWh/t O_2 produced (540 kJ/kg), and the electrical energy necessary for

this process would be approximately 80 MW, causing a significant reduction of about 7–11% in the efficiency of net electricity generation (Chorowski and Gizicki 2015).

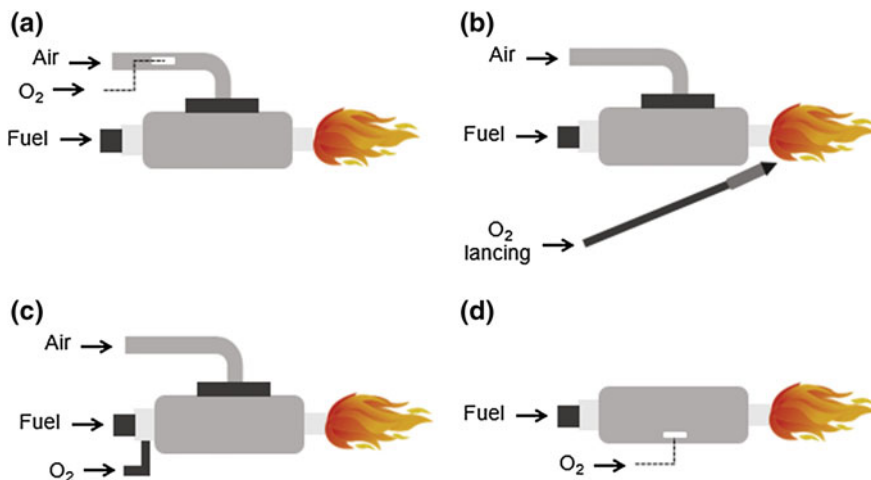## 3.2 Oxygen-Enrichment Methods in Combustion Systems

In addition to purity issues, another important point is the site for oxygen injection production. Oxygen enrichment in combustion processes provides many benefits as mentioned above; however, if the feeding system is not properly designed, problems such as furnace wall damage, non-uniform heating, and increased pollutant emissions can be potentiated (Baukal 2013). According to Daood et al. (2012), techniques for oxygen enrichment in oxycombustion are significantly different from one another, due to the different equipment design requirements, but are similar in regard to the reduced gas flows through the burner, increased residence time in combustion zones, and improvement in fuel burnout.

Thus, there are four main oxygen-enrichment methods in oxycombustion systems, as shown in Fig. 1. One is by adding O_2 in the incoming combustion air stream, also referred to as premix enrichment. Some systems use almost 100% oxygen at the main combustion inlet. However, performance is lower due to the large difference in the oxidizer speed of pure O_2 when compared to air (IHEA 2007). According to Lacava et al. (2006), most burners show enhanced performance and boost productivity with low-level enrichment (about 26% O_2), and only some operate at higher enrichment levels (about 35% O_2). Generally, when O_2 is added to the premix, the flame intensifies, the mixture between fuel/oxidizer is adequate, and the gas stream is dried. However, there is a greater risk of burner damage and explosion, due to the higher temperature, besides higher NO_x emission (Toftegaard et al. 2010).

The second method is the strategic injection of oxygen beside, beneath, or through the air/fuel flame, also referred to as O_2 lancing. This method is generally used for low O_2 levels. Its main advantage is that the flame can be better controlled, and released heat is evenly distributed. Nevertheless, furnace design has to be reconsidered (Baukal 2013).

The third method is to separate the injection of combustion air and O_2 into the burner, referred to as air/oxygen/fuel combustion. O_2 concentration in the burner will possibly be the same, as is the case for operation with air. In addition, it has the flexibility to operate with dual fuels (liquid and gaseous) and the enrichment of higher O_2 levels; however, significant risks are associated with the injection of nearly pure oxygen into a high-temperature stream of fuel and flue gas (Baukal 2013).

The last method consists in the complete replacement of air by high-purity O_2, referred to as oxyfuel combustion, where O_2 and fuel remain, and separation and mixing only occur when they are inserted into the furnace. For safety reasons,

Fig. 1 Scheme of oxygen-enrichment methods in oxycombustion systems. **a** premix enrichment with air; **b** air/fuel flame (O_2 lancing); **c** air/oxygen/fuel combustion; and **d** oxyfuel combustion

there is no premix due to the high-level O_2 (>90%), which is extremely reactive. By this type of enrichment, an overall improvement in the combustion process is achieved, despite the higher operating costs (Baukal 2013).

3.3 Fuel Supply

Most industrial combustion processes require large amounts of energy, which is commonly generated by the burning of fossil fuels. These fuels are composed of hydrocarbons and sulfur, which readily combine with oxygen to produce a particular compound, and release a rather large amount of heat (Cengel 2003). Table 2 shows the main fuels (solids, liquids, and gaseous) with different heating value, oxygen supply, and estimated CO_2 emissions. For burning of 1 kg of natural gas, for example, one of the most commonly used gaseous fuels in combustion, it is necessary to provide about 2.11 kg of oxygen, which emits an average of 2.63 kg of CO_2 and presents potential energy of about 47 MJ/kg. The oxygen supply ranges from 2.00 to 3.73 kg; i.e., the required amount of O_2 can be almost 4 times the amount of fuel burned.

On the other hand, the use of oxygen-enrichment systems, besides improving the combustion efficiency, reduces energy loss and also increases fuel economy, depending on the exhaust gas temperature and the percentage of oxygen in the combustion air (ITP 2005). According to the US Department of Energy and the Industrial Heating Equipment Association (IHEA), the conversion to oxygen-enriched combustion is followed by an increase in furnace temperature and

Table 2 Heating value, oxygen supply, and estimated CO_2 emissions for combustion of different fuels (Griffiths and Barnard 1995; Cengel 2003)

Fuel	Heating value (MJ/kg)	O_2 supply $\left(kg_{O_2}/kg_{fuel}\right)$	CO_2 emissions $\left(kg_{fuel}/kg_{CO_2}\right)$
Methane	50.00	2.00	2.75
Ethane	47.80	3.73	1.46
Propane	46.35	3.63	1.00
Butane	45.75	3.58	0.75
Ethanol	27.70	2.08	0.95
Natural gas	47.00	2.11	2.63
Gasoline	44.40	3.50	0.38
Diesel oil	43.40	3.46	0.19
Petroleum coke	29.00	2.69	3.30
Coal	23.00	2.50	2.89

a simultaneous decrease in furnace gas flow around the product. Considering an oxycombustion furnace operating at a temperature of 1000 °C, and combustion air composed of 95% oxygen, fuel reduction is about 68%. This shows a fuel saving of approximately 35% in relation to a conventional combustion system. Additionally, the control of parameters such as air supply (fuel/air ratio), removal of combustion gases, carrier gas velocity, vapor pressure, and oxygen purity assists in fuel supply to achieve optimum energy efficiency in the furnace.

The remarkable advantages of oxycombustion show the feasibility of its implementation in power generation industries, despite their current operation only on pilot-scale. Meantime, original research and review articles have highlighted many barriers associated with the main operating parameters of the technology, which must be overcome to achieve industrial scale, as shown in Table 3.

4   Oxygen Produced by Photosynthesis

Green plants and photosynthetic microorganisms, such as cyanobacteria and microalgae, perform photosynthesis. Commonly, it is necessary mainly CO_2, which is converted into organic compounds, and light energy to carry out photosynthesis, releasing oxygen molecules and water through a sequence of different chemical reactions in distinct cellular compartments. This mechanism can be subdivided into two stages: light reactions or photochemical step, which occur only when the cells are illuminated, and dark reactions or carbon fixation step, which are not directly influenced by light, also occurring in the dark (Fay 1983).

During photosynthesis, more specifically in light reactions, there is the formation of highly energetic compounds, such as ATP (adenosine triphosphate) and NADPH

Table 3 Critical issues in oxycombustion systems

Parameter	Technical barrier
Oxygen supply	An oxycombustion plant requires large amounts of high-purity oxygen. The only option available on the market is ASU, which requires intense energy demand, operating expenses (OPEX), and capital expenditure (CAPEX)
Cost	The technology is expensive. Demand for electricity can increase plant cost by 70–80%
Scale-up	Although there is an oxygen–air separation process commercially available, it has not been deployed at the scale required for large power plants applications
Energy integration	Steam required for regeneration can only be extracted at conditions defined by the power plants steam cycle. Additionally, mitigation can result in the generation of significant quantities of waste heat. Energy integration can improve plant efficiency
Auxiliary power for CO_2 mitigation	Auxiliary power is also required to operate CO_2 mitigation technologies. This decreases the power plant's net electrical generation and significantly reduces net power plant efficiency
Mechanical integration	Any CO_2 mitigation system must fit within the boundaries of the power plant. This is a significant barrier when dealing with existing plants that have fixed layouts and limited open space
Flue gas pollutants	Constituents of the combustion exhaust gases, mainly sulfur, can damage the equipment and reduce its useful life
Water usage	A significant amount of water is used in current technologies for cooling during CO_2 compression

(nicotinamide adenine dinucleotide phosphate), essential for the assimilation of inorganic carbon and for oxygen production (Williams and Laurens 2010). This process begins in two photosystems (I and II), where pigments such as chlorophyll are responsible for absorbing mainly photons and transferring energy to an electron-accepting substance (located in the thylakoid membranes). From this stage, the excited chlorophyll recovers 6 lost electrons, where the energy is used for the water photolysis, also referred to as Hill reactions (Heldt and Piechulla 2011). By removing the light electrons, water molecules decompose into H^+ ions, releasing oxygen atoms to form the gaseous O_2 molecule, a significant product of microalgae metabolism. Figure 2 shows the schematic representation of water photolysis and oxygen generation during photosynthesis in a microalgae eukaryotic cell. This is an important aspect of photosynthesis, because all the oxygen generated in the process comes from the water photolysis (Barber 2017). The reaction can be described, in chemical terms, as follows (Eq. 1):

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \tag{1}$$
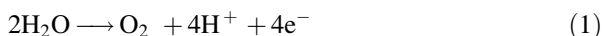
Additionally, the theoretical and realistic conversion efficiencies of water photolysis can be obtained by biological estimates, in terms of quantum efficiency, i.e., through the energy fraction of absorbed photons, or calculated from the solar
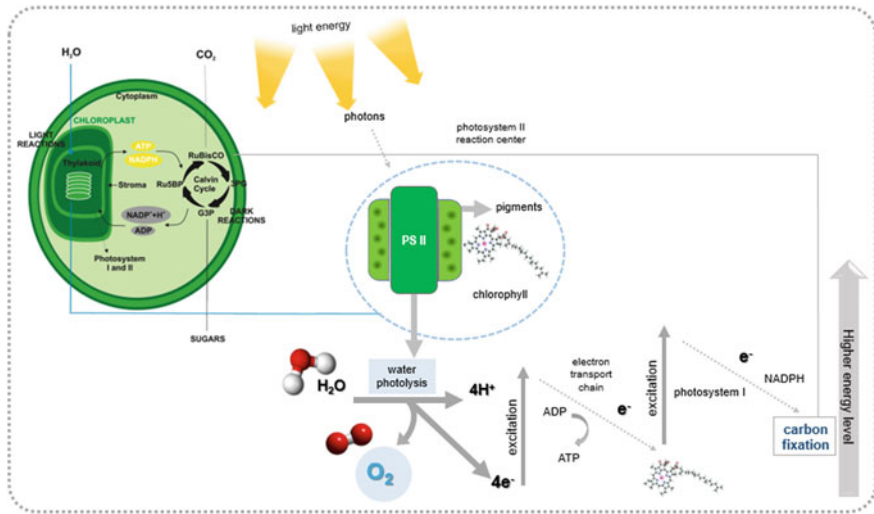
Fig. 2 Schematic representation of the oxygen generation in the photosynthesis

energy conversion point of view, through the solar spectrum. According to Bergene (1996), this ratio provides the value of process efficiency. In this work, the theoretical upper efficiency of water photolysis by microalgae was 0.11. Comparatively, commercial photovoltaic solar cells convert solar energy with efficiency in the range of 0.10–0.15.

Another important measure is the photosynthetic quotient (PQ), which provides more accurate values of the components involved in photosynthesis. The PQ is the molar ratio between released oxygen (gross primary production) in water photolysis during light reactions and CO_2 converted during the Calvin–Benson–Bassham cycle, and it varies as a function of the nitrogen source, carbon/nitrogen ratio assimilated, microalgae species used, type of organic molecule produced, luminous intensity, and photoperiods (Eriksen et al. 2007; Smith et al. 2012).

To accurately measure the photosynthetic activity, the PQ can be calculated according to Eq. 2 (Kliphuis et al. 2010):

$$PQ = \frac{OPR}{CUR} \tag{2}$$

where OPR is the oxygen production rate, and CUR is the carbon dioxide consumption rate.

Generally, the experimental values of the PQ are close to 1.0 (Burris 1981). Table 4 shows the experimental values of the PQ found in different microalgae. Jacob-Lopes et al. (2010) found a PQ of 0.74, which result corroborates the theoretical value estimated through the photosynthetic equation, establishing that each 1 kg of CO_2 consumed corresponds to a release of 0.73 kg O_2.

Table 4 Photosynthetic quotients (PQ) found by different species of microalgae

Microalgal species	Bioreactor type	PQ	References
Arthrospira platensis	Membranes	1.38	Cogne et al. (2005)
Chlamydomonas reinhardtii	Bubble column	1.00	Eriksen et al. (2007)
Chlorella sp.		1.30	
Aphanothece microscopica Nägeli	Bubble column	0.74	Jacob-Lopes et al. (2010)
Chlorella sorokiniana	Bubble column	1.40	Kliphuis et al. (2010)
Tetraselmis striata	Bubble column	1.50	Holdt et al. (2013)
Synechococcus PCC7002	Bubble column	1.30–1.40	Bernal et al. (2014)
Synechocystis sp.			
Anabaena PCC7120			
Chaetoceros wighamii	Bubble column	1.26	Spilling et al. (2015)

Both the efficiency values and PQ show the ability of these photosynthetic microorganisms to convert the solar energy and, consequently, the water photolysis. However, these quantitative relations can only be considered if parameters such as photobioreactor configuration, light incidence, mixing, and ecological aspects are properly determined.

5   Volatile Organic Compounds as Energy Source

Besides the biological oxygen generation, other products are biotransformed by microalgae photosynthetic cultures, being the volatile organic compounds (VOCs) of great relevance. These compounds correspond to the larger fraction (gas phase) of carbon bioconverted in photobioreactors that satisfy the global mass balance in the system, in addition to biomass (solid phase), carbonates, bicarbonates, and extracellular polymers (liquid phase) (Jacob-Lopes and Franco 2013).

The VOCs are organic chemical molecules with high vapor pressure and low boiling point, passing freely through biological membranes, which causes them to easily evaporate into the atmosphere (Dudareva et al. 2013). Additionally, VOCs are among the fastest growing molecules in aquatic ecosystems, and many of these compounds with specific biological activity are generated and released from the metabolism of photosynthetic microorganisms, both in marine and in freshwater phytoplankton (Goldstein and Galbally 2007).

According to Zepka et al. (2015), the VOCs produced by microalgae can be divided into terpenoids, phenylpropanoids/benzenoids, carbohydrate derivates, fatty acids derivates, and amino acid derivates, besides specific compounds not represented in those major classes. Microalgae are able to generate and release substantial amounts of VOCs belonging to different classes of compounds, such as alcohol, aldehydes, ketones, hydrocarbons, esters, terpenes, carboxylic acids,

and sulfurized compounds, with chains that can contain up to 10 carbon atoms (Muñoz et al. 2004; Fink 2007; Sun et al. 2012).

Many studies of commercial interest have been conducted to identify VOCs produced by microalgae and cyanobacteria and point out their potential uses. Compounds such as β-cyclocyclal, 2-methyl-1-butanol, and 3-methyl-1-butanol were excreted in the extracellular fraction of *Microcystis aeruginosa* (Hasegawa et al. 2012). A wide variety of compounds, such as β-ionone, hexanol, hexanal, propanol, butanol, among others, were produced by *Phormidium autumnale* (Santos et al. 2016). In a study by Eroglu and Melis (2010), the microalgae *Botryococcus braunii* synthesized long-chain hydrocarbons, which can be commercially exploited for the synthesis of chemicals and biofuels feedstock. Schirmer et al. (2010) found in different cyanobacteria alkanes, such as heptadecane, pentadecane, and methyl heptadecane, besides alkenes, that have desirable properties for combustion. All these compounds have great potential as biofuels.

Most research on microalgae VOCs is focused on their use as industrial chemicals. Meantime, there are few studies demonstrating the feasibility of applying these compounds as fuels. Recently, Jacob-Lopes et al. (2017) developed a bioprocess in an attempt to make feasible the VOCs production in photobioreactors for use as gaseous fuels. A total of 17 compounds of different chemical structures were produced by microalgae *Scenedesmus obliquus* and released from photobioreactor exhaust gases (Fig. 3), which can potentially be used as energy source in combustion systems. Therefore, assuming that the estimated energy potential of these compounds is approximately 86.30 MJ/kg, and comparing them quantitatively with other conventional fuels, VOCs total energy content is superior to the value of natural gas (47.00 MJ/kg) and diesel oil (43.40 MJ/kg), for example. The several VOCs generated in photobioreactors could, therefore, be used for the gaseous fuels production, representing an important step in the consolidation of strategies to reduce dependence on fossil fuels and the expansion of renewable energy sources.

6   Photobioreactors Design

A photobioreactor can be defined as a lighted system designed for the development of photosynthetic reactions. In order for the CO_2 bioconversion in photosynthetic products to occur efficiently, it is necessary to consider some basic requirements, such as adequate light energy and CO_2, dissolved oxygen concentration, efficient mixing system, temperature control, nutrient availability, and scale-up (Wang et al. 2012).

A wide variety of cultivation systems have been reported for microalgae-based processes. Photobioreactors are generally classified into two designs: open or closed systems (Borowitzka 1999). Open systems are most commonly used in large-scale processes and are based on circular ponds and raceway tanks. They are simple to operate, cheap, and easy to expand. However, performance is poor, since the culture
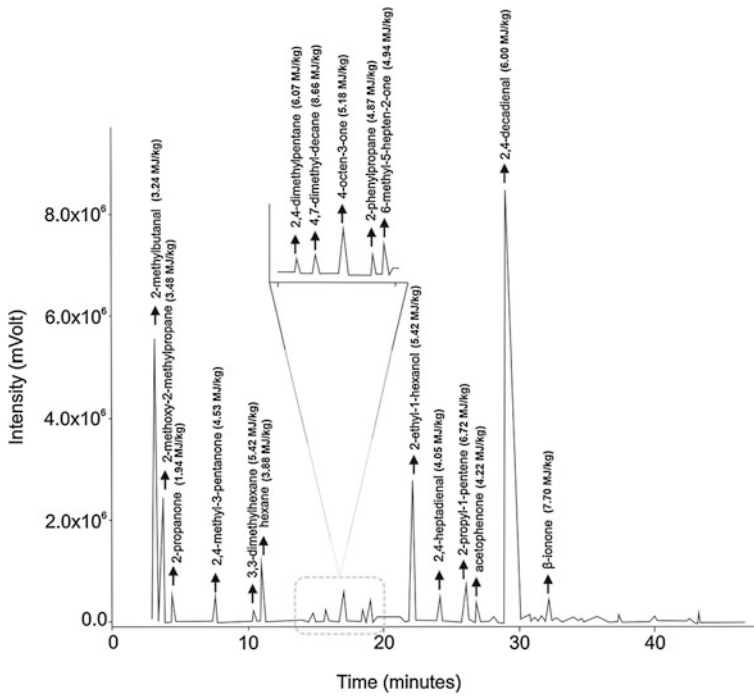
Fig. 3 Identification of VOCs produced by *Scenedesmus obliquus* and released from the photobioreactor exhaust gases. Adapted of Jacob-Lopes et al. (2017)

medium is exposed to variations in weather conditions, affecting the light intensity and temperature, besides low mass transfer, high evaporation rate, and susceptibility to contamination, which makes it unfeasible for an effective CO_2 conversion (Razzak et al. 2017).

On the other hand, closed systems included flat-plate, bubble column, airlift, tubular, hybrid, and biofilm photobioreactors, which enable high rates of CO_2 biotransformation in a wide variety of high-value bioproducts (Medipally et al. 2015; Tao et al. 2017). Moreover, they provide an easily controlled medium, safe against contamination. Despite their greatest potential for commercial application, closed systems are more expensive, due to the requirement of very transparent material, like glass or acrylic (Vasumathi et al. 2012). Another limiting factor is that losses of about 70% of non-bioconverted carbon are predicted when high CO_2 loads are injected (Jacob-Lopes et al. 2009).

Given these varied configurations, currently, one of the most widely accepted configurations for mass culture of microalgae is the closed tubular photobioreactors. This type is basically designed to achieve a maximum surface/volume (S/V) ratio and can be classified based on the horizontal, vertical, inclined, or helical arrangement of the tubes. They are suitable for CO_2 conversion due to their homogeneous mixture, greater gas transfer, smaller hydrodynamic stress,

and uniform light distribution, which implies enhanced performance on the microalgae growth. In addition, they can be operated easily, their cell density is 5–6 times higher than that of open ponds, and their capacity can reach up to 25,000 L and occupy a restricted area of about 10 m^2 (Raeesossadati et al. 2014; Jacob-Lopes et al. 2015; Pawar 2016). However, in addition to the drawbacks related to over-heating, the main critical issue in these systems is photo-inhibition, energy consumption, high costs, and dissolved oxygen (DO) accumulation (Huang et al. 2017).

As oxygen is a product of photosynthetic metabolism, its formation and solubilization in tubular photobioreactors indicate high inorganic carbon consumption rates, reaching O_2 generation rates of up to 10 mg/L min, even with a very frequent gas exchange (Chisti 2007). To prevent inhibition by O_2 accumulation, the DO concentration in the culture medium should not exceed the maximum tolerable value of 400% of the saturation level achieved in the presence of air. In a study by Raso et al. (2012), O_2 concentration increased from 75 to 250%; air saturation inhibited the growth of microalgae. To improve productivity in tubular photobioreactors, the oxygen level must be controlled or removed. However, optimal control parameters have not yet been well established to improve productivity in these systems.

With regard to operation, in a tubular photobioreactor, the airlift column circulates the broth with the culture medium to ensure light penetration through the solar collector, in which place most of the photosynthesis occurs, with ensuing DO accumulation. This, in turn, cannot be easily removed from the tubes (Molina-Grima et al. 2001). Therefore, in theory, if the oxygen is not removed within about one minute after accumulation, the inhibitory effect on the cells will occur immediately (Huang et al. 2017). In this case, the collecting tubes should be designed with restricted length for continuous DO removal, as well as the insertion of degasser systems.

Despite the fact that tubular photobioreactors are currently the most suitable configurations for application in oxygen generation, the main bottleneck of this type of equipment is its configuration, especially characterized by the geometry of these systems.

Due to the currently limited operational scale, the conventional configurations meet the basic requirements of the photosynthetic process. However, for a potential scale-up of the production process, operational failures must be overcome. Parameters such as the ratio of height/diameter column (H/D) are fundamental to build industrial photobioreactors. For this reason, hybrid photobioreactors compensate the drawbacks caused by limitation of S/V ratio and scale-up, since these systems can be based on a proper H/D ratio, generating configurations of reactors with heavy workloads in contrast to very long tubes or shallow ponds (Jacob-Lopes et al. 2016). If these aspects are considered, photobioreactors could be a fundamental step forward for the consolidation of the industrial biological oxygen generation.

## 7   Process Integration in Bio-oxycombustion Systems

Process integration has been widely used to further increase production systems efficiency. This concept focuses on the combination of technologies, in which the raw materials used can generate various types of products. Biobased systems may be suitable to minimize environmental impact, use of fossil inputs, and capital expenditures and to maximize the overall efficiency of an energy generation process or industry, provided they are obtained by total chain integration (Budzianowski and Postawa 2016).

Microalgae-mediated processes have recently seen growing demands for research and technological development, due to the versatility of these microorganisms in the CO_2 biotransformation within photobioreactors into valuable metabolic products (Jacob-Lopes et al. 2010).

Therefore, process integration using microalgae is a sustainable and economically viable route for improved sustainability, and it can be achieved by two types of integration basically: (i) mass integration, through effluents reuse and water recycling, and (ii) energy integration by heat recovery (Moncada et al. 2016).

By way of example, Fig. 4 describes a bioprocess, which represents the gain in thermal performance of a bio-oxycombustion furnace integrated into a photobioreactor. The thermal images show the superiority of use of the photobioreactor exhaust gases when compared to the injection of different oxidizers and at different cell residence times, during petroleum coke burning (Jacob-Lopes et al. 2017).

In this context, for bio-oxycombustion system proposed, mass integration occurs by direct conversion of GHG, especially CO_2 (gaseous effluent integration) in photobioreactors. Subsequently, part of the CO_2 is converted into photosynthetic metabolism by-products, such as biomass, inorganic salts, exopolymers, O_2, and VOCs. In parallel, energy integration is made by recovering of the photobioreactor gaseous phase, which contains the compounds of interest: VOCs (heat integration), O_2, and unconverted CO_2 released from the exhaust gases. These are integrated into
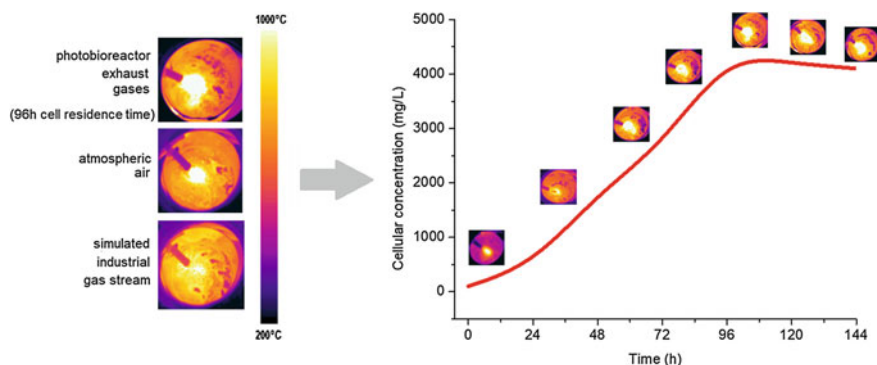
Fig. 4 Thermal performance of the integrated bio-oxycombustion system. Adapted of Jacob-Lopes et al. (2017)

Table 5 Challenges facing bio-oxycombustion technology

R&D challenges to integrated bio-oxycombustion systems scale-up	Comments
Photobioreactor design	Aspects associated with engineering, maintenance, economics, and microalgae species are the key to the construction of industrial photobioreactors for oxygen production
Collection of photobioreactor exhaust gases	Closed photobioreactors would be potentially suitable equipment for the oxygen supply and VOCs generation. For the removal mainly of the accumulated O_2, it would be necessary to design a degassing zone equipped with valves to control the flow and pressure of the gaseous fluid
Humidity of the photobioreactor exhaust gases	The gaseous phase of photobioreactor contains water vapor. When recovering exhaust gases, water should be removed in a separate unit to not interfere in the combustion
Pre-heating of the gases for injection	After removal of humidity, gases can be cooled; it would be necessary to do their pre-heating for injection into the burner system so as to avoid system thermal efficiency reduction
Injection site in the furnace	The injection zone must be defined so as to optimize energy utilization potential of O_2 and VOCs
Concentration of O_2 and VOCs	The bio-oxycombustion system requires high loads of the substances released from the photobioreactor exhaust gases. The photobioreactors currently available are not able to meet this demand, due to the lack of an ideal configuration
Process integration	Due to technical barriers of oxycombustion, process integration should be taken into account in order to balance the cost of CO_2 capture, oxygen, and fuel supply and to improve energy performance
Process life cycle analysis	Although bio-oxycombustion eliminates N_2 from flue gas and presents a potential increase in thermal efficiency, issues related to GHG emissions, more specifically CO_2, and energy consumption must be properly addressed, in order to reduce the environmental impact over its entire life cycle
Economic impacts	Microalgae-based processes are currently economically viable only on the fine chemicals production. It is necessary to develop new technological routes to the potential bulk chemical production

a combustion furnace such as oxidizer, gaseous fuels, and nitrogen diluent, respectively. After oxidation of the fuel, the resulting combustion CO_2 returns to the photobioreactor (mass integration) partially or totally, integrating the process globally.

8 Challenges Facing Bio-oxycombustion Technology

The implementation of bio-oxycombustion technology is a cost-effective means of BCCU, which could significantly reduce emissions from various industrial manufacturing sectors. R&D needs regarding fundamentals and performance of the oxycombustion system, scale-up of photobioreactors, and the integration and optimization of processes are identified in Table 5, for that the integrated bio-oxycombustion system can be fully scalable in the future.

9 Final Considerations

The growing development of oxycombustion systems has proven to be a viable strategy to mitigate CO_2 and increase the thermal efficiency of industrial processes. The integration of this technology with microalgae-based processes is considered an important engineering approach to promote sustainable development. Therefore, the full use of the photobioreactors exhaust gases could provide overall improvements in the thermal performance of integrated bio-oxycombustion systems. However, the CO_2 industrial biotransformation into O_2 and VOCs is very limited due to lack of an ideal photobioreactor design. Conversely, considering that combustion systems have extensive infrastructure, it would be necessary to design a photobioreactor that would operate at large volumes for the production of these substances in a mature industrial process. In this sense, for that bio-oxycombustion technology to present viability, efficiency, and productivity, operational problems must be solved in order to meet industrial demand for photobioreactors with applicability in full scale at field conditions.

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