UNIVERSIDADE FEDERAL DE SANTA MARIA
CENTRO DE CIÊNCIAS RURAIS
PROGRAMA DE PÓS-GRADUAÇÃO EM CIÊNCIA E TECNOLOGIA DE ALIMENTOS

Ihana de Aguiar Severo

INTEGRAÇÃO DE PROCESSOS PARA O DESENVOLVIMENTO DE SISTEMAS DE BIO-OXICOMBUSTÃO EM INDÚSTRIAS DE ALIMENTOS

Santa Maria, RS
2017

Ihana de Aguiar Severo

INTEGRAÇÃO DE PROCESSOS PARA O DESENVOLVIMENTO DE SISTEMAS DE BIO-OXICOMBUSTÃO EM INDÚSTRIAS DE ALIMENTOS

Dissertação apresentada ao Curso de Mestrado do Programa de Pós-Graduação em Ciência e Tecnologia dos Alimentos, Área de Concentração em Qualidade de Alimentos, da Universidade Federal de Santa Maria (UFSM, RS), como requisito parcial para obtenção do título de **Mestre em Ciência e Tecnologia de Alimentos.**

Orientador: Prof. Dr. Eduardo Jacob Lopes

Santa Maria, RS
2017

Ihana de Aguiar Severo

INTEGRAÇÃO DE PROCESSOS PARA O DESENVOLVIMENTO DE SISTEMAS DE BIO-OXICOMBUSTÃO EM INDÚSTRIAS DE ALIMENTOS

Dissertação apresentada ao Curso de Mestrado do Programa de Pós-Graduação em Ciência e Tecnologia dos Alimentos, Área de Concentração em Qualidade de Alimentos, da Universidade Federal de Santa Maria (UFSM, RS), como requisito parcial para obtenção do título de **Mestre em Ciência e Tecnologia de Alimentos.**

Aprovado em 06 de março de 2017:

Eduardo Jacob Lopes

Prof. Dr. Eduardo Jacob Lopes (Presidente/Orientador)

Rodrigo F. S. Salazar

Prof. Dr. Rodrigo F. dos Santos Salazar (UNICRUZ)

ROGER WAGNER

Prof. Dr. Roger Wagner (UFSM)

Santa Maria, RS

2017

AGRADECIMENTOS

À Deus, por sempre guiar o meu caminho e dar-me forças.

Ao professor Dr. Eduardo Jacob Lopes, pela valiosa orientação, oportunidades proporcionadas, incentivo e por compartilhar seus conhecimentos e experiências.

Aos meus colegas de laboratório, pela agradável convivência, especialmente ao Rodrigo, pela ajuda na execução dos experimentos, e a Mariany pela contribuição no desenvolvimento do trabalho e ideias partilhadas.

Aos colegas do NTA, pelos momentos de descontração.

Aos professores, Dr. Juliano Smanioto Barin e Dr. Roger Wagner, pela colaboração no presente trabalho.

Aos meus amigos, pelo carinho e companheirismo.

Ao órgão de fomento à pesquisa: CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior) pela concessão da bolsa de mestrado.

À Universidade Federal de Santa Maria, pela formação proporcionada.

Por fim, tendo consciência que sozinha nada disto teria sido possível, agradeço aos meus pais, José Carlos de Oliveira Severo e Isabel Cristina Severo de Aguiar, por toda a dedicação a minha educação e criação, pelo amor incondicional e incentivo para que eu chegasse até aqui, além dos meus irmãos Morgana e Murillo, pelo apoio a cada conquista. A eles dedico este trabalho!

“Você nunca sabe que resultados virão da sua ação.
Mas se você não fizer nada, não existirão resultados. ”
(Mahatma Gandhi)

RESUMO

INTEGRAÇÃO DE PROCESSOS PARA O DESENVOLVIMENTO DE SISTEMAS DE BIO-OXICOMBUSTÃO EM INDÚSTRIAS DE ALIMENTOS

AUTOR: Ihana de Aguiar Severo
ORIENTADOR: Eduardo Jacob Lopes

O desenvolvimento de tecnologias alternativas para mitigação de dióxido de carbono atmosférico têm sido o foco de muitas pesquisas científicas, com ênfase na economia e sustentabilidade dos processos de produção. A oxicombustão é considerada como uma estratégia promissora para este propósito, entretanto ela possui algumas limitações, às quais podem ser contornadas com a aplicação de fotobiorreatores microalgais. Essa rota tecnológica propõe melhorar a eficiência térmica de equipamentos de combustão com uso simultâneo dos compostos formados, através da técnica de bio-oxicombustão. Nesse sentido, o trabalho teve por objetivos: (i) construir um forno de oxicombustão integrado a um fotobiorreator; (ii) estabelecer o quociente fotossintético do fotobiorreator; (iii) caracterizar a fração volátil do fotobiorreator; e (iv) avaliar o desempenho térmico do forno de oxicombustão. Os resultados demonstraram que através do enriquecimento dos gases de exaustão do fotobiorreator, obteve-se um ganho significativo na eficiência térmica do sistema, com taxas de aquecimento de 30,5% e 45,8% superiores ao uso do ar atmosférico e da corrente gasosa industrial simulada, respectivamente. Em relação a composição dos gases de exaustão do fotobiorreator, foi possível gerar cerca de 40% de oxigênio que foi utilizado como comburente. Dentro desse contexto, foi evidenciado que a integração destes processos é altamente potencial para captura de carbono e utilização biológica, além de melhorar substancialmente a eficiência energética dos sistemas de combustão industrial.

Palavras-chave: Oxicombustão. Fotobiorreatores. Integração de processos. Captura de carbono e utilização biológica. Indústrias de alimentos.

ABSTRACT

PROCESS INTEGRATION FOR THE DEVELOPMENT OF BIO-OXYCOMBUSTION SYSTEMS IN FOOD INDUSTRIES

AUTHOR: Ihana de Aguiar Severo
ADVISOR: Eduardo Jacob Lopes

The development of alternative technologies for mitigation of atmospheric carbon dioxide have been the focus of many scientific research, with emphasis on the economy and sustainability of production processes. Oxycombustion is considered a promising strategy for this purpose, however it has some limitations, which can be circumvented with the application of microalgal photobioreactors. This technological route proposes improve the thermal efficiency of combustion equipment with the simultaneous use of the formed compounds, through the bio-oxycombustion technique. In this sense, the aims of this work were: (i) build an oxycombustion furnace integrated with a photobioreactor; (ii) establishing the photosynthetic quotient of photobioreactor; (iii) characterize the volatile fraction of photobioreactor; and (iv) evaluated the thermal performance of the oxycombustion furnace. The results demonstrated that through of enhancement of photobioreactor exhaust gases, a significant gain in the thermal efficiency of the system was achieved, with heating rates of 30.5% and 45.8% superior to use of atmospheric air and the simulated industrial gas stream, respectively. Regarding the composition of photobioreactor exhaust gases, was possible generated about 40% of oxygen that was used as oxidizer. In this context, was demonstrate that the integration these processes is highly potential for biological carbon capture and utilization, besides substantially improving the energy-efficiency for industrial combustion systems.

Keywords: Oxycombustion. Photobioreactors. Process integration. Biological carbon capture and utilization. Food industries.

LISTA DE ILUSTRAÇÕES

MANUSCRITO 1

MANUSCRITO 3

LISTA DE TABELAS

MANUSCRITO 1

MANUSCRITO 3

LISTA DE ANEXOS

SUMÁRIO

APRESENTAÇÃO

Essa dissertação está dividida em quatro capítulos, sendo que o **Capítulo 1** contempla os itens **Introdução** e **Objetivos**. O **Capítulo 2** é composto pela **Revisão Bibliográfica**, que está na forma de dois trabalhos científicos publicados: o **Manuscrito 1**, na forma de um capítulo de livro, e o **Manuscrito 2**, um artigo de revisão. As seções Materiais e Métodos e Resultados e Discussão encontram-se no **Manuscrito 3**, na forma de um artigo em processo de submissão, dentro do item **Parte Experimental**, contemplando o **Capítulo 3**. No **Capítulo 4**, está o item **Conclusão geral**, que aborda uma compilação de intepretações a respeito dos resultados obtidos nesse trabalho. As **Referências** pertencem somente às citações que aparecem no item Introdução. Ao final dessa dissertação, encontra-se o item **Anexos** referente ao depósito de duas Patentes Internacionais.

Capítulo 1

INTRODUÇÃO E OBJETIVOS

1. INTRODUÇÃO

O aumento das concentrações de gases de efeito estufa (GEE) é atribuído como a principal causa do aquecimento global, um problema ambiental com potencial para alterar o equilibro climático terrestre. O dióxido de carbono (CO_2), emitido principalmente da queima de combustíveis fósseis, tem impacto negativo representando a maior parcela das emissões (IPCC, 2014).

Atualmente, o setor industrial é responsável por cerca de 7% das emissões globais de efluentes gasosos. Apesar de uma produtividade relativamente baixa em comparação aos demais setores, a indústria de alimentos utiliza amplamente diferentes fontes energéticas o que, inevitavelmente, favorecem o acúmulo de CO_2 na atmosfera (LIN & XIE, 2016). De acordo com os dados obtidos do Carbon Disclosure Project (CDP), as dez maiores empresas do ramo alimentício, quando juntas, emitem cerca de 263,7 milhões de toneladas de GEE por ano (OXFAM, 2017). Dessa forma, existe uma ligação explícita entre as alterações climáticas e a produção de alimentos (ZHAO et al., 2017).

A fim de mitigar esse problema, diversas pesquisas foram sendo desenvolvidas com o foco na captura de carbono e subsequente armazenamento (CCS) ou utilização (CCU). Diversos autores relatam que estas opções devem ser avaliadas tendo em vista a crescente demanda de energia, infraestrutura, bem como a economia do processo (SCHEFFKECHT et al., 2011; CUÉLLAR-FRANCA & AZAPAGIC, 2015; RAHMAN et al., 2017).

Uma das rotas tecnológicas mais promissoras para a captura de carbono é a oxicombustão, a qual está fundamentada na substituição parcial ou total do ar utilizado nos processos convencionais de combustão por atmosferas enriquecidas de oxigênio. Como consequência, há um ganho na capacidade térmica, resultando em uma elevada eficiência energética dos equipamentos, redução no consumo de combustível e não há formação de poluentes (YIN & YAN, 2016).

Embora a oxicombustão seja tecnicamente exequível, a principal desvantagem inerente a esta tecnologia refere-se à obtenção de oxigênio de alta pureza e em grandes volumes. Dentre os métodos para produção de oxigênio, o criogênico através de uma unidade de separação do ar (ASU) é considerado a única opção disponível comercialmente para este propósito. Contudo, essa unidade requer um alto consumo de energia e custo de produção, além de apresentar uma configuração de difícil flexibilidade operacional, inviabilizando sua aplicação em escala industrial (JIN et al., 2015).

Em contrapartida, essa limitação pode ser contornada através da aplicação de fotobiorreatores, utilizando microrganismos fotossintéticos, como as microalgas, as quais geram como co-produto metabólico o oxigênio através das reações de fotólise da água (HELDT & PIECHULLA, 2011). Através dessa rota tecnológica, é possível obter aproximadamente 0,75 kg de oxigênio para cada 1 kg de CO_2 bioconvertido, o que demonstra a potencialidade de produção dessa substância nesse tipo de equipamento. Estes bioprocessos produzem em paralelo inúmeros compostos orgânicos voláteis (COVs) (JACOB-LOPES et al., 2010; JACOB-LOPES & FRANCO, 2013), que em função das suas estruturas químicas, apresentam considerável valor energético, além de liberarem nos gases de exaustão substanciais concentrações de CO_2.

Alternativamente, o desenvolvimento de novas tecnologias, como a captura de carbono e utilização biológica (BCCU), podem ser consideradas como uma estratégia altamente potencial para aplicação industrial. Essa rota tecnológica converte CO_2 em bioprodutos de valor agregado (SEVERO et al., 2016).

Diante desse contexto, para satisfazer a demanda de oxigênio requerida nos processos industriais de oxicombustão e a captura de carbono, o presente trabalho está fundamentado no desenvolvimento de um sistema integrado de bio-oxicombustão. Através dessa técnica, é possível gerar biologicamente oxigênio e CO_2 provenientes da conversão direta em fotobiorreatores de GEE, principalmente CO_2, que são reutilizados para uso como comburentes e diluentes de nitrogênio, respectivamente, em fornos industriais. Ainda, este trabalho é inovador do ponto de vista da integração de processos, pois minimiza o consumo de energia e maximiza a eficiência, melhorando o desempenho térmico de sistemas industriais de combustão, contribuindo de forma efetiva para o desenvolvimento sustentável.

2. OBJETIVOS

2.1. OBJETIVO GERAL

Desenvolver sistemas integrados de bio-oxicombustão em indústrias de alimentos.

2.2. OBJETIVOS ESPECÍFICOS

- Construir um forno de oxicombustão integrado a um fotobiorreator;
- Estabelecer o quociente fotossintético do fotobiorreator;
- Avaliar o desempenho térmico do forno de oxicombustão.

Capítulo 2

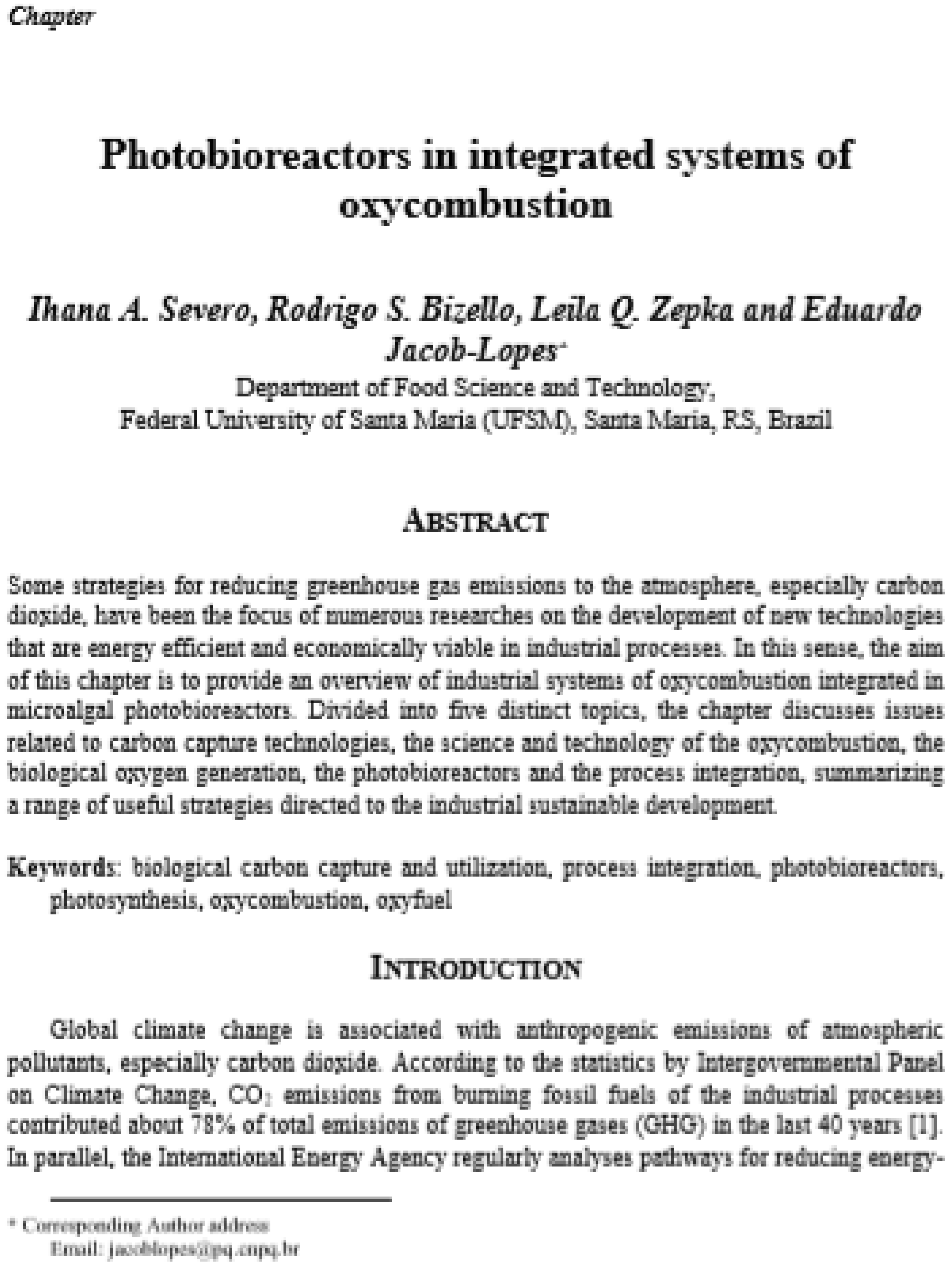
REVISÃO BIBLIOGRÁFICA

1. MANUSCRITO 1

Photobioreactors in integrated systems of oxycombustion

Ihana Aguiar Severo, Rodrigo Stefanello Bizello, Leila Queiroz Zepka e Eduardo Jacob-Lopes

Capítulo publicado no Livro Photobioreactors: Advancements, Applications and Research, Nova Science Publishers, Inc., New York, 2016.



Chapter

Photobioreactors in integrated systems of oxycombustion

Ihana A. Severo, Rodrigo S. Bizello, Leila Q. Zepka and Eduardo Jacob-Lopes[*]
Department of Food Science and Technology,
Federal University of Santa Maria (UFSM), Santa Maria, RS, Brazil

ABSTRACT

Some strategies for reducing greenhouse gas emissions to the atmosphere, especially carbon dioxide, have been the focus of numerous researches on the development of new technologies that are energy efficient and economically viable in industrial processes. In this sense, the aim of this chapter is to provide an overview of industrial systems of oxycombustion integrated in microalgal photobioreactors. Divided into five distinct topics, the chapter discusses issues related to carbon capture technologies, the science and technology of the oxycombustion, the biological oxygen generation, the photobioreactors and the process integration, summarizing a range of useful strategies directed to the industrial sustainable development.

Keywords: biological carbon capture and utilization, process integration, photobioreactors, photosynthesis, oxycombustion, oxyfuel

INTRODUCTION

Global climate change is associated with anthropogenic emissions of atmospheric pollutants, especially carbon dioxide. According to the statistics by Intergovernmental Panel on Climate Change, CO_2 emissions from burning fossil fuels of the industrial processes contributed about 78% of total emissions of greenhouse gases (GHG) in the last 40 years [1]. In parallel, the International Energy Agency regularly analyses pathways for reducing energy-

---

[*] Corresponding Author address
Email: jacoblopes@pq.cnpq.br

related CO_2 emissions. This information suggests the necessity of researches on the development and management of alternative technologies that are economical and energy-efficient in industrial processes, enabling mitigation of these compounds [2].

The oxycombustion has proven to be one of the best forms of carbon capture from stationary sources, due to its ability to mitigate emissions and improve combustion performance. This technological route is based on the replacement of the air used in combustion processes by oxygen-rich atmospheres [3; 4]. As a consequence of the increased partial pressure of oxygen in combustion processes, there is a gain in thermal capacity, resulting in greater overall efficiency of equipment, reducing fossil fuel consumption and consequently emissions of greenhouse gases [5].

Despite the oxycombustion be an attractive technology, this approach has faced significant difficulties in implementation related to the cost and the purity of the oxygen produced, beyond control of operating system variables, unfeasible their application in industrial scale [6].

Regarding these issues, the limitations can be circumvented through the photobioreactors, using photosynthetic microorganisms, as the microalgae, which have as a metabolic co-product the oxygen supported by the water photolysis reactions. Additionally, the bioprocess mediated by microalgae produce in parallel numerous volatile organic compounds that have considerable energy content, besides releasing substantial concentrations of CO_2 in exhaust gases, serving as nitrogen diluent [7; 8].

Prompted by government actions and in order to reduce the carbon footprint, several alternative technologies have been developed focusing on the capture, storage and/or use of carbon [9]. The biological carbon capture and utilization (BCCU) is a high potential technology for industrial application, because it converts biologically carbon dioxide with their integration into a oxycombustion process. Therefore, the bio-oxycombustion technique is discussed in this review, including fuels derived from biological conversion processes of GHG through photosynthesis.

These strategies are highlighted for being economically viable and for improving the thermal performance of industrial combustion systems, effectively contributing to sustainable development. In this sense, the aim of this chapter was to provide an overview of integrated systems of industrial oxycombustion in microalgal photobioreactors.

CARBON CAPTURE TECHNOLOGIES

Global emissions of carbon dioxide reach more than 20 billion tons per year. In contrast, it is estimated that such emissions should be reduced by at least 50% to mitigate the increase in global temperature. In this scenario, the oxycombustion technology have been proposed as a viable option to capture approximately 90% CO_2 in large point sources of emissions, consisting basically of compression stages, capture, transport and storage or utilization [10].

In carbon capture and storage (CCS), the CO_2 is captured, compressed and transported through pipelines to be stored in an appropriate location, generally in the deep ocean, in geological formations underground or in the form of mineral carbonate [11]. According to the International Energy Agency, currently the CCS is employed in some energy sectors around the world, but it is a relatively expensive technology, requiring a complex infrastructure, being in development for the generation energy in other industrial processes. Moreover, the storage is not an entirely safe option, because may occur leakage to the atmosphere, followed by possible environmental impacts [12; 13].

On the other hand, carbon capture and utilization (CCU) have also been explored with the possibility of using CO_2 in commercial processes, either in pure form or as raw material in the synthesis of numerous chemical products in different areas, such as food and beverages, pharmaceutical, mineral, chemical solvents, plastics, fuels and enhanced oil recovery. However, there are some barriers to that the CCU to performed in these sectors, as the large amount of additional power and supply capacity and product demand in the market [14; 15].

Recently, biological carbon capture and utilization (BCCU) may be a viable alternative in comparison to the CCU and CCS, representing a concrete step toward the goal of a sustainable chemical industry, with concomitant reduction in overall costs of the CO_2 capture process and emissions [16; 17; 18]. This technological route consists of the biological conversion of CO_2 into biomass through photosynthesis, for the extraction of high value-added products. Mechanisms involving the CO_2 use specific catalysts, some of which are mediated by biological systems. Microorganisms capable of fixing CO_2 are prokaryotes or eukaryotes. In this context, the microalgae, for example, present high photosynthetic rates, which provide an attractive form of BCCU, recycling the CO_2 from different sources of industrial emissions [4].

SCIENCE AND TECHNOLOGY OF THE OXYCOMBUSTION

Process overview

The use of pure oxygen as oxidant in combustion processes is a relatively new approach to the greenhouse gases mitigation. The oxycombustion technology was developed in 1982 to produce a CO_2 rich gas used in advanced oil recovery [19]. Currently, the oxycombustion is already being applied in combustion processes in industrial scale, and the focus of researches has been directed to the new or existing power generation plants [13].

The main characteristic of oxycombustion technology is the partial or total replacement of the air by high purity oxygen. More specifically, this technological route is based on fossil fuels combustion in an atmosphere enriched with high purity oxygen free nitrogen, differing from conventional processes that use air as oxidant [20].

Once this separation occurs, one obtains a high purity O_2 concentration (> 95%) and this is directed to a power conversion unit which will mix it with the recycled flue gas of concentrated CO_2. The combustion performed in an atmosphere with a mixture of O_2/CO_2 produces a gas stream comprising CO_2 (> 80% by vol.) and H_2O. The water is easily removed by condensation and the remaining CO_2 is purified and compressed. The CO_2 volume obtained can vary by the type of process used, the type of fuel, the air losses, the purity of the CO_2 and the excess O_2 [21].

During combustion, some oxidized components are also formed, such as the sulfur residues which are removed during compression of CO_2. After this step, CO_2 is highly concentrated (95-99% vol.) and is ready for its separation and subsequent capture [22].

Thus, due to the high flame temperature resulting from burns with practically pure O_2, part of the gas from combustion, rich in CO_2, returns to the system to refund the volume of gas lost when N_2 is removed from the air and to prevent the excessive increasing temperature in the system. A consequence of the increased concentration of O_2 is the gain in overall heat capacity of the equipment, because it increases radiation heat transference into the system and reduces fuel consumption [23]. In theory, the oxycombustion can be used with any fuel to thermal energy production [24].

Besides the improvement in the energy performance, the oxycombustion has the advantage of decreasing the volume of exhaust gas due to the absence of oxidizer N_2, which provides a longer residence time in the burner. This is crucial factor for the NO_x formation reduction in approximately 50%. On these conditions, it is possible to reduce the pipeline gas output, an important factor to optimize limited space plants [25].

In terms of applicability, the oxycombustion has been directed to the implementation of new thermal power generation facilities. Moreover, it can be adapted to existing installations, such as thermal power plants, cement, iron and steel, industrial furnaces, boilers and oil refineries [5; 26; 27].

In contrast, one of the drawbacks regarding in relation to this technology refers to the cost when one is working with high purity oxygen. In this case, it is necessary a purification system coming from the oxycombustion, which shows an additional cost for the plant and increased energy consumption. Disregarding the pre-treatment unit and the CO_2 cleaning, the impurities presented in the flue gas can negatively interact with the material of the pipelines, forming corrosive acids and causing damage to the equipment [24]. In this sense, disadvantages regarding to the costs in the production of oxygen combined with high energy consumption has great impact on the overall efficiency of the plant. These are the main challenges to be overcome [10].

Chemical aspects of oxycombustion

The most industrial combustion processes use air as oxidizing agent, and in many cases, these processes can be substantially improved by using oxygen as the oxidizing gas [22].

Combustion reactions occur when the chemical elements present in a fuel reacts with an oxidant (usually oxygen from the air) releasing large amounts of heat. The main chemical elements in fuels that release heat are carbon, hydrogen and sulfur [28]. In addition, several compounds, including oxygen (O_2), carbon monoxide (CO), nitrogen oxides (NO_x), sulfur oxides (SO_x), methane (CH_4), hydrocarbons, water vapor, hydrochloric acid, heavy metals, particulate materials, among others, are also present in combustion gases [29; 20].

Based on this information, the replacement of nitrogen for oxygen will impact on the temperature, the stability, the propagation velocity and delay in the flame ignition, the heat transfer and reduction of pollutants emissions. These effects are based on differences in properties of the combustion gases, like oxygen (used as oxidizing) and carbon dioxide (used as nitrogen diluent) which are shown in Table 1.

In relation to flame temperature, it is necessary to recirculate about 60% of the oxycombustion of gases so that the temperature is the same as that in the combustion with air. High concentrations of O_2 in the system increase the adiabatic flame temperature, which is the largest attained temperature in the combustion products without heat exchanging inside or outside the system. On the other hand, low concentrations of O_2 may result in instability of flame, and consequently there can be no burning of the total fuel. In this case, to maintain a satisfactory stability, the O_2 enrichment should be sufficient to ensure the flame ignition and to correctly select the amount of flue gas that is recycled, establishing the optimum heat transfer balance [30]. This fact is evidenced by the heat capacity ($C\rho$) of molecules, because in 1400K the N_2 presents a $C\rho$ of 34.18 kJ/k mol, whereas CO_2 has $C\rho$ 57.83 kJ/k mol. In addition to this information, the emissivity (ε) of triatomic substances such as CO_2 and H_2O are greater than diatomic molecule such as N_2, resulting in greater heat transfer in the system. This occurs because molecules can undergo a transition to a higher energy level by absorbing or emitting energy radiation [31; 32].

The flame propagation velocity is another important aspect to be considered. As the molecular weight of CO_2 (44) is higher than the molecular weight of N_2 (28), the flue gas has a higher density and, consequently, there is a delay in the flame ignition. This characteristic is also related to the lowest O_2 diffusion rate into the particle used as fuel. In this sense, since there is enriched with O_2, the velocity of the combustion reaction will be higher, which implies a lower residence time in the overall system [33].

In the case of oxycombustion, pollutant emissions such as NO_x, SO_x and mercury are generated in minimal amounts due to the elimination of nitrogen from the air and recycled flue gas. The most important factors that influence the formation of these acid gases are the flame conditions, especially the oxygen concentration and the flame temperature. High temperatures enable the formation of NO_x, a problem which can be minimized by using pure oxygen instead of air [26].

[Table 1]

Oxygen production by conventional technologies

The atmospheric air comprises a mixture of gases, such as nitrogen (79%) and oxygen (21%). Oxygen is the key component to any oxycombustion system. Thus, there are four main methods for oxygen enrichment in a oxycombustion system: (i) the addition of O_2 at the entrance of the combustion air flow; (ii) injection of O_2 in the air-fuel flame; (iii) the total replacement of the combustion air with high purity O_2; and (iv) injection separately from the O_2 in the combustion air to the burner [35].

However, to make it possible to enrich oxycombustion system with oxygen, it is first necessary to make the separation of air into its individual components, and such process requires a high energy demand [36]. The air can be separated by four main technologies including: cryogenic distillation processes, adsorption, absorption and membrane separation, which are summarized in Table 2.

Currently, cryogenic air distillation process is the most used by industry producing substantial volumes (100-300 ton/day) of high purity oxygen (> 99%). This process consists in several unit operations, comprising compression steps, pre-treatment of air purification, cooling until the point of liquefaction, cryogenic distillation in the chamber and obtaining the final concentrate product [37].

Thus, an air separation unit (ASU) is required to separate oxygen and other compounds, with low emissions pollutants. However, the ASU is not an attractive technology for industrial application, considering that the power consumption in the compression step is excessive high [25; 38].

On the other hand, the production of oxygen by a pressure adsorption swing (PSA) is done by removing one or more substances from a gas mixture by intermolecular forces with the aid of a solid adsorbent at high pressure and low temperature, which will oscillate at low pressure (usually atmospheric pressure). Several factors influence this process, such as temperature, partial pressure, type of adsorbent, adsorption pore size and surface strength [39; 40]. The PSA process provides very pure product (> 95%) and it is suitable for small and medium-sized plants (20-100 ton/day). However, besides its high energy consumption, the PSA has low efficiency in the separation of O_2 compared with other technologies, depending on the adsorbent possess low selectivity and adsorption capacity [37].

Other air separation method is the process of absorption, which can happen through a chemical reaction from an aqueous alkaline solvent. In this reaction it is generally used amine and acid, or by means of a physical solvent at elevated partial pressures [41]. The gases absorption occurs with the separation of one or more components from a gas stream and through its interaction with a solvent, the dissolution of these components occurs. In turn, the desorption is the inverse process in which a component in liquid phase passes into the gas phase. This process will depend on the solubility of the solute in the liquid solvent [42]. Although these processes are widely used in industrial sectors, the main problems with the use of chemical solvents are the corrosion of the absorption column and the large amount of energy required for the solvent regeneration process. For the physical method, the operation cost becomes lower when compared to the use of chemical absorbents. However, in this method, the solvent absorption capacity is lower, causing loss in solvent circulation, obtaining, therefore, higher costs to the chemical method [27].

Finally, nevertheless it is a technology that is still being developed, air separation can also be done by using membranes. The process occurs with retention and passage of some components in a gas flow through different mechanisms. The membranes are semi-permeable, and selective barriers can be made of various materials, organic (polymer) or inorganic (zeolite, ceramic, carbon or metallic), porous or non-porous [43]. Despite being simple, flexible and low power consumption technology, the membranes cannot separate a mixture of gases selectively neither have good heat resistance and chemical and physical stability, which is the necessity for further researches on industrial scene [44]. Considering these aspects, the technology for air separation currently available are considered unattractive because of the limitations of cost and/or purity of the produced oxygen. In this sense, it is needed development of more efficient and economic methods that decrease the energy use in industrial scene.

[Table 2]

BIOLOGICAL OXYGEN GENERATION

Plants and photosynthetic microorganisms perform oxygenic photosynthesis, releasing oxygen. Although there are some differences in the photosynthetic process between these three groups, the overall process is very similar in these organisms. In general, photosynthesis is a physical-chemical process that converts carbon dioxide into biomass using light energy and producing oxygen molecules through a sequence of different chemical reactions in distinct cellular compartments [48]. The general equation (Eq. 1) to describe photosynthesis is [49]:

$$6CO_2 + 12H_2O \xrightarrow{\text{Light}} C_6H_{12}O_6 + 6O_2 + 6H_2O \qquad (1)$$

Photosynthesis is characterized by a two-stage mechanism: a series of photochemical reactions that occur only when the cells receive light and carbon fixation reactions, also denominated dark reactions, occurring both in the presence of light as in the dark [50].

In the simplest organisms (prokaryotes) such as cyanobacteria, the photosynthesis occurs in cytoplasm, where the thylakoids are located. They contain many chlorophyll molecules associated to the plasma membrane invaginations. Moreover, other algae groups (eukaryotes) perform photosynthesis completely inside the chloroplast [51]. These special organelles are coated with a watery fluid membrane, the stroma, containing stacks of flat disks bounded by the thylakoid membrane. Immersed membranes thylakoids are the photosynthetic pigments that promote the light reactions and the synthesis of ATP. Furthermore, the stroma contains the biochemical apparatus necessary for the CO_2 sequestration through the carboxylation reactions of photosynthesis, also known as the Calvin-Benson cycle [52].

In the light reactions, there is the formation of high-energy compounds such as ATP (adenosine triphosphate) and NADPH (nicotinamide adenine dinucleotide phosphate), essential for the assimilation of inorganic carbon and for the oxygen production. The overall equation (Eq. 2) for the light reactions is [53]:

$$2H_2O + 2NADP^+ + 3ADP + 3P_i + \xrightarrow{\text{Light}} 2NADPH + 2H^+ + 3ATP + O_2 \qquad (2)$$

Therefore, the light energy is retained in two photoreactions prepared by two pigment-protein complexes, called photosystem I and II [54]. The photosystems are formed by the reaction center of the complex and the complex antenna, comprising accessory pigments such as chlorophyll *b*, *c* and *d*, carotenoids and phycobiliproteins. They are responsible by absorbing mainly photons and transferring the energy to the reaction center complex. In this sense, therefore, the chlorophyll *a* molecules are excited and their electrons are transferred to a molecule electron acceptor [48].

The electrons then flow through a series of membrane bound transporters, including cytochromes, quinones, and iron-sulfur proteins. Simultaneously, protons are pumped by the thylakoid membrane in order to generate an electrochemical potential. Part of the released energy is incorporated during this electron transport to ATP in the process of photophosphorylation. The ultimate source of electrons for photosynthesis is water, which yields in the process of photolysis, or "Hill reaction", hydrogen atoms (protons), electrons and free oxygen, an important microalgae product and green plants photosynthesis [55]. The Hill reaction is represented by the equation (Eq. 3) [56]:

$$2H_2O \xrightarrow{\text{Light}} 4H^+ + 4\bar{e} + O_2 \qquad (3)$$

In chemical terms, the Hill reaction occurs when isolated chloroplasts release O_2 when illuminated by sunlight in the presence of a suitable electron acceptor. The receiver is reduced and molecular O_2 is released. Thus, this reaction is an important aspect of photosynthesis, because the O_2 in the process is generated from the water photolysis [57].

In the dark reactions or Calvin Cycle, there is the synthesis of sugars (monosaccharides) from the CO_2 fixation. The cycle starts with the reaction of ribulose 1,5-bisphosphate (Ru5BP) with CO_2, which is catalyzed by the enzyme ribulose 1,5-bisphosphate carboxylase/oxygenase (RuBisCo). The reaction product is broken into two three-carbon molecules of 3-phosphoglycerate or 3-phosphoglyceraldehyde (PGA or PGAL). In the presence of ATP and NADPH, the PGA is reduced to glyceraldehyde 3-phosphate (G3P). The most of the G3P produced is used to regenerate Ru5BP, so that the cycle can be closed. One out of the six Ru5BP molecules is not recycled and then condenses to form intermediate phosphorous sugars and subsequently glucose [57]. The overall equation (Eq. 4) for the light-independent reactions is [53]:

$$3CO_2 + 9ATP + 6NADPH + 6H^+ \rightarrow C_3H_6O_3\text{-phosphate} + 9ADP + 8P_i + 6NADP^+ + 3H_2O$$
(4)

The process of oxygen generation at the cellular level can be illustrated in Fig. 1 in eukaryotic and prokaryotic microorganisms.

[Figure 1]

On the other hand, the photosynthetic quotient (PQ) is defined as the molar ratio between O_2 released during photolysis of water in the light-dependent reactions and CO_2 absorbed during the light-independent reactions and this varies as a function of the nitrogen source used. This ratio provides more accurate values of the components involved in photosynthesis, such as absorption of CO_2 from measures of primary production of oxygen and generally the value is close to 1.0 [59]. According to Jacob-Lopes et al. [7], the average value of PQ found using the culture *Aphanothece microscopica Nägeli* has been 0.74, result which corroborates the value estimated through the photosynthetic equation, establishing that each 1 g of CO_2 consumed corresponds to a release of 0.73 g O_2.

The values of PQ can change depending on various physiological factors, such as the species of microalgae used, the type of organic molecule produced, the source of nitrogen and the ratio of carbon and nitrogen assimilated [59].

High PQ may be associated with the conversion of nitrate to ammonia, which results in the production of two molecules of O_2 absorbed by N_2 atom. Likewise, the formation of photosynthetic products or organic compounds may also increase the values of PQ. In addition, once the nitrogen source is depleted, the photosynthetic apparatus is affected, influencing the composition of the produced biomass and consequently the PQ [60; 61].

In contrast, low values of PQ are associated with photorespiration. This process is similar to the metabolism of cellular respiration, with the assimilation of O_2 and glucose or other organic substances, and the production of CO_2, energy and water; but it occurs only in the presence of light [62].

Other volatiles compounds released by microalgae

Despite the existence of many studies considering the fraction of non-volatile metabolites, it is also observed that the yield in biomass does not completely fulfill the total carbon balance of the system. One should consider, however, that other products are involved in carbon dioxide conversion in photosynthetic cultures, as exopolymers, carbonates, bicarbonates and, of particular interest volatile organic compounds (VOCs) [7; 8].

The VOCs are unexplored biomolecules, which are influenced by the culture parameters may be of great importance in biochemical elucidation. Are substances of low polarity and high pressure vapor passing freely through biological membranes, being easily emitted to the atmosphere [63]. Some of these compounds, such as halocarbons and aldehydes, are described in photosynthetic cultures of microalgae, which in turn play a role in chemical processes in the atmosphere. Moreover, microalgae are capable of synthesizing specific VOCs, which indicate a great commercial interest in biomolecules from renewable sources such as hydrocarbons and short chain alcohols. These compounds can be used for the biofuels production, representing sustainable solutions for the energy sector and possibly for the traditional petrochemical industry [64; 65].

Microalgae are able to form and release substantial amounts of VOCs belonging to different classes of compounds such as alcohol, esters, hydrocarbons, terpenes, ketones, carboxylic acids and sulfurized compounds, with chains that can contain up to 10 carbon atoms [66; 67]. Some cyanobacteria are known to synthesize alkanes or alkenes that have desirable properties for combustion [68]. Unlike bacteria that need to synthesize genetic alkanes, microalgae need not be engineered for achieving this. Schirmer et al. [69] found in microalgae alkanes such as heptadecane, pentadecane and methyl heptadecane.

The occurrence of VOCs in microalgae is a consequence of their metabolism. Based on this knowledge, can be suggested applicable routes for the synthesis of VOCs both for their better ecological understanding as to their potential commercial applications [70]. Figure 2 represents some volatile compounds obtained in photobioreactor that can be used as oxyfuel.

Once the biosynthetic origin is elucidated, these VOCs can be divided into terpenoids, phenylpropanoids/benzenoids, carbohydrate derivates, fatty acids derivates and amino acid derivates, in addition to specific compounds not represented in those major classes. These compounds could therefore be a source of useful chemical products, based on a nonconventional technological route [71].

In photosynthetic metabolism, so that the CO_2 is converted into carbohydrates, at the end of the Calvin cycle one obtains a pyruvate molecule. It is through this molecule occurs VOCs biosynthesis and moreover, this mechanism will depend on the availability of carbon, nitrogen and energy from the primary metabolism. The formation of compounds from pyruvate can follow the route of terpenoids. With the formation of Acetyl-CoA has the biosynthesis of fatty acids. On arriving at the tricarboxylic acid cycle, they are formed several compounds derived from amino acids. Moreover, at this stage, there is the formation of intermediate amino acids, 2-keto acids. These 2-keto acids can also form through a series of reactions, alcohols, aldehydes, acids and esters [63].

Still, microalgae contain high concentrations of carotenoids, which can be degraded by the same synthetic route fatty acids via Acetyl-CoA reductase enzyme. Using saturated fatty acids is the formation of hydroperoxides which are then converted to aldehydes, such as 1-

hexanal, hexanol and nonanal, which are reduced to alcohols. In this synthesis, may also be unbranched hydrocarbons produced by the action of enzymes. Some species of microalgae are rich in polyunsaturated fatty acids (PUFAs), the which directs the formation of compounds as aldehydes, ketones and alcohols from the lipid degradation. Considering that short chain aldehydes are derivatives of lipid oxidation, aldehydes are formed because of lipid oxidation and enzymatic protein [68].

Is possible to note that some compounds can be produced metabolically (by enzymes present in microalgae) and also by primary degradation compounds, such as lipids and proteins. In this sense, the complete characterization of metabolic pathways of these microorganisms can contribute to the production of specific compounds, besides the obtaining of a wide variety of raw materials of commercial interest [72].

[Figure 2]

PHOTOBIOREACTORS

The cultivation of photosynthetic microorganisms presents a unique demand in industrial biotechnology, which is the appropriate supply of light energy to the cells. This characteristic substantially modify the configuration of photobioreactors for the microalgae cultivation. Besides this process parameter, photobioreactors should present some appropriate requirements in microalgae cultivation, such as nutrient availability, efficient supply of CO_2, temperature control, agitation, mass transfer, ease of control of the reaction conditions and ease of scale up [73].

Phenomena of photo-limiting and photo-inhibition are common in inadequately illuminated cultures, causing significant loss of kinetic performance in photobioreactors [74]. Moreover, one must consider the nature of light incident on the systems. Natural or artificial lighting can be used according to the characteristics required in culture systems. Aspects such as location, seasonal variations, variations over the light photoperiod and photoperiod occurrence of light/dark are the main issues of naturally illuminated systems [75].

The composition of microalgal biomass is predominantly composed of carbon, nitrogen and phosphorus, in proportions of approximately 50, 8 and 1%, respectively. Consequently, the availability of these nutrients is essential to support a robust mobile performance in photobioreactors. At the level of photosynthetic cultivation, the CO_2 is the main carbon source used in cultivations, which may be in their normal or dissociated form (HCO_3^-) [76]. Once the atmospheric CO_2 concentration (0.034%) is not sufficient to support intensive cultivations, this gas is supplied through concentrated stationary sources (compressed carbon dioxide, primary standard and industrial flue gases mixtures) that allow to obtain concentrations the input gases photobioreactors in amounts usually between 3 and 15%. There is a wide expectation on the availability and use of CO_2 originating from industrial combustion gases to the support microalgal photosynthetic cultures [50]. However, the nature of these gases not only contains high concentrations of CO_2, but also the high level of impurities such as CO, CH_4, NO_x, SO_x, H_2 and particulate matter, beyond the temperature of the gases, which normally attains values above 1000 °C, two characteristics that can negatively influence the bio-based processes [77; 78]. Many studies utilizing microalgae presented excellent tolerance to fix the flue gas CO_2 from various industrial sectors, suggesting to its application to mitigate these compounds [79; 80; 81; 82; 83; 84].

Temperature is another important factor associated with microalgal cultures. In general, the optimum growth temperature is in the mesophilic region (25-35), although some thermophilic strains resistant to temperatures in the range of 60 °C. The majority of culture systems assumes the variation in temperature as a result of ambient variation, although the use of heating jackets, serpentines and external heat exchanger can be installed to the control of photobioreactors microalgal temperature [85].

Finally, the agitation is a necessary operation in the cultivation of microorganisms photosynthetic once it ensures that the spatial uniformity of reaction vessels, favoring the light exposure of the cells, heat transfer, and thermal stratification and improve the exchange of gases. A suitable mixture further minimizes the formation of cell aggregates which increase the overall inefficiency of the photobioreactor [86].

Besides these elements, should be considered in the design and construction of cultivation systems the biology of the species, the cost and availability of area, labor, energy, water, nutrients, climatic conditions and the characteristics desired in the final product. Thus, the photobioreactors for microalgae cultivation and for bioremediation of polluting compounds must be sized based on some criteria, such as high efficiency of utilization of light energy, have efficient mixing system and control the reaction conditions, low stress hydrodynamic the cells and ease of scaling [87].

In terms of configuration, photobioreactors can be classified into open or closed systems [88]. For scale-up issues and capita and operational costs, open systems dominate the overall operating large scale processes based on microalgae. These cultivation systems have two main configurations: circular ponds and raceway tanks. Although simple in construction, such systems are inefficient as reaction vessels because of the limited transfer of light energy and carbon dioxide, usually leading to low productivities. These systems have as main limitations higher water evaporation rates, producing significant variations in the composition of the culture medium, requirement of wide areas for the construction, operational control difficulties, limited light energy transfers and dioxide carbon, resulting in low productivity, besides high risk of contamination, not allowing recovery of the exhaust gases [53; 89].

An alternative to open photobioreactors, are closed systems, which allow greater control of the conditions of biological reaction, besides enabling a variety of configurations and significantly increase the photosynthetic rates. On the other hand, the construction of closed systems has higher cost, since they are operationally more complex and difficult stagger. The optimization of these systems must be made according to the species of microorganisms used because the physiological and growth characteristics that will determine the proper performance of the systems. In this sense, three main configurations dominate arrangements of closed photobioreactors, tubular systems, flat plates and the vertical columns [90].

With a special focus on tubular photobioreactors, these are considered to be more promising for the large scale production of bio-products obtained from the cultivation of microalgae, with the simultaneous removal of CO_2 [91]. However, the dissolved oxygen accumulation in this type of system can occur due to water dissociation activity of photosystem II, excessively producing oxygen during photosynthesis. As a consequence, can generate photo-oxidative damage to cells, reducing the efficiency photosynthetic [92]. For this reason, considering these problems, the removal and utilization of the accumulated oxygen and their integration in processes that require the enrichment of this compound as oxidizer are two potentials examples to show their applicability in industrial bioprocess and economically viable.

PROCESS INTEGRATION

The process integration can be defined as a series of techniques and methods in the design of integrated production systems that combine several unit operations inside an industrial plant [93]. An integrated process relies on material recycling to minimize raw material use and emissions, and to make extensive use of heat recovery, improving energy efficiency. This approach is a relatively new term and has been widely implemented in most industrial production processes [94; 95].

Therefore, a reduction in operating costs of existing facilities (*retrofit*) is expected. As for the new processes (*newbuilt*), the design project may have lower investment in operating costs. Moreover, there is the replacement of large equipment which requires high energy demand by clean technology; that is, smaller, more secure and efficient devices [96].

As an alternative to the traditional processes, some approaches have been proposed to replace the processes using fossil inputs for bio-based processes, such as processes mediated by microalgae, that meet the principles of green engineering and represent the key to sustainable industrial development. The bioprocess integration is a suitable and innovative strategy to comply with these requirements [97; 98; 99]. Figure 3 represents a possible strategy of process integration of the bio-based in the carbon dioxide conversion in photobioreactors integrated into an industrial oxycombustion process.

This technological route has, as a direct consequence, lowered its overall energy consumption of the process, which implies the reduction of fossil raw materials, potable water consumption and minimizing emissions. Additionally, a higher efficiency is attained when there is the integration of these bioprocesses, impacting on the increased flexibility and the control and intensification of the process [95; 100]. Several integrated processes have been developed and some possibilities are considered through the reuse, the recovery and the possibly recycling of surpluses mass, effluents, water and energy for industrial application [101].

A specific application of sustainable processes using microalgae is focused on mass integration. Currently, the efficient use of resources is performed in several production plants. Therefore, the mass of integration adds value to industry byproducts, which can be used as adducts in other processes. Applied to the cultivation of microalgae, biomass contributes to the numerous value-added products, creating the idea of biorefinery [102].

On the other hand, there is the possibility of integration of gaseous effluents. The use of CO_2 and NO_x from industrial processes of combustion allows input of inorganic carbon and nitrogen in photosynthetic cultures. This type of integration is considered an efficient bioprocess, allowing direct biofixation CO_2 from stationary sources [103].

Considering that the microalgae can be grown heterotrophically, the supply of essential nutrients such as carbon, nitrogen and phosphorus can be given efficiently by integrating liquid effluents. Thus, besides to reducing costs during the process of cultivation of these microorganisms, the effluent is treated in an appropriate way [99]. Both effluents integration strategies also allow the reuse of the thermal energy contained in waste, which can be used in the maintenance of the medium temperature culture in the mesophilic range. This type of integration is highly dependent on the type of industrial waste [104].

In parallel to the integration of liquid effluents, it is also possible to integrate water through its reuse. Water is a basic resource in various industrial processes and are extremely used. In this case, water can be reused directly in other processes without being treated (i.e., cooling equipment) considering that the contaminants do not interfere in the process; it also can be regenerated through treatment for partial removal of contaminants and later reuse; and it can still be recycled, where there is partial removal of contaminants to be reused in the same process generated [105]. Therefore, the microalgae can play a valuable role in the treatment of waste and contribute to the water reuse, as well as nutrients recycling [53].

In conclusion, the integration of energy can be employed to minimize energy consumption and to maximize heat recovery. It may also be used internally in the process. This approach is thermodynamic oriented cycles in order to increase the thermal efficiency in industrial combustion processes and, thereby, to reduce costs of the plant [77; 106]. The different strategies of integration of the bio-based processes are considered important approaches towards sustainable development. When it obtains an end product in high volumes and sold at low prices, these technological routes significantly contribute to the bioeconomy of the future.

[Figure 3]

REFERENCES

[1] International Panel on Climate Change (2014). Climate change 2014: Mitigation of Climate Change. Contribution of Working Group III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

[2] International Energy Agency (2015). Energy and climate change. World Energy Outlook Special Report. OECD/IEA, Paris.

[3] Bu, C.; Gómez-Barea, A.; Chen, X.; Leckner, B.; Liu, D.; Pallarès, D.; Lu, P. (2016). Effect of CO_2 on oxy-fuel combustion of coal-char particles in a fluidized bed: Modeling and comparison with the conventional mode of combustion. *Applied Energy* 177, 247-259.

[4] Cheah, W. Y.; Ling, T. C.; Juan, J. C.; Lee, D-J.; Chang, J-S.; Show, P. L. (2016). Biorefineries of carbon dioxide: From carbon capture and storage (CCS) to bioenergies production. *Bioresource Technology* 215, 346-356.

[5] Escudero, A. I.; Espatolero, S.; Romeo, L. M. (2016). Oxy-combustion power plant integration in an oil refinery to reduce CO_2 emissions. *International Journal of Greenhouse Gas Control* 45, 118-129.

[6] International Energy Agency (2011). Cost and performance of carbon dioxide capture from power generation. OECD/IEA, Paris.

[7] Jacob-Lopes, E.; Scoparo, C. H. G.; Queiroz, M. I.; Franco, T. T. (2010). Biotransformations of carbon dioxide in photobioreactors. *Energy Conversion and Management* 51, 894-900.

[8] Borowitzka, M. A. (2013). High-value products from microalgae their development and commercialization. *Journal Applied Phycology* 25, 743-756.

[9] Jajesniak, P.; Ali, H. E. M. O.; Wong, T. S. (2014). Carbon Dioxide Capture and Utilization using Biological Systems: Opportunities and Challenges. *Bioprocessing and Biotechniques* 4, 3.

[10] Cuéllar-Franca, R. M.; Azapagic, A. (2015). Carbon capture, storage and utilization technologies: A critical analysis and comparison of their life cycle environmental impacts. *Journal of CO_2 utilization* 9, 82-102.

[11] International Panel on Climate Change (2005). Special Report on Carbon Dioxide Capture and Storage, United Kingdom and New York, 107-171.

[12] International Energy Agency (2013). Technology roadmap: carbon capture and storage. OECD/IEA, Paris.

[13] International Energy Agency (2016). Tracking Clean Energy Progress 2016, edition Energy Technology Perspectives (ETP 2016). OECD/IEA, Paris.

[14] National Energy Technology Laboratory (2016). CO_2 utilization focus area, 2016. [Acessed: 10.08.16] Avaiable from: URL: https://www.netl.doe.gov/research/coal/carbon-storage/research-and-development/co2-utilization.

[15] Bruhn, T.; Naims, H.; Olfe-Kräutlein, B. (2016). Separating the debate on CO_2 utilisation from carbon capture and storage. *Environmental Science & Policy* 60, 38-43.

[16] Oh, S. T.; Martin, A. (2016). Thermodynamic efficiency of carbon capture and utilisation in anaerobic batch digestion process. *Journal of CO_2 utilization* 16, 182-193.

[17] Rezvani, S.; Moheimani, N. R.; Bahri, P. A. (2016). Techno-economic assessment of CO_2 bio-fixation using microalgae in connection with three different state-of-the-art power plants. *Computers and Chemical Engineering* 84, 290-301.

[18] Moreira, D.; Pires, J. C. M. (2016). Atmospheric CO_2 capture by algae: Negative carbon dioxide emission path. *Bioresource Technology* 215, 371-379.

[19] Abraham, B. M.; Asbury, J. G.; Lynch, E. P.; Teotia, A. P. S. (1982). Coal-oxygen process provides CO_2 for enhanced recovery. *Oil and Gas Journal* 80, 68-70.

[20] Stanger, R.; Wall, T. (2011). Sulphur impacts during pulverized coal combustion in oxy-fuel technology for carbon capture and storage. *Progress in Energy and Combustion Science* 37, 69-88.

[21] Chen, L.; Yong, S. Z.; Ghoniem, A. F. (2012). Oxy-fuel combustion of pulverized coal: Characterization, fundamentals, stabilization and CFD modeling. *Progress in Energy and Combustion Science* 38, 156-214.

[22] Wall, T.; Liu, Y.; Spero, C.; Elliott, L.; Khare, S.; Rathnam, R.; Zeenathal, F.; Moghtaderi, B.; Buhre, B.; Sheng, C.; Gupta, R.; Yamada, T.; Makino, K.; Yu, J. (2009). An overview on oxyfuel coal combustion – State of the art research and technology development. *Chemical Engineering Research and Design* 87, 1003-1016.

[23] Irfan, M. F.; Arami-Niya, A.; Chakrabarti, M. H.; Daud, W. M. A. W.; Usman, M. R. (2012). Kinetics of gasification of coal, biomass and their blends in air (N_2/O_2) and different oxy-fuel (O_2/CO_2) atmospheres. *Energy* 37, 665-672.

[24] Toftegaard, M. B.; Brix, J.; Jensen, P. A.; Glarborg, P.; Jensen, A. D. (2010). Oxy-fuel combustion of solid fuels. *Progress in Energy and Combustion Science* 36, 581-625.

[25] Spigarelli, B. P.; Kawatra, S. K. (2013). Opportunities and challenges in carbon dioxide capture. *Journal of CO_2 utilization* 1, 69-87.

[26] Carrasco-Maldonado, F.; Spörl, R.; Fleiger, K.; Hoenig, V.; Maier, J.; Scheffknecht, G. (2016). Oxy-fuel combustion technology for cement production – State of the art research and technology development. *International Journal of Greenhouse Gas Control* 45, 189-199.

[27] Leung, D. Y. C.; Caramanna, G.; Maroto-Valer, M. M. (2014). An overview of current status of carbon dioxide capture and storage technologies. Renewable and Sustainable *Energy Reviews* 39, 426-443.

[28] Griffiths, J. F.; Barnard, J. A. (1995). *Flame and Combustion*. 3rd ed, Chapman and Hall, London, UK.

[29] Hende, S. V. D.; Vervaeren, H.; Boon, N. (2012). Flue gas compounds and microalgae: (Bio-)chemical interactions leading to biotechnological opportunities. *Biotechnology Advances*, 30, 1405-1424.

[30] Scheffkecht, G.; Al-Makhadmeh, L.; Schnell, U.; Maier, J. (2011). Oxy-fuel coal combustion – A review of the current state-of-the-art. *International Journal of Greenhouse Gas Control* 5, 16-35.

[31] Buhre, B. J. P.; Elliott, L. K.; Sheng, C. D.; Gupta, R. P.; Wall, T. F. (2005). Oxy-fuel combustion technology for coal-fired power generation. *Progress in Energy and Combustion Science* 31, 283–307.

[32] Yin, C.; Yan, J. (2016). Oxy-fuel combustion of pulverized fuels: Combustion fundamentals and modeling. *Applied Energy* 162, 742-762.

[33] Stanger, R.; Wall, T.; Spörl, R.; Paneru, M.; Grathwohl, S.; Weidmann, M.; Scheffknecht, G.; McDonald, D.; Myöhänen, K.; Ritvanen, J.; Rahiala, S.; Hyppänen, T.; Mletzko, J.; Kather, A.; Santos, S. (2015). Oxyfuel combustion for CO_2 capture in power plants. *International Journal of Greenhouse Gas Control* 40, 55-125.

[34] NIST. (2016). Chemistry WebBook: thermophysical properties of fluid systems. [Acessed: 28.08.16] Avaiable from: URL: http://webbook.nist.gov/chemistry/.

[35] Baukal, C. E. (2013). Oxygen-enhanced combustion, Second Edition, CRC Press.

[36] Olajire, A. A. (2010). CO_2 capture and separation technologies for end-of-pipe applications – A review. *Energy* 35, 2610-2628.

[37] Belaissaoui, B.; Moulec, Y. L.; Hagi, H.; Favre, E. (2014). Energy efficiency of oxygen enriched air production technologies: Cryogenic vs membranes. *Separation and Purification Technology*, 125, 142-150.

[38] Aneke, M.; Wang, M. (2015). Potential for improving the energy efficiency of cryogenic air separation unit (ASU) using binary heat recovery cycles. *Applied Thermal Engineering* 81, 223-231.

[39] Riboldi, L.; Bolland, O. (2015). Evaluating Pressure Swing Adsorption as a CO_2 separation technique in coal-fired power plants. *International Journal of Greenhouse Gas Control* 39, 1-16.

[40] Vinson, D. R. (2006). Air separation control technology. *Computers and Chemical Engineering* 30, 1436-1446.

[41] Figueroa, J. D.; Fout, T.; Plasynski, S.; McIlvried, H.; Srivastava, R. D. (2008). Advances in CO_2 capture technology – The U.S. Department of Energy's Carbon Sequestration Program. *International Journal of Greenhouse Gas Control* 2, 9-20.

[42] Mondal, M. K.; Balsora, H. K.; Varshney, P. (2012). Progress and trends in CO_2 capture/separation technologies: A review. *Energy* 46, 431-441.

[43] Kosinov, N.; Gascon, J.; Kaptejin, F.; Hensen, E. J. M. (2016). Recent developments in zeolite membranes for gas separation. *Journal of Membrane Science* 499, 65-79.

[44] Hashim, S. S.; Mohamed, A. R.; Bhatia, S. (2011). Oxygen separation from air using ceramic-based membrane technology for sustainable fuel production and power generation. *Renewable and Sustainable Energy Reviews* 15, 1284-1293.

[45] Tranier, J-P.; Dubettier, R.; Darde, A.; Perrin, N. (2011). Air separation, flue gas compression and purification units for oxy-coal combustion systems. *Energy Procedia* 4, 966-971.

[46] Luis, P.; Gerven, T. V.; Bruggen, B. V. D. (2012). Recent developments in membrane-based technologies for CO_2 capture. *Progress in Energy and Combustion Science* 38, 419-448.

[47] Zhang, Y.; Sunarso, J.; Liu, S.; Wang, R. (2013). Current status and development of membranes for CO_2/CH_4 separation: A review. *International Journal of Greenhouse Gas Control* 12, 84-107.

[48] Zhao, B.; Su, Y. (2014). Process effect of microalgal-carbon dioxide fixation and biomass production: A review. *Renewable and Sustainable Energy Reviews* 31, 121-132.

[49] Williams, P. J. B.; Laurens, L. M. L. (2010). Microalgae as biodiesel & biomass feedstocks: Review and analysis of the biochemistry, energetics & economics. *Energy & Environmental Science* 3, 554-590.

[50] Cheah, W. Y.; Show, P. L.; Chang, J-S.; Ling, T. C.; Juan, J. C. (2015). Biosequestration of atmospheric CO_2 and flue gas-containing CO_2 by microalgae. *Bioresource Technology* 184, 190-201.

[51] Checchetto, V.; Teardo, L.; Carraretto, L.; Formentin, E.; Bergantino, E.; Giacometti, G. M.; Szabo, I. (2013). Regulation of photosynthesis by ion channels in cyanobacteria and higher plants. *Biophysical Chemistry* 182, 51-57.

[52] Calvin, M.; Benson, A. A. (1948). The Path of Carbon in Photosynthesis. *Science* 107, 476-480.

[53] Razzak, S. A.; Hossain, M. M.; Lucky, R. A.; Bassi, A. S.; Lasa, H. D. (2013). Integrated CO_2 capture, wastewater treatment and biofuel production by microalgae culturing – A review. *Renewable and Sustainable Energy Reviews* 27, 622-653.

[54] Carr, N. G.; Whitton, B. A. (1982). The biology of cyanobacteria. Univ. California Press, 19.

[55] Bergene, T. (1996). The efficiency and physical principles of photolysis of water by microalgae. *International Journal of Hydrogen Energy* 21, 189-194.

[56] Heldt, H-W; Piechulla, B. (2011). *Plant Biochemistry*. 4ª ed. German edition: Academic Press in an imprint of Elsevier, 618.

[57] Fay, P. (1983). The Blue-Greens (Cyanophyta-Cyanobacteria). 5ª ed. London: Edward Arnold Publishers, Studies in Biology 160, 88.

[58] Taddei, D.; Cuet, P.; Frouin, P.; Esbelin, C.; Clavier, J. (2008). Low community photosynthetic quotient in coral reef sediments. *Comptes Rendus Biologies* 331, 668-677.

[59] Smith, L. M.; Silver, C. M.; Oviatt, C. A. (2012). Quantifying variation in water column photosynthetic quotient with changing field conditions in Narragansett Bay, RI, USA. *Journal of plankton research* 34, 437-442.

[60] Burris, J. E. (1981). Effects of oxygen and inorganic carbon concentrations on the photosynthetic quotients of marine algae. *Marine Biology* 65, 215-219.

[61] Eriksen, N. T.; Riisgård, F. K.; Gunther, W. S.; Iversen, J. J. L. (2007). On-line estimation of O_2 production, CO_2 uptake, and growth kinetics of microalgal cultures in a gas-tight photobioreactor. *Journal Applied Phycology* 19, 161-174.

[62] Hoefnagel, M. H. N.; Atkin, O. K.; Wiskich, J. T. (1998). Interdependence between chloroplasts and mitochondria in the light and the dark. *Biochimica et Biophysica Acta*, 1366, 235-255.

[63] Dudareva, N.; Klempien, A.; Muhlemann, J. K.; Kaplan, I. (2013). Biosynthesis, function and metabolic engineering of plant volatile organic compounds. *New Phytologist* 198, 16-32.

[64] Keppler, F.; Eiden, R.; Niedan, V.; Pracht, J.; Schöler, H. F. (2000). Halocarbons produced by natural oxidation processes during degradation of organic matter. *Nature*, 403, 298-301.

[65] Eroglu, E.; Melis, A. (2010). Extracellular terpenoid hydrocarbon extraction and quantitation from the green microalgae *Botryococcus braunii* var. Showa. *Bioresource Technology* 101, 2359-2366.

[66] Sun, S-M.; Chung, G-H.; Shin, T-S. (2012). Volatile compounds of the green alga, *Capsosiphon fulvescens*. *Journal of Applied Phycology* 24, 1003-1013.

[67] Muñoz, J.; Mudge, S. M.; Sandoval, A. (2004). Effects of ionic strength on the production of short chain volatile hydrocarbons by *Dunaliella salina* (Teodoresco). *Chemosphere* 54, 1267-1271.

[68] Lau, N-S.; Matsui, M.; Abdullah, A. A-A. (2015). Cyanobacteria: Photoautotrophic Microbial Factories for the Sustainable Synthesis of Industrial Products. *BioMed Research International* 2015, 1-9.

[69] Schirmer, A.; Rude, M. A.; Li, X.; Popova, E.; Cardayre, S. B. (2010). Microbial Biosynthesis of Alkanes. *Science* 329, 559-562.

[70] Zepka, L. Q.; Santos, A. B.; Fernandes, A. S.; Wagner, R.; Queiroz, M. I.; Jacob-Lopes, E. (2015). Biogeneration of volatile compounds from microalgae. Chapter: *Flavour Generation*, 257-260.

[71] Santos, A. B.; Fernandes, A. S.; Wagner, R.; Jacob-Lopes, E.; Zepka, L. Q. (2016). Biogeneration of volatile organic compounds produced by *Phormidium autumnale* in heterotrophic bioreactor. *Journal of Applied Phycology* 28, 1561-1570.

[72] Draaisma, R. B.; Wijffels, R. H.; Slegers, P. M. E.; Brentner, L. B.; Roy, A.; Barbosa, M. J. (2013). Food commodities from microalgae. *Current Opinion in Biotechnology* 24, 169-177.

[73] Singh, R. N.; Sharma, S. (2012). Development of suitable photobioreactor for algae production – A review. *Renewable and Sustainable Energy Reviews* 16, 2347-2353.

[74] Abu-Ghosh, S.; Fixler, D.; Dubinsky, Z.; Iluz, D. (2016). Flashing light in microalgae biotechnology. *Bioresource Technology* 203, 357-363.

[75] Jacob-Lopes, E.; Scoparo, C. H. G.; Lacerda, L. M. C. F.; Franco, T. T. (2009). Effect of light cycles (night/day) on CO_2 fixation and biomass production by microalgae in photobioreactors. *Chemical Engineering and Processing: Process Intensification*, 48, 306-310.

[76] Markou, G.; Vandamme, D.; Muylaert, K. (2014). Microalgal and cyanobacterial cultivation: The supply of nutrients. *Water Research* 65, 186-202.

[77] Jacob-Lopes, E.; Franco, T. T. (2013). From oil refinery to microalgal biorefinery. *Journal of* CO_2 *utilization* 2, 1-7.

[78] Maity, J. P.; Bundschuh, J.; Chen, C-Y.; Bhattacharya, P. (2014). Microalgae for third generation biofuel production, mitigation of greenhouse gas emissions and wastewater treatment: Present and future perspectives – A mini review. *Energy* 78, 104-113.

[79] Douskova, I.; Doucha, J.; Livansky, K.; Machat, J.; Novak, P.; Umysova, D.; Zachleder, V.; Vitova, M. (2009). Simultaneous flue gas bioremediation and reduction of microalgal biomass production costs. *Applied Microbiology and Biotechnology* 82, 179-185.

[80] Borkenstein, C. G.; Knoblechner, J.; Frühwirth, H.; Schagerl, M. (2011). Cultivation of *Chlorella emersonii* with flue gas derived from a cement plant. *Journal Applied Phycology* 23, 131-135.

[81] Jiang, Y.; Zhang, W.; Wang, J.; Chen, Y.; Shen, S.; Liu, T. (2013). Utilization of simulated flue gas for cultivation of *Scenedesmus dimorphus*. *Bioresource Technology*, 128, 359-364.

[82] Zhao. B.; Su, Y.; Zhang, Y.; Cui, G. (2015). Carbon dioxide fixation and biomass production from combustion flue gas using energy microalgae. *Energy* 89, 347-357.

[83] Lara-Gil, J. A.; Senés-Guerrero, C.; Pacheco, A. (2016). Cement flue gas as a potential source of nutrients during CO_2 mitigation by microalgae. *Algal Research* 17, 285-292.

[84] Li, T.; Xu, G.; Rong, J.; Chen, H.; He, C.; Giordano, M.; Wang, Q. (2016). The acclimation of Chlorella to high-level nitrite for potential application in biological NO_x removal from industrial flue gases. *Journal of Plant Physiology* 195, 73-79.

[85] Ho, S-H.; Ye, X.; Hasunuma, T.; Chang, J-S.; Kondo, A. (2014). Perspectives on engineering strategies for improving biofuel production from microalgae – A critical review. *Biotechnology Advances*, 32, 1448-1459.

[86] Borowitzka, M. A. (1999). Commercial production of microalgae: ponds, tanks, tubes and fermenters. *Journal of Biotechnology* 70, 313-321.

[87] Wang, B.; Lan, C. Q.; Horsman, M. (2012). Closed photobioreactors for production of microalgal biomasses. *Biotechnology Advances* 30, 904-912.

[88] Huang, G.; Chen, F.; Wei, D.; Zhang, X.; Chen, G. (2010). Biodiesel production by microalgal biotechnology. *Applied Energy*, 87, 38-46.

[89] Fernandes, B. D.; Mota, A.; Teixeira, J. A.; Vicente, A. A. (2015). Continuous cultivation of photosynthetic microorganisms: Approaches, applications and future trends. *Biotechnology Advances* 33, 1228-1245.

[90] Brennan, L.; Owende, P. (2010). Biofuels from microalgae – A review of technologies for production, processing, and extractions of biofuels and co-products. *Renewable and Sustainable Energy Reviews* 14, 557-577.

[91] Jacob-Lopes, E.; Scoparo, C. H. G.; Franco, T. T. (2008). Rates of CO_2 removal by *Aphanothece microscopica Nägeli* in tubular photobioreactors. *Chemical Engineering and Processing* 47, 1365-1373.

[92] Molina, E.; Fernández, J.; Acién, F. G.; Chisti, Y. (2001). Tubular photobioreactor design for algal cultures. *Journal of Biotechnology* 92, 113-131.

[93] International Energy Agency (2000). Tutorial on Process Integration. A Process Integration Primer. SINTEF Energy Research.

[94] Friedler, F. (2010). Process integration, modelling and optimisation for energy saving and pollution reduction. *Applied Thermal Engineering* 30, 2270-2280.

[95] Baldea, M. (2015). From process integration to process intensification. *Computers and Chemical Engineering* 81, 104-114.

[96] El-Halwagi, M. M. (1998). Pollution prevention through process integration. *Clean Products and Processes* 1, 5-19.

[97] Wohlgemuth, R. (2009). The locks and keys to industrial biotechnology. *New Biotechnology* 25, 204-213.

[98] Zydney, A. L. (2015). Perspectives on integrated continuous bioprocessing – opportunities and challenges. *Current opinion in Chemical Engineering* 10, 8-13.

[99] Francisco, E. C.; Franco, T. T.; Zepka, L. Q.; Jacob-Lopes, E. (2015). From waste-to-energy: the process integration and intensification for bulk oil and biodiesel production by microalgae. *Journal of Environmental Chemical Engineering* 3, 482-487.

[100] Sanders, J. P. M.; Clark, J. H.; Harmsen, G. J.; Heeres, H. J.; Heijnen, J. J.; Kersten, S. R. A.; Swaaij, W. P. M. van; Moulijin, J. A. (2012). Process intensification in the future production of base chemicals from biomass. *Chemical Engineering and Processing: Process Intensification* 51, 117-136.

[101] Klemeš, J. J. (2013). Handbook of Process Integration (PI) – Minimisation of Energy and Water Use, Waste and Emissions. Woodhead Publishing Limited.

[102] Fresewinkel, M.; Rosello, R.; Wilhelm, C.; Kruse, O.; Hankamer, B.; Posten, C. (2014). Integration in microalgal bioprocess development: Design of efficient, sustainable, and economic processes. *Engineering in Life Sciences* 14, 560-573.

[103] Moncada, J. B.; Aristizábal, V. M.; Cardona, C. A. A. (2016). Design strategies for sustainable biorefineries. *Biochemical Engineering Journal, In Press.*

[104] Aziz, M.; Takuya, O.; Takao, K. (2014). Integration of energy-efficient drying in microalgae utilization based on enhanced process integration. *Energy* 70, 307-316.

[105] El-Halwagi, M. M. (2006). Process Integration. Process Systems Engineering, *Elsevier Science*, Amsterdam, 1st Edition.

[106] Klemeš, J. J.; Friedler, F.; Bulatov, I.; Varbanov, P. S. (2011). Sustainability in the Process Industry-Integration and Optimization. McGraw-Hill, New York.

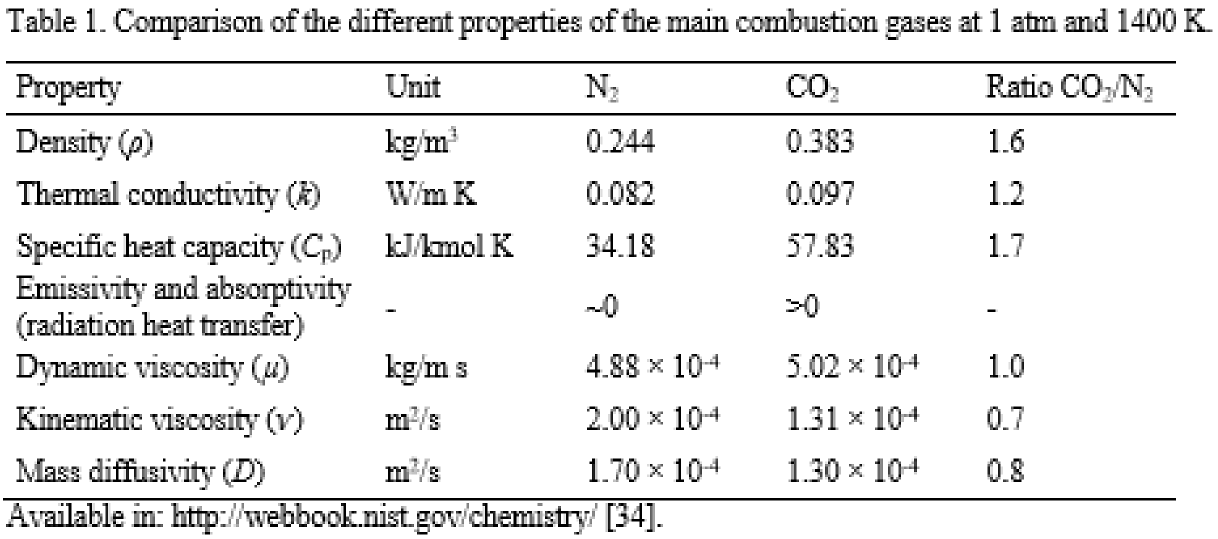


Table 1. Comparison of the different properties of the main combustion gases at 1 atm and 1400 K.

Property	Unit	N_2	CO_2	Ratio CO_2/N_2
Density (ρ)	kg/m^3	0.244	0.383	1.6
Thermal conductivity (k)	W/m K	0.082	0.097	1.2
Specific heat capacity (C_p)	kJ/kmol K	34.18	57.83	1.7
Emissivity and absorptivity (radiation heat transfer)	-	~0	>0	-
Dynamic viscosity (μ)	kg/m s	4.88×10^{-4}	5.02×10^{-4}	1.0
Kinematic viscosity (ν)	m^2/s	2.00×10^{-4}	1.31×10^{-4}	0.7
Mass diffusivity (D)	m^2/s	1.70×10^{-4}	1.30×10^{-4}	0.8

Available in: http://webbook.nist.gov/chemistry/ [34].

[Table 1]

Table 2. Current technologies in the production of oxygen by air separation.

Processes	Technology	Advantages	Disadvantages	Purity O_2 (vol.%)	Status	References
Cryogenic distillation	ASU (Air Separation Unit)	• More economical than other technologies • Capability to produce high concentrations of oxygen	• High cost • Low purity oxygen • High energy demand	30-99	Mature	[45; 38; 37]
Adsorption	PSA or VPSA (Pressure or Vacuum Swing Adorption)	• Appropriate for producing small volumes of O_2 (small to medium-sized plant)	• High energy demand • High cost	90-95	Semi-mature	[37; 39]
Absorption	Chemical and/or physical	• Reduced energy demand compared to cryogenic processes	• System corrosion due to the solvents used (economic losses) • Operational limitations • Using of toxic solvents • High cost	99	Semi-mature	[46; 42; 27]
Membranes	Organic Inorganic Porous Non-porous	• Simple process design • Ease of scale-up	• Production of low oxygen concentrations • High cost of producing oxygen in large scale • Low permeability, selectivity, resistance and thermal stability	25-40	Developing	[47; 43]

[Table 2]

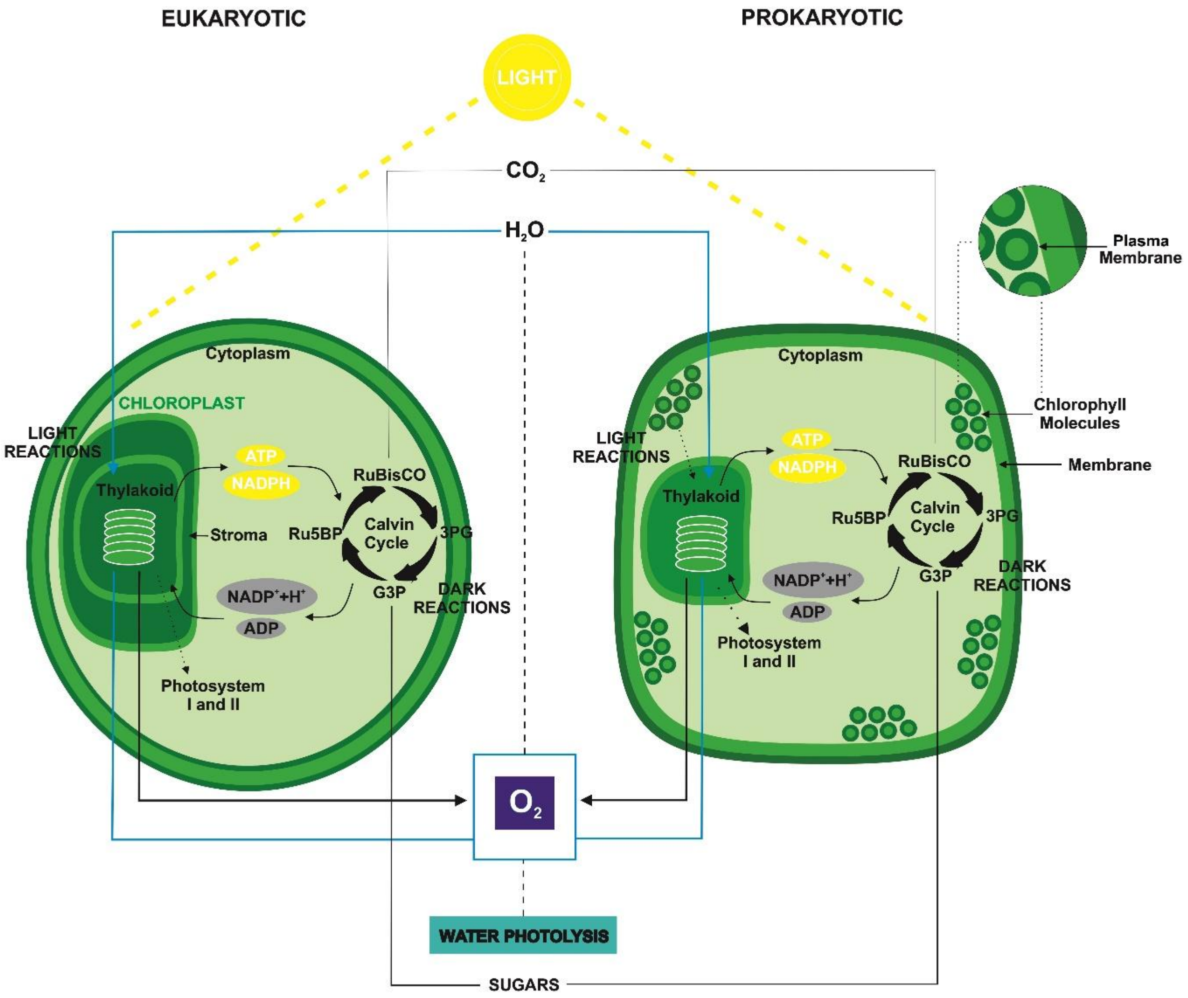


Figure 1. Overview of the oxygen generation in eukaryotic and prokaryotic microorganisms.

[Figure 1]

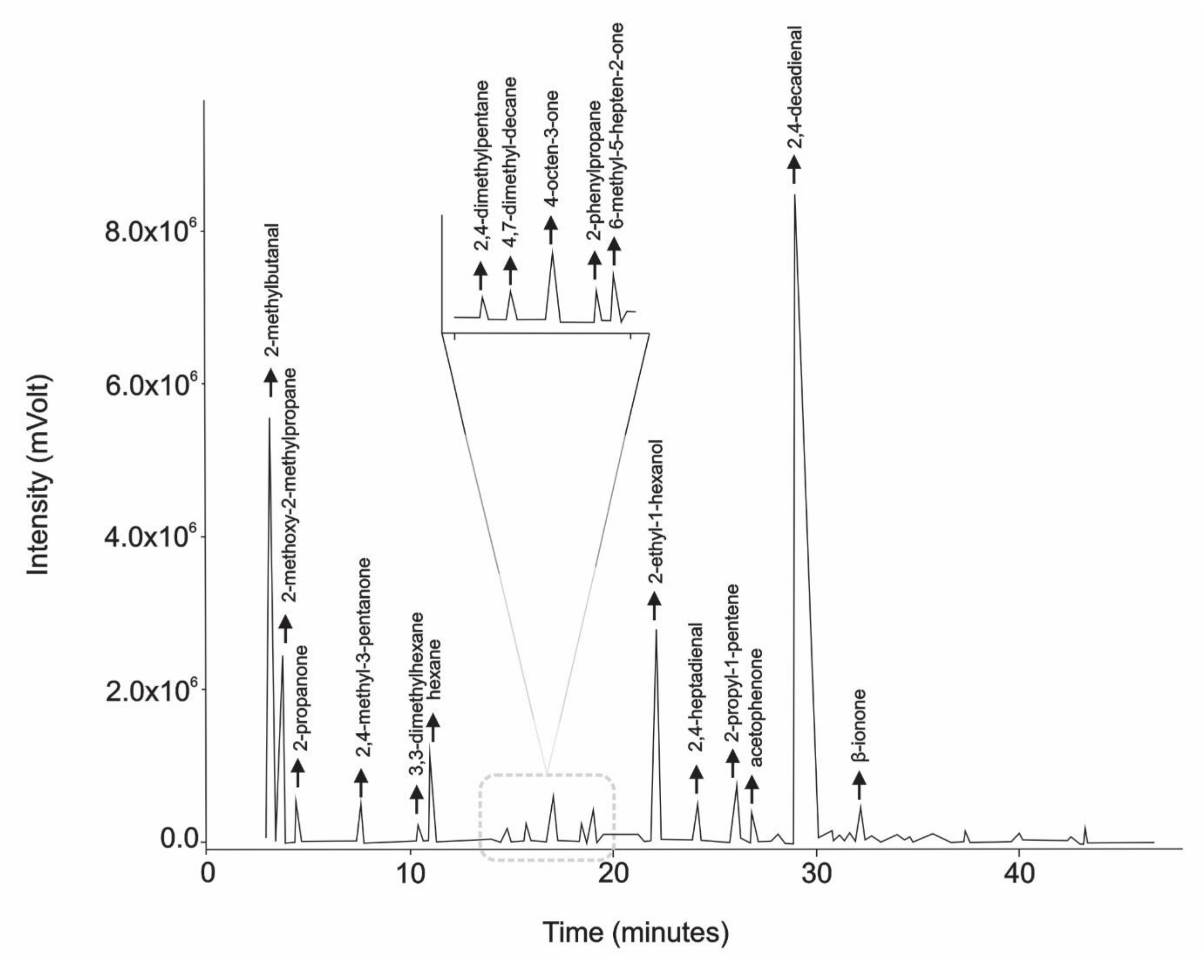


Figure 2. Characterization of volatile organic compounds produced by *Phormidium autumnale* generated from photobioreactor [70].

[Figure 2]

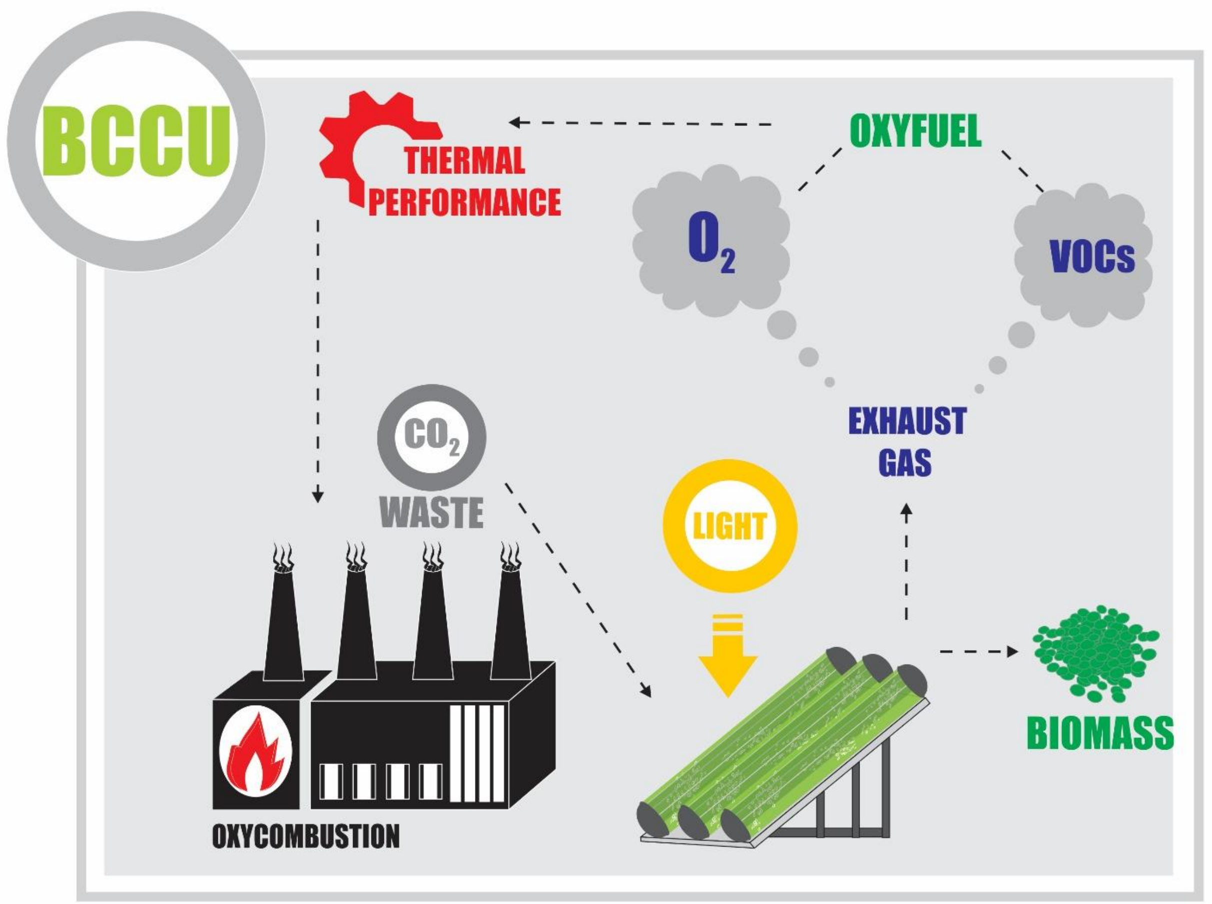


Figure 3. Conceptual diagram of process integration.

[Figure 3]

2. MANUSCRITO 2

Photobioreactors and Oxycombustion: A Mini-Review on the Process Integration

Ihana Aguiar Severo, Mariany Costa Deprá, Leila Queiroz Zepka e Eduardo Jacob-Lopes

Artigo de Revisão publicado na revista Journal of Chemical Engineering & Process Technology, volume 7, número 4, páginas 7-4, 2016.

Journal of
Chemical Engineering & Process Technology

Severo et al., J Chem Eng Process Technol 2016, 7:4
DOI: 10.4172/2157-7048.1000310

Short Communication Open Access

Photobioreactors and Oxycombustion: A Mini-Review on the Process Integration

Severo IA, Deprá MC, Zepka LQ and Jacob-Lopes E*

Department of Food Science and Technology, Federal University of Santa Maria, Santa Maria, RS, Brazil

Abstract

Some strategies for reducing greenhouse gas emissions to the atmosphere, especially carbon dioxide, have been gaining growing attention by researchers with the aim of develop new technologies that are energy-efficient and economically viable in industrial processes. In this sense, the aim of this paper is to provide a mini review of industrial systems of oxycombustion integrated in microalgal photobioreactors. Divided into four distinct topics, the paper discusses issues related to biological carbon capture and utilization, the elements of oxycombustion technology, the reuse of exhaust gases from photobioreactor and the process integration, summarizing a range of useful strategies directed to the industrial sustainable development.

Keywords: Biological carbon capture and utilization; Bio-oxycombustion; Oxyfuel; Microalgae

Introduction

Concerns over global climate change lead efforts on developing technologies to reduce carbon dioxide emissions from anthropogenic activities. Technological solutions to this problem includes research and development systems and alternative techniques that are economical and energy-efficient in industrial processes, enabling mitigation of polluting compounds [1]. The oxycombustion has proven to be one of the best forms of carbon capture from stationary sources, due to its ability to mitigate emissions and improve combustion performance. This technological route is based on the replacement of the air used in combustion processes by oxygen-rich atmospheres. As a consequence, there is a gain in thermal capacity, resulting in greater overall efficiency of equipment and reducing fossil fuel consumption [2]. Despite the oxycombustion be an attractive technology, this approach has faced significant difficulties in implementation related to the high cost and the purity of the oxygen produced, unfeasible their application in industrial scale [3].

These issues can be circumvented through the photobioreactors, using photosynthetic microorganisms, as the microalgae, which have as a metabolic co-product the O_2 supported by the water photolysis reactions. Additionally, the bioprocess mediated by microalgae produce in parallel numerous volatile organic compounds that have considerable energy content, besides releasing substantial concentrations of CO_2 in exhaust gases, serving as N_2 diluent [4,5].

Several technologies have been proposed for reducing CO_2 emission focusing on the capture, storage and/or utilization of carbon [6]. The biological carbon capture and utilization (BCCU) is a highly potential technology for industrial application, because it converts biologically carbon dioxide with their integration into a oxycombustion process [7]. Therefore, the bio-oxycombustion technique is discussed in this mini review, including fuels derived from biological conversion processes of greenhouse gases through photosynthesis.

Biological Carbon Capture and Utilization

Global emissions of carbon dioxide reach more than 20 billion tons per year. In contrast, it is estimated that such emissions should be reduced by at least 50% to mitigate the increase in global temperature. In this scenario, the oxycombustion technology have been proposed as a viable option to capture approximately 90% CO_2 in large point sources of emissions, consisting of compression stages, capture, transport and storage or utilization [8]. Complementing the carbon capture and storage (CCS) and carbon capture and utilization (CCU) technologies, more recently the BCCU technology represents a potential strategy for CO_2 capture from polluting sources. This technological route consists of the biological conversion of CO_2 into biomass through photosynthesis, for the extraction of high value-added products. In this context, the microalgae-based processes, for example, present high conversion rates, which provide an attractive form of BCCU, recycling the CO_2 from different industrial processes [7,9].

Elements of Oxycombustion Technology

The use of pure oxygen as oxidant in combustion processes is a relatively new approach to the greenhouse gases mitigation. In oxycombustion, the fuel is burnt in an atmosphere enriched with high purity oxygen and free nitrogen, differing from conventional processes that use air as oxidant. The flue gas are recycled, producing a stream containing mainly CO_2 and H_2O. After this step, CO_2 is ready for capture after purification and compression [10]. Due to the high flame temperature resulting from burns with practically pure O_2, part of the gas from combustion, rich in CO_2, returns to the system to refund the volume of gas lost when N_2 is removed from the air and to prevent the excessive increasing temperature in the system [11]. The main differences in the replacement of N_2 for O_2 are in relation to the temperature, the stability, the propagation velocity and delay in the flame ignition, the heat transfer and reduction of pollutants emissions, impacting positively in the overall heat capacity of the equipment. Many of these effects can be explained by differences in gas properties CO_2 and N_2, which influence both heat transfer and combustion reaction kinetics (density, heat capacity, diffusivity and radiative properties of

---

*Corresponding author: Jacob-Lopes E, Department of Food Science and Technology, Federal University of Santa Maria, Roraima Avenue, 1000, 97105-900, Santa Maria, RS, Brazil, Tel: 555532208822; E-mail: jacoblopes@pq.cnpq.br

Received October 04, 2016; Accepted October 07, 2016; Published October 07, 2016

Citation: Severo IA, Deprá MC, Zepka LQ, Jacob-Lopes E (2016) Photobioreactors and Oxycombustion: A Mini-Review on the Process Integration. J Chem Eng Process Technol 7: 310. doi: 10.4172/2157-7048.1000310

the gases). The oxycombustion can be used with any fuel to thermal energy production [12]. Despite the inherent advantages of this technology, one of the main drawbacks associated with oxycombustion refers to O_2 production of high purity. In this case, a unit for separation and purification is necessary, which causes an additional cost for the plant and increased energy consumption. These problems are the main challenges to be overcome [13].

Reuse of Exhaust Gases from Photobioreactors

Photobioreactors may be defined as systems utilized for the development of photosynthetic reactions. These equipments present different configurations, although the most common designs for the cultivation of microalgae are open or closed systems. Besides, some process parameters should be taken into account to achieve good yields, such as nutrient availability, efficient supply of CO_2, temperature control, agitation, mass transfer, ease of control of the reaction conditions and ease of scale-up [14]. Regardless of these questions, growth of microalgae in photobioreactors occurs through the photosynthetic mechanism. This in turn, consists in a chemical process that converts carbon dioxide into biomass using light energy and producing oxygen molecules [15]. Photosynthesis is characterized by two interdependent phases. Firstly, carbon dioxide is incorporated into ribulose 1,5-biphosphate (rubisco) energy being required during the catalytic reaction of the enzyme rubisco carboxylase. The reaction product is broken into three-carbon molecules, 3-phosphoglyceraldehyde (PGA). In the presence of ATP (adenosine triphosphate) and NADPH (nicotinamide adenine dinucleotide phosphate), the PGA is reduced to glyceraldehyde 3-phosphate (G3P), leads to the production of sugars and subsequently glucose. This sequence of metabolic transformations is known as the Calvin-Benson cycle. Therefore, the light energy is retained in two photoreactions prepared by two pigment-protein complexes, called photosystem I and II, exciting the chlorophyll a molecule and their electrons are transferred to a molecule electron acceptor. Part of the energy liberated is incorporated into ATP in the phosphorylation process [16]. The ultimate source of electrons for photosynthesis is H_2O, which yields in the process of photolysis, or Hill's reaction, hydrogen atoms, electrons and free oxygen. Thus, this reaction is an important product obtained from photosynthesis microalgae, because the O_2 in the process is generated exclusively from the water photolysis [17].

Despite the existence of many studies considering the fraction of non-volatile metabolites, it is also observed that the yield in biomass does not completely fulfill the total carbon balance of the system. One should consider that other products are involved in the photosynthetic conversion of the CO_2, including the secretion of biopolymers into the culture media, and of particular interest, the release of volatile organic compounds (VOCs) [4]. The VOCs are unexplored biomolecules, which are influenced by the culture parameters. This way, microalgae are capable of synthesizing and release specific compounds which indicate a great commercial interest in biomolecules from renewable sources, such as alcohol, esters, hydrocarbons, terpenes, ketones, carboxylic acids and sulfurized compounds [18]. Some cyanobacteria are known to synthesize alkanes or alkenes that have desirable properties for combustion. These VOCs can be used for the biofuels production, representing sustainable solutions for the energy sector [19]. The occurrence of VOCs in photosynthetic microorganisms is a consequence of their metabolism, and their biosynthesis, will depend exclusively on the availability of carbon, nitrogen and energy from the primary metabolism. The possible metabolic pathways CO_2 conversion for the synthesis of VOCs, were previously described in other studies [4,20,21]. These compounds could, therefore, be considered a source of useful chemical products with potentiality for commercial applications.

Process Integration: Photobioreactors Integrated to Oxycombustion Systems

The process integration is a relatively current concept and has been implemented in most industrial production processes. This technological route is defined as a series techniques and methods in integrated production systems that combine several unit operations inside an industrial plant [22]. Thus, the main objectives this strategy is to reduce the operational costs of the plant and the minimization of large equipment. As result, there is a lower energy consumption and increased overall efficiency in the system [23].

Alternatively, industrial processes which using fossil inputs have been gradually replaced by biobased processes. Microalgae-based processes, for example, are a potential way to a sustainable and economically viable production of consumables. The integration of microalgae into industrial processes is a suitable and innovative strategy to comply with the requirements of green engineering. For this technological route, is possible lowered its overall energy consumption of the process, which implies the reduction of fossil raw materials, potable water consumption and minimizing emissions [24,25]. Several integrated processes have been developed and some possibilities are considered through the reuse, the recovery and the possibly recycling of surpluses mass, effluents, water and energy for industrial application [26]. These strategies are highlighted for being economically viable and for improving the thermal performance of industrial combustion systems, effectively contributing to sustainable development.

The different strategies of integration of the bio-based processes are considered important approaches towards sustainable development. For this reason, the use of oxygen biologically generated in photobioreactors and their integration in processes that require the enrichment of this compound as oxidizer, such as bio-oxycombustion process, are considered potential examples for industrial application. These technological routes can significantly contribute to the bioeconomy of the future.

References

1. IPCC - International Panel on Climate Change (2014) Climate change 2014: Mitigation of Climate Change. Contribution of Working Group III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
2. Escudero AI, Espatolero S, Romeo LM (2016) Oxy-combustion power plant integration in an oil refinery to reduce CO_2 emissions. International Journal of Greenhouse Gas Control 45: 118-129.
3. IEA - International Energy Agency (2011) Cost and performance of carbon dioxide capture from power generation. OECD/IEA, Paris.
4. Jacob-Lopes E, Scoparo CHG, Queiroz MI, Franco TT (2010) Biotransformations of carbon dioxide in photobioreactors. Energy Conversion and Management 51: 894-900.
5. Borowitzka MA (2013) High-value products from microalgae their development and commercialization. Journal Applied Phycology 25: 743-756.
6. Gladysz P, Ziebik A (2016) Environmental analysis of bio-CCS in an integrated oxy-fuel combustion power plant with CO_2 transport and storage. Biomass and Bioenergy 85: 109-118.
7. Jajesniak P, Ali H, Wong TS (2014) Carbon Dioxide Capture and Utilization using Biological Systems: Opportunities and Challenges. Bioprocessing and Biotechniques 4: 155.
8. Cuéllar-Franca RM, Azapagic A (2015) Carbon capture, storage and utilisation technologies: A critical analysis and comparison of their life cycle environmental impacts. Journal of CO_2 utilization 9: 82-102.

9. Oh ST, Martin A (2016) Thermodynamic efficiency of carbon capture and utilisation in anaerobic batch digestion process. Journal of CO_2 utilization 16: 182-193.

10. Stanger R, Wall T (2011) Sulphur impacts during pulverised coal combustion in oxy-fuel technology for carbon capture and storage. Progress in Energy and Combustion Science 37: 69-88.

11. Irfan MF, Arami-Niya A, Chakrabarti MH, Daud WMAW, Usman MR (2012) Kinetics of gasification of coal, biomass and their blends in air (N2/O2) and different oxy-fuel (O2/CO2) atmospheres. Energy 37: 665-672.

12. Yin C, Yan J (2016) Oxy-fuel combustion of pulverized fuels: Combustion fundamentals and modeling. Applied Energy 162: 742-762.

13. Toftegaard MB, Brix J, Jensen PA, Glarborg P, Jensen AD (2010) Oxy-fuel combustion of solid fuels. Progress in Energy and Combustion Science 36: 581-625.

14. Singh RN, Sharma S (2012) Development of suitable photobioreactor for algae production – A review. Renewable and Sustainable Energy Reviews 16: 2347-2353.

15. Zhao B, Su Y (2014) Process effect of microalgal-carbon dioxide fixation and biomass production: A review. Renewable and Sustainable Energy Reviews 31: 121-132.

16. Calvin M, Benson AA (1948) The Path of Carbon in Photosynthesis. Science 107: 476-480.

17. Heldt HW, Piechulla B (2011) Plant Biochemistry. 4th edn. German edition: Academic Press in an imprint of Elsevier, p. 618.

18. Keppler F, Eiden R, Niedan V, Pracht J, Schöler HF (2000) Halocarbons produced by natural oxidation processes during degradation of organic matter. Nature 403: 298-301.

19. Lau NS, Matsui M, Abdullah AA (2015) Cyanobacteria: Photoautotrophic Microbial Factories for the Sustainable Synthesis of Industrial Products. BioMed Research International 2015: 1-9.

20. Jacob-Lopes E, Franco TT (2013) From oil refinery to microalgal biorefinery. Journal of CO_2 utilization 2: 1-7.

21. Santos AB, Fernandes AS, Wagner R, Jacob-Lopes E, Zepka LQ (2016) Biogeneration of volatile organic compounds produced by Phormidium autumnale in heterotrophic bioreactor. Journal of Applied Phycology 28: 1561-1570.

22. International Energy Agency (2000) Tutorial on Process Integration. A Process Integration Primer. SINTEF Energy Research.

23. Baldea M (2015) From process integration to process intensification. Computers and Chemical Engineering 81: 104-114.

24. Francisco EC, Franco TT, Zepka LQ, Jacob-Lopes E (2015) From waste-to-energy: the process integration and intensification for bulk oil and biodiesel production by microalgae. Journal of Environmental Chemical Engineering 3: 482-487.

25. Wohlgemuth R (2009) The locks and keys to industrial biotechnology. N Biotechnol 25: 204-213.

26. Posewinkel M, Rosello R, Wilhelm C, Kruse O, Hankamer B, et al. (2014) Integration in microalgal bioprocess development: Design of efficient, sustainable, and economic processes. Engineering in Life Sciences 14: 560-573.

Citation: Severo IA, Deprá MC, Zepka LQ, Jacob-Lopes E (2016) Photobioreactors and Oxycombustion: A Mini-Review on the Process Integration. J Chem Eng Process Technol 7: 310. doi: 10.4172/2157-7048.1000310

Capítulo 3

PARTE EXPERIMENTAL

1. MANUSCRITO 3

Bio-oxyfuel petroleum coke combustion: The process integration with photobioreactors

Ihana Aguiar Severo, Mariany Costa Deprá, Juliano Smanioto Barin, Roger Wagner, Leila Queiroz Zepka and Eduardo Jacob-Lopes

O artigo será submetido para a revista Bioresource Technology e foi redigido conforme as normas da mesma.

Bio-oxyfuel petroleum coke combustion: The process integration with photobioreactors

Ihana Aguiar Severo[1], Mariany Costa Deprá[1], Juliano Smanioto Barin[1], Roger Wagner[1], Leila Queiroz Zepka[1] and Eduardo Jacob-Lopes[1*]

[1]Department of Food Science and Technology, Federal University of Santa Maria (UFSM), 97105-900 Santa Maria, RS, Brazil

* Corresponding author.

E-mail address: jacoblopes@pq.cnpq.br

Abstract: The aim of this work was to develop a bio-oxycombustion system integrated with a photobioreactor. Different concentrations of oxidizers were injected into the combustion chamber and the temperature and flame stability, fuel conversion and heating rate were analyzed. The results showed that the use of photobioreactor exhaust gases as oxidizer in the oxycombustion furnace increased the thermal efficiency of the system, with heating rates 30.5% and 45.8% higher than the atmospheric air and the simulated industrial gas stream, respectively. This improvement occurred because the photobioreactor exhaust gases contain until 40% of oxygen. Thus, the integration of these processes could be considered as a viable strategy to improve the thermal performance of oxycombustion systems, with simultaneous use of the compounds formed and contributing effectively to the sustainability and the economy of industrial processes.

Keywords: oxycombustion, photobioreactors, microalgae, process integration, biological carbon capture and utilization.

1. Introduction

The abundant use of fossil fuels has become a cause of concern due to their adverse effects on the environment, particularly related to the emission of carbon dioxide (CO_2), a major greenhouse gas (GHG). From the economic point of view, as long as fossil fuels and carbon-intensive industries play dominant roles in this sector, carbon capture and storage or utilization will remain a critical solution for reducing these emissions. However, these technologies face numerous barriers that must be overcome before they can be used on a large scale (Bruhn et al., 2016).

More recently, a related alternative – biological carbon capture and utilization (BCCU) – has started to attract attention in comparison to the CCU and CCS, representing a possible strategy for CO_2 capture from polluting sources. BCCU converts biologically CO_2 into biomass through photosynthesis to obtain value-added products (Severo et al., 2016).

In this context, there are some CO_2 capture methods associated with different combustion processes, and oxycombustion has proven to be an attractive option mainly due to the increase in thermal efficiency (Cuéllar-Franca and Azapagic, 2015). Additionally, others benefits are related to oxygen-enrichment in combustion systems, such as the ability to be integrated into current energy production facilities, lower loss of heat energy through the flue gas and higher heating rates (Wu et al., 2010). The oxycombustion is the process of using pure oxygen for the combustion of fuel, resulting in a gas stream with high CO_2 concentrations and nitrogen-free, which can be easily be separated and used. This process is technically feasible, but the main disadvantage is the consumption of large amounts of oxygen coming from an energy intensive air separation unit (ASU) (Leung et al., 2014).

In order to circumvent this problem, photobioreactors are considered promising equipment to generate substantial amounts of pure oxygen, since they serve as photosynthetic microorganism culture medium, such as microalgae. Metabolically O_2 is generated by water photolysis, an important chemical step in photosynthesis (Walker, 2002). Through this technological route is obtained about 0.75 kg of O_2 for every 1 kg of bioconverted CO_2, which demonstrates its production potentiality. In addition, some authors report the oxygen accumulation produced in tubular photobioreactors. With this configuration, the concentrations of dissolved oxygen can reach up to 400% of air saturation, suggesting that continuous O_2 removal is essential in these systems (Molina et al., 2001; Solimeno et al., 2017). Simultaneously, substantial concentrations of CO_2 are released into photobioreactor exhaust gases.

Process integration is a methodology for energy saving and mitigation of emissions, that has been studied for resource conservation, besides being widely used in processing and power generation industries (Liew et al., 2017). As an alternative to processes using fossil inputs, integration of the bio-based processes, as for example tubular photobioreactors in oxycombustion systems, is considered as important approach towards sustainable development. Therefore, an integrated system for biological conversion GHG into oxygen to be used as oxidizer, and CO_2 for use as nitrogen diluent in oxycombustion systems, is an innovative technology with large potential for industrial application.

In this sense, the aim of this work was to develop a bio-oxycombustion system integrated into photobioreactor. The study focused on the evaluation of the thermal performance of the oxycombustion furnace and the characterization of the exhaust gases of photobioreactor.

2. Materials and methods

2.1. Microorganism and culture conditions

Axenic cultures of *Scenedesmus obliquus* CPCC05 were obtained from the Canadian Phycological Culture Centre. Stock cultures were propagated and maintained in synthetic BG-11 medium (Braun-Grunow medium) (Rippka et al., 1979) and pH 7.6. The incubation conditions used were 30 ºC, photon flux density of 15 µmol m^{-2} s^{-1} and a photoperiod of 12 h.

2.2. Photobioreactor design

Measurements were made in a bubble column photobioreactor (Maroneze et al., 2016). The system was built in 4 mm thick glass with internal diameter of 7.5 cm, height of 75 cm and nominal working volume of 2.0 L. The dispersion system for the reactor consisted of a 1.5 cm diameter air diffuser located in the center of the column. The reactor was illuminated with forty-five 0.23 W LED lamps (total consumption of 0.01125 kW h), located in a photoperiod chamber. The CO_2/air mixture was adjusted to achieve the desired concentration of carbon dioxide in the airstream, through three rotameters that measured the flow rates of carbon dioxide, air and the mixture of gases, respectively.

2.3. Obtaining the kinetic data in photobioreactor

The experiments were carried out in photobioreactors operating in intermittent regime, fed with 2.0 L of culture medium. The experimental conditions were as follows: initial cell concentration of 0.1 g L^{-1}, isothermal reactor operating at a temperature of 26 °C, photon flux density of 150 μmol m^{-2} s^{-1} and continuous aeration of 1 VVM (volume of air per volume of culture per minute) with the injection of air enriched with 15% carbon dioxide (Jacob-Lopes and Franco, 2013). The cell density, carbon dioxide and oxygen concentrations were monitored every 24 h during the growth phase of the microorganism. The tests were carried out in triplicate and the kinetic data referred to the mean of six repetitions.

2.4. Kinetic parameters

Carbon dioxide and oxygen concentration data were used to calculate the gaseous exchange rates [$r = (C_o - C_i) \cdot Q \cdot V_R^{-1}$, mg/L min] and removal efficiency [$RE = ((C_i - C_o)/C_i) \times 100$, %], where Co and Ci correspond to the inlet and outlet CO_2 concentration, respectively, Q is the gas flow and V_R is the reactor volume. Photosynthetic quotient data were determined using equation [$PQ = (d(O_2)/dt/d(CO_2)/dt)$], where dO_2/dt and dCO_2/dt corresponds to the variation of the concentration of O_2 and CO_2 over time, respectively.

2.5. Analytical methods

2.5.1. General analysis of process control

The temperature and pH of the culture medium were determined using a polarographic probe (Mettler Toledo, Switzerland). Cell concentration was gravimetrically determined by filtering a known volume of culture medium through a 0.45 µm filter (Millex FG, Billerica-MA, USA) and drying at a temperature of 60 °C for 24 h. Luminous intensity was determined by using a quantum sensor (Apogee Instruments, Logan-UT, USA).

2.5.2. Determinations of CO_2 and O_2 concentration profiles

Gas chromatograph (GC) was used to determine the concentrations of CO_2/O_2 of exhaust gases of photobioreactor. The equipment used was a GC-Greenhouse (Shimadzu, Kyoto, Japan), equipped with two packed columns connected the flame ionization detector (FID) and thermal conductivity (TCD) and helium as carrier gas. The amounts of carbon dioxide removed and oxygen produced was determined from samples 50 µL, taken from the gaseous phase of the system (inlet and outlet) with a gas-tight microsyringe (Hamilton, Bellefonte-PA, USA). The areas obtained using the integrator Software GCsolution were compared with reference curves to determine the CO_2 and O_2 concentrations.

2.6. Bio-oxycombustion system

The experiments were performed in an oxycombustion system constructed in laboratory scale (Fig. 1). The experimental apparatus was constituted by a stainless steel furnace, with coating composed of refractory material. The chamber has 3 cm thick in the inner part, a height of 40 cm, length 20 cm and width 20 cm. The furnace was equipped with two electric resistance of 300 W. A ceramic support was inserted in the center combustion chamber which was used for sample introduction. The photobioreactor exhaust gases were directed to the furnace through of a stainless steel pipe, located on the bottom, containing 80 cm in length and 3 mm internal diameter. The gases resulting of the combustion in the furnace were referred by the output channel, located at the top of the chamber. The system presents a filter for humidity and two pumps to control the gas flow.

2.6.1. Fuel composition

The fuel used in the experiments of oxycombustion was the petroleum coke. The sample was characterized through elemental analysis using an elemental analyzer Perkin Elmer 2400 CHNS/O (Perkin Elmer, Waltham-MA, USA), where 2 mg coke were oxidized at 1000 °C and the resulting gases were measured by thermal conductivity. Acetanilide was used as reference standard containing 71.09% carbon, 11.84% oxygen, 6.71% hydrogen and 10.36% nitrogen. The gaseous emissions of a clinkering furnace of the industrial unit InterCement (Apiaí, São Paulo, Brazil) was considered as source of stationary industrial emissions for photobioreactor feed, with the following composition: 5.5% O_2, 18% CO_2 and 76.5% N_2. The composition of this emission was simulated through a primary standard mixture (Praxair, Inc., Brazil).

2.6.2. Oxidizers

Different oxidants were tested in the experiments: atmospheric air, a gaseous mixture containing 5.5% O_2, 18% CO_2 and 76.5% N_2, corresponding to a typical industrial conditions used in clinkering furnaces, and the exhaust gases of the photobioreactor.

2.6.3. Obtaining kinetic data in bio-oxycombustion furnace

The experiments were monitored every 24 h during the growth phase of the microorganism, through the injection of different oxidizers in the furnace of bio-oxycombustion and in different cell residence times. The experimental conditions were: initial mass of coke 1.0 g, combustion time of 20 minutes and aeration rate of 1.0 L/min. During the oxycombustion, the temperature and flame stability, and the heating rate were continuously monitored. At the end of reaction, fuel conversion was determined. The tests were carried out in triplicate.

2.6.4. Thermal performance parameters of bio-oxycombustion system

2.6.4.1. Flame temperature

The flame temperature monitoring was carried through the thermal image of the combustion reaction using a long wave infrared camera Flir SC 305 (Flir Systems, Wilsonville-OR, USA) obtaining images of 320×240 pixels at a rate of 3.75 Hz (3.75 thermal images each second). The camera was positioned at 60 cm of combustion zone. The images were processed using FLIR Tools+ software. The emissivity of material (0.68) was determined through previous heating of coke at 100 ºC and all measurements were corrected for ambient temperature and relative humidity.

2.6.4.2. Flame stability

The flame stability in furnace was evaluated based on the values average of temperature during the combustion kinetics [FS = (σ_T/T) × 100, %], where σ_T corresponds to the standard deviation of the average temperature and T is the average flame temperature.

2.6.4.3. Fuel conversion

At the end of combustion reaction, the mass of coke converted was calculated [X = (M_i - M/M_i - M_c), %], where X corresponds to the converted fraction and M represents the mass of coke in different stages of combustion.

2.6.4.4. Heating rate

The heating rate was determined [dT/dt = (Tn – To)/(tn – to), ºC/s], where Tn is the instantaneous furnace temperature, To is the initial furnace temperature, tn – to is the time taken from the start of the experiment till the furnace reach final temperature.

2.7. Statistical analyses

Analysis of variance (one-way ANOVA) and Tukey's test ($p < 0.05$) were used to test differences between the oxidants studied. The analyses were performed with the software Statistica 7.0 (StatSoft, Tulsa-OK, USA).

3. Results and Discussion

3.1. Evaluation of the thermal performance of the oxycombustion furnace

Figure 2 shows the thermal performance of the oxycombustion furnace with the injection of different oxidizers in the combustion chamber at different cell residence times. The analysis of the flame temperature dynamics in the oxycombustion furnace operated with the different oxidizers evidence that the use of the photobioreactor exhaust gases presents the highest flame temperatures in parallel with the heating rates of the furnace. A clear difference is observed between the thermal profiles obtained through the different oxidizers used in the experiment, because with the utilization of the photobioreactor exhaust gases, the flame temperature reaches the peak in a reduced period of time (about 80 s). On the other hand, with the use of atmospheric air as oxidizer, the flame temperature is also high, however it presents a long time period, with about of 180 s to that the maximum temperature is achieved in the furnace. Despite the difference in the combustion time, these two oxidizers have very similar thermal profiles. This is because the heat released during combustion and the heat transferred are quite similar both in O_2/N_2 and O_2/CO_2 atmospheres (Bu et al., 2016). In contrast, the simulated industrial gas stream presents a more differentiated behavior of the other analyzed conditions, since the flame temperature increases slowly and reaches the peak in approximately 720 s of combustion, characterizing an unsatisfactory thermal performance.

Comparatively, an experimental study, conducted by Wu et al. (2010) on the temperature variation as a function of the concentration of oxygen in the oxidizer, shows that the variation of the oxygen level from 21% to 30% in the oxidizer promotes the elevation temperature in the combustion chamber. For

21% of O_2, the time required to heat the chamber at 1200 ºC was 3700 s and is only 2000 s for 30% O_2. This reduction in delay is explained by the decrease of the nitrogen amount in the oxidizer which limits the thermal losses.

In order to test the variation of the injection of the different oxidizers, the thermal parameters of the oxycombustion furnace performance were analyzed and can be better visualized in Table 1. The results obtained from the present experiment confirm the superiority of use of the photobioreactor exhaust gases in relation to the other oxidizers tested. For the 96 h cell residence time, considered the best condition in the furnace thermal performance, the highest values were obtained, with a flame temperature of 1000.5 ºC, flame stability of 6.2%, fuel conversion of 99.2% and heating rate (dT/dt) of 5.9 ºC/s. According to Wall et al. (2009), many of these effects are explained by differences in gas properties between CO_2 and N_2, the main diluting gases in oxycombustion and combustion with air, respectively, impacting both heat transfer as the combustion reaction kinetics. Additionally, the molecular weight of CO_2 is 44 $g.mol^{-1}$, compared to 28 for N_2 $g.mol^{-1}$, thus the density of the flue gas is higher in oxycombustion.

Similarly, the heat capacity of triatomic molecules such as CO_2 and H_2O, is higher than diatomic molecules, such as N_2. These characteristics is related to the greater emissivity of the oxycombustion gases, resulting in a high transfer of heat by radiation in the furnace. Moreover, the O_2 diffusion rate in CO_2 is 0.8 times higher than in N_2 (Scheffknecht et al., 2011; Yin and Yan, 2016). In contrast, for the simulated industrial gas stream, low oxygen concentrations can lead to an unstable flame and reduced temperature. Thus, the oxygen-enrichment has an extremely important role on increasing the temperature and flame stability, energy efficiency, heating rate and reduction of fuel consumption (Riahi et al., 2016).

Finally, Figure 3 shows the thermograms of the oxycombustion furnace, comparing the different oxidizers used, during 20 min of petroleum coke combustion. As can be seen, in the clearer parts of the thermogram in relation to the color scale, the maximum temperature was obtained with the enrichment of the photobioreactor exhaust gases at a combustion time between 2-6 minutes. Likewise, the higher temperatures for the atmospheric air are distributed in the region corresponding to the combustion time between 6-10 minutes and for the simulated industrial gas stream between 14-18 minutes. In this sense, the thermal images reinforce the superiority of the use of the photobioreactor exhaust gases to be applied as gaseous fuels in the bio-oxycombustion furnace.

3.2. Analysis of the composition of photobioreactor exhaust gases

Despite the existence of many studies considering only biomass, it is also observed that other products are involved in carbon dioxide conversion in photosynthetic cultures, since O_2 is the most relevant when generated in these bioprocesses (Jacob-Lopes et al., 2010). The Figure 4 shows the CO_2 conversion, O_2 release and photosynthetic quotient (PQ) in the photobioreactor.

The behavior of both rates are similar throughout the experiment, presenting low rate values at early and late cultivation times and reaching maximum rates at 96 h of cultivation (18.3 ± 0.5 mg_{CO_2}/L/min and 16.0 ± 0.7 mg_{O_2}/L/min for CO_2 sequestration and O_2 release, respectively).

The ratio between the converted CO_2 and the O_2 produced resulted in a PQ in the order of 0.71. This result is consistent with the expected value by photosynthetic equation which establishes that each 1 g of CO_2 consumed is correspondent to a release of 0.73 g of O_2. Comparatively, the mean value of PQ found by Jacob-Lopes et al. (2010) to measure CO_2 sequestration rates and O_2 release was 0.74, using the culture of *Aphanothece microscopica Nägeli* in a bubble column photobioreactor. For Spilling et al. (2015), the value obtained was similar, with PQ of 1.2 to a planktonic diatom species. This ratio provides more accurate values of the components involved in photosynthesis, such as absorption of CO_2 from measures of primary production of oxygen, and generally, the value is close to 1.0. Additionally, the values of PQ vary according to physiological factors, as the species of microalgae used, the type of organic molecule produced, as well as the source and proportion of assimilated nutrients (Eriksen et al., 2007).

Based on these aspects, the photolysis reactions of water provided in the experimental conditions the generation and consequently the desorption of approximately 40% of oxygen to photobioreactor exhaust gases. This concentration of oxidizer strengthened the thermal performance of furnace of bio-oxycombustion, as presented previously.

In order to compare quantitatively, the technologies for obtaining pure oxygen are usually in the range of 25 to 99% (Belaissaoui et al., 2014). The cryogenic method through an ASU is considered the only commercial technology available for this purpose, and to satisfy the demand of oxycombustion, oxygen production should be large volumes (7000–9000 ton/day of oxygen), implying an energy expenditure of 500 MW (Jin et al., 2015). According to the U.S. Department of Energy (DOE) Industrial Technologies Program (ITP) and the Industrial Heating Equipment Association (IHEA), some systems use almost 100% oxygen in the main combustion header, while others blend in oxygen to increase the oxygen in the incoming combustion air. However, about 30% of oxygen is effectively injected into oxycombustion chambers. For the clinkering furnaces, for example, they normally operate with an excess air rate in the order of 5 to 15%, which corresponds to percentage of injectable oxygen in the combustion chamber in the range of 1 to 6% of O_2. In addition, for this type of furnace, oxygen-enrichment can reduce fuel requirements by around 7-12% (DOE; IHEA, 2007).

Finally, should be consider that only the oxygen-enrichment close to 40% in furnaces operated at 1000 ºC provides an energy savings close to 60%. Thus, as in some industries, the energy consumption can account for 10% or more of total operating costs (IHEA, 2007). Specifically, for the petroleum coke, these improvements represent an economy of the USD 240 per metric ton of fuel burned (OCI, 2013). In this way, the bio-oxycombustion technology proposed in this study, can represent an opportunity in the systems improvements aiming to increase efficiency, reduce emissions and boost productivity.

4. Conclusions

Based on the different oxidizers tested, the thermal parameters of the system increased proportionally to the amount of oxygen supplied to the furnace. The results proved that the photobioreactor exhaust gases were able to provide a superior overall thermal performance in the bio-oxycombustion system, suggesting their application as oxidizer in combustion systems. The process integration was a potential engineering approach in order to promote the sustainability and economy of these industrial processes.

Acknowledgement

Funding for this research was provided by InterCement Brazil S/A.

References

Belaissaoui, B. et al. 2014. Energy efficiency of oxygen enriched air production technologies: Cryogeny vs membranes. Sep Purif. Technol. 125, 142-150.

Bruhn, T. et al. 2016. Separating the debate on CO_2 utilisation from carbon capture and storage. Environ. Sci. Policy. 60, 38-43.

Bu, C. et al. 2016. Oxy-fuel combustion of a single fuel particle in a fluidized bed: Char combustion characteristics, an experimental study. Chem. Eng. J. 287, 649-656.

Cuéllar-Franca, R. M., Azapagic, A. 2015. Carbon capture, storage and utilization technologies: A critical analysis and comparison of their life cycle environmental impacts. J. CO_2 Utilization. 9, 82-102.

Eriksen, N. T. et al. 2007. On-line estimation of O_2 production, CO_2 uptake, and growth kinetics of microalgal cultures in a gas-tight photobioreactor. J. Appl. Phycol. 19, 161-174.

Industrial Heating Equipment Association (IHEA). 2007. Improving Process Heating System Performance: A Sourcebook for Industry, Second Edition.

Jacob-Lopes, E., Franco, T. T. 2013. From oil refinery to microalgal biorefinery. J. CO_2 Utilization. 2, 1-7.

Jacob-Lopes, E. et al. 2010. Biotransformations of carbon dioxide in photobioreactors. Energy Conv. Manage. 51, 894-900.

Jin, B. et al. 2015. Plantwide control and operating strategy for air separation unit in oxy-combustion power plants. Energy Conv. Manage. 106, 782-792.

Leung, D. Y. C. et al. 2014. An overview of current status of carbon dioxide capture and storage technologies. Renew. Sustain. Energy Rev. 39, 426-443.

Liew, P. Y. et al. 2017. Total Site Heat Integration planning and design for industrial, urban and renewable systems. Renew. Sustain. Energy Rev. 68, 964-985.

Maroneze, M. M. et al. 2016. The role of photoperiods on photobioreactors – A potential strategy to reduce costs. Bioresour. Technol. 219, 493-499.

Molina, E. et al. 2001. Tubular photobioreactor design for algal cultures. J. Biotechnol. 92, 113-131.

Oil Change International (OCI). Petroleum Coke: The Coal Hiding in the Tar Sands 2013. Washington DC, USA.

Riahi, Z. et al. 2016. Experimental study of natural gas flame enriched by hydrogen and oxygen in a coaxial burner. Appl. Therm. Eng. 108, 287-295.

Rippka, R. et al. 1979. Generic assignments, strain histories and properties of pure cultures of cyanobacteria. J. Gen. Microbiol. 111, 1-61.

Scheffknecht, G. et al. 2011. Oxy-fuel combustion – A review of the state-of-the-art. In. J. Greenhouse Gas Control. 5, 16-35.

Severo, I. A. et al. 2016. Photobioreactors and Oxycombustion: A Mini-Review on the Process Integration. J. Chem. Eng. Process Technol. 7, 7-4.

Solimeno, A. et al. 2017. Mechanistic model for design, analysis, operation and control of microalgae cultures: Calibration and application to tubular photobioreactors. Algal Res. 21, 236-246.

Spilling, K. et al. 2015. Interaction Effects of Light, Temperature and Nutrient Limitations (N, P and Si) on Growth, Stoichiometry and Photosynthetic Parameters of the Cold-Water Diatom *Chaetoceros wighamii*. PLoS One, 10.

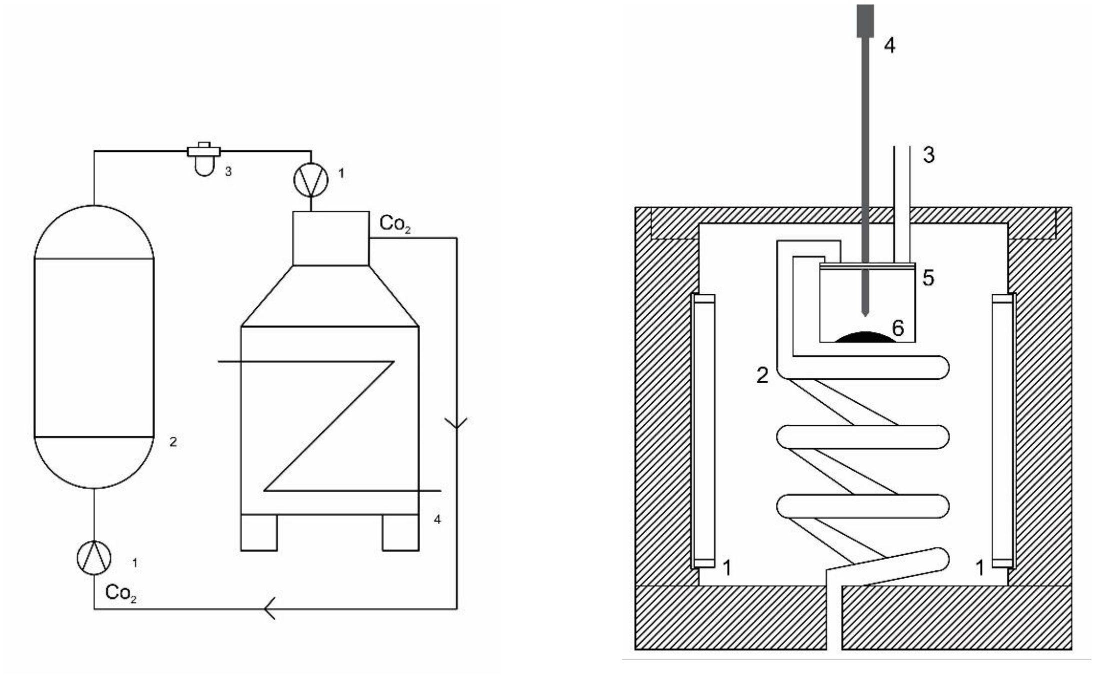
Yin, C.; Yan, J. 2016. Oxy-fuel combustion of pulverized fuels: Combustion fundamentals and modeling. Appl. Energy 162,742-762.

Walker, D. A. 2002. ‘And whose bright presence’ – an appreciation of Robert Hill and his reaction. Photosynth. Res. 73, 51-54.

Wall, T. et al. 2009. An overview on oxyfuel coal combustion—State of the art research and technology development. Chem. Eng. Res. Des. 87, 1003-1016.

Wu, K-K. et al. 2010. High-efficiency combustion of natural gas with 21–30% oxygen-enriched air. Fuel 89, 2455-2462.

U.S. Department of Energy (DOE). <https://energy.gov/>.



(A) (B)

Figure 1. Schematic diagram of bio-oxycombustion system. (A) 1: Pumps for the flow control and mixing of gases; 2: Photobioreactor; 3: Dehumidifier; 4: Oxycombustion furnace; (B) 1: Electrical resistances; 2: Photobioreactor exhaust gases inlet channel; 3: Output channel of the exhaust gases; 4: Thermal sensor; 5: Ceramic support; 6: Combustion chamber.

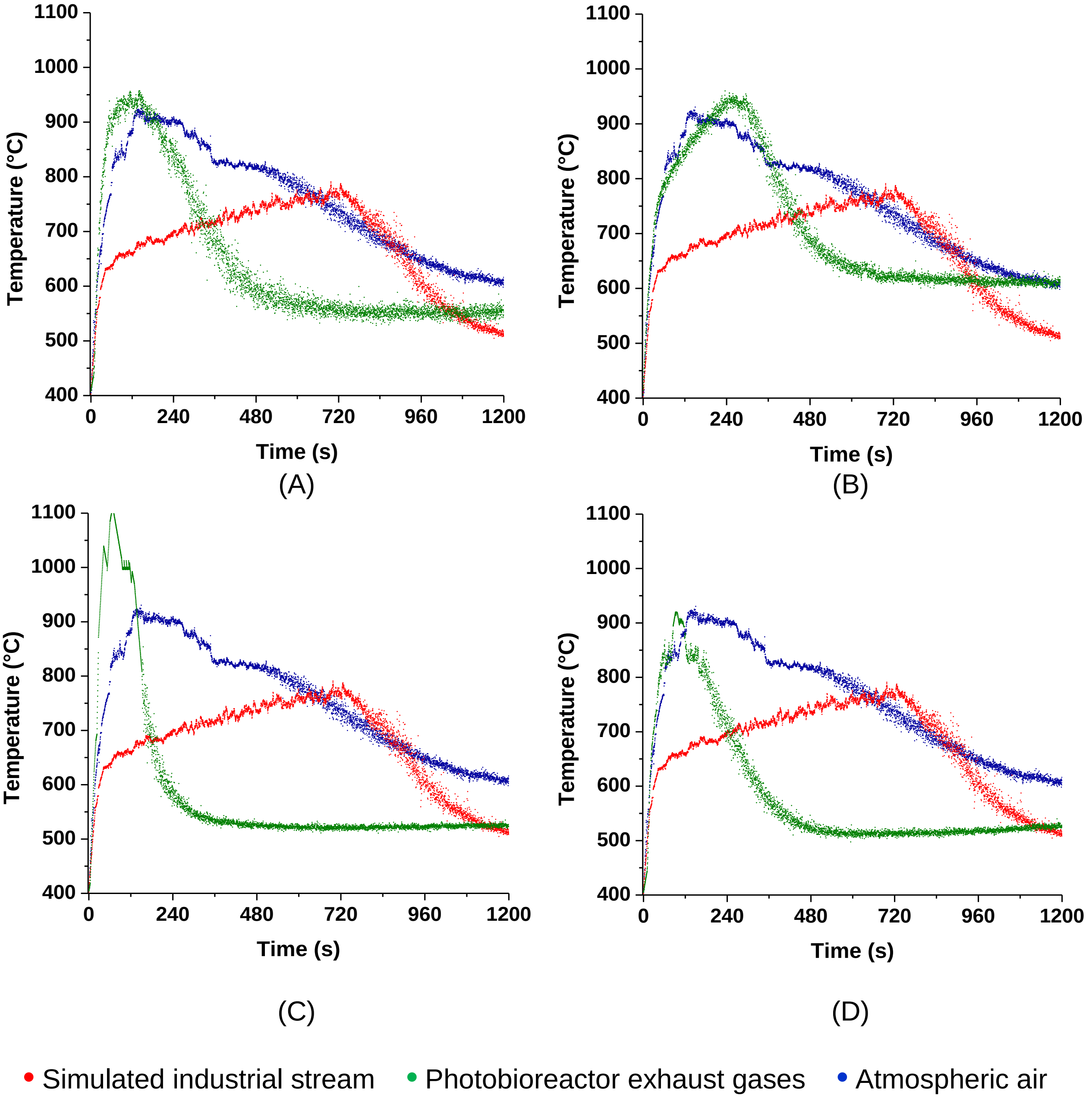


Figure 2. Dynamic of flame temperature in the oxycombustion furnace. Photobioreactor exhaust gases in: (A) 0 h, (B) 48 h, (C) and (D) 144 h.

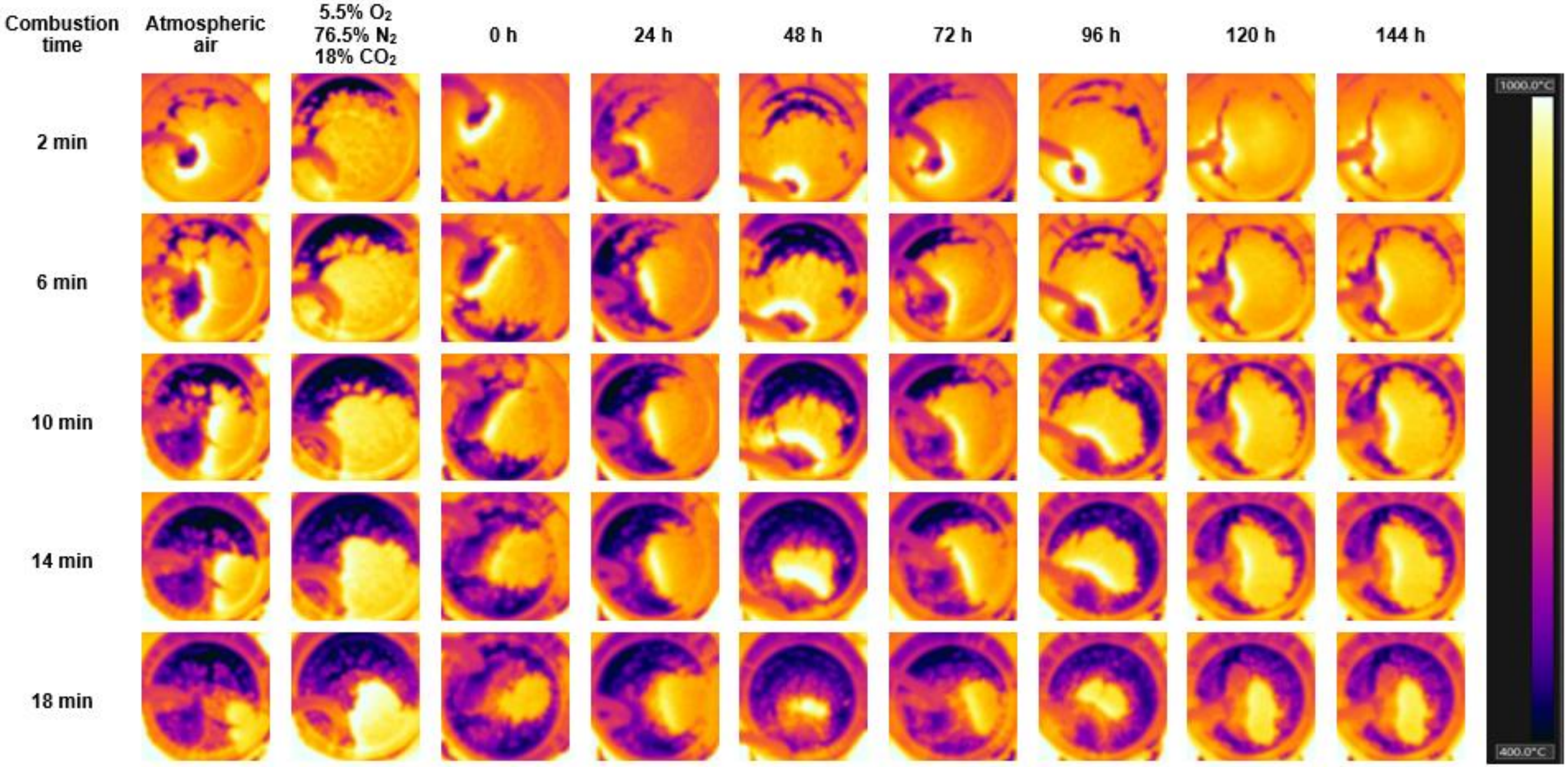


Figure 3. Thermograms of furnace of bio-oxycombustion.

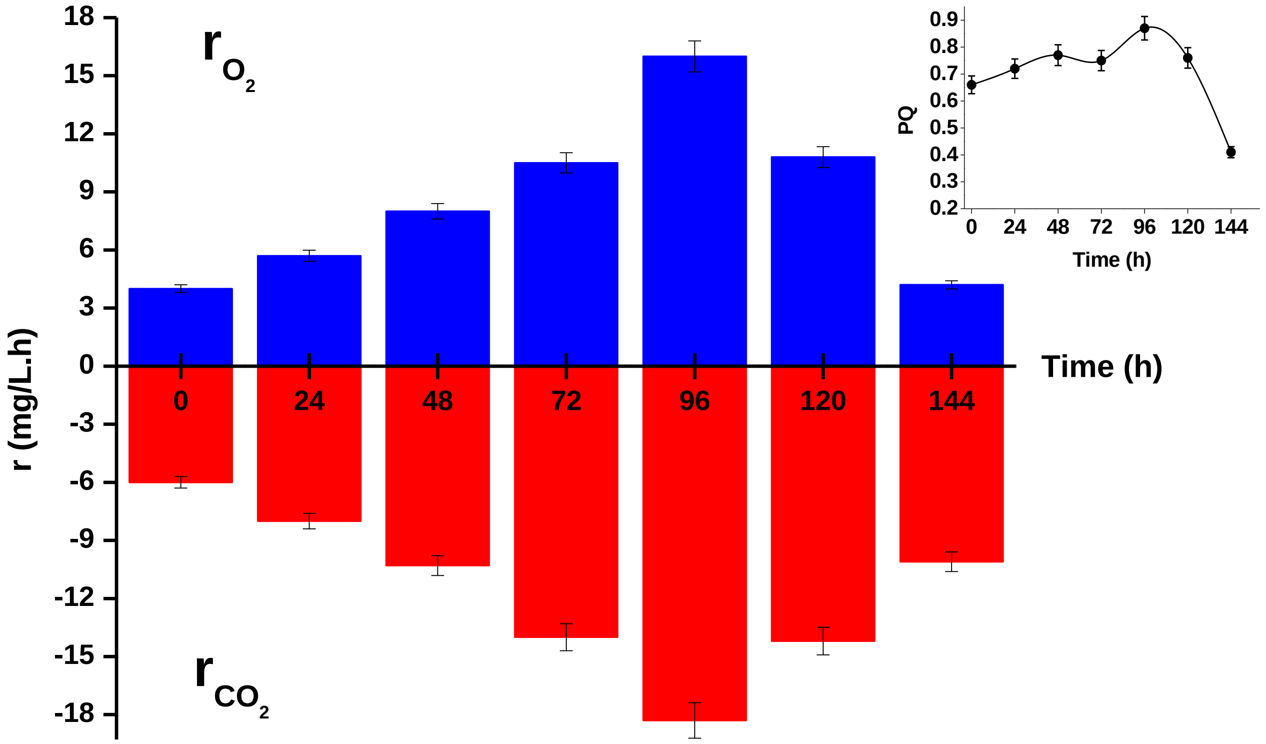


Figure 4. Carbon dioxide conversion, oxygen release rates and photosynthetic quotient (PQ) in the photobioreactor.

Table 1. Thermal performance parameters of bio-oxycombustion system.

Parameter	Atmospheric air	5.5 O_2 + 17% CO_2 + 76.5 N_2	PBR (0 h)	PBR (24 h)	PBR (48 h)	PBR (72 h)	PBR (96 h)	PBR (120 h)	PBR (144 h)
Flame temperature (ºC)	907.3^{e} ± 7.0	822.8^{j} ± 8.2	925.9^{d} ± 16.6	879.7^{g} ± 16.9	929.9^{c} ± 13.8	953.8^{b} ± 16.1	1003.5^{a} ± 62.4	900.1^{f} ± 39.1	856.0^{h} ± 34.0
Flame stability (%)	0.8^{f} ± 0.00	1.0^{ef} ± 0.00	1.8^{d} ± 0.00	1.9^{d} ± 0.00	1.5d^{e} ± 0.00	3.4^{c} ± 0.02	6.2^{a} ± 0.01	4.4^{b} ± 0.04	4.0^{b} ± 0.02
Fuel conversion (%)	99.1^{ab} ± 1.90	99.1^{d} ± 0.70	99.6^{a} ± 1.1	98.0^{e} ± 0.90	99.5^{a} ± 1.30	98.8^{b} ± 0.50	99.2^{ab} ± 1.00	99.3^{ab} ± 1.70	99.4^{a} ± 0.60
Heating rate (ºC/s)	4.1^{cde} ± 0.12	3.2^{f} ± 0.05	4.6^{bc} ± 0.15	4.2^{cde} ± 0.2	4.6^{bc} ± 0.1	5.0^{b} ± 0.25	5.9^{a} ± 0.45	4.6^{bc} ± 0.97	4.3^{cd} ± 0.34

Different letters in the same line differ significantly by Tukey test (α = 0.05)

Capítulo 4

CONCLUSÃO GERAL

3. CONCLUSÃO GERAL

O sistema integrado de bio-oxicombustão desenvolvido demonstrou ser uma estratégia potencial para captura de carbono e utilização biológica;

Considerando o forno de oxicombustão, todos os parâmetros de desempenho térmico foram substancialmente melhorados com o enriquecimento dos gases de exaustão do fotobiorreator;

Para o tempo de residência celular de 96 horas, considerado a melhor condição experimental, obteve-se um ganho significativo na eficiência térmica do sistema, com taxas de aquecimento de 30,5% e 45,8% superiores ao uso do ar atmosférico e da corrente gasosa industrial simulada, respectivamente;

Em relação à composição dos gases de exaustão do fotobiorreator, foi possível gerar uma concentração de aproximadamente 40% de oxigênio, para uso como comburente;

Desta forma, através da integração destes processos, foi possível desenvolver um sistema de combustão superior às tecnologias atualmente disponíveis industrialmente.

REFERÊNCIAS

CUÉLLAR-FRANCA, R. M.; AZAPAGIC, A. Carbon capture, storage and utilization technologies: A critical analysis and comparison of their cycle environmental impacts. **Journal of CO_2 Utilization**, v. 9, p. 82-102, 2015.

HELDT, H-W.; PIECHULLA, B. **Plant Biochemistry**. Academic Press is an imprint of Elsevier, Fourth edition, 2011.

IPCC. Intergovernmental Panel on Climate Change. **Climate Change 2014: Synthesis Report**. IPCC, Geneva, Switzerland, 151 pp., 2014.

JACOB-LOPES, E. et al. Biotransformations of carbon dioxide in photobioreactors. **Energy Conversion and Management**, v. 51, p. 894-900, 2010.

JACOB-LOPES, E.; FRANCO, T. T. From oil refinery to microalgal biorefinery. **Journal of CO_2 Utilization**, v. 2, p. 1-7, 2013.

JIN, B. et al. Plantwide control and operating strategy for air separation unit in oxy-combustion power plants. **Energy Conversion and Management**, v. 106, p. 782-792, 2015.

LIN, B.; XIE, X. CO_2 emissions of China's food industry: an input-output approach. **Journal of Cleaner Production**, v. 112, p. 1410-1421, 2016.

OXFAM. **Oxfam International – Feeding climate change**. Oxford, UK, 2017. Disponível em: <https://www.oxfam.org/en/research/feeding-climate-change>. Acesso em: 15 jan. 2017.

RAHMAN, F. A. et al. Pollution to solution: Capture and sequestration of carbon dioxide (CO_2) and its utilization as a renewable energy source for a sustainable future. **Renewable and Sustainable Energy Reviews**, v. 71, p. 112-126, 2017.

SCHEFFKNECHT, G. et al. Oxy-fuel coal combustion – A review of the current state-of-the-art. **International Journal of Greenhouse Gas Control**, v. 5, p. 16-35, 2011.

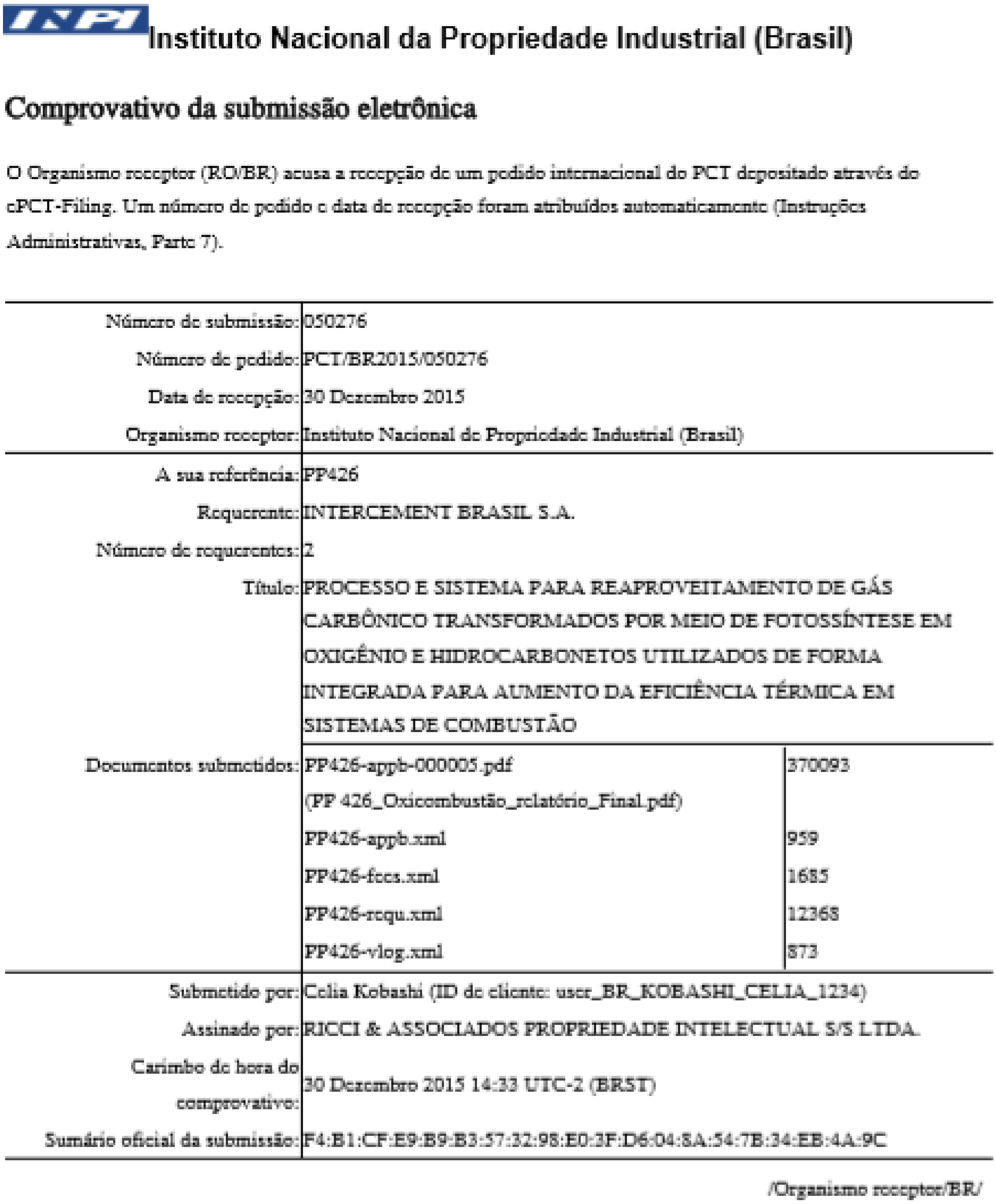
SEVERO, I. A. et al. Photobioreactors and Oxycombustion: A Mini-Review on the Process Integration. **Journal of Chemical Engineering & Process Technology**, v. 7, p. 7-4, 2016.

YIN, C.; YAN, J. Oxy-fuel combustion of pulverized fuels: Combustion fundamentals and modeling. **Applied Energy**, v. 162, p. 742-762, 2016.

ZHAO, R. et al. Allocation of carbon emissions among industries/sectors: An emissions intensity reduction constrained approach. **Journal of Cleaner Production**, v. 142, p. 3083-3094, 2017.

ANEXOS

ANEXO A – PATENTE DEPOSITADA NO *PATENT COOPERATION TREATY* (PCT – TRATADO INTERNACIONAL DE PATENTES)



Instituto Nacional da Propriedade Industrial (Brasil)

Comprovativo da submissão eletrônica

O Organismo receptor (RO/BR) acusa a recepção de um pedido internacional do PCT depositado através do ePCT-Filing. Um número de pedido e data de recepção foram atribuídos automaticamente (Instruções Administrativas, Parte 7).

Número de submissão:	050276	
Número do pedido:	PCT/BR2015/050276	
Data de recepção:	30 Dezembro 2015	
Organismo receptor:	Instituto Nacional de Propriedade Industrial (Brasil)	
A sua referência:	FP426	
Requerente:	INTERCEMENT BRASIL S.A.	
Número de requerentes:	2	
Título:	PROCESSO E SISTEMA PARA REAPROVEITAMENTO DE GÁS CARBÔNICO TRANSFORMADOS POR MEIO DE FOTOSSÍNTESE EM OXIGÊNIO E HIDROCARBONETOS UTILIZADOS DE FORMA INTEGRADA PARA AUMENTO DA EFICIÊNCIA TÉRMICA EM SISTEMAS DE COMBUSTÃO	
Documentos submetidos:	FP426-appb-000005.pdf (FP 426_Oxicombustão_relatório_Final.pdf)	370093
	FP426-appb.xml	959
	FP426-fees.xml	1685
	FP426-requ.xml	12368
	FP426-vlog.xml	873
Submetido por:	Celia Kobashi (ID de cliente: user_BR_KOBASHI_CELIA_1234)	
Assinado por:	RICCI & ASSOCIADOS PROPRIEDADE INTELECTUAL S/S LTDA.	
Carimbo de hora do comprovativo:	30 Dezembro 2015 14:33 UTC-2 (BRST)	
Sumário oficial da submissão:	F4:B1:CF:E9:B9:B3:57:32:98:E0:3F:D6:04:8A:54:7B:34:EB:4A:9C	

/Organismo receptor/BR/

PCT REQUERIMENTO

Print Out (Original em Formato Electrónico)

0	**Reservado para o Organismo receptor**	
0-1	Pedido internacional No.	PCT/BR2015/050276
0-2	Data do depósito internacional	30 Dezembro 2015 (30.12.2015)
0-3	Nome do Organismo receptor e "Pedido internacional PCT"	RO/BR

0-4	**Formulário PCT/RO/101 Requerimento PCT**	
0-4-1	Preparado Utilizando	ePCT-Filing Version 3.2.003 MT/FOP 20151028/0.20.5.24
0-5	**Petição** O abaixo assinado solicita que o presente pedido internacional seja processado de acordo com o Tratado de Cooperação em matéria de Patentes	
0-6	**Organismo receptor (especificado pelo requerente)**	Instituto Nacional de Propriedade Industrial (Brasil) (RO/BR)
0-7	**Referência do processo do requerente ou do mandatário**	PP426
I	**Título da invenção**	PROCESSO E SISTEMA PARA REAPROVEITAMENTO DE GÁS CARBÔNICO TRANSFORMADOS POR MEIO DE FOTOSSÍNTESE EM OXIGÊNIO E HIDROCARBONETOS UTILIZADOS DE FORMA INTEGRADA PARA AUMENTO DA EFICIÊNCIA TÉRMICA EM SISTEMAS DE COMBUSTÃO
II	**Requerente**	
II-1	Esta pessoa é:	Apenas requerente
II-2	Requerente para	Todos os Estados designados
II-4	Nome	INTERCEMENT BRASIL S.A.
II-5	Endereço	Av. das Nações Unidas, 12495, 13 e 14 andares Torre Nações Unidas A 04578-000 São Paulo Brasil
II-6	Nacionalidade (nome do Estado)	BR
II-7	Domicílio (nome do Estado)	BR
II-8	No. de telefone	(55 11) 5581-5707
II-10	Endereço de correio electrónico	riccipat@riccipi.com.br
II-10(a)	Autorização relativa ao correio electrónico O Organismo receptor deve obter junto de uma biblioteca digital e transmitir à Secretaria Internacional uma cópia autenticada do(s) pedido(s) anterior(es) acima identificado(s) no(s) ponto(s):	como notificações prévias por via electrónica seguidas de notificações em papel

PP426

2/6

PCT REQUERIMENTO

Print Out (Original em Formato Electrónico)

III-1	**Requerente e/ou inventor**	
III-1-1	Esta pessoa é:	Apenas requerente
III-1-2	Requerente para	Todos os Estados designados
III-1-4	Nome	UNIVERSIDADE FEDERAL DE SANTA MARIA
III-1-5	Endereço	Av. Roraima, 1000 Bairro Camobi 97105-900 Santa Maria Brasil
III-1-6	Nacionalidade (nome do Estado)	BR
III-1-7	Domicílio (nome do Estado)	BR
III-1-8	No. do telefone	(55 11) 5581-5707
III-1-10	Endereço de correio electrónico	riccipat@riccipi.com.br
III-1-10(a)	Autorização relativa ao correio electrónico O Organismo receptor deve obter junto de uma biblioteca digital e transmitir à Secretaria Internacional uma cópia autenticada do(s) pedido(s) anterior(es) acima identificado(s) no(s) ponto(s):	como notificações prévias por via electrónica seguidas de notificações em papel
III-2	**Requerente e/ou inventor**	
III-2-1	Esta pessoa é:	Apenas inventor
III-2-3	Inventor para	Todos os Estados designados
III-2-4	Nome (APELIDO, nome próprio)	LOPES, Eduardo Jacob
III-2-5	Endereço	R. João Atilio Zampieri 62/603 97105-490 Santa Maria Brasil
III-3	**Requerente e/ou inventor**	
III-3-1	Esta pessoa é:	Apenas inventor
III-3-3	Inventor para	Todos os Estados designados
III-3-4	Nome (APELIDO, nome próprio)	BARIN, Juliano Smanioto
III-3-5	Endereço	R. Esmeralda 405, Parque Residencial Santa Lúcia 97110-767 Santa Maria Brasil
III-4	**Requerente e/ou inventor**	
III-4-1	Esta pessoa é:	Apenas inventor
III-4-3	Inventor para	Todos os Estados designados
III-4-4	Nome (APELIDO, nome próprio)	TISCHER, Bruna
III-4-5	Endereço	R. Presidente Vargas 2116/304 97015-513 Santa Maria Brasil

III-5	**Requerente e/ou inventor**	
III-5-1	Esta pessoa é:	Apenas inventor
III-5-3	Inventor para	Todos os Estados designados
III-5-4	Nome (APELIDO, nome próprio)	MENEZES, Cristiano Ragagnin De
III-5-5	Endereço	R. Cristalino Machado Soares 311/401 97110-210 Santa Maria Brasil
III-6	**Requerente e/ou inventor**	
III-6-1	Esta pessoa é:	Apenas inventor
III-6-3	Inventor para	Todos os Estados designados
III-6-4	Nome (APELIDO, nome próprio)	WAGNER, Roger
III-6-5	Endereço	R. José Paulo Teixeira, 174 97110-750 Santa Maria Brasil
III-7	**Requerente e/ou inventor**	
III-7-1	Esta pessoa é:	Apenas inventor
III-7-3	Inventor para	Todos os Estados designados
III-7-4	Nome (APELIDO, nome próprio)	BIZELLO, Rodrigo Stefanello
III-7-5	Endereço	R. Quadra 58, 19, Bairro Tancredo Neves 97032-410 Santa Maria Brasil
III-8	**Requerente e/ou inventor**	
III-8-1	Esta pessoa é:	Apenas inventor
III-8-3	Inventor para	Todos os Estados designados
III-8-4	Nome (APELIDO, nome próprio)	SEVERO, Ihana De Aguiar
III-8-5	Endereço	R. Conde De Porto Alegre 891/204 97015-110 Santa Maria Brasil
III-9	**Requerente e/ou inventor**	
III-9-1	Esta pessoa é:	Apenas inventor
III-9-3	Inventor para	Todos os Estados designados
III-9-4	Nome (APELIDO, nome próprio)	CICHOSKI, Alexandre José
III-9-5	Endereço	R. Fernando Ferrari, 1820/301 97050-800 Santa Maria Brasil
III-10	**Requerente e/ou inventor**	
III-10-1	Esta pessoa é:	Apenas inventor
III-10-3	Inventor para	Todos os Estados designados
III-10-4	Nome (APELIDO, nome próprio)	ZEPKA, Leila Queiroz
III-10-5	Endereço	R. João Atilio Zampieri 62/603 97105-490 Santa Maria Brasil

PP426

4/6

PCT REQUERIMENTO

Print Out (Original em Formato Electrónico)

III-11	**Requerente e/ou inventor**	
III-11-1	Esta pessoa é:	Apenas inventor
III-11-3	Inventor para	Todos os Estados designados
III-11-4	Nome (APELIDO, nome próprio)	SUZUKI, Seiiti
III-11-5	Endereço	Rua Tabor 647 - apto. 154 - Bloco D 04202-021 São Paulo Brasil
III-12	**Requerente e/ou inventor**	
III-12-1	Esta pessoa é:	Apenas inventor
III-12-3	Inventor para	Todos os Estados designados
III-12-4	Nome (APELIDO, nome próprio)	MENEZES, Mariana Figueira Lacerda De
III-12-5	Endereço	Rua Indiana, 437 - apto. 31 - Brooklin 04562-000 São Paulo Brasil
III-13	**Requerente e/ou inventor**	
III-13-1	Esta pessoa é:	Apenas inventor
III-13-3	Inventor para	Todos os Estados designados
III-13-4	Nome (APELIDO, nome próprio)	PEREIRA, Taynara Ribas
III-13-5	Endereço	Avenida Santo Antônio, 595 - apto. 12 - Vila Osasco 06086-070 Osasco Brasil
III-14	**Requerente e/ou inventor**	
III-14-1	Esta pessoa é:	Apenas inventor
III-14-3	Inventor para	Todos os Estados designados
III-14-4	Nome (APELIDO, nome próprio)	ZOTTIN, Ligia Silvestre
III-14-5	Endereço	Rua Dr. Franco da Rocha, 205 - Apto 132 - Perdizes 05015-040 São Paulo Brasil

PP428

5/6

PCT REQUERIMENTO

Print Out (Original em Formato Electrónico)

IV-1	**Mandatário ou representante comun; ou endereço para a correspondência** A pessoa abaixo-identificada é/foi, por este meio, designada para actuar em nome do(s) requerente(s) perante as Autoridades Internacionais competentes, na qualidade de:	Mandatário	
IV-1-1	Nome	RICCI & ASSOCIADOS PROPRIEDADE INTELECTUAL S/S LTDA.	
IV-1-2	Endereço	Avenida Indianópolis, 2504 - Planalto Paulista 04062-002 São Paulo Brasil	
IV-1-3	No. de telefone	(55 11) 5581-5707	
IV-1-4	No. de fax	(55 11) 2276-9864	
IV-1-5	Endereço de correio electrónico	riccipat@riccipi.com.br	
IV-1-5(a)	Autorização relativa ao correio electrónico O Organismo receptor deve obter junto de uma biblioteca digital e transmitir à Secretaria Internacional uma cópia autenticada do(s) pedido(s) anterior(es) acima identificado(s) no(s) ponto(s):	como notificações prévias por via electrónica seguidas de notificações em papel	
IV-1-6	No. do registo do requerente junto do Organismo	API 1745	
V	**DESIGNAÇÕES**		
V-1	**O depósito deste requerimento constitui, de acordo com a Regra 4.9.a), a designação de todos os Estados Contratantes vinculados pelo PCT na data do depósito internacional, para os fins da concessão de qualquer tipo de protecção disponível e, se for caso disso, para os fins da concessão tanto de patentes regionais como de patentes nacionais.**		
VI-1	**Reivindicação de prioridade**	NENHUMA(S)	
VII-1	**Autoridade Responsável pela Pesquisa Internacional Escolhida**	Instituto Nacional de Propriedade Industrial (Brasil) (ISA/BR)	
VIII	**Declarações**	Número de declarações	
VIII-1	Declaração relativa à identidade do inventor	-	
VIII-2	Declaração relativa ao direito do requerente, na data do depósito internacional, de pedir e obter uma patente	-	
VIII-3	Declaração relativa ao direito do requerente, na data do depósito internacional, de reivindicar a prioridade do pedido anterior	-	
VIII-4	Declaração de autoria da invenção (apenas para os fins da designação dos Estados Unidos da América)	-	
VIII-5	Declaração relativa a divulgações não prejudiciais ou excepções à falta de novidade	-	

PCT REQUERIMENTO

Print Out (Original em Formato Electrónico)

IX	Lista de controle	Número de folhas	Ficheiro(s) electrónico(s) anexado(s)
IX-1	Requerimento (incluindo as folhas de declaração)	6	✓
IX-2	Descrição	14	✓
IX-3	Reivindicações	4	✓
IX-4	Resumo	1	✓
IX-5	Desenhos	2	✓
IX-7	TOTAL	27	
	Itens anexos	Documento(s) em papel anexado(s)	Ficheiro(s) electrónico(s) anexado(s)
IX-8	Folha de cálculo das taxas	–	✓

IX-20	**Figura dos desenhos que deve acompanhar o resumo**	1
IX-21	**Língua do depósito do pedido internacional**	Português
X-1	**Assinatura do requerente, do mandatário ou do representante comun**	/Helcio Ferro Ricci/
X-1-1	Nome	RICCI & ASSOCIADOS PROPRIEDADE INTELECTUAL S/S LTDA.
X-1-2	Nome de quem assina	RICCI, Helcio Ferro
X-1-3	Qualidade (se tal qualidade não for evidente para quem ler o requerimento)	Socio

RESERVADO PARA O ORGANISMO RECEPTOR

10-1	**Data efectiva de recepção do alegado pedido internacional**	30 Dezembro 2015 (30.12.2015)
10-2	**Desenhos:**	
10-2-1	Recebida	
10-2-2	Não recebida	
10-3	**Data efectiva de recepção, corrigida devido à recepção ulterior, mas dentro do prazo, de documentos ou desenhos que completam o alegado pedido internacional**	
10-4	**Data da recepção, dentro do prazo, das correcções exigidas de acordo com o Artigo 11.2) do PCT**	
10-5	**Autoridade responsável pela pesquisa internacional**	ISA/BR
10-6	**Transmissão da cópia de pesquisa diferida até ao pagamento da taxa de pesquisa**	

RESERVADO PARA A SECRETARIA INTERNACIONAL

11-1	**Data da recepção da via original pela Secretaria Internacional**	

Relatório Descritivo de Patente de Invenção para "Processo e sistema para reaproveitamento de gás carbônico transformados por meio de fotossíntese em Oxigênio e hidrocarbonetos utilizados de forma integrada para aumento da eficiência térmica em sistemas de combustão".

CAMPO DA INVENÇÃO

[001] A presente invenção encontra seu campo de aplicação dentre os processos e sistemas para o aumento de eficiência térmica em fornos de combustão industrial através da técnica de bio-oxicombustão. De forma mais especifica a invenção trata de geradores biológicos de oxigênio, combustíveis gasosos e diluentes de nitrogênio oriundos de processos de conversão biológica de gases do efeito estufa ou mais especificamente, dióxido de carbono, que são regenerados para uso como comburentes, combustíveis e diluentes respectivamente em fornos de combustão industrial.

[002] Neste documento o termo bio-oxicombustão é definido como a substituição parcial ou total do ar, utilizado nos processos de combustão, por: oxigênio, como comburente; compostos orgânicos voláteis e/ou semivoláteis como combustíveis e dióxido de carbono como diluentes de nitrogênio oriundos de processos de conversão biológica de gases do efeito estufa por meio de fotossíntese.

FUNDAMENTOS DA INVENÇÃO

[003] A atual preocupação mundial com as emissões industriais de gases de efeito estufa e as consequentes mudanças climáticas têm acelerado o desenvolvimento de tecnologias alternativas visando o desenvolvimento sustentável. As fábricas de cimento, por exemplo, são responsáveis por aproximadamente cinco por centro das emissões antropogênicas globais de gases de efeito estufa. A elaboração do cimento e a extração dos agregados para o concreto têm impactos ambientais significativos - estima-se que os fornos cimenteiros gerem em torno de 700 quilogramas de CO_2 para cada tonelada métrica de cimento produzido.

[004] Diante destes números torna-se imperativo a redução da pegada de carbono dos processos industriais. Alguns acordos internacionais têm sido propostos com este objetivo, embora as barreiras tecnológicas e econômicas limitem a aplicação das tecnologias de captura e estocagem ou captura e utilização de gases de efeito estufa.

[005] Uma das rotas tecnológicas que vêm ganhando considerável atenção é a oxicombustão, que está baseada na substituição do ar (que contem aproximadamente 79% de nitrogênio e 21% de oxigênio), utilizado nos processos de combustão, por oxigênio puro. Como consequência do aumento da pressão parcial de oxigênio nos processos de combustão há um ganho na capacidade térmica global dos equipamentos, reduzindo o consumo de combustíveis e consequentemente as emissões de gases de efeito estufa.

[006] A tecnologia de oxicombustão está fundamentada nas diferenças existentes em relação à combustão com ar, nas propriedades do gás usado como comburente, nas reações de combustão e nas propriedades dos gases de combustão. As principais diferenças são provenientes da mudança na composição dos gases, ou seja, na substituição do gás nitrogênio (N_2) pelo gás oxigênio (O_2), em paralelo a outros gases, como o gás carbônico (CO_2) como diluente do gás oxigênio.

[007] Em termos de capacidade térmica (Cp), verifica-se que a 800K o N_2 apresenta um Cp=31,4 J/kmol, enquanto que o CO_2 possui Cp=51,4 J/kmol. Adicionalmente, a emissividade (ε), que é a capacidade de emitir energia por radiação, de substâncias triatômicas, como o CO_2 e H_2O são superiores a moléculas diatômicas como o N_2. Estas caracteristicas de composição do gás comburente impactam principalmente na (i) estabilidade e temperatura da chama, (ii) transferência de calor, (iii) transferência de massa, (iv) cinética da combustão, e (v) corrosividade do gás.

[008] Em adição a estas considerações, a pureza do oxigênio é considerada a principal variável operacional dos processos de

oxicombustão, sendo uma função apenas dos aspectos econômicos de sua produção. As tecnologias atualmente comercialmente disponíveis para a produção de oxigênio são baseadas em unidades de separação criogênica de ar (ASU) e em sistemas de adsorção com variação de pressão (PSA), que por limitações de custo e/ou grau de pureza do oxigênio produzido, são consideradas pouco atrativas. Em adição, processos de separação com membranas têm sido desenvolvidos, mas ainda não apresentam a maturidade necessária para o escalonamento industrial.

[009] A limitação da geração de oxigênio para uso como oxicombustível pode ser contornada através da sua produção em reatores biológicos, que utilizam micro-organismos fotossintéticos como as microalgas. O oxigênio metabólico é gerado como um coproduto do metabolismo fotossintético através das reações de fotólise da água. Por esta rota tecnológica é possível produzir em média 0,75 kg de oxigênio para cada 1 kg de dióxido de carbono bioconvertido, o que demonstra o amplo potencial de produção desta substância neste tipo de processo. Estes bioprocessos produzem em paralelo inúmeros compostos orgânicos voláteis e semivoláteis, que apresentam considerável valor energético, além de liberar nos gases de exaustão substanciais concentrações de CO_2.

[010] O processo de bio-oxicombustão aplica-se a qualquer processo de combustão industrial para geração de energia térmica. Podendo ser aplicado em novas unidades (*new-built*) ou adaptado a unidades já existentes (*retrofit*).

[011] Assim, um sistema integrado para a conversão biológica de dióxido de carbono em Oxigênio, combustíveis gasosos e diluente de nitrogênio para uso em sistemas de oxicombustão é algo ainda não conhecido do estado da técnica.

TÉCNICA RELACIONADA

[012] Inúmeras rotas tecnológicas têm sido desenvolvidas visando à captura, uso e estocagem de carbono. A conversão biológica de dióxido de carbono em fotobiorreatores e os processos de oxicombustão são considerados dois exemplos de

elevado potencial de aplicação industrial (Chen C, Lu Z, Ma X, Long J, Peng Y, Hu L, Lu Q. Oxy-fuel combustion characteristics and kinetics of microalgae *Chlorella vulgaris* by thermogravimetric analysis. Bioresource Technology 2013; 144:563-571).

[013] A conversão direta de gases de efeito estufa, principalmente dióxido de carbono em fotobiorreatores por microalgas é uma técnica potencial, pois além de mitigar os poluentes gera inúmeros produtos do metabolismo fotossintético, como, biomassa, sais inorgânicos, exopolímeros, oxigênio e compostos orgânicos voláteis (álcoois, ésteres, hidrocarbonetos, terpenos, aldeídos, cetonas e ácidos carboxílicos), que podem ser reutilizados como insumos intermediários e/ou produtos finais de diferentes processos de manufatura industrial (Jacob-Lopes, E, Franco, TT. From oil refinery to microalgal biorefinery Journal of CO_2 Utilization 2013; 2:1-7).

[014] As tecnologias de oxicombustão, por outro lado, estão baseadas no enriquecimento dos equipamentos de combustão industrial com o gás Oxigênio, aumentando a eficiência térmica dos processos e, por conseguinte, reduzindo o gasto com combustíveis fósseis, geradores de gases de efeito estufa (Chen C, Lu Z, Ma X, Long J, Peng Y, Hu L, Lu Q. Oxy-fuel combustion characteristics and kinetics of microalgae *Chlorella vulgaris* by thermogravimetric analysis. Bioresource Technology 2013; 144:563-571).

[015] Recentemente, alguns pedidos de patentes têm sido depositados na tentativa de viabilizar processos de oxicombustão com aplicação industrial.

[016] O documento de patente EP 2292974 A2, refere-se a uma caldeira de oxicombustão em que existe uma unidade de separação física de oxigênio do ar. O oxigênio separado por esta unidade é encaminhado através de um sistema de recirculação ao forno para a oxicombustão. O forno de oxicombustão compreende ainda uma unidade de controle de fluxo de combustível ajustável aos teores de oxigênio injetado na caldeira.

[017] O documento de patente norte americano US 20080115500 refere-se a um sistema de geração de energia a partir da queima de hidrocarbonetos, utilizando elevadas concentrações de oxigênio comburente, obtido por separadores físicos. O processo propõe o uso de um combustível à base de água, através da diluição dos hidrocarbonetos com este solvente.

[018] O documento de patente brasileiro PI 0715471-2 A2 descreve um equipamento e método de oxicombustão baseado em um combustível, um comburente e um gás majoritário inerte, visando proporcionalizar adequadamente esta mistura para o aumento da eficiência térmica de sistemas de combustão industrial.

[019] O documento de patente EP 2309185 relata um equipamento e processo para o enriquecimento com Oxigênio de uma caldeira a carvão, conectada a uma unidade de separação física de Oxigênio do ar, que busca aumentar a eficiência térmica global do processo.

[020] O documento de patente WO 2013116667 cita um sistema de purificação de oxigênio, para uso em processos de oxicombustão, baseado em membranas poliméricas cerâmicas que são adaptadas ao sistema de combustão.

[021] Estes cinco documentos de patentes acima descritos possuem limitações comuns, que é a geração de Oxigênio por processos de separação física do ar, que são pouco atrativos sob o ponto de vista comercial, uma vez que produzem oxigênio a custos incompatíveis com a maioria das operações industriais.

[022] Os documentos de patente norte-americanos US 20130224841 e US20140113275 referem-se a métodos de uso combinado de combustíveis fósseis e renováveis em sistemas de oxicombustão enriquecidos por oxigênio oriundo de unidades de separação física e oxigênio metabólico gerado por biorreatores microalgais. Esses documentos desconsideram a produção conjunta de combustíveis voláteis em paralelo a produção de oxigênio nos fotobiorreatores, além de não considerarem o uso de parte do dióxido de carbono, não convertido no fotobiorreator, como

diluente do nitrogênio, dois fatores que aumentam substancialmente o desempenho térmico dos fornos.

[023] Diante das limitações do estado da técnica, desenvolveu-se o presente processo e sistema integrado e intensivo para combustão em sistemas industriais através de bio-oxicombustíveis. Os bio-oxicombustíveis são aqui entendidos como os combustíveis oriundos de processos de conversão biológica de gases do efeito estufa por meio de fotossíntese.

[024] A presente invenção é uma solução tecnológica que permite integrar a geração e reuso de dióxido de carbono industrial em um circuito parcialmente ou totalmente fechado, para a produção de bioprodutos fotossintéticos, principalmente oxigênio e compostos orgânicos voláteis e semivoláteis que serão utilizados como comburente e combustíveis em fornos industriais respectivamente. As tecnologias existentes propõem o enriquecimento dos fornos de combustão com oxigênio oriundo de processos de separação física do ar ou oxigênio produzido biologicamente por micro-organismos. A invenção aqui ensinada compreende ainda o uso de metabólitos voláteis produzidos conjuntamente com o oxigênio como coprodutos do metabolismo microalgal em fotobiorreatores, além de regenerar parte do dióxido de carbono para uso como diluente dos gases comburentes.

SUMÁRIO DA INVENÇÃO

[025] O processo integrado para a produção e uso de oxigênio em sistemas de bio-oxicombustão, revelado na presente invenção, tem como objetivo aumentar a eficiência térmica de fornos industriais.

[026] O oxigênio é produzido por reações de fotólise em fotobiorreatores mediados por microalgas. Estes fotobiorreatores, que podem apresentar configuração variada, são alimentados preferencialmente com dióxido de carbono industrial, cuja ação dos micro-organismos converte o CO_2 em produtos gasosos do metabolismo fotossintético, particularmente Oxigênio e outros compostos orgânicos voláteis e/ou semivoláteis, que serão recuperados e utilizados como oxicombustíveis para injeção

em fornos de combustão industrial. Adicionalmente, a fração não convertida do dióxido de carbono injetado no fotobiorreator é regenerada para uso como diluente do nitrogênio. Estas reações são controladas pela energia luminosa incidente no fotobiorreator, que pode ser de origem natural (solar) e/ou artificial (lâmpadas fluorescentes, LED, fibra ótica).

[027] O sistema aqui revelado compreende uma unidade de geração biológica, preferencialmente um fotobiorreator (1), que fornece oxigênio, compostos voláteis e/ou semivoláteis e dióxido de carbono, duas unidades de bombeamento de gases (2) e (8) e dois sistemas de tratamento e purificação de gases (3) e (4) e (6) e (7), um forno de combustão (5) e dois conjuntos de medidores e controladores (9) e (10), que operam de forma integrada.

BREVE DESCRIÇÃO DAS FIGURAS

[028] A Figura 1 mostra uma representação esquemática de um fotobiorreator (1) para geração biológica de comburentes e combustíveis voláteis e/ou semivoláteis e um processo integrado e intensivo de oxicombustão conectado ao forno de combustão (5) por meio de uma bomba (2) e sistemas de tratamento e purificação de gases. Os gases de saída do forno de combustão passam ainda por um sistema de tratamento e purificação de gases e são bombeados no todo ou em parte para a entrada do fotobiorreator (1). As setas indicam a direção do fluxo de gases. Uma saída de gases também é prevista antes da bomba (8).

[029] A Figura 2 mostra a caracterização compostos orgânicos voláteis gerados pelo fotobiorreator (1) e usados como combustível no forno de combustão:

(11) 2-metilbutanal,
(12) 2-metoxi-2-metil-propano,
(13) 2-propanona,
(14) 2,4-dimetil-3-pentanona,
(15) 3,3-dimetil-hexano,
(16) hexanal,
(17) 2,4-dimetilheptano,

(18) 4,7-dimetil-undecano,

(19) 4-octen-3-ona,

(20) 2-fenillpropeno,

(21) 6-metil-5-hepten-2-ona,

(22) 2-etil-1-hexanol,

(23) 2,4-heptadienal,

(24) 2-propil-1-heptanol,

(25) acetofenona,

(26) 2,4-decadienal, (E,Z) e

(27) β-ionona.

[030] Figura 3 apresenta um exemplo de desempenho térmico de um forno de combustão, alimentado com coque de petróleo, operando integrado ao sistema de bio-oxicombustão.

DESCRIÇÃO DETALHADA DA INVENÇÃO

[031] As características do processo e sistema de bio-oxicombustão, objeto da presente invenção, serão mais bem percebidas a partir da descrição detalhada que se fará a seguir.

[032] O processo aqui revelado ocorre por meio das etapas de:

(a) recuperação da fase gasosa de um fotobiorreator;

(b) tratamento dos gases;

(c) injeção do oxigênio, compostos orgânicos voláteis e/ou semivoláteis, nitrogênio e dióxido de carbono em um forno de combustão;

(d) regeneração dos gases de exaustão do forno de combustão, no todo ou em parte, para uso no fotobiorreator;

[033] Em um aspecto detalhado, a fase gasosa do fotobiorreator é recuperada e bombeada a uma unidade de tratamento, para remoção do excesso de vapor d'agua e demais interferentes (óxidos de nitrogênio, óxidos de enxofre, dentre outros). Os gases purificados são injetados no forno de combustão (5), atuando como comburentes (oxigênio), combustíveis (compostos orgânicos voláteis e/ou semivoláteis) e diluidores de nitrogênio. Em uma última etapa, a oxidação dos combustíveis no

forno de combustão resultará na produção de dióxido de carbono e demais gases de exaustão, que retornarão ao fotobiorreator, no todo ou em parte, após passarem pela unidade de tratamento de gases, integrando globalmente o processo.

[034] O meio de cultura armazenado no fotobiorreator (1) recebe uma mistura de ar e CO_2 proveniente das emissões industriais que é bombeada continuamente para o interior do sistema, proporcionando o aporte de carbono inorgânico as culturas, em paralelo a agitação e mistura para o meio reacional. Este meio de cultura recebe a energia luminosa, permitindo a captação da energia pelas células, que desencadeiam a reação fotossintética, convertendo o dióxido de carbono ou outros gases do efeito estufa nos bioprodutos gasosos do metabolismo fotossintético: oxigênio e compostos orgânicos voláteis e/ou semivoláteis, além de liberar nos gases de exaustão parte do CO_2 injetado e não convertido. Esta operação é repetida por tempos de residência variáveis. No caso da operação descontínua o tempo de residência será definido pela exaustão dos nutrientes presentes no meio de cultura. Estes tempos de residência variam normalmente entre 3 e 10 dias, no caso de operações descontínuas.

[035] Por outro lado, no caso da operação contínua, haverá a alimentação de meio de cultura em taxas de diluição proporcionais a velocidade de crescimento das células, com a retirada de meio de cultura em vazões equivalentes as vazões de alimentação. A operação continua será mantida por tempo de residência indefinido, que permita a manutenção das culturas em estado estacionário.

[036] O controle de um processo continuo é realizado através do ajuste da taxa de diluição (D, h^{-1}). Por definição, D equivale ao inverso do tempo de residência, ou seja, $D=1/t$ (h^{-1}), ou ainda $D=F/V$ (h^{-1}).

[037] Como a velocidade especifica de crescimento celular é dada nas mesmas unidades da taxa de diluição (μ, h^{-1}), podemos relacioná-las fazendo com que $D=\mu$.

[038] Finalmente, a vasão de alimentação e a vasão de retirada de meio de cultura do biorreator operado continuamente, são obtidas através do produto de D=µ com o volume útil do sistema (V, m^3), obtendo-se o valor em m^3/h. A manutenção desse equilíbrio é chamada de operação em estado estacionário e pode ser indefinidamente mantida, desde que o crescimento celular esteja equilibrado com a alimentação/retirada de meio de cultura.

[039] A descrição do sistema de bio-oxicombustão é feita de acordo com a identificação dos respectivos componentes, conforme identificados na figura-1. A presente invenção refere-se a um equipamento principal, constituído pelo fotobiorreator, forno, filtros e condensadores) e seus acessórios necessários para a condução do processo.

[040] O referido sistema de bio-oxicombustão compreende basicamente os seguintes componentes:

- um fotobiorreator (1) de mistura perfeita usado para converter dióxido de carbono e outros gases de efeito estufa, oriundos dos fornos de combustão industrial, em oxigênio e demais compostos orgânicos voláteis. O sistema regenera o dióxido de carbono não convertido. O fotobiorreator pode ser operado de forma descontínua, descontínua alimentada e contínua;
- duas estações de bombeamento de gases (2) e (8) dotadas de bombas pneumáticas, de potência dimensionada de acordo com a capacidade operacional do sistema, suficiente para integrar o fotobiorreator (1) com o forno (5);
- dois conjuntos de tratamento de gases (3) e (4) e (6) e (7), dotados de um filtro (mangas ou coalescência) ou ainda um precipitador eletrostático acoplados a um condensador, utilizados para a para a purificação parcial de interferentes gasosos, particulados e vapor de água;
- um forno de combustão industrial (5), usado para geração de energia térmica em diferentes processos industriais. O forno (5) é alimentado com o oxigênio e

compostos orgânicos voláteis e/ou semivoláteis gerados pelo fotobiorreator, além de dióxido de carbono não convertido (1) e fornece o dióxido de carbono para alimentar o fotobiorreator (1). A alimentação dos gases de exaustão pode ocorrer em diferentes regiões do forno industrial de clinquer, incluindo o maçarico, a caixa de fumaça ou o calcinador.

- um conjunto de medidores e controladores (9) e (10) dos parâmetros do sistema (pH, temperatura, dióxido de carbono, monóxido de carbono, nitrogênio, oxigênio e carbono orgânico total) que são interligados a um sistema de controle, que auxilia nos ajustes dos parâmetros do processo e sistema.

[041] Os medidores podem servir a uma operação não automatizada apenas como auxiliares na caracterização do processo, enquanto com os medidores associados aos controladores podem contribuir, além da caracterização do processo ao efetivo controle e ajuste das condições operacionais.

EXEMPLOS

[042] Um exemplo de um bioprocesso de conversão do CO_2 da presente invenção trata de um da conversão do CO_2 em bioprodutos gasosos, através das etapas de:

(a) seleção e adaptação de microalgas as condições físico, químicas e biológicas operacionais do sistema para gerar uma cepa mutante;

(b) inserção no reator da cepa mutante gerada na etapa (a) com concentração inicial do inoculo de cerca de 0,1 a 0,3 g/L, juntamente com o meio de cultura liquido;

(c) propagação da cepa mutante através da manipulação das condições operacionais de temperatura, pH, agitação por aeração de ar comprimido contaminado com dióxido de carbono (1-25%).

[043] Em um aspecto particular, as células microalgais utilizadas como biocatalisador do processo, deverão passar por

uma etapa de adaptação genética, produzindo células mutantes. O procedimento de produção de mutantes pré-seletivos consiste em duas etapas: (1) cultivo axênico da espécie de microalga em tubos de ensaio contendo meio sintético BG11 enriquecido com 20 g/L de agar-agar, mantidos a temperatura de 20°C e luminosidades de 1,0 klux, em uma câmara de incubação provida de lâmpadas fluorescentes do tipo luz do dia (400-700nm). As culturas são mantidas em crescimento balanceado através de transferências periódicas de inóculos a meio de cultura fresco e (2) submissão das culturas axênicas a um ambiente seletivo, que mimetiza as condições impostas industrialmente, que consistem na exposição das células a concentrações crescentes (3, 5, 10, 15, 25% v/v) dos gases de combustão industrial, ricos em CO_2, a condições de temperatura entre 10-40°C, pH entre 3 a 10, luminosidade entre 0 a 100 klux, em uma segunda câmara de incubação provida de lâmpadas fluorescentes do tipo luz do dia (400-700nm). Estas duas etapas geram células resistentes às condições de operação do sistema. As células resistentes ao ambiente extremo são mantidas por 30 dias e então analisadas visualmente por microscopia ótica, determinando o número de células mutantes resistentes ao ambiente adaptativo.

[044] De forma opcional, o bioprocesso de conversão de efluentes gasosos provê uma etapa de tratamento preliminar da emissão gasosa através de sistemas de separação para a contenção de material particulado, metais pesados e outros constituintes do gás poluente.

[045] A proporção de inoculo/meio de cultura da etapa (b) do processo pode variar entre 10% (100/1000) a 30% (300/1000).

[046] Em uma incorporação do bioprocesso de conversão de CO_2, a etapa (c) de propagação da cepa mutante ocorre em temperaturas de cerca de 10 a 40°C, pH inicial do meio ajustado para aproximadamente 7,0 a 8,0, agitação por aeração de ar comprimido de 0,5 a 1,5 VVM (volume de ar por volume de meio de cultura por minuto), sendo este ar enriquecido/contaminado com uma proporção de gases de emissão do processamento industrial,

que resulte em um teor de CO_2 entre 1 a 25%, preferencialmente 15%, e intensidades luminosas que variam de 10 a 100 klux.

[047] Outro aspecto do bioprocesso de conversão de gases do efeito estufa, da presente invenção, é a utilização de microalgas pertencentes às classes das cianobactérias, cloroficeas e diatomáceas, como *Aphanothece*, *Scenedesmus*, *Synechocystis*, *Nostoc*, *Phormidium*, *Chlorella* e *Phaeodactylum*, incluindo monoculturas ou consórcios microalgais.

[048] Outro exemplo de realização da invenção pode ser descrito a partir de um fotobiorreator de coluna de bolhas (1) operado a partir de uma cepa mutante de *Chlorella vulgaris*, em meio sintético BG11, a 25°C, 10 klux e com uma taxa de alimentação de dióxido de carbono de 1,8 $kg/m^3/d$. Nestas condições ocorre uma bioconversão de 0,56 $kg_{CO2}/m^3/d$, sendo perdido nos gases de exaustão aproximadamente 1,25 $kg_{CO2}/m^3/d$. O dióxido de carbono é convertido em 0,52 $kg/m^3/d$ de compostos orgânicos voláteis, em paralelo a 0,42 $kg/m^3/d$ de oxigênio, que estariam disponiveis para alimentação de fornos de combustão industrial.

[049] A título de exemplificação, uma realização pode ser descrita através da caracterização dos compostos orgânicos voláteis gerados pelo fotobiorreator (1) e usados como combustível no forno de combustão, conforme a figura 2. Nas mesmas condições descritas no exemplo anterior, correspondentes a uma taxa de produção de 0,52 $kg/m^3/d$ de compostos orgânicos voláteis, há a formação de cetonas (2-propanona, 2,4-dimetil-3-pentanona, 4-octen-3-ona, 6-metil-5-hepten-2-ona, acetofenona e β-ionona), aldeidos (2-metilbutanal, hexanal, 2,4-heptadienal e 2,4-decadienal), hidrocarbonetos (2-metoxi-2-metil-propano, 3,3-dimetil-hexano, 2,4-dimetilheptano e 4,7-dimetil-undecano), álcoois (2-etil-1-hexanol e 2-propil-1-heptanol) e terpenos (2-fenillpropeno) que juntos totalizam a fração orgânica dos gases de exaustão do fotobiorreator em um tempo de residência celular de 96h.

[050] A título de exemplificação, um evento real pode ser descrito através da Figura 3, que representa o desempenho térmico de um forno de combustão, alimentado com coque de petróleo, operando integrado ao sistema de bio-oxicombustão. As imagens de termografia por infravermelho sugerem ganhos de desempenho na ordem de 37,0% na temperatura da chama, 31,6% na estabilidade da chama e 0,5% na conversão adicional global de coque quando comparado ao uso de ar atmosférico como agente comburente. O aumento do desempenho destes três parâmetros irá ocasionar economia no consumo de combustíveis dos sistemas de combustão em paralelo a redução da emissão de gases de efeito estufa.

[051] A descrição que se fez até aqui do processo e sistema integrado, objetos da presente invenção, devem ser consideradas apenas como uma possível concretização e quaisquer características particulares nela introdusida devem ser entendidas apenas como algo que foi descrito para facilitar sua compreensão. Desta forma, não podem de forma alguma ser consideradas como limitantes da invenção, a qual está limitada pelo escopo das reivindicações que seguem.

REIVINDICAÇÕES

1) Um processo para reaproveitamento de gás carbônico transformados por meio de fotossíntese em Oxigênio e hidrocarbonetos **caracterizado pelo** fato da injeção integrada do Oxigênio, como um comburente, dos compostos orgânicos voláteis e/ou semivoláteis, como combustíveis, e do dióxido de carbono, como um diluente de Nitrogênio em um forno de combustão.

2) O processo para reaproveitamento de gás carbônico transformados por meio de fotossíntese em Oxigênio e hidrocarbonetos, de acordo com a reivindicação 1, **caracterizado pelo** fato de compreender as seguintes etapas:

(a) recuperação da fase gasosa de um fotobiorreator (1);

(b) tratamento dos referidos gases;

(c) injeção do Oxigênio, compostos orgânicos voláteis e/ou semivoláteis e dióxido de carbono em um forno de combustão;

(d) regeneração dos gases de exaustão do forno de combustão, no todo ou em parte, para uso no fotobiorreator (1);

3) O processo para reaproveitamento de gás carbônico transformados por meio de fotossíntese em Oxigênio e hidrocarbonetos, de acordo com a reivindicação 2, **caracterizado pelo** fato da fase gasosa do fotobiorreator (1) ser recuperada e bombeada, por meio da bomba (2) à unidade de tratamento (3) e (4) para remoção do excesso de vapor d'agua, de óxidos de nitrogênio e de óxidos de enxofre, sendo a referida fase gasosa purificada injetada no forno de combustão (5), onde a oxidação dos combustíveis no forno de combustão (5) resultará na produção de dióxido de carbono e demais gases de exaustão, que passarão ainda pela unidade de tratamento de gases (6) e (7) e serão bobeados, por meio da bomba (8), retornando, no todo ou em parte, ao fotobiorreator (1) integrando o processo.

4) O processo para reaproveitamento de gás carbônico transformados por meio de fotossíntese em Oxigênio e hidrocarbonetos, de acordo com a reivindicação 1, caracterizado pelo fato de um meio de cultura armazenado no fotobiorreator (1) receber uma mistura de ar e dióxido de carbono proveniente de emissões, que é bombeado continuamente ou descontinuamente ou descontinuamente alimentada para o interior do sistema, proporcionando o aporte de carbono inorgânico às culturas, em paralelo a agitação e mistura para o meio reacional, onde o referido meio de cultura recebe ainda energia luminosa, permitindo a captação dessa energia pelas células, convertendo o dióxido de carbono ou outros gases do efeito estufa nos bioprodutos gasosos do metabolismo fotossintético.

5) O processo para reaproveitamento de gás carbônico transformados por meio de fotossíntese em Oxigênio e hidrocarbonetos, de acordo com a reivindicação 4, caracterizado pelo fato dos compostos orgânicos voláteis compreenderem cetonas (2-propanona, 2,4-dimetil-3-pentanona, 4-octen-3-ona, 6-metil-5-hepten-2-ona, acetofenona e β-ionona), aldeidos (2-metilbutanal, hexanal, 2,4-heptadienal e 2,4-decadienal), hidrocarbonetos (2-metoxi-2-metil-propano, 3,3-dimetil-hexano, 2,4-dimetilheptano e 4,7-dimetil-undecano), álcoois (2-etil-1-hexanol e 2-propil-1-heptanol) e terpenos (2-fenillpropeno).

6) O processo para reaproveitamento de gás carbônico transformados por meio de fotossíntese em Oxigênio e hidrocarbonetos, de acordo com a reivindicação 4, caracterizado pelo fato de que na operação continua a alimentação do meio de cultura ocorrerá em taxas de diluição proporcionais à velocidade de crescimento das células, com a retirada de meio de cultura em vazões equivalentes às vazões de alimentação, sendo a operação continua mantida por tempo de residência indefinido.

7) O processo para reaproveitamento de gás carbônico transformados por meio de fotossíntese em Oxigênio e hidrocarbonetos, de acordo com a reivindicação 4, caracterizado

pelo fato de que na operação descontínua o tempo de residência será definido pela exaustão dos nutrientes presentes no meio de cultura, sendo os referidos tempos de residência entre 3 e 10 dias.

8) Um sistema para reaproveitamento de gás carbônico transformados por meio de fotossíntese em Oxigênio e hidrocarbonetos caracterizado pelo fato de compreender um fotobiorreator (1), que fornece uma fase gasosa contendo oxigênio, compostos orgânicos voláteis e/ou semivoláteis e dióxido de carbono para uma estação de bombeamento (2), que por sua vez envia os referidos gases a uma unidade de tratamento de gases, composta por um filtro (3) acoplado a um condensador (4), que entregam gases para injeção no forno de combustão (5), onde o referido forno (5) possui ainda medidores e controladores (10) dos parâmetros do sistema, onde os gases provenientes do forno (5) são então encaminhados para uma unidade de tratamento de gases, composta por um filtro (6) acoplado a um condensador (7), que entregam por meio de uma bomba (8) os gases para alimentar o fotobiorreator (1), onde o referido fotobiorreator (1) possui ainda um medidor e controlador (9).

9) Um sistema para reaproveitamento de gás carbônico transformados por meio de fotossíntese em Oxigênio e hidrocarbonetos, de acordo com a reivindicação 8, caracterizado pelo fato do fotobiorreator ser operado de forma descontínua, descontínua alimentada e contínua.

10) Um sistema para reaproveitamento de gás carbônico transformados por meio de fotossíntese em Oxigênio e hidrocarbonetos, de acordo com a reivindicação 8, caracterizado pelo fato das bombas (2) e (8) serem pneumáticas.

11) Um sistema para reaproveitamento de gás carbônico transformados por meio de fotossíntese em Oxigênio e hidrocarbonetos, de acordo com a reivindicação 8, caracterizado pelo fato dos filtros (3) e (6) serem filtros de mangas ou filtros de coalescência ou precipitadores eletrostáticos.

12) Um sistema para reaproveitamento de gás carbônico transformados por meio de fotossíntese em Oxigênio e hidrocarbonetos, de acordo com a reivindicação 8, <u>caracterizado pelo</u> fato da entrega dos gases para injeção no forno de combustão (5) industrial de clinquer ser realizada no maçarico ou na caixa de fumaça ou no calcinador.

13) Um sistema para reaproveitamento de gás carbônico transformados por meio de fotossíntese em Oxigênio e hidrocarbonetos, de acordo com a reivindicação 8, <u>caracterizado pelo</u> fato da injeção dos gases ser realizada por meio da técnica de bio-oxicombustão.

14) Um sistema para reaproveitamento de gás carbônico transformados por meio de fotossíntese em Oxigênio e hidrocarbonetos, de acordo com a reivindicação 8, <u>caracterizado pelo</u> fato dos medidores e controladores (9) e (10) serem de pH, temperatura, dióxido de carbono, monóxido de carbono, nitrogênio, oxigênio e carbono orgânico total.

15) Um sistema para reaproveitamento de gás carbônico transformados por meio de fotossíntese em Oxigênio e hidrocarbonetos, de acordo com a reivindicação 14, <u>caracterizado pelo</u> fato dos referidos medidores (9) e (10) serem utilizados em uma operação não automatizada como auxiliares na caracterização do processo.

16) Um sistema para reaproveitamento de gás carbônico transformados por meio de fotossíntese em Oxigênio e hidrocarbonetos, de acordo com a reivindicação 14, <u>caracterizado pelo</u> fato dos referidos medidores (9) e (10) serem interligados ainda a um sistema de controle para o ajuste das condições operacionais do sistema.

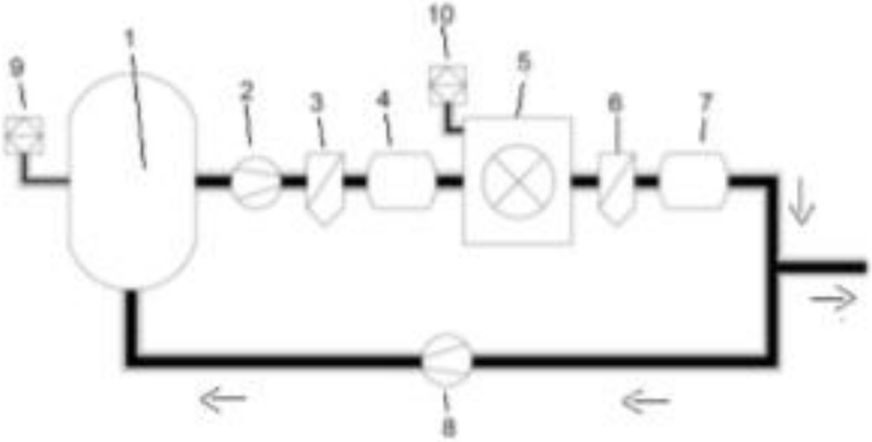


Figura - 1

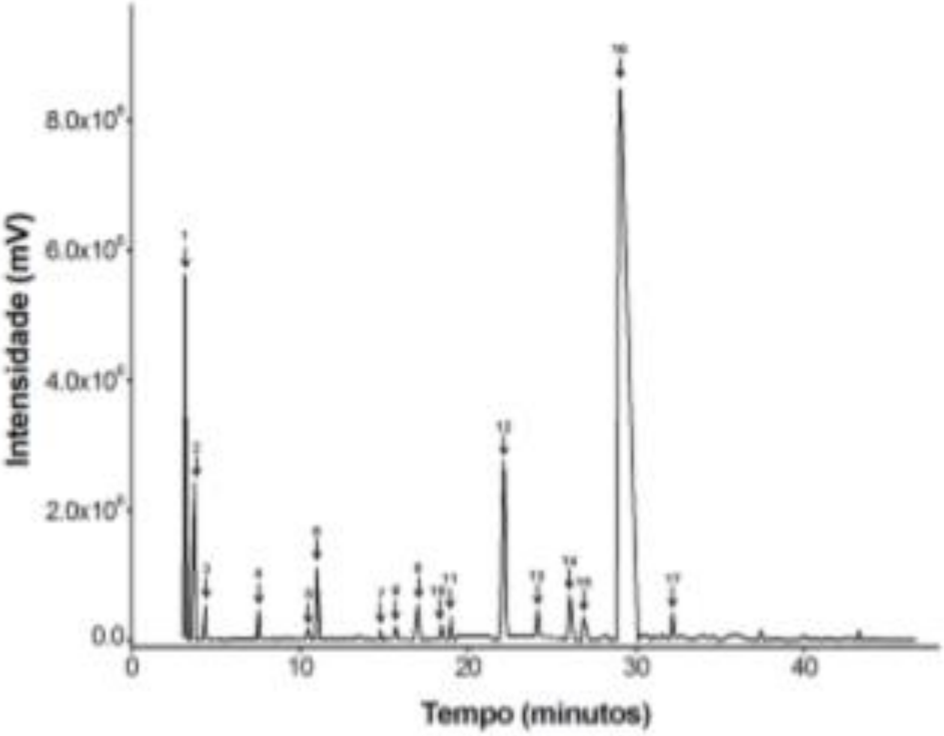


Figura - 2

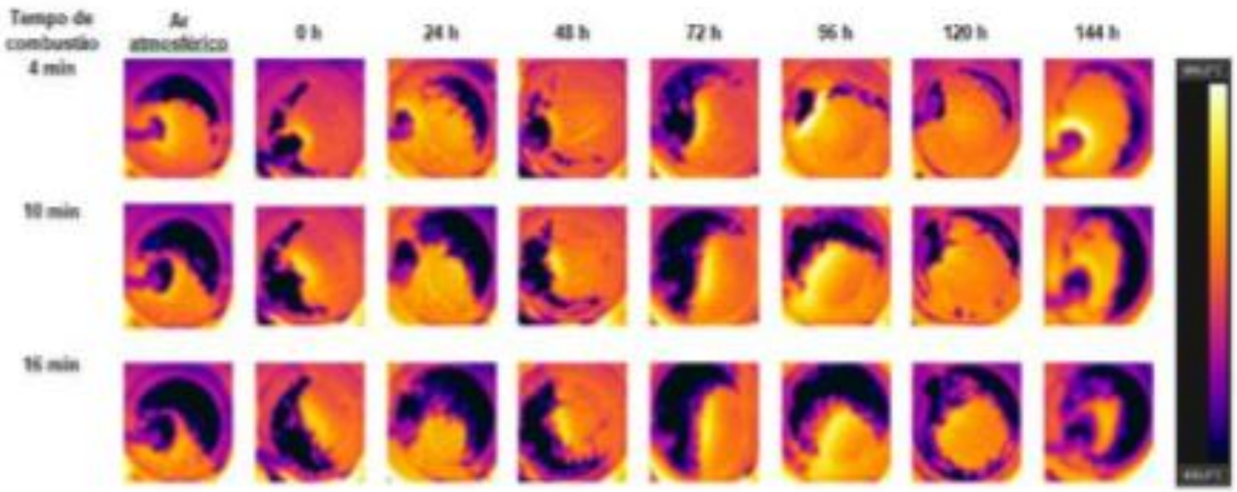

Tempo de combustão
4 min
10 min
16 min
Ar atmosférico
0 h
24 h
48 h
72 h
96 h
120 h
144 h

Figura - 3

RESUMO

PROCESSO E SISTEMA PARA REAPROVEITAMENTO DE GÁS CARBÔNICO TRANSFORMADOS POR MEIO DE FOTOSSÍNTESE EM OXIGÊNIO E HIDROCARBONETOS UTILIZADOS DE FORMA INTEGRADA PARA AUMENTO DA EFICIÊNCIA TÉRMICA EM SISTEMAS DE COMBUSTÃO

A presente invenção encontra seu campo de aplicação dentre os processos e sistemas para o aumento de eficiência térmica em fornos de combustão através da técnica de bio-oxicombustão. O processo integrado para a produção e uso de Oxigênio, como um comburente, dos compostos orgânicos voláteis e/ou semivoláteis, como combustíveis, e do dióxido de carbono, como um diluente de Nitrogênio em um forno de combustão, tem como objetivo aumentar a eficiência térmica de fornos industriais. O Oxigênio é produzido em fotobiorreatores, que podem apresentar configuração variada, sendo alimentados com dióxido de carbono industrial, cuja ação dos micro-organismos converte o CO_2 em produtos gasosos do metabolismo fotossintético. Adicionalmente, a fração não convertida do dióxido de carbono injetado no fotobiorreator é regenerada para uso como diluente do Oxigênio. O sistema aqui revelado compreende uma unidade de geração biológica, preferencialmente um fotobiorreator, que fornece a sua fase gasosa; duas unidades de bombeamento de gases (2) e (8) e dois sistemas de tratamento e purificação de gases (3) e (4) e (6) e (7), um forno de combustão (5) e dois conjuntos de medidores e controladores (9) e (10), que operam de forma integrada.

ANEXO B – PATENTE DEPOSITADA NO INSTITUTO NACIONAL DE LA PROPRIEDAD INDUSTRIAL – *ADMINISTRACIÓN NACIONAL DE PATENTES* (INPI – ARGENTINA)

En caso de ser Modificatoria indicar el Nº

PARA U
NACIONA

INPI Exp.: 20160104025
Trámite: 16245423 PATENTES Importe: $4580.-
Fecha/Hora: 27/12/2016 11:36:18.100
Agente: ALONSO, FERNANDO MARTIN

REPUBLICA ARGENTINA

INSTITUTO NACIONAL DE LA PROPIEDAD INDUSTRIAL
ADMINISTRACION NACIONAL DE PATENTES

SOLICITUD DE PATENTE DE INVENCION	X
SOLICITUD DE MODELO DE UTILIDAD	

Hoja 1 de 3

I. SOLICITANTE (S) CANTIDAD DE SOLICITANTES 2

INTERCEMENT BRASIL S.A.
Consignar Nombre y Apellido o Denominación Social (de uno de ellos el resto en ANEXO)
C.U.I.T./C.U.I.L./C.D.I.:
D.N.I.:
Personas Físicas:
Estado Civil:
Nupcias:
Nombre y apellido del cónyuge:
D.N.I.:

Av. das Nações Unidas 12495, 13º e 14º.Torre Nações Unidas A
Domicilio Real - Calle; Nº Piso Dpto

Localidad: Sao Paulo -SP
C.P. Nº: 04578-000
País de Residencia: BR

TTE. GRAL JUAN D. PERÓN 555, PISO 3º, "A"
Domicilio Legal - Calle - Nº - Localidad - Provincia
Código Postal: C1038AAK
Dirección de e-mail: nat@pagbam.com.ar
Teléfono: 5032-3640

II. OBJETO

Título de la invención: Proceso y sistema para reciclar dióxido de carbono transformado por medio de fotosíntesis en oxígeno, e hidrocarburos, que se utilizan de manera integrada para aumentar la eficiencia térmica de los sistemas de combustión.

Carácter de la Patente / Modelo de Utilidad:

Adicional a: Patente Nº
Solicitud Nº
Divisional de la Solicitud Nº

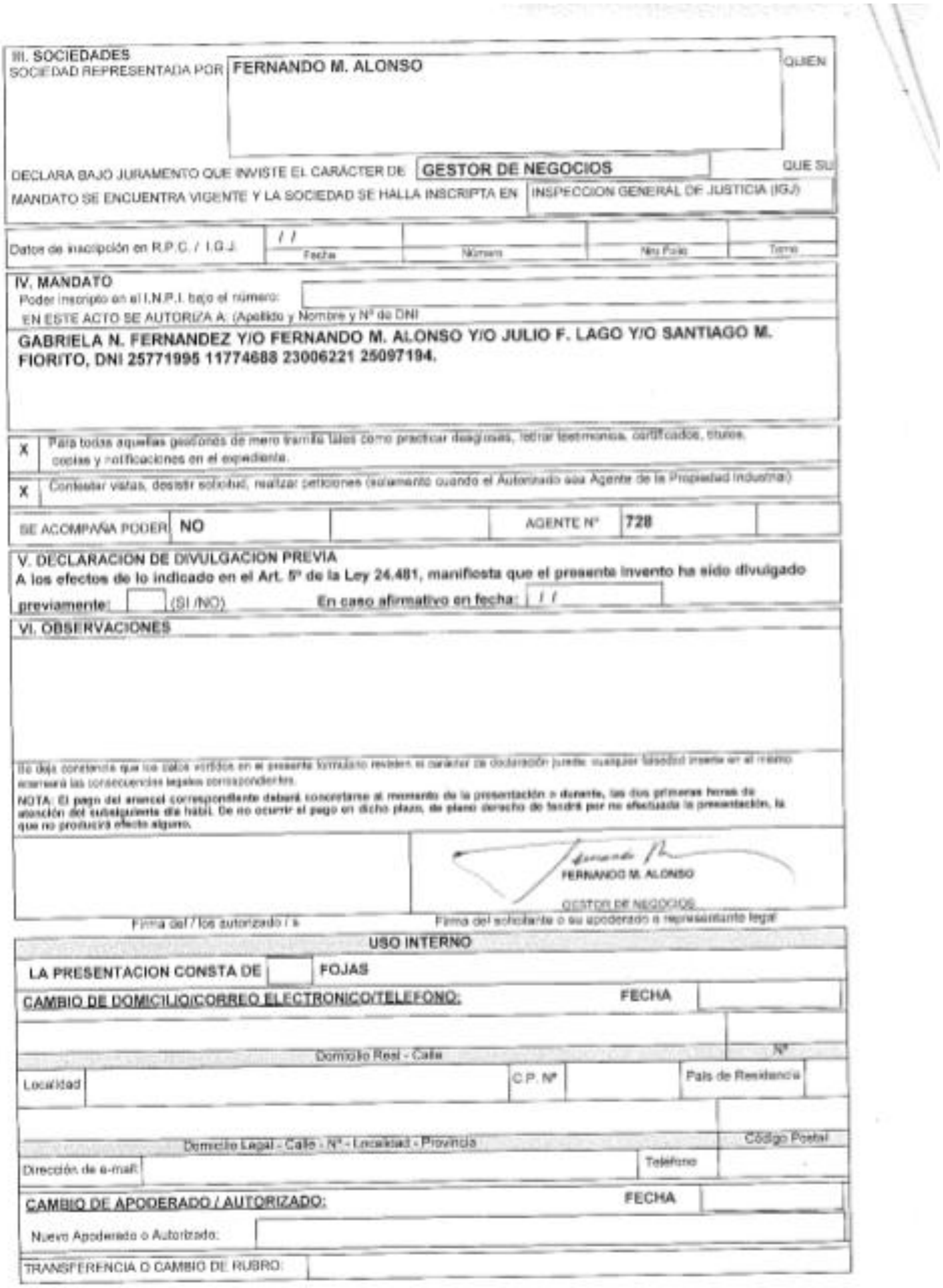
PRIORIDAD (LEY 17.011)

País	Número	Fecha
BR	2015/050276	30/12/2015

DEPOSITO DE MICROORGANISMOS

FECHA DE DEPOSITO:
Nº DE ACCESO AL DEPOSITO:
Nombre de la Institución Depositaria
Domicilio de la Institución
País
Datos del Depositante
Origen del Material Biológico y Genético

Continúa en hoja anexa:



III. SOCIEDADES

SOCIEDAD REPRESENTADA POR **FERNANDO M. ALONSO** QUIEN

DECLARA BAJO JURAMENTO QUE INVISTE EL CARÁCTER DE **GESTOR DE NEGOCIOS** QUE SU MANDATO SE ENCUENTRA VIGENTE Y LA SOCIEDAD SE HALLA INSCRIPTA EN INSPECCION GENERAL DE JUSTICIA (IGJ)

Datos de inscripción en R.P.C. / I.G.J.	/ / Fecha	Número	Nro Folio	Tomo

IV. MANDATO

Poder inscripto en el I.N.P.I. bajo el número:

EN ESTE ACTO SE AUTORIZA A: (Apellido y Nombre y Nº de DNI

GABRIELA N. FERNANDEZ Y/O FERNANDO M. ALONSO Y/O JULIO F. LAGO Y/O SANTIAGO M. FIORITO, DNI 25771995 11774688 23006221 25097194.

X	Para todas aquellas gestiones de mero trámite tales como practicar desgloses, retirar testimonios, certificados, títulos, copias y notificaciones en el expediente.
X	Contestar vistas, desistir solicitud, realizar peticiones (solamente cuando el Autorizado sea Agente de la Propiedad Industrial)

SE ACOMPAÑA PODER **NO** AGENTE Nº **728**

V. DECLARACION DE DIVULGACION PREVIA

A los efectos de lo indicado en el Art. 5º de la Ley 24.481, manifiesta que el presente invento ha sido divulgado previamente: ☐ (SI /NO) **En caso afirmativo en fecha:** / /

VI. OBSERVACIONES

Se deja constancia que los datos vertidos en el presente formulario revisten el carácter de declaración jurada; cualquier falsedad inserta en el mismo acarreará las consecuencias legales correspondientes.

NOTA: El pago del arancel correspondiente deberá concretarse al momento de la presentación o durante, las dos primeras horas de atención del subsiguiente día hábil. De no ocurrir el pago en dicho plazo, de pleno derecho se tendrá por no efectuada la presentación, la que no producirá efecto alguno.

FERNANDO M. ALONSO
GESTOR DE NEGOCIOS

Firma del / los autorizado / s

Firma del solicitante o su apoderado o representante legal

USO INTERNO

LA PRESENTACION CONSTA DE ☐ **FOJAS**

CAMBIO DE DOMICILIO/CORREO ELECTRONICO/TELEFONO: **FECHA**

Domicilio Real - Calle Nº

Localidad C.P. Nº País de Residencia

Domicilio Legal - Calle - Nº - Localidad - Provincia Código Postal

Dirección de e-mail: Teléfono

CAMBIO DE APODERADO / AUTORIZADO: **FECHA**

Nuevo Apoderado o Autorizado:

TRANSFERENCIA O CAMBIO DE RUBRO:

PARA USC
DE L/
IAL

INPI Exp.: **20160104025**

Trámite: 16245423 PATENTES Importe: $4580.-
Fecha/Hora: 27/12/2016 11:36:18.100
Agente: ALONSO, FERNANDO MARTIN

INSTITU
ADMINISTRACION NACIONAL DE PATENTES

REPUBLICA ARGENTINA

HOJA TECNICA

Hoja 2 de 3

(10) PUBLICACION N°: AR ☐ **(12)** ☒ **PATENTE DE INVENCION** ☐ **MODELO DE UTILIDAD**

(21) SOLICITUD N°: **(51) INT.CL.:**

(22) FECHA DE SOLICITUD / /

(30) DATOS PRIORIDAD BR 2015/050276 30/12/2015

(71) SOLICITANTE (S):
INTERCEMENT BRASIL S.A.
UNIVERSIDADE FEDERAL DE SANTA MARIA

(72) INVENTOR(ES):
Eduardo Jacob Lopes, Juliano Smanioto Barin, Bruno Tischer, Cristiano Ragagnin De Menezes, Roger Wagner, Rodrigo Stefanello Rizello (*)continua abajo.

(41) FECHA DE PUBLICACION / /
BOLETIN N°:

(61) ADICIONAL A :

(62) DIVISIONAL DE :

(74) AGENTE: 728

(83) DEPOSITO DE MICROORGANISMOS / /

(54) TITULO DE LA INVENCION: **Proceso y sistema para reciclar dióxido de carbono transformado por medio de fotosíntesis en oxígeno, e hidrocarburos, que se utilizan de manera integrada para aumentar la eficiencia térmica de los sistemas de combustión.**

(57) RESUMEN:

En el campo de la aplicación de procesos y sistemas para aumentar la eficiencia térmica en hornos de combustión mediante la técnica de biooxicombustión, un proceso integrado para la producción y el uso de oxígeno, como comburente, de compuestos orgánicos volátiles y/o semivolátiles, como combustibles, y de dióxido de carbono, como diluyente de nitrógeno en un horno de combustión, que tiene el objetivo de aumentar la eficiencia térmica de los hornos industriales. El oxígeno se produce en fotobiorreactores, que pueden tener diversas configuraciones, y se alimentan con dióxido de carbono industrial, donde la acción de los microorganismos convierte el CO2 en productos gaseosos de metabolismo fotosintético. Adicionalmente, la fracción que no se convierte de dióxido de carbono que se inyecta en el fotobiorreactor se regenera para usar como diluyente del oxígeno. El sistema que se divulga aquí comprende una unidad de generación biológica, preferentemente un fotobiorreactor, que suministra una fase gaseosa; dos unidades de bombeo de gases (2) y (8) y dos sistemas de tratamiento y purificación de gases (3) y (4) y (6) y (7), un horno de combustión (5) y dos conjuntos de medidores y controladores (9) y (10), que operan de manera integrada.

(*) Ihana De Aguiar Severo, Alexandre José Cichoski, Leila Queiroz Zepka, Seiti Sasaki, Mariana Figueira Lacerda De Menezes, Tayuara Ribas Pereira, Ligia Silveira Zottin.

FIGURA MAS REPRESENTATIVA N°:

INPI Exp.: **20160104025**

Trámite: 16245423 PATENTES Importe: $4580.-

Fecha/Hora: 27/12/2016 11:36:18.100

Agente: ALONSO, FERNANDO MARTIN

PARA
NACIO

REPUBLICA ARGENTINA

INSTITUT
ADMINISTRACION NACIONAL DE PATENTES

ANEXO TITULARES

Hoja 3 de 3

Titulo de la invención: **Proceso y sistema para reciclar dióxido de carbono transformado por medio de fotosintesis en oxigeno, e hidrocarburos, que se utilizan de manera integrada para aumentar la eficiencia térmica de los sistemas de combustión.**

Carácter de la Patente / Modelo de Utilidad:

UNIVERSIDADE FEDERAL DE SANTA MARIA

Consignar Nombre y Apellido o Denominación Social

C.U.I.T./C.U.I.L. / C.D.I.:

D.N.I.:

Personas Fisicas: Estado Civil: Nupcias:

Nombre y apellido del cónyuge: D.N.I.:

Av. Roraima 1000.

Localidad: **Barrio Camobi, Santa Maria RS** C.P. N°: **97105-900** Pais de Residencia: **BR**

Persona Jurídica: Datos de inscripción en R.P.C. / I.G.J.

Fecha	Número	Nro Folio	Tomo
/ /			

Dirección de e-mail: Teléfono:

FERNANDO M. ALONSO
TTE. GRAL. JUAN D. PERÓN 565, PISO 3º, "A"(C1038AAM)
EN CARACTER DE GESTOR DE NEGOCIOS AGENTE Nº 728
EMAIL nat@pogban.com.ar TEL 5032-3540

FERNANDO M. ALONSO
GESTOR DE NEGOCIOS

Datos del representante legal — Firma del solicitante o su representante legal

Consignar Nombre y Apellido o Denominación Social

C.U.I.T./C.U.I.L. / C.D.I.:

D.N.I.:

Personas Fisicas: Estado Civil: Nupcias:

Nombre y apellido del cónyuge: D.N.I.:

Localidad: C.P. Nº: Pais de Residencia:

Persona Jurídica: Datos de inscripción en R.P.C. / I.G.J.

Fecha	Número	Nro Folio	Tomo
/ /			

Dirección de e-mail: Teléfono:

Datos del representante legal — Firma del solicitante o su representante legal