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INTEGRAÇÃO MÁSSICA E ENERGÉTICA EM SISTEMAS DE OXICOMBUSTÃO NA INDÚSTRIA DE ALIMENTOS

Santa Maria, RS
2020

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

Orientador: Prof. Dr. Eduardo Jacob Lopes

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“A sorte segue a coragem.”

RESUMO

INTEGRAÇÃO MÁSSICA E ENERGÉTICA EM SISTEMAS DE OXICOMBUSTÃO NA INDÚSTRIA DE ALIMENTOS

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O desenvolvimento de tecnologias alternativas orientadas para mitigação de dióxido de carbono têm sido o alvo de diversas pesquisas científicas, destacando a sustentabilidade e economia dos processos industriais de produção. A captura de carbono através da oxicombustão é considerada como uma abordagem potencial para cumprir com esses requisitos, entretanto, apresenta algumas limitações, em função da demanda de oxigênio e energia, às quais podem ser contornadas com a integração de fotobiorreatores microalgais. A integração de processos propõe melhorar a eficiência térmica de sistemas de combustão, reduzindo os custos e emissões nocivas, por meio da técnica de captura de carbono e utilização biológica. Nesse sentido, o objetivo do presente trabalho foi desenvolver um sistema de oxicombustão através da integração mássica e energética. Primeiramente, o estudo se concentrou em construir um forno em escala laboratorial, avaliar os parâmetros de desempenho térmico, bem como avaliar os parâmetros cinéticos, o quociente fotossintético e os gases de exaustão do fotobiorreator. Posteriormente, a análise do ciclo de vida e da bioeconomia do processo integrado foi realizada e, ao final, um estudo sobre a prospecção tecnológica de patentes. Os resultados obtidos evidenciaram que através do enriquecimento dos gases de exaustão do fotobiorreator, obteve-se um ganho na eficiência térmica do sistema. Paralelamente, foi evidenciado potenciais melhorias no desempenho ambiental em relação as métricas de sustentabilidade e redução nos custos dos utilitários, incluindo o consumo de combustível e comburente. Ainda, o processo cumpriu com os requisitos de inovação e atividade inventiva, demonstrando potencial para a transferência da tecnologia ao setor industrial.

Palavras-chave: Microalgas. Fotobiorreator. Captura de carbono e utilização biológica. Integração de Processos. Análise de Ciclo de Vida. Bioeconomia.

ABSTRACT

MASS AND ENERGY INTEGRATION IN OXYCOMBUSTION SYSTEMS IN THE FOOD INDUSTRY

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The development of alternative technologies aimed at mitigating carbon dioxide has been the target of several scientific pieces of research, highlighting the sustainability and economy of industrial production processes. Carbon capture through oxy-combustion is considered a potential approach to meet these requirements; however, it has some limitations due to the demand for oxygen and energy, which can be overcome with the microalgal photobioreactors integration. The process integration proposes to improve the thermal efficiency of combustion systems, reducing costs and harmful emissions, through the technique of biological carbon capture and utilization. In this sense, the objective of the present work was to develop an oxy-combustion system through mass and energy integration. First, the study focused on building a laboratory-scale furnace, evaluating the thermal performance parameters, as well as evaluating the kinetic parameters, the photosynthetic quotient, and the photobioreactor exhaust gases. Subsequently, the life cycle assessment and the bioeconomy of the integrated process was carried out and, in the end, a study on the technological prospecting of patents. The results obtained showed that through the enrichment of the photobioreactor exhaust gases, a gain in the system's thermal efficiency was obtained. Simultaneously, potential improvements in environmental performance were evidenced concerning sustainability metrics and reduction in utility costs, including fuel and oxidizer consumption. The process also met the requirements for innovation and inventiveness, demonstrating the potential for technology transfer to the industrial sector.

Keywords: Microalgae. Photobioreactor. Biological Carbon Capture and Utilization. Process integration. Life cycle assessment. Bioeconomy.

APRESENTAÇÃO

Esta tese de doutorado está organizada em nove itens principais, sendo os dois primeiros compostos pela **Introdução** e **Objetivos**. Os demais itens encontram-se divididos na forma de capítulos temáticos. Nesse sentido, o **Capítulo 1** é composto pela Revisão bibliográfica acerca dos tópicos que fundamentam esta pesquisa. **Nos Capítulos 2, 3, 4 e 5**, encontram-se todos os resultados do doutoramento e as discussões, que são apresentados na forma de: um depósito e uma concessão de patente, dois artigos publicados, um manuscrito em fase de submissão, e cinco capítulos de livros publicados, respectivamente. O **Capítulo 6** contempla a conclusão geral do trabalho, integrando a temática da tese. Ao final, no **Capítulo 7**, encontram-se algumas sugestões para a realização de trabalhos futuros. O item **Referências** refere-se somente àquelas inseridas na Introdução e Revisão bibliográfica.

SUMÁRIO

1. INTRODUÇÃO

No atual contexto global, há um enorme interesse em dar novas respostas a um dos principais desafios da sociedade: a sustentabilidade. O setor industrial, por exemplo, contribui significativamente para o cenário das alterações climáticas, com uma parcela de 17% de emissões de poluentes atmosféricos (EPA, 2020).

Apesar de uma produtividade relativamente baixa em comparação aos demais setores, a indústria de processamento de alimentos utiliza amplamente insumos energéticos fósseis, o que inevitavelmente favorece o acúmulo de emissões de gases de efeito estufa (GEE) na atmosfera, especialmente o dióxido de carbono (CO_2) (ISLAM et al., 2021). De acordo com os dados obtidos do *Carbon Disclosure Project* (CDP), as dez maiores empresas do ramo alimentício, quando juntas, emitem cerca de 264 milhões de toneladas de GEE por ano (OXFAM, 2020). Além disso, em resposta às políticas ambientais, o setor da manufatura de alimentos tem realizado algumas transformações para atingir metas de redução a longo prazo na demanda de energia, incluindo a substituição de combustíveis fósseis, investimento em novos equipamentos energeticamente eficientes e tecnologias de baixo carbono. No entanto, em um cenário onde a população mundial cresce, a demanda por alimentos deverá aumentar em 60% até 2050 (FAO, 2017).

A fim de mitigar esse problema, diversas pesquisas têm sido desenvolvidas nas últimas décadas para a captura de CO_2. Uma das opções promissoras é a oxicombustão, que está baseada na substituição total ou parcial do ar atmosférico, o qual é utilizado nos processos convencionais de combustão, por atmosferas enriquecidas de oxigênio. Tal alteração, favorece o aumento da eficiência energética do sistema de queima. Consequentemente, há um decréscimo nos requisitos por combustível e nas emissões (YIN & YAN, 2016). Contudo, a principal barreira inerente a oxicombustão é o oxigênio, o qual é fornecido por uma unidade de separação do ar (ASU), que demanda elevado consumo de energia, impactando nos custos de produção e operação (TAFONE et al., 2018).

Por outro lado, essa limitação poderia ser contornada através de processos baseados em microalgas, desenvolvidos essencialmente em fotobiorreatores. Esses sistemas de cultivo são adequados para a bioconversão de CO_2 em biomassa e outros bioprodutos. Dentre eles, destaca-se o oxigênio biológico, um co-produto do metabolismo fotossintético, gerado através das reações de fotólise da água (HELDT

& PIECHULLA, 2011). Paralelamente, esses bioprocessos produzem inúmeros compostos orgânicos voláteis (COVs), os quais possuem considerável conteúdo energético, além de liberarem nos gases de exaustão do fotobiorreator substanciais concentrações de CO_2 não convertido (JACOB-LOPES & FRANCO, 2013; SEVERO et al., 2018; SEVERO et al., 2020).

Nesse sentido, este trabalho apresenta uma nova rota tecnológica envolvendo a abordagem de integração de processos por meio do reuso dos excedentes de massa e energia. O processo integrado proposto aqui é destinado a gerar O_2, COVs e CO_2 em um fotobiorreator microalgal, através da técnica de captura de carbono e utilização biológica, cujos produtos foram recuperados para uso como comburente, combustíveis gasosos e diluente de nitrogênio, respectivamente, em um sistema de bio-combustão. Dessa forma, o estudo desta estratégia se faz necessário para avaliar o potencial de minimizar o consumo de insumos e maximizar o desempenho ambiental e econômico das indústrias de base energética. Finalmente, os termos incluídos no presente trabalho, como processos biotecnológicos, bioengenharia, sistemas integrados, sustentabilidade e bioeconomia, são cada vez mais destacados em todos os aspectos do desenvolvimento técnico-científico.

2. OBJETIVOS

2.1. OBJETIVO GERAL

Desenvolver um sistema de oxicombustão na indústria de alimentos através da integração mássica e energética.

2.2. OBJETIVOS ESPECÍFICOS

- Construir um forno de oxicombustão integrado a um fotobiorreator;
- Avaliar os parâmetros de desempenho térmico do forno de oxicombustão;
- Avaliar os parâmetros cinéticos do fotobiorreator;
- Estabelecer o quociente fotossintético do fotobiorreator;
- Caracterizar os gases de exaustão do fotobiorreator;
- Analisar o ciclo de vida do processo integrado;
- Avaliar a bioeconomia do processo integrado;
- Realizar um estudo sobre prospecção tecnológica de patentes.

3. CAPÍTULO 1

REVISÃO BIBLIOGRÁFICA

3.1 MICROALGAS E METABOLISMO FOTOSSINTÉTICO

O termo microalgas é uma terminologia comercial sem valor taxonômico. As microalgas compreendem um grupo diversificado de microrganismos amplamente conhecidos na superfície terrestre, com cerca de 72.500 espécies catalogadas de forma consistente. Atualmente, os padrões de divisão taxonômica dependem de suas características morfofisiológicas e estruturais, incluindo 16 classes desses organismos (*Cyanophyceae*, *Rhodophyceae*, *Chlorophyceae*, *Charophyceae*, *Euglenophyceae*, *Raphidophyceae*, *Xanthophyceae*, *Bacillariophyceae*, *Chrysophyceae*, *Haptophyceae*, *Phaeophyceae*, *Dinophyceae*, *Cryptophyceae*, *Synurophyceae*, *Eustigmatophyceae* e *Glaucophyceae*). As mais abundantes são as diatomáceas (*Bacillariophyceae*), as algas verdes (*Crysophyceae*) e as algas douradas (*Chrysophyceae*). Por outro lado, as cianobactérias (*Cyanophyceae*), as algas verdes e as diatomáceas são as mais significativas em termos de exploração e uso biotecnológico (JACOB-LOPES et al., 2019).

Do ponto de vista morfológico, as microalgas são altamente diversificadas em forma e tamanho, exibindo uma ampla faixa que varia de 0,5 a 200 µm. Tal conformação é denominada talo, independentemente de ser unicelular ou multicelular e pode se apresentar como caules unicelulares, coloniais e multicelulares (VAN den HOEK et al., 1995).

Em contrapartida, a estrutura celular das microalgas é dividida em procariótica e eucariótica. Os organismos procarióticos incluem bactérias e duas divisões de microalgas (*Cyanophyta* e *Prochlorophyta*). Já os eucariontes incluem as divisões da maioria das algas, sendo *Chlorophyta*, *Euglenophyta*, *Rhodophyta*, *Haptophyta*, *Heterokontophyta*, *Cryptophyta*, *Dinophyta*, *Glaucophyta* e *Chlorarachniophyta*. Embora cada grupo apresente características peculiares, esses microrganismos possuem comportamentos fisiológicos semelhantes, tendo como principal modelo metabólico a fotossíntese, tal como nos vegetais superiores (SUGANYA et al., 2016).

O processo fotossintético em microalgas e cianobactérias ocorre nos cloroplastos e na membrana tilacóide (localizada no citoplasma), respectivamente. Esse mecanismo, que é impulsionado pelo ciclo de Calvin-Benson Bassham, envolve um metabolismo complexo e pode ser subdividido em duas etapas: as reações fotoquímicas, que ocorrem apenas quando as células recebem luz (fase clara), e as reações de conversão de carbono, ocorrendo tanto na presença de luz, quanto no escuro (fase escura). De um modo geral, a fotossíntese é um processo físico-químico, onde as microalgas utilizam a energia luminosa para bioconverter o CO_2 em moléculas orgânicas (CALVIN & BENSON, 1948). A reação global da fotossíntese é descrita pela Eq. 1:

$$6\mathrm{CO_2} + 12\mathrm{H_2O} + \mathrm{nutrientes} \overset{\mathrm{Luz}}{\rightarrow} \mathrm{C_6H_{12}O_6} + 6\mathrm{O_2} + 6\mathrm{H_2O} \qquad (1)$$

No que se refere a bioconversão de CO_2, as microalgas possuem altas taxas fotossintéticas, o que explica o modo como diferentes espécies se adaptam a uma ampla faixa de concentração de carbono e, portanto, está diretamente relacionado a um processo biofísico essencial, conhecido como mecanismo de concentração de carbono (MCC). Esses MCCs correspondem ao uso e acúmulo de diferentes concentrações e formas de carbono inorgânico (GHOSH & KIRAN, 2017). Existem seis diferentes vias de assimilação de carbono por microalgas, sendo que as enzimas anidrase carbônica e ribulose-1,5-bifosfato carboxilase/desidrogenase (RuBisCO) são as responsáveis pela biocatálise dessas reações e são capazes de aumentar consideravelmente os níveis de CO_2 intracelular (SINGH et al., 2014).

Ao mesmo tempo, através de balanços de massa de carbono, a bioconversão de CO_2 resulta em diversos produtos. De acordo com Jacob-Lopes & Franco (2013), em um balanço de massa global, cerca de 70% do carbono injetado nos cultivos microalgais é perdido, indicando que 30% é efetivamente convertido em produtos químicos. A biomassa representa apenas uma pequena fração. Em contrapartida, os COVs correspondem a fração de maior representatividade.

3.2 SISTEMAS DE CULTIVO

A seleção adequada do sistema de cultivo de microalgas é um fator crucial para a bioconversão eficiente de CO_2. Normalmente, esses sistemas são classificados em abertos ou fechados. Entretanto, recentemente, os sistemas híbridos foram investigados para alcançar níveis mais elevados de conversão de dióxido de carbono (JACOB-LOPES et al., 2016).

Estabelecidos no início dos anos 1960, os sistemas abertos são os mais comumente utilizados em larga escala para o cultivo de microalgas. Atualmente, diferentes modelos estão sendo estudados: lagoas rasas, sistemas inclinados ou em cascata, lagoas circulares, lagoas mistas e lagoas de pista ou também conhecidas como lagoas *raceway*. De todas as configurações apresentadas, os sistemas do tipo *raceway* são de longe os mais aceitos para aplicação comercial (BOROWITZKA, 2013). Embora sejam de fácil construção e mais baratos, os sistemas abertos possuem extensos requisitos de área de terra e as condições operacionais oscilam amplamente. Além disso, o risco de contaminação por agentes externos e as perdas por evaporação são elevadas; são altamente vulneráveis às condições climáticas, devido à difusão de CO_2 para a atmosfera, irradiação e temperatura, o que afeta negativamente a produtividade (VERMA & SRIVASTAVA, 2018).

Mais tarde, em 1980, os sistemas fechados começaram a ser desenvolvidos, os quais atualmente são denominados de fotobiorreatores. Diversas versões têm sido patenteadas nos últimos anos para superar as limitações que os sistemas abertos apresentam (BOROWITZKA, 2013). Dentre as configurações existentes, as mais comuns são os fotobiorreatores tubulares, painéis de placas planas, coluna de bolhas e *air-lift*. As últimas versões desenvolvidas com alta performance e flexibilidade são os fotobiorreatores de membranas, biofilmes e do tipo *soft-frame* (VO et al., 2019).

A maioria das *startups* e empresas do setor de microalgas optam por utilizar os fotobiorreatores, preferencialmente porque cada uma dessas configurações apresenta parâmetros eficientes e robustos, proporcionando condições artificiais que garantem a base necessária para melhor controle e monitoramento do meio de cultura. Além desses requisitos, as razões para selecionar esses sistemas de cultivo são também devido à baixa propensão de contaminação, reduzido estresse hidrodinâmico, adequada relação de área/volume (A/V) e altura/diâmetro (A/D), altas produtividades e eficiência na captura de CO_2 e mínimas perdas por evaporação nos gases de exaustão (ACIÉN et al., 2017).

Os principais fatores que devem ser considerados para o desempenho do crescimento celular nos fotobiorreatores são o fornecimento de energia luminosa e CO_2, temperatura e pH controlados, disponibilidade de nutrientes, adequado sistema de mistura e equilibro de gases, facilidade de controle das condições da reação e de aumento de escala (CHANG et al. 2017). Paralelamente, a configuração ideal de um fotobiorreator para aplicação industrial deve levar em consideração a espécie da microalga utilizada, o rendimento do processo, os custos de produção e o produto-alvo desejado (HUANG et al. 2017).

Em termos de custos, no entanto, os fotobiorreatores são provavelmente os equipamentos mais caros nos processos de microalgas. Essa desvantagem é devido a sua sofisticação, que está relacionada ao elevado consumo de energia e qualidade do material de construção. O preço de venda de um fotobiorreator comercial varia muito de uma configuração para outra e, normalmente, o custo incorrido representa cerca de 50% dos custos totais da planta de processamento de microalgas. Nesse sentido, os sistemas de cultivo ainda enfrentam muitas dificuldades em termos de custos de operação e construção, e de aumento de escala, demonstrando que esses fatores devem ser cuidadosamente equilibrados na escolha de um reator ideal (TREDICI et al. 2016).

3.3 OXICOMBUSTÃO

Embora o ar atmosférico seja frequentemente usado como comburente, o nitrogênio no ar pode ter impactos negativos em qualquer processo de combustão industrial. Essencialmente, o calor absorvido pelo nitrogênio durante a combustão é perdido, o que diminui a eficiência de todo o sistema queimador, e a liberação de gases de efeito estufa (principalmente CO_2 e NO_x) é potencializada (WU et al., 2018).

Os processos de combustão podem ser melhorados diminuindo a quantidade de nitrogênio usada no ar de combustão e aumentando a quantidade de oxigênio. Dessa forma, as tecnologias de captura de carbono têm sido rapidamente desenvolvidas para esse propósito. A captura baseada na oxicombustão, também conhecida como combustão enriquecida com oxigênio, é uma das opções mais aceitas, a qual está fundamentada na combustão de um combustível fóssil em uma atmosfera rica em oxigênio, variando de 30 a 95% (SONG et al., 2019). A combustão em níveis elevados de oxigênio produz uma corrente gasosa rica em CO_2 (em torno de 80%) e água, favorecendo a separação e posterior captura. Uma vez capturado, o CO_2 é comprimido e pode ser armazenado, em formações geológicas, ou utilizado, como matéria-prima para a produção de diversos produtos (YAN & ZHANG, 2019).

Como consequência do aumento da pressão parcial de oxigênio, há um ganho na capacidade térmica, resultando em uma elevada eficiência energética dos equipamentos, com redução do consumo de combustível e, portanto, reduzida formação de poluentes (YIN & YAN, 2016). Quimicamente, esses fenômenos ocorrem graças as diferenças nas propriedades dos gases diluentes, N_2 e CO_2, na combustão convencional e na oxicombustão, respectivamente. Os principais impactos serão nas características da cinética de combustão, que é determinada por parâmetros como transferência de calor e massa, temperatura, estabilidade e velocidade de chama, ignição e formação de poluentes (QI et al., 2021).

Embora apresente inúmeras vantagens, a principal barreira a ser superada na oxicombustão refere-se ao requisito por oxigênio, que normalmente deve ser fornecido em grandes quantidades (> 1.000 ton./dia$_{O2}$). Dentre os métodos para a produção de oxigênio, o criogênico através de uma unidade de separação do ar (ASU) é a única opção atualmente disponível no mercado. Entretanto, uma ASU demanda alto consumo de eletricidade, o que penaliza a eficiência energética de todo o processo e inviabiliza a sua operação industrial (WU et al., 2018). Além disso, as elevadas despesas de capital, para implementação da ASU em plantas de captura novas (*new-built*) ou já existentes (*retrofit*) são dominantes, seguida das despesas operacionais, não limitada apenas ao oxigênio, mas também ao aporte de combustível (TANG & YOU, 2018). Por outro lado, apesar da oxicombustão contribuir para a pegada de carbono e demais gases poluentes, existem algumas etapas do processo que podem contribuir para outros impactos ambientais adversos (CUÉLLAR-FRANCA & AZAPAGIC, 2017).

3.4 INTEGRAÇÃO DE PROCESSOS

A integração de processos foi inicialmente desenvolvida como uma resposta à crise energética, causada pelo uso massivo de insumos fósseis. A técnica apresentou muitas vantagens diretas em instalações industriais e, atualmente, tem sido amplamente difundida em diversos domínios da manufatura, como no setor de alimentos, químico, petroquímica e geração de energia (KLEMEŠ, 2013).

Um processo integrado baseia-se em estratégias de engenharia orientadas para o uso efetivo dos recursos industriais, combinando operações unitárias, equipamentos e técnicas de processamento. Como resultado, é possível recuperar, reciclar e/ou reutilizar os excedentes de massa, água e energia, minimizando as emissões, consumo de energia e gastos desnecessários, e maximizando a eficiência do processo. Além disso, o uso de equipamentos de grande porte que exigem alta demanda de energia fóssil podem ser substituídos por novos dispositivos de energia renovável (KLEIN et al., 2018).

Os processos e produtos baseados em microalgas têm sido considerados como a nova tendência da indústria frente à abordagem de integração de processos, justamente porque esses sistemas biológicos cumprem com os requisitos de engenharia e química verde, desenvolvimento biotecnológico e sustentabilidade. Considerando a versatilidade que as tecnologias de microalgas oferecem, diferentes estratégias de integração podem ser realizadas, como a integração de massa (efluentes), energia e água (DEPRÁ et al., 2018).

A integração de massa compreende o uso de resíduos industriais, como efluentes líquidos, sendo uma maneira eficiente de contribuir com o aporte de massa de carbono inorgânico, nitrogênio e fósforo para as culturas microalgais; ou efluentes gasosos, através do uso de gases de combustão industrial de fontes estacionárias de emissão. Esses gases, ricos em CO_2 e NO_x, podem servir como fonte de carbono inorgânico e nitrogênio em cultivos fotossintéticos (FRESEWINKEL et al., 2014; SEVERO et al., 2019). Além disso, apesar da toxicidade, algumas espécies de microalgas conseguem assimilar como um recurso de nutriente compostos como SO_x, os quais são também liberados nos gases de exaustão de combustão (LARA-GIL et al., 2016).

Em contrapartida, a integração de energia considera o uso de calor, através da recuperação da energia térmica de equipamentos ou qualquer outro tipo de sistema de aquecimento (KLEMEŠ, 2013), bem como a energia contida nos materiais derivados dos efluentes, que podem ser empregadas para manter a temperatura do meio de cultivo, na faixa mesofílica, aumentando a produtividade da biomassa de microalgas (MONCADA et al., 2016). A energia a partir do processamento termoquímico da biomassa, para obtenção de bioenergia e biocombustíveis, também pode ser considerada como uma estratégia de integração (WALMSLEY et al., 2018). Recentemente, uma rota potencial de integração de energia pode ser realizada através do uso dos compostos orgânicos voláteis liberados nos gases de exaustão de fotobiorreatores, melhorando a eficiência térmica de processos de combustão (SEVERO et al., 2018; SEVERO et al., 2020).

Finalmente, a integração de água está baseada no uso direto ou indireto de água para os cultivos microalgais ou para qualquer outra etapa do processo que necessite de tal recurso, seja através da água do mar, água doce ou água residuária parcialmente ou totalmente tratada (água de reuso) (DEPRÁ et al., 2018).

Dessa forma, tanto os processos, quanto os produtos baseados em microalgas, desempenham um papel fundamental para a produção de insumos utilizando substratos de baixo custo, reduzindo a pegada de carbono e hídrica e melhorando o desempenho técnico-operacional dos processos integrados.

3.5 ANÁLISE DE CICLO DE VIDA E BIOECONOMIA

As crescentes preocupações ambientais e econômicas para as indústrias são as duas principais motivações para o desenvolvimento de tecnologias alternativas de base biológica. Os processos baseados em microalgas são relativamente prematuros e emergentes em comparação àqueles baseados em insumos fósseis (CHANDRA et al., 2018). Dessa forma, melhorias são necessárias para contribuir com o fornecimento sustentável e lucrativo sobre os bioprodutos e bioprocessos. No entanto, antes da implantação comercial, a viabilidade econômica e ambiental precisa ser elucidada (THOMASSEN et al., 2017).

A análise de ciclo de vida (ACV) tem sido extensivamente estudada como uma ferramenta para ajudar a avaliar e quantificar os possíveis impactos ambientais associados a um produto ou processo, bem como identificar e melhorar os principais pontos críticos durante o ciclo de vida global dos sistemas industriais para reduzir os impactos no meio ambiente (KETZER et al., 2018). Regida pela Organização Internacional de Padronização (ISO - *International Organization for Standardization*), a ACV consiste em uma série de diretrizes que aborda todos os potenciais aspectos e impactos do produto/processo desde a extração e aquisição de matérias-primas, passando pelas etapas de produção, utilização, reciclagem, até sua destinação final (ISO 14040, 2006). Adicionalmente, a ACV inclui quatro fases que permitem uma avaliação mais detalhada: (i) definição do objetivo e escopo; (ii) análise de inventário; (iii) avaliação de impacto; e (v) interpretação. Essas informações são utilizadas para melhorar os processos, corrigir possíveis erros e dar suporte para a futura tomada de decisão (CURRAN, 2006).

Por outro lado, a análise técnico-econômica, uma poderosa ferramenta que está fundamentada em elementos básicos relacionados aos custos de capital e nas despesas operacionais de uma cadeia produtiva, poderá auxiliar na avaliação da viabilidade e lucratividade de qualquer indústria baseada em microalgas, seja na produção de energia, químicos, produtos alimentares ou outros materiais (KERN et al., 2017). A bioeconomia, como também é conhecida tal ferramenta, refere-se também a toda atividade econômica utilizando um recurso biológico, proporcionando melhorias de processos e identificando maiores requisitos de pesquisa e desenvolvimento durante os estágios iniciais de diferentes tecnologias microalgais (GUO & SONG, 2019).

Portanto, ambas ferramentas são essenciais para eliminar qualquer fonte de incerteza que poderá afetar a exploração de uma série de potenciais processos e produtos baseados em microalgas. Aprimorar essas rotas tecnológicas é, sem dúvidas, o principal desafio a ser superado para garantir a implementação industrial bem-sucedida de bioprocessos ambientalmente e economicamente viáveis (DUTTA et al., 2016).

4. CAPÍTULO 2

4.1 DEPÓSITO DE PATENTE

O Pedido de Patente Internacional "*Process and system for re-using carbon dioxide transformed by photosynthesis into oxygen and hydrocarbons used in an integrated manner to increase the thermal efficiency of combustion systems*" foi depositado na Organização Mundial da Propriedade Intelectual (WIPO - World Intellectual Property Organization), em 06 de julho de 2017, sob número de registro WO2017/112984A1.

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(Continua na página seguinte)

(54) Title : PROCESS AND SYSTEM FOR RE-USING CARBON DIOXIDE TRANSFORMED BY PHOTOSYNTHESIS INTO OXYGEN AND HYDROCARBONS USED IN AN INTEGRATED MANNER TO INCREASE THE THERMAL EFFICIENCY OF COMBUSTION SYSTEMS

(54) 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

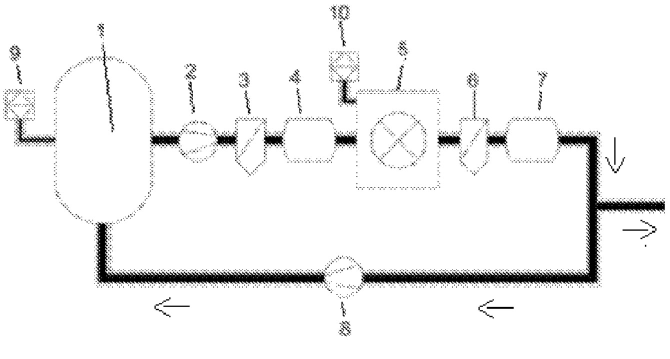

Figura - 1

(57) Abstract : The present invention is used in the field of processes and systems for increasing the thermal efficiency of combustion furnaces through bio-oxicombustion technology. The purpose of the integrated process for producing and using oxygen to oxidise volatile and/or semi-volatile organic compounds used as fuel and carbon dioxide used to dilute nitrogen in a combustion furnace, is to increase the thermal efficiency of industrial furnaces. Oxygen is produced in photobioreactors that can have various configurations and are supplied with industrial carbon dioxide, the activity of micro-organisms converting CO2 into gaseous products of the photosynthetic metabolism. In addition, the unconverted fraction of the carbon dioxide injected into the photobioreactor is regenerated for use as oxygen dilutent. The disclosed system comprises a biological generation unit, preferably a photobioreactor, which supplies the gaseous phase; two gas pumping units (2 and 8) and two gas treatment and purification systems (3 and 4) and (6 and 7), a combustion furnace (5) and two measuring and controlling assemblies (9 and 10) which operate in an integrated manner.

(57) Resumo :

(Continua na página seguinte)

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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 CO2 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.

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 características 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 contínua será mantida por tempo de residência indefinido, que permita a manutenção das culturas em estado estacionário.

[036] O controle de um processo contínuo 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 específica 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 vazão de alimentação e a vazão 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 líquido;

(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, clorofíceas 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 disponíveis 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), aldeídos (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 introduzida 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), aldeídos (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 contínua 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 contínua 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, **caracterizado pelo** 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, **caracterizado pelo** 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, **caracterizado pelo** 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, **caracterizado pelo** 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, **caracterizado pelo** fato dos referidos medidores (9) e (10)serem interligados ainda a um sistema de controle para o ajuste das condições operacionais do sistema.

REIVINDICAÇÕES MODIFICADAS
Recebidas pela Secretaria Internacional no dia 19 Novembro 2016 (19.11.2016)

REIVINDICAÇÕES

1) Um processo para reaproveitamento de gás carbônico transformado 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 processo de oxicombustão.

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), aldeídos (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 contínua 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 contínua 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), sendo a referida injeção dos gases realizada por meio da técnica de oxicombustão, 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, **caracterizado pelo** 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, **caracterizado pelo** fato dos medidores e controladores (9) e (10) serem de pH, temperatura, dióxido de carbono, monóxido de carbono, nitrogênio, oxigênio e carbono orgânico total.

14) Um sistema para reaproveitamento de gás carbônico transformados por meio de fotossíntese em Oxigênio e hidrocarbonetos, de acordo com a reivindicação 13, **caracterizado pelo** fato dos referidos medidores (9) e (10) serem utilizados em uma operação não automatizada como auxiliares na caracterização do processo.

15) Um sistema para reaproveitamento de gás carbônico transformados por meio de fotossíntese em Oxigênio e hidrocarbonetos, de acordo com a reivindicação 13, **caracterizado pelo** fato dos referidos medidores (9) e (10)serem interligados ainda a um sistema de controle para o ajuste das condições operacionais do sistema.

A fim de tornar mais clara a reivindicação independente de no. 1 o adjetivo “transformados” foi passado para o singular “transformado”, para concordar com o substantivo “gás carbônico”. Tal modificação esclarece que quem é de fato transformado é o gás carbônico.

Com intuito de melhor esclarecer que a invenção se limita a ser utilizada em um processo de oxicombustão, em substituição a “forno de combustão” foi incluído “processo de oxicombustão”.

As modificações na reivindicação independente de no. 1 revestem a mesma de atividade inventiva, pois agora foi especificado que a aplicação conjugada de Oxigênio, dos compostos orgânicos voláteis e/ou semivoláteis e do dióxido de carbono em processos de oxicombustão matéria essa não antecipada por nenhuma combinação de documentos do estado da técnica. Tendo em vista as modificações acima, as reivindicações dependentes de processo de 2 a 7 foram inalteradas.

A reivindicação independente de sistema de no. 8 foi emendada a fim de especificar que a injeção dos gases ocorre por meio da técnica de oxicombustão. Dessa forma, limita-se o escopo de proteção da presente invenção a fim de torna-la inventiva frente ao estado da técnica. Ou seja, nenhuma combinação de documentos do estado da técnica torna óbvia para um técnico no assunto o sistema aqui ensinado e reivindicado.

A reivindicação dependente de no. 13 perdeu a sua função, uma vez que a característica nela reivindicadas é agora pleiteada na reivindicação independente de N°8. Dessa forma, a reivindicação de no. 13 foi excluída do quadro reivindicatório. As reivindicações de 14 a 16 foram renumeradas transformando-se nas reivindicações de 13 a 15.

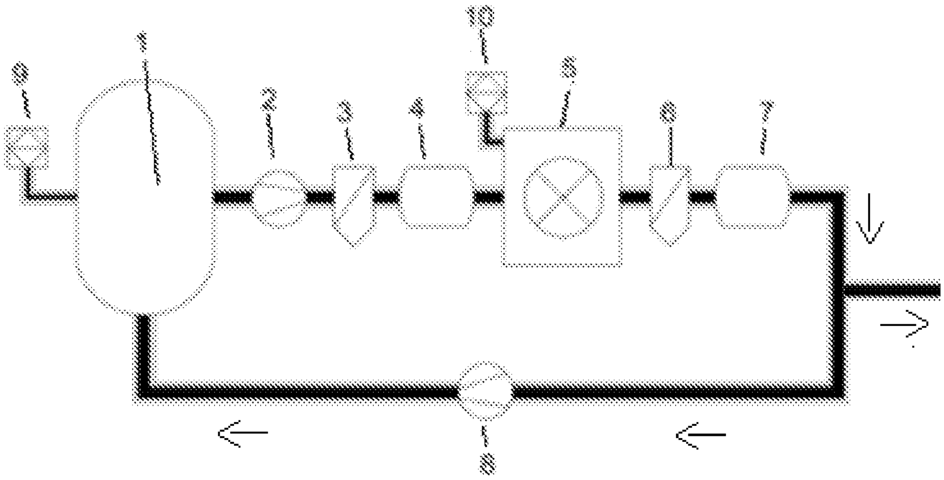

Figura - 1

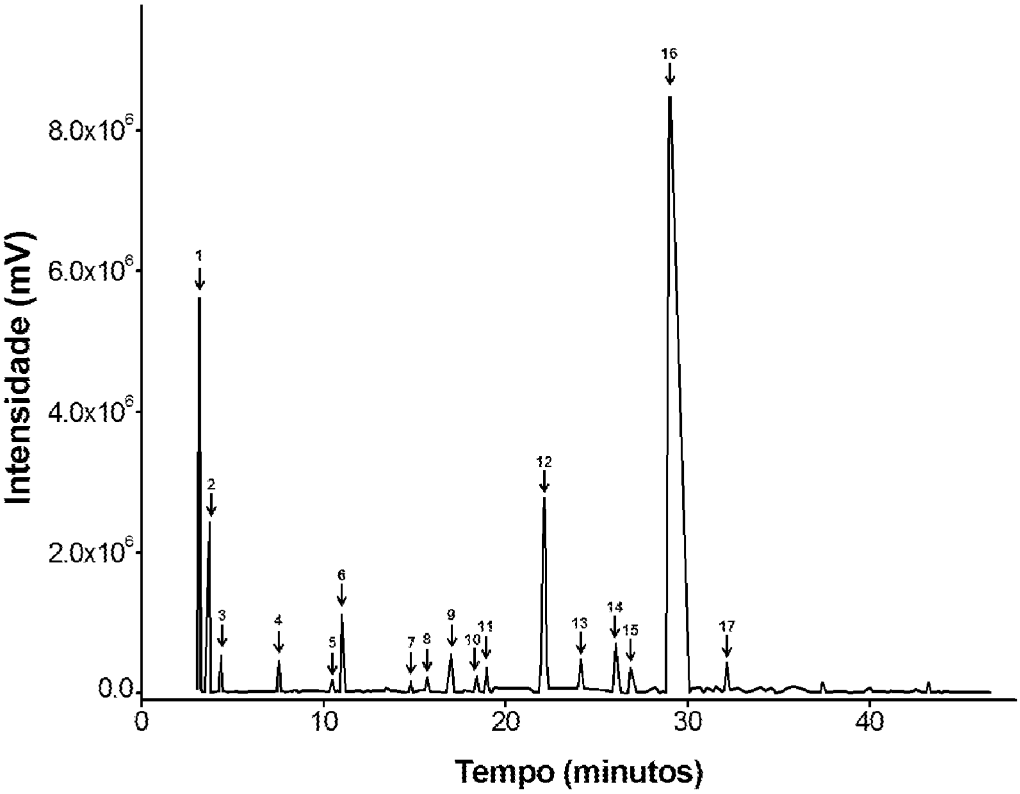

Figura - 2

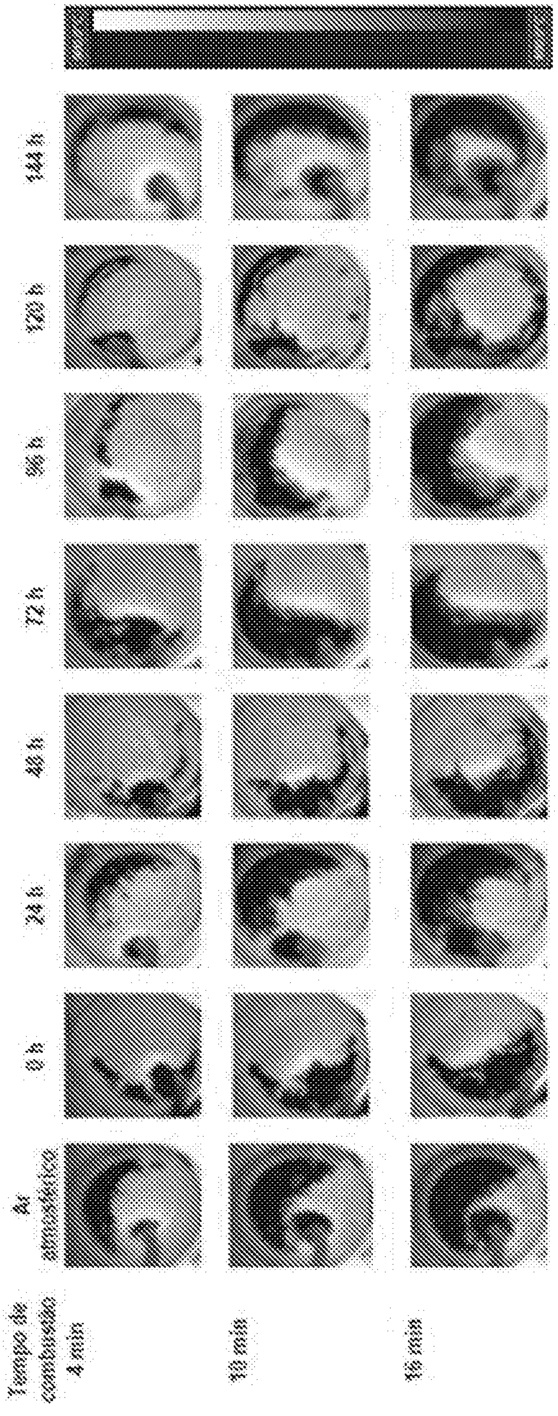
Tempo de combustão
4 min
10 min
16 min
Ar atmosférico
0 h
24 h
48 h
72 h
96 h
120 h
144 h

Figura - 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/BR2015/050276

A. CLASSIFICATION OF SUBJECT MATTER
F23L 7/00 (2006.01), B01D 53/62 (2006.01), C12N 1/12 (2006.01), F23N 5/00 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

F23L, B01D, C12N, C12M, F23N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Banco de Patentes Brasileiro - INPI-BR

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC, USPTO

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	**US 2005260553 AI (BERZIN ISAAC [US]) 24 November 2005 (2005-11-24) paragraphs 0002 to 0013, 0094, 0095, 0158 and 0164 figures 6a and 9 abstract**	1-4, 8, 14, 16 5-7, 9-13, 15
Y A	**US 2008178739 AI (GREENFUEL TECHNOLOGIES CORP [US]) 31 July 2008 (2008-07-31) paragraphs 0002 to 0009, 0060 and 0112 abstract**	1-4, 8, 14, 16 5-7, 9-13, 15
Y A	**WO 2010068288 A2 (JOULE BIOTECHNOLOGIES INC [US]) 17 June 2010 (2010-06- 17) paragraphs 0002, 0003, 0017, 0024, 0054, 0138 and 0242 to 0247 abstract**	1-5, 8, 14, 16 6-7, 9-13, 15

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search **02/09/2016**	Date of mailing of the international search report **09/09/2016**
Name and mailing address of the ISA/ INSTITUTO NACIONAL DA PROPRIEDADE INDUSTRIAL Rua Sao Bento nº 1, 17º andar cep: 20090-010, Centro - Rio de Janeiro/RJ Facsimile No. +55 21 3037-3663	Authorized officer **Denise Neves Menchero Palacio** Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/BR2015/050276

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	**US 2012252105 AI (BIOPROCES SH20 LLC [US])** **04 October 2012 (2012-10-04)** **paragraphs 0002, 0249, 0250, 0415 and 0618** **figures 1, 2 and 122**	1-5, 8, 14, 16 6-7, 9-13, 15
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Y A	**E. Jacob-Lopes, T. T. Franco. Journal of C02 Utilization, 2, 1-7,** **From oil refinery to microalgal biorefinery, 2013.** **pages 1 and 5**	1-5, 8, 14, 16 6-7, 9-13, 15
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RELATÓRIO DE PESQUISA INTERNACIONAL

Depósito internacional Nº
PCT/BR2015/050276

A. CLASSIFICAÇÃO DO OBJETO

F23L 7/00 (2006.01), B01D 53/62 (2006.01), C12N 1/12 (2006.01), F23N 5/00 (2006.01)

De acordo com a Classificação Internacional de Patentes (IPC) ou conforme a classificação nacional e IPC

B. DOMÍNIOS ABRANGIDOS PELA PESQUISA

Documentação mínima pesquisada (sistema de classificação seguido pelo símbolo da classificação)

F23L, B01D, C12N, C12M, F23N

Documentação adicional pesquisada, além da mínima, na medida em que tais documentos estão incluídos nos domínios pesquisados

Banco de Patentes Brasileiro - INPI-BR

Base de dados eletrônica consultada durante a pesquisa internacional (nome da base de dados e, se necessário, termos usados na pesquisa)

EPODOC, USPTO

C. DOCUMENTOS CONSIDERADOS RELEVANTES

Categoria*	Documentos citados, com indicação de partes relevantes, se apropriado	Relevante para as reivindicações Nº
Y	US 2005260553 A1 (BERZIN ISAAC [US])	1-4, 8, 14, 16
A	24 novembro 2005 (2005-11-24)	5-7, 9-13, 15
	parágrafos 0002 a 0013, 0094, 0095, 0158 e 0164	
	figuras 6a e 9	
	resumo	
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Y	US 2008178739 A1 (GREENFUEL TECHNOLOGIES CORP [US])	1-4, 8, 14, 16
A	31 julho 2008 (2008-07-31)	5-7, 9-13, 15
	parágrafos 0002 a 0009, 0060 e 0112	
	resumo	
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Y	WO 2010068288 A2 (JOULE BIOTECHNOLOGIES INC [US])	1-5, 8, 14, 16
A	17 junho 2010 (2010-06-17)	6-7, 9-13, 15
	parágrafos 0002, 0003, 0017, 0024, 0054, 0138 e 0242 a 0247	
	resumo	
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☒ Documentos adicionais estão listados na continuação do quadro C ☒ Ver o anexo de famílias das patentes

* Categorias especiais dos documentos citados:

"A" documento que define o estado geral da técnica, mas não é considerado de particular relevância.

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"&" documento membro da mesma família de patentes.

Data da conclusão da pesquisa internacional

02/09/2016

Data do envio do relatório de pesquisa internacional:

09/09/2016

Nome e endereço postal da ISA/**BR**

INSTITUTO NACIONAL DA
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Funcionário autorizado

Denise Neves Menchero Palacio

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RELATÓRIO DE PESQUISA INTERNACIONAL

Depósito internacional Nº
PCT/BR2015/050276

C. DOCUMENTOS CONSIDERADOS RELEVANTES

Categoria*	Documentos citados, com indicação de partes relevantes, se apropriado	Relevante para as reivindicações Nº
Y A	US 2012252105 A1 (BIOPROCESSH20 LLC [US]) 04 outubro 2012 (2012-10-04) parágrafos 0002, 0249, 0250, 0415 e 0618 figuras 1, 2 e 122	1-5, 8, 14, 16 6-7, 9-13, 15
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Y A	E. Jacob-Lopes, T. T. Franco. Journal of CO2 Utilization, 2, 1-7, From oil refinery to microalgal biorefinery, 2013. páginas 1 e 5	1-5, 8, 14, 16 6-7, 9-13, 15
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RELATÓRIO DE PESQUISA INTERNACIONAL
Informação relativa a membros da família da patentes

Depósito internacional Nº
PCT/BR2015/050276

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4.2 CONCESSÃO DE PATENTE

A Patente Internacional “*Process and system for re-using carbon dioxide transformed by photosynthesis into oxygen and hydrocarbons used in an integrated manner to increase the thermal efficiency of combustion systems*” foi concedida ao Instituto Nacional da Propriedade Industrial de Portugal, em 15 de janeiro de 2019, sob número de registro PP/426-PT.

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PORTUGAL

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N.º 2017112984

O Instituto Nacional da Propriedade Industrial (INPI) passa o presente título para prova do direito sobre a invenção identificada na(s) folha(s) anexa(s), devidamente autenticada(s).

Lisboa, 30 de abril de 2019

Ana Bandeira

Ana Bandeira
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EPÍGRAFE

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

RESUMO

A PRESENTE INVENÇÃO ENCONTRA O SEU CAMPO DE APLICAÇÃO ENTRE OS PROCESSOS E SISTEMAS PARA O AUMENTO DE EFICIÊNCIA TÉRMICA EM FORNOS DE COMBUSTÃO ATRAVÉS DA TÉCNICA DE BIO OXI-COMBUSTÃO. O PROCESSO INTEGRADO PARA A PRODUÇÃO E USO DE OXIGÉNIO, COMO UM COMBURENTE, DOS COMPOSTOS ORGÂNICOS VOLÁTEIS E/OU SEMI-VOLÁTEIS, COMO COMBUSTÍVEIS, E DO DIÓXIDO DE CARBONO, COMO UM DILUENTE DE AZOTO NUM FORNO DE COMBUSTÃO, TEM COMO OBJETIVO AUMENTAR A EFICIÊNCIA TÉRMICA DE FORNOS INDUSTRIAIS. O OXIGÉNIO É PRODUZIDO EM FOTOBIORREATORES, QUE PODEM APRESENTAR CONFIGURAÇÃO

VARIADA, SENDO ALIMENTADOS COM DIÓXIDO DE CARBONO INDUSTRIAL, CUJA AÇÃO DOS MICRO-ORGANISMOS CONVERTE O CO2 EM PRODUTOS GASOSOS DO METABOLISMO FOTOSSINTÉTICO. ADICIONALMENTE, A FRAÇÃO NÃO CONVERTIDA DO DIÓXIDO DE CARBONO INJETADA NO FOTO-BIORREATOR É REGENERADA PARA USO COMO DILUENTE DO OXIGÉNIO. O SISTEMA AQUI REVELADO COMPREENDE UMA UNIDADE DE GERAÇÃO BIOLÓGICA, PREFERENCIALMENTE UM FOTO-BIORREATOR, 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.

RESUMO

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

A presente invenção encontra o seu campo de aplicação entre os processos e sistemas para o aumento de eficiência térmica em fornos de combustão através da técnica de bio oxi-combustão. O processo integrado para a produção e uso de oxigénio, como um comburente, dos compostos orgânicos voláteis e/ou semi-voláteis, como combustíveis, e do dióxido de carbono, como um diluente de azoto num forno de combustão, tem como objetivo aumentar a eficiência térmica de fornos industriais. O oxigénio é produzido em foto-biorreatores, 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 injetada no foto-biorreator é regenerada para uso como diluente do oxigénio. O sistema aqui revelado compreende uma unidade de geração biológica, preferencialmente um foto-biorreator, 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.

5. CAPÍTULO 3

5.1 ARTIGO 1

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

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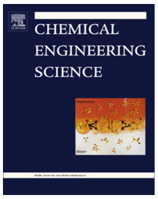

Bio-combustion of petroleum coke: The process integration with photobioreactors

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HIGHLIGHTS

- Photobioreactor exhaust gases were used as oxidizers, fuels and nitrogen diluent.
- Photobioreactor exhaust gases enhance the thermal performance of combustion system.
- The process has potential to supply energy and fuel economy in industrial facilities.

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ABSTRACT

The objective of this study is to develop a bio-combustion system integrated into a photobioreactor. Different oxidizers (a simulated industrial gas stream containing 5.5% O_2, 18% CO_2 and 76.5% N_2, the atmospheric air and the photobioreactor exhaust gases in different residence times) were injected into the combustion chamber, and combustion temperature, combustion stability, heating rate, and fuel conversion were analyzed. The results have shown that the use of photobioreactor exhaust gases as oxidizer, biofuel, and nitrogen diluent in the combustion furnace, have 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. Thus, the integration of these processes could be considered a viable strategy to improve the combustion systems thermal performance, efficiently contributing to the sustainability and economy of industrial operations.

1. Introduction

The continued growth in anthropogenic emissions of air pollutants, from burning fossil fuels, has become an issue of concern due to their adverse effects on the environment, particularly related to the carbon dioxide (CO_2), a major greenhouse gas (GHG) (Dowell et al., 2017). From an economic point of view, as long as fossil fuels and carbon-intensive industries play dominant roles in this sector, carbon capture and storage (CCS) or utilization (CCU) will remain a critical solution for reducing the emissions (IEA, 2013). These technologies face numerous barriers that must be overcome before they can be used on a large scale (Bruhn et al., 2016).

Recently, an associated alternative – biological carbon capture and utilization (BCCU) – has started to get more attention in comparison to the CCU and CCS, representing a possible strategy for CO_2 capture through polluting sources. BCCU directly converts CO_2 into biomass and other valuable products through photosynthetic cultures (Choi et al., 2017).

In this context, there are some CO_2 capture methods associated with different combustion processes, and bio-combustion has proven to be an attractive option mainly due to the increase in thermal efficiency. Bio-combustion is the process of combined use of oxygen (O_2), CO_2 and volatile organic compounds (VOCs) generate biologically by microalgae cultures in photobioreactors (Jacob-Lopes et al., 2017).

Photobioreactors are considered promising equipment to generate substantial O_2 and VOCs concentrations, since they work as a photosynthetic microorganism culture medium, such as microalgae. Metabolically, the O_2 is generated by water photolysis reactions, an essential chemical step in the photosynthesis process (Walker, 2002). Through this technological route, it is obtained close to 0.75 kg O_2 for every 1 kg bioconverted CO_2, which demonstrates its excellent production potentiality (Eriksen et al., 2006). Some authors have reported the O_2 accumulation produced in tubular photobioreactors, where the dissolved oxygen

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concentrations can reach up to 400% of air saturation, suggesting the high potential O_2 generation in these systems (Molina et al., 2001; Raso et al., 2012).

Additionally, these bioprocesses simultaneously produce several VOCs, and once the biosynthetic routes are known, the compounds can be divided into terpenoids, carbohydrate, fatty acids and amino acids derivatives, and phenylpropanoids/benzenoids (Santos et al., 2016). The VOCs belong to different chemical classes, such as alcohol, esters, hydrocarbons, terpenes, ketones, sulfur compounds and carboxylic acids, presenting a significant energetic value (Van Durme et al., 2013). Furthermore, a part of the injected CO_2 into the photobioreactor is lost through the exhaust gases, because most of the closed systems achieve CO_2 removal efficiency rates under 30%. It corresponds to a fraction of unconverted carbon in these systems, assisting in the nitrogen (N_2) dilution (Jacob-Lopes et al., 2009).

Therefore, the process integration through the bio-combustion technique for biological GHG conversion in O_2, VOCs and CO_2, which could be reused as oxidizers, gaseous fuels and nitrogen diluent, respectively, is considered an innovative technology with large potential for industrial application (Berzin, 2005; Lewnard and Wu, 2008; Van et al., 2010; Ahrens et al., 2012; Bliss, 2013, Gonzalez et al., 2014; Jacob-Lopes et al., 2015; Jacob-Lopes et al., 2016; Jacob-Lopes et al., 2017). Moreover, this is an approach for energy saving and emissions mitigation, that has been studied according to resource conservation.

Conversely, should be considered that in an integrated process, with the nitrogen removal from the gaseous stream, O_2 concentration increases parallelly, so the oxygen mass transfer to the culture medium also increases and a new equilibrium is established. These high O_2 levels in the medium may potentially damage the performance of microalgal cells, and cause growth-inhibiting effects (Solimeno et al., 2017).

In this sense, the objective of this study is to develop a bio-combustion system integrated into photobioreactor. The research focuses on the evaluation of the combustion furnace thermal performance and the photobioreactor exhaust gases characterization.

2. Materials and methods

2.1. Bio-combustion system

The experiments were performed in a bio-combustion system manufactured in lab-scale (Fig. 1). The experimental apparatus was constituted by a furnace made of stainless steel plates, with the coating composed of the refractory material to reduce heat loss through walls. The internal dimensions of the combustion chamber were height (H) = 40 cm, depth (D) = 20 cm and width (W) = 20 cm. The furnace was equipped with two 300 W electrical resistors. A ceramic support was inserted in the center combustion chamber, which was used to introduce the fuel sample. The photobioreactor exhaust gases were directed to the chamber through a stainless steel pipe, located on the bottom of the furnace, measuring length (L) = 80 cm and internal diameter (ID) = 3 mm. The gases resulting from the combustion were forwarded 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.

2.2. Fuel composition

The fuel used in the combustion experiments was the petroleum coke. The sample was characterized using a PerkinElmer 2400 CHNS/O elemental analyzer (PerkinElmer, Waltham-MA, USA), in which two milligrams of 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.

2.3. Oxidizers

For furnace feed, three oxidizers were used in the experiments: (i) the typical gaseous emissions of a clinkering furnace was simulated, through a primary standard mixture (Praxair, Inc., Brazil), containing 5.5% O_2, 18% CO_2 and 76.5% N_2; (ii) atmospheric air (constituted by 21% O_2 and 79% N_2); and (iii) photobioreactor exhaust gases in different residence times.

2.4. Obtaining kinetic data in bio-combustion furnace

The experiments were monitored every 24 h during the microorganism growth phase by the injection of photobioreactor exhaust gases and the other oxidizers tested in the bio-combustion furnace. The experimental conditions were the following: initial coke mass 1.0 g, total combustion time of 20 min and airflow rate 1.0 L/min. During the bio-combustion, combustion temperature, combustion stability, heating rate, and fuel conversion were continuously monitored. The tests were carried out in triplicate.

2.5. Thermal performance parameters of bio-combustion system

The evaluation of thermal performance of the bio-combustion system was performed by using a long wave infrared camera Flir SC 305 with a resolution of 320 × 240 pixels at a rate 3.75 Hz and maximum temperature at 1200 °C (Flir Systems, Wilsonville-OR, USA). The camera was positioned 60 cm from the combustion zone. The images were processed using FLIR Tools + software. The material emissivity (0.68) was determined through previous petroleum coke heating at 100 °C, and all measurements were corrected at ambient temperature and relative humidity.

The use of such device recorded the fuel particles superficial temperature during combustion in the chamber. Therefore, each pixel presents both a temperature and an average temperature value. Distribution could be estimated by image processing. An area of 180 pixels was selected in the software for the temperature monitoring, and it has covered at least 90% of the sample surface inside the chamber. Considering the monitoring of reaction during 20 min and the frame rate 3.75 Hz, around 4.500 images were obtained. It corresponds to 810.000 temperature values for the construction of each temperature plot.

The combustion temperature (°C) was calculated from the average of maximum temperature values measured by the infrared camera. It has corresponded to a two minutes interval during the combustion reaction.

The combustion stability (%) was evaluated based on the fuel temperature distribution inside the combustion chamber (Eq. (1)):

$$CS = \left(\frac{\sigma_T}{T}\right) \times 100 \tag{1}$$

where σ_T corresponds to the standard deviation of fuel temperature values inside the chamber and T is the combustion temperature.

The heating rate (°C/min) was determined from Eq. (2):

$$\frac{dT}{dt} = \frac{(Tn - T_0)}{(tn - t_0)} \tag{2}$$

where Tn is the instantaneous furnace temperature, To is the initial furnace temperature, $tn - to$ is the time taken from the experiment starting point until the furnace has reached the final temperature.

At the end of combustion reaction, fuel conversion (%) was determined (Eq. (3)):

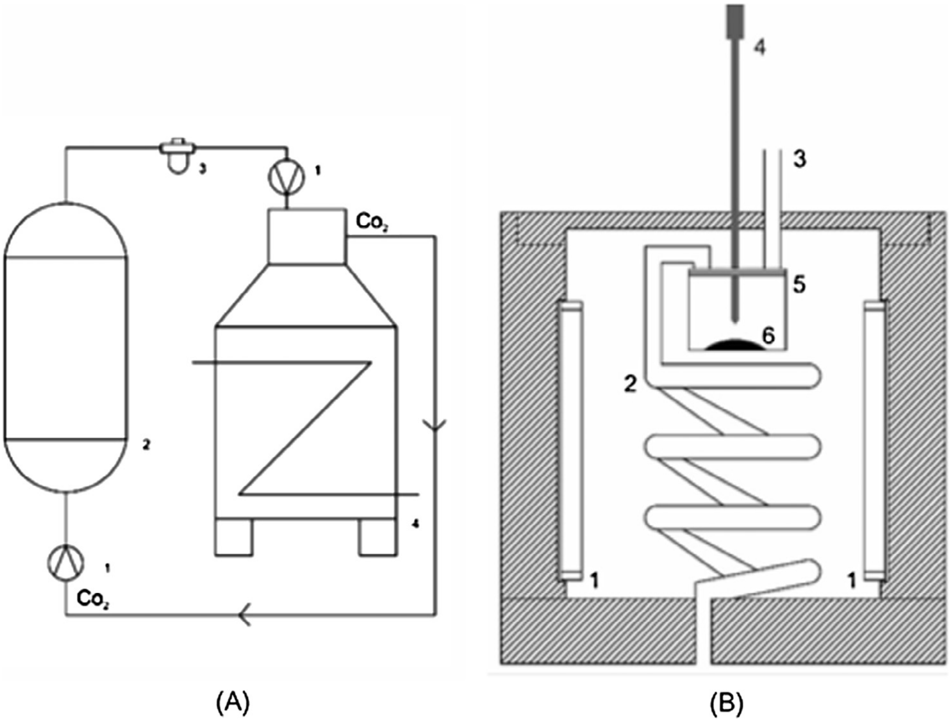

Fig. 1. Schematic diagram of the bio-combustion system. (A) 1: Pumps for the flow control and mixing of gases; 2: Photobioreactor; 3: Filter for humidity; 4: Bio-combustion furnace; (B) 1: Electrical resistances; 2: Photobioreactor exhaust gases inlet channel; 3: Output channel of the exhaust gases;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

$$X = \frac{(M_i - M)}{(M_i - M_C)} \times 100 \tag{3}$$

where X corresponds to the converted fraction and M represents the mass of coke in different stages of combustion.

2.6. 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 °C, photon flux density 15 μmol/m^2/s and a photoperiod 12 h.

2.7. 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 7.5 cm, height 75 cm and nominal working volume 2.0 L. The dispersion system for the reactor consisted on 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, located in a photoperiod chamber. The CO_2/air mixture was adjusted to achieve the desired carbon dioxide concentration in the airstream, through three rotameters that measured the CO_2 flow rates, air and the mix of gases, respectively.

2.8. Obtaining the kinetic data in photobioreactor

The experiments were carried out in photobioreactors operating in an intermittent regime, fed with 2.0 L of culture medium. The experimental conditions were the following: initial cell concentration 0.1 g/L, isothermal reactor operating at 26 °C, photon flux density of 150 μmol/m^2/s and continuous aeration of 1 VVM (volume of air per volume of culture per minute) with air injection enriched with 15% CO_2 (Jacob-Lopes and Franco, 2013). The empty-bed residence time (EBRT) of the gaseous compounds in photobioreactor was kept constant at 1 min. The cell density, carbon dioxide, oxygen, inorganic carbon and total carbon concentrations were monitored every 24 h during the microorganism growth phases. Residence times of up to 144 h were considered for all the experiments. The tests were carried out in triplicate.

2.9. Kinetic parameters

Carbon dioxide concentration data were used to calculate the elimination capacity (kg/m^3/d) and removal efficiency (%) (Eqs. (4) and (5)):

$$EC = \frac{(C_0 - C_i) \times Q}{V_R} \tag{4}$$

$$RE = \frac{(C_i - C_0)}{C_i} \times 100 \tag{5}$$

where C_0 and C_i correspond to the inlet and outlet CO_2 concentration, respectively, Q is the gas flow and V_R is the reactor volume.

Oxygen concentration data were used to calculate the production capacity (kg/m^3/d) and photosynthetic quotient (Eqs. (6) and (7):

$$PC = \frac{(C_0 - C_i) \times Q}{V_R} \tag{6}$$

where C_0 and C_i correspond to the inlet and outlet O_2 concentration.

$$PQ = \frac{\frac{d(O_2)}{dt}}{\frac{d(CO_2)}{dt}} \tag{7}$$

where dO_2/dt and dCO_2/dt corresponds to the variation of the O_2 and CO_2 concentration over time, respectively.

2.10. Analytical methods

2.10.1. General analysis of process control

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

2.10.2. Determinations of CO_2 and O_2 concentration profiles

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

2.10.3. Analysis of total organic carbon (TOC)

Total carbon (TC) and inorganic carbon (IC) have been measured in the liquid and gaseous phases using the carbon analyzer TOC-VCSN (Shimadzu, Kyoto, Japan) with a normal sensibility catalyst (platinum on 1/8″ Alumina Pellets). Organic carbon (OC) was calculated by the difference between TC and IC. In the liquid phase measurements, 20 mL of the medium was filtered through a 0.2 μm filter. In the total carbon analysis, 27 μL samples were carried to the combustion tube at 680 °C, where the CO_2 catalytic oxidization has occurred. For the inorganic carbon analysis, samples of 27 μL have reacted with hydrochloric acid 2 M to convert all the inorganic carbon into CO_2. In both cases, the carbon dioxide was quantified by non-dispersive infrared absorption, and the concentrations were calculated from analytical curves (peak area × concentration) previously constructed by standard solutions of potassium hydrogen phthalate for TC and sodium hydrogen carbonate for IC. The gaseous measuring has made collecting gas samples in the photobioreactor entrance flow and exit flow. To measure the total carbon, 50 μL samples were injected and carried over a flow provided by an analytical O_2 cylinder in the combustion tube (680 °C).The samples were catalytic oxidized to CO_2. Finally, to analyze inorganic carbon, 40 μL samples were injected and carried directly to the detector. They were quantified by a non-dispersive infrared detector, and the concentrations achieved by analytical curves of peak × concentration were observed at the same conditions, with pure CO_2.

2.10.4. Analysis of volatile organic compounds by GC/MS

The VOCs formed in the bioprocess were extracted using the technique of headspace solid-phase micro-extraction (HS-SPME) with a 50/30 μm divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) fiber (Supelco, Bellefonte-PA, USA) (Santos et al., 2016). The extraction temperature was 40 °C, with 5 min of equilibration time and exposure of the fiber for 45 min. The analysis of the VOCs was performed by a gas chromatograph coupled to a mass spectrometer (Shimadzu, Kyoto, Japan), separated on a DB-Wax fused silica capillary column, 60 m length, 0.25 mm id, and 0.25 μm film thickness (Chrompack Wax 52-CB) in a Shimadzu QP 2010 Plus gas chromatograph mass spectrometer. The initial oven temperature for the DB-Wax column was set at 35 °C for 5 min, followed by a linear increase at 5 °C/min–220 °C, and this temperature was held for 5 min. For identification, an electron-impact ionization voltage of 70 eV was applied, and helium was used as the carrier gas.

The VOCs were identified by a comparison of their MS spectra to those provided by the computerized library (NIST MS Search). Also, to assist with identification, each volatile linear retention index (LRI) was calculated using the retention times of a paraffin homologues standard mixture, prepared in hexane and compared to the LRI values published in the literature for columns with the same polarity (Acree and Arn, 2017). Sample co-injection and the standard mixture have provided experimental LRIs to the compounds, which were compared with those standards analyzed under similar conditions.

2.10.5. Mass and energy balances

The mass balance of the photobioreactor was performed through Eq. (8):

$$C_{in} - C_{out} = V_R M_c \left(\frac{d[C_{biomass}]}{dt}\right) + V_H M_c \left(\frac{d[C_{headspace}]}{dt}\right) \tag{8}$$

where C_{in} and C_{out} correspond to the carbon mass flow rate at the inlet and outlet of photobioreactor, V_H is the volume of the headspace, M_C is the atomic weight of carbon, $(d[C_{biomass}])/dt$ is the rate of change in carbon concentration converted into biomass, and $(d[C_{headspace}])/dt$ is the rate of change in carbon concentration in headspace.

The energy balance of the bio-combustion furnace was calculated from Eq. (9):

$$Q = m_F \times c_F \times (T_{\mathrm{out}} - T_{in}) \tag{9}$$

where Q is the amount of heat lost in the exhaust gases, m_F is the total mass of fuel, c_F is the average specific heat of fuel, T_{out} is the combustion temperature of the exhaust gases, and T_{in} is the temperature before the fuel is burned.

The net energy ratio (NER) of the system was calculated through Eq. (10):

$$NER = \frac{\sum E_{out}}{\sum E_{in}} \tag{10}$$

where E_{out} is the sum of the total energy produced, and E_{in} is the sum of the energy content required in all system operations.

2.10.6. Estimation of production and power generation rate of volatile organic compounds

The VOCs production rate (kg/m^3/d) was estimated corroborating the TOC data measured in the photobioreactor gaseous phase. The total compounds have been identified and quantified in the GC/MS using the Eq. (11):

$$r_{VOCs} = \frac{\left(\frac{(OC_i - OC_O)\times Cc}{100}\right) \times Q}{V_R} \tag{11}$$

where OC_i and OC_O correspond to the inlet and outlet carbon organic concentration, respectively, and Cc is the VOC concentration. Additionally, the power generation rate was estimated based on calorific power of the carbon (34,000 kJ/kg) and hydrogen (120,000 kJ/kg) atoms of organic molecule (Hanby, 1994).

2.11. Statistical analyses

Analysis of variance (one-way ANOVA) and Tukey's test ($p < .05$) were used to check the differences between the studied oxidants. The analyses were performed on the software Statistica 7.0 (StatSoft, Tulsa-OK, USA).

3. Results and discussion

3.1. Evaluation of the thermal performance of the bio-combustion furnace

Fig. 2 shows the bio-combustion furnace thermal performance with the injection of different oxidizers. Based on the temperature dynamics analysis in the furnace, it is evident that the photobioreactor exhaust gases use presents the highest combustion temperatures in parallel to the heating rates. The difference is visually apparent among the thermal profiles obtained by different oxidizers, since photobioreactor exhaust gases lead to a faster combustion, reaching the peak temperature in a reduced period (about 2 min). The similar profile has been observed for atmospheric air; however, the maximum reached temperature is slightly smaller. This happens because the released heat during combustion and the transferred heat are quite similar, both in O_2/N_2 and O_2/CO_2 atmospheres (Bu et al., 2016). On the other hand, the simulated industrial gas stream has presented more differentiated behavior, offering slower combustion (about 12 min to reach the peak) at a lower maximum temperature, characterizing an unsatisfactory thermal performance.

Comparatively, a study carried by Wu et al. (2010), on the temperature variation as a function of the oxygen concentration in the oxidizer, has showed that the 9% increase in the oxygen level promoted a rise in the heating rate of 53.6%.

To test the petroleum coke combustibility with the injection of different oxidants, thermal kinetic parameters have been established (Table 1). All experimental parameters analyzed have been substantially improved by the photobioreactor exhaust gases enrichment in the developed bio-combustion furnace. In the 96 h cell residence time, the best thermal performance is obtained: combustion temperature of 1003.51 °C, combustion stability of 6.22%, heating rate of 5.90 °C/min and fuel conversion of 99.18%. In general, in oxygen-enriched atmospheres, the temperature, the stability, and the combustion velocity are increased in the oxidizer mixture due to the enhanced chemical kinetics (Moroń and Rybak, 2015; Rashwan et al., 2017).

According to Wall et al. (2009), many of these effects are explained by differences in CO_2 and N_2 properties, the main diluting gases in combustion processes. Both impact on the heat transfer and combustion reaction kinetics. The molecular CO_2 mass is 44 g/mol, while it is 28 g/mol for N_2 and, therefore, the flue gas density is higher in bio-combustion. Similarly, the triatomic

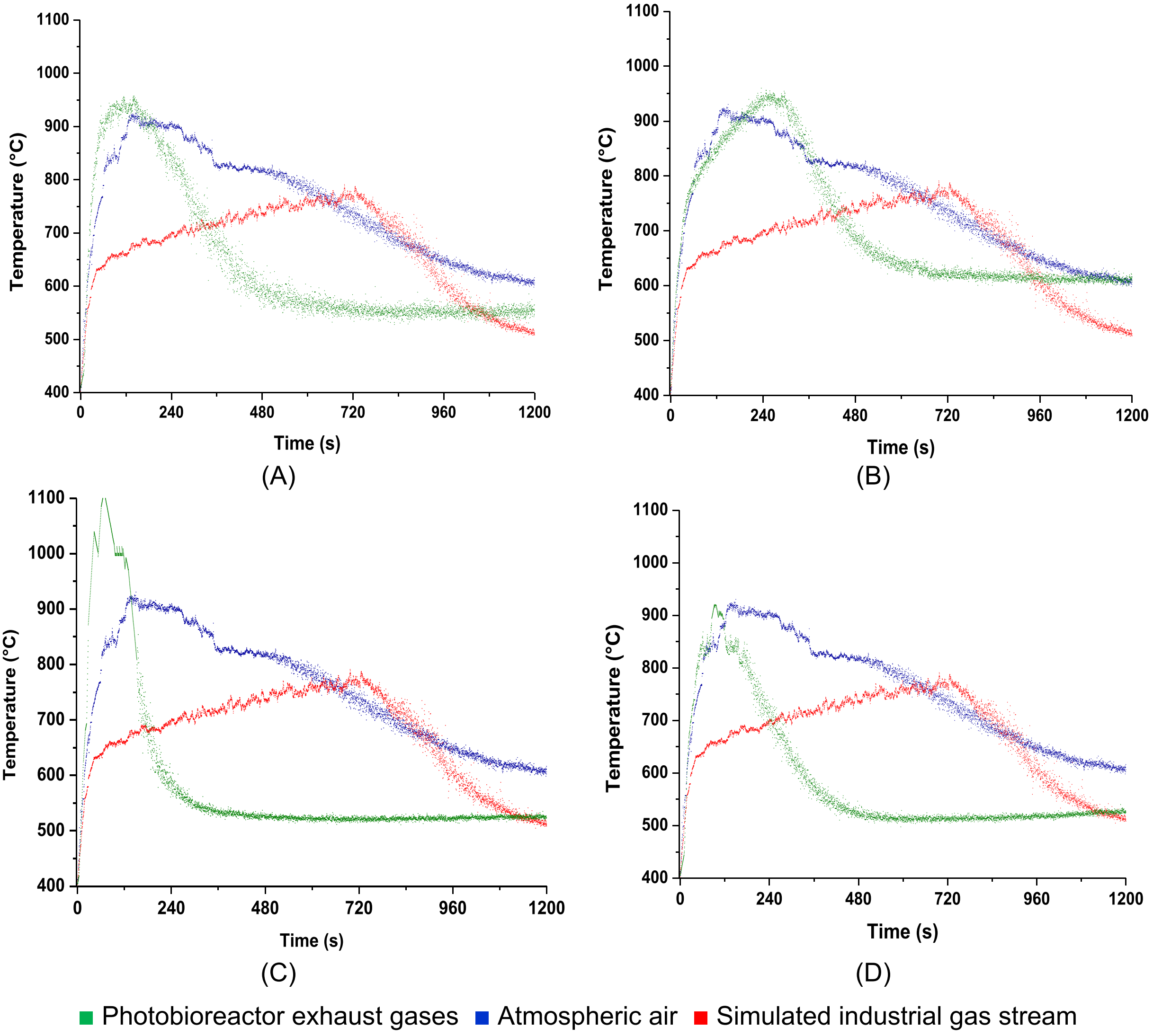

Fig. 2. Dynamic of temperature in the bio-combustion furnace. Photobioreactor exhaust gases in: (A) 0 h, (B) 48 h, (C) 96 h and (D) 144 h.

Table 1
Thermal performance parameters of bio-combustion 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)
Combustion temperature (°C)	$907.25^{e} \pm 7.00$	$822.80^{j} \pm 8.16$	$925.86^{d} \pm 16.64$	$879.72^{g} \pm 16.94$	$929.87^{c} \pm 13.78$	$953.58^{b} \pm 16.10$	$1003.51^{a} \pm 62.42$	$900.01^{f} \pm 39.15$	$856.03^{h} \pm 34.00$
Combustion stability (%)	$0.77^{f} \pm 0.00$	$0.91^{ef} \pm 0.00$	$1.80^{d} \pm 0.00$	$1.93^{d} \pm 0.00$	$1.48^{de} \pm 0.00$	$3.43^{c} \pm 0.02$	$6.22^{a} \pm 0.01$	$4.35^{b} \pm 0.04$	$3.97^{b} \pm 0.02$
Heating rate (°C/min)	$4.13^{cde} \pm 0.12$	$3.22^{f} \pm 0.05$	$4.57^{bc} \pm 0.15$	$4.18^{cde} \pm 0.20$	$4.57^{bc} \pm 0.10$	$4.98^{b} \pm 0.25$	$5.90^{a} \pm 0.45$	$4.63^{bc} \pm 0.97$	$4.29^{cd} \pm 0.34$
Fuel conversion (%)	$99.12^{ab} \pm 1.90$	$97.00^{d} \pm 0.70$	$99.58^{a} \pm 1.10$	$98.01^{e} \pm 0.90$	$99.46^{a} \pm 1.30$	$98.78^{b} \pm 0.50$	$99.18^{ab} \pm 1.00$	$99.30^{ab} \pm 1.70$	$99.36^{a} \pm 0.60$

Different letters in the same line differ significantly by Tukey test ($\alpha = 0.05$).

molecules thermal capacity, such as CO_2, is higher than diatomic molecules, like N_2. These characteristics are associated with high emissivity gases from combustion, which have high heat transfer in the furnace (Scheffknecht et al., 2011; Yin and Yan, 2016).

In contrast, for the simulated industrial gas stream, the thermal parameters have been substantially decreased, with a combustion temperature of 822.80 °C, combustion stability of 0.91%, heating rate of 3.22 °C/min and fuel conversion of 97.00%. At low oxygen concentrations in the gaseous mixture, the temperature is lower. Consequently, the burning time becomes longer and the determining character of the chemical kinetics becomes more evident (Bhunia et al., 2017; Nunes and Marcílio, 2015).

Additionally, the fuel conversion parameter has presented similar values in all oxidizers tested. The fuel conversion close to 100% occurs due to the high temperatures and to the residence time reducing the fuel particles in the combustion chamber. It is also noted that the fuel conversion was slightly lower when subjected to the simulated industrial gas stream (Czakiert et al., 2006).

Finally, Fig. 3 shows the bio-combustion furnace thermograms comparing the different oxidizers during 20 min of combustion. As it can be seen in the thermogram lighter parts, the maximum temperature has been obtained through the enrichment of the photobioreactor exhaust gases at a combustion time between 2 and 6 min. Likewise, the higher temperatures for the atmospheric air are distributed in the region corresponding to the combustion time between 6 and 10 min and for the simulated industrial gas stream between 14 and 18 min. In this way, the thermal images emphasize the superiority of the photobioreactor exhaust gases use to be applied as oxidizer, biofuel, and nitrogen diluent in bio-combustion systems.

3.2. Analysis of the composition of photobioreactor exhaust gases

Although there are many studies only focusing on biomass production, it corresponds to a small fraction of the total CO_2 amount injected in the photobioreactor. It is also observed that other products are involved in carbon conversion in photosynthetic cultures (Jacob-Lopes and Franco, 2013). Fig. 4 shows the dynamic of CO_2

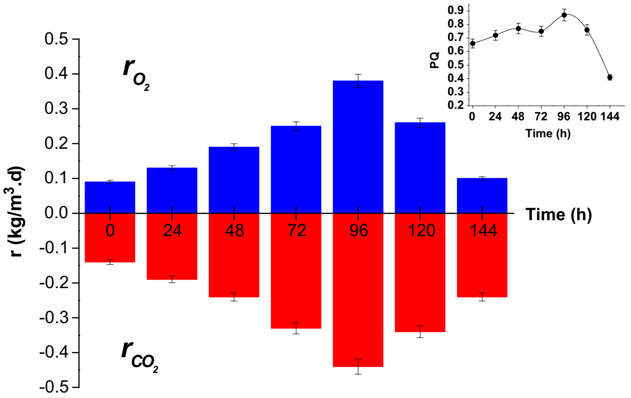

Fig. 4. Carbon dioxide sequestration and oxygen release rates and relation with the experimental value of PQ.

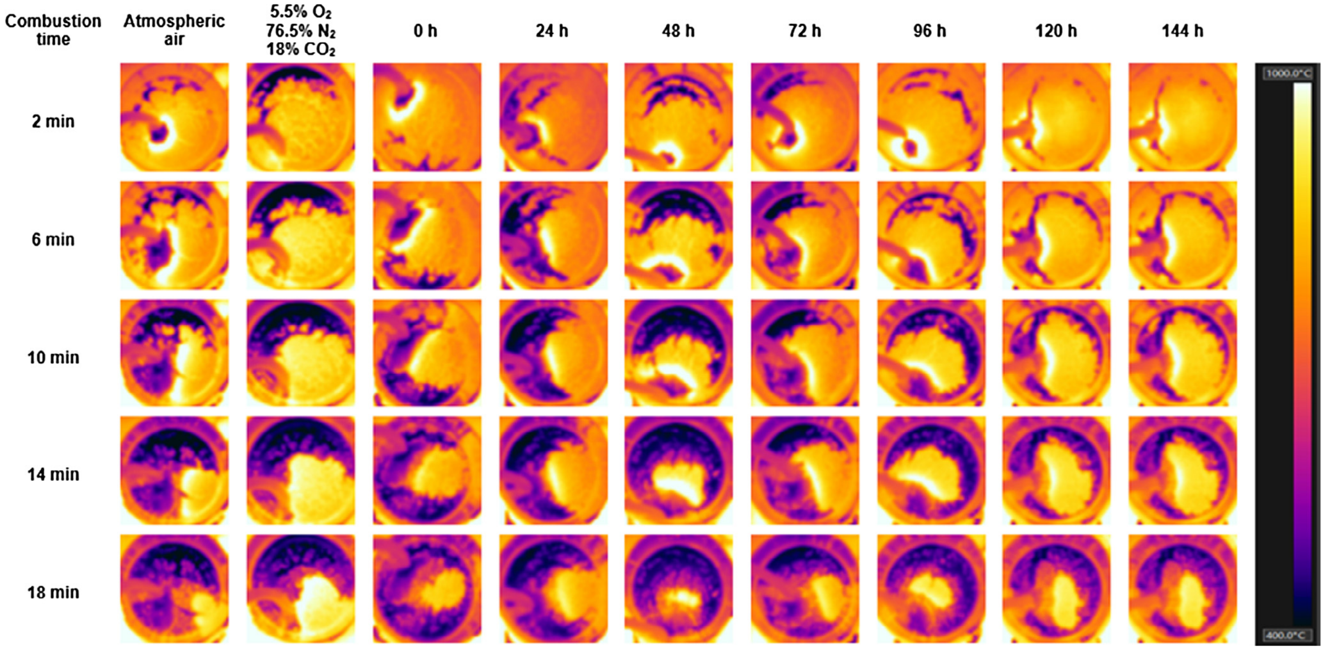

Fig. 3. Thermograms of bio-combustion furnace.

Table 2
Production and power generation rate of volatile organic compounds generated in photobioreactor.

Compound	Linear retention indices	Concentration[a] (%)	Production rate (kg/m^3/d)	Energy potential (kJ/kg)	Power generation rate (kJ/m^3/d)
Alcohols					
2-ethyl-1-hexanol	1481	14.23	0.49	5420	2655.80
2-propyl-1-heptanol	1528	5.86	0.20	6720	1344.00
Aldehydes					
2-methylbutanal	806	16.62	0.57	3240	1846.80
Hexanal	1083	ND	–	3880	–
2,4-heptadienal	1487	ND	–	4050	–
2,4-decadienal, (E, Z)	1753	4.60	0.16	6000	900
Hydrocarbons					
2-methoxy-2-methylpropane	828	31.84	1.09	3480	3793.20
3,3-dimethylhexane	1022	0.29	0.0097	5420	52.03
2,4-dimethylheptane	1097	1.28	0.0441	6070	262.22
4,7-dimethyl-undecane	1107	1.90	0.0654	8660	568.09
Ketones					
2-propanone	942	1.12	0.0384	1940	74.49
2,4-dimethyl-3-pentanone	1007	9.56	0.3296	4530	1493.08
4-octen-3-one	1303	1.75	0.0596	5180	314.94
6-methyl-5-hepten-2-one	1387	2.92	0.0987	4940	497.95
Acetophenone	1636	4.43	0.1526	4220	641.44
β-ionone	1912	2.09	0.0704	7700	554.40
Terpenes					
2-phenylpropene	1351	1.49	0.0513	4870	249.34
TOTAL		99.98	3.42	86,320	15,247.78

ND: not detected.

[a] Mean values corresponding to the residence time of 96 h.

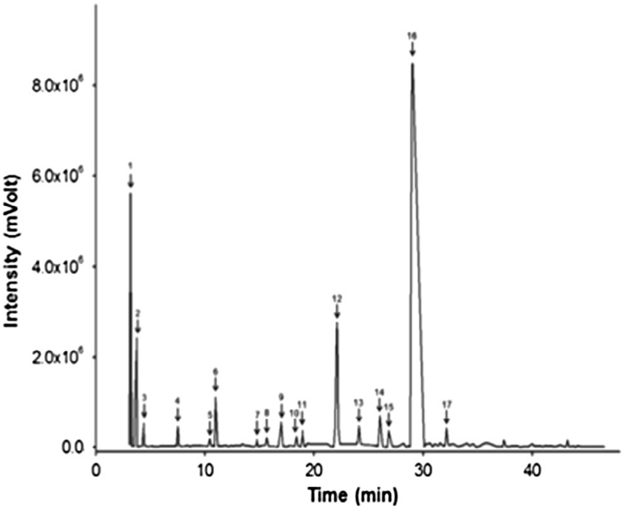

Fig. 5. Chromatogram obtained in 96 h of residence time in the photobioreactor. (1) 2-methylbutanal; (2) 2-methoxy-2-methylpropane; (3) 2-propanone; (4) 2,4-dimethyl-3-pentanone; (5) 3,3-dimethylhexane; (6) hexanal; (7) 2,4-dimethylheptane; (8) 4,7-dimethylundecane; (9) 4-octen-3-one; (10) 2-phenylpropene; (11) 6-methyl 5-hepten-2-one; (12) 2-ethyl-1-hexanol; (13) 2,4-heptadienal; (14) 2-propyl-1-heptanol; (15) acetophenone; (16) 2,4-decadienal, (E, Z); (17) β-ionone.

sequestration and O_2 releasing in the photobioreactor, and the experimental value of PQ.

The behavior of both rates is similar throughout the experiment, presenting low rate values at early and late cultivation times, reaching maximum rates at 96 h of cultivation (0.44 ± 0.50 $kg_{CO2}/m^3/d$ and 0.38 ± 0.70 $kg_{O2}/m^3/d$ for CO_2 sequestration and O_2 releasing, respectively).

The ratio between the converted CO_2 and the produced O_2 has resulted in a PQ of 0.71. This result is consistent with the expected theoretical value by the photosynthetic equation, which establishes that each 1 kg CO_2 consumed is correspondent to a 0.73 kg O_2 released (Jacob-Lopes et al., 2010). Comparatively, the average PQ value found by Jacob-Lopes et al. (2010) to measure CO_2 sequestration rates and O_2 releasing has been 0.74, using the culture of *Aphanothece microscopica Nägeli* in a bubble column photobioreactor. According to Spilling et al. (2015), the obtained value has been similar, with a PQ of 1.20 to a planktonic diatom species. This ratio provides more accurate values of the components involved in photosynthesis, such as CO_2 conversion from measures of primary oxygen production during water photolysis, and, generally, the value is close to 1.0. Additionally, the PQ values vary according to physiological factors, such as the used microalgae species, the luminous intensity, the type of organic molecule produced, as well as the source and proportion of assimilated nutrients (Eriksen et al., 2006).

Based on these aspects, the water photolysis reactions provided in the experimental conditions the generation and desorption of approximately 12% of oxygen released in photobioreactor exhaust gases. This oxidizer concentration has strengthened the biocombustion furnace thermal performance, as presented previously.

According to the U.S. Department of Energy (2017) and the Industrial Heating Equipment Association (2007), some systems use almost 100% of oxygen in the main combustion header, while others blend the oxygen to increase it in the incoming combustion air. However, about 30% of oxygen is effectively injected into combustion chambers. For the clinkering furnaces, for example, they usually operate with an excess air rate 5 to 15%, which corresponds to the injectable oxygen percentage in the combustion chamber up to 6% O_2. Besides, for this type of oxygen-enriched furnace, fuel requirements can reduce by around 7–12%.

In addition, the VOCs produced and released in the photobioreactor should be considered. The Table 2 and Fig. 5 show the generated VOCs in 96 h of the experiment. A total of 17 compounds of various chemical structures have been found in the photobioreactor exhaust gases. The most representative chemical classes have been the hydrocarbons (35.31%), ketones (21.87%), aldehydes (21.22%) and alcohols (20.09%), totalizing 98.49% of the total identified compounds. A small amount of terpenes (1.49%) has also been detected. Among the identified chemical classes, 2-methoxy-2-methylpropane (31.84%), 2-methylbutanal (16.62%), 2-ethyl-1-hexanol (14.23%) and 2,4-dimethyl-3-pentanone (9.56%) has been identified as the major.

According to Jacob-Lopes et al. (2010) and Jacob-Lopes and Franco (2013), under photosynthetic conditions, CO_2 conversion occurs predominantly in VOCs, mainly when higher CO_2 loading rates are injected into the reactor. These biotransformations are the most representative conversion forms during the microalgae cultivation in photobioreactors. Furthermore, the compounds characterization may contribute to potential applications of the formed bioproducts. Many studies report the production of different types of VOCs released in many of microalgae species (Eroglu and Melis, 2010; Muñoz et al., 2004; Xu et al., 2017; Zuo et al., 2012). Some cyanobacteria are notorious because they synthesize alkanes or alkenes that have desirable properties for combustion (Lau et al., 2015).

Regarding energy potential, the compounds have estimated values ranging from 1940 to 8660 kJ/kg, resulting in a total energy content 86,320 kJ/kg. Volumetrically, a power generation rate 15,247.78 kJ/m^3/d is estimated in this experimental condition. These values are higher than those other conventional fuels used in combustion processes, e.g. gasoline (47,300 kJ/kg), liquefied petroleum gas (46,100 kJ/kg), diesel (44,800 kJ/kg), and natural gas (39,360 kJ/kg), potentiating the bio-combustion systems thermal performance (Metz et al., 2007). Therefore, the VOCs formed in this bioprocess are an additional fuel that has a significant contribution to the better combustion performance.

From the mass and energy balances of the combustion systems (Fig. 6), we can estimate that 1 kg of CO_2 was injected into the photobioreactor, and about 0.70 kg was not converted, thus being lost in the exhaust gases. However, the bioconverted fraction resulted in 0.02 kg of biomass, 0.12 kg of oxygen and 0.16 kg of VOCs. In contrast, the combustion of 1 kg of petroleum coke was able to generate 650 kJ of energy. Comparatively, the other analyzed conditions presented energy generation values in the order of 550 kJ and 450 kJ for the atmospheric air and simulated industrial gas stream, respectively. Besides, the NER estimated in the bio-combustion system was 0.0054. This value is 5.55% and 22.22% higher than the values obtained for the combustion system with atmospheric air (0.0051) and the simulated industrial gas stream (0.0042), confirming the energetic improvement of the integrated system.

Finally, it also should be considered that only the oxygen-enrichment close to 15% in furnaces operating at 1000 °C provides energy savings close to 25%. Thus, 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 USD 240 per metric ton of burned fuel (OCI, 2013). In this sense, the bio-combustion technology proposed in this study may represent an opportunity for systems improvements, aiming to increase efficiency, to reduce emissions and to boost productivity.

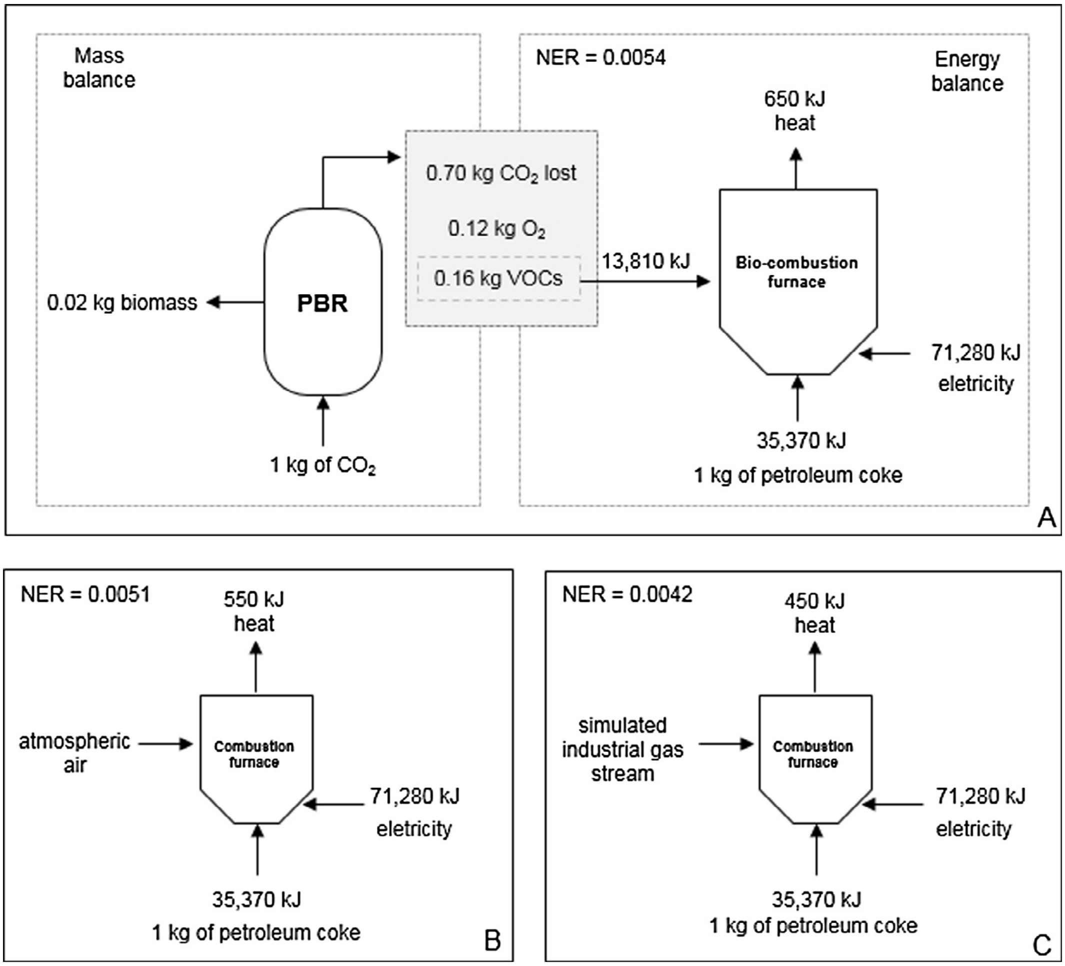

Fig. 6. Global mass and energy balances and calculated NER of the combustion systems. (A) integrated bio-combustion system; (B) conventional combustion with atmospheric air; and (C) combustion with the simulated industrial gas stream.

4. Conclusions

Based on the different oxidizers tested, the system thermal parameters have proportionally increased compared to the oxygen provided to the furnace. The results have proved the photobioreactor exhaust gases have been able to offer a superior overall thermal performance in the bio-combustion system, proposing their application as an oxidizer, biofuels, and nitrogen diluent in combustion systems. The process integration has been a potential engineering approach to promote the sustainability and the economy for these industrial processes.

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5.2 ARTIGO 2

Bio-combustion of petroleum coke: The process integration with photobioreactors. Part II – Sustainability metrics and bioeconomy

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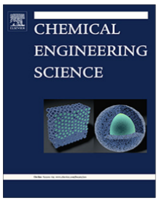

Bio-combustion of petroleum coke: The process integration with photobioreactors. Part II – Sustainability metrics and bioeconomy

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HIGHLIGHTS

- Process integration of a photobioreactor with a combustion furnace was demonstrated.
- The most widely-deployed sustainability metrics evidenced improved performance.
- Fuel consumption cost during the bio-combustion was reduced.
- The process utilities have the potential to generate substantial revenues.
- The BCCU approach further extend the system revenues through carbon credits trading.

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ABSTRACT

In this study, we evaluated the sustainability metrics and bioeconomy of the integrated bio-combustion system. Based on previous experiments, inventory data were standardized for a functional unit of 1 kg of mass, 1 MJ of energy, 1 m^3 of water, and a stream factor of 0.90. The impact categories resulted in a net energy ratio of 0.71, greenhouse gas emissions of 0.70 kg_{GHG}/kg_{fuel}, global warming potential of 12,523.60 $kgCO_{2eq}/yr$, water footprint of 56.40 $m^3/m^3/yr$, acidification potential of 33 $kgSO_{2eq}/yr$, eutrophication potential of 4.42×10^{-3} kgN_{eq}/yr, and ozone depletion potential of 2.15×10^{-8} kgCFC-11 $_{eq}/yr$. Regarding the utilities, fuel consumption cost was reduced close to 40%, and the oxygen and volatile organic compounds productions were responsible for the majority revenue generation. Besides, both avoided and captured carbons obtained potential revenues through carbon credits. The current contribution of the integrated process has shown improved environmental performance and is a promising approach towards circular bioeconomy.

1. Introduction

The global energy crisis, based on overexploitation of non-renewable resources, has propelled a tremendous advance for the industry, resulting in improvements in energy efficiency. But at the same time, several technical, environmental, economic, and political challenges have arisen in manufacturing processes. Today, decision-makers' primary concern is to expand further the energy supply and use it in a carbon-constrained era (World Energy Council, 2016).

Taking this into account, power generation, petrochemical, basic chemicals, and food sectors, are the most representative manufacturing industries that require intensive amounts of energy resources and produce massive emissions, exerting profound environmental impacts (EPA, 2016). These traditional plants are composed of combustion equipment, such as furnaces, kilns, boilers, heaters, thermal oxidizers, or any other type of burning machinery, which are the basic building block to produce practically everything that our society needs (IHEA, 2015). However, these burners are still exceedingly energy inefficient because they use high excess air and elevated temperatures without heat recovery from combustion products (Turns, 2011). Therefore, to withstand the massive industry workloads, there are substantial fuel requirements. Due to environmental issues, mainly CO_2 emissions, related to the type and quantity of fuel used, regulatory constraint, environmental taxes, and charges, will have a significant effect on overall process costs. It is noteworthy that the primary role of any combustor is to produce with the minimal operational expense, which is based on capital costs, costs incurred with fuel and other

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utilities, as well as maintenance costs (Mullinger and Jenkins, 2014).

Thereby, process integration emerged as a response to energy-savings, and it was a leap toward troubleshooting on large-scale. This concept is based on the adoption of chemical engineering methods, supported by energy and material balances, to couple unit operations, equipment, or processing techniques. Thus, it is possible to reduce resource consumption, emissions, process time, product losses, as well as maximize productivity and efficiency (Baleta et al., 2019). An integrated process takes advantage of thermal energy (waste heat recovery from heating or cooling streams), mass (effluent reuse), and water (recycling of reuse water and wastewater) surpluses. Still, the main reason for these integrations has been the realization of entrepreneurs and industrial engineers that this is a strategy for upgrading a plant site with better capital gains (Klemeš, 2013).

The numerous advantages of process integration motivate increasingly sustainable projects. This is all thanks to the research and development (R&D) partnerships between academic and industrial sectors, which are now joining an even more intense wake-up call in an attempt to pursue smart technology routes to attach with conventional plants (Varbanov et al., 2018).

Biological carbon capture and utilization (BCCU) is a robust technology with potential applicability for this purpose. The BCCU is mediated by microalgae-based processes, which can be developed in both open and closed systems. However, the first has many limitations that are overcome by the second culture system, called photobioreactors (Verma and Srivastava, 2018). These equipment are designed with parameters that allow adequate and controlled conditions for efficient CO_2 capture and conversion into biomass and other bioproducts of commercial interest (Jacob-Lopes et al., 2017; Severo et al., 2018a, 2018b; Merchuk et al., 2019). New photobioreactor designs have been claimed to meet scaling requirements. Such attributes should enable high operating volumes to obtain commodity products proportionally to industrial demands (Deprá et al., 2019).

The BCCU technology in an integrated process of biologically-assisted combustion was first demonstrated in Severo et al. (2018b), referring to Part I of this sequential research. The process recovers photobioreactor exhaust gas and injects them into a bio-combustion furnace. More specifically, gaseous bioproducts of the photosynthetic metabolism, such as volatile organic compounds (VOCs), oxygen, and part of unconverted CO_2, are reused as gaseous biofuels, oxidizer, and nitrogen diluent, respectively. Through bio-combustion, it was possible to increase the furnace efficiency close to 30% with parallel energy savings of 25%, compared to conventional combustion. In addition to being able to be retrofitted to existing combustion systems rather than newly built units, increasing the thermal performance parameters of this potential process indicates a crucial advantage concerning the reduction in fuel consumption and greenhouse gas emissions.

Considering these aspects, the process integration approach proposed here provides a broad view of industrial systems that lead to sustainability and circular bioeconomy (Walmsley et al., 2019). First, because we are dealing with a bio-based structure that increases cyclic flows in a combustion process. Afterward, these two indicators serve as powerful extensive project planning tools. They can guide them in the detailed evaluation of its future performance. Nevertheless, many industries still do not see the advance of engineering and technology innovation towards a sustainable economy pathway (Arastoopour, 2019). The actual development of environmentally and economically viable systems has been held back by the lack of a comprehensive metric methodology (Batterham, 2006). In this sense, the integrated bio-combustion system now needs to be subjected to a set of meaningful metrics to deal with this gap and highlight how this target can be achieved.

This is what we propose in Part II of this current research. Here, we evaluate the sustainability metrics and bioeconomy of the photobioreactor integrated into the bio-combustion furnace. We consider the most critical aspects that will determine the viability of the microalgae-based processes, such as life cycle assessment (LCA), assigned by the indicators of six environmental impact categories (net energy ratio, global warming potential, water footprint, acidification potential, eutrophication potential, and ozone depletion potential). As one of the typical steps that support the bioeconomy, we estimate utility costs and carbon credits. Moreover, according to the best of our knowledge, a theoretical-experimental approach of LCA oriented to this type of process has not yet been reported in the scientific literature.

2. Material and methods

The LCA tool was used to evaluate the environmental aspects and potential impacts of the microalgae-based process. According to the International Organization for Standardization (ISO) 14,000 series, there are four sequential phases in the LCA study: (i) goal and scope definition, (ii) Life Cycle Inventory (LCI), (iii) Life Cycle Impact Assessment (LCIA), and (iv) interpretation of results (ISO, 2006). The procedures considered in each step are detailed below.

2.1. Goal and scope definition

The goal of the LCA in this study was to evaluate the environmental profile of the integrated process, which consisting of the photobioreactor and bio-combustion furnace, whose data were previously obtained in Part I (Severo et al., 2018b). The system boundaries of gate-to-gate have been performed based on the integrated process (Fig. 1). The main steps included are the microalgae cultivation and the petroleum coke bio-combustion. Essential inputs for these operations include electricity, fuels, water, and greenhouse gas. The laboratory-scale experiments provided all the requirements for data inventory, which were then standardized for a functional unit of 1 kg of mass, 1 MJ of energy, and 1 m^3 of water. Besides, a total of 330 days per year was considered, resulting in a stream factor (SF) of 0.90.

2.2. Summary of the integrated bio-combustion system

The process developed was based on the biological CO_2 capture inside the leading equipment, consisting of a bubble column photobioreactor, which served as a reaction vessel for the *Scenedesmus obliquus* microalgae cultivated in synthetic BG-11 medium, fed with 15% of industrial CO_2 in the airstream. The microorganism metabolic activity allowed the CO_2 conversion into gaseous products of photosynthesis such as O_2 and VOCs, which were recovered and reused as an oxidizer and gaseous biofuels, respectively, for injection in the bio-combustion furnace. Additionally, the unconverted CO_2 fraction injected into the photobioreactor was regenerated for use as a nitrogen diluent. The bio-combustion furnace built on a laboratory scale consisted of a system for thermal energy generation with sufficient operational capacity to be coupled to the photobioreactor. The furnace was fed with O_2, VOCs, and unconverted CO_2 through a recirculation channel, in addition to the use of petroleum coke as the primary fuel (see Fig. 1, Part I). The specifications of the technique we described in patent WO2017/112984A1 (Jacob-Lopes et al., 2017). Besides, obtaining the kinetic data and the analytical methods used to control the photobioreactor and furnace are reported in detail in Part I of this study (Severo et al., 2018b).

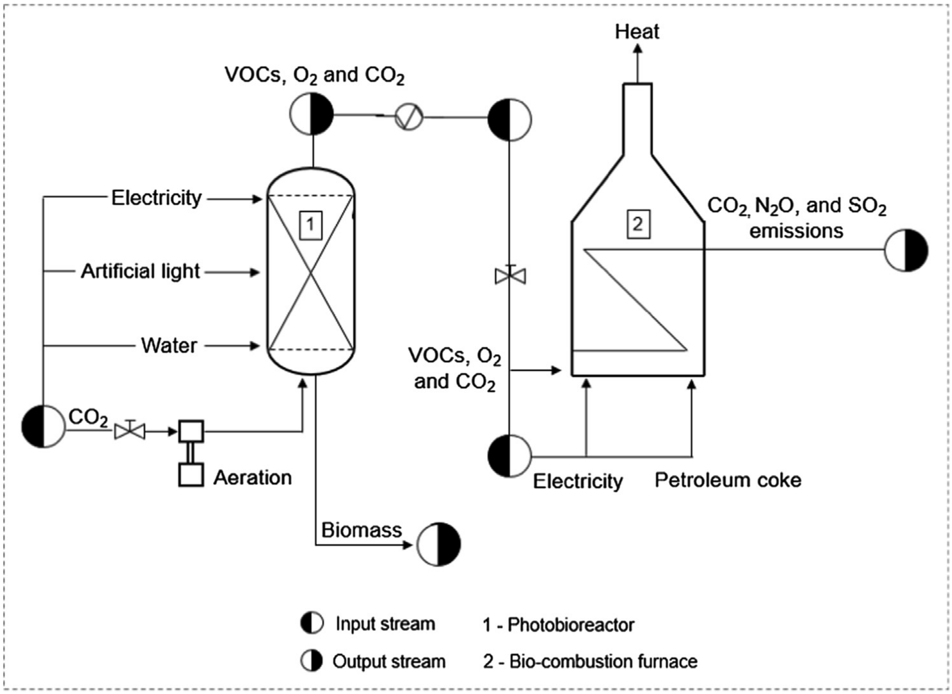

Fig. 1. Integrated bio-combustion system boundary based on the process flow diagram. Adapted from Severo et al. (2018b).

2.3. Experimental determination of greenhouse gas emissions

The GHGs emissions were daily measured in the bio-combustion furnace. A gas chromatograph (GC) was used to determine the CO_2 and N_2O. The equipment used was a GC Greenhouse Gas Analyzer (Shimadzu GC-2014, Kyoto, Japan), equipped with six-packed chromatographic columns (Supelco, Bellefonte-PA, USA) connected to the following detectors: thermal conductivity detector (TCD), flame ionization detector (FID), and electron capture detector (ECD). The FID and ECD were used for the determination of the CO_2 and N_2O, respectively. Helium was used as a carrier gas. Gaseous samples at the furnace output were collected in previously evacuated vials; 5 mL of sample was injected using a gas-tight syringe. The peak areas obtained using the integrator Software GC solution were compared with reference curves to determine the gas concentrations (Jacob-Lopes and Franco, 2013).

2.4. Life cycle inventory (LCI)

Table 1 summarizes the primary data sources and information involved in the operation of the integrated process. Most of the data were based on the identification and quantification of consumption flows and production (input and output) of each step of the process.

2.5. Life cycle impact assessment (LCIA)

The LCIA method is related to elementary flows, which considers the implementation of combined mid-point parameters. Thus, it is possible to derive the characterization factors and express the significance of the emissions with a higher level of reliability. The selected impact categories were: net energy ratio, global warming potential, water footprint, acidification potential, eutrophication potential, and ozone depletion potential, and their characterization factors are shown in Supporting Information (Table S1).

2.5.1. Impact categories

2.5.1.1. Energy balance and net energy ratio (NER). The energy balance (MJ) of the bio-combustion furnace was established from Eq. (1), and subsequently, the NER (dimensionless) was calculated (Turns, 2011; Jorquera et al., 2010).

$$Q = m\, c_p (T_{out} - T_{in}) \tag{1}$$

Table 1
Inputs and outputs of process data inventory.

Stage	Input/output	Materials/consumables	Unit	Value
Photobioreactor	In	Electricity	kWh	15,840
		Artificial light	kWh	81.97
		Aeration	kWh	104.54
		Water	m^3	2×10^{-3}
	Out	VOCs	MJ	5,031.76
		CO_2	MJ	1.10
		Biomass	MJ	58,990
Bio-combustion furnace	In	Electricity	kWh	7,128
		Petroleum coke	MJ	35.12
		VOCs	MJ	805.08
	Out	Heat	MJ	0.65
		GHGs emissions	MJ	0.28

where Q is the amount of heat loss in the exhaust gas, m is the fuel mass, Cp is the average specific heat of fuel, T_{out} is the combustion temperature of the exhaust gas, and T_{in} is the temperature before the fuel is burned.

The NER, which is defined as the ratio of the total renewable energy produced over the fossil-energy required, was calculated for the photobioreactor from Eq. (2):

$$\mathrm{NER} = \frac{\sum \mathrm{E_{out}}}{\sum \mathrm{E_{in}}} \tag{2}$$

where E_{out} is the sum of the total energy produced, and E_{in} is the sum of the total energy required.

Afterward, the NER of the integrated process was calculated considering the ratio between the total quantification of output energy of the photobioreactor plus the furnace over the input energy thereof.

2.5.1.2. Global warming potential (GWP). The determination of the GWP ($kgCO_{2eq}$/yr) was evaluated according to the CO_2 and N_2O emissions measured from the experimental data. These values of GHGs were integrated with their respective emission factors and expressed as CO_2 equivalence ($kgCO_{2eq}$), based on a time horizon of 100 years, as described in Eq. (3) (Laratte et al., 2014):

$$\mathrm{GWP} = \mathrm{GWP_i} \times \mathrm{m_i} \tag{3}$$

where GWP_i is the equivalence factor for the substance i and m_i is the emission of the substance i.

2.5.1.3. Water footprint (WF). The WF (m^3/m^3/yr) was quantified considering direct and indirect water consumption, according to Eq. (4) (Hoekstra, 2011):

$$\mathrm{WF} = \sum \mathrm{WF_{blue}} + \mathrm{WF_{green}} + \mathrm{WF_{gray}} \tag{4}$$

where WF_{blue}, WF_{green}, and WF_{gray} correspond to blue, green, and gray water footprints, respectively.

2.5.1.4. Acidification potential (AP). The AP ($kgSO_{2eq}$) was quantified using the AP of substances such as sulfur, as described in Eq. (5) (Hauschild and Wenzel, 1998):

$$\mathrm{AP} = \sum_{i} \mathrm{AP_i} \times \mathrm{m_i} \tag{5}$$

where AP_i is the equivalence factor for the substance i, and m_i is the emission of substance i.

2.5.1.5. Eutrophication potential (EP). The EP ($kgPO_{4eq}$) can be measured according to Eq. (6) (Hauschild and Wenzel, 1998):

$$\mathrm{EP} = \sum_{i} \mathrm{EP_i} \times \mathrm{m_i} \tag{6}$$

where EP_i is the equivalence factor for the substance i and m_i is the emission of the substance i.

2.5.1.6. Ozone depletion potential (ODP). The ODP (kgCFC-11) was estimated through Eq. (7), where the values are related to the equivalence factor relative to chlorofluorocarbons-11 (Hauschild and Wenzel, 1998).

$$\mathrm{ODP} = \sum \mathrm{ODP_i} \times \mathrm{m_i} \tag{7}$$

where ODP_i is the equivalency factor for the substance i and m_i is the mass of the emission substance i.

2.6. Normalization

The normalization was determined according to Eq. (8) described by ILDC (2010). During this step, each of the environmental impact potentials was divided by reference value, corresponding to the world environmental impact normalization factor (Table S1).

$$\mathrm{N_k} = \frac{\mathrm{S_k}}{\mathrm{R_k}} \tag{8}$$

where k denotes the impact category, N is the normalized indicator, S is the category indicator from the characterization phase, and R is the reference value or the normalization factor.

2.7. Bioeconomy of the integrated system

2.7.1. Estimation of manufacturing costs

For estimating operating costs associated with supplying utilities to the bio-combustion system, the approach taken here was to assume that the capital investment required to build a facility to supply the utility has already been made. The costs associated with providing a given utility were obtained by calculating the operational costs to generate it. The manufacturing and related expenses were reported in terms of USD per unit time, according to the methodology proposed by Turton (2009). An SF of 0.90 was considered to calculate the yearly cost of utilities. The elements of manufacturing expenses and revenues were focused on the utility streams required by the bio-combustion process. In this regard, the primary fuel (petroleum coke), the oxidizer (oxygen), and the additional biofuel (VOCs) were considered. The selling prices of the utilities were obtained from Chemical Market Reporter (CMR, 2019). The selling price of VOCs was estimated based on the prices of petroleum coke equivalent.

2.7.2. Estimation of carbon credits

The carbon credits were estimated according to the carbon footprint of the bio-combustion system, and the current average carbon prices suggested by the World Bank Group (World Bank, 2018). The streams of carbon dioxide not produced and avoided (Eqs. (9)–(10)) were considered, according to the methodology proposed by Pérez-Fortes et al. (2016).

$$\mathrm{CO_{2\,notproduced}} = \mathrm{CO_{2\,conventional}} - \mathrm{CO_{2\,emitted}} \tag{9}$$

$$\mathrm{CO_{2\,avoided}} = \mathrm{CO_{2_{notproduced}}} + \mathrm{CO_{2_{captured}}} \tag{10}$$

where $CO_{2conventional}$ is the amount of CO_2 released in the conventional process, while $CO_{2emitted}$ and $CO_{2captured}$ refer to the bio-combustion system.

3. Results and discussion

3.1. Net energy ratio and energy balance

The NER is an essential indicator that, in addition to investigating the global energy balance and the net income of a given process, it also assesses the feasibility of industrial scaling. Thus, Table 2 shows the energy balance and the NER for each life cycle stage of the process.

As shown in Table 2, the NER of the photobioreactor resulted in 1.04. This indicates that the amount of renewable energy produced during the cultivation stage is 3.7% greater than the fossil energy consumed. The output energy, related to the production of VOCs and biomass, has considerable potential to sustain a positive energy balance in the photobioreactor (Slade and Bauen, 2013).

Table 2
Energy balance and NER for life cycle stages of the integrated bio-combustion system.

Stage	Input (MJ)	Output (MJ)	NER
Photobioreactor	57,695.43	59,795.88	1.04
Bio-combustion furnace	26,501.00	0.93	0.000035
Integrated process	82,719.92	59,796.16	0.71

The sustainability of microalgae-based processes strongly depends on the value of NER. Most of the research reports very extreme values, ranging from less than 0.05 to greater than 19, since the energy requirements are directly influenced by the type of photobioreactor and the downstream steps involved (Hullat and Thomas, 2011; Tredici et al., 2015; Jacob et al., 2015). In this context, many attempts have been made in recent years to improve the NER of these bioprocesses. Deprá et al. (2019) showed a new hybrid photobioreactor design with an NER of 2.49, which, despite the relative energy consumption, presents considerable return energy in parallel to the superior volumetric productivity. This trade-off is favorable to the energetic bioreactor viability, which can still be enhanced by optimizing operational parameters.

Regarding the bio-combustion furnace, the energy balance resulted in a very low NER (0.000035). Thus, it should be considered that thermal energy consumed in furnaces represents the major part of the total energy consumption of traditional industrial combustion processes. This is because these devices typically depend on higher fuel mass input associated with superior temperatures (IHEA, 2015). From the chemical point of view, these processes are characterized by exothermic reactions, where the combustion products are less energetic than the reactants, that is, the losses of substantial amounts of heat are frequent, dissipating it through the chamber walls by conduction and thermal radiation (Glassman et al., 2015).

Finally, regarding the integrated process, there was a reduction in the energy input requirements of the furnace, resulting in an NER of 0.71. This means that the photobioreactor exhaust gas integration into the bio-combustion furnace, associated with petroleum coke as the primary fuel, providing substantial improvements in the energy performance of the whole system. By way of comparison, Tredici et al. (2015) showed the benefit of process integration, whose NER value doubled in the microalgae-based process. Therefore, the photobioreactor integration could be an advanced technique to energy retrofit existing combustion systems.

3.2. Greenhouse gas emissions

Harmful gas emissions from combustion processes are among the most critical aspects to reverse the trends of global warming. So, the environmental impact category related to greenhouse gas is the most addressed in the LCA studies. However, the theoretical values that are often extrapolated can provide unrealistic and imprecise data (Collet et al., 2015). In this research, this is overcome because we perform experimental measurements for the quantification of GHGs emissions of the bio-combustion system, as shown in Figs. 2 and 3.

Based on Figs. 2 and 3, the GHGs emissions profile shows that in a hydraulic retention time of 120 h, considered the best experimental condition, 0.70 kg of CO_2 is released for every 1 kg of petroleum coke burned. Similar behavior was obtained for N_2O emissions, however, in an extremely deficient range, with a value of 1.03×10^{-4} kg_{N2O}/kg_{fuel}.

The results obtained for both GHGs emissions corroborate, firstly, with the microalgae cell growth kinetics, following a bell-shaped curve pattern. In the initial and final cultivation stages, there is less production of the metabolites. In the intermediate steps, in hydraulic retention times between 96 and 120 h, there is the maximum production of these bioproducts (Jacob-Lopes et al., 2010). This means that the furnace emissions vary to the same extent as substances such as VOCs, O_2, and unconverted CO_2 are desorbed in the photobioreactor exhaust gas and subsequently injected into the combustion chamber. As described in our previous work (Fig. 4, Part I), this profile is also co-related to the rates of CO_2 consumption and O_2 and VOCs release, which corresponds to values of 0.44, 0.38, and 3.42 kg/m^3/d, respectively (Severo et al., 2018b).

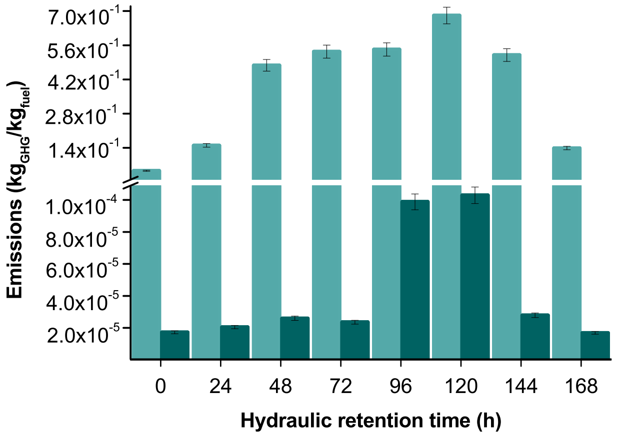

Fig. 2. Kinetics of gaseous emissions in the bio-combustion furnace at different hydraulic retention times.

Secondly, about CO_2 and N_2O emissions, low concentrations in the furnace exhaust gas is related to the impact of oxygen-enrichment on the intake air and amount of fuel burned. Regarding CO_2, in this study, the values were substantially below that established by the stoichiometry of petroleum coke air-combustion, whose value is 3.30 kg_{CO2}/kg_{fuel}. This demonstrates that the integrated bio-combustion system emits 78.8% less CO_2 when compared to conventional combustion.

Such a phenomenon can be explained by the fact that when feeding the furnace inlet air with 12% of biological O_2 from the photobioreactor (Fig. 6, Part I), there is a change in the thermodynamic properties of the gas inside the combustion chamber. The inert N_2 is diluted by the volumetric increase of O_2, causing the heat loss by radiation in the furnace to be reduced. This increases the temperature and intensifies the faster fuel combustion, so a higher thermal-efficiency is obtained. Such an effect allows less fuel to be expended to maintain the same performance as in the air-combustion and, as a result, less CO_2 is formed (Yin and Yan, 2016).

In terms of N_2O emissions, they can also be justified for reasons similar to the CO_2. As O_2 partial pressure and local temperature increase, N_2 is displaced from air-combustion and, consequently, reduces its formation. Besides, the typical conversion of solid fuels, such as petroleum coke, to N_2O is about 1% under certain temperature conditions; this means that N_2O emissions are often in trace values (below 0.1 ppm) (Wang et al., 2019), which corroborates the data of this study.

According to the U. S. Department of Energy and the Industrial Heating Equipment Association, emissions from combustion devices depend directly on three variables: fuel consumption, oxidizer concentration in the combustion air, and system temperature. Enriching a furnace with 12% O_2 and operating at a constant temperature of 1000 °C, immediate fuel savings results are expected, generally exceeding 15%. Therefore, the emissions would be reduced proportionally to the reduction of fuel requirements. By spending less fuel per unit of production, decreasing incidences of emission-related penalties (IHEA, 2015; DOE, 2019).

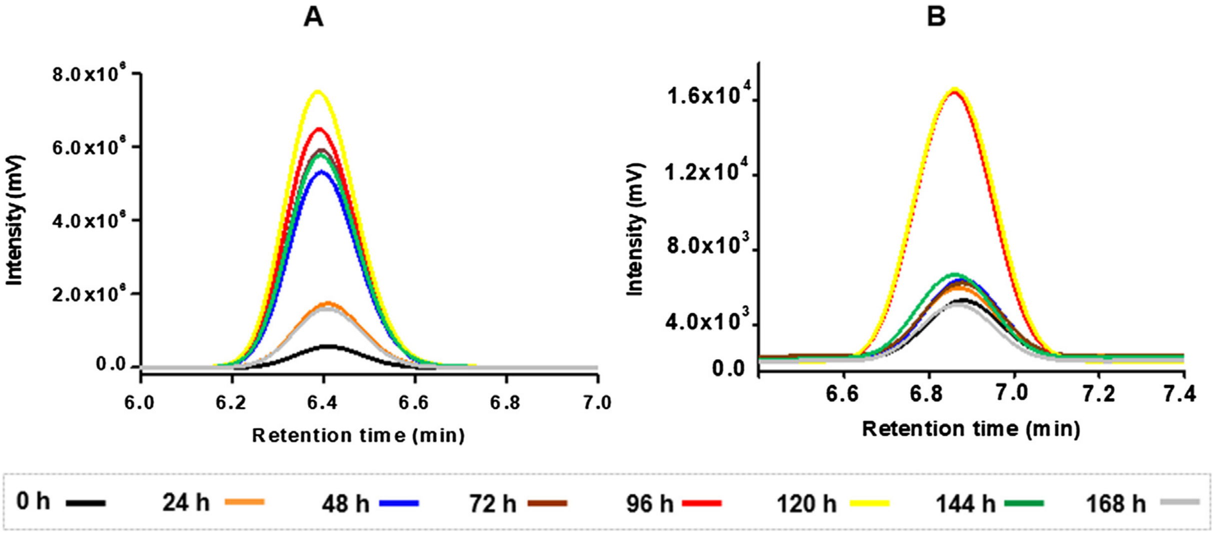

Fig. 3. Chromatogram detail representing gas release in the bio-combustion furnace. Greenhouse gas emissions: (A) CO_2 and (B) N_2O. The color of each peak represents the different hydraulic retention times. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

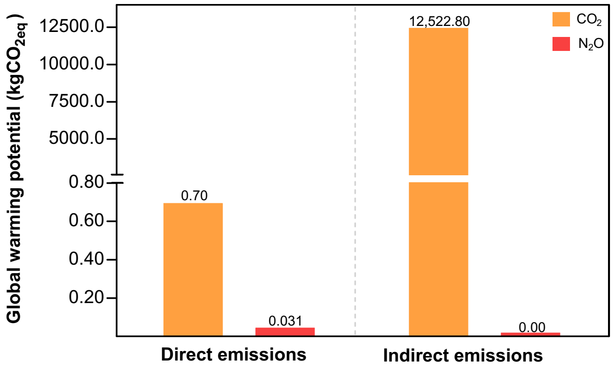

Fig. 4. Distribution of direct and indirect emissions contributors to the global warming potential.

Another essential factor to be considered about emissions is inferred not only to oxygen-enrichment but also to the joint injection of renewable energy from additional biofuels (VOCs) and nitrogen diluent (unconverted CO_2). All of them, when combined, lead to even more significant savings, close to 25%. The VOCs of microalgae are the main products of CO_2 biotransformation in the photobioreactor, accounting for about 90%. For this reason, their substantial quantities are released into the exhaust gas (Jacob-Lopes and Franco, 2013; Deprá et al., 2019). These metabolites belong to different chemical classes of low molecular weight carbonic chain compounds like alcohols, aldehydes, esters, hydrocarbons, ketones, terpenes, and sulfur compounds, which have the potential to be recovered as gaseous biofuels from microalgae cultivation (Santos et al., 2016). They have a high energy density, around 86.32 MJ/kg, which enhances the petroleum coke burning in the bio-combustion furnace, as reported in Part I of this study (Severo et al., 2018b). That is, if this source of renewable energy boosts combustion, it is expected that the fuel requirements and GHGs emissions are restricted.

3.2.1. Global warming potential analysis

In addition to the quantitative determination of each of the evaluated gas, it is essential to adopt a way of comparing them in a single unit. So, the direct and indirect GHGs emissions were estimated through the Global Warming Potential (GWP), whose sustainability metric provides a fundamental link between the process and the environmental impact caused by them. Besides, the accumulative GHGs emissions of microalgae-based processes are usually determined by each process step, which includes the production and consumption of electricity and materials production (Sun et al., 2019). Fig. 4 shows the distribution of GHGs emissions in the bio-combustion system.

Based on Fig. 4, the process indicated a GWP of 12,523.60 $kgCO_{2eq}$. Notably, direct GHGs emissions were practically negligible due to the low quantification of the gaseous compounds in furnace exhaustion. On the other hand, 99% of the indirect emissions accounted for virtually the entire GWP of the process, due to activities related to electricity consumption and fuel use heat. The cultivation stage by itself required a primary energy expenditure of 16,026.50 kWh. It is noteworthy that despite the energy outlay of the photobioreactor, it also generates a substantial fraction of renewable energy, contained in the VOCs, which assists the petroleum coke burning. Energy integration, in this case, allows higher indirect emissions to be converted into lower direct emissions, which minimizes GWP effects. Thus, the system could be adopted as a low-emission technology.

3.3. Water footprint

The Water Footprint (WF) usually includes the water consumed in the whole process, whose spending volume is not returned to the source for reuse. The WF analysis helps identify the intensive operations in the consumption of different water types: blue, green, and grey (Hoekstra, 2011). In microalgae-based processes, blue water is associated with the removal of freshwater in operations per temporal functional unit; green water refers to the evaporation rate and the volume incorporated into biomass; and grey water is related to the amount of water used to dilute a pollutant load which reaches a water body, taking as basis its natural conditions (Farooq et al., 2015). In this study, however, only the blue and green water footprint were considered because the water requirements in the integrated bio-combustion system solely come from the photobioreactor. Table 3 shows the water footprints evaluated.

According to Table 3, the blue water footprint of the process is approximately 47 $m^3/m^3/yr$. Considering that an average of 20% of cultivation water is incorporated into biomass, about 9.4 $m^3/m^3/yr$ of green water is spent in the process. The evaporation resulted in a water loss of 0.094 $m^3/m^3/yr$, which is attributed to the aeration rate. The total water footprint was estimated close to 56.4 $m^3/m^3/yr$.

Table 3
Water footprints of the integrated bio-combustion system.

Water footprint	Cultivation stage ($m^3/m^3/yr$)
Blue	47
Green	9.4
Grey	nc
Evaporation	0.094
Total water footprint	56.4

All values are expressed in 1 m^3 of water demand per 1 m^3 of reactor operating continuously with seven daily cycles and considering an SF of 0.90.
*nc: denotes a parameter not considered in the study.

Regarding the WF evaluation of microalgae-based processes, few studies are available in the literature, and the results of impacts differ greatly depending on the different cultivation systems, conversion methods, climatic, and geographical variations. Regardless, although the focus here is on a combustion system, there is a freshwater displacement, even minimal, to support this technological route. The results obtained show that about 79% of the water footprint could be reduced through partial or total integration of the volume of water demanded in the process, or still allocated as water credits, as suggested by Batan et al. (2013).

3.4. Potential of acidification, eutrophication, and ozone depletion

The mid-point impact related to the acidification (AP) and eutrophication potential (EP) is attributed to the SO_x and NO_x emissions. Both come entirely from the furnace due to the petroleum coke burning, which could cause a wide range of damages on terrestrial and aquatic ecosystems, organisms, and materials (Valderrama et al., 2012).

In this specific case, the AP refers to the SO_2 released in the combustion, which combines with the air humidity and forms sulfuric acid, the main compound responsible for the climatic phenomenon of acid rain (Ye et al., 2018). Therefore, the AP of the bio-combustion furnace was estimated in 33 $kgSO_{2eq}/yr$. The impact of this acidifying substance is minimal when compared to microalgae-based processes for biofuels and bioenergy production (Grierson et al., 2013).

On the other hand, the EP was 4.42×10^{-3} kgN_{eq}/yr, which is represented by small N_2O concentrations emitted in the bio-combustion furnace. The EP is due to the terrestrial eutrophication as a function of air nitrogenous compounds deposition. Usually, eutrophication is also related to phosphorus surplus and other nitrogen compounds released into marine and freshwater ecosystems (Czyrnek-Delêtre et al., 2017). In addition, NO_x contributes to the smog formation potential, whose impact category examines the mass of O_{3eq} released into the troposphere (Ye et al., 2018). However, it was disregarded because the concentrations would be insignificant during the bio-combustion.

Concerning ozone depletion potential (ODP), it is an impact related to the chlorofluorocarbons (CFCs) emissions and other halogenated ozone layer depleting substances in the atmosphere. Although ozone (O_3) plays a crucial role in the stratosphere, it is harmful in the troposphere and can cause damage to human health and change ecosystems (Koiwanit et al., 2014). The ODP of the integrated bio-combustion system was 2.15×10^{-8} kgCFC-11 $_{eq}$/yr, whose environmental impact is mainly due to indirect emissions from electric power requirements. Direct emissions of CFCs in the system were insignificant.

3.5. Impact categories

Environmental profiles comparison reveals the absolute performance in the context of each metric analyzed. Although it seems simple, such patterns cannot be easily interpreted. For a better understanding between scores and emissions magnitude, all categories were normalized (ILDC, 2010). The environmental impacts of the integrated bio-combustion system are compared in Fig. 5.

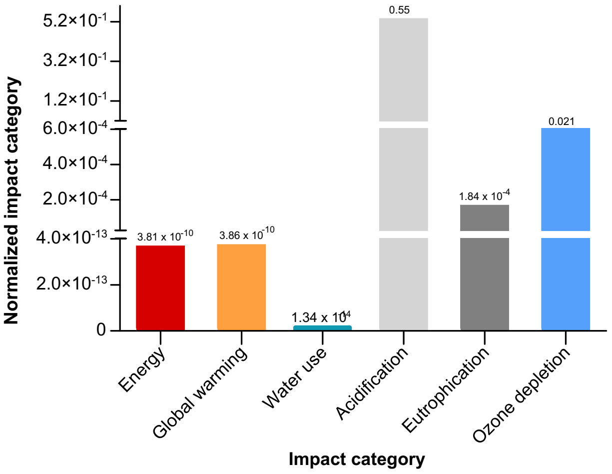

Fig. 5. Normalized impact categories of integrated bio-combustion system.

As shown in Fig. 5, acidification was the most representative impact category in the process (0.55), followed by ozone depletion (0.021). Even so, these values are much lower when compared to the microalgae-based processes with multiple unit operations. In the same tendency, other evaluated categories, such as eutrophication (1.84×10^{-4}), global warming (3.86×10^{-10}), energy (3.81×10^{-10}), and water use (1.34^{-14}), practically did not have any environmental impact.

About the acidification, data normalization indicated that this category is more expressive due to the release of sulfur dioxide (SO_2) from the petroleum coke combustion, accounting for 56% of the environmental impact when compared to the reference (ILDC, 2010). In contrast, the ozone depletion represents 20.3% of the total impact and is attributed exclusively to electricity consumption.

In most cases, the role played by the energy requirements, whether from fossil fuel or electricity use, accounts for more than 90% of the total environmental burden. As expected, the photobioreactor is the central hotspot of this study. This means that the electricity consumption impact during the cultivation stage comprises the environmental onus for almost all categories analyzed. This fact is consistent with other studies; however, with contributions significantly higher than that of the bio-combustion system (Pérez-López et al., 2017).

Given this scenario, the broad adoption of renewable energy sources is imperative. But although electricity has been produced efficiently from wind, solar, hydro, and geothermal power in recent years, the fact is that coal sustains, predominantly, the global energetic matrix. At this moment, alternative approaches, including the drastic reduction in non-renewable energy demand, would be needed. However, the main bottleneck persists in the economic unfeasibility for the full implementation of these alternative technologies worldwide.

3.6. Bioeconomy

3.6.1. Estimation of manufacturing costs and revenues

The fundamental components of manufacturing costs are raw materials, utilities, and waste treatment. The costs related to a day-to-day facility procedure must be estimates before the economic feasibility of a process can be evaluated. Regarding this, Fig. 6 shows the fuel consumption and production of oxygen and

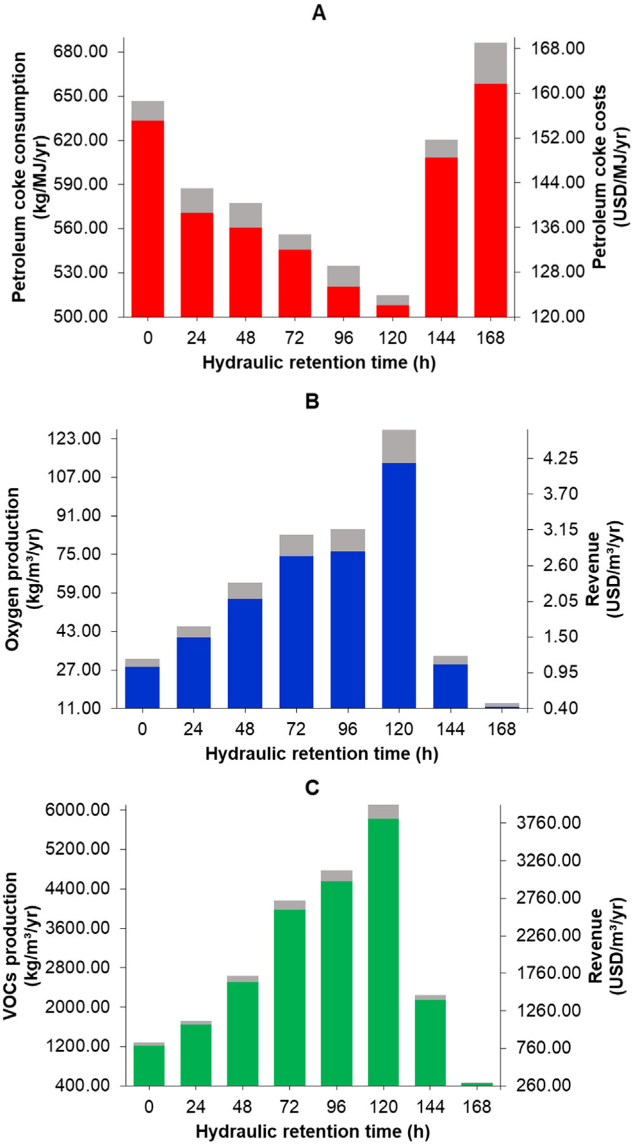

Fig. 6. Utility costs and revenues of the integrated bio-combustion system. (A) Petroleum coke, (B) Oxygen*, and (C) Volatile organic compounds**. Note: The left y-axis represents materials mass (gray bars), and the right y-axis represents the costs (red bars) and revenues (blue and green bars). *Considering oxygen selling price of 33 USD/metric ton (CMR, 2019). **Considering fuel selling price of 240 USD/metric ton and expressed in petroleum coke equivalents (CMR, 2019). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

volatile organic compounds with their costs and revenues generated in the integrated bio-combustion system.

The main direct manufacturing costs of the bio-combustion system is related to fuel consumption, which is estimated close to 514.8 kg of petroleum coke per MJ of energy generated yearly, resulting in a utility cost of 122.1 USD/MJ/yr (Fig. 6A). Compared with other experimentally tested conditions (data from Table 1, Part I), fuel consumption and its costs in the combustion with the atmospheric air enrichment and with the simulated industrial gas stream (composition of 5.5% O_2, 17% CO_2, and 76.5% N_2) were estimated in values of 594 and 726 kg/MJ/yr, and 141.9 and 171.6 USD/MJ/yr, respectively. This represents more than 16% and 40%, respectively, of expenses concerning bio-combustion. The main parameter in the differentiation of these values is related to the concentration of oxygen injected into the furnace (IHEA, 2015). At the industrial level, combustion systems, in general, are highly energy-intensive. By way of exemplification, the typical fuel expenditure in a clinker furnace can reach up to 3.5 MJ/ton of processed clinker. Nonetheless, energy use has always been enhanced by economic reasons. In contrast, there are few options available for further optimization (Oliveira et al., 2019).

Besides, the integrated bio-combustion system generates two materials that can be classified as utilities (oxygen as oxidizer and VOCs as additional biofuel), and these revenues are demonstrated in Fig. 6B and 6C. Data analysis indicates that the system has the potential to produce 125.4 kg/m^3/yr of oxygen that results in a revenue of 4.2 USD/m^3/yr (data from Fig. 4, Part I). The impact of the volumetric oxygen productivity is not very representative in the process.

Regarding the VOCs, an energy potential of 5,029.20 MJ/m^3/yr is generated in the photobioreactor. Associated with this, about 6,107.40 kg/m^3/yr of VOCs are produced (data from Table 2 and Fig. 6, Part I), and this energetic fraction results in a possible revenue of 3,817 USD/m^3/yr in terms of petroleum coke equivalents. These compounds represent a substantial net energy gain and can expand the revenues of the integrated system.

3.6.2. Carbon credits

Equally impactful to leverage the bioeconomy of the present process is the CO_2 capture and utilization in the photobioreactor, which would provide a new opportunity to generate additional revenues through the sale of carbon credits. Ultimately, this relevant economic aspect, which is often overlooked, could reduce other costs in the facility (Wiesberg et al., 2017). In this sense, Table 4 shows carbon credits associated with the integrated process.

According to Table 4, the relative mass of carbon captured in the photobioreactor was predicted to be 145 kg/m^3/yr. While the carbon avoided from bio-combustion was close to 221.2 kg per MJ of energy produced yearly. In this sense, the bioeconomy of the integrated process showed that the facility could earn in terms of yearly carbon credits around 3.2 USD. This additional value represents only the 0.09% share of total revenue projected in the system. It is worth noting that the majority revenue (3,821.2 USD/m^3/yr), related to utilities produced VOCs and oxygen, when accounted for together, forecast a possible amount that surpasses the fuel consumption expenses. Therefore, this is the point at which microalgae-based processes, primarily represented by photobioreactors, come into focus. If these BCCU technologies could be integrated, even partially and without any modernization into the retrofitting existing thermal system, they would be considered as ancillary equipment in utility costs.

However, while potential revenues are evident, the bioeconomy of the integrated system still does not hold up in practice. To date, there is no photobioreactor design, among other aspects, with operational capacity for CO_2 capture and bioconversion into bulk or commodity products (Severo et al., 2018a). This is also due to industrial combustion processes that would require such utilities in quantities high enough to withstand the daily workload. The same probably would not apply to the achievement of economic

Table 4
Carbon credits generated from the integrated process of biological carbon capture and utilization.

BCCU	Relative carbon mass	Carbon credits
Carbon captured	145 kg/m^3/yr	1.30 USD/m^3/yr
Carbon avoided	211.2 kg/MJ/yr	1.90 USD/MJ/yr

*The values were based on the experimental condition represented by the simulated industrial gas stream, assuming it as a conventional process (Severo et al., 2018b).

profits in combustion processes. Overall expenses of these facilities are undoubtedly more expressive, since they face much higher demand for other utilities, typically including process steam, electricity, compressed air, hot oil, and cooling and heating water. And this without taking into account the other elements of determining manufacturing costs, such as capital, labor, and general expenses (Ulrich and Vasudevan, 2006). Thus, the preliminary estimates of the integrated bio-combustion system could be used merely to further direct R&D efforts to cost-cutting improvement opportunities.

4. Conclusion

The integrated bio-combustion system based on BCCU has subjected a rigorous analysis across sustainability metrics and bioeconomy. Following the life cycle assessment, all scores had enhanced environmental performance. The normalization indicated that the most impacting factor in the categories evaluated is attributed often to non-renewable energy requirements, accounting 90% of the environmental burden. From the engineering costs analysis standpoint, fuel consumption was substantially inferior compared to air-enriched combustion and simulated industrial gas stream, reducing the cost of this utility by 16% and 40%, respectively. Besides, although the revenue obtained from oxygen productivity is not very expressive, the process generates jointly the VOCs, whose utilities represent 99% of the total revenue. Finally, carbon captured and avoided could further improve the bioeconomy earning additional revenues through potential carbon credits sale. These highlights seem hopeful, yet still problematic. Today, microalgae-based processes face a myriad of obstacles that need to be overcome, some of which have already been pointed out. This would require a combined effort among researchers, entrepreneurs, and policymakers to make these technologies viable in the future.

CRediT authorship contribution statement

Ihana A. Severo: Formal analysis, Data curation. **Mariany C. Deprá:** Methodology, Validation. **Rosangela R. Dias:** Methodology, Validation. **Juliano S. Barin:** Resources. **Cristiano R. de Menezes:** Writing - review & editing. **Roger Wagner:** Resources. **Leila Q. Zepka:** Supervision, Funding acquisition. **Eduardo Jacob-Lopes:** Conceptualization, Writing - review & editing.

Declaration of Competing Interest

We declare that we have no conflict of interest.

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Appendix A. Supplementary material

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6. CAPÍTULO 4

6.1 MANUSCRITO

Photobioreactors integrated into combustion process: A patent landscape analysis

Manuscrito a ser submetido para o periódico

Renewable Energy

(FI: 6.274; Estrato: B1)

Abstract: Combustion systems contribute significantly to the emission of deleterious products to the environment. This has stimulated the development of technologies with mitigation potential, which race with climate change in real-time, such as microalgae-based processes. Its application is a technological goal; however, it can be subject to several hurdles. Many reviews on this topic are often published, but the quantification of technological prospection involving patents has been little studied. In this sense, this work aimed to investigate the disruptive microalgae technologies using photobioreactors integrated with combustion systems through the patent analysis. For this, the Cooperative Patent Classification criteria were considered. More than 700 patent families were mapped, and after the screening, about 100 were analyzed. The results indicated an increase in the number of applications since 2007-2013 and a reduction in new documents' contributions over the last years. The leading countries in patents are represented by the USA and China, responsible for 20 and 12%, respectively. Besides, the company GreenFuel Technologies contributes 15% of innovations in the area. Our findings suggest that microalgae technologies have motivated environmental and economic interest, allowing retrofit of combustion processes that can be applied by the current industry and optimize existing ones. With these insights, it is possible to inform the decision-makers' long-term investment strategies and help researchers identify technical barriers and potential research.

Keywords: Combustion technology, Biological carbon capture and use (BCCU), Microalgae, Photobioreactor, Patent landscape, Innovation.

1. Introduction

Future combustion processes will be diversified, and the noticeable increase in energy supply will be renewable energy, which will require a robust platform for new strategies for converting and generating energy from coal-based fossil resources. Technologies, applications, and processes of combustion, burning, or heating with efficiency and potential for mitigation or adaptation against climate change will play a key role in the large-scale implementation of renewable and sustainable energy (REN21, 2020).

These systems are divided into some basic categories: fuel-based process heating, electric-based or steam-based, as well as heat recovery, heat exchange, and fluid heating systems. They are essential to produce practically all the consumer and industrial services that modern societies need. This includes a wide range of applications in various manufacturing sectors, such as food, chemicals, petrochemical, power, cement, and primary metals. Besides, they usually demand multiple unit operations, such as drying, heating/reheating, incineration, thermal oxidation, and other general heat treatments. The most common types of equipment and machinery include furnaces, kilns, boilers, reactors, dryers, greenhouses, and resistance heaters (U.S Department of Energy, Industrial Technologies Program, and Industrial Heating Equipment Association, 2015).

The problem is that most of these combustion-based processes equipment are fueled with coal, fuel oil, gas, or electricity. Other waste product fuels represent a large part of energy use in many industrial facilities, such as petroleum coke, refinery gas, and blast furnace gas (U.S Department of Energy, Industrial Technologies Program, and Industrial Heating Equipment Association, 2015). These fossil fuels are supplied in high loads and, when burned, emit deleterious products to the environment, including CO, CO_2, N_2O, NO_x, SO_x, and particulate materials. Greenhouse gas emissions (GHG) are directly associated with fuel consumption. Thus, as a total-system regime, energy efficiency promotes improvements in the control of fuel use (Kohse-Höinghaus, 2020).

Considering these aspects, innovative approaches to improve a particular combustion or heating process with a reduction in fossil energy demand have been considered and adopted worldwide to mitigate emissions, especially CO_2 (Leung et al., 2014). Options generally include ways to improve energy efficiency and promote conservation or reduction in energy intensity, by (i) increasing the use of low-carbon fuels (i.e., drop-in biofuels); (ii) renewable energies (i.e., biomass and bioenergy); and (iii) pre-combustion, oxy-combustion, post-combustion, or chemical looping combustion processes combined with carbon capture storage (CCS) or utilization (CCU) technologies using physical-chemical (direct capture) or biological (indirect capture) methods of the atmospheric CO_2 separation (Cuéllar-Franca and Azapagic, 2015; Nogia et al., 2016; Bhatia et al., 2019; Pires, 2019; Hetti et al., 2020).

These options have different technological readiness levels (TRL), whose scale assesses projects from the basic principles until full demonstration (Zimmermann and Schomäcker, 2017). Although they are in proof-of-concept stages up to actual systems “flight-proven” through successful operations, the hottest point is that for their implementation and competitiveness, it is necessary to redesign conventional processes, not to mention the high capital and operational costs (Babacan et al., 2020).

Given the above approaches, biological systems have stood out to reduce CO_2 emissions, especially the microalgae-based processes, which have become important disruptive technologies for the energy market. Microalgae are microorganisms photosynthetic, which convert CO_2 into metabolic products. Unlike terrestrial organisms, microalgae grow much faster and achieve high photosynthetic rates. They contain highly specialized structures, as carbon concentration mechanisms (CCMs), which increase the intracellular CO_2 levels at the site of enzyme ribulose-1,5-bisphosphate carboxylase/oxygenase (Rubisco). The carbonic anhydrase enzyme supplies CO_2 to Rubisco, playing a key role in photosynthesis efficiency (Jacob-Lopes et al., 2010; Ho et al., 2011).

Nevertheless, it should be mentioned that the performance of microalgae in converting CO_2 depends, among many factors, on the cultivation systems. There are open systems, such as raceway ponds; however, closed systems, such as photobioreactors, are equipment of central importance for the microalgae mass culture, as reported by Raeesossadati et al. (2014). This is because of its robust design that allows better control of reactions. Photobioreactors have different configurations and geometries, such as tubular, flat-plates, bubble columns, and hybrids. A comprehensive review of these aspects is shown in Verma and Srivastava (2018). Advances in photobioreactors have increasingly boosted the microalgae market, paving the way for investments and new research. They will provide lucrative opportunities for market players. The forecast is approximately USD 3.2 billion to be reached by 2030-end in this segment (Transparency Market Research, 2020). Several researchers have also declared that microalgae are valuable sources of a myriad of commercial products of high added value, including chemical specialties based on pigments and fatty acids, and low value, such as bulk chemicals, fertilizers and various biofuels and bioenergies (Deprá et al., 2020; Jacob-Lopes et al., 2020). In this scenario, studies on microalgae photobioreactors are intensified and envisage the need for technological improvements for scale operation and, therefore, the very CO_2 capture and use.

Thus, many research and development (R&D) efforts in collaborative alliances with industries, companies, universities, and all stakeholders began to invest in disruptive microalgae technologies combined with conventional combustion or heating systems for CO_2 conversion towards potential commercial competitiveness (Borkenstein et al., 2011; Li et al., 2011; Chen et al., 2013; Jacob-Lopes and Franco, 2013; Zhao et al., 2015). By way of exemplification, in the sequential study by Severo et al. (2018) and Severo et al. (2020), an integrated bio-combustion process was evaluated. In Part I, the thermal performance of a furnace fed with the photobioreactor exhaust gases, which captured CO_2 and converted it into O_2, VOCs, and untransformed-CO_2 and used as an oxidizer, gaseous fuels, and nitrogen diluent, respectively, in said combustion apparatus, was demonstrated, showing improvements in energy-efficiency and lower fuel consumption. In Part II, metrics and sustainability indicators and bioeconomy analysis indicated improved environmental performance and reduced fuel and utility costs.

This action is under massive scrutiny involving cutting-edge process integration techniques and is associated with a paradigm shift towards sustainable and economic issues. In addition, the progress of these surveys can show the trends in technical improvements, problems that need solutions, the TRL, as well as justifying investor decisions. This is often reflected in articles and other documents of scientific literature. However, it is better clarified when exploring information on Intellectual Property protection of high technological value, as are patent documents (Míguez et al., 2018).

Patents are representations of technological innovations in a country or organization and are, in effect, an agreement between the inventor and the government or agency. The use of patent documents to map a particular domain's development levels is valuable for industrial and business applications in several aspects. For example, patent analysis helps determine novelty and its inventions, in intellectual property and technological competitiveness (strengths and weaknesses) of the competitors, and in estimating their evolution or decline over a given period of time (Abbas et al., 2014).

In this sense, few studies on the patent status analysis of approaches to mitigate climate change are available, such as Li et al. (2013), Albino et al. (2014), Sampaio et al. (2018), Sharifzadeh et al. (2019), Karvonen and Klemola (2019), Hussin and Aroua (2020), and Yin et al. (2020). However, they focus on physical-chemical methods. To an even lesser extent, patent analyzes based on biological systems are found, for example, in Norhasyima et al. (2018), Míguez et al. (2018), and Míguez et al. (2020). Still, the authors explore microalgae processes in a purely superficial way. On the other hand, the patent landscape on microalgae photobioreactors is well documented in Kirnev et al. (2020); however, the study presents specific information, such as design and geometry.

Based on these published investigations, our work intends to take a step forward concerning the available literature. Here, we aim to present the state-of-the-art on disruptive microalgae technologies using photobioreactors integrated with combustion or heating systems to improve process efficiency through a technological mapping based on patent analysis.

2. Methodology and data

2.1 Patent analysis

In order to understand the Intellectual Property (IP) landscape in the research scope of this study, a patent analysis was performed using the software developed by Orbit Intelligence Questel (version 1.9.8) (Questel, 2020). It consists of a worldwide platform containing a database published by more than 100 patent authorities, providing a snapshot of the level of patenting activities over a given period. Through the search results, the tool uses several algorithms to cluster international documents into families based on the FamPat Collection, which incorporates the strict rules of the European Patent Office (EPO) with that supplementary publication of the EP and/or Patent Cooperation Treaty (PCT) and links between provisional and published US applications. Moreover, this database allows access to publications from 22 offices (WO, US, EP, AT, BE, BR, CA, CH, CN, DE, ES, FR, GB, JP, RU, DK, FI, SE, IN, TW, TH, and KR), which assign codes and definitions based on International Patent Classification (IPC), Cooperative Patent Classification (CPC), EPO, US Patent and Trademark Office (USPTO), World Intellectual Property Organization (WIPO), and Japanese classifications, and also includes results from various sources of scientific literature.

2.2 Search strategy

The patents search was done on September 17, 2020, selecting in the software the advanced research option. The quest method comprised a three-step procedure: (1) search using the CPC classification codes, which are organized by section, and in them, the classes, subclasses, groups, and subgroups are embedded (https://www.cooperativepatentclassification.org/index). The fields selected are presented in Table 1.

Table 1. CPC classification codes.

Section	Code	Description

B	B01D 53/00	Separation; Separation of gases or vapors; Recovering vapors of volatile solvents from gases; Chemical or biological purification of waste gases, e.g. engine exhaust gases, smoke, fumes, flue gases, aerosols.
C	C12M 1/002	Apparatus for enzymology or microbiology; apparatus for culturing microorganisms for producing biomass, for growing cells or for obtaining fermentation or metabolic products, i.e. Bioreactors or fermenters; • {Photo bio reactors}
	C12M 21/02	{Bioreactors or fermenters specially adapted for specific uses}; • {Photobioreactors (culturing algae)}
	C12N 1/12	Microorganisms or enzymes; compositions thereof; propagating, preserving, or maintaining microorganisms; mutation or genetic engineering; culture media; • Unicellular algae; Culture media therefor.
F	F23N	Combustion apparatus; combustion processes. Regulating or controlling combustion.
Y	Y02E	Reduction of greenhouse gas [GHG] emissions, related to energy generation, transmission or distribution

These codes are standardized to classify patents according to the different technological areas to which they belong, providing a high level of detail in searches with more accurate results. Based on this strategy, more than 700 patent families, resulting in approximately 3580 individual patents.

After that, (2) the screening of data was taken to withdraw documents not belonging to the scope of the present study by searching with keywords and their variants using the syntax: [(“photobioreactor”+, “photo-bioreactor”+, “photo bioreactor”+, “bioreactor”+, “cultur”+, “cultiv”+, “grow”+, “microalg”+, “alg”+, or “cyanobacteri”+) and (“combust”+ and “heat”+, “burn”+, or “fuel”+)], among others combinations, reducing the data set to about 260 patent families. The truncation “+”, which refers to a symbol that replaces one or more characters and allows to retrieve different relevant variations linked to a term (plural, synonym, and genres) plus the Boolean operators "AND" (used to find all terms in the search) and "OR" (refers to any one of the search terms) were inserted among those keywords. The use of CPC codes combined with the words for every family serves to refine further the results obtained. The fields considered for the search query were: Title, Abstract, and Claims.

Subsequently, (3) a new screening was carried out to filter documents related to potential improvements in energy-based processes combined with microalgae photobioreactors, resulting in more than 100 patent families. Finally, they were tabulated and analyzed carefully.

Figure 1 outlines the distribution of the main concepts contained in the fields of invention sought here. It is evident that the words “algae” and “CO_2” or “carbon dioxide” are the most representative, justifying the portfolio analyzed in this study.

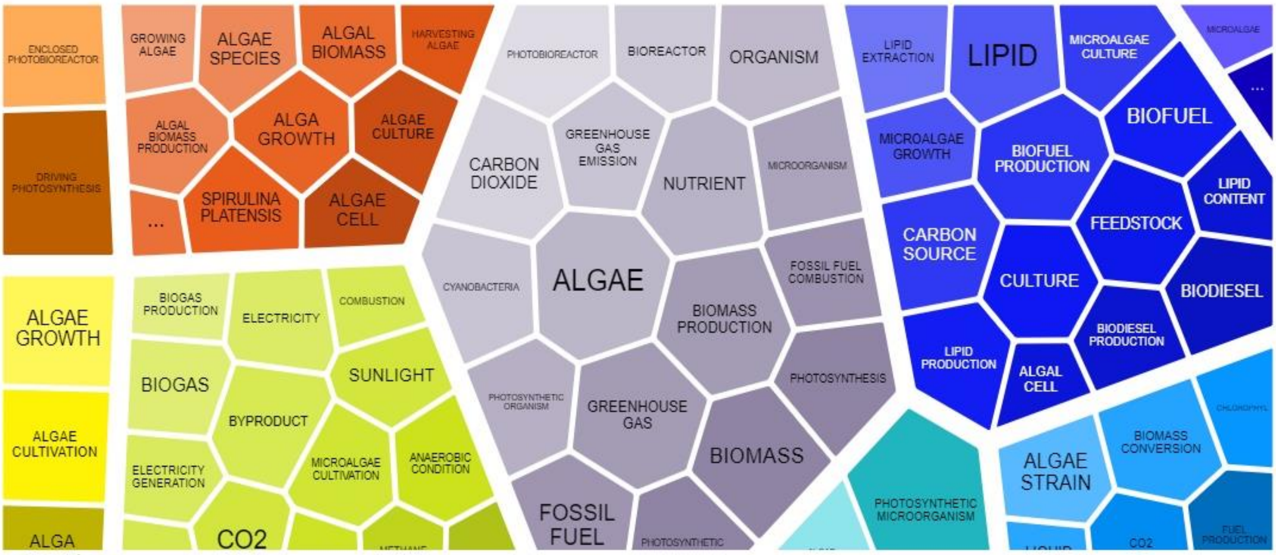

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Figure 1. Concept clusters of the analyzed portfolio.

The principal subgroups of the CPC classification codes in which the innovations are identified comprise Y02E-050 (Reduction of greenhouse gas [GHG] emissions, related to energy generation, transmission or distribution; Technologies for the production of fuel of non-fossil origin), C12M-021 (Bioreactors or fermenters specially adapted for specific uses […]), C12N-001 (Microorganisms, e.g. protozoa; Compositions thereof […]), and Y02P-020 (Technologies for climate change mitigation technologies in the production or processing of goods related to chemical industry), representing more than 52% of patents. To a lesser proportion, it was found that significant subgroups like Y02C-020 (Capture, storage, sequestration or disposal of greenhouse gases [GHG]), and Y02A-050 (Technologies for adaptation to climate change related to human health protection, e.g. against extreme weather), accounting about 27% of the patents identified.

Regarding the data interpretation, it is worth noting that there is no single method of searching and analyzing patents. The efficiency of research depends, among other factors, on the object under study and the intended objective. Besides, only documents that have already been published can be mapped during the search. The time between the submission of the patent application and its publication modifies substantially between different offices worldwide; thus, it can cause a certain margin of error when carrying out the search queries.

3. Results and discussion

3.1 Historical trend in patenting activity

According to the mapped documents, Figure 2 illustrates the evolution of patent applications submitted and published over time. The timeline dynamics show that in the early years (2000 - 2006), there were only 6 patent families. Since then, there has been a sharp increase until 2013, with a slight decline in 2012, showing a production activity of approximately 10 - 12 patent families per year. This jump in the number of patents may be related to the consolidation of intergovernmental agreements on global climate change, such as the Kyoto Protocol, which came into force in 2005 and expired in 2012. This treaty postulated strict guidelines for reducing GHG emissions for member countries, especially developed ones. In the same context, the Nations Framework Convention on Climate Change (UNFCCC) was a treaty signed by almost all countries worldwide in an attempt to stabilize the GHG concentration in the atmosphere. International climate agreements boost technological progress and financial investments.

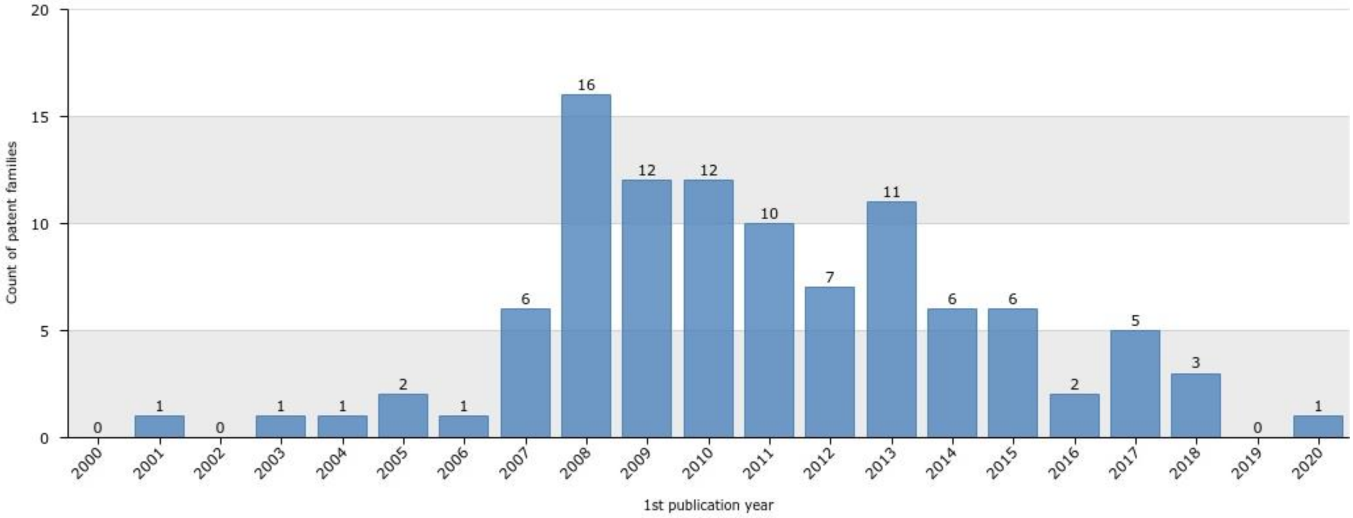

Figure 2. Timeline of patents published worldwide in the last 20 years (2000 – 2020).

After this period, there was a drop in the number of patents filed, which is usually symptomatic of a substantial decline in R&D or intellectual property budgets. In this case, it may be attributed to the consolidation of microalgae-based processes, mainly concerning photobioreactors. This shows that investment in this area can be relatively low, probably because additional costs are expected compared to the available models – which today are technically and economically reasonable – forcing changes in the R&D budget. That is, technological maturity has been reached in the sector. Importantly, the low number of patents does not necessarily represent a low degree of inventiveness. This means that other points in these systems require additional improvements. It is also worth mentioning that there is a backwardness of approximately 18-month (2018 to the current year) between the filing of an application and its publication.

3.2 Global geographical distribution of patents

The origin of the technologies from the countries and several assignee international offices can be seen in Figure 3. It is observed that North America, China, India, and EPO are the leaders in the ranking of innovations in microalgae photobioreactor technologies combined with energy-based systems, including combustion or heating, contributing 26, 17, 17 and 16 patents families, respectively, in the last two decades.

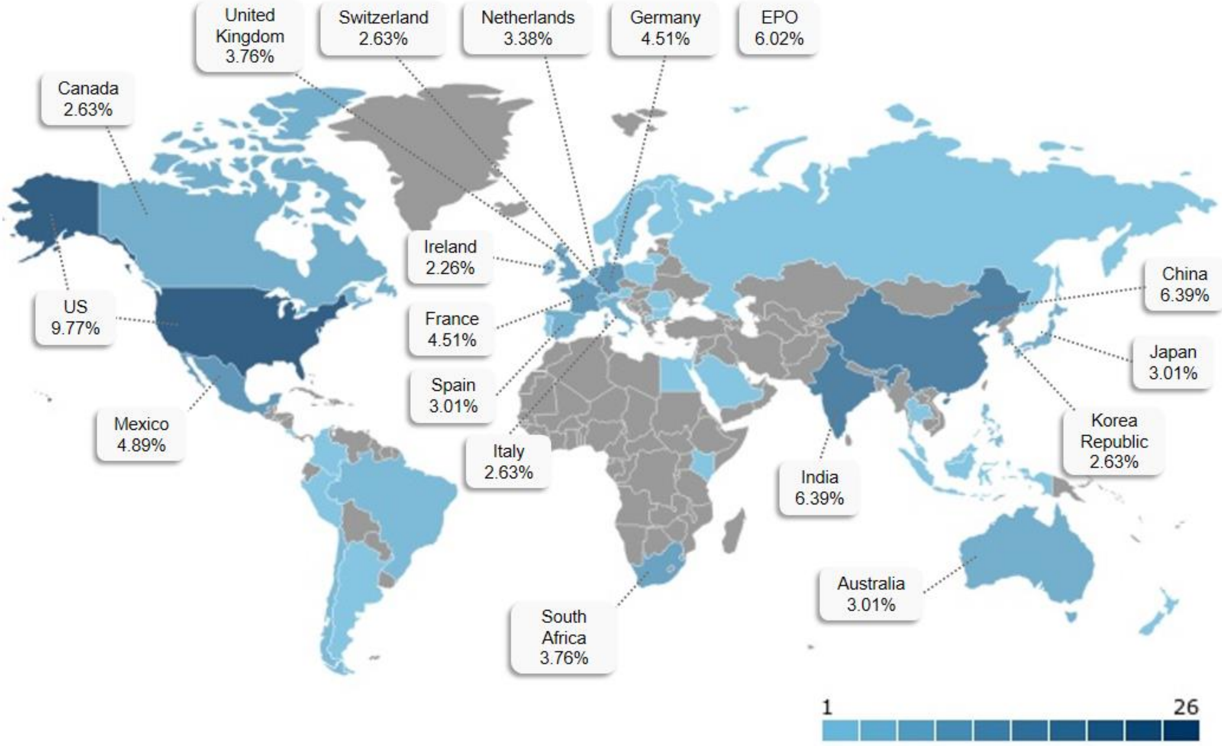

Figure 3. Geographic origin of technologies based on alive patents protected.

This fact is related to the engagement and participation of each country in mitigating GHG emissions from its different sectors of industrial manufacturing, especially in energy ones. This, in turn, emitted 6% more in 2013 than in 2010, that is, more than 18 GtCO_2eq. Also, for the cement production industries, for example, all fossil fuels are used, with coal predominating (about 43% of CO_2 emissions) in areas such as China, USA, and India (IPCC, 2014). These countries are considered the top 3 annual CO_2 emitters, accounting for 10.06, 5.41, and 2.65 Gt, respectively, in 2018 (IEA, 2020). Despite this, the two major world powers, the USA and China, are at the forefront of technological progress and innovations. They use this argument to accelerate commercialization, competitiveness and maintain a high market share on emerging microalgae-based processes.

For example, the USA concentrates most companies producing microalgae due to high public funding for their development. From a private point of view, there are also many industrial and commercial efforts on the rise compared to other countries in the world. The USA remains the major driving force to boost R&D in this field, in addition to being involved in major cooperation with other countries, such as Australia, which has propitious environmental conditions for the microalgae production (IEA Bioenergy, 2017).

In contrast, in China, the microalgae area was stimulated by the Medium and Long Term Development Plan for Renewable Energy promulgated by The National Development and Reform Commission of the People’s Republic of China (NDRC) in 2007 (Kirnev et al., 2020). In 2010, strategies for capturing and using CO_2 by photobioreactors were included in the country's objectives to deal with severe environmental degradation, in addition to efforts to produce cleaner energy, biofuels (biodiesel), green manufacturing, and sustainable services (IEA Bioenergy, 2017).

3.3 Analysis of patent families by assignee

The assignee, developer, or creator refers to the entity that holds the exclusive legal right to protect intellectual property over a certain period of time. Besides, applicants may include companies, public or private agencies, including universities, research centers, and institutes, or individual inventors (Norman and Eisenkot, 2017). Figure 4 shows the main active assignees in the patent pool analyzed in this study and their impact indicators.

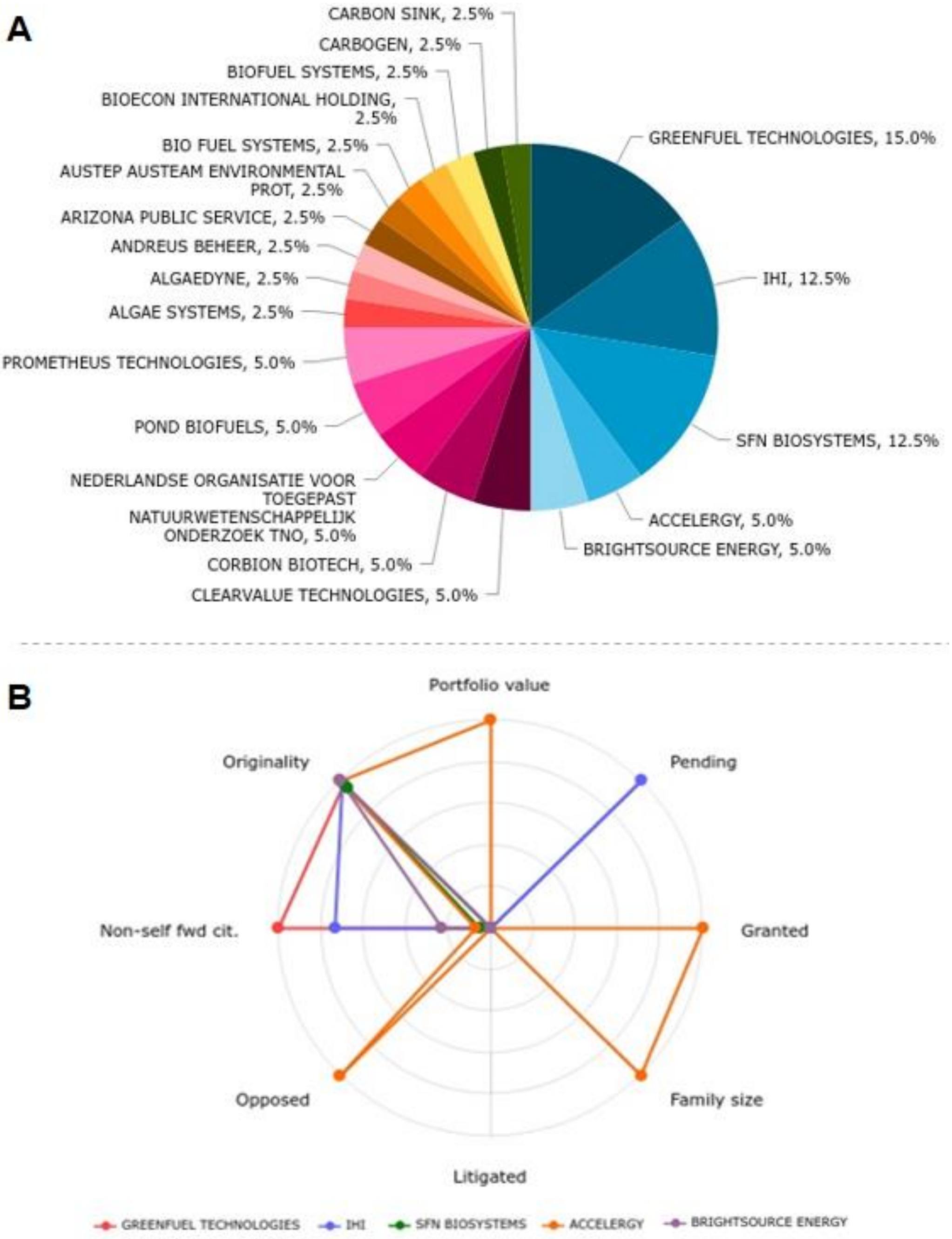

Figure 4. Portfolio of main active assignees. (A) Top 20 players from the patent families; (B) Impact indicators of the top 5 players.

According to Figure 4A, the 20 names shown of the companies lead the patenting on disruptive technologies involving microalgae photobioreactors, combined with combustion processes, indicating the level of inventiveness. Therefore, the development of these technological routes is dominated by three companies: GreenFuel Technologies Corporation, IHI Corporation, and SFN Biosystems Inc., with 6, 5, and 5 published patent families, respectively. GreenFuel Technologies Corporation patents deal with processes for microalgae cultivation integrated with fossil fuel emissions to produce biofuel. They correspond to publications US20080009055A1 and WO2003094598A1, with great relevance in terms of citation. In this sense, through this analysis, it is possible to demonstrate the applicant's propensity to collaborate and identify their preferred partners.

Figure 4B shows the total score of the portfolio value index by assignees with impact indicators. Because it is considered the top 1, GreenFuel Technologies Corporation's patents show originality scores close to 0.93, 496 non-self-citations, and 0 opposition or annulment procedures. On the other hand, the Accelergy Corporation patents had an impact on the categories of originality (0.95), portfolio value (11.5), granted (2), family size (13), litigated (0), and opposed (1); however, it had a relatively low impact on non-self-citations (35). In general, these quality indicators suggest that these patents are particularly valuable because they obtained the highest originality scores, considering the scale of 0 to 1 (Harhoff et al., 2003). The other categories indicate that patents are positively correlated to the value of rights.

Additionally, patent families by assignees can also be analyzed by the technological domain in which they are contained, which is based on classification codes, and can appear in different categories. Figure 5 provides an overview of the main technology areas covered by the top players.

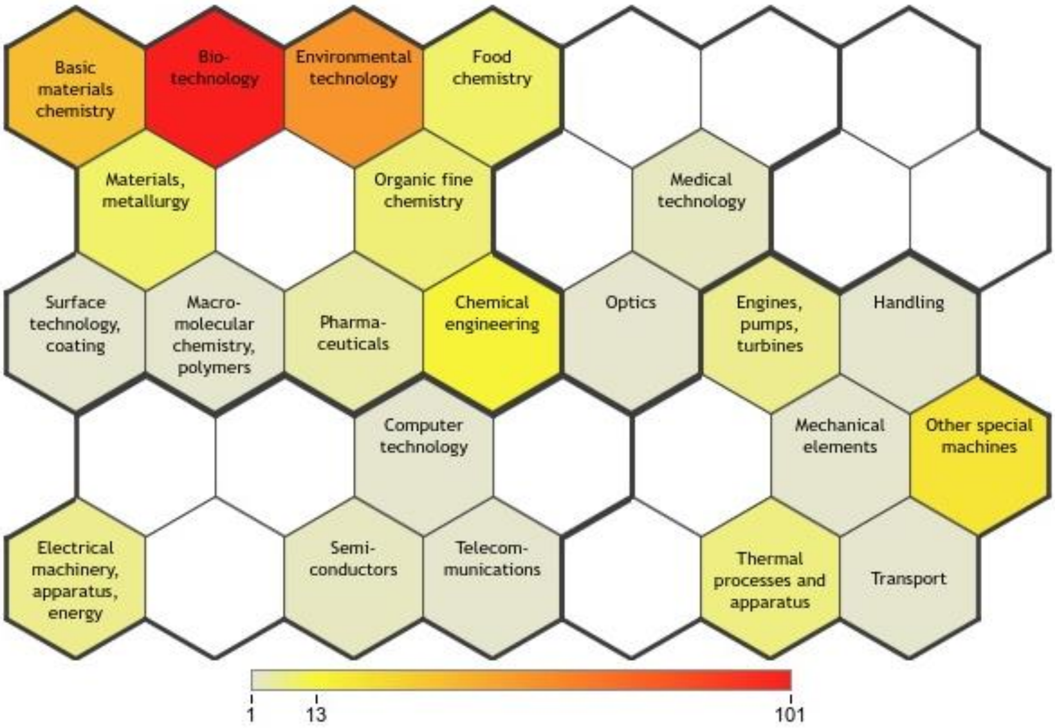

Figure 5. Patent families by technology domain.

Through this thematic concept map, it is possible to identify that the companies' patents are mainly concentrated in the areas of biotechnology and environmental technology. Evidently, these areas are the pillars that support the microalgae-based processes, which are currently considered extremely relevant to the industry in the search for innovation and new knowledge. These disruptive approaches show the strong relationship between scientific research in the area, emphasizing the important role of science in the generation of some technologies, and inventions in the sector.

Thus, it is possible to quickly identify the main business of a specific company and the potential partners in the market (WIPO, 2016).

3.4 Analysis of key patented inventions

The patent families that meet the quality requirements (as discussed in Section 3.3) were ranked as the top 30 and are presented in Table 2. They were analyzed and ordered according to the percentage of the relevance score obtained on the search platform.

As previously discussed, disruptive microalgae technologies combined with combustion processes and with the potential to mitigate climate change have been studied by several authors in the scientific literature. The papers generally report efforts to improve the photobioreactors design, studies on the parameters that affect culture performance when integrated to capture and use CO_2 and other GHG generated from flue gases, and renewable energy generation. Although the articles provide valuable information on the results of a scientific process, whether experimental or not, and the inferences established, the patent documents offer technical reports that describe the processes, methods, and devices along with their intended industrial applications (Abbas et al., 2014).

According to the first patent shown in Table 2, the leading company GreenFuel Technologies has several patents to capture and use CO_2 and produce energy-based products in parallel. By way of exemplification, the patent number WO2008008262A2, entitled "*Photobioreactor systems and methods for treating* CO_2*-enriched gas and producing biomass*", claims a microalgal photobioreactor fed with high concentrations of CO_2 as part of a fuel generation system. In certain embodiments, the invention uses the biomass generated as biofuel in an integrated combustion device, such as a power plant. The described process is similar to that presented in documents WO2003/094598 "*Photobioreactor and process for biomass production and mitigation of pollutants in flue gases*" (ranking #3), WO2008/008263 "*Integrated photobioreactor-based pollution mitigation and oil extraction processes and systems*” (ranking #24), and WO2007/011343 "*Photobioreactor and process for biomass production and mitigation of pollutants in flue gases*" (ranking #30).

On the other hand, in the second score in Table 2, the patent WO2012/024758 "Extraction of CO_2 gas" comprises a photobioreactor used to remove CO_2 from the exhaust gases of a combustion engine and recover heat (energy integration technique) as a kind of heat exchanger device for cooling the exhaust gas and heating the liquid container using heat.

Other patents such as WO2014/110668 "*Process for managing photobioreactor exhaust*" (ranking #14), BRPI0720662A2 "*Closed system photobioreactors and biofuel production method*" (ranking #18), and US20130224841 "*Method for establishing synergism between renewable energy production and fossil energy production*" (ranking #25) also present relevant processes, both as an individual inventor and as well-known companies in the microalgae industry.

Regarding applications from universities, the patent WO2017112984A1 "*Process and system for re-using carbon dioxide transformed by photosynthesis into oxygen and hydrocarbons used in an integrated manner to increase the thermal efficiency of combustion systems*” (ranking #4), from the Federal University of Santa Maria, Brazil, in collaboration with the company InterCement S/A, is the most representative document. The invention deals with the partial or total replacement of the air used in combustion processes by oxygen as an oxidizer, volatile and/or semi-volatile organic compounds as gaseous fuels, and carbon dioxide as nitrogen diluent, originating from biological GHG conversion through photosynthesis in a photobioreactor. More specifically, this document claims the treatment and conversion of said gases, the recovery of the photobioreactor gaseous phase, the integration of O_2, volatile organic compounds, and unconverted-CO_2 for use as an adjuvant in a petroleum coke combustion furnace, and the total or partial regeneration of the furnace exhaust gases for use in the photobioreactor. The present invention finds its field of application among the processes and systems for increasing thermal efficiency in industrial furnaces through the "bio-oxycombustion" technique. Later, the term was reframed as “bio-combustion” in the scientific two-part works developed by Severo et al. (2018) and Severo et al. (2020).

The most technologically impacting patent documents analyzed above, in general, present many unit operations for the treatment of microalgal biomass and conversion into biofuels or bioenergy. Some, on the other hand, address integrated processes with more simplified steps. The point is that these documents do not anticipate the direct use of photobioreactor exhaust gases to increase the energy efficiency of industrial combustion furnaces compared to the bio-combustion technique. That is, no records were found of a process with claims as peculiar as this one. This process was also subjected to strict metrics and sustainability indicators and bioeconomy analysis, foreseeing to be a disruptive innovation with environmental, economic, and social influence. The findings show that the process integration approach provided an improved performance on these questions. This is particularly important when dealing with the impactful and stable industrial combustion structures.

Table 2. Main innovations according to relevance score.

#	Publication number	Title	Year	Applicant/Assignee	Valid till or legal status
#1	WO2008008262A2	Photobioreactor systems and methods for treating CO_2-enriched gas and producing biomass	2006	GreenFuel Technologies (original); Tron Group LLC, IHI Inc., and Algae Systems (acquisition)	Lapsed
#2	WO2012/024758	Extraction of CO_2 gas	2010	SFN Biosystems	Lapsed
#3	WO2003/094598	Photobioreactor and process for biomass production and mitigation of pollutants in flue gases	2003	GreenFuel Technologies; IHI Inc.,	Lapsed
#4	WO2017112984A1	Process and system for re-using carbon dioxide transformed by photosynthesis into oxygen and hydrocarbons used in an integrated manner to increase the thermal efficiency of combustion systems	2017	Intercement Brazil, Federal University of Santa Maria	2035
#5	WO2010068288A2	Solar biofactory, photobioreactors, passive thermal regulation systems and methods for producing products	2010	Joule Biotechnologies, Inc.	Lapsed
#6	WO2009/112624	Liquid-phase gas collection	2008	Endesa Generacion	2028
#7	EP3150697	Method for treating liquid effluent and producing microalgae, comprising a pyrolysis step	2015	CEA - Commissariat al Energie Atomique & Aux Energies Alternatives	2035
#8	WO2008/042919	Method and apparatus for extracting carbon dioxide from air	2007	Kilimanjaro Energy (original); Carbon Sink (acquisition)	2027
#9	CA2630297	Extraction of CO_2 gas from engine exhaust	2008	SFN Biosystems	Lapsed
#10	CN104962476	Coal-mine-goaf-based carbon dioxide underground sealing method and system	2015	China Shenhua Energy	2035
#11	WO2007/101172	Process for the production of ethanol from algae	2006	Propulsion Logic	Lapsed

#12	WO2011/163111	Process for the selective production of hydrocarbon based fuels from algae utilizing water at subcritical conditions	2011	Old Dominion University Research Foundation	2032
#13	WO2013/106932	Integrated process for dual biocatalytic conversion of CO_2 gas into bio-products by enzyme enhanced hydration	2013	CO_2 Solutions (original); Saipem (acquisition)	Pending
#14	WO2014/110668	Process for managing photobioreactor exhaust	2013	Pond Biofuels (original); Pond Technologies (acquisition)	Pending
#15	EP2159195	Accelerated method for converting carbon dioxide into energy	2007	Stroiazzo-Mougin, Bernard A. J.	2027
#16	BRPI0806678	Process sped up for the conversion of energy of carbon dioxide	2007	Stroiazzo-Mougin, Bernard A. J.	2027
#17	CA2780103	Growing microorganisms using exhaust gas as a nutrient supply	2012	SFN Biosystems	Lapsed
#18	BRPI0720662A2	Closed system photobiorreators and biofuel production method	2007	Solix Biosystems; Colorado State University	2035
#19	DE4212334C1	Burning fuel oil or natural gas with pure oxygen to obtain heat with high efficiency without harmful emissions, with photosynthetic conversion using bioreactor	1992	Henry Schwetzingen De Tischmacher	Lapsed
#20	WO2013/089814	Integrated bioprocessing for fuel production	2011	ExxonMobil Research & Engineering	2033
#21	WO2010/116611	Micro-alga belonging to genus navicula, process for production of oil by culture of the micro-alga, and oil collected from the micro-alga	2010	Electric Power Development	Pending
#22	CN107899375	Carbon dioxide mixed capturing and microalgae carbon fixation coupling technology for coal-fired power plant flue gas	2017	Yang Zhengshan	Pending

#23	US20050064577	Hydrogen production with photosynthetic organisms and from biomass derived therefrom		GreenFuel Technologies; IHI Inc.	Lapsed
#24	WO2008/008263	Integrated photobioreactor-based pollution mitigation and oil extraction processes and systems	2007	GreenFuel Technologies	Lapsed
#25	US20130224841	Method for establishing synergism between renewable energy production and fossil energy production	2012	Charles Bliss	Lapsed
#26	US20110283618	Supplying bioreactor gaseous effluent to combustion process	2010	Pond Biofuels	Lapsed
#27	EP2582783	System for supporting algae growth with adsorbed carbon dioxide	2010	General Atomics	2032
#28	EP2046938	Photobioreactor systems and methods for treating co2-enriched gas and producing biomass	2007	Algae System; GreenFuel Technologies	Expired
#29	US20140011263	Photobioreactor cell culture systems, methods for pre-conditioning photosynthetic organisms, and cultures of photosynthetic organisms produced thereby	2013	IHI Inc.	Lapsed
#30	WO2007/011343	Photobioreactor and process for biomass production and mitigation of pollutants in flue gases	2005	GreenFuel Technologies	Lapsed

3.5 Process applicability

The processes claimed in the patents have certain limitations in terms of scale-up and capital cost of implementation. Some considerations about the photobioreactors configuration must be carefully analyzed before they can be engineered in the open market. At the current stage, some of these technologies undertook development during the commercial installation reaching TRL of 9; however, others remain at the lowest TRL.

Closed photobioreactors are essential to manufacturing compounds with high added value. Some authors have suggested methods to increase productivity in large-scale facilities. However, despite these advances, overcoming the deficit in the yield of cultivation systems has been discouraging. Associated with this, the problems caused many mistaken attempts in terms of dimensioning. There are several companies with outdoor mass cultivation systems for the production of microalgae biomass and bioproducts. However, as far as is known, no photobioreactor has been designed to operate with large production volumes and withstand the high CO_2 loads that industrial combustion processes deal with.

In an attempt to find a suitable photobioreactor, technological innovation systems (TIS) have been used as a *proxy* to direct continuous developments and identify potential technologies (Berg et al., 2019). On the other hand, as the costs are exorbitant, technical-economic analyzes need to be continuously updated to guarantee the viability and economy of scale in all phases of technology development, from its conception, prototyping, demonstration to full commercialization. In practical terms, implementation is not an easy task. There is a real and strong demand for systems, methods, techniques, and apparatus to produce high capacity microalgae for commercial competitiveness.

4. Conclusions

The use of disruptive technologies with the potential to mitigate against climate change will be increasingly necessary, considering the current patterns of energy consumption and generation, world population growth, public policy trends, which subsidize stimulus for innovation. Technological prospecting involving patent analysis in this field of knowledge contributes to the considerable advance to be optimized by other industries. Certainly, these approaches could be implemented in a way that complements the traditional industrial combustion processes. Besides, the process integration would allow for more sustainable development and contribute to the circular bioeconomy of the current industry portfolio.

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7. CAPÍTULO 5

7.1 CAPÍTULO DE LIVRO 1

Biofuels from Microalgae: Photobioreactor Exhaust Gases in Oxycombustion Systems

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

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

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

1 Introduction

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

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

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

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

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

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

2 Fundamentals of the Oxycombustion

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

In a conventional combustion system, air is used as the oxidizer, and the coming CO_2 from the flue gas is diluted by N_2 of air, resulting in a reduced CO_2 concentration per capture (about 15% v/v). In oxycombustion, a combination of practically pure oxygen (usually 95% v/v) and recycled flue gas is used as the oxidizer for burning the fuel. Such flue gas is composed mainly of CO_2 and H_2O, which is used to control the flame temperature in the burner and fill the volume removed N_2, ensuring that there is enough gas to carry heat through the system (Stanger et al. 2015). Carbon dioxide concentration in the flue gases increases by approximately 17–70%, depending on the fuel used, and can then be captured, stored, or used (Buhre et al. 2005).

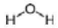
By determining the physical and chemical processes that the fuel experiences during oxycombustion, characteristics such as heat and mass transfer, temperature, stability and flame velocity, ignition, and pollutant formation are affected globally (Chen et al. 2012a, b). The main impacts are related to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

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

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

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

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

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

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

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

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

3 Operational Implications for Oxycombustion-Enhanced Performance

3.1 Oxygen Supply

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

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

In terms of capacity, ASUs have been designed with design features to meet total oxygen production from 1000 tons (30,000 Nm^3/h) to 5500 tons (165,000 Nm^3/h). Today, the world's largest plant with an ASU for oxygen supply operates at a capacity of 4000 ton/d O_2 (Linde Group 2017). Therefore, assuming that, on a 500 MW oxycombustion power plant operating on an industrial scale, the oxygen supply should be around 10,000 ton/d (Higginbotham et al. 2011), 3 more ASU plants would necessarily have to operate simultaneously, or an ASU with greater capacity than the existing ones should be developed. At the same time, the expected energy consumption to separate 1 ton of oxygen from the air would be 150–200 kWh/t O_2 produced (540 kJ/kg), and the electrical energy necessary for this process would be approximately 80 MW, causing a significant reduction of about 7–11% in the efficiency of net electricity generation (Chorowski and Gizicki 2015).

3.2 Oxygen-Enrichment Methods in Combustion Systems

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

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

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

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

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

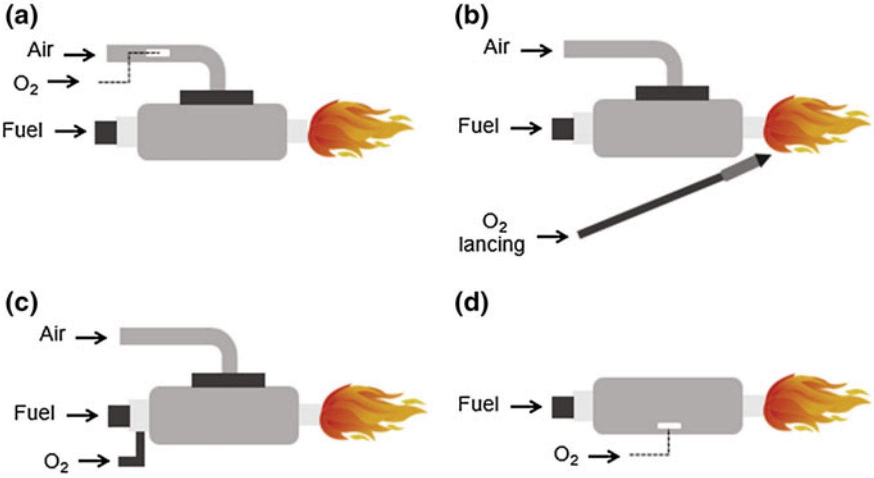


Fig. 1 Scheme of oxygen-enrichment methods in oxycombustion systems. **a** premix enrichment with air; **b** air/fuel flame (O_2 lancing); **c** air/oxygen/fuel combustion; and **d** oxyfuel combustion

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

3.3 *Fuel Supply*

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

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

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

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

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

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

4 Oxygen Produced by Photosynthesis

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

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

Table 3 Critical issues in oxycombustion systems

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

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

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \tag{1}$$

Additionally, the theoretical and realistic conversion efficiencies of water photolysis can be obtained by biological estimates, in terms of quantum efficiency, i.e., through the energy fraction of absorbed photons, or calculated from the solar

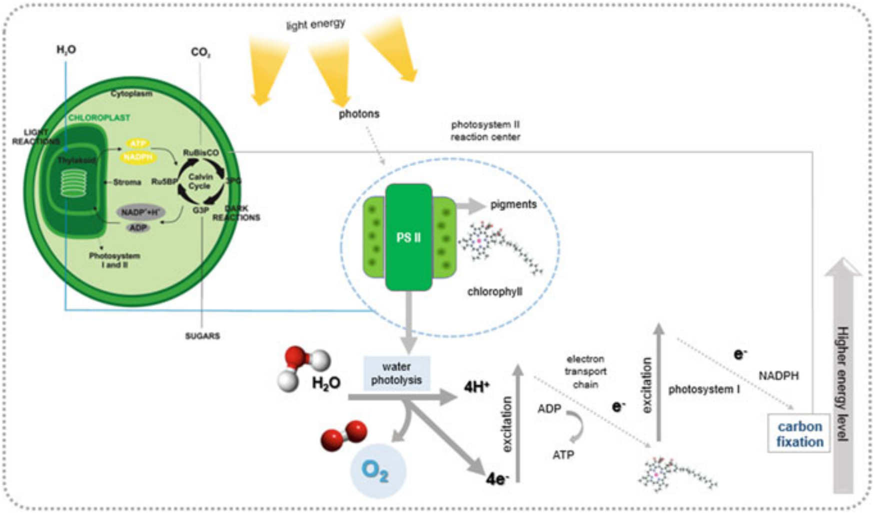


Fig. 2 Schematic representation of the oxygen generation in the photosynthesis

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

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

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

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

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

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

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

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

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

5 Volatile Organic Compounds as Energy Source

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

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

According to Zepka et al. (2015), the VOCs produced by microalgae can be divided into terpenoids, phenylpropanoids/benzenoids, carbohydrate derivates, fatty acids derivates, and amino acid derivates, besides specific compounds not represented in those major classes. Microalgae are able to generate and release substantial amounts of VOCs belonging to different classes of compounds, such as alcohol, aldehydes, ketones, hydrocarbons, esters, terpenes, carboxylic acids, and sulfurized compounds, with chains that can contain up to 10 carbon atoms (Muñoz et al. 2004; Fink 2007; Sun et al. 2012).

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

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

6 Photobioreactors Design

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

A wide variety of cultivation systems have been reported for microalgae-based processes. Photobioreactors are generally classified into two designs: open or closed systems (Borowitzka 1999). Open systems are most commonly used in large-scale processes and are based on circular ponds and raceway tanks. They are simple to operate, cheap, and easy to expand. However, performance is poor, since the culture

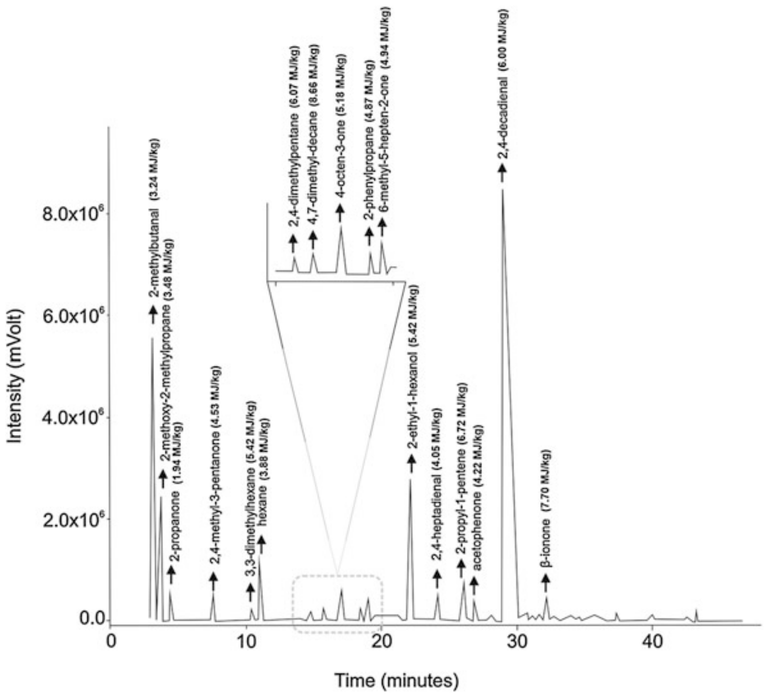


Fig. 3 Identification of VOCs produced by *Scenedesmus obliquus* and released from the photobioreactor exhaust gases. Adapted of Jacob-Lopes et al. (2017)

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

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

Given these varied configurations, currently, one of the most widely accepted configurations for mass culture of microalgae is the closed tubular photobioreactors. This type is basically designed to achieve a maximum surface/volume (S/V) ratio and can be classified based on the horizontal, vertical, inclined, or helical arrangement of the tubes. They are suitable for CO_2 conversion due to their homogeneous mixture, greater gas transfer, smaller hydrodynamic stress, and uniform light distribution, which implies enhanced performance on the microalgae growth. In addition, they can be operated easily, their cell density is 5–6 times higher than that of open ponds, and their capacity can reach up to 25,000 L and occupy a restricted area of about 10 m^2 (Raeesossadati et al. 2014; Jacob-Lopes et al. 2015; Pawar 2016). However, in addition to the drawbacks related to overheating, the main critical issue in these systems is photo-inhibition, energy consumption, high costs, and dissolved oxygen (DO) accumulation (Huang et al. 2017).

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

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

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

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

7 Process Integration in Bio-oxycombustion Systems

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

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

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

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

In this context, for bio-oxycombustion system proposed, mass integration occurs by direct conversion of GHG, especially CO_2 (gaseous effluent integration) in photobioreactors. Subsequently, part of the CO_2 is converted into photosynthetic metabolism by-products, such as biomass, inorganic salts, exopolymers, O_2, and VOCs. In parallel, energy integration is made by recovering of the photobioreactor gaseous phase, which contains the compounds of interest: VOCs (heat integration), $O_{2,}$ and unconverted CO_2 released from the exhaust gases. These are integrated into

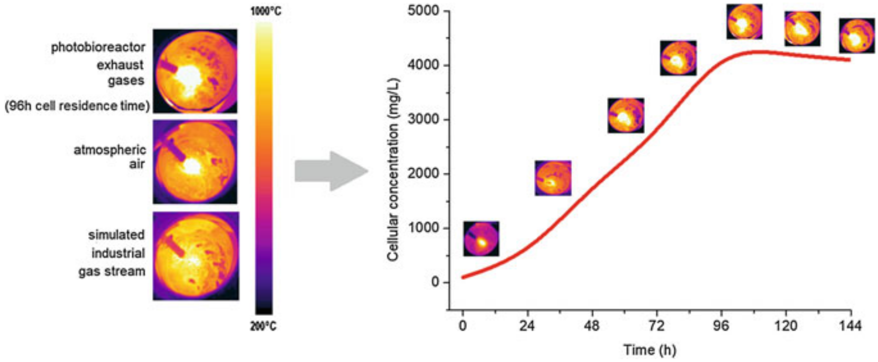


Fig. 4 Thermal performance of the integrated bio-oxycombustion system. Adapted of Jacob-Lopes et al. (2017)

Table 5 Challenges facing bio-oxycombustion technology

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

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

8 Challenges Facing Bio-oxycombustion Technology

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

9 Final Considerations

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

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7.2 CAPÍTULO DE LIVRO 2

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Chapter 12

BIOLOGICALLY-ASSISTED COMBUSTION: A WASTE-TO-ENERGY APPROACH

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ABSTRACT

The objective of this chapter is to address aspects related to biologically-assisted combustion focusing on waste-to-energy. Divided into six different sections, the chapter reports issues that outline the combustion science and technology, the oxygen and fuel requirements in combustion systems, the biologically-assisted combustion, the photobioreactors, the mass and energy integration, the environmental performance evaluation and the bioeconomy of the process, summarizing a series of sustainable approaches for the industrial combustion processes.

Keywords: photobioreactors, process integration, oxycombustion, mass balance, energy balance, life cycle assessment, bioeconomy

1. INTRODUCTION

The most source of carbon dioxide (CO_2) emissions is from consumption of fossil fuels. Besides, heavy dependence on these fuels causes worldwide and governmental concerns regarding the generation and use of energy from inherently non-renewable

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sources (IPCC, 2014). According to International Energy Agency (IEA), the average concentration of CO_2 in 2015 was about 40% higher than in the past two decades. Still, it is estimated that at least half to mitigate the environmental impact should reduce such emissions in the coming years (IEA, 2017).

In an attempt to mitigate climate change, some engineering strategies have been considered, including carbon capture by microalgae-based processes, which are now being found to have a dual benefit: (i) use of CO_2 from flue gases and (ii) biotransformation in high-value products (Choi et al., 2017). This waste-to-energy strategy is to make use of waste resources in a manner that eliminates or at least significantly minimizes adverse effects on the environment, contributes to sustainability factors, and provides a net positive energy result (Skaggs et al., 2018).

Among the available options, combustion processes have been extensively studied for carbon capture. However, even if CO_2 capture is fully effective, there are harmful emissions in previous stages such as extraction, processing, and receipt of raw materials and fuels, which shows that the technology may have other environmental impacts (Gładysz and Ziebik, 2016).

The microalgae-mediated processes are attractive due to the perspectives that they offer in the current scenario of decreasing energy and carbon footprint. However, the main limitation to the use of microalgal technologies at commercial scale is associated, primarily, to an ideal photobioreactor design and, secondarily, to their relatively high cost and negative energy balance, which is less favorable than traditional renewable resources (Tredici et al., 2015).

Recently, an integrated process of biologically-assisted combustion was developed, whose technology is based on the biological conversion of greenhouse gases (GHG), primarily CO_2, into volatile organic compounds (VOCs) and oxygen (O_2). Besides, a considerable fraction of CO_2 injected into the photobioreactor is lost through the exhaust gases, due the most of the closed systems achieve CO_2 removal efficiency rates under 30%. These substances are reused as gaseous fuels, oxidizer, and nitrogen diluent, respectively, in a combustion system, aiming at an improvement in energy-efficiency, fuel and oxidizer saving and, minimize emissions (Jacob-Lopes et al., 2017; Severo et al., 2018). Although the process integration approach is widely widespread within the new dimensions of sustainability (Manan et al., 2017), the bio-combustion system proposed by these authors can achieve other potential environmental impacts throughout the entire process.

For this, life cycle assessment (LCA) is a promising tool to guide decision-making in ecologically sound processes. It contributes to quantification, identification, and comparison of energy, water and materials use, as well as waste emissions, analyzing their potential impacts on the environment, and enabling opportunities for improvement throughout the life cycle (Pragya and Pandey, 2016). Therefore, the chapter aims to present aspects related to biologically-assisted combustion with an approach in waste-to-energy. Therefore, the objective of this is to present aspects related to biologically-assisted combustion with a waste-to-energy approach. The focus of the chapter is the integration of mass and energy of photobioreactors with bio-combustion processes, the environmental performance assessment, as well as the bioeconomy.

2. COMBUSTION SCIENCE AND TECHNOLOGY

The behavior of fuel combustion involves complex reactions characterized by physical-chemical phenomena of both fundamental interest and practical relevance. There are important exothermic reactions which release substantial energy with the ability to affect the combustion performance, as the combustion kinetics and heat and mass transfer, and as such is governed from the first law of thermodynamics (Glassman and Yetter, 2008).

The overall combustion process involves two necessary steps: the devolatilization and the ignition and are strongly influenced by the change in the composition of the oxidizer and fuel, where new chemical substances are formed (Yin and Yan, 2016). In most industrial processes, atmospheric air is used as the oxidizer agent, and the CO_2 from the flue gas, which contains a concentration of 10 to 15%, is used as a chemically inert nitrogen diluent. Under these conditions, the reactive O_2 removes part of the thermal energy from the exhaust gases, and the combustion efficiency is affected by the amount of unburned fuel and excess air. The largest portion losses presented by combustion with air is perceived by flue gases whose furnace cannot obtain a clean burning and operates at high excess air rates. Thus, the flame temperature is reduced, and the fuel demand increases, drastically decreasing the efficiency of the system (Lalović et al., 2011).

On the other hand, given the current state of technological development of energy generation processes, oxygen-enrichment combustion systems have been suggested as a possible technology to improve industrial combustion. This is a CO_2 capture technology considered as technically feasible and economically competitive for future commercial applications (Sher et al., 2018). Unlike conventional combustion, oxygen-enrichment combustion employs an additional air separation unit (ASU) to produce an almost pure O_2 stream as the oxidizer (more than 21%, reaching up to 99%), and recycled flue gas, containing about 80% CO_2, for fuel burning (Skorek-Osikowska et al., 2015). The flue gas recycling is necessary to nitrogen dilution and for moderate the otherwise excessively high flame temperature. Increasing O_2 can reduce the energy loss and improve the heating system efficiency (Luo et al., 2013). Figure 1 shows the simplified diagram of a combustion process with oxygen-enrichment.

According to Yin and Yan (2016), the perceived improvements in oxygen-enriched combustion about conventional combustion come from the differences in physicochemical properties of the diluent gases. The heat transfer by radiation is much higher due to the superior thermal capacity of CO_2 compared to N_2; the concentration of tri-atomic gas molecules in the flue gas increases drastically, and consequently, the absorptivity and emissivity will also be higher. Additionally, the density of the flue gas is increased, due to the higher molecular weight CO_2, when compared to the N_2. When considering these aspects, is possible to obtain a more stable combustion, high flame temperatures, better burning speed, heat and mass transfer, combustion kinetics, ignition and lower formation of pollutants.

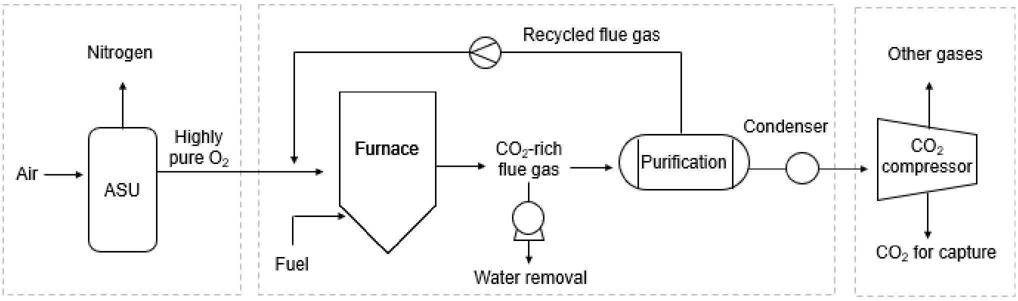

Figure 1. Combustion process steps with oxygen-enrichment.

Processes that use combustion technology with oxygen-enrichment have not yet been implemented at the industrial scale. Meantime, worldwide, there are many researches concerning of this type of system in laboratory or pilot scales being conducted, since it is considered as an acceptable methodology for controlling GHG emissions (Kumar, 2017).

2.1. Oxygen and Fuel Requirements in Combustion Systems

The improved efficiency of combustion systems could be influenced by various factors, including mainly the amounts of O_2 and fuel requirements, and suitable air/fuel mixture (Buhre et al., 2005).

Industrial oxygen is produced in an ASU, in which the atmospheric air is cleaned, compressed and cooled, and the liquefied stream is introduced into the cryogenic distillation column to separate air into its components (CO_2, H_2O, hydrocarbons). An ASU may deliver sizeable O_2 flow rate, producing more than 3,000 tons of O_2 per day with purity close to 100% and consumption about 0.24 kWh/kg O_2 (Chen et al., 2012; Ebrahimi et al., 2015).

The main challenges of this system include the high cost associated with the additional equipment required and the excessive thermal energy consumption, which is more than 14% of the cost of electricity. The system performance significantly depends on how the various equipment’s or subsystems are designed and integrated as a whole in the plant (Yin and Yan, 2016).

The cost of electricity used depends on the design of the O_2 production plant and its purity. According to a report by International Energy Agency, a combustion plant that needs approximately 10,000 tons of O_2 per day at a purity of 95%, energy consumption is in the order of 200 kWh/tons of O_2. Additionally, ASU's capital cost is about USD 258 million. Considering a capital of 10%, and operation of 7500 hours/year, energy expenditure reaches approximately USD 47.5 million per year, which represents on average 65% of the cost of O_2 (IEA GHG, 2007).

Other emerging methods of O_2 production are under development: the pressure swing adsorption (PSA) process, chemical absorption, and polymer membranes or ion carriers, which have the same level of energy expenditure (Banaszkiewicz et al., 2014).

On the other hand, the consumption of fossil fuels in combustion processes is another crucial issue to be considered. Several studies report that the more O_2 is supplied to the burner system, the better the combustion performance. The enrichment technique can reduce up to 50% of fuel required, and the emissions can be reduced up to 90% (Luo et al., 2009; Wu et al., 2010; Baskar and Senthil Kumar, 2016).

A combustion system with enrichment of high O_2 concentrations and high exhaust gases temperature can reduce fuel requirements when compared to a conventional system. However, when taking into account the costs of O_2 production, some industries choose to inject low O_2 concentrations, around 5 to 15%, and therefore, it is necessary to use more fuel (IHEA, 2007). Thus, considering the estimates of the IEA, the price of petroleum could rise to USD 100 per barrel by 2020. With the current global trend in energy supply and consumption, it shows that such an increase is inevitable (IEA, 2017). A detailed analysis of O_2 and fuel requirements should be performed to avoid operating expenses.

3. BIOLOGICALLY-ASSISTED COMBUSTION

3.1. O_2 Production

Many microorganisms are capable using light as a source of energy, in a process known as photosynthesis. Of these, cyanobacteria and microalgae are of particular interest because they are oxygenic, using the water as an electron transfer during the photosynthetic process. Similar to the higher plants, these microorganisms are responsible for the biological O_2 generation at significant levels, despite the existence of specific aspects in some species (Fay, 1983).

Photosynthesis is driven by Calvin–Benson–Bassham (CBB) cycle, which is the metabolic pathway for the CO_2 bioconversion in microalgae. This mechanism involves a complex metabolism and can be subdivided into two steps: light reactions or photochemical step, and dark reactions or carbon fixation step (Calvin and Benson, 1948).

The microalgae have high photosynthetic rates, and this can be explained by the presence of an essential biophysical process known as carbon concentration mechanism (CCM), allowing the use and accumulation of different concentrations and forms of inorganic carbon (Badger and Price, 2003). Three different inorganic carbon assimilation routes by microalgae are possible: (i) direct CO_2 assimilation via the plasmatic membrane; (ii) the use of bicarbonate by inducing the carbonic anhydrase enzyme, which converts the HCO_{3^-} into CO_2; and (iii) direct transport of bicarbonate via the plasmatic membrane. The carbonic anhydrase enzyme is able by increasing the intracellular CO_2 levels, demonstrating the efficiency elevated of bioconversion of these microorganisms. Thus, CCMs is a potential tool for photosynthetic performance (Singh et al., 2014).

Firstly, the CO_2 is incorporated into ribulose 1,5 diphosphate, catalyzed by the enzyme ribulose-1,5-bisphosphate carboxylase oxygenase (RuBisCO). The reaction product is divided into the following molecules: PGA (phosphoglyceric acid), which is reduced by NADPH (nicotinamide adenine dinucleotide phosphate), leads to the production of ATP (adenosine triphosphate) and a series of intermediary phosphorylated sugars and finally to the glucose molecule (Calvin and Benson, 1948).

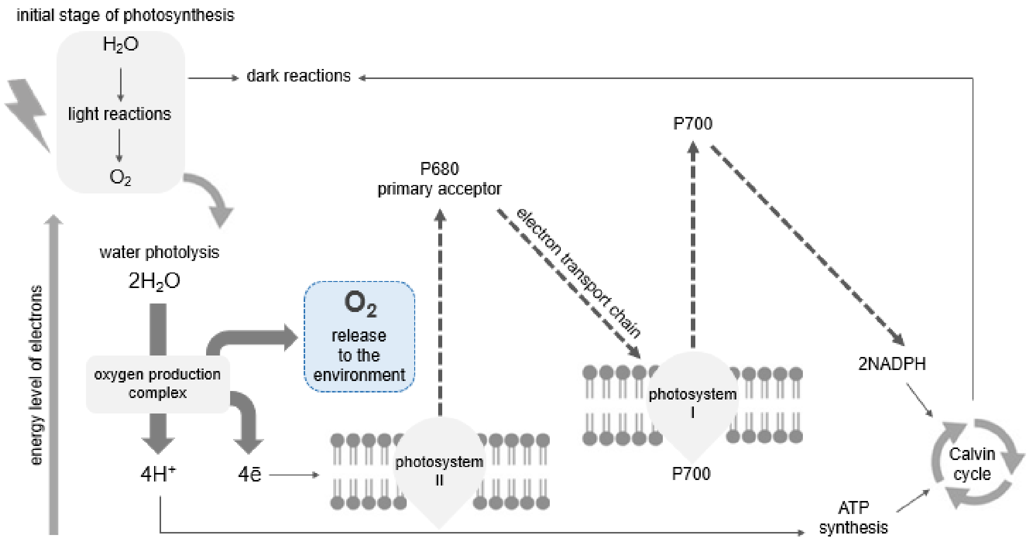

Figure 2. Scheme of water photolysis and O_2 production in photosynthesis.

In the CO_2 fixing process, which is not directly light dependent, the requirements for energy in the form of ATP and NADPH are coming of CBB cycle, entirely dependent on the photochemical step, which occurs in the thylakoid membranes. In this place, are the photosystems I (P700 acceptor) and II (P680 acceptor), where pigments such as chlorophyll are responsible for absorbing mainly photons and transferring energy to an electron-accepting substance. Part of the energy liberated is incorporated into ATP in the phosphorylation process during electron transport, and used for the water photolysis, the last electron source in the photosynthesis (Williams and Laurens, 2010). The water photolysis is also referred to as Hill's reaction, which releases O_2 atoms, a fundamental volatile bioproduct generated by microalgae (Heldt and Piechulla, 2011). Figure 2 shows the water photolysis and O_2 production in photosynthesis.

In order to obtain more information about the O_2 production efficiency during the water photolysis, estimates may be made through the photosynthetic quotient (PQ). PQ refers to the moles of O_2 produced per mole of converted CO_2 and is based on the stoichiometry of photosynthetic equation, which establishes a theoretical value of 0.73 kg of O_2 produced for every 1 kg of CO_2 consumed. Experimentally, the PQ values found in the literature range from 0.62 to 1.50 (Eriksen et al., 2007; Jacob-Lopes et al., 2010; Holdt et al., 2013; Spilling et al., 2015; Undurraga et al., 2016).

3.2. CO_2 Losses

Microalgal growth requires CO_2 as an inorganic carbon source, and at the same time, their supply contributes to control of pH of the medium. In the closed photobioreactors, the carbon availability is controlled by injecting pure CO_2. The most suitable forms of supply are by direct injection, either mixed in the airflow, directly in the culture medium, or using a mixing absorber. Nevertheless, a significant problem associated to the microalgae cultivation is the expense with the CO_2 supply and its transfer to the culture, totaling approximately 30% of the production costs in large-scale systems (Sánchez et al., 2003).

Such problems occur mainly because when high CO_2 loads are injected into the system inlet, the real losses are higher than 70%. These issues are considered as a fundamental factor that affects productivity and can determine the performance of converting CO_2 in the photobioreactors (Fernández et al., 2010).

Even if the microalgae present the CCM as a metabolic pathway that supports high levels of inorganic carbon retained intracellularly, some studies have shown that part of this substance is lost in the exhaust gases (Rubio et al., 1998; Fuentes et al., 1999; Jacob-Lopes et al., 2008). Metabolically, the carbonic anhydrase enzyme, involved in the photosynthetic process, reduces its efficiency as a function of the dissolved inorganic carbon saturation that is transferred for the gas-liquid interface in the culture medium (Sobczuk et al., 1999).

Their excess addition causes considerable losses that are not used by microalgae cultures, resulting in unnecessary availability and release into the environment. Such losses could only be reduced to less than 30% if the ideal design and operational strategies were adequately developed to improve the performance of photobioreactors.

However, there is still no system that meets these requirements (Jacob-Lopes et al., 2009; Fernández et al., 2010).

Thus, the recovery of unconverted CO_2 and lost in the photobioreactor exhaust gases can be considered. The reuse in combustion systems, for example, as a gaseous nitrogen diluent, could be a factor in enhancing the thermal performance of these processes. The reduction of the N_2 volume contributes to the increase of the concentration of molecules with a triatomic spatial configuration, as in the case of CO_2, which has the power to emit more energy in the form of heat and, thus, allowing greater productivities (Buhre et al., 2005).

3.3. VOCs Production

Even with the scarcity of information with respect to carbon mass balance analysis in microalgae cultivation, it is known that the formation of VOCs is the main CO_2 biotransformation pathway in photosynthetic cultures under conditions of high carbon availability (Jacob-Lopes and Franco, 2013). Based on the mass balance, VOCs represent on average 90% of the total bioconverted substrate in photobioreactors, in addition to O_2, biomass, soluble biopolymers, carbonates and bicarbonates, whose variations will depend on the microalgae species and operation conditions (Cabello et al., 2017).

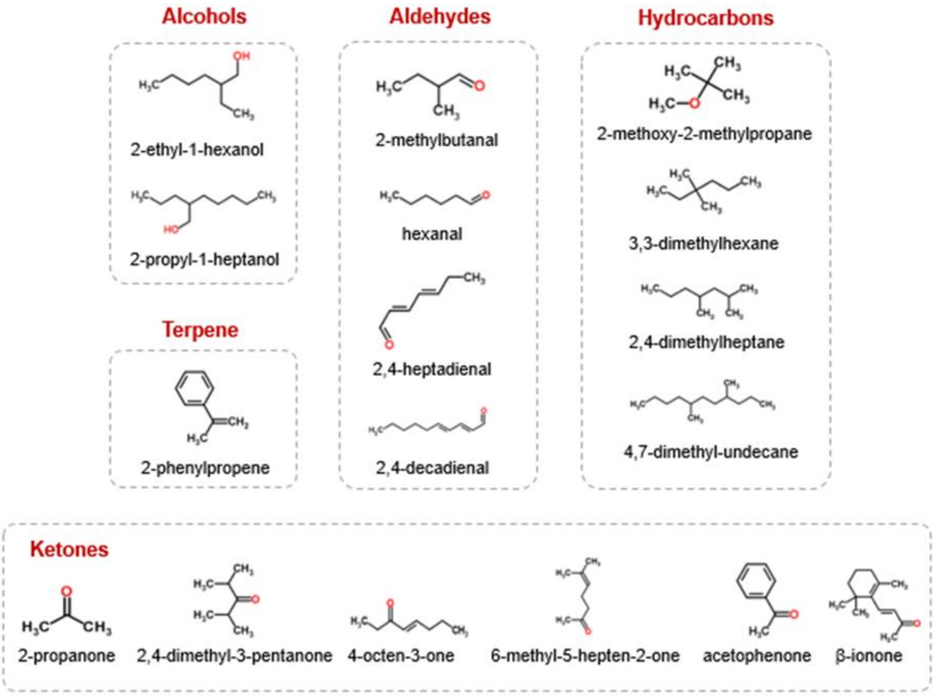

Figure 3. Volatile organic compounds produced by microalgae in a photobioreactor.

The VOCs come from the end step of the CBB cycle, where one molecule of G3P (glyceraldehyde-3-phosphate) is formed, which specialized enzymes present in microalgae catalyze reactions that incorporate carbon atoms to form phosphoenolpyruvate, and finally, the pyruvate molecule. The formation of VOCs from pyruvate can follow the route of terpenoids, phenylpropanoids/benzenoids, carbohydrate derivates, derivates short to medium-chain free fatty acids, and amino acid derivates. Some studies have reported the biosynthetic origin of these compounds to facilitate the knowledge of their production (Santos et al., 2016).

Depending on species, culture medium and environmental conditions, microalgae are capable of producing a wide variety of VOCs, and are originated from different chemical classes of compounds such as alcohol, aldehydes, ketones, hydrocarbons, esters, terpenes, carboxylic acids and sulfurized compounds, which are released into the environment (Hosoglu, 2018).

The detailed identification of such compounds is essential due to their direct impacts on the properties of the final product. Several sources report the production of VOCs by microalgae and cyanobacteria (Muñoz et al., 2004; Eroglu and Melis, 2010; Hasegawa et al., 2012). Figure 3 shows some compounds produced by microalgae in photobioreactors (Jacob-Lopes and Franco, 2013; Jacob-Lopes et al., 2017; Severo et al., 2018). Because the carbon chain is extensive, these secondary metabolites present considerable energy potential. Regarding applicability, they can be considered as promising sources of bioenergy.

4. PHOTOBIOREACTORS

The microalgae cultivation is performed in open or closed photobioreactors. Open systems are the most applied at commercial scale and are based on circular and raceway ponds. They have low capital and operating costs and can be built more easily. However, the productivity is limited due to poor utilization of light and the higher risk of contamination. Also, CO_2 conversion is not satisfactory because the water evaporation rate is rapid, resulting in a low retention time (Pires et al., 2017).

Another open system that is being developed is the biofilm technology, where the cells are immobilized in matrixes, forming a thin film and present relatively good productivity. Besides, microalgae biofilms can reduce the costs of biomass processing, because they can be integrated into the cultivation and harvesting stage. However, biofilm activity is relatively low due to limited light penetration (Fu et al., 2017).

On the other hand, closed systems can have different configurations such as flat-plate, bubble column, air-lift, tubular, and hybrid photobioreactors, which enable high rates of CO_2 biotransformation in a wide variety of high-value bioproducts (Tao et al., 2017). Due to the design, closed photobioreactors allow greater control of CO_2, can achieve high biomass productivities, low risk of contamination, and better control of cultivation variables. Although these systems are potentially suitable for microalgae cultivation, the scale-up is limited mainly by issues related to costs and energy consumption during operation (Wang et al., 2012). The different microalgae culture systems and their characteristics are listed in Table 1.

Among the various types of photobioreactors, the most exploited for outdoor mass cultures and is currently in operation in the worldwide are tubular. Concerning configuration, they are classified based on the horizontal, vertical or helical arrangement of the transparent tubes, known as solar collectors. These systems are designed to achieve a maximum surface/volume (S/V) ratio, can be installed indoors, receive artificial lighting, or be arranged outdoors, receiving solar energy and, still, achieve high productivity (Fernández et al., 2012). Nonetheless, the high concentration of dissolved O_2 is the main problem in tubular photobioreactors. The accumulation of metabolically produced O_2 is toxic to cells, inhibiting microalgal growth (García-Galán et al., 2018).

The photosynthetic efficiency of microalgae is accompanied by the ratio of CO_2 consumed and O_2 produced. Thus, O_2 levels above air saturation (250 to 400% at 25°C) can inhibit photosynthesis, even if higher loads of CO_2 are maintained in the photobioreactor. To an ideal balance, gas exchange and an efficient mixture system are required for mass transfer between the gas-liquid phases. In this sense, the O_2 removal dramatically improves the productivity in tubular photobioreactors (Huang et al., 2017). However, such systems for O_2 accumulation control have still been well developed to operate on the required scale (Molina-Grima et al., 2001).

At intermediate levels of scale, the tubular photobioreactors available in the market can meet the demand of the photosynthetic process, as well as generate several fine chemicals products. But, for the bulk production of O_2, for instance, operational problems must be solved to expand the industrial production process (Ramírez-Mérida et al., 2015).

Table 1. Comparison between different microalgae culture systems (Wang et al., 2012; Singh and Sharma, 2012; Razzak et al., 2017)

Design	Cultivation system	Possibility of exhaust gas collection	Accumulation of dissolved oxygen	Scale up	Relative cost	Energy input	Productivity	Land space
Open	Circular ponds	Low	Low	High	Low	Low	Low	High
	Raceway ponds	Low	Low	High	Low	Low	Low	High
	Biofilm	Low	Low	Low	High	Low	Medium	High
Closed	Flat-plate	High	Low	Low	High	Low	High	High
	Bubble column	High	Low	Medium	High	High	High	High
	Air-lift	High	Low	Medium	High	High	High	High
	Tubular	High	High	Medium	High	High	High	High
	Hybrid	High	Low	High	Low	High	High	Low

In an effort to advance the status of microalgae cultivation systems, arise hybrid photobioreactors with a new design to equilibrate the failures of other types of equipments. They combine open and closed reactors as a configuration more productive, low-cost and, specially developed with a ratio height/diameter column (H/D) appropriate to withstand high workloads, which demonstrates the possibility of scale up (Jacob-Lopes et al., 2016). Even with the existence of a considerable number of photobioreactors, to date, no type of equipment has been adequately designed for industrial scale deployment. In the future, photobioreactors could be developed to generate high volumes of biological O_2 and, therefore, assist other production processes in an economically viable way.

5. MASS AND ENERGY INTEGRATION IN BIOLOGICALLY-ASSISTED COMBUSTION PROCESSES

Industrial complexes allow highly integrated and efficient production of multiple products. The integration is based on engineering projects that focus primarily on mass and energy integration, both separately and simultaneously (Manan et al., 2017).

The concept of process integration represents a rigorous framework to determine the efficient use of energy resources, water, effluents, and materials, minimizing environmental impacts and leading to higher net profit. The laws of thermodynamics are applied to understand the nature of production systems with an emphasis on the mass and energy balances in integrated processes (Fan et al., 2018).

In this regard, the current trend towards integrating processes for cleaner production is centered on advanced biotechnological platforms and the bioprocesses integration, which can be mediated by microalgae, whose focus is to develop technologies to transfer the logic of the fossil-based industry to potential renewable industries (Fresewinkel et al., 2014).

Specifically, biologically-assisted combustion processes with the waste-to-energy approach, deal with mass flows that can be recovered and reused within production systems through the integration of effluents and water.

As an alternative to conventional end-of-pipe effluent treatments, the integration of gaseous effluents generated by chemical plants may be appropriate for the microalgae cultivation in photobioreactors, since the combustion gases contain substances such as CO_2, NO_x, and SO_x, which serve as sources of carbon inorganic and other nutrients (Klein et al., 2018). Several studies have shown the possibility of integrating flue gases by microalgae through the biofixation of gaseous compounds (Zhao et al., 2015; Lara-Gil et al., 2016; Aslam et al., 2017).

Because it is a basic resource in industrial production processes, the water required for culture medium composition in the photobioreactor can also be integrated. Microalgae production is known as a highly demanding process of water. Among all possible forms of water loss in the cultivation, the evaporation rate of the photobioreactor should be considered when scaling-up an integrated system. The recycling of cultivation water is essential to minimize the water footprint and for avoiding waste (Klein et al., 2018). Therefore, both strategies of mass integration are interesting options to tackle economic issues, such as the use of low-cost substrates, and environmental, in a single step.

As for the energy flows, the recovery of surpluses can be done through heat integration in heating systems, power generation and consumption, and fuels. Strategically, when heat is integrated through its internal recovery in the equipments, the energy consumption is minimized, and the overall thermal efficiency is maximized (Klemeš, 2013).

Thus, it is possible to integrate the energy released in the photobioreactor exhaust gases contained in the fraction of VOCs and CO_2 unconverted in the biologically-assisted combustion processes. VOCs have energy content with potential for to be used as gaseous fuels in processes that require heating (Jacob-Lopes et al., 2017; Severo et al., 2018). Different aspects can be evidenced as direct advantages of mass and energy integration and they emerge as a real opportunity to leverage bioprocesses. But, regardless of the chosen strategy, aspects related to the microalgae cultivation in photobioreactors must still be well planned on a laboratory scale to eventually be transferred to the industrial sector.

6. ENVIRONMENTAL PERFORMANCE EVALUATION

Microalgae-based systems can significantly improve the sustainability and economy of a process when globally integrated. Thus, decision-making on how to distribute and prioritize production processes will undoubtedly be affected by the demands of materials and energy flows, which will have a direct impact on water and carbon footprint, as well as emissions (Ledda et al., 2016).

For this, the LCA is applied, an important emergent industrial ecology tool, which accompanies the production cycles and helps identify alternatives for interaction between processes. According to US Environmental Protection Agency, the LCA holistically evaluates a product or process throughout its life cycle and the amount of energy and raw materials used from the extraction, production, distribution, consumption, use, until its transformation into waste (Curran, 2006).

The detailed mapping of these flows consists mainly of mass and energy balances, where all input flows must correspond to a quantified output flow such as product, waste or emission. The balances enable evaluation of the overall performance indicators, whether in process optimization, such as commercial viability assessment (Nanou et al., 2016).

Mass and energy balances for the processes are calculated using basic conservation principles and the first law of thermodynamics for different scenarios. For mass, it is possible to analyze how much product and by-products are produced by the process for each unit of raw material. The input and output material reacts and transforms according to process specifications. On the other hand, the energy balance is performed to determine the general heat requirements (Ong et al., 2017). Energy is also reported in terms of Net Energy Ratio (NER), which is the ratio of energy output to energy input (Jorquera et al., 2010).

By way of example, Figure 4 describes the overall mass and energy balance of an integrated bio-combustion process, a conventional combustion process and a combustion process using a simulated industrial gas stream. The quantified base data were adapted from Severo et al., (2018).

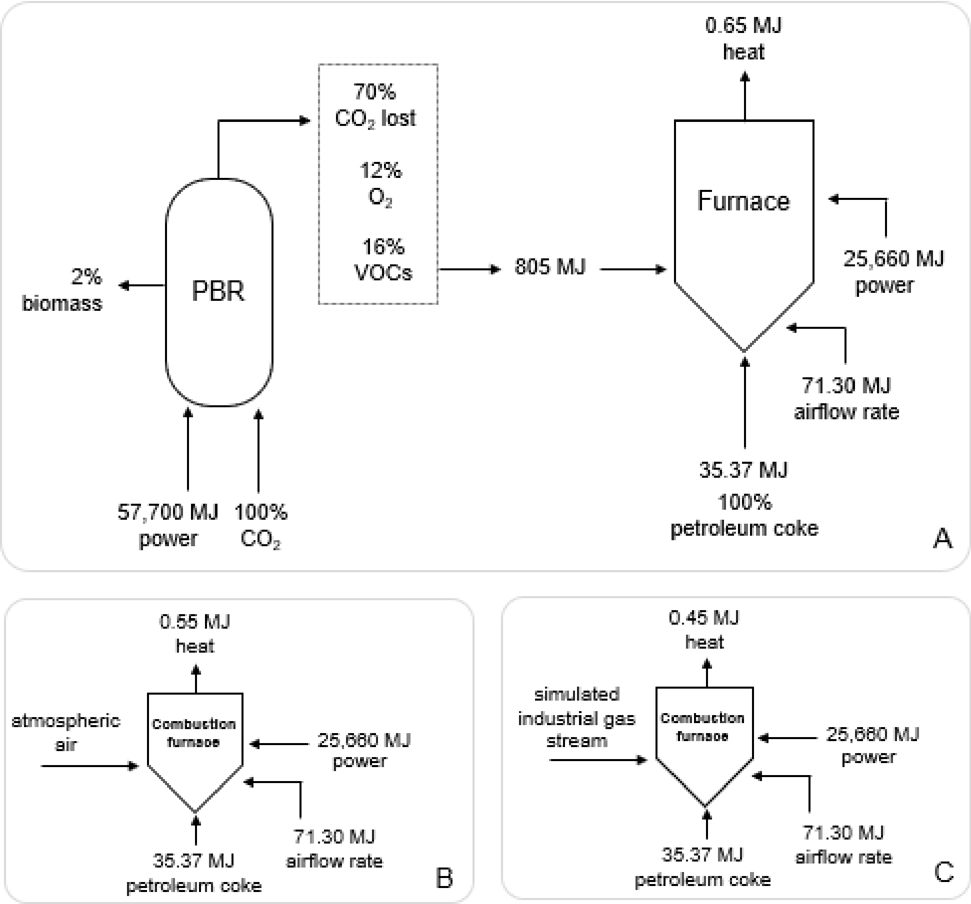

Figure 4. Global mass and energy balances of the combustion systems. (A) integrated biologically-assisted combustion system; (B) conventional combustion with atmospheric air; and (C) combustion with the simulated industrial gas stream. Adapted from Severo et al. (2018).

For the integrated bio-combustion process, the obtained NER value was 0.000077, being unfavorable from the environmental point of view. The ideal NER value should be positive (NER > 1) for microalgae-based processes, which would be able to supply the entire production chain, producing real gains and reducing GHG emissions considerably. Therefore, to improve the performance of the integrated bio-combustion process, it would be necessary to consider other steps along the chain. One of the possibilities, in an attempt to improve the process, would be through the use of biomass generated in the cultivation as an extra energy source. In this case, the NER value found was 0.71, proving to be a superior option to scenario A. When considering additional steps, the bioproducts obtained can provide market benefits and financial viability to industrial processes. Thus, the microalgae-to-energy technologies are beginning to be developed and have significant potential for additional innovations.

7. BIOECONOMY

The techno-economic evaluations are a set of methods for quantifying the profit or loss potential of a process, through the determination of the capital (CAPEX) and operating (OPEX) expenditures. They are considered to be very useful tools for strategic planning and can help evaluate cost viability of microalgae-based processes (Tredici et al., 2016). In this context, a cost analysis was estimated for the combustion process with oxygen-enrichment and for the biologically-assisted combustion process.

For the combustion process with oxygen-enrichment, petroleum coke was considered as fuel and the oxidizer come from an ASU with a capacity to produce 4,000 tons of O_2/day. Considering the combustion stoichiometry, to burn 1 ton of petroleum coke are needed on average 2.8 tons of O_2. According to the US Department of Energy, the costs of fuel and oxidizer are USD 240 and 75, respectively, per ton used (DOE, 2018). Therefore, the daily expenses with the O_2 production, which varies according to the purity level, are USD 300,000.00 in addition to the high installation cost of ASU, which is greater than USD 60 million. For this volume of oxidizer, about 1,428.57 tons of fuel is required, representing an expenditure of USD 342.720.00/day.

To circumvent these values, two factors must be taken into account simultaneously for improving efficiency and costs savings: combustion temperature and purity of enriched O_2. Table 2 can be used to estimate energy savings commonly used process combustion applications. Considering a combustion system operating at 2000 °C and 95% of the combustion air is oxygen, fuel requirements can be reduced by up to 38%, representing a fuel saving of approximately USD 130,285.00. Meantime, there is still no economic balance on the appropriate supply of O_2 and fuel in these oxygen-enrichment combustion systems.

Table 2. Estimative of energy savings (%) from different levels of oxygen-enrichment. Adapted from US Department of Energy and IHEA (2007)

Combustion temperature (°C)	**Oxygen-enrichments (%)**				
	25	30	35	45	100
500	2	3	4	6	8
1000	4	7	8	11	15
1500	7	11	15	18	26
2000	11	19	24	30	38
2500	18	30	35	42	53
3000	32	47	54	62	70

Alternatively, the combustion biologically-assisted process may in the future represent substantial gains for the bioeconomy. In theory, this integrated system can have a reduction in costs with oxidizer and fuel, because these substances are produced in a single step, without the need for extra energy-intensive equipment (Severo et al., 2018).

To produce 1 ton/day of biological O_2, it would be necessary to design a photobioreactor with a capacity of approximately 2,700 m^3. However, taking into account that an industrial combustion system with oxygen-enrichment requires 4,000 tons of O_2/day, this capacity would increase by up to 400 times more, making the process unfeasible.

Additionally, the VOCs generated can be used as gaseous fuels, since they have an estimated energy potential of 13,810 MJ for each ton produced. On the other hand, if consider the burning of 1 ton of petroleum coke, about 35,370 MJ is generated, that is, it contains 60% more energy. Yet, if VOCs are used as an additional energy source in combustion processes, the fossil fuel requirement and costs would be reduced.

Finally, CO_2 unconverted in the photobioreactor can be used as an air-nitrogen diluent in combustion systems, due to the higher energy emissivity and, consequently, greater heat transfer. CO_2 has an energy potential of 815.75 MJ/ton of fuel burned, which helps maximize energy-efficiency. If these three are used simultaneously as an oxidizer, biofuels, and nitrogen diluent, the overall combustion productivity could improve considerably.

CONCLUSION

The mass and energy integration into biologically-assisted combustion processes is a potential route to improve the sustainability of industrial facilities. The use of photobioreactor exhaust gases could play a fundamental role in the energy-efficiency of combustion systems, besides presenting feasibility for the bioeconomy and lower environmental impact. But, even if such benefits are evident, research has shown that to enable the scale-up of microalgae-based technologies, the inherent obstacles mainly to photobioreactors must be overcome since these equipments do not have sufficient maturity to meet the needs of an actual combustion process.

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7.3 CAPÍTULO DE LIVRO 3

Carbon dioxide capture and use by microalgae in photobioreactors

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CHAPTER

8

Carbon dioxide capture and use by microalgae in photobioreactors

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8.1 Introduction

Energy-related carbon dioxide (CO_2) emissions have become a major concern due to the adverse climatic effects of greenhouse gases (GHGs) [1]. In this context the continued reliance on fossil fuel combustion for many energy applications leads to the need for the development of different low-carbon technologies. As a precautionary measure, the International Energy Agency estimates that these low-carbon technologies could result in a 39% reduction in CO_2 emissions by 2035 [2].

Potentially scalable technologies for managing GHG emissions consist of carbon capture and storage (CCS) or utilization. These strategies can contribute about 19% of the reductions needed by 2050 [2]. However, due to technical–operational and cost limitations, they are considered unattractive [3]. On the other hand, biological processes can be applied and enhanced to carbon capture, with simultaneous production of value-added compounds. Thus microalgae-based processes become promising for carbon bioconversion and integration into other industrial systems [4].

From the engineering point of view, photobioreactors are considered the core of microalgae-based processes. In order to design suitable culture systems, it is essential to understand the main phenomena that limit the performance of microalgae cells, such as nutrient supply, pH, gas exchange (CO_2 addition, O_2 removal), requirements for temperature and lighting (photolimitation, photoinhibition, seasonal periods, and photoperiods) [5]. Different essential design concepts for photobioreactors have been proposed. Their complementary and coexisting functions are important for improving operational performance, rise in height/diameter and surface/volume ratio, providing highest workload, increasing CO_2 capture rates and minimizing energy and cost requirements [6].

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In order to take commercial consolidation, microalgae-based processes should also be subjected to tools to assess environmental and economic performance. For this the life cycle assessment (LCA) integrated with economic analysis can provide results that demonstrate the viability of the processes, both in terms of sustainability as a circular bioeconomy [7–9]. Given this scenario, the objective of this chapter is to provide an overview of aspects related to CO_2 capture and use by microalgae in photobioreactors.

8.2 Biological carbon capture and utilization

Thousands of tons of CO_2 are emitted annually into the atmosphere by various manufacturing sectors, whether through the industrial processes sector, electricity and heat generation, transportation, land-use change and forests, buildings or waste [1]. These sectors face an expensive problem: reduce emissions or pay penalties. But what if these companies could promote the reduce carbon footprint and benefit from CO_2 savings? These issues have been discussed by many researchers, scientists, and environmental experts worldwide.

Driven by environmental protection policies, carbon capture technologies are increasingly exploited, even presenting several obstacles for implementation. One of the potentially scalable technologies to mitigate CO_2 emissions is CCS, which has been developed aiming store CO_2 in geological formations [10]. However, CCS is extremely expensive and energy intensive, the infrastructure is complex and is not a fully safe method. It is merely a temporary solution, making unfeasible full development on the scale required [11].

Wherever possible, CO_2 should not be stored but used as a chemical building block to add value to the production of other products. Complementing the CCS, the carbon capture and utilization (CCU) technology basically meets these requirements. It includes the physical, chemical, and biochemical use of CO_2 previously captured, which can be applied in the manufacture of chemicals, fuels and power, carbonates, polymers, and in the food and pharmaceutical sector. But for the chemical industry, CCU can only contribute a small portion to the total mitigation of CO_2 emitted, because the conversion efficiency in products is low, and the production costs are high. In this case, only an overall assessment of the energy and CO_2 balance, and economic analysis, to establish a cost-benefit strategy, could contribute to a real utilization of CO_2 [3,12].

New opportunities in the CO_2 economy must be explored, which is the case of biological CCU (BCCU), an emerging technology with high potential for monetizing and mitigating CO_2 emissions [13]. Once captured from the anthropogenic or industrial sources, CO_2 and other compounds can be used directly or indirectly by photosynthetic microorganisms, such as bacteria, algae, and microalgae [9,14].

Microalgae, for example, are the most important microorganisms in aquatic ecosystems for the global carbon budget, playing crucial roles in CO_2 fixation. Through photosynthesis, several carbon assimilation pathways are involved in its biotransformation into a wide range of fine chemicals as bulk products [15]. Carbon concentration mechanisms (CCMs) in microalgae, in addition to actively working to transport and accumulate intracellular inorganic carbon, can be an efficient route for biofix CO_2 from stationary sources of emissions. While complex and sometimes inefficient in some species, CCM is beneficial for microalgal cells, since they increase their photosynthetic productivity [16].

8.3 Microalgae

Morphological, physiological, and structural characterization of microalgae make these organisms beings of extraordinary adaptive capacity, capable of surviving in an environmental diversity [17]. The biodiversity of microalgae is enormous and represents an almost unexplored resource. With over 40,000 species already identified and with many more yet to be identified, it is estimated that there are about 20,000–800,000 species [18].

The morphological conformation of the microalgae is denominated thallus and may present as unicellular, colonial, and multicellular stalks. Regarding the size of these microorganisms, depending on the species, they can vary from a few micrometers (μm) to a few hundred micrometers (0.5–200 μm) [19].

Under the structural aspect, microalgae include two types of cell structure: the eukaryotic, with representatives in the divisions *Chlorophyta*, *Euglenophyta*, *Rhodophyta*, *Haptophyta*, *Heterokontophyta*, *Cryptophyta*, and *Dinophyta* and the prokaryotic, which includes the two divisions: *Cyanophyta* and *Prochlorophyta* [20]. Independent of the characteristics among the individuals that integrate the different divisions, the microalgae present similar physiological behaviors, having as fundamental metabolic characteristic the photosynthesis [21].

Usually, the photosynthetic process in microalgae occurs in chloroplasts, while in cyanobacteria, photosynthesis occurs in plasmalemma. The chloroplasts are surrounded by a membrane, containing an aqueous fluid, a stroma, which contains the biochemical apparatus necessary for CO_2 fixation, through the photosynthesis carboxylation reactions, also known as the Calvin–Benson–Bassham cycle. The stroma contains stacks of flat disks bounded by a membrane denominated thylakoid, the photosynthetic pigments, which promote light reactions and the synthesis of chemical energy [22]. This process can be divided into two phases of reaction, which differ because the first one is dependent on luminosity, and in the later phase, the products of the reactions with light are subsequently consumed by the reduction of CO_2 to carbohydrates [23].

In the light dependent phase the light energy is absorbed as photons and converted to adenosine triphosphate (ATP). This phase occurs in the internal membranes of the chloroplasts, in the thylakoids and branches of the plasma membrane, where photosynthetic pigments (chlorophylls, carotenoids, and in some cases in phycobilins) are found and the enzymes necessary for the use of light and fixation of CO_2. The pigments are in highly organized structures, known as photosystem I (PSI), or reaction center (P700) and photosystem II (PSII), or reaction center (P680), which are interconnected through a series of electron carriers. This energy is used by PSII in the oxidation of water, releasing protons, electrons, and molecules of oxygen, known as Hill reaction. Electrons are transferred through the electron transport chain to PSI and lead to the reduction of ferredoxin to the formation of the nicotinamide adenine dinucleotide phosphate (NADPH) reducing intermediate. The formed photosynthetic products (NADPH and ATP) serve as substrates for the second phase [24].

TABLE 8.1 Carbon concentration mechanisms in microalgae.

Mechanism	Location within organism	Phylogenetic distribution
1. Passive CO_2 entry, energized conversion to HCO_3^-	Plasmalemma, thylakoid; $HCO_3^- \rightarrow CO_2$ and assimilation by RuBisCO in carboxysomes	Cyanobacteria
2. Energized entry of HCO_3^-	Plasmalemma, carboxysomes	Cyanobacteria
3. Energized entry of CO_2	RuBisCO in stroma/pyrenoid	Microalgae
4. Energized flux of H^+ to cell wall, conversion of HCO_3^- to CO_2	Plasmalemma, CO_2 flux to RuBisCO in stroma	Some microalgae
5. Energized flux of H^+ to thylakoid lumen, conversion of HCO_3^- to CO_2	Thylakoids, CO_2 flux to RuBisCO in pyrenoid	Freshwater green microalgae *Chlamydomonas*
6. C_4 metabolism in single-cell type	Inorganic C + C_3 acid → C_4 acid in cytosol, C_4 acid → C_3 acid + CO_2 in chloroplast stroma (or nearby), RuBisCO in stroma	Marine diatom, marine green acellular macroalgae

Adapted from J.A. Raven, C.S. Cockell, C.L. De La Rocha, The evolution of inorganic carbon concentrating mechanisms in photosynthesis, Philos. Trans. R. Soc. B: Biol. Sci. 363 (2008) 2641–2650. http://rstb.royalsocietypublishing.org/content/363/1504/2641.abstract [29].

Afterwards, in the light-independent phase, the microalgae convert CO_2 through three phases: carboxylation, reduction, and regeneration. In the carboxylation phase, CO_2 is incorporated into ribulose-1,5-bisphosphate (RuBP) catalyzed by ribulose-1,5-bisphosphate carboxylase/oxygenase (RuBisCO), resulting in two molecules of 3-phosphoglycerate (3-PGA). Then, 3-PGA undergoes phosphorylation and reduction, catalyzed by 3-PGA kinase and glyceraldehyde phosphate dehydrogenase, respectively, to produce glyceraldehyde 3-phosphate. Finally, the RuBP is regenerated through a series of reactions and enters the next fixation cycle. During the transfer process the transport resistance and diffusion of CO_2 are the main limiting factors that influence the fixation of CO_2 [25].

Faced with limiting factors in carbon sequestration, the way that different species of microalgae adapt to a wide range of carbon concentration is directly related to the CCM [26]. These mechanisms correspond to complex metabolic pathways, since different forms of inorganic carbon are involved in these biological processes (Table 8.1) [27]. The function of CCMs is to raise intracellular inorganic carbon levels, responsible for pumping CO_2 to the carboxylation sites [28].

8.4 Photobioreactors

The selection of the microalgae cultivation system is the key to the effective bioconversion of the CO_2 [30]. Generally, microalgae culture systems are classified as open or closed systems. Meantime, recently, hybrid systems have been investigated to achieve higher levels of carbon dioxide conversion [31].

Established since the 1950s, open systems have been widely used for the cultivation of microalgae. Currently, different projects and configurations are presented, being the shallow ponds, inclined (cascade) systems, circular central-pivot ponds, simply mixed ponds, and raceway ponds. However, raceway ponds are by far the most commonly used [32]. Structurally, these models are based on constructions with a blade wheel to allow the flow and circulation of microalgal cells, water, and nutrients due to the limited depth of sunlight penetration, as well as to move the algae close to the surface for absorption of CO_2 [33].

Open systems are widely used by most companies for industrial scale. These cultures are characterized by being more extensive as to the area requirements, however, they present low energy and operation costs. In contrast, their performance may be greatly affected by climatic conditions and contamination problems. In addition, the practicality of using microalgae ponds to sequester CO_2 is limited. Studies report that raceway ponds showed low values CO_2 removal rate of 0.20 g/L/day for *Botryococcus braunii Kutz* [34]. According to Basu et al. [35] for *Scenedesmus obliquus*, in raceway ponds presenting values in order to 0.18 g/L/day of CO_2 removal rate. In view of these values the limitations of these systems are evident. Thus significant losses by evaporation, CO_2 diffusion to the atmosphere, irradiance, temperature, and loss of productivity in the dark and winter months are barriers to be overcome [36].

Conversely, closed systems (e.g., photobioreactors) are cultivation systems that underwent structural improvements to compensate for the drawbacks of open systems. These configurations of photobioreactors were rethought to allow better control of the culture conditions, in order to maintain a greater variety of species, preserve the culture without contaminations, and allow adjustment of factors, such as pH, concentration and insertion of gases, temperature, and nutrients [37].

In addition, while photobioreactors enable a reduction of surface area when compared to open tanks, these equipment are being improved to maximize workloads, ensuring high biomass production and certifying reduction in production costs. In this context the control and modeling of these reactors along with BCCU technology also face many barriers in practical applications continue to be an important bottleneck for processes based on microalgae (Table 8.2).

Given this scenario, innumerable configurations of closed photobioreactors were designed for the growth of microalgae. These photobioreactors can be constructed in different materials and formats, the most used being tubular photobioreactors, flat plates, bubble columns, airlift, big-bags, biofilms, and hybrid photobioreactors.

8.4.1 Tubular photobioreactors

Tubular photobioreactors are described as a set of transparent tubes, glass, or plastic, arranged horizontally, inclined, or vertically. The tubes have a diameter of approximately 5–10 cm are arranged in a stack in the form of loops arranged toward the sunlight so that the penetration of light is sufficient in the culture medium in order to promote high biomass productivities [38]. Frequently, these tubes are coupled to a common degassing unit to remove accumulated O_2. Likewise, the carbon dioxide can be fed to the system in the same degassing unit, thus allowing the gas exchanges and maintaining the mixing process. In addition, microalgae cultured in tubular photobioreactors are recycled with a

TABLE 8.2 Barriers and opportunities associated to the biological carbon capture and utilization by microalgae in photobioreactors.

Type of approach	Barriers	Opportunities
Technical	Large-scale CO_2 fixation capacity is very low due to lack of an ideal photobioreactor design Engineering expertise demand	Can use flue gases directly Genetic engineering approaches have the potential to increase the efficiency of CO_2 fixation Can be integrated into new build or retrofit installations
Economic	High production costs associated with the cultivation system, corresponding increase in the cost of electricity Microalgae-based products are still expensive, making it impossible to actual entry in the market The cost of a CO_2 mitigation technology is higher than current carbon prices	Financial return with coproduction of food, fuel, fine chemicals, and others The cost benefits will be the driving force to balance the costs of traditional capture technologies in the future
Environmental	Significant losses of CO_2 (up to 30%) to the atmosphere through the photobioreactor exhaust gases Currently, there is no microalgae process that can capture CO_2 and treat wastewater simultaneously	Possibility of using marginal and nonarable land Integration of sea water and industrial wastes as a nutrient source, and flue gases as inorganic carbon source for growth Develop effective negative carbon technology
Policy	Lack of more stringent environmental regulations and incentives to reduce CO_2 emissions, coupled with the desire to improve industrial competitiveness	Implementation of an appropriate policy framework to enable effective certified trading of carbon credits in the market Initiatives to address regulatory issues of public perception, serving as a basis for increase the policy interest in BCCU technology

BCCU, Biological carbon capture utilization.

mechanical or air transport pump. However, disadvantages such as the high energy consumption of the mechanical agitation, when compared to other photobioreactor configurations, and the low surface/volume ratio limit its large-scale application. Yet, the increase in tube length increases the chances of CO_2 and pH gradient in liquid, the formation of air pockets during photosynthesis, preventing CO_2 sequestration [39]. In contrast, to date, tubular photobioreactors, along with runways, are the only configurations with the commercial representativeness.

8.4.2 Flat plate photobioreactors

Flat plate photobioreactors are represented by cubic-shaped glass reactors. These photobioreactors are usually arranged horizontally or vertically in the land [40]. The thickness of the flat plate is only a few millimeters to allow optimum penetration of radiation into the microalgae culture. It can be made from transparent materials such as glass, plastic, and polycarbonate. The mixing system is provided through air bubbling or mechanical rotation, thus requiring less power supply than tubular photobioreactors for mass transfer, mixing and heat transfer ability [41]. CO_2 supplied through the perforated tube at the base of plate provides only air movement parallel to the plates resulting in large dead pockets where microalgae might be present with limited CO_2 sequestration [42]. They have a high lighted surface area, which theoretically results in a high cell density. Furthermore, they tend to have a lower accumulation of dissolved oxygen and greater photosynthetic efficiency when compared to tubular photobioreactors [43]. Nevertheless, they are difficult to operationalization evenly because of their large surface area for volume ratio.

8.4.3 Bubble column and airlift photobioreactors

A bubble column reactor (BCR) is basically cylindrical vessels with a gas distributor at the bottom [44]. Dimensionally, they are up to 4 m high, with measurements of the radius of up to 0.2 m, usually presenting difficulties in scaling due to the relation height/diameter. In addition, they are relatively simple and inexpensive to produce. Nonetheless, the scaling processes are impaired, since the luminous intensity inside the columns may be insufficient as the scale increases [45]. Nevertheless, as advantages, these photobioreactors, on the laboratory scale, require low shear forces, without growth of microorganisms in the vessel wall. Yet, these models have high efficiency of use of CO_2 inserted for carbon sequestration processes by microalgae, obtaining high values of cell density [46].

In addition, as a variant of the BCR, airlift bioreactors (ALRs) are typically cylinder shaped, developing distinct vertical streams known as risers and downcomers. The ALR has better mixing, more suitable heat, and mass transfer than bubble column due to the existence of the draft tube, and some of its advantages include simple construction without moving parts such as agitator and low consumption of energy [47,48]. A disadvantage of airlift photobioreactors is that they are built with low-resistance materials, making them fragile when staggered [49]. Further, as a consequence of stagger, light path length may be a problem in airlift photobioreactors even as in BCR. Yet, capital costs and cleanliness can also be considered disadvantages of large-scale application. This way, the bubble bursting, gas retention, gas transfer, and temperature control at the top of airlift photobioreactors are also the areas of concern with these systems [50].

8.4.4 Big-bag photobioreactors

These photobioreactors consist of sterile big-bags of up to 0.5 m, with gas diffusion system and suspended in appropriate structures. Although big-bag photobioreactors have been favored by many researchers, since they are inexpensive and easy to construct, they have many disadvantages [50]. First, photolimitation usually occurs due to the distortion of the bags by gravity. Still, this photobioreactors may suffer from inadequate mixing, and cell growth is inhibited in some areas. The bags are inherently fragile, so the leak happens more than occasionally. This circumstance can be disastrous for mass culture. Consequently, the life of the bags is short (≤1 year), because of the cleaning and leaking problems, so they are not economical in the long run. In addition, as the volume of a photobioreactor is usually small for presenting a thin optical thickness for the sake of light transfer; hence, the temperature has a significant increase, this way an alternative able to control the temperature is the immersion of the bags in pools of water. Lastly, the disposal of large quantities of big-bags presents a potential problem [51].

8.4.5 Biofilms

The cultivation of biofilm photobioreactors has recently received great attention due to its low water requirement and cost of harvesting [52]. The system consists of (1) a biofilm growth surface, (2) a nutrient medium recirculation system, and (3) a lighting system. The heating plate usually has a layer of 8 mm thickness [53]. These cultures assume the characteristic profile of achieving rapid cell growth, in the fact that the microorganisms tend to grow adhered to the containers. Biofilm culture is a different method of suspension. The dense algae cells are immobilized and fixed in the artificial carrier material, and the liquid medium is supplied to the biofilm to keep the algae cells under moist conditions [54]. Many studies prove that the biofilm system is a promising method for its long-term stability, free of contamination, low total energy consumption, and even a high efficiency in the use of CO_2. Although serial models are used, workloads are extremely low [55].

8.4.6 Hybrid photobioreactors

Recently, hybrid photobioreactors have emerged as one of the most prominent alternatives for adequate microalgae growth. These photobioreactors are characterized by the incorporation of two structural elements characteristic of open and closed systems [56]. In addition, these configurations aim to compensate for the disadvantages caused by limiting the surface/volume ratio and the scale-up of conventional photobioreactors. These systems are based on a suitable height/diameter ratio, generating configurations of reactors with heavy workloads [6].

On the other hand, to date, no ideal photobioreactor exists for mass CO_2 conversion, due to the practical difficulties, that is, scale, cost of capital, operational cost, and lifetime. However, it becomes clear that in recent years, much research and development (R&D) efforts were made with the aim of overcoming these barriers. Therefore Table 8.3 shows the main characteristics of photobioreactors for carbon capture. Furthermore, Table 8.4 presents some parameters relevant as area and energy requirements, biomass productivities, and carbon removal rate to the use of a photobioreactor integrated system for carbon capture.

8.5 Microalgae-based products

Microalgae have been highlighted from the biotechnological point of view since these microorganisms present multiple metabolic diversities. In this sense, besides the application in environmental processes, microalgal biomass is considered a promising source for the generation of several bioproducts [19].

Currently, with the depletion of fossil fuel reserves and consequently increasing demand for renewable energies, microalgae have received great attention for application

TABLE 8.3 Characteristics of the main photobioreactors for carbon bioconversion.

System	Reactor	Characteristics	Configuration remarks based on CO_2 bioconversion
	Tubular	High volumetric biomass density O_2 accumulation Photoinhibition Large requirement of land	CO_2/O_2 concentration imbalance throughout the tubular length due to CO_2 utilization In case $O_2 + CO_2$ added with tube then it becomes configuration similar to bubble column
	Bubble column	Greatest gas exchange Best photosynthetic efficiency Best exposure to light and dark cycles Less land requirement but high cost Scalability problem	Bigger bubbles rise may cause shear effects Best CO_2 conversion rates can be expected from this configuration as compared to tubular and flat plate configuration
Closed	Airlift	No moving mechanical parts High mass transferability Satisfactory mixing with low energy and shear stress	Higher photosynthetic rates Removal of accumulated oxygen by aeration High solubility of CO_2 in the medium
	Flat plate	Low power consumption Shortest O_2 path Low photosynthetic efficiency Shear damage to cells from aeration	There might be dead pockets in the flat panels due to imperfect gas mixing
	Hybrid	Highest workload Higher productivity Lower energy consumption Low cost	Best CO_2 conversion rates There is no accumulation of O_2 Hydrodynamic parameters present similar values to the other configurations
Open	Raceway	Low biomass concentration High risk of contamination Difficulty in controlling process parameters High evaporation rate	High CO_2 losses Low-carbon bioconversion rates

Adapted from R. Verma, A. Srivastava, Carbon dioxide sequestration and its enhanced utilization by photoautotroph microalgae, Environ. Dev. 27 (2018) 95–106. doi:10.1016/j.envdev.2018.07.004.

TABLE 8.4 Relevant parameters of photobioreactor configurations applied to an integrated carbon conversion system.

System	Configuration	Area requirements (m^2/m^3)	Energy requirements (W/m^3)	Biomass productivities (g/L/day)	CO_2 removal rate (g/L/day)	References
	Tubular photobioreactor	14.28	2500	0.05–1.5	0.14–0.19	[57]
	Flat plate photobioreactor	14.42	53	0.27–2.9	1.02–1.57	[58]
Closed	Bubble column photobioreactor	350	280	0.03–0.77	0.14–4.58	[59]
	Biofilms photobioreactors	550	11.55	0.015–7.07	0.068	[60]
	Hybrid photobioreactor	0.22	52	0.57–0.66	3.9	[61]
Open	Raceway ponds	6.67	12.2	~0.5	0.48–1.8	[62]

in third-generation biofuels, including biodiesel, biogas, biohydrogen, and bioethanol [63]. Nonetheless, biodiesel is by far the most thoroughly investigated option, but further research and progress will be necessary before microalgal biofuels become a scalable reality [64].

Given this scenario, microalgae biofuels remain to date unviable, however, the biorefinery approach to exploitation of microalgae biomass, thus bringing microalgae closer to sustainability [65]. In this way, intracellular compounds and metabolites, with biological activities, have received a renewed interest due to their high market values [66]. Chemically, the classification of these compounds can be grouped into fatty acids, sterols, pigments, proteins/enzymes, vitamins, alkaloids, mycosporine-like amino acids (MAAs), and other compounds not included in these classes.

Several species of microalgae are able to synthesize lipids, which include ω-3 long-chain fatty acids such as linolenic, eicosapentaenoic, and docosahexaenoic and ω-6 acids such as linoleic, gamma-linolenic, and arachidonic acids [67].

In addition to cholesterol, some species of microalgae produce unconventional sterols such as brassicasterol, campesterol, stigmasterol, and sitosterol. Due to the high levels of sterols, these species have been used in formulating rations for the growth of juveniles, especially oysters [68,69].

Another aspect of relevance in the exploration of microalgal bioproducts is associated with the pigments. In addition to chlorophyll, microalgae contain auxiliary pigments such as carotenoids and, in some cases, phycobiliproteins. These extracts include β-carotene, astaxanthin, and phycocyanin, which when applied industrially are widely used as color enhancers in natural foods and pharmacological applications [70–72].

Microalgae are also classified a good source of minerals, such as magnesium, calcium, phosphorus, and potassium in higher concentrations, as well as trace minerals (manganese, zinc, aluminum, iron, and copper). These minerals making biomass a source susceptible to be used as a food supplement in aquaculture and also as fertilizer [73]. Still, these microorganisms also present in their composition valuable sources of essential vitamins, such as vitamins A, B1, B2, B6, B12, C, E, nicotinate, biotin, folic acid, and pantothenic acid [74].

Some proteins, peptides, and amino acids have biological functions associated with nutritional benefits and human health. Thus as most species of microalgae present levels above 50% protein in dry weight, these biopolymers can be used as nutraceuticals or included in functional food formulations. At the enzyme level, some metalloenzymes such as superoxide dismutase have been identified in microalgal cells, whose activity is associated with protection against oxidative damage in cells [75,76].

Furthermore, important sun blockers derived from microalgae have emerged as an alternative to synthetic molecules and/or molecules of botanical origin. Compounds with photoprotective action include two major classes: the MAAs and the scytonemin. These compounds exhibit high blocking efficiency, photostability, and low toxicity [77]. Although it does not fit in any of the previous chemical groups, compounds, such as ciguatoxin, karatungiol, okadaic, gambieric, and gamma-aminobutyric acids, have been identified in microalgal extracts, presenting antimicrobial action [78].

In addition to many beneficial properties, microalgae also produce numerous volatile organic compounds (VOCs), which can be used as an important source of alternative aromas for bulk and fine chemicals [79]. According to Santos et al. [80], the VOCs produced by microalgae can be divided into terpenoids, phenylpropanoids/benzenoids, carbohydrate derivatives, fatty derived from acids, and amino acid derivatives. In contrast, recent research has shown the production of VOCs for application as gaseous biofuels, which have an energy potential of 86.32 MJ/kg, with values higher than other traditional fuels such as gasoline (47.30 MJ/kg) and diesel (44.80 MJ/kg) [81]. These synthesized compounds could be potential competitors to traditional energy sources [82].

Although there is a wide availability of microalgae bioproducts to be explored, should be considered the choice of the ideal bioproduct for an integrated carbon capture system, which presents attractive commercial value to effectively contribute to the sustainability of industrial activities.

8.6 Process integration based on microalgae: a holistic approach

To the detriment of the problems reported, process integration could be a potential engineering approach that can systematically develop products and processes in a wide range of industrial manufacturing domains. An integrated process consists essentially of combining unit operations or separate processes to add value to CO_2 conversion, reduce costs, and improve environmental performance [83].

In addition, it can be broadly categorized into energy integration, in the form of heat or power, and mass integration, whether in the form of effluents or water. These flows, which would be disposed of due to lack of economic viability or without possibilities of additional use, are recovered and reused as input to a new process. Thus feedstock use, emissions, waste generation, and primary energy consumption could be reduced from the global process integration [84].

Unlike traditional integration approaches, the trend in recent years has been focused on R&D of integrated bioprocesses. Microalgae-based processes, for example, have played a valuable role in the field of industrial biotechnology [85]. In terms of carbon capture and use by microalgae, Fig. 8.1 shows an example of the integration of mass and energy in a photobioreactor.

In this process the CO_2 mass is integrated directly into a photobioreactor, which converts a part of this compound in bioproducts of photosynthetic metabolism, such as biomass, inorganic salts, exopolymers, and especially O_2 and VOCs. At the same time the integration of mass and energy occurs through the recovery of photobioreactor exhaust gases that, besides containing the O_2 and VOCs, also containing a part of unconverted CO_2 in the bioprocess, and which are reused simultaneously as oxidizer, gaseous fuels, and nitrogen diluent in a bio-combustion furnace, enhancing overall system thermal performance [13,81,86].

There is in the literature several forms of integrated microalgae processes with emphasis on CO_2 capture, as recently reported by Deprá et al. [87]. In this sense the different possibilities of integration and subsequent use of the final product are vital to demonstrate the benefits that microalgae can represent in the future in systems designed on large scales. These bioprocesses will act as a springboard for a new generation of sustainable and economically viable technologies.

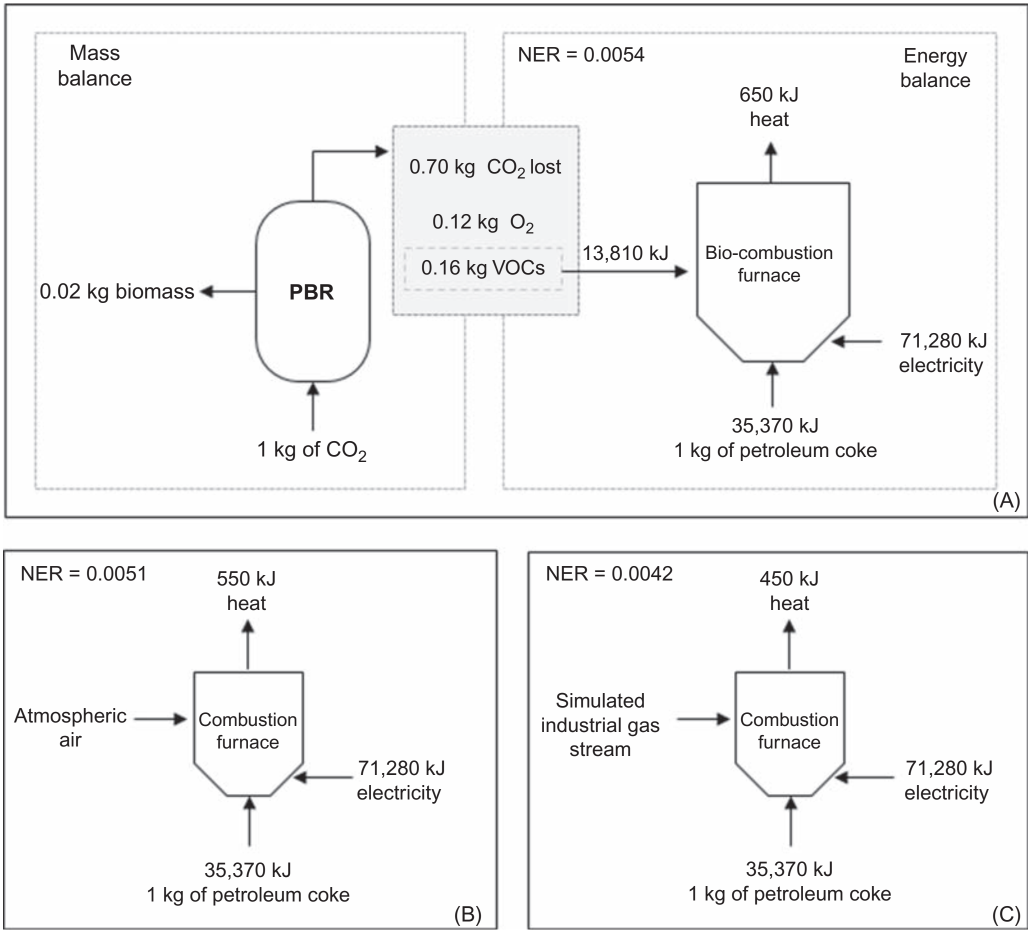

FIGURE 8.1 Process integrated of carbon capture and use in a photobioreactor. (A) integrated bio-combustion system; (B) conventional combustion withatmospheric air; and (C) combustion with the simulated industrial gas stream. Source*: Adapted from I.A. Severo, M.C. Deprá, J.S. Barin, R. Wagner, C.R. de Menezes, L.Q. Zepka, et al., Bio-combustion of petroleum coke: the process integration with photobioreactors, Chem. Eng. Sci. 177 (2018). doi:10.1016/j.ces.2017.12.001.*

But, there are some limitations that must be overcome for this to happen, such as (1) the domestication of a larger number of suitable strains and improvements through the application of molecular biology tools; (2) the same microalgae strains must tolerate extreme environments and have greater stability; (3) maximizing process performance in relation to CO_2 removal efficiency and elimination capacity; (4) the downstream processing step regarding the concentration of dilute microalgae suspensions; (5) the concept of biorefinery should be introduced to enable the commercial exploration of products and coproducts and ensure the economy; (6) improvements in photobioreactor design; and (7) the application of microalgae technologies for the CO_2 integration should take into account not only the economic aspects but also the possible environmental impacts [7].

8.7 Life cycle assessment for sustainable engineering

Recently, the LCA tool has been applied to support different decision-making procedures in product life cycle management, such as eco-design, process optimization, supply chain management, and strategic marketing decisions [88]. However, LCA is rarely applied in industrial production systems [89].

The CO_2 capture with photobioreactors can also be submitted to the LCA with the intention of evaluating the environmental performance or improving the bioprocess energy balance. Therefore considering an integrated carbon capture system, as exemplified in Fig. 8.1, Table 8.5 presents the input and output values required in the system based on [13].

Starting from a functional unit of 1 m^3 of cultivation with energy requirements computed in a total of 32.06 MJ, and bioproducts generated with the energy potential of 0.46 and 13.81 MJ for biomass and VOCs, respectively, the total energy return is 14.17 MJ [13]. According to Jorquera et al. [90], for a process to be sustainable, the values must be net energy ratio >1. In this case the integrated process showed values in order to 0.44 is energetically not adequate. Meantime, some alternatives for the increase of the energy ratio can be achieved, such as increase lipid content through metabolic engineering, the cell productivity and density, and, consequently, more final bioproduct for exploration as return energy.

As for the water footprint requirement, the system needs only workload for cultivation. Only 20% is incorporated in the microalgal biomass, and the values of evaporation are not significant in photobioreactors when compared with open systems [60], and it is still possible to have a net reuse of 0.8 m^3. However, if arising from wastewater from the industrial process, it can be said that the microalgae through the assimilation of nutrients treat this volume and also proportionately reduce the costs of the final disposal of this effluent [91].

In addition, as a parameter of major relevance, when referring to carbon capture, atmospheric emissions can be quantifiable in relation to the fossil energy required for the operation of the systems, together with CO_2 lost by the photobioreactor, resulting in values of the order of 17.75 $kgCO_{2eq}$.

Thus it is known that the emerging BCCU technologies are considered negative carbon systems, that is, carbon negativity is the reduction of the carbon footprint to less than the neutral, so that the system in question has a net effect of removing CO_2 from the atmosphere rather than adding it. However, even if incoming carbon is reused from an industrial source in the integrated carbon capture system, in general, photobioreactors have only 30% carbon conversion efficiency [92]. Thus even if this loss is not considered a new

TABLE 8.5 Inputs and outputs required from the use of a photobioreactor integrated system for carbon capture and use.

Requirements	Input	Output	Final balance
Net energy ratio (MJ)	32.06	14.17	0.44
Water footprint (m^3)	1.0	0.80	0.20
Carbon footprint ($kgCO_{2eq}$)	17.37	0.379	17.75

emission, there is no way to classify it as a negative carbon system. Therefore the system is characteristic of systems with neutral carbon footprint, since being carbon neutral means balancing the amount of CO_2 released into the atmosphere by a specific activity such as the use of fossil energy with an equal amount or compensations of carbon sequestration [93]. Yet, the use of microalgal biomass is considered a carbon-neutral process because the CO_2 released during the generation of energy is balanced by what is absorbed during its growth [94]. It is important to emphasize that the integrated process, besides bioconverting the main GHG, becomes a potential alternative of clean technology for the treatment of gaseous wastes. Nevertheless, environmental analysis will only be a determining factor in an industrial process, once it is submitted to economic analysis and these results indicate commercial viability.

8.8 Bioeconomy

The CO_2 capture and use can open up a new niche market and change our vision from a linear economy toward a circular bioeconomy. Integrated processes, in which carbon flows in a closed loop, could be a sustainable research direction, fueling the industrial sector and, above all, forming a solid economic platform [95]. But, at the same time that microalgae-based processes are gaining increasing prominence, it is crucial to optimize the upstream and downstream processing stages so that economic viability is achieved for future large-scale commercialization [96].

The most of economic analysis of microalgae systems using photobioreactors are based on unrealistic data, since the values are obtained in laboratory-scale or in small-scale plants, being extrapolated from parameters such as productivity and photosynthetic efficiency. These data generally do not match with what should occur in practice, being that the major hurdle is relatively high product cost. In addition, many studies do not target a specific bioproduct, which could be marketed to obtain investment returns [97].

There are other limitations that prevent a complete economic analysis of these bioprocesses: (1) type of photobioreactor, to estimate investment and maintenance costs; (2) choice of location and distribution, which will influence in the land, construction, labor costs, and system productivity; (3) water and nutrients source for supply; (4) plant size; and (5) ancillary processes. The neglect of this information can affect the product selling price, as well as in the projection of financial viability and profitability of the plant [98].

Economic analysis provides a vision of market viability and steps to minimize production costs or to neutralize them. It is one of the most basic tools applied to evaluate scale-up of microalgae-based processes and generally is associated with process modeling, assessing essentially the capital expenses (CAPEX), operational expenses (OPEX), and annual total costs of investment (TCI) [99].

Photobioreactors have a high energy demand, reflecting in CAPEX increase, which generally represents up to 50% of the TCI. However, in terms of productivity and capture efficiency, they have an enhanced capacity. By way of example, Wiesberg et al. [12] analyzed the economic performance of a process similar to BCCU and compared with a conventional CCS technology. The results indicated that the photobioreactor is economically infeasible in terms of CAPEX and OPEX. Although the photobioreactor and CCS capture efficiencies are 73% and 48%, respectively, and the cost per net metric ton of CO_2 captured is USD 139 and 304, respectively, the amount of CO_2 tax payment captured is USD 50/t CO_2, which makes both processes expensive. In addition, the area required for the photobioreactor would be 1000 ha, and CO_2 capture process would account for 70% of CAPEX.

While these trends highlight the importance of new bioprocesses in minimizing environmental impacts and have economic opportunities, the cost of capture is much higher than the fee to be paid from the environmental tax. It is noteworthy that, according to Word Bank Group [100], the carbon prices have varied substantially, from less than USD 1/t CO_2 to a maximum of USD 139/t CO_2, values considered to be very low. Therefore microalgal CO_2 capture systems can be promising to the same extent that can capture high CO_2 loads with lower OPEX. The bioeconomy for the operation of these systems may be feasible if captured CO_2 is seen as revenue, that is, as carbon credits.

While the research and economic tools of bioprocesses emerge to assist in project decision-making, there are still many issues to be evaluated. Among the main ones the cultivation systems should be improved and integrated, toward a complementary other process and not more autonomous. In sum, until it can balance the cost of products and processes in terms of carbon capture and use in photobioreactors, and that CO_2 mitigation is really offset by higher sales prices, today a biomass biorefinery approach for production of multiple value-added products as food, feed, and especially products, will be able to equilibrate the aspects related to the bioeconomy and viability of microalgae-based processes [7].

8.9 Final considerations and recommendations

Carbon dioxide capture and use in photobioreactors arises as a new effort in the attempt to reduce the concentration of atmospheric pollutants. In parallel, microalgae have several characteristics that make them promising to obtain many bioproducts of commercial interest. Therefore this win–win relationship, in which microalgae-based processes are designed on a single platform for multiple purposes, is considered enormously sustainable and economical. Nonetheless, there are many bottlenecks related to microalgae technology for it to become an industrial reality. Some recommendations for future research are listed as follows:

- Find microalgae strains tolerant at relatively high temperatures, elevated concentrations of CO_2, and compounds such as NO_x and SO_x from flue gases, including the possibility of genetic engineering manipulation;
- The photobioreactors engineering should be improved for environmental applications. The best photobioreactor design must be able to achieve a suitable surface/volume ratio, providing high workloads, higher CO_2 conversion rates, lower energy consumption, and low capital and operational costs;
- Develop a strategy for the intensification of microalgae-based processes and at the same time integrate energy, mass, water, and effluents to optimize the operation of facilities, minimizing unit operations and expenses with raw materials;
- Establish a more robust analysis to evaluate the real environmental viability of these bioprocesses;

- The technical-economic shortcomings are already known. Sensitivity analyzes to trace the roadmap of long-term research should be better explored to assess the bioeconomy of microalgae-based technologies. Thus it is possible to point the main hindrance in establishing the economic viability;
- Finally, once the barriers mentioned above are overcome, companies that adopt these alternative technologies will be able to receive carbon credits, enabling new business opportunities, and prepare for the transition to a low-carbon economy.

Acronyms

3-PGA	3-phosphoglycerate
ALR	airlift bioreactor
ATP	adenosine triphosphate
BCCU	biological carbon capture and utilization
BCR	bubble column reactor
CAPEX	capital expenses
CCM	carbon concentration mechanism
CCS	carbon capture and storage
CCU	carbon capture and utilization
GHG	greenhouse gas
LCA	life cycle assessment
MAA	mycosporine-like amino acid
NADPH	nicotinamide adenine dinucleotide phosphate
OPEX	operational expenses
PSI	photosystem I
PSII	photosystem II
R&D	research and development
RuBisCO	ribulose-1,5-bisphosphate carboxylase/oxygenase
RuBP	ribulose-1,5-bisphosphate
TCI	total costs of investment
VOC	volatile organic compound

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7.4 CAPÍTULO DE LIVRO 4

Biological Conversion of Carbon Dioxide into Volatile Organic Compounds

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Chapter 2
Biological Conversion of Carbon Dioxide into Volatile Organic Compounds

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Abstract Biological processes for the carbon dioxide conversion into high value-added biomolecules are of interest to the chemical, energy, food, and pharmaceutical industries. A closer look has been directed mainly at microalgae-based processes and products. Depending on the cultivation systems, species, and other engineering aspects, microalgae produce a variety of metabolites, including volatile organic compounds (VOCs). These molecules are originated from distinct chemical classes such as alcohol, aldehydes, hydrocarbons, ketones, terpenes, esters, and sulfurized compounds. However, it is crucial to know how these compounds are formed to target specific commercial applications. Besides, recent studies are demonstrating the use of volatiles as environmental indicators and also addressing the technical aspects that could be used to recover them. In this sense, the objective of this chapter is to provide a comprehensive view of the biological conversion of carbon dioxide into VOCs. Furthermore, the characteristics of microalgae and photosynthetic metabolism, the VOC biosynthesis mechanism, the culture systems, the environmental implications, and the insights on industrial applications were presented and discussed.

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2.1 Introduction

Carbon dioxide (CO_2) is a chemical molecule that constitutes the carbon cycle of the terrestrial atmosphere. As an outcome of the anthropogenic action, the natural emissions and CO_2 absorptions have been adversely affected. Without a doubt, we can point to the massive use of fossil fuels as the primary source of greenhouse gases (GHGs), of which CO_2 is the most significant contributor to global climate change (Chaudry 2019). According to the International Energy Agency, in 2016, CO_2 emissions were 32.31 Gt_{CO2}, in 2017 emissions increased by around 1.5%, and the forecast for the coming years is that the levels increase more and more (IEA 2017).

These data encourage scientists, researchers, government agencies, and public and private companies around the world to seek the development and improvement of technologies for carbon capture and storage or utilization. However, both techniques face technical and economic limitations, in addition to the low knowledge and public acceptance, which makes industrial rollout unsuccessful (Arning et al. 2019).

Among the various options, biological carbon capture has gained substantial attention because it offers a double solution: the conversion into multiple complex value-added molecules of commercial interest associated with improved environmental performance (Choi et al. 2019). Thus, autotrophic organisms and some microorganisms such as bacteria, cyanobacteria, and microalgae can reduce CO_2 to produce organic compounds from key enzymes, such as carbonic anhydrase and ribulose-1,5-bisphosphate carboxylase/oxygenase (RuBisCO) during the photosynthesis, and this is considered as the biological mechanism of nature quantitatively more efficient in the CO_2 bioconversion (Hicks et al. 2017).

Microalgae, for example, are recognized as the atmospheric carbon sink, and, for this reason, they have been the target of many works in the field of biotechnology. These microorganisms have relatively simple growth requirements (nutrients, CO_2, luminosity, pH, and temperature) and high photosynthetic rates, which induce a better CO_2 conversion. Regarding cultivation, microalgae can grow both in open or closed systems, and the latter (photobioreactors) is the most acceptable because of better control of the operating conditions (Vo et al. 2019).

At the same time, CO_2 is removed from the emissions when submitted to microalgae-based processes; this molecule can be simultaneously biotransformed into biomass, which can be applied for food production, animal feed, biofertilizer, biofuels, bioenergy, and other products of photosynthetic metabolism. These, in turn, are represented by the production of oxygen, exopolymers, carbonate, bicarbonate, and, especially, volatile organic compounds (VOCs) (Jacob-Lopes et al. 2010).

Volatile organic compounds are compounds of low molecular weight, high vapor pressure, and low boiling point, promoting the rapid passage from the liquid or solid phase to the gaseous phase and can be desorbed and dispersed at the water-air interface (Jerković et al. 2018). The metabolic profile of these compounds assumes an important category in the volatolomic branch, one of the new research fields in the “omic” sciences (Achyuthan et al. 2017).

Depending on the species, photosynthetic activity, and the growing circumstance, microalgae and cyanobacteria have been reported as a prosperous source for the production of VOC blends with up to 15 carbon atoms belonging to distinct chemical classes, such as alcohol, aldehydes, ketones, esters, terpenes, hydrocarbons, and sulfurized compounds (Santos et al. 2016b; Hosoglu 2018). However, there is a scarcity of consolidated information about how these compounds are formed, which could help identify them and target the most appropriate industrial application sector. According to Jacob-Lopes and Franco (2013), the elucidation of VOC formation occurs through the global CO_2 sequestration rates associated with the carbon mass balances, which shows the possible routes of carbon fractions incorporation. Still, according to these authors, about 90% of the carbon-based compounds generated in microalgal processes are represented by the release of VOCs, which could be profitable if they were collected adequately by efficient recovery systems.

Therefore, the objective of this chapter was to provide a comprehensive view of the biological conversion of CO_2 into VOCs. Here, we cover topics related to the characteristics of microalgae and photosynthetic metabolism, the VOC biosynthesis mechanism, the culture systems, the environmental implications, and, finally, the insights on industrial applications.

2.2 Microalgae and Photosynthetic Metabolism

Microalgae are a group of living microorganisms widely known on the terrestrial surface, whose screening comprises approximately 72,500 species. The classification of microalgae has undergone many changes over the years. Currently, the taxonomic division patterns rely upon their morphophysiological and structural characteristics, dividing these organisms into 16 classes (*Cyanophyceae*, Rhodophyceae, Chlorophyceae, Charophyceae, Euglenophyceae, Raphidophyceae, Xanthophyceae, Bacillariophyceae, Chrysophyceae, Haptophyceae, Phaeophyceae, Dinophyceae, Cryptophyceae, Synurophyceae, Eustigmatophyceae, and Glaucophyceae), but the most abundant in nature are the golden algae (Chrysophyceae), the green algae (Chrysophyceae), and the diatoms (Bacillariophyceae). Concerning biotechnological exploitation, the green algae, the cyanobacteria (*Cyanophyceae*), and the diatoms are the most relevant (Jacob-Lopes et al. 2019).

From a morphological point of view, microalgae are highly diversified in shape and size, displaying a wide range which ranges from 0.5 to 200 µm. Such a conformation is denominated thallus, independent of being unicellular or multicellular, and may present as unicellular, colonial, and multicellular stalks (Van den Hoek et al. 1995).

In contrast, the cellular structure of microalgae is divided into prokaryotic and eukaryotic. Prokaryotic organisms include bacteria and two microalgae divisions (*Cyanophyta* and *Prochlorophyta*). Already the eukaryotes include the divisions of most algae, being Chlorophyta, Euglenophyta, Rhodophyta, Haptophyta, Heterokontophyta, Cryptophyta, Dinophyta, Glaucophyta, and Chlorarachniophyta. Although each group presents peculiar characteristics, these microorganisms have similar physiological behaviors. Metabolically, photosynthesis is the preferred energetic route of microalgae (Suganya et al. 2016).

The photosynthesis in microalgae and cyanobacteria occurs into chloroplasts and thylakoids (located in the cytoplasm), respectively. This mechanism involves a complex metabolism and can be subdivided into two stages: (i) the photochemical (or light reactions) and (ii) carbon bioconversion (dark reactions). Usually, microalgae use light energy to generate reducing equivalents and incorporate CO_2 into organic molecules (Calvin and Benson 1948). The overall reaction of the photosynthesis is described by Eq. 2.1:

$$6CO_2 + 12H_2O \xrightarrow{\text{Light}} C_6H_{12}O_6 + 6O_2 + 6H_2O \tag{2.1}$$

About CO_2 bioconversion, microalgae can adapt to specific carbon concentrations. Therefore, there are inorganic carbon bioconversion mechanisms that involve many biochemical reactions in these biological processes that will give rise to VOCs.

2.3 Biosynthesis Mechanism of Volatile Organic Compounds

Through the photosynthesis and carboxylation reactions, also known as the Calvin–Benson–Bassham cycle, six different mechanisms for inorganic carbon bioconversion have been reported to date, as shown in Table 2.1.

The first bioconversion pathway of discovered carbon dioxide was the Calvin–Benson–Bassham cycle and after by the reductor tricarboxylic acid cycle, the Wood–Ljungdahl route, the 3-hydroxypropionate bicycle, the dicarboxylate-4-hydroxybutyrate cycle, and the 3-hydroxypropionate-4-hydroxybutyrate cycle (Calvin and Benson 1948; Evans et al. 1966; Schulman et al. 1972; Strauss and Fuchs 1993; Huber et al. 2008; Claassens et al. 2016).

In general terms, a carboxylating enzyme unites carbon dioxide or bicarbonate ions into an acceptor molecule, to be regenerated in the subsequent phases of the route. For the inorganic carbon bioconversion into cellular carbon to occur, energy

Table 2.1 Comparison of the reported natural inorganic carbon bioconversion pathways in microalgae

Pathways	Energy sources	Input	Output	References
Calvin–Benson–Bassham cycle	Light	3 CO_2, 9 ATP, 6 NADPH	Glyceraldehyde-3-phosphate	Calvin and Benson (1948)
Reductive tricarboxylic acid cycle	Light and sulfur	2 CO_2, 2 ATP, 4 NADPH	Acetyl-CoA	Evans et al. (1966)
Wood–Ljungdahl pathway	Hydrogen	2 CO_2, 1 ATP, 4 NADPH	Acetyl-CoA	Schulman et al. (1972)
3-Hydroxypropionate bicycle	Light	3 HCO_3^-, 5 ATP, 5 NADPH	Pyruvate	Strauss and Fuchs (1993)
Dicarboxylate-4-hydroxybutyrate cycle	Hydrogen and sulfur	1 CO_2, 3 HCO_3^-, 3 ATP, 4 NADPH	Acetyl-CoA	Berg et al. (2007)
3-Hydroxypropionate-4-hydroxybutyrate cycle	Hydrogen and sulfur	2 HCO_3^-, 4 ATP, 4 NADPH	Acetyl-CoA	Huber et al. (2008)

Adapted from Gong et al. (2018)

CO_2 carbon dioxide, *NADPH* nicotinamide adenine dinucleotide phosphate, *ATP* adenosine triphosphate

input is needed, which is provided by the adenosine triphosphate molecule hydrolysis (Berg 2011).

The Calvin–Benson–Bassham cycle, shown in Fig. 2.1, is the biologically ubiquitous pathway and, therefore, has received more scientific attention, where more than 90% of inorganic carbon of nature is bioconverted by this cycle (Ducat and Silver 2012; Gong et al. 2018). The metabolic Calvin cycle comprises 13 reactions catalyzed by 11 different enzymes and subdivided into 3 steps: (i) carboxylation, (ii) reduction, and finally (iii) regeneration (Paul 2013; Noreña-Caro and Benton 2018).

The carboxylation phase is catalyzed by ribulose-1,5-bisphosphate carboxylase/oxygenase, which is the most relevant enzyme in the Calvin–Benson–Bassham cycle, and probably the earth's most abundant protein, where three molecular structures of carbon dioxide are fused with three molecular structures of ribulose 1,5-bisphosphate to obtain six 3-phosphoglycerate (Blankenship 2008; Paul 2013).

During the reduction phase, nicotinamide adenine dinucleotide phosphate and adenosine triphosphate, generated during photosynthesis, are used to reduce 3-phosphoglycerate to 1,3-bisphosphoglycerate, being degraded to glyceraldehyde-3-phosphate and dihydroxyacetone phosphate (Noreña-Caro and Benton 2018).

Carbon atom gets out the Calvin cycle for the biosynthesis of multiproduct, such as glyceraldehyde-3-phosphate, to synthesize structures with six carbon atoms (hexose). A representative fraction of microalgae uses the Embden–Meyerhof–Parnas pathway to transform hexose molecule to pyruvate. However, five-sixths of the carbon is withheld in cycle itself to regenerate the acceptor molecule and thus keep it running (Paul 2013).

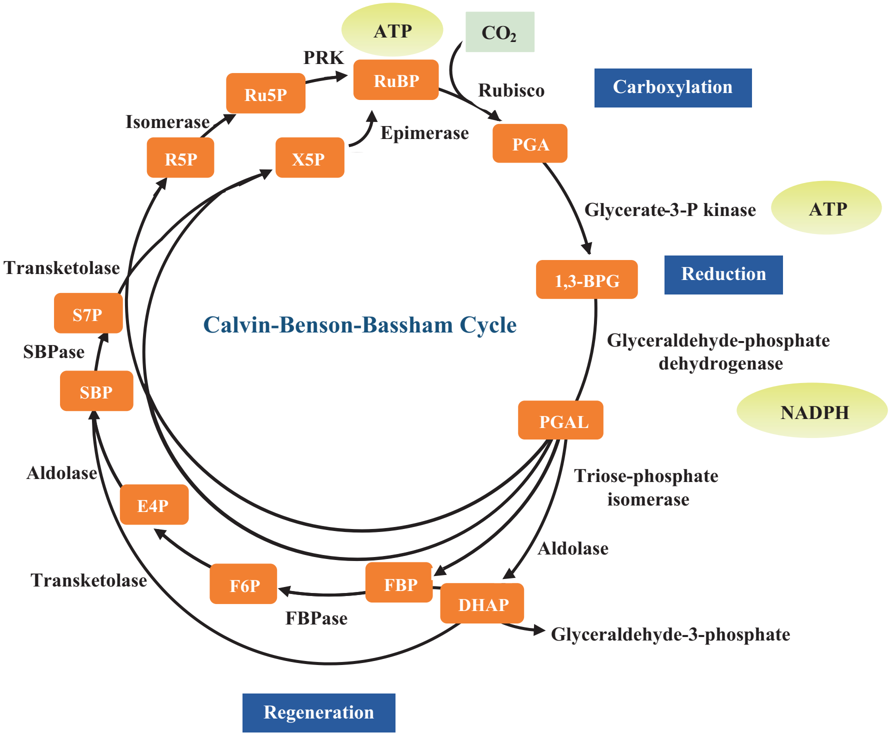

Fig. 2.1 Calvin cycle mechanism that incorporates carbon dioxide into glyceraldehyde-3-phosphate and regenerates ribulose-1,5-bisphosphate for continued inorganic carbon bioconversion. Compound abbreviations are specified as follows: CO_2, carbon dioxide; RuBisCO, ribulose-1,5-bisphosphate carboxylase/oxygenase; PGA, 3-phosphoglyceric acid; 1,3-BPG, 1,3-bisphosphoglyceric acid; PGAL, glyceraldehyde-3-phosphate; DHAP, dihydroxyacetone phosphate; FBP, fructose-1,6-bisphosphate; FBPase, fructose-1,6-bisphosphatase; F6P, fructose-6-phosphate; E4P, erythrose-4-phosphate; SBP, sedoheptulose-1,7-bisphosphate; SBPase, sedoheptulose-1,7-bisphosphatase; S7P, sedoheptulose-7-phosphate; X5P, xylulose-5-phosphate; R5P, ribose-5-phosphate; Ru5P, ribulose-5-phosphate; PRK, phosphoribulokinase; RuBP, ribulose-1,5-bisphosphate

In the regeneration phase of ribulose-1,5-bisphosphate occurs a series of biochemical mechanisms where glyceraldehyde-3-phosphate is converted into fructose-1,6-bisphosphate what is later transformed to fructose-6-phosphate and fused with glyceraldehyde-3-phosphate to produce erythrose-4-phosphate and xylulose-5-phosphate. Thereafter, the compounds erythrose-4-phosphate and dihydroxyacetone phosphate are combined to obtain sedoheptulose-1,7-bisphosphate, which is subsequently converted to sedoheptulose-7-phosphate. Ribulose-1,5-bisphosphate five carbon sugars are obtaining by combining sedoheptulose-7-phosphate with glyceraldehyde-3-phosphate. Finally, ribose-5-phosphate and xylulose-5-phosphate are isomerized to ribulose-5-phosphate, which is next phosphorylated to form ribulose-1,5-bisphosphate (Noreña-Caro and Benton 2018).

Inorganic carbon bioconversion metabolizes pyruvate or acetyl-CoA. Several pathways enzymatic or by a reaction degradation can convert these metabolites into volatile organic compounds, comprising the keto acid, fatty acid derivatives, and the isoprenoid pathway (Fig. 2.2). The distinct volatile organic compounds belong to various chemical classes such as terpenes, alcohol, ketones, aldehydes, esters, hydrocarbons, carboxylic acids, and sulfurized compounds (Liao et al. 2016; Santos et al. 2016a, b).

Two distinct routes can synthesize the isoprenoids: mevalonate pathway or methylerythritol phosphate pathway (Chappell 1995; Lichtenthaler et al. 1997), responsible for the synthesis of isopentenyl diphosphate and its molecular isomer

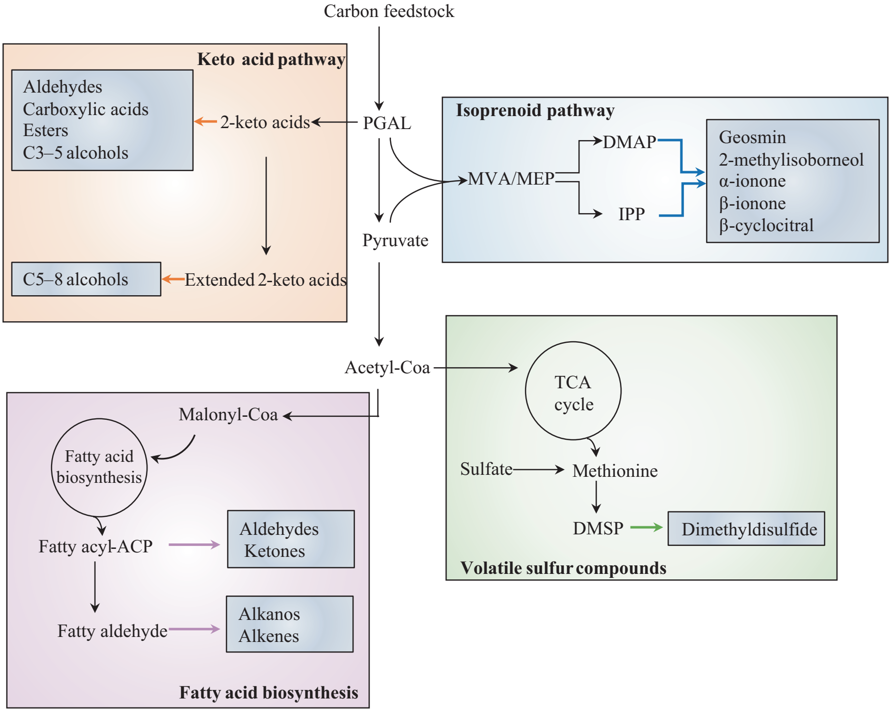

Fig. 2.2 General schematic of biosynthetic pathways leading to the microalgae volatile organic compound formation. The keto acid pathway (orange arrows) can be used to generate aldehydes, carboxylic acids, esters, and alcohols. It uses portions of amino acid synthesis routes for keto acid structure extension. Fatty acid synthesis mechanism (purple arrows) using malonyl-CoA as a substrate, where compounds such as aldehydes and ketones can be derived from fatty acids and alkanes and alkenes are possibly derived from unsaturated fatty aldehydes. The volatile sulfur compound (green arrows) the dimethylsulfoniopropionate (DMSP) is derived from amino acid methionine (arises from TCA cycle (tricarboxylic acid cycle)), initially, decarboxylation, reduce, and finally methylation mechanism to form dimethyl sulfide. Glyceraldehyde-3-phosphate (PGAL) and pyruvate synthesize isopentenyl diphosphate (IPP) and dimethylallyl diphosphate (DMAPP), the general precursors of isoprenoid synthesis (blue arrows), which are formed by methylerythritol phosphate (MEP) or mevalonate (MVA) routes

dimethylallyl diphosphate. They are consecutively condensed producing geranyl, farnesyl, and geranylgeranyl diphosphate; the series of reactions are catalyzed by enzymes geranyl diphosphate synthase, farnesyl diphosphate synthase, and geranylgeranyl diphosphate synthase, respectively (Liao et al. 2016).

These carbon precursors are rapidly transformed into different terpenoids, as carotenoids and their oxidative and enzymatic cleavage products, for example, volatile organic compounds as α-ionone, β-ionone, and β-cyclocitral (Durme et al. 2013; Santos et al. 2016a; Lee et al. 2017; Hosoglu 2018).

Through geranyl diphosphate, the sesquiterpenes can be formed as 2-methylisoborneol (Watson et al. 2016; Lee et al. 2017). In microalgae system, the cyclization of farnesyl diphosphate can produce geosmin, in three distinct phases: where farnesyl diphosphate form germacradienol which is converted the 8,10-dimethyl-1-octalin to form geosmin finally, this mechanism is catalyzed by geosmin synthase (Giglio et al. 2008).

In the keto acid pathway, any longer-structure keto acid can be decarboxylated and reduced to higher alcohols. This reaction comprises chain extension at the level of 2-keto acids, which in turn are utilized as building blocks in branched-chain amino acid synthesis. Keto acid structure extension is catalyzed through the acetohydroxyacid enzyme in the leucine synthesis pathway, or the valine, followed by reactions of isomerization, reduction, dehydration, and esterification. Besides, it can produce aldehydes, carboxylic acids, esters, and alcohols. For example, in the isobutanol, 2-methyl-1-butanol, 3-methyl-1-butanol, and 1-butanol, the reaction can be extended to form 1-hexanol and other alcohols (Hasegawa et al. 2012; Lan and Liao 2012; Liao et al. 2016).

The de novo fatty acid pathway starts with acetyl-CoA using malonyl-CoA as a building block based on cyclic series mechanisms catalyzed by the multienzyme system, denominated fatty acid synthase (Peralta-Yahya et al. 2012; Zhou et al. 2018). Aldehydes, hydrocarbons, and ketones can be fatty acid derivatives (Santos et al. 2016a).

Aldehyde compounds 2,4-decadienal and 2,4,7-decatrienal are degradation products of arachidonic or eicosapentaenoic acid, catalyzed by lipoxygenase/hydroperoxide lyase. The fatty acids, linoleic or linolenic acid, are the precursors of aldehydes such as nonanal, hexanal, and 2-pentanal (Adolph et al. 2003; Yu et al. 2014; Santos et al. 2016b; Jerković et al. 2018). The alkanes such as heptadecane and pentadecane, along with alkenes, presumably derived from unsaturated fatty aldehydes and aliphatic ketones can be lipid oxidation products (Schirmer et al. 2010; Santos et al. 2016a, b).

Sulfur compounds are another group of volatile organic compounds that are released by many microalgae, such as dimethyl sulfide, dimethyl disulfide, and dimethyl trisulfide, generated by a diversity of biota, biochemical pathways, enzymes, and precursors. Interestingly, in microalgae (in species that this pathway has been reported), dimethyl sulfide is dependent of dimethylsulfoniopropionate by senescing microalgae (Giordano et al. 2005; Achyuthan et al. 2017).

In the dimethylsulfoniopropionate biosynthesis, the methionine is the forerunner of the 2-keto acid, 4-methylthio-2-oxobutyrate, through a transamination (perhaps the amino group is forwarded to keto acid; see Giordano et al. 2005 and their references), followed by a reduction reaction, converting in 4-methylthio-2-hydroxybutyrate, using nicotinamide adenine dinucleotide phosphate molecule. This mechanism is catalyzed by 4-methylthio-2-oxobutyrate reductase, and the activity of this enzyme is usually high in dimethylsulfoniopropionate-producing species (Giordano and Prioretti 2016).

The next stage in the reaction is that the S-methylation of 4-methylthio-2-hydroxybutyrate to 4-dimethylsulfonio-2-hydroxybutyrate finally is converted to dimethylsulfoniopropionate through oxidative decarboxylation (Giordano et al. 2005; Giordano and Prioretti 2016). The demethiolation of dimethylsulfoniopropionate form to methanethiol which can be transformed into dimethyl sulfide by methylation (Achyuthan et al. 2017; Curson et al. 2017).

Given the above, the establishment of biochemical pathways can target the production of the specific biomolecules of microalgae metabolism. However, the biogeneration of these molecules is strongly influenced by the cultivation conditions as well as other key factors that can be improved.

2.4 Culture Systems for Volatile Organic Compound Production

The CO_2 conversion into VOCs could be excellent and efficient if certain conditions were considered, two of which are the injection of high CO_2 loads and the design of appropriate culture system. Among them, there are open and closed systems for microalgae cultivation, which are operated under different aspects (Jacob-Lopes and Franco 2010).

The state-of-the-art and argumentative opinions on the use of open systems for large-scale cultivation as well as engineering requirements began in the 1960s. Today, different models are being studied: shallow lagoons and ponds, circular ponds, mixed ponds, inclined systems, and raceway ponds, the latter being the most accepted for commercial application (Borowitzka 2013). Although they are easy to build and cheap, open systems rely on operational conditions that oscillate wildly. They can be rapidly contaminated by external agents and are vulnerable to inclement weather, which directly affects microalgal productivity, limiting the CO_2 conversion (Verma and Srivastava 2018). Another obvious disadvantage is the considerable increase in evaporation rates. Undoubtedly, these issues make it difficult to increase the production and collection of gaseous products such as VOCs.

Later, in the 1980s in the United States, work began on closed systems, which are now commonly called photobioreactors. Many versions have been patented in recent decades aiming to overcome the bottlenecks that closed systems show (Borowitzka 2013). Among the designs accepted, the most common are flat-plate panels, tubular photobioreactors, airlift, and bubble columns. Recently, innovative models have emerged such as biofilms, membrane, soft-frame, and hybrid photobioreactors (Vo et al. 2019).

Most start-ups in the microalgae sector choose to use photobioreactors, preferably because each of these configurations has efficient and robust parameters, providing artificial conditions that give the whole basis for better control and monitoring of the culture medium. In addition to these requirements, the reasons for selecting these vessel reactions are also due to the lower propensity to contamination, smaller hydrodynamic stress, higher surface/volume (S/V) and height/diameter (H/D) ratio, and CO_2 capture and productivities and, ultimately, closed systems can reduce losses by evaporation in the exhaust gases, which is very favorable for obtaining volatile substances (Chauton et al. 2015; Jacob-Lopes et al. 2016; Acién et al. 2017).

The main factors that should be considered to avoid poor cell growth performance in photobioreactors are light, temperature, pH, nutrient supply, and CO_2/O_2 balance and mixing (Chang et al. 2017). Associated with these issues, the ideal photobioreactor design for industrial application should take into account the species of microalgae used, process yield, production costs, and product obtained (Huang et al. 2017).

In terms of costs, however, photobioreactors are probably the most expensive equipment in microalgae cultivation. This is because its sophistication is related to high energy consumption and cost with construction materials. The cost of a photobioreactor can range from USD 55 to 150/m^2, which represents about 50% of the total cost of the plant. Some companies around the world provide values of commercial photobioreactors ranging from USD 80,000 to 668,000 and can reach extremely high costs of USD 20 million (AlgaeLink 2019). Although they face many fluctuations in the sale price, the values of the photobioreactors depend almost entirely on capital and operational expenditures, and this is because they are still far from becoming an industrial reality (Christiansen et al. 2012; Tredici et al. 2016). If all of these aspects were addressed, photobioreactors could be an essential milestone in VOC research. This is a challenging question that depends not only on the culture conditions but also on various environmental factors.

2.5 Environmental Implications

In addition to the GHG emissions such as CO_2, methane, fluorinated gases, and nitrous oxide, substantial quantities of VOCs are also released into the atmosphere from anthropogenic activities, including sources such as fossil fuel combustion, industrialization, agriculture, mining, transportation, construction, and wastewater treatment process, impacting negatively the environment (Franco et al. 2014; EPA 2016; Bonan and Doney 2018). In parallel with the issues mentioned above, they contribute to photochemical pollution and for being the precursors of tropospheric ozone (Fu et al. 2019).

It is also useful to highlight that VOCs have a wide range of adverse effects on human health due to their toxicity. According to the World Health Organization, problems are generally mutagenic and carcinogenic, causing respiratory damage;

Table 2.2 Odorants produced in microalgae cultures

Chemical name	Odor description	Threshold odor ($\mu g\ L^{-1}$)	Microalgae
Dimethyl sulfide	Cabbage/sulfurous	1	*Chlamydomonas globosa*; *Phormidium autumnale*; *Oscillatoria tenuis*
Dimethyl disulfide	Septic/garlic/putrid	4.0	*Microcystis wesenbergii*; *Microcystis aeruginosa*
Dimethyl trisulfide	Septic/garlic/putrid/swampy	0.01	*Microcystis aeruginosa*; *Microcystis wesenbergii*
β-Cyclocitral	Tobacco/smoky/moldy	19.3	*Scenedesmus subspicatus*; *Microcystis aeruginosa*; *Microcystis botrys*
2-Methylisoborneol	Earthy/musty/camphorous	0.015	*Oscillatoria limosa*; *Phormidium tenue*; *Oscillatoria tenuis*
Geosmin	Earthy/musty	0.004	*Anabaena circinalis*; *Phormidium amoenum*; *Pseudanabaena catenata*
2,4-Decadienal	Rancid/fishy	19.8	*Dinobryon divergens*; *Cryptomonas rostratiformis*; *Synura petersenii*

Adapted from Lee et al. (2017)

lung damage; eye, nose, and throat irritation; headaches; nausea; fatigue; and dizziness (WHO 2010; Capelli et al. 2011).

Concerning ecophysiological studies, microalgae have shown the natural production of several VOCs (Steinke et al. 2002; Durme et al. 2013). These compounds commonly occur as part of secondary metabolism, which plays important roles in chemical communications (Amavizca et al. 2017). Curiously, they also act as sex pheromones, in the chemical defense against herbivores, and suppressors of competitive neighbors (López-Pérez et al. 2017).

Microalgae in their natural habitat have been recognized as significant factories of VOCs, including sulfates, isoprenes, and monoterpenes (Achyuthan et al. 2017). These VOCs can be released by microalgae intracellularly and extracellularly with the potential to cause multiple problems in water quality, such as the generation of odoriferous compounds (López-Pérez et al. 2017; Lee et al. 2017). Table 2.2 shows different odorants and microalgae species.

The different types of odor compounds fluctuate in their intensity, chemical composition, and production patterns about different rates of growth of the microorganism. Geosine and 2-methylisobornel are responsible for the taste and odor of water in drinking water (Watson et al. 2008; Suurnäkki et al. 2015; Lee et al. 2017).

Other metabolites also associated with flavor problems are β-ionone and β-cyclocitral (Achyuthan et al. 2017). β-Cyclocitral forms the blue color that is caused by lysis of microalgae, creating mold/tobacco smell in surface water (Jüttner 1984; Lee et al. 2017). Derivatives of polyunsaturated fatty acids (PUFA) from microalgae release fish/rancid scents. Cucumber odor can be caused by the 2,6-nonadienal compound (Hosoglu 2018).

Sulfur is abundant in microalgae cells and is released as a mechanism of responses to the distinct environmental conditions in which these microorganisms are exposed, both biotic and abiotic (Giordano and Raven 2014; Lee et al. 2017). The release of sulfur compounds can contribute significantly to the biogeochemical sulfur cycle, contributing to environmental disturbances related to acid rain (Giordano and Raven 2014). Sulfur compounds are responsible for strong putrid odors and are produced during bacterial degradation of microalgae in natural water sources (Suurnäkki et al. 2015; Watson et al. 2016).

In fact, microalgae VOCs have some undesirable environmental implications. But these robust microorganisms have so many other favorable forward skills to sustainability that these issues become small. Microalgae-based process for CO_2 conversion into useful VOCs is one of the options. Associated with this, microalgae may be a promising alternative to alter the formation of odoriferous compounds.

Recent studies on laboratory scale have shown the application of microalgae for the production of a variety of volatile bioproducts for industrial purposes (Durme et al. 2013; Santos et al. 2016a, b; López-Pérez et al. 2017).

Santos et al. (2018) evaluated the biogeneration of aromatic VOCs from *Phormidium autumnale* cultivated mixotrophically in a photobioreactor. With the same strain, Santos et al. (2016b) did not detect the compounds that cause unpleasant odor such as 2-methylisoborneol and geosmin. In the study by Hosoglu (2018), were identified as characteristic aroma compounds of five species of microalgae that could minimize aesthetically unpleasant effects. In contrast, Severo et al. (2018b) developed an integrated process, where a photobioreactor captures CO_2 and biologically generates VOCs for use as gaseous biofuels in a combustion system.

Therefore, it is perceived that the VOC detection has a wide reach of implications in nature. At the same time, these molecules can open up a new perspective to be exploited facing the industry.

2.6 Insights on Industrial Applications

Microalgae-based products have been very successful in the academic and manufacturing sectors. These microorganisms can biosynthesize CO_2 very efficiently and biotransform it into VOCs. These, in turn, present potential industrial application in the chemical, petrochemical, food, and pharmaceutical sectors (Jacob-Lopes and Franco 2013; Claassens et al. 2016; Gong et al. 2018).

Numerous are the VOCs originated by microalgae, covering several classes of small molecular weight carbonic chain compounds (Achyuthan et al. 2017). About the commercialization of these molecules, the sale price can be 1000 times superior to the synthetic sources. Some investments in research and development are being made by companies that aim to manufacture volatile compounds of biological origin. This has excellent potential to expand revenue and market business in the coming years (Abdel-Raouf et al. 2012).

Microalgae fabricate a variety of volatile organic compounds that can be used as an important alternative resource of bulk and fine chemicals (Santos et al. 2016b). Due to their low odor thresholds, aldehydes are important VOCs generated by microalgae because they contribute desirable aromas. Saturated aldehydes have a green-like grass odor, while unsaturated aldehydes have a rancid odor (Hosoglu 2018; Santos et al. 2016a).

Concerning the petrochemical industry, hydrocarbons and short-chain alcohols are interesting to generate bioenergy (Severo et al. 2018a). Alternatively, renewable biofuels could be produced from these so-called “greener” routes. Some studies have shown that short-chain alcohols or higher alcohols could in the future be inserted to gasoline as oxygenated or, in other cases, substituted for it because it has high energy density and low solubility in water and butanol has comparable energy to gasoline (Peralta-Yahya et al. 2012).

Ketones, such as 1-penten-3-one, 2,3-butanedione, and 2,3-pentenedione, are used as flavors and floral fragrances. The esters are used in the flavor and fragrance industry; methyl octanoate, for example, is applied in the food and perfumery industries as a flavoring and scent additive, respectively (Durme et al. 2013; Hosoglu 2018).

Already terpenes are a class of compounds applied as aromas and pharmaceuticals; however, they also could be used as biofuels due to the branches and rings in their hydrocarbon chain (Peralta-Yahya et al. 2012). Table 2.3 shows the main VOCs from microalgae found in scientific studies with potential industrial application.

Despite the possibility of broad industrial application of VOCs, there is a bottleneck concerning the isolation and fractionation of specific molecules (Severo et al. 2018b): firstly, because it is generally not possible to obtain high yields in the photobioreactor and secondly, due to the biosynthesis of volatile substances by microalgae being very low. So, although not an easy task, it is imperative to select a suitable system for this purpose. Currently, some techniques can be exploited for the separation and recovery of VOCs in the photobioreactor exhaust gases, which may assist microalgae-based processes when it is desired to obtain a compound or a group thereof separately (Wylock et al. 2015). In this sense, Table 2.4 summarizes the main available technologies for the recovery of volatile organic compounds.

Continuous and nondestructive recovery can be through technologies based on condensation, adsorption, membranes, distillation, and supercritical fluid extraction (SFE). Many studies reported in the scientific literature aim to minimize losses and recover useful volatile compounds and, therefore, have a final product of high quality (Akacha and Gargouri 2015).

Among the various technologies, the most accepted is distillation for the recovery of volatiles, for its simplicity. When it is desired to obtain a final product with peculiar characteristics, it is recommended to use the adsorption technology, which has the potential to be used as a highly selective recovery method. Already membrane-based technology may be a promising alternative to be used in conjunction with other conventional processes. It offers ideal conditions for optimizing the recovery system and increases the selectivity of specific target compounds.

Table 2.3 Volatile organic compounds from microalgae with potential industrial application

Chemical name	Industrial application	Species to produce the odorants	Companies	References
α-Ionone	Analytical standard, flavor and fragrance agents	*Botryococcus braunii*, *Rhodomonas* sp., *Tetraselmis chuii*, *Nannochloropsis*	Penta international, Phoenix Aromas & Essential Oils, and sigma-Aldrich	Durme et al. (2013)
β-Cyclocitral	Analytical standard and fragrance agents	*Botryococcus braunii*, *Chlorella vulgaris*, *Nannochloropsis oculata*, *Nostoc* sp., *Phormidium autumnale*, *Rhodomonas* sp., *Spirulina platensis*, *Tetraselmis chuii*	Penta international and sigma-Aldrich	Durme et al. (2013), Milovanovic et al. (2015), Santos et al. (2016b), Lee et al. (2017)
β-Ionone	Analytical standard, flavor and fragrance agents	*Botryococcus braunii*, *Rhodomonas* sp., *Tetraselmis chuii*, *Nannochloropsis*, *Spirulina platensis*, *Nostoc* sp.	Advanced biotech, Phoenix Aromas & Essential Oils, and sigma-Aldrich	Durme et al. (2013), Milovanovic et al. (2015)
Benzaldehyde	Analytical standard, flavor and fragrance agents	*Chlorella vulgaris*, *Botryococcus braunii*, *Rhodomonas* sp., *Tetraselmis chuii*, *Nannochloropsis oculata*, *Nitzschia closterium*	Advanced biotech, Phoenix Aromas & Essential Oils, and sigma-Aldrich	Durme et al. (2013), Zhou et al. (2017)
Benzothiazole	Analytical standard, fragrance agents and cosmetic	*Phormidium autumnale*, *Nitzschia closterium*, *Chaetoceros calcitrans*, *Dicrateria inornata*, *Platymonas helgolandica*, *Nannochloropsis* sp., *Thalassiosira weissflogii*	Penta international, TCI America, and sigma-Aldrich	Santos et al. (2016b), Zhou et al. (2017)
Benzyl alcohol	Analytical standard, analytical reagent, flavor and fragrance agents	*Phormidium autumnale*, *Crypthecodinium cohnii*, *Schizochytrium limacinum*, *Chlorella protothecoides*, *Tetraselmis chuii*, *Nannochloropsis oculata*, *Chlorella vulgaris*, *Nitzschia closterium*	Advanced biotech, Phoenix Aromas & Essential Oils, and sigma-Aldrich	Santos et al. (2016b), Zhou et al. (2017), Hosoglu (2018)

(continued)

Table 2.3 (continued)

Chemical name	Industrial application	Species to produce the odorants	Companies	References
2,3-Butanedione	Analytical standard, flavoring agents and cosmetic	*Botryococcus braunii*, *Rhodomonas* sp., *Chlorella vulgaris*, *Tetraselmis chuii*, *Nannochloropsis oculata*, *Nitzschia closterium*	Axxence aromatic, Phoenix Aromas & Essential Oils, and sigma-Aldrich	Durme et al. (2013), Zhou et al. (2017)
cis-2-penten-1-ol	Fragrance agents	*Botryococcus braunii*, *Rhodomonas* sp., *Chlorella vulgaris*, *Tetraselmis chuii*, *Nannochloropsis oculata*, *Nitzschia closterium*	Parchem, Penta international, and sigma-Aldrich	Durme et al. (2013), Zhou et al. (2017)
2,4-Dimethylheptane	Fuel/energy and analytical standard	*Scenedesmus obliquus*	Santa Cruz biotechnology and TCI America	Severo et al. (2018b)
Dimethyl disulfide	Analytical standard, flavor and fragrance agents	*Rhodomonas* sp., *Tetraselmis chuii*	Axxence aromatic, Penta international, and sigma-Aldrich	Durme et al. (2013), Lee et al. (2017)
Dimethyl sulfide	Analytical standard, analytical reagent, flavor and fragrance agents	*Chaetoceros calcitrans*, *Chlorella protothecoides*, *Chlorella vulgaris*, *Crypthecodinium cohnii*, *Nannochloropsis* sp., *Phormidium autumnale*, *Oscillatoria chalybea*, *Oscillatoria tenuis*, *Platymonas helgolandica*, *Plectonema boryanum*, *Schizochytrium limacinum*, *Synechococcus cedrorum*, *Tetraselmis chuii*, *Thalassiosira weissflogii*	Advanced biotech, Axxence aromatic, and sigma-Aldrich	Watson (2003), Durme et al. (2013), Zhou et al. (2017), Hosoglu (2018), Lee et al. (2017)
Dimethyl trisulfide	Analytical standard, flavor and fragrance agents	*Rhodomonas* sp., *Tetraselmis chuii*	BOC sciences, Penta international, and sigma-Aldrich	Durme et al. (2013), Lee et al. (2017)
Dodecane	Analytical standard, fuel/energy	*Microcystis flos-aquae*, *Microcystis aeruginosa*	BOC sciences, EMD Millipore, and sigma-Aldrich	Xu et al. (2017), Zuo et al. (2018)

(continued)

Table 2.3 (continued)

Chemical name	Industrial application	Species to produce the odorants	Companies	References
Ethanol	Analytical standard, solvent and fuel/energy	*Botryococcus braunii*, *Rhodomonas* sp., *Tetraselmis chuii*, *Nannochloropsis oculata*, *Chlorella vulgaris*, *Nitzschia closterium*	Penta international	Durme et al. (2013), Zhou et al. (2017)
2-Ethyl-1-hexanol	Analytical standard, flavor and fragrance agents	*Tetraselmis chuii*, *Nannochloropsis oculata*, *Chlorella vulgaris*, *Nitzschia closterium*, *Spirulina platensis*, *Nostoc* sp.	Badische Anilin & Soda Fabrik (BASF), BOC sciences, and sigma-Aldrich	Milovanovic et al. (2015), Zhou et al. (2017)
2-Ethylfuran	Analytical standard, flavoring agents	*Botryococcus braunii*, *Rhodomonas* sp., *Tetraselmis chuii*, *Nannochloropsis oculata*, *Chlorella vulgaris*, *Nitzschia closterium*	Alfrebro, Penta international, and sigma-Aldrich	Durme et al. (2013), Zhou et al. (2017)
Geosmin	Fragrance agents and standard material for GC	*Anabaena lemmermannii*, *Anabaena circinalis*, *Anabaena crassa*, *Anabaena macrospora*, *Anabaena planctonica*, *Anabaena solitaria*, *Anabaena viguieri*, *Anabaena millerii*, *Aphanizomenon gracile*, *Geitlerinema splendidum*, *Leibleinia subtilis*, *Microcoleus* sp., *Phormidium allorgei*, *Phormidium amoenum*, *Phormidium breve*, *Phormidium cortianum*, *Phormidium formosum*, *Phormidium simplicissimum*, *Phormidium uncinatum*, *Phormidium viscosum*, *Phormidium* sp.	Pell Wall perfumes	Watson (2003), Liato and Aïder (2017), Lee et al. (2017)

(continued)

Table 2.3 (continued)

Chemical name	Industrial application	Species to produce the odorants	Companies	References
Heptadecane	Analytical standard, analytical reagent, fragrance agents and fuel/energy	*Spirulina platensis*, *Nostoc* sp., *Nitzschia closterium*, *Chaetoceros calcitrans*, *Thalassiosira weissflogii*, *Platymonas helgolandica*, *Nannochloropsis* sp., *Dicrateria inornata*, *Microcystis flos-aquae*, *Microcystis aeruginosa*	Penta international and sigma-Aldrich	Milovanovic et al. (2015), Zhou et al. (2017), Xu et al. (2017), Zuo et al. (2018)
Heptanal	Analytical standard, flavor and fragrance agents	*Botryococcus braunii*, *Rhodomonas* sp., *Thalassiosira weissflogii*, *Dicrateria inornata*	Alfrebro, Penta international, and sigma-Aldrich	Durme et al. (2013), Zhou et al. (2017)
Hexadecane	Analytical standard, solvent, fuel/energy, flavor and fragrance agents	*Spirulina platensis*, *Nostoc* sp., *Nitzschia closterium*, *Chaetoceros calcitrans*, *Thalassiosira weissflogii*, *Platymonas helgolandica*, *Nannochloropsis* sp., *Dicrateria inornata*, *Microcystis flos-aquae*, *Microcystis aeruginosa*	Penta international and sigma-Aldrich	Milovanovic et al. (2015), Zhou et al. (2017), Xu et al. (2017), Zuo et al. (2018)
Hexanal	Analytical standard, flavor and fragrance agents	*Botryococcus braunii*, *Rhodomonas* sp., *Tetraselmis chuii*, *Nannochloropsis oculata*, *Chlorella vulgaris*, *Phormidium autumnale*, *Schizochytrium limacinum*	Advanced biotech, Phoenix Aromas & Essential Oils, and sigma-Aldrich	Durme et al. (2013), Santos et al. (2016b), Hosoglu (2018)
1-Hexanol	Cosmetic, analytical reagent, flavor and fragrance agents	*Tetraselmis chuii*, *Nannochloropsis oculata*, *Chlorella vulgaris*, *Phormidium autumnale*	Advanced biotech, Axxence aromatic, and sigma-Aldrich	Durme et al. (2013), Santos et al. (2016b)
3-Hexen-1-ol	Flavor and fragrance agents	*Chlorella vulgaris*	BOC sciences and fine chemicals	Durme et al. (2013)

(continued)

Table 2.3 (continued)

Chemical name	Industrial application	Species to produce the odorants	Companies	References
3-Hydroxy-2-butanone	Analytical standard, flavor and fragrance agents	*Botryococcus braunii*, *Rhodomonas* sp., *Tetraselmis chuii*, *Nannochloropsis oculata*, *Chlorella vulgaris*, *Nitzschia closterium*	Advanced biotech, Penta international, and sigma-Aldrich	Durme et al. (2013), Zhou et al. (2017)
Isobutanol	Analytical standard, analytical reagent, energy and fragrance agents	*Phormidium autumnale*	Badische Anilin & Soda Fabrik (BASF), Phoenix Aromas & Essential Oils, and sigma-Aldrich	Santos et al. (2016b)
Methyl octanoate	Analytical standard, cosmetic, flavor and fragrance agents	*Botryococcus braunii*, *Rhodomonas* sp., *Tetraselmis* sp., *Nannochloropsis*, *Crypthecodinium cohnii*, *Chlorella protothecoides*, *Tetraselmis chuii*, *Schizochytrium limacinum*	Advanced biotech, Penta international, and sigma-Aldrich	Durme et al. (2013), Hosoglu (2018)
Methyl phenylacetate	Analytical standard, flavor and fragrance agents	*Botryococcus braunii*, *Rhodomonas* sp., *Tetraselmis chuii*, *Nannochloropsis*, *Crypthecodinium cohnii*, *Chlorella protothecoides*, *Schizochytrium limacinum*	Advanced biotech, Santa Cruz biotechnology, and sigma-Aldrich	Durme et al. (2013), Hosoglu (2018)
2-Methoxy-2-methylpropane	Analytical standard, fuel/energy and solvent	*Scenedesmus obliquus*	Sigma-Aldrich	Severo et al. (2018b)
2-Methylbutanol	Analytical standard, analytical reagent, fragrance agents; fuel/energy	*Tetraselmis* sp.; *Nannochloropsis*, *Chlorella vulgaris*	Advanced biotech, Alfrebro, Penta international, and sigma-Aldrich	Durme et al. (2013)

(continued)

Table 2.3 (continued)

Chemical name	Industrial application	Species to produce the odorants	Companies	References
2-Methylisoborneol	Analytical standard	*Oscillatoria curviceps*, *Oscillatoria limosa*, *Oscillatoria tenuis*, *Oscillatoria variabilis*, *Phormidium autumnale*, *Phormidium breve*, *Phormidium calcícola*, *Phormidium favosum*, *Phormidium tenue*, *Phormidium* sp.	Santa Cruz biotechnology and sigma-Aldrich	Watson et al. (2016), Lee et al. (2017)
2-Methylpropanal	Analytical standard, analytical reagent, cosmetic, flavor and fragrance agents	*Phormidium autumnale*, *Nannochloropsis oculata*, *Chaetoceros calcitrans*, *Thalassiosira weissflogii*, *Platymonas helgolandica*, *Nitzschia closterium*	Advanced biotech, Augustus oils, and Badische Anilin & Soda Fabrik (BASF)	Santos et al. (2016a, b), Zhou et al. (2017)
3-Methylbutanal	Analytical standard, flavor and fragrance agents	*Rhodomonas* sp., *Tetraselmis chuii*, *Nannochloropsis oculata*, *Chlorella vulgaris*, *Phormidium autumnale*	Advanced biotech, Badische Anilin & Soda Fabrik (BASF), Augustus oils, and sigma-Aldrich	Durme et al. (2013), Santos et al. (2016a, b)
3-Methylbutanol	Analytical standard, analytical reagent, solvent, flavor and fragrance agents	*Tetraselmis chuii*, *Nannochloropsis oculata*, *Chlorella vulgaris*, *Phormidium autumnale*	Advanced biotech, Badische Anilin & Soda Fabrik (BASF), and sigma-Aldrich	Hasegawa et al. (2012), Durme et al. (2013), Santos et al. (2016b)
6-Methyl-5-hepten-2-one	Analytical standard, flavor and fragrance agents	*Botryococcus braunii*, *Rhodomonas* sp., *Tetraselmis chuii*, *Nannochloropsis*, *Phormidium autumnale*	Advanced biotech, Augustus oils, and sigma-Aldrich	Durme et al. (2013), Santos et al. (2016b)

(continued)

Table 2.3 (continued)

Chemical name	Industrial application	Species to produce the odorants	Companies	References
Nonanal	Analytical standard, flavor and fragrance agents	*Botryococcus braunii*, *Rhodomonas* sp., *Nannochloropsis oculata*, *Chlorella vulgaris*, *Thalassiosira weissflogii*, *Nitzschia closterium*, *Chaetoceros calcitrans*, *Platymonas helgolandica*, *Crypthecodinium cohnii*, *Schizochytrium limacinum*, *Chlorella protothecoides*	Advanced biotech, Penta international, and sigma-Aldrich	Durme et al. (2013), Zhou et al. (2017), Xu et al. (2017), Hosoglu (2018)
2,6-Nonadienal	Flavor and fragrance agents	*Nitzschia closterium*, *Chaetoceros calcitrans*, *Thalassiosira weissflogii*, *Platymonas helgolandica*, *Nannochloropsis* sp., *Dicrateria inornata*, *Chlorella vulgaris*	Alfrebro, Augustus oils, and sigma-Aldrich	Zhou et al. (2017), Hosoglu (2018).
2-Octanedione	Flavoring agents	*Botryococcus braunii*, *Rhodomonas* sp., *Tetraselmis chuii*, *Nannochloropsis oculata*, *Chlorella vulgaris*, *Nitzschia closterium*	Penta international and Parchem	Durme et al. (2013), Zhou et al. (2017)
2-Octenal	Analytical standard, fragrance agents	*Botryococcus braunii*, *Nannochloropsis oculata*, *Thalassiosira weissflogii*, *Nitzschia closterium*, *Chaetoceros calcitrans*, *Dicrateria inornata*	Advanced biotech, Penta international, and sigma-Aldrich	Durme et al. (2013), Zhou et al. (2017)
1-Octen-3-ol	Analytical standard, flavor and fragrance agents	*Rhodomonas* sp., *Nannochloropsis oculata*, *Chlorella vulgaris*, *Crypthecodinium cohnii*, *Chlorella protothecoides*, *Tetraselmis chuii*, *Schizochytrium limacinum*	Advanced biotech, Phoenix Aromas & Essential Oils, and sigma-Aldrich	Durme et al. (2013), Hosoglu (2018)
3,5-Octadien-2-one	Flavoring agents	*Botryococcus braunii*, *Rhodomonas* sp., *Tetraselmis chuii*, *Nannochloropsis oculata*, *Chlorella vulgaris*, *Nitzschia closterium*, *Chaetoceros calcitrans*, *Dicrateria inornata*, *Platymonas helgolandica*	Penta international and BOC sciences	Durme et al. (2013), Zhou et al. (2017)

(continued)

Table 2.3 (continued)

Chemical name	Industrial application	Species to produce the odorants	Companies	References
Pentadecane	Analytical standard, flavor and fragrance agents	*Spirulina platensis*, *Nostoc* sp., *Nitzschia closterium*, *Chaetoceros calcitrans*, *Thalassiosira weissflogii*, *Platymonas helgolandica*, *Nannochloropsis* sp., *Dicrateria inornata*	BOC sciences, Santa Cruz biotechnology, and sigma-Aldrich	Milovanovic et al. (2015), Zhou et al. (2017)
1-Pentanol	Analytical reagent, flavor and fragrance agents	*Botryococcus braunii*, *Rhodomonas* sp., *Tetraselmis chuii*, *Nannochloropsis oculata*, *Chlorella vulgaris*, *Nitzschia closterium*	Augustus oils, BASF, and sigma-Aldrich	Durme et al. (2013), Zhou et al. (2017)
1-Penten-3-ol	Analytical standard, flavor and fragrance agents	*Botryococcus braunii*, *Rhodomonas* sp., *Tetraselmis chuii*, *Nannochloropsis oculata*, *Chlorella vulgaris*, *Nitzschia closterium*	Advanced biotech and sigma-Aldrich	Durme et al. (2013), Zhou et al. (2017)
1-Penten-3-one	Analytical standard, flavor and fragrance agents	*Botryococcus braunii*, *Rhodomonas* sp., *Tetraselmis chuii*, *Nannochloropsis oculata*, *Chlorella vulgaris*, *Nitzschia closterium*, *Chaetoceros calcitrans*, *Dicrateria inornata*, *Platymonas helgolandica*	M&U International and sigma-Aldrich	Durme et al. (2013), Zhou et al. (2017)
2-Pentenal	Analytical standard, flavor and fragrance agents	*Botryococcus braunii*, *Rhodomonas* sp., *Tetraselmis chuii*, *Nannochloropsis oculata*, *Chlorella vulgaris*, *Nitzschia closterium*	Penta international, Santa Cruz biotechnology, and sigma-Aldrich	Durme et al. (2013), Zhou et al. (2017)
2-Penthylfuran	Analytical standard, flavor and fragrance agents	*Botryococcus braunii*, *Rhodomonas* sp., *Tetraselmis chuii*, *Nannochloropsis oculata*, *Chlorella vulgaris*, *Nitzschia closterium*	Advanced biotech, Penta international, and sigma-Aldrich	Durme et al. (2013), Zhou et al. (2017)
2-Phenylethyl alcohol	Analytical standard, flavor and fragrance agents	*Crypthecodinium cohnii*	Advanced biotech, Phoenix Aromas & Essential Oils, and sigma-Aldrich	Hosoglu (2018)

(continued)

Table 2.3 (continued)

Chemical name	Industrial application	Species to produce the odorants	Companies	References
2-propanone	Energy and analytical reagent	*Scenedesmus obliquus*	Sigma-Aldrich	Severo et al. (2018b)
2,3-Pentenedione	Analytical standard, flavor and fragrance agents	*Botryococcus braunii*, *Rhodomonas* sp., *Tetraselmis chuii*, *Nannochloropsis oculata*, *Chlorella vulgaris*, *Nitzschia closterium*	Advanced biotech, Phoenix Aromas & Essential Oils, and sigma-Aldrich	Durme et al. (2013), Zhou et al. (2017)
Tetradecane	Analytical standard and fuel/energy	*Spirulina platensis*, *Nostoc* sp., *Nitzschia closterium*, *Chaetoceros calcitrans*, *Thalassiosira weissflogii*, *Platymonas helgolandica*, *Nannochloropsis* sp., *Dicrateria inornata*, *Microcystis flos-aquae*, *Microcystis aeruginosa*	Sigma-Aldrich	Milovanovic et al. (2015), Zhou et al. (2017), Xu et al. (2017), Zuo et al. (2018)
Tridecane	Analytical standard and fuel/energy	*Microcystis flos-aquae*, *Microcystis aeruginosa*	Sigma-Aldrich	Xu et al. (2017), Zuo et al. (2018)

Condensation could be used singly or integrated, since it has several geometries such as enhanced tubes and compact heat exchangers, to achieve a high recovery efficiency. On the other hand, although it can be applied in batch, the SFE may have higher costs, depending on the operation scale (Saffarionpour and Ottens 2018; Try et al. 2018).

The improvement and development of these types of techniques are crucial factors when it comes to industrial application. Some global benefits can be obtained: (i) better recovery capacity; (ii) economic viability; and (iii) production of highly fractioned and concentrated volatile compounds (Podstawczyk et al. 2017). Thus, with the adaptation of the photobioreactor to the recovery techniques and methods associated with additional biotechnological research, microalgae-based processes appear to be a mighty tool for the VOC production on an industrial scale in the future.

Table 2.4 Technologies available for the recovery of volatile organic compounds

Recovery technology	Technique	Principle	Auxiliary equipment/ substance	Comments
Condensation	Solid/liquid equilibrium	A condenser system (also described in some research as cryogenic), operating at a temperature below the boiling point of the target volatile substance, is inserted into the bioreactor outlet to retain the cooled exhaust gases	Filter; condenser; trap column; security column; liquid nitrogen	Offers great flexibility to change columns and present several geometries
Adsorption		The process is based on the physical adsorption capacity of a solid (adsorbent or adsorbent pores), which are led to a fast and reversible equilibrium, to link a component of a gas (adsorbate) in its area, where there is a greater force of attraction	Filter; dehumidifier column; adsorbent column	Presents greater selectivity, is more accepted for the recovery of volatile, and can be integrated with other processes
Membranes	Vapor/liquid equilibrium	The technique can be done by the pervaporation, which is the parting of liquid mixtures by vaporization using a membrane (which can be polymeric or ceramic) with a gaseous flux. Similarly, the technique can be applied for the pertraction; however, the difference is the use of liquid phase in the downstream step	Vacuum pump; membrane module; feed and retention system	Can be used for conventional separation processes such as liquid solvent extraction, vacuum distillation, and distillation; present greater selectivity; the membrane material should be appropriate to recover the compound of interest
Distillation		The principle of distillation is to remove the aqueous stream which feeds the system containing the volatile compounds and concentrate them by fractional distillation. Generally, the stripping is combined with the rectifying and enrichment of the VOCs	Centrifugal distillation; spinning cone column	Very recently used for the separation of hydrocarbons, terpenes, alcohols, ketones, and aldehydes; is cost-competitive technology; high permeability flow can be achieved

(continued)

Table 2.4 (continued)

Recovery technology	Technique	Principle	Auxiliary equipment/ substance	Comments
Supercritical fluid extraction	Liquid and/or solid and supercritical fluid equilibrium	The operation is based on the use of substances, under optimized conditions of pressure and temperature, above the critical point (thermodynamic principle) as solvents; they will separate one component from another to extract volatile compounds. The most widely used supercritical fluid is carbon dioxide	Storage tank; compressor; heater; cosolvents	Higher selectivity and velocity; although initial high capital expenditures, operational expenses would be small, as it is performed as a continuous mode

Adapted from Akacha and Gargouri (2015), Saffarionpour and Ottens (2018), Try et al. (2018)

2.7 Conclusion

Microalgae have received noticeable attention in the last years as potential cellular factories for the production of several products. Microalgae-based processes when subjected to CO_2 bioconversion into VOCs enable exploitation for many relevant commercial applications. Associated with this, it is crucial to know first and foremost the structural characterization and morphology of microalgae, metabolic pathways, VOC biosynthesis, and optimization of culture systems. However, some hurdles must be overcome for these bioprocesses to be successful in the market, such as improving genetic engineering strategies to boost VOCs production, the choice of appropriate microalgae strains and the culture systems should be refined for best cost-benefit results on industrial scales. Besides, volatile molecule recovery technologies must be designed to follow the photobioreactor scale-up, ensuring an efficient gathering. Many advances regarding experimental and analytical techniques have been obtained on a laboratory scale to understand the volatile profile of microalgae. So, if these aspects are addressed in the following years, microalgal processes could be a springboard for the alternative production of many products of low environmental impact on different markets.

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7.5 CAPÍTULO DE LIVRO 5

Process integration applied to microalgae-based systems

Livro: ***Handbook of Microalgae-Based Processes and Products - Fundamentals and Advances in Energy, Food, Feed, Fertilizer, and Bioactive Compounds* (Academic Press, Elsevier, Cambridge)**

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CHAPTER 26

Process integration applied to microalgae-based systems

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Chapter outline

26.1 Introduction

The world energy crisis boosted advances in the industrial sector, resulting in considerable improvements in processes efficiency. At the same time, numerous technical, economic, environmental, and political challenges have arisen, which manufacturing facilities had—and still have—to face. Concerning prominent ecological crises—including global climate change, water scarcity, food raw materials, land misuse, and energy consumption—decision-makers are now thinking collaboratively for an even more intense wake-up call, inspiring sustainability ideas, driven by research and development (R&D) partnerships (FAO, 2017; D'Amato et al., 2019).

The chemical, petrochemical, energy, pharmaceutical, and food industries are based on fossil inputs, which exert some of the most profound impacts on the ecosystem. These facilities

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require high energy demands, mass, and water flows to operate, and generate a pollutant load, whether solid, liquid, or gaseous (Varbanov et al., 2018).

Today, it is imperative to adopt alternative technologies to optimize production chains, and global R&D activities provide much of the innovation. An example is the bioengineering and related fields for consumer goods production (Mattiasson, 2013). Microalgae-based processes, in particular, have a strong influence on current topics of study. These bioprocesses are unique because they associate the use of residual raw materials or not with the production of multiple valuable products that are in considerable demand in the market (Sathasivam et al., 2019). However, microalgae technologies have many bottlenecks, many of which are still far from being eliminated to become viable.

However, on the journey toward industrial competition, a trend that began in the 1970s was process integration, which is focused on connecting unit operations, equipment, or manufacturing techniques within a process. This approach would reduce costs, process time, workload, and product losses, and would increase productivity, efficiency, and sustainability (Walmsley et al., 2019).

Several process integration options have been proposed to enhance the cost-effectiveness of microalgae-based systems. Thus, three main types can be highlighted: mass, energy, and water integration. Moreover, when microalgae-based processes have low requirements for these inputs, they are undoubtedly preferable, since they provide more significant conservation of energy and mass. However, due to the complexity of integrations, there are still many bottlenecks that need to be elucidated, and these can only be well-explained by applying systematic tools for sustainability and cost assessments (Walmsley et al., 2018).

In this chapter, therefore, we display a comprehensive view of process integration applied to microalgae-based systems. In addition, we discuss the processes and products of interest in the microalgae market, as well as the fundamentals of integrated facilities with their respective integration elements. Finally, to assess all this potential, a study of environmental and economic insights is presented.

26.2 A general overview of microalgae-based processes and products

Microalgae is not a taxonomic term, but a merely commercial designation. The current situation of the species already identified is founded on a database and literature information (i.e., www.algaebase.org and Guiry, 2012). So what are microalgae and what is their application? As a brief answer, they constitute a vast group of microorganisms of very diverse morphology and physiology, which present simple culture requirements, developing rapidly and efficiently, inhabiting niches of extreme environments. Although photoautotrophic metabolism is preferable, microalgae can also grow under heterotrophic and mixotrophic conditions. Because of these peculiar traits, microalgae symbolize an exceptional matrix for the bioprospecting of countless interesting metabolites. They derive from major molecules such as lipids, proteins, carbohydrates, and pigments (Borowitzka, 2018).

Given this general explanation, commercial exploitation of microalgae worldwide has evolved enormously over the years. The researchers, jointly with the industry, discovered the potential of these microorganisms for application in several sectors: food and feed (nutraceuticals and aquaculture nutrients), pharmaceuticals, cosmetics, chemicals (materials), and energy (biofuels, power, and heat). At the same time, these microorganisms are also promising for ecological uses, such as greenhouse gases mitigation and wastewater treatment (Severo et al., 2019).

As the advantages are many, start-ups and companies were founded in the past initially to manufacture microalgal whole biomass using cyanobacteria such as *Spirulina* and green algae *Chlorella*. Currently, many other small/medium-sized facilities and also pilot/demonstrative operations have been created, and the value of microalgae-based products has been improved (Gaignard et al., 2019); examples include Algenol, PetroSun, Solix Biofuels, Solazyme, Cyanotech Corporation, Cellana Inc., Fermentalg, AlgoSource, Isua Biotechnologie & Compagnie, Euglena, Algatech International, Simris, Algenuity, and Microsynbiotix. In addition, some technologies have also been developed and patented. The patents that are found on access platforms claim applications of the bioproducts in many segments, some of which are Sepal Technologies Ltd., Heliae Development LLC, Ecopetrol SA, and Synthetic Genomics Inc. (Khanra et al., 2018; Gifuni et al., 2019).

Regardless of the numerous examples of progress, the timeline shows that technical and economic barriers concerning microalgae commercialization persist today. Biomass production and other bioproducts, in general, are very onerous and require a massive volume of culture to satisfy the process design priorities. Thus, the cultivation systems are the centerpiece that hinders the large-scale economic viability of these bioprocesses (see Box 26.1 for more details).

When considering industrial manufacturing of microalgae-based products, one should take into account the market into which they are being sold and the facility objectives. Therefore, innumerable products can be divided into two broad classes for a better understanding: (i) commodity or bulk products, which must be produced in large quantities and purchased based on chemical composition, purity, and selling price; and (ii) fine or specialty chemicals, which must be produced in small quantities and are purchased due to their impact or function rather than their chemical composition (Xiong et al., 2019).

Additionally, production scale also differs between these products classes in terms of larger or smaller production volume and high or low added value (Smith, 2005). Fig. 26.1 demonstrates an overview of the classes of microalgae-based products and their respective values, volumes, and downstream expenditures for manufacturing.

The classes of specialty and fine chemicals, including pharmaceuticals, cosmetics, nutrients, and some chemicals, are high value-added products obtained, but in low volumes. On the other

BOX 26.1 CULTIVATION SYSTEMS

There are the open and closed systems, being raceway ponds and photobioreactors or heterotrophic bioreactors (fermenters), respectively. These cultivation systems are often based on the same mode, requiring: (i) energy light input, whether solar or artificial (except the heterotrophy); (ii) a carbon source (organic or inorganic); and (iii) agitation, aeration, and other operating conditions particular to each system (Gaignard et al., 2019). Open systems were the pioneers for microalgae culture and are currently responsible for 95% of worldwide industrial biomass production. Despite low capital expense, raceway ponds require large land areas (0.2–0.5 ha). They exhibit inferior productivity (0.7 g/L) due to the high evaporation rate, contamination, and inefficient mixing. In addition, the geographical location influences final product costs and overall process viability (Verma and Srivastava, 2018). Closed systems have already overcome almost all these barriers. They have the additional benefit of being equipped with monitors and controllers for better productivity performance, which can reach up to 3.5 g/L. The designs of these reaction vessels are numerous and have varied configurations, as described in Mantzorou and Ververidis (2019), but only tubular photobioreactors are widely commercially exploited. Of the three main disadvantages of photobioreactors, including the intense energy demand and difficulty in scaling up, undoubtedly the high purchase cost of equipment is the most critical factor. The value can be up to 100 times larger than an open system (Kumar et al., 2015). Finally, heterotrophic bioreactors have better kinetic performance and are easily scalable. Although they are exempt from the light requirements, and some strains use low-cost organic substrates as a carbon source, bioreactors need greater asepsis to avoid competition with other microorganism heterotrophs (Ramírez-Mérida et al., 2017). Deprá et al. (2019) estimated the purchased-equipment cost for raceway ponds, tubular and flat plate photobioreactors, and fermenters, whose values were in the range of 4–6 kUSD/m^3, 40–50 kUSD/m^3, 150 kUSD/m^3, and 8.5 kUSD/m^3, respectively. All commercially available cultivation systems have a win-lose relation. However, the focus should remain on the target product and company business needs.

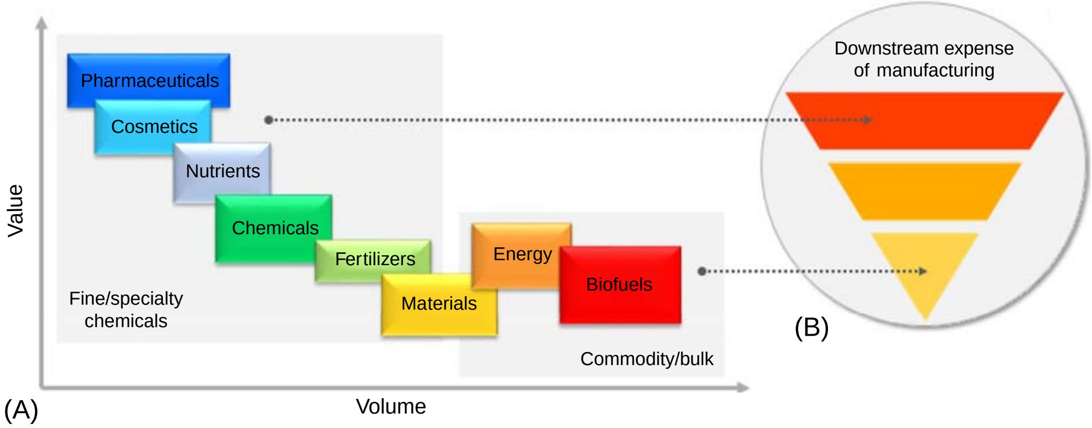

Fig. 26.1
Overview of microalgae-based products: (A) correlation between volume (x-axis) versus value (y-axis); and (B) hierarchy of downstream expenses for product classes manufacturing.

hand, commodities and bulk products, such as bioenergies and biofuels, are considered low value-added and are required in larger volumes (Fig. 26.1A) (Budzianowski, 2017).

For instance, pigments such as carotenoids, chlorophylls, and phycobiliproteins are found in microalgal biomass. However, the first commercial uses were from β-carotene and astaxanthin as food colorant agents. Although there are other products, pigments are predominant. The market share for these compounds expands to use as vitamins in food, animal feed, additives, products with antioxidant and anti-inflammatory properties, bioactive compounds to promote human health, and biomaterials (Jacob-Lopes et al., 2019). These biomolecules, despite being less competitive than traditional sources, are preferentially exploited because they attract the attention of niche consumers. However, they are not obtained in large quantities from the raw biomass at the factory gate due to intracellular compounds, which generate very low concentrations. In addition, pigments can be obtained at a relatively reasonable cost because some products are justified by their attributes, producing potential profitability for the manufacturing industry. For this reason, they reach sufficiently high sales prices, enabling the current market (Gerardo et al., 2015).

Nevertheless, it should not be overlooked that commercialization is based only on the extraction of a single compound, while the other co-products are depreciated or rejected. This does not take into account the sophisticated techniques of extraction and purification, which is the second hottest point of the process (further details in Box 26.2). In addition to the many unit operations, these steps are intense in materials, utilities, and energy, accounting for up to 90% of the product manufacturing expenses (Fig. 26.1B).

BOX 26.2 DOWNSTREAM PROCESSING

Another barrier to economic implementation of microalgae-based processes concerns downstream processing steps of biomass. Starting with harvesting methods, which include centrifugation, flocculation, flotation, filtration, and sedimentation, they are considered energy-intensive, expensive, and still inefficient for industrial use. This step also depends on the type of strain, cultivation condition, and cell density, affecting the final product yield. After that, drying, including methods such as spray-drying, convective drying, drum-drying, fluidized bed drying, and freeze-drying, may be efficient, but this will depend on the desired product, and the water content, which is often high, requiring a large surface to dry and the possibility of losing some compounds is high. In addition, cell disruption, which may be mechanical (bead mill, pressing, and high-pressure homogenization), biochemical (alkaline and acid treatment, enzymes, and osmotic shock), or physical (microwave, autoclave, pulsed electric field, and ultrasound), depends on the efficiency of the chosen process. This will require more or less energy and is also affected by the chemical composition and microalgae cell wall structure. Ultimately, the extraction method, including the use of solvents or supercritical fluid, has environmental demerits or requires expensive and sophisticated equipment, respectively (Kam et al., 2018; Gifuni et al., 2019). In this sense, it is imperative to streamline the unit operations that integrate the current downstream processing steps of microalgae-based processes.

Regardless of the bottlenecks inherent to the process, the marketing of microalgae-based products of high value-added continues to increase. It is expected by manufacturing companies that new market segments will be achieved, with duplicate sales prices exceeding production costs. Some pipeline bioproducts from the survey, whether commercialized or regulatory pipeline or at an advanced/early stage of development, will be introduced to the sales business, increasing the chances of successful large-scale applications (Enzing et al., 2014). However, these predictions are based on conservative assumptions, and the actual status of the pipeline product is unknown.

Because of this, the production of low-value commodities and bulk products would today be the highest priority to increase gross revenue from microalgae-based processes and boost the bioeconomy[a] of these facilities. Biodiesel, bioethanol, biogas, and bioelectricity, including heat generation, are the major, albeit distant, examples of what societies worldwide require and with selling prices as affordable as petroleum-derived fuel (Fig. 26.1A). In addition, the widespread protein supply in the human food chain or as an animal feed additive, and some chemicals, such as biopolymers and bioplastics, are also demanded but not forecasted for biomanufacturing in the coming years (Wijffels et al., 2010; Ruiz et al., 2016). This is because to make them successfully competitive, these products require massive production volumes. In fact, the technology is not available, among other aspects (i.e., microalgae strains selections and genetic engineering techniques), for processing biomass at the appropriate amount.

The key to the reported problems comes not from the attempt to optimize the overall plant design, but rather from an effort to streamline auxiliary operations. The integration and co- and sub-integration of other process units, whether partial or total, such as microalgae-based processes and products, can benefit all parties and are scenarios closer to real industrial exploitation. If subjected to these synergistic strategies and of smart interconnection, they could reduce the time and financial commitments involved, improving facilities' performance.

26.3 Process integration fundamentals

Process integration has experienced tremendous development, dating back more than 50 years, and is currently a well-established and mature methodology. Originally, the method was applied for heat recovery by thermal energy integration, reducing hot or cold utilities consumption. Over time, it has been used in many fields of research to minimize resource use, among other aspects. Therefore, it extended to mass integration through the materials usage, of which water integration was the most common branch. Today, water integration can be a separate branch, referring to the context of different water networks (Klemeš, 2013). In general,

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[a] Bioeconomy: Despite numerous concepts, in a practical sense, the bioeconomy is based on the use of renewable biological resources as feedstock for the conversion and supply products, processes, and services of value, within a sustainable economic system.

to reduce resource demand, it is necessary to maximize internal recycling or recovery and the reuse of material and energy flows. Process integration improves the efficiency of these features, benefiting plant (see Box 26.3, which describes process integration).

Although process integration metrics are more often applied to traditional manufacturing industries (chemical sites), this approach has spread much more broadly covering microalgae-based systems. Therefore, the next sections discuss critically the different types of integration in these facilities.

26.3.1 Energy integration

Energy can be defined as the capacity to produce work, that is, of two systems interacting with each other. According to the conservation law, the total amount of energy is conserved; however, it can be transformed from one type to another. There are several types of energy and energetic resources that derive from thermal energy, electrical energy, chemical energy, kinetic energy, and mechanical energy. Already, energy integration is one of the process integration methodologies, which is fundamentally based on thermodynamic principles, from energy and exergy balance insights (Sinnott and Towler, 2020).

In microalgae facilities, energy integrations are used to define the heating, cooling, and power needs of given equipment, unit operations, thermal systems, or products. At an operational level, this will help show the energy usage pattern in the production chain and identify sites where there is a need to conserve and save energy forms. In this sense, the overall target is to achieve maximum integration levels for improved energetic efficiency and reduce costs (Aziz et al., 2014).

Based on these fundamentals, the starting point is to understand the location of energy-generating sources, as well as dissipating energy sources, in order to minimize external heating

BOX 26.3 WHAT IS PROCESS INTEGRATION?

Process integration is conceptualized as an engineering approach toward design and operation for application in industrial systems, which has been implemented in the most varied areas of knowledge (Klemeš et al., 2018). The central objective of process integration is to address a system holistically—that is, integrate individual operations, envisioning synergy to improve overall production chain efficiency. Originally, the use of the concept of integrated processes was in the field of heat recovery. However, it extended to many industrial complexes: materials, emissions, water, energy systems, energy, and logistics. As process integration adopts immense proportions, the installation design becomes more complex and, consequently, the overall benefits increase. In this sense, critical discussion of environmental policy issues, including resource conservation, sustainability metrics, and bioeconomy, is also a contribution of this methodology (Walmsley et al., 2019).

and cooling requirements. Typically, power and heat expenses are present in almost all downstream processing steps, which should not be treated as standalone operations at the end-of-pipe.

In this sense, the first form of energy integration may be at the reactor level. There is a specific persistent problem in the performance of the microalgal culture indirectly related to reactor design: the temperature. This dominant environmental factor requires substantial attention. The efficiency of microalgae cultivation systems to obtain a specific product depends on the optimal temperature, and activity of these microorganisms is in the mesophilic range, between 25°C and 35°C. Cell growth rates usually decrease at temperatures above 35°C and below 16°C, although the pre-adaptation of some strains in extreme temperature ranges (thermophilic conditions) has been considered in aiming the optimization of reactors for industrial-scale application (Huang et al., 2017).

Regardless, considerable variations are experienced by mass outdoor commercial cultivation due to daytime temperature fluctuations and seasonality. Thus, an economical temperature control system is essential to keep the culture temperature within a favorable range. In both cold and warm seasons, heat exchangers are usually installed next to the photobioreactor (Chang et al., 2017).

In winter, for example, these systems need to be heated; however, this operation increases the process power demand. Therefore, heat integration from solar energy would be a cheap method of temperature control. Of course, this would be possible with the installation of alternative devices, such as photovoltaic panels to generate electrical energy (Fresewinkel et al., 2014). Tredici et al. (2015) demonstrated photovoltaic integration and the potential energy gain exceeded 600 GJ ha/yr. Since this is a sustainable bioprocess, at first glance this strategy seems incoherent for microalgae, but reasonable to the extent that 15% of light-to-electricity conversion efficiency of this auxiliary source would cover conventional electrical power requirements.

On the other hand, in summer, photobioreactors present a problem of overheating. Solar radiation is so intense through the transparent walls, due to the small surface area, that it can cause damage to microalgae cells by photoinhibition. Depending on the geographical, weather conditions, including irradiation, can raise the temperature 10–30°C higher than the ambient temperature in summer (Huang et al., 2017). For this reason, the control and monitoring of reactor overheating are indispensable. Even in middle-latitude zones, cooling systems are adopted as a preventive measure. Some ideas for greener cooling control have been employed, but are often ineffective because they significantly reduce light irradiation. There is also submersion in water reservoirs, but with specific penalties. Spraying water to cool the reactor surface has been considered the most preferred option. However, spray-cooling capacity is deficient, and its effective use is only possible under certain environmental conditions (temperature vs. humidity). A heat-exchange pump enables this procedure, yet incurs extra energy expenditure (Sierra et al., 2008).

It should be noted that the adoption of any temperature control system requires expensive components on a large scale. In this sense, energy integration through waste heat recirculation from other hot sources would be a promising approach. Song et al. (2015) proposed the optimization of an integrated process by coupling hot and cold streams of heat exchangers via exergetic recovery. Notably, these energy integration strategies from heating and cooling systems will only be viable if a suitable location for photobioreactor installation is chosen. The location should have available energy, waste heat, and water resources to maintain the temperature to the set point and then reduce energy consumption.

Going further, energy integration from the stages after cultivation is crucial. Depending on the product that the facility targets, downstream microalgal biomass processing goes through many operations, including equipment and thermal systems, which are often extremely energy-intensive. In the harvesting stage, the biomass dryer, for example, is a device that can consume up to 85% of the total energy required in the process due to the high moisture content (Aziz et al., 2014). Alternative minimal energy intensity drying routes are urgently needed. Several methodologies have been developed, but unfortunately the options to integrate or co-integrate energy from other sources are not yet viable. To date, no technology is applicable due to the low level of heat recovery and the enormous exergy destruction in equipment.

Furthermore, as a bioresource of varied chemical composition, microalgae biomass can be converted and processed by thermochemical and biochemical routes, which generate different types of bioenergy. Through these routes, energy integration can be done during gasification, pyrolysis, liquefaction, hydrogenation, fermentation, transesterification, or direct thermal combustion, whose steps produce heat, syngas, and biofuels, with substantial energy content (Lee et al., 2019). After that, the integration of these products in other burning processes, either by co-combustion (with other fossil fuels) or independently (biomass direct combustion or association of conversion routes and power generation, such as integrated gasification combined cycle) can be considered for enhancing energetic efficiency (IEA, 2017). Waste heat utilities could be collected and regenerated in these procedures that provide thermal streams.

Finally, other biomass-independent products, such as volatile organic compounds, oxygen, and partial carbon dioxide, which are released into photobioreactor exhaust gases, can be integrated as an energy source into combustion systems. Severo et al. (2018a,b) demonstrated that this energy integration approach has the potential to improve equipment thermal performance by more than 40%. It is worth mentioning that this process is performed in a single operation because the bioproducts are excreted by the microalgal cells, eliminating the biomass processing intermediate steps. Despite all the advantages, integration of gaseous molecules is particularly challenging. The main issues are that these products are quite heterogeneous and in low concentrations, which would require an appropriate collection or recovery technique from exhaust stream to be commercially established (Lukin et al., 2018).

26.3.2 Mass integration

Mass is a property of an object, so mass integration techniques are based on the identification of the chemical constituents of a physical body. However, there are some problems related to the law of conservation of mass, which are dependent on material flows properties and not necessarily on chemical compositions (Klemeš, 2013). Analogous to what happens in heat integration, mass integration in industrial processes provides an understanding of global material flows, using mass balances, in order to track the best pathway of allocation, separation, recovery, and generation stream of the mass species (El-Halwagi, 2017).

Typical industrial microalgae plant designs require different types of masses, including carbon, nitrogen, phosphorus, and sulfur. They can be integrated in culture systems, since microalgae are able to assimilate these elements in both organic and inorganic form, aiming at the maintenance of cellular structures.

Carbon is the predominant element in microalgal biomass composition, with an average proportion of 50%, being considered the basis for robust bioproducts production. In the inorganic form, the main carbon integration route is from carbon dioxide (CO_2). Metabolically, microalgae bioconvert free CO_2 during photosynthesis, which is transported across the plasma membrane, being stored in cells, as a kind of reservoir. This procedure is known as the carbon concentration mechanism, through six distinct routes. High-efficiency enzymes catalyze these reactions, carbonic anhydrase and ribulose 1,5 bisphosphate carboxylase/dehydrogenase, which accumulate CO_2 concentrations up to 1000 times greater than that of the external circulating flows (Cheng et al., 2019).

Given the above, free CO_2 integration has been widely envisioned for environmental management reasons. Rather than integrating CO_2 from the atmosphere, which is inefficient for sustaining intensive cultivations due to the low CO_2 level in the air (380 ppmv), direct CO_2 integration from highly concentrated stationary sources is a promising strategy for balancing the economic interests of microalgae-based processes. The flue gases concentrations can usually reach 30%, allowing adjustment to values between 3% and 15% for input in photobioreactors (Van Den Hende et al., 2012). Typical examples are the use of off-gas streams from clinker and lime kilns, coal-fired boilers, exhaust pipes, internal combustion engines, as well as flue gases from chemical and petrochemical plants and other available CO_2 emitters (Anbalagan et al., 2017; Aslam et al., 2019). Integrating CO_2 from these sources would avoid, in principle, logistical problems. This attractive carbon mass integration strategy is often proposed for input into microalgae photobioreactors; however, it is seldom implemented at the demanded scale. Firstly, these flue gases contain not only CO_2, but also hundreds of substances, most of which are toxic to cells (CO, CH_4, NO_x, SO_x, H_2, heavy metals, halogen acids, and particulate matter). Secondly, flue gas temperature is above 1200°C (Jacob-Lopes and Franco, 2013). These two problems are enough to inhibit photosynthetic activity.

In contrast, microalgae heterotrophic cultivation systems require an organic carbon exogenous source. However, to overcome the money-consuming processes, the use of low-cost organic carbon is interesting. The integration of cheap substrates including agricultural waste, municipal waste, molasses, fruit extracts, vinasse, and glycerol have been reported as efficient resources for this purpose (Katiyar et al., 2017). High lipid productivity is one of the advantages. Crude glycerol, for example, a by-product of biodiesel production, would be a potential integration form, since it is a particularly abundant feedstock in some regions and of difficult final disposal (Klein et al., 2018). Of course, any of these integrations will depend upon the physicochemical composition of the compounds, which later may or may not impair microalgae uptake. This option is by far a merely economic criterion.

After carbon, nitrogen is the most important element for microalgae cultivation. These microorganisms are able to metabolize various nitrogenous compounds to support cell growth and maintenance, such as ionized ammonia (NH_4^+), free ammonia (NH_3^-), nitrate (NO_3^-), and nitrite (NO_2^-) (Van Den Hende et al., 2012). For this reason, industrial effluents integration (i.e., dairy effluent, poultry, and swine slaughterhouse effluent), has been commonly suggested as an efficient method to supply organic nitrogen, and to reduce nutrient discharge, eutrophication in receptor streams, and downstream biomass processing costs. This source is rich in amino acids and urea, which have entry within the cell by active transport. In terms of amino acids, some of them have been used as carbonaceous and nitrogenous substrates for microalgal growth in the dark. However, the most common source is still urea, which is hydrolyzed to NH_3^- and CO_2, whose generated compounds can be co-used in cultivations. Another target of these microalgae-based processes is to reduce the purchase and degradation of nitrogen-based substances, such as fertilizers and proteins, for use in the effluent treatment plant itself. But what comes up is that the neutral form of NH_3^-, even at low concentrations (1.2 mM/20 mg/L), has detrimental effects on microalgae due to its toxicity (Peccia et al., 2013).

Additionally, other nitrogen compounds in inorganic form, also derived from industrial flue gases, can be integrated into the cultivation systems. In addition to air N_2, NO and NO_2 are the main NO_x species, while N_2O, NO_3, and other trace-level forms can be used by microalgae (Singh et al., 2019). However, research on NO_x integration into photobioreactors is progressing at a slow pace. If on the one hand there are questions about tolerance and effects on microalgae species, on the other there is the limitation on the dissolution of these nitrogen compounds in the culture medium.

Phosphorus is the third most in-demand element in these systems. Although the microalgae metabolize this essential macronutrient at deficient concentrations (1% by weight), reactive phosphorus is the most straightforward form to assimilate, despite hydrolysable acid phosphorus and organic phosphorus being efficiently used (Solovchenko et al., 2016). Similarly to the other elements, the integration of phosphorus-rich industrial effluents has been widely required for microalgal cultivation, since it is the second-largest contaminant in these sources—typical total phosphorus concentrations in swine effluents range from 100 to 620 mg/L (Nagarajan et al., 2019). However, besides the regulation and assimilation mechanism not yet being well understood, there is another considerable obstacle for the integration: microalgae strains are not yet able to metabolize phosphorus so quickly, as well as other pollutants present in the medium, and withstand high loads of real-world effluent.

Finally, sulfur integration also has the potential for application to microalgae cultivation systems. Although some sulfur compounds, such as dimethyl sulfonic propionate (DMSP) and dimethyl sulfide (DMS), are released by some species under specific conditions, this element is a component of the amino acids (cysteine and methionine) of microalgae, and is present in the thylakoid membrane (anionic sulfolipid) (Giordano et al., 2005). Regardless, in the same case of CO_2 and NO_x, flue gases simultaneously release sulfur oxides (SO_x), in the forms of SO_2 and SO_3, depending on the chemical reaction with the fuel. Therefore, some studies have shown that these compounds could be integrated into photosynthetic cultivations (Van Den Hende et al., 2012). However, as far as we know, very few strains can tolerate the sulfur compounds formation, due to the high solubility in aqueous media, and the mechanism leading to this is unknown.

In this sense, the different mass integration possibilities seem very attractive at first sight, because they would be a cheap source of nutrient enrichment to cultures. In practical terms, the biggest problem inherent to these integrations is that coupling of reactors for microalgae processing near industrial areas for the surpluses reuse is very complicated. Generally, there is no land available around these facilities to integrate the supplied effluents.

26.3.3 Water integration

Water is an essential natural resource for the survival of all living beings that inhabit the Earth. It is abundant, covering most of the terrestrial surface. However, effects on the quality and quantity of available water (surface and groundwater) are already evident in many parts of the world. The threat of its scarcity and impacts on ecosystems may seem exaggerated, but it is not (Damerau et al., 2019).

The industrial sector is the second largest water consumer, accounting for about 22% of worldwide consumption, below only agriculture. Regardless, all industrial activities need to be supported by these limited water resources to transform feedstock into products. In addition, the rising price of freshwater, its scarcity, pollution, stricter environmental regulations, and wastewater treatment costs raise the need for better management and distribution in a process. Therefore, routes should be sought out to minimize water requirements in industrial facilities (De-León Almaraz et al., 2016).

Following this trend, microalgae-based processes are water-intensive, which makes this a strong constraint for marketing them. This critical issue is fundamentally related to water expenditure in the cultivation stage, alongside the substantial evaporation losses due to aeration rate, and secondarily in some downstream processing steps of the biomass, such as harvesting. For biodiesel production in photobioreactors, for example, it is estimated that freshwater requirements range from 80 to 291 m^3/GJ (Batan et al., 2013). Yet, according to these same authors, it has been shown that the global water volume for the manufacture of other biofuels is between 90 and 420 billion m^3 of water, equivalent to the additional direct consumption of up to three times the volume of water spent to support agricultural irrigation activity. Chinnasamy et al. (2010) demonstrated that microalgae biomass production in open ponds demands 11–13 million L/ha/yr of water. However, these water withdrawal numbers fluctuate due to the geographic location and climate resolution for a stable microalgae process.

The most obvious solution to this barrier is to integrate seawater to offset water requirements, since the oceans are considered as abundant natural resources. The use of seawater can significantly minimize the amount of demanded drinking water for cultivation preparation. This type of integration has a double benefit: in addition to volumetric water input, mass integration is possible. Seawater is composed of all the chemical elements supporting marine biology, such as carbonates, nitrates, phosphates, minerals, and other dissolved ions (Na^+, Cl^-, Mg_2^+, SO_4^{2-}, Ca_2^+, and K^+). Nutrient-enriched seawater supply can be an efficient way to replace partially some of the key elements of synthetic culture media. $MgSO_4$, $CaCl_2$, and $NaCO_3$ are examples that constitute the BG-11 medium, considered the universal broth for microalgae cell maintenance (Jung et al., 2015).

Additionally, square-kilometer-scale photobioreactors for outdoor marine microalgae cultivation are available in some coastal areas near the sea (i.e., Cyanotech Corporation, Hawaii, USA). A considerable number of practical investigations have been made using seawater integration, as is the case of the plant made of "Green Wall Panel-II" (GWP-II) photobioreactors (Tredici et al., 2016) and the emerging offshore cultivation photobioreactors floating on the ocean surface (Maeda et al., 2018). On the other hand, there are also laboratory studies addressing the cultivation of individual species in artificially manipulated brackish water (Sheets et al., 2014). Although some halophilic microalgae thrive in high saline concentrations and even present exceptional biodesalination potential, the number of domesticated salt-tolerant strains is very limited (Sahle-Demessie et al., 2019). Further evaluations of microalgae gene modifications for screening individual mutant strains are needed in this field.

In addition to the implications mentioned above, there are other restrictions on seawater integration. Firstly, to supply a commercial microalgae plant, the use of seawater would be intensive. The reality here is that it would necessary to consider desalination as an alternative source for water security. But for industrial purposes, this is burdensome, and therefore still regarded as something remote (Förster, 2014). Secondly, as regards the guardianship of natural water resources, the legislation is aimed at protecting freshwater bodies, such as rivers, lakes, and underground reservoirs (Cosgrove and Loucks, 2015). For example, the European Water Policy, declared in the Water Framework Directive (2000/60/EC), exerts pressure on water bodies by estimating water abstraction and pollution from industrial activities. Perhaps to be taken as an inexhaustibility factor or the high cost of the desalination process, seawater is not treated by law as an isolated natural resource. In general, in this regard, the legislation is flawed in that fully effective measures cannot be implemented in the qualitative and quantitative management of seawater withdrawal and allocation. It is worth mentioning, however, that conflicts may be generated in the future about seawater integration because, as no universal standard exists, it is not known to what regime the use of this resource will be subject. On the one hand, there may be a requirement for a legal grant; on the other, fees may be charged for its use.

Another attractive option for water integration to offset expenses is through reuse of water and its coupling in microalgae-based processes. The amount of reused water is proportional to water demand in the process; that is, it reduces the need for further exploitation of this resource (Gude, 2015). Similarly to what happens with mass effluent integration, instead of nutrient cycling to cultures, the residual aqueous fraction of this material, from a given industrial process, can be incorporated into other operations. Water reuse, sometimes referred to as water recycling, can be viable for various applications, depending on site-specific conditions (EPA, 2019). For the microalgae industry, the destination of this “purified water” may be for incorporation into the cultivation reactor itself, or as cooling and heating water for auxiliary equipment (i.e., boiler makeup water in a process to generate bioenergy or biofuels) (Mo and Zhang, 2013). For this, the reused water usually goes through a wastewater treatment plant, considering some quality parameters (solids, color, turbidity, alkalinity, etc.) to fit the standards established by legislation for the intended use (EPA, 2012).

As mentioned above, although some microalgae species can assimilate the pollutants contained in the recycled liquid medium, the growth of the vast majority is often affected due to the toxicity of certain compounds that are not eliminated in treatment (Farooq et al., 2015). Waters from industrial activities include oils, pesticides, and heavy metals, among other constituents, whose toxic organic compounds often combine with the persistence and bioaccumulation potential (Priyadarshani et al., 2011). Another significant limitation of this type of reuse water integration is related to locality issues (Fresewinkel et al., 2014). For example, the installation of a microalgae mass cultivation system requires a vast area of land and it is usually located far from the large industrialization sites to supply this water source, and its transport in tanks would be costly. This fact alone makes integration unfeasible. The integrations of the different types of water shown here are quite promising, but present real challenges to microalgae-based processes.

26.4 Environmental and economic indicators of microalgae integrated systems

26.4.1 Life cycle assessment

The challenge of understanding mass, energy, and water integrations and approaching them under the sustainable aspect appear complex. However, process integration strategies associated with environmental assessment tools play a key role in the practical and sustainable development of microalgae-based industrial systems. This is because using systematic methodologies, such as a life cycle assessment, presents significant potential to address and quantify the inherent environmental burdens (Mongkhonsiri et al., 2018). This methodology simultaneously enables costs improvements that are also achieved through the waste hierarchy, which consists of the three R's: reuse, recovery, and recycling, making them fundamental tools for implementation in industrial systems (Johnson, 2018).

An established consensus reports energy demands as a critical bottleneck in the development of any microalgae-based process. In this way, energy integration has become an issue widely discussed in energy management in industrial processes. Therefore, reducing energy requirements (conversion, supply, and consumption) should be investigated further for resource efficiency and the economy as well as environmental footprints (Chen et al., 2019). For this reason, the global energy and associated environmental impacts have been explored in detail in an attempt to optimize more sustainable technological routes by verifying the process steps that can be integrated (Banerjee et al., 2019).

Given this scenario, initial studies on integration strategies promoted using the residual heat of the combustion gases of the plants for the drying of algae (Chowdhury et al., 2012). About 8% of the energy used in coal plants is lost with the flue gases. Thus, when integrating the exhaust gases of coal plants with the unitary microalgal drying operation, it would result in approximately 10% less direct environmental impacts associated with the energy resource category. Moreover, since we would probably consider fossil energy as a source for the operating system, we would be indirectly interfering in the categories of ozone depletion, global warming, smog, acidification, eutrophication, and ecotoxicity. Therefore, the most efficient method to reduce environmental impacts is by minimizing external inputs of fossil energy as well as fossil-derived feedstock materials.

Another possibility for heat integration is wet algal biomass to biofuel production (Kouhia et al., 2019). Studies report that the direct combustion of biomass results in a gas mixture with substantial heat potential. This, in turn, can be used in industrial heating systems or can also be used for the production of steam and consequently applied in the production of electricity. It is estimated that the energy content of the biomass represents about 60%–85% of the total heat of the steam in a boiler (Kumar and Singh, 2017). In addition, the energy integration from biomass ensures decreased demand for fossil energy required for the system, providing a reduction of energy resources. Still, once energy is related indirectly to the categories of global warming and ecotoxicity potentials, this will be slightly minimized since, for the obtaining of energy, environmental factors of extraction of natural resources influence them.

In the same way, the VOCs generated in microalgal photobioreactors have been reported as promising heat sources to be integrated into a bio-combustion process (Jacob-Lopes et al., 2017; Severo et al., 2020). The VOCs produced in this bioprocess were considered as a supplementary biofuel, presenting energy potentials and a power generation rate of 86,320 kJ/kg and 15,247.78 kJ/m^3/d, respectively, contributing to a better combustion performance (Severo et al., 2018a,b). From an environmental point of view, the results showed improvements in the thermal efficiency of 30.5% compared to conventional combustion and about 25% of total energy, indicating energy resource potential proceeds. Moreover, greenhouse gas emissions represented a reduction of about 80% in global warming potential.

Simultaneously, as well as the depletion of energy resources, the persistent volumes of freshwater used in industrial processes have contributed to the establishment of legislative and policy requirements for effluent reduction (Ramos et al., 2016). As a consequence, water integration strategies have been designed to ensure the minimum demand for natural resources. In addition, numerous aspects can be considered as real advantages of integrating water in microalgae-based industrial processes such as minimizing water footprint through the use of seawater and freshwater as well as the reuse of effluents and consequently the reduction of effluents sent to treatment (Klein et al., 2018).

The considerable demand for limited natural resources is one of the main obstacles to the economic viability of microalgal products (Ishika et al., 2017). Given this aspect, studies employing seawater integration as an alternative to freshwater have been presented (Ishika et al., 2019). This resource could replace losses by evaporation, or cultivations could be filled exclusively with seawater. In contrast, another alternative for water integration occurs through water resulting from centrifugation processes (Förster, 2014). In the freshwater integration scenarios, the water footprints associated with the evaporation and recirculation system of water in the centrifugation and drying procedures would allow recirculation of 75% of the blue water footprint. In addition, 90% of the gray water footprint would be avoided, since there would be no wastewater to be treated. Therefore, the possibility of recovery of water volumes can reach about 80% of the total water footprint required in microalgae cultivation systems.

The wastewater integration strategy is the primary alternative for minimizing environmental indicators. In this context, Guldhe et al. (2017) proposed microalgae cultivation in wastewater. Thus, the wastewater requires about 90% less freshwater. It is essential to note that in addition to the integration of a substantial fraction of water, in parallel there is a considerable amount of mass integration, resulting in the reduction of the nitrogen requirement by up to 94%. This is because, depending on the composition of the effluent, the microalgae can remove approximately 85% of nitrates and 75% of ammonia, besides other nutrients such as phosphates and organic carbon demand (Rawat et al., 2013). Moreover, if we consider the energy resources and greenhouse gas emissions related to chemical fertilization, when integrating wastewater, a reduction of up to 50% is possible in these categories (Lam and Lee, 2012). Beyond the significant decrease of these impact categories, considerable values of acidification and potential eutrophication are minimized, since these categories are directly related to ammonia, nitrate, and phosphate emissions in water and terrestrial ecosystems.

Where the use of mass integration strategies is necessary to control excess waste in industrial practices, Deprá et al. (2019), simulating combustion gases, provided carbon concentrations of 15% as the sole source of carbon in a hybrid photobioreactor. The results showed maximum conversion efficiencies of 45.32 $kgCO_2/m^3/d$, resulting in a global carbon conversion of 30%. As an environmental indicator, the energy relation to the energy potential of the biomass produced and the required operational energy demand was determined, and the ecological viability was therefore achieved, resulting in a net energy ratio of 2.49. In addition, the carbon footprint attributed to this system can offer a reduction of approximately 41% of global warming potential.

Alternatively, among a wide range of possible uses of mass integration, glycerol is an attractive alternative in terms of environmental aspects (Ren et al., 2017). The results found in the literature show that microalgal growth and lipid content, 16.7 $g/m^2/d$ and 23.6%, respectively, were improved with the integration of glycerol in the culture. Moreover, the removal of nutrients such as nitrogen and phosphorus were increased when compared to the control treatment (without glycerol). Under a sustainability assessment, this integration has advantages over environmental equilibrium, since the reuse of a by-product can be reintroduced into the production of renewable energy (biodiesel) (Ma et al., 2016). Acidification and eutrophication potentials can be significantly reduced as they are directly related to organic carbon demand.

Besides carbon mass, nitrogen is the second most abundant element in biomass and, consequently, also represents a strong economic influence on nutrient demand during cultivation (Gao et al., 2019). Given this aspect, organic nitrogen, such as urea, was integrated into a microalgal system to raise biomass and lipid production when compared to the preferential sources of nitrogen (ammonia) (Batista et al., 2019). The results demonstrated that the use of urea did not modify cell growth rates. At the same time, the integration of nitrogenous nutrients has a relevant character regarding the impact reduction associated with terrestrial and mainly aquatic eutrophication categories.

Likewise, nitrogen oxides (NO_x) may be used as nutrients during cultivation (Vuppaladadiyam et al., 2018). It is known that coal-fired flue gases present 90% NO_x as the major compound (Van Den Hende et al., 2012). Because of the above, microalgal strains were exposed under-treated with flue gas as a strategy to reduce greenhouse gases to the atmosphere. The microalgae presented NO removal of about 2.86 mg/L/d, resulting in global values of 96% of the converted nitrogen (Ma et al., 2019). However, it is important to note that the environmental footprint associated with photochemical oxidation, eutrophication, and acidification, according to these results, shows a drastic reduction in these impact categories. Furthermore, indirectly, the human toxicity category can be decreased since the excessive emission of these compounds poses a threat to respiratory health (Zhao et al., 2018).

Similarly, sulfur oxide (SO_x) emissions negatively influence the health of both biotic and human flora and fauna (Singh et al., 2019). The concentration levels of these compounds vary according to the combustion processes; however, values of the order of 200%–1500% are found in waste incineration systems. In view of this, gaseous effluents require proper treatment before being disposed to the atmosphere. Studies by Kumar et al. (2019), proposed the incorporation of exhaust gases from a coal-burning boiler composed of 180 ppm SO_x into microalgal cultures in sewage wastewater. The results showed that the SO_x removal efficiency was 45%, resulting in biomass productivities of 0.6 g/L. However, attention should be paid when exposing microalgal strains to high concentrations of SO_x, as this may inhibit their growth (Choi et al., 2019). Environmentally, by reducing the emitted levels, it is suggested that the acidification potentials be minimized by approximately 50% since sulfur compounds are directly related to acid rain. Furthermore, indirectly, this pollutant participates in photochemical smog, and consequently impacts on the category of photochemical ozone formation at ground level, which results in undesirable effects on human health.

Finally, several scenarios of partial mass, water, and energy integrations have been proposed to reduce the environmental impacts associated with the high demand of materials essential for the production and processing of microalgae processes. Therefore, the reuse of these surpluses could be a strategy to strengthen the non-generation of new wastes. However, although efforts have focused on determining key environmental indicators, these in turn represent only part of the sustainability metrics. The joint evaluation of economic aspects is crucial to try to reach a common denominator in the future.

26.4.2 Economic outlooks

From an economic point of view, the numerous evaluations of microalgae-based processes indicate a generally unfavorable economy (Doshi et al., 2016). Crucially, among ostensible factors related to the processes viability are those associated with the costs of nutrient and energy supply. In addition, basic principles of process engineering such as the design and location of the plant, as well as economy of scale, make all these factors of a complex nature (Judd et al., 2017).

Since energy demand in microalgal processes is accentuated, metrics related to energy efficiencies and requirements are often accounted for in order to reduce the costs of this nature (Arcigni et al., 2019). Thus, through energy return on investment (EROI), this indicator can be an auxiliary measure of economic viability, since it quantifies energy inputs and outputs (Brigagão et al., 2019). An ideal option for microalgae production, $\text{EROI} > 3$, would be able to supply the entire production chain (Medeiros et al., 2015). Therefore, valuation strategies of the energy potential of biomass, integrating the co-product for the energy supply system, decrease the input demands of energy resource. Still, studies report that the use of renewable energy as a source of energy significantly increases EROI values to 8.35, while fossil energies are reduced to 1.25 and 2.13 (Beal et al., 2015).

Additionally, carbon dioxide is considered the most expensive consumable commodity (Wu et al., 2019). Theoretically, to produce 1 kg of biomass, about 1.83 kg of carbon dioxide is needed (Sepulveda et al., 2019). However, when considering microalgal processes where the supply of pure carbon dioxide values of 125.00 USD/kgCO_2 are estimated, this results in a cost of 228.75 USD/kg of biomass. In contrast, to integrate exhaust gases associated with a carbon capture and storage system, the Carbon Capture and Storage Association (CCSA) estimates that costs per ton of carbon dioxide are equivalent to around 95.00 USD/ton (Service, 2016). However, although the value is lower when compared to pure carbon dioxide, this value is still onerous. Furthermore, according to the Department of Energy, technological advances will make it possible in the short term to reduce to 20.00 USD/ton by 2025 (DOE, 2019).

Still, associated with carbon pricing, a strategy accessible to financial markets is related to carbon credits (Settre et al., 2019). It is estimated that around 16.1 million carbon credits have been sold in voluntary carbon markets in recent years (CER, 2018). In this sense, the possibility of acquiring additional carbon credits to affect the emission limit may reduce emissions. Moreover, the growing interest in carbon emissions indicates a substantial number of investors paying higher prices for carbon-neutral projects and technologies for the ease of selling surplus credits as it can be used to subsidize future projects in the plant (Günther et al., 2018).

Likewise, fertilization with nitrates and phosphates is indispensable to supply microalgal productivities. Currently, according to the United States Department of Agriculture, it is estimated that the costs of ammonium nitrate and superphosphates are approximately USD/ton 550 and 300, respectively (USDA, 2019). In addition, fertilizer production accounts for 1%–2% of global energy consumption (Winkler and Straka, 2019). Studies conducted by Zhang and

Kendall (2019) report requirements of ammonium nitrate 0.15 kg/kg of biomass and superphosphate in the order of 0.10 kg/kg of biomass. Therefore, in an estimated production of 1 ton of microalgal biomass, the required costs involving nutrient demand would be around 82.5 USD for nitrates and USD 30.00 for phosphates. Thus, a viable cost-reduction strategy is presented through the partial integration of nutrients. Besides, according to De Bhowmick et al. (2018), the cultivation of microalgae using liquid effluent nutrients in a closed circular biorefinery model, that is, total integration, results in a cost reduction of 35%–86%.

Microalgae cultivation requires large volumes of water. However, studies show that in the process of obtaining 1 kg of biomass without water recycling, values of the order of 1.08 m^3 are required. On the other hand, if there is total water integration, about 0.24 m^3 is required (Mayers et al., 2016). From an economic point of view, it is estimated that water prices in the world show values of approximately 1.50 USD/m^3. However, the values associated with wastewater treatment are around 3.0–4.0 USD/m^3 for sewage discharge, resulting in an approximate direct cost of 5.00 USD/m^3 (Clere, 2016). Since the water volumes represent a capital demand of approximately 1.62 USD/kg of biomass, with 100% of the recycled water, the values can reduce by up to 22% of the costs. In addition, considering that wastewater can be included integrally to microalgae cultures, in a hypothetical scenario, a medium-sized industry has about 16 m^3/d. If we think of the integration of this wastewater to the microalgae cultivation, it is possible to avoid spending about 26.4 million USD/year.

Thereby, it is believed that entire processes integration is aimed at reducing greenhouse gas emissions, as well as the remediation of wastewater associated with energy generation and high value-added co-products. In addition, other benefits are expected through carbon capture and carbon storage of carbon credits as an integral part of a process. Therefore, the microalgae-based systems would become economically viable and environmentally sustainable from the point of view of the circular biorefinery (Fig. 26.2.). In this way, it is suggested that there should be efficient recycling of the products generated within the integrated system. Exhaust gases would serve the nutrients for the development of biomass microalgae, in addition to wastewater with a high concentration of nutrients. Thus, the products and co-products generated could return to the industry in a closed loop. Therefore, this concept should be considered as a potential strategy to solve and to establish new green engineering associated with the environmental and economic benefits related to microalgal processes.

26.5 Concluding remarks

When considering that microalgae-based processes and products still face barriers to full market competitiveness, the process integration strategy seems, at first glance, to be a promising solution. However, by looking more closely at the reality of the facts, it is not enough

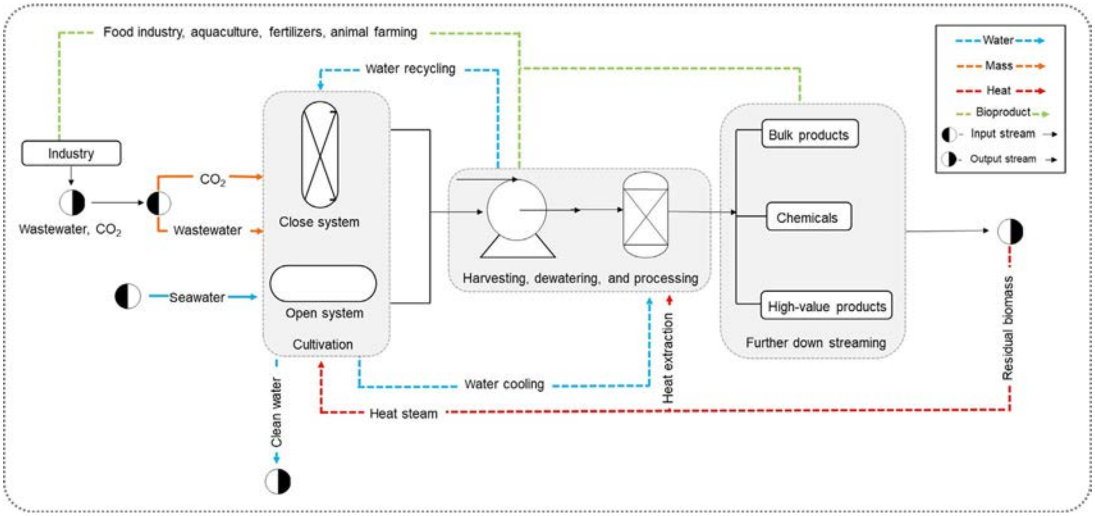

Fig. 26.2
An ideal process integration model in a microalgae-based biorefinery.

to integrate and co-integrate energy, mass, or water, as discussed here. The most important point now is to consider synergistically environmental and economic assessments, as well as the biorefinery approach, in an attempt to find a scenario for industrial deployment.

In this sense, for a better understanding, we separated the pros and cons of the different types of integration in Table 26.1, along with open questions for each of the categories. In general, it is complex to find a balance in each type of process integration category. All of them depend on seasonality and geographical conditions, which are considered the main factors for a stable microalgae system. Tools for strategically exploring the optimal sites for large-scale cultivation (e.g., the geographic information system, or GIS) are today one of the priorities of process integration; they consider global and local mapping, including several parameters, such as ideal temperature, solar irradiation, availability of land and inputs near industrial areas (CO_2 or wastewater supply), groundwater salinity, and rainfall. In addition to this information, many other vital factors must be addressed: the inherent requirements of microalgae strains under genetic engineering perspectives, and the technical, economic, social, governmental, and environmental aspects of the selected potential site.

Once adjusted, the progress of process integration applied to microalgae-based systems on a commercial scale will considerably reduce costly demands and then will result in inexpensive, safe, and sustainable technologies.

Table 26.1: Pros and cons of different types of integration and open questions for each category in microalgae-based systems.

Type of integration	Pros	Cons	Open questions
Energy	• Reduced electricity expense • Waste heat recovery from thermal operations	• Nonexistence of a cheap temperature control system • Poor heat recovery techniques	• What would be the best geographical location to adopt as the ideal climatic model for microalgae-based processes temperature control? • What recovery technique would be more suitable to optimize for application in large-scale manufacturing processes?
Mass	• Ability to remove surplus compounds from indus trial activities	• Limited assimilation of certain substances • Availability of geographically appropriate sites to introduce a microalgae plant	• How can we improve both strains' performance and cultivation systems to support the high abundance of effluents from industries?
Water	• Reduced water footprint • Combination of integration approaches (water vs. mass)	• Insufficient environmental regulation • Characteristics of cell toxicity and bioaccumulation	• How should genome editing techniques be engineered to improve the metabolism required for different types of water use?

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8. CAPÍTULO 6

8.1 CONCLUSÃO

O processo proposto neste trabalho demonstrou ser uma estratégia com considerável potencial para a captura de dióxido de carbono e paralela utilização dos produtos formados. Em relação ao forno de combustão projetado laboratorialmente, todos os parâmetros de desempenho térmico foram substancialmente melhorados com o enriquecimento dos gases de exaustão do fotobiorreator, em um tempo de residência celular de 96 horas, considerada a melhor condição experimental. Dessa forma, obteve-se um ganho na eficiência térmica do sistema, com taxas de aquecimento na ordem de 30,5% e 45,8% superiores ao uso do ar atmosférico e da corrente gasosa simulada, respectivamente. Por outro lado, através da composição dos gases de exaustão do fotobiorreator, cerca de 40% de oxigênio biológico foi gerado para posterior uso como comburente, além dos compostos orgânicos voláteis, que apresentaram substancial potencial energético para uso como combustíveis gasosos, e do CO_2 não convertido, que foi utilizado como diluente de nitrogênio.

Adicionalmente, quando submetido a ferramenta de análise de ciclo de vida, o processo integrado apresentou ganhos em termos de desempenho ambiental, considerando as métricas e indicadores de sustentabilidade mais amplamente utilizadas para avaliar processos. Em termos de bioeconomia, os custos com consumo de combustível durante a bio-combustão foram reduzidos em aproximadamente 40%, uma vez que as produções de oxigênio e compostos orgânicos voláteis foram as responsáveis por pela maior geração de receitas.

Dessa forma, através da integração destes processos, foi possível desenvolver uma rota tecnológica que atendeu aos requisitos de inovação e atividade inventiva, demonstrando potencial para transferência ao setor industrial.

9. CAPÍTULO 7

9.1 SUGESTÕES PARA NOVOS TRABALHOS

Os conhecimentos obtidos através do desenvolvimento desta Tese de Doutorado podem ser consideravelmente ampliados através de pesquisas em escala semi-industrial ou industrial sobre a integração de processos. A disponibilidade de sistemas baseados em microalgas em maiores escalas de operação viabilizaria diversos ensaios experimentais adicionais que embasariam estudos complementares acerca da temática aqui considerada. Assim, seria possível agilizar e reduzir os custos do desenvolvimento de um processo microalgal com maior robustez e identificar com maior precisão as condições ideais para sua aplicação. Diante do exposto, as sugestões para trabalhos futuros estão listadas a seguir:

- Operar um sistema de cultivo de microalgas em maior escala;

- Realizar testes em outras configurações de fotobiorreatores;

- Avaliar outras espécies de microalgas para obtenção de cepas com características aprimoradas, visando maximizar a conversão de dióxido de carbono e a produção de bioprodutos;

- Verificar a possibilidade de recuperar os produtos metabólicos liberados nos gases de exaustão de fotobiorreatores;

- Explorar os produtos energéticos da biomassa de forma integrada com outras operações unitárias, consolidando uma biorrefinaria;

- Realizar estudos de Prospecção Tecnológica para diferentes configurações e geometrias de fotobiorreatores, bem como para diferentes produtos energéticos de microalgas;

- Elaborar um livro acerca da temática desta tese, enfatizando as abordagens de integração de processos, incluindo massa, energia e água.

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