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REVIEW

Biomass valorization via pyrolysis in microalgae-based wastewater treatment: Challenges and opportunities for a circular bioeconomy

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Abstract
Microalgae-based wastewater treatment technology is a sustainable and environmentally friendly alternative to conventional treatment systems. The biomass produced during microalgae-based wastewater treatment can be valorized via pyrolysis to generate multiple valuable products, such as biochar, bio-oil, and pyrolytic gas. This study summarizes the potential of pyrolysis for valorizing microalgal biomass produced from wastewater treatment. It shows how pyrolysis can provide a variety of valuable products, the composition of which is influenced by the type of microalgae used, the operating conditions of the pyrolysis process, and the presence of contaminants in the biomass. It also highlights the main challenges to be addressed before pyrolysis can be adopted to valorize microalgae biomass. These challenges include the high energy requirements of pyrolysis, the need for further research to optimize the process, and the potential for pyrolysis to produce harmful emissions. Despite this, pyrolysis appears as a promising technology with potential to contribute to the sustainable development of a circular economy. Future research should address these challenges and develop more efficient and environmentally friendly pyrolysis processes.

Keywords Circular biosystem · microalgae technology · Pyrolysis · Syngas · Wastewater treatment

Introduction

Access to good quality water is becoming increasingly scarce and it is essential for the sustainability of ecosystems, human health, and social and economic development. As the global population continues to grow and natural environments become degraded, there is an increase in water demand and wastewater generation (Mishra et al. 2021). Wastewater is generated from various sources including agriculture, industries, and municipalities, and is typically rich in nitrogen, phosphorus and organic carbon. Depending on the type of wastewater, it can also contain a wide range of contaminants, such as heavy metals, pathogenic microorganisms, and contaminants of emerging concern, including microplastics, pharmaceuticals, pesticides, and personal care products (Ahmed et al. 2022). Treating wastewater before

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its discharge is crucial in order to prevent environmental pollution and ensure safe water reuse. Doing so can help mitigate the negative impacts on the environment and human health, while also contributing to sustainable development (Obaideen et al. 2022).

Traditional primary and secondary wastewater treatments are designed to remove easily settling solids and to oxidize organic matter, resulting in a seemingly clear effluent. However, this treated (secondary) effluent, which is discharged into natural water bodies, may still have organic micropollutants and heavy metals which can pose long-term problems (Abdel-Raouf et al. 2012). In addition to the environmental concerns, conventional activated sludge wastewater treatment systems are burdened with high costs due to the energy demand of aeration tanks and the treatment of produced sludge (Siatou et al. 2020). Hence, there is an urgent need for more cost-effective and sustainable solutions.

Microalgae offer an alternative to conventional biological wastewater treatments due to their high flexibility to changing conditions, such as nutrient availability and light intensity, and their ability to grow photoautotrophically, heterotrophically, or mixotrophically. These microscopic organisms are capable of removing excess nutrients (such as nitrogen and phosphorus) from wastewater and incorporating them into their biomass in the form of organic compounds. This biomass can then be used as a feedstock for producing biofuels, biofertilizers, animal feed, and bioactive compounds (Morais et al. 2021), thus promoting the circular bioeconomy principles. In addition, microalgae also possess the ability to remove organic contaminants from wastewater through processes such as bioaccumulation (Gojkovic et al. 2019), biosorption (Abbas et al. 2014) or biodegradation (Matamoros et al. 2015), providing an added advantage to their use in wastewater treatment. Despite the advantages of using microalgae for wastewater treatment, biomass contamination often impedes its reuse as food or feed, among other applications. Therefore, the biomass needs to undergo conversion processes that either degrade the contaminants or concentrate them into ash form (Abdel-Raouf et al. 2012).

An alternative and novel approach is to pyrolyze the microalgal biomass cultivated in wastewater. Pyrolysis is a thermochemical process that involves heating organic materials in the absence of oxygen or with limited oxygen supply, causing them to decompose into volatile gases, liquids, and solid residues. This process enables the conversion of various organic substances, including biomass, plastics, and waste materials, into valuable products such as bio-oil, pyrolytic gas, and biochar (Sekar et al. 2021) while mitigating environmental impacts by minimizing emissions and reducing the reliance on landfill disposal or traditional combustion methods. These pyrolysis products may have applications in other systems. For instance, bio-oil can be utilized as biofuel (Zhang et al. 2007), thereby contributing to the sustainability of fuels production; and pyrolytic gas can be used to generate thermal and electrical energy (Chen et al. 2017). As far as biochar is concerned, it could be applied as a filter within the microalgae wastewater treatment system, creating a closed-loop system (Xiang et al. 2020).

This review focuses on the valorization of the biomass produced during microalgae-based wastewater treatment via pyrolysis. While several reviews have already discussed wastewater treatment by microalgae (Yu et al. 2017; Lage et al. 2018; Daverey et al. 2019; Nagarajan et al. 2019; Hussain et al. 2021; Yadav et al. 2021), the present one highlights pyrolysis not only as a process for bioenergy conversion, but also for obtaining high-value products. The review summarizes different sources of wastewater, contaminants, microalgae species or consortia, and compares the composition of the biomass produced for potential valorization. Since pyrolysis involves the thermal degradation of biomass in the absence of oxygen, not only can contaminated biomass be used in this process, but it can also lead to the formation of multiple products, namely biochar, bio-oil and pyrolytic gas, thereby transforming waste into valuable products.

Microalgae and wastewater treatment

Biomass production in wastewater treatment systems

Two main characteristics of microalgae strains for wastewater treatment are high productivity and tolerance to extreme conditions (Morais et al. 2021). Generally, the strains that are most suitable for this type of cultivation are either genetically modified or have been isolated from environments with harsh conditions, such as those near power plants or waste treatment facilities (Lage et al. 2018). Among the different genera, *Chlorella* and *Scenedesmus* have demonstrated the best performance in developing under adverse conditions, as they are more robust (Álvarez-Díaz et al. 2017).

A notable feature of wastewater treatment with microalgae is that it seldom involves monoculture. Typically, microorganisms present in the medium grow rapidly and coexist with the inoculated strain. Mixed cultures are better adapted to wastewater and offer greater stability (Lage et al. 2018). Moreover, there is a symbiosis between microalgae and heterotrophic bacteria, by which microalgae provide oxygen through their photosynthesis wheras heterotrophic bacteria consume it in their respiration and release CO_2 which is again consumed by microalgae. Recently, research has also focused on other consortia such as fungi-microalgae (Leng et al. 2021). Mixed consortia have proven to be highly effective in wastewater bioremediation and biomass harvesting, owing to their larger morphology.

The treatment of waste effluents via microalgae is mainly conducted by green algae (such as *Chlorella*, *Scenedesmus*, *Botryococcus*, *Chlamydomonas*) and cyanobacteria (including *Spirulina/Arthrospira*, *Phormidium*, *Microcystis*, and *Synechococcus*) (Cai et al. 2013; Passos et al. 2015). Additionally, microalgae have the capacity to remove heavy metals and some toxic organic compounds, thus preventing secondary pollution (Abdel-Raouf et al. 2012; García-Galán et al. 2018; Moondra et al. 2020; Chaudry 2021).

Considering the concept of microalgae biorefinery, biomass from wastewater treatment has great potential to produce various bioproducts, such as proteins, fatty acids, pigments, biofertilizers, biochar and animal feed (Cai et al. 2013; Moondra et al. 2020). The composition of wastewater affects the growth of microalgae and the production of bioproducts. Some examples of wastewater that can be treated with microalgae culture include agricultural (García-Galán et al. 2018), municipal (Tang et al. 2023), and industrial wastewater (Amin et al. 2022). Microalgal treatment is also outlined as one of the technologies appropriate for the remediation of wastewater from the textile industry, often polluted with dyes. These effluents are highly toxic and comprise intricate, harmful, and challenging-to-treat components (Shabir et al. 2022).

The process of urbanization and the consequent increase in urban populations have led to the production of higher quantities of municipal wastewater containing relatively large amounts of heavy metals such as lead, zinc, and copper compared to liquid effluents from animal sources (Cai et al. 2013). Municipal wastewater used for microalgae cultivation can be broadly classified into the following categories: (1) raw sewage, which refers to municipal wastewater prior to primary settling; (2) primary effluent, which refers to municipal wastewater after primary settling for suspended solids removal; and (3) secondary effluent, which refers to municipal wastewater after biological treatment for organic matter removal. The nutritional profiles of different types of municipal wastewater can vary significantly, leading to significant differences in microalgal growth (Arashiro et al. 2019). For example, the biomass productivity of microalgae cultured in primary effluent can be as low as 25% of that in Tris–acetate phosphate medium, which may be overcome by using combined cultures with high concentrations of CO_2 (5–15%) (Zhao and Su 2014).

Agricultural wastewaters, particularly those from animal manure, are typically rich in nitrogen and phosphorus. About half of the nitrogen in animal waste is in the form of ammonium, while the rest is in organic nitrogen form. The nutrient content is significantly influenced by factors such as animal diet, age, use, productivity, management, and location. The nitrogen-to-phosphorus ratio (N/P) typically ranges from 2 to 8 for wastewater from confined dairy, swine, and bovine cattle operations (Cai et al. 2013; Li et al. 2019b). However, the high suspended solid and ammonia contents make this type of wastewater unsuitable for direct use in microalgae-based treatment systems. To treat manure, anaerobic digestion is typically used, followed by land application of the digestate. During the process, most of the organic carbon is converted into methane, an important greenhouse gas, leaving nitrogen and phosphorus in the digested effluent (Zhu et al. 2013; Bohutskyi et al. 2015). The C/N ratio is relatively low compared to that of concentrated manure, making digested manure an ideal medium for the growth of certain microalgae, such as *Rhizoclonium hieroglyphicum*, *Chlorella*, *Micractinium*, and *Actinastrum* (Pittman et al. 2011). However, the high concentration of nutrients can inhibit the growth of many strains (Pittman et al. 2011; Zhu et al. 2013).

Most industrial wastewater contains higher levels of heavy metals and lower amounts of nitrogen or phosphorus than other types of wastewaters, depending on the source (Morais et al. 2021). Certain species of microalgae can effectively remove toxic heavy metals in wastewater through absorption and adsorption, while others are sensitive to metal toxicity. Microalgae cells can assimilate heavy metals in low concentrations through micronutrient transporters, ultimately detoxifying them in specific cellular compartments, or removing them using the unique extracellular ultrastructure of the microalgae (Morais et al. 2021), making it possible to treat industrial wastewater with low levels of heavy metals. *Chlorella*, *Ankistrodesmus*, and *Scenedesmus* have been found to be effective in treating industrial wastewater (Rawat et al. 2011; Li et al. 2019b), along with some cyanobacteria (Arashiro et al. 2020). Concerning wastewater from textile industries, it is characterized by high salinity, temperature, variable pH, and strong colors, as well as a high chemical oxygen demand (COD). Microalgae can remove these colored dyes through biosorption or reducing mechanisms (Wang et al. 2016).

Microalgae present a versatile and environmentally beneficial approach to wastewater treatment. They excel in removing nutrients, such as nitrogen and phosphorus, from various types of wastewaters, including agricultural, municipal, and industrial effluents, thereby preventing the pollution of natural water bodies. Furthermore, microalgae possess the unique capability to absorb heavy metals and toxic organic compounds, contributing to the remediation of contaminated water sources. This dual capacity for nutrient removal and pollutant mitigation makes microalgae-based systems highly effective in sustainable wastewater management. Additionally, the resulting biomass from microalgae cultivation in wastewater can be harnessed for energy production, particularly through processes like pyrolysis, where heavy metals are transformed into stable forms, minimizing secondary pollution risks. Thus, microalgae offer a promising and holistic solution for wastewater treatment, environmental protection, and bioenergy production.

Nutrients and pollutants removal from wastewater

The primary purpose of using microalgae-based wastewater treatment systems is to remove nutrients and convert them into biomass. Additionally, certain pollutants such as heavy metals found in wastewater can directly affect the growth of microalgae. Therefore, it is crucial to understand the potential mechanisms by which microalgae can remove/metabolize the nutrients and pollutants from wastewater (Abdelfattah et al. 2023).

Microalgae can utilize two sources of carbon: inorganic carbon (such as CO_2 and HCO_3^-) and organic carbon (such as sugars, alcohols, and acids). Autotrophic microalgae can fix CO_2 from the atmosphere and industrial exhaust gases through photosynthesis. On the other hand, some microalgae exhibit heterotrophic behavior and can use organic forms of carbon for growth. Certain microalgae even display both autotrophic and heterotrophic characteristics (Cai et al. 2013; Liu and Hong 2021). In heterotrophic mode, microalgae metabolize organic carbon compounds present in wastewater (such as glucose, galactose, glycerol, ethanol, and acetate) for growth. These organic carbon sources enter the microalgae cells either through the plasma membrane or phagocytosis (Perez-Garcia et al. 2011).

Microalgae can use various forms of nitrogen, including ammonium (NH_4^+), nitrate (NO_3^-), nitrite (NO_2^-), urea, and amino acids present in wastewater to synthesize proteins, nucleic acids and phospholipids (Raven & Giordano 2016; Sniffen et al. 2018). Ammonium nitrogen is the preferred form because it does not require a redox reaction and consumes less energy (Morais et al. 2022). However, nitrate, being more oxidized and thermodynamically stable, is also an important source of nitrogen for microalgae, as it can induce reductase nitrate activity. In wastewaters with high concentrations of ammonium, it can be efficiently used for the rapid growth of microalgae (Cai et al. 2013; Barsanti and Gualtieri 2014) although high concentrations may be toxic (Ayre et al. 2017).

Inorganic phosphate (such as PO_4^{3-}, HPO_4^{2-}, and $H_2PO_4^-$) is the preferred form of phosphorus assimilated by microalgae, playing a significant role in their growth and metabolism (Su 2021). While microalgae primarily utilize inorganic forms of phosphorus, some species are capable of using organic esters as a source of phosphorus for growth. Although orthophosphate is generally considered a limiting nutrient in freshwater systems, excess phosphorus from wastewater drainage can contribute to eutrophication. Phosphorus removal from wastewater occurs not only through absorption by the cell, but also by precipitation. Since phosphorus does not exist in a gaseous state, elevated pH and dissolved oxygen concentration can prompt phosphate precipitation (Cai et al. 2013).

Some heavy metals, such as boron, copper, iron, zinc, cobalt, and molybdenum, are essential trace elements for the growth of microalgae, promoting enzymatic reactions and cellular metabolism (Durai and Rajasimman 2010). Heavy metals are commonly found in wastewater as pollutants, and microalgae have the ability to absorb them (Mehta and Gaur 2005; Bucková et al 2022). Biosorption is considered the main mechanism for the removal of heavy metals by microalgae (Liu and Hong 2021), so proper reuse/valorization of microalgal biomass is crucial to avoid secondary pollution caused by metal contamination in the generated biomass.

Microalgae have the ability to also remove antibiotics from wastewater (Villar-Navarro et al. 2018). The mechanisms involved in the removal of antibiotics by microalgae include biosorption, bioaccumulation, biodegradation, photodegradation and hydrolysis (Liu and Hong 2021). Antibiotics found in urban sewage originate from various sources, such as hospitals, households, and pharmaceutical industries (Szekeres et al. 2017). They are also used in the prevention and treatment of diseases in livestock and poultry, resulting in their presence in animal manure effluents (Zhang et al. 2018). The removal of antibiotics using microalgae has been studied but the mechanisms involved in the simultaneous removal of multiple antibiotics and the toxicity of intermediate products in the degradation process require further investigation (Liu and Hong 2021).

Consequences of microalgae composition and contamination in biomass valorisation

Heavy metals, drugs, xenobiotics, and other contaminants present in wastewater tend to accumulate in microalgal biomass cultivated in such media (Lage et al. 2018). Thus, the resulting biomass cannot be used for food and feed production, and in some cases, the algal biomass cannot even be used as a fertilizer. Typically, biomass obtained from wastewater cultivation is intended for energy production, such as the generation of heat, electricity, or fuel (Morais et al. 2021). Indeed, extensive research has been conducted on the production of biofuels from microalgae treating wastewater (Uggetti et al. 2017), following biological, chemical or thermal processes.

In the pyrolysis process, the fate of heavy metals present in the raw material depends on the characteristics of these metals. Metals with lower thermal stability, such as mercury, cadmium, arsenic and lead, are volatilized, while thermally stable metals, such as chromium, manganese and nickel, are enriched in the waste (Chanaka Udayanga et al. 2018). The enrichment in heavy metals is not problematic during pyrolysis, as the temperatures used (usually between 400 and 900 °C) result in minimal distribution of heavy metals in the gaseous and oil phases, and most of these compounds are concentrated in the biochar (Chanaka Udayanga et al. 2018). Moreover, biochar does not generate secondary pollution, as there is low leaching of heavy metals due to their conversion to stable forms during the process (Devi and Saroha 2014).

Pyrolysis as a downstream process in biomass biorefinery

Pyrolysis is a thermochemical decomposition process that involves the heating of organic materials (Chen and Lin 2016) in the absence of oxygen to produce useful products such as biochar, bio-oil, and pyrolytic gas and their distribution depends on the operating parameters of the reaction (Bridgwater 2012). The specific products obtained depend on factors such as temperature, residence time, pressure and the nature of the biomass, as well as other reactor conditions (Kesari et al. 2021; Sekar et al. 2021). Figure 1 shows the pyrolysis types and the most comon reactors used for each.

Microalgal biomass is a promising feedstock for pyrolysis due the high growth rate, high lipid, and low lignin contents of algae, which result in higher yields of bio-oil and pyrolitic gas compared to woody biomass (Maliutina et al. 2017). Microalgal biomass has a high nutrient content, making the resulting biochar an excellent soil amendment (Ağbulut et al. 2023). The application of pyrolysis to microalgal biomass produced in wastewater can provide a sustainable and renewable source of energy and reduce the environmental impact of waste disposal (Morais et al. 2021). The pyrolysis application on microalgal biomass can be: 1) direct pyrolysis of microalgae biomass, when this is too contaminated for valuable products extraction, and 2) a two-stage process, where high-value compounds are first extracted and the left-over biomass is then pyrolyzed. Li et al. (2022b) conducted direct pyrolysis on the biomass and Li et al. (2022a) a two-stage process involving lipid extraction from the biomass followed by pyrolysis of the residual biomass from the first stage. In both studies, *Desmodesmus* sp. EJ 8–10 was cultivated in anaerobic digestion effluent sourced from a pig farming facility, adjusted with small quantities of reagents to achieve adequate Fe, P, and Mg concentration, as these nutrients were identified as insufficient for microalgae cultivation in the effluent. Both studies produced increased value pyrolysis products (aliphatic hydrocarbons and fatty acids) and low amounts of toxic compounds (nitrogen-containing compounds and polycyclic aromatic hydrocarbons). These approaches also significantly contributed to reduce environmental impacts, as indicated by Life Cycle Assessment (LCA). Thus, this can be an outstanding key for the biorefinery process through microalgal biomass produced in wastewater and circular economy.

The main difference between slow, fast, and flash pyrolysis is the heating rate and the residence time of the biomass in the reactor. Slow pyrolysis takes place at low heating rates (0.1 to 10 °C min^{-1}) and long residence times (30 min to several hours), producing high-quality biochar with low yields of bio-oil and pyrolitic gas. Fast pyrolysis, on the other hand, involves high heating rates (100–1000 °C s^{-1}) and short residence times (seconds to minutes), resulting in higher yields of bio-oil and pyrolitic gas but lower-quality biochar. However fast pyrolysis is still the recommended technique for obtaining biochar from microalgal biomass, as it is easier to operate and allows for the vapour to remain inside the reactor for up to 60 min, resulting in a higher yield of solids (Sekar et al. 2021). Flash pyrolysis occurs at higher heating rate (HHV) and with much shorter annealing time than conventional pyrolysis, thus favoring the yield of

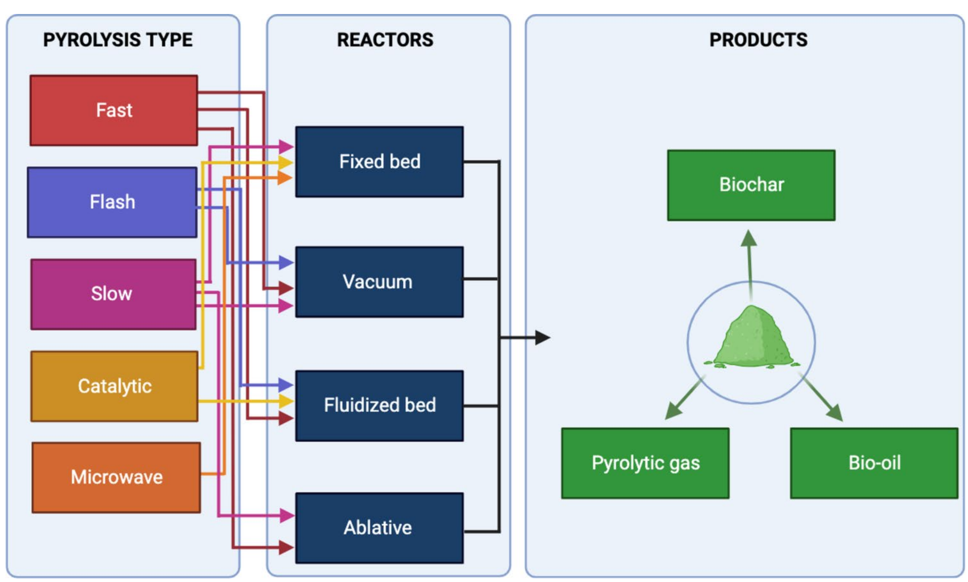

Fig. 1 Pyrolysis classification, reactors, and the main products produced from microalgae biomass

bio-oil and gases over biochar. For the flash pyrolysis to be effective, temperature, heating rate and residence time should be within the range of 450–600 °C, 103 – 104 °C s^{-1}, and < 1 s, respectively (Ighalo et al. 2022). Pyrolysis can be carried out in various types of reactors, including fixed-bed, fluidized-bed, and vacuum reactors (Ağbulut et al. 2023).

Catalyst pyrolysis is generally conducted at temperatures between 300 and 600 ºC, and could reduce the entire pyrolysis temperature and duration, and enhance the effectiveness and performance of the procedure (Sun et al. 2022). Catalytic biomass pyrolysis is categorized into three main groups of catalytic reactions: non-metallic catalysis (e.g., zeolite and activated carbon), monometallic catalysis, and bimetallic catalysis (Lee et al. 2022). The catalysts play a role on the deoxygenating and denitrification, converting O-containing compounds into aromatic compounds and N-containing compounds into ammonia, being used mainly for bio-oil production (Sun et al. 2022). Bio-oil generated from conventional pyrolysis processes typically exhibits drawbacks such as high oxygen and biomass moisture contents, along with low higher heating value (HHV), high viscosity, and elevated total acidity number (Park et al. 2021). Catalytic pyrolysis effectively overcomes these issues and reduces the activation energy during pyrolysis (Wang et al. 2021). Thus, catalytic pyrolysis is the most suitable process to address these deficiencies. However, it is necessary to select the ideal catalyst to achieve the desired product characteristics. This ideal catalyst might vary, given the utilization of different biomasses and pyrolysis process configurations (Seo et al. 2022). Catalytic pyrolysis of cow manure over HZSM-5 zeolite exhibited high potential for the production of valuable biofuels such as benzene, toluene, ethylbenzene, xylene, and naphthalene (BTEXN), as well as greater capacity to suppress harmful products compared to other zeolites (HBeta and HY) (Valizadeh et al. 2022). Meanwhile, in the catalytic pyrolysis of a commercial wood-plastic composite (HBeta) produced a larger quantity of aromatics compared to the other zeolite catalysts (HZSM-5 and HY) (Park et al. 2019).

Microwave and catalyst pyrolysis are considered advanced methods of pyrolysis that, compared to the conventional slow and fast pyrolysis, have less energy and lower temperature requirements as well as the possibility to eliminate contaminants from bio-oil like solid residues and decrease its oxygen, sulfur, nitrogen and phosphorus content. These methods can improve product selection by altering the pyrolysis reaction pathways (Ağbulut et al. 2023).

Microwave-assisted pyrolysis creates heat from the center of the biomass towards the outside and has as advantages the short process time and selective and uniform internal heating being therefore indicated for high moisture content raw materials (Chen et al. 2021). This technique uses radiofrequency waves in the range of 0.3 to 300 GHz (Sekar et al. 2021) and thus could be unfavorable for producing bio-oil as the chemical bonds of molecules of macronutrients could be easily broken under the directly-transferred energy of microwaves resulting in rapidly degradability of this compounds in the process reducing bio-oil yield (Ağbulut et al. 2023).

In summary, the downstream process in microalgae biomass biorefinery, specifically pyrolysis, plays a crucial role in transforming microalgae biomass into valuable products. Pyrolysis can be tailored to suit different scenarios, either as a direct process for contaminated biomass or as a two-stage approach with lipid extraction preceding pyrolysis. Bio-oil derived from microalgae can serve as a source of green transportation fuels or valuable chemicals, although it may require further upgrading to match the properties of fossil fuels. Pyrolytic gas generated in the process is a cost-effective and sustainable source of energy, with potential applications in thermal and electrical energy generation and hydrocarbon synthesis. Biochar, another valuable product of pyrolysis, has diverse applications, including carbon sequestration, soil improvement, wastewater treatment, and even as a precursor for manufacturing nanoparticles. These downstream processes demonstrate the versatility and potential of microalgae biomass generated in wastewater treatment systems can contribute to a circular economy and sustainable biorefinery processes.

Bio-oil

Bio-oil derived from microalgal biomass pyrolysis is typically a dark brown liquid with a smoky odor, composed of a complex mixture of several hundreds of organic compounds, primarily aliphatic and aromatic hydrocarbons, oxygen-containing compounds, and nitrogen-containing compounds (Saber et al. 2016). The chemical composition highly depends on the type of biomass, pyrolysis process and operating conditions, resulting in different physical properties of bio-oils (Table 1). Generally, bio-oil has been considered a sustainable source of green transportation fuels or feedstock for valuable chemicals. However, bio-oil has some drawbacks, such as higher density, higher water content, higher viscosity, and lower heating value when compared to fossil fuels (Zhang et al. 2007). Nevertheless, bio-oils produced from microalgae typically exhibit HHV ranging from 25 to 41 MJ kg^{-1} (Table 1), lower oxygen content and a desirable pH, showing their tremendous potential as biofuel products compared to conventionally used lignocellulosic biomass, where HHV range between 16 and 19 MJ kg^{-1} (Isahak et al. 2012).

To further enhance both the yield and quality of bio-oil, fast pyrolysis has been utilized for the biomass of *Chlorella protothecoides* and *Microcystis aeruginosa*, with higher HHV resulting in lower viscosity compared to those produced by slow pyrolysis (Miao et al. 2004). Additionally,

Table 1 Pyrolysis conditions and bio-oil yields for different microalgae species and treatments

Microalgae	Pyrolysis type	Bio-oil (%)	C	H (% dry mass)	N	O	Water (% mass)	HVV (MJ kg^{-1})	Reference
Chlorella protothecoides	fast, 500 °C	17.5	62.07	8.76	9.74	19.43	-	30	Miao and Wu (2004)
Chlorella protothecoides (heterotroph)	fast, 500 °C	57.9	76.22	11.61	0.93	11.24		41	
Chlorella vulgaris	fast, 400 °C	42	59.5	7.6	8.0	24.9	29	27.9 ± 0.5	Belotti et al. (2014)
C. vulgaris N-starved	fast 400 °C	-	61.0	8.2	6.0	24.8	30	28.9 ± 0.8	
C. vulgaris remnants	fast 500 °C	53	51.4	8.34	12.8	27.46	15.89	24.57	Wang et al. (2013)
Chlorella sp.	fast, 500 °C	35.5	54.52	9.06	11.51	25.69	-	25.5	Campanella and Harold (2012)
Chlorella sp.	catalytic (zeolites crystallites), 500 °C	28.9–34.6	58.54–63.64	8.44–8.99	9.18–10.96	19.41–23.58	-	26.8–29.1	
Chlorella sp.	microwave-assisted		65.4	7.84	10.28	16.48	-	30.7	Du et al. (2013)
Chlorella sp.	batch, 450 °C	34	54.4	9.6	7.3	28.2	17.9	29.8	Rizzo et al. (2013)
C. vulgaris	catalytic (Ni loaded zeolites), 500 °C	10	47	-	30	10			Zainan et al. (2018)
Chlorella sp.	catalytic, 450 °C	40	-	-	-	-	32	32.2	Babich et al. (2011)
Microcystis aeruginosa	fast 500 °C	23.7	60.99	8.23	9.83	20.95	-	29	Miao et al. (2004)
Nannochloropsis sp. residue	slow, 400 °C	31.1	56.13	7.63	5.34	30.09		24.4	Pan et al. (2010)
Nannochloropsis sp. *residue*	catalytic, slow, 400 °C	19.7	65.21	9.83	5.43	19.5		32.7	
Pavlova sp.	500 °C	18.68	68.31	8.84	8.75	14.10		33.32	Aysu et al. (2017)
Pavlova sp.	catalytic (titania-based)	20.04–22.55	72.27–75.20	9.02–9.47	6.12–6.58	9.47–12.48		35.21–37.07	
Scenedesmus sp.	fast, 480 °C	55	51.9	9.0	8.6	27.6		18.4	Harman-Ware et al. (2013)
Spirulina platensis	500 °C	28.5	74.66	10.57	7.13	6.81		33.62	Jena and Das (2011)
Spirulina spp.	slow, 550 °C	45	46.05	7.97	9.7	36.28	32.42	21.68	Chaiwong et al. (2013)

controlling the growth conditions of microalgae can alter the biomass composition, thereby changing the properties of the bio-oil produced by pyrolysis. For instance, fast pyrolysis of heterotrophically grown *C. protothecoides* led to 3.4 times more bio-oil than those grown autotrophically, resulting in bio-oil with lower viscosity and a HHV of 41 MJ kg^{-1} (Miao and Wu 2004). In another study, fast pyrolysis of nitrogen-starved *C. vulgaris* resulted in a bio-oil yield of 42%, with an increased HHV of 28.9 MJ kg^{-1} and a lower nitrogen content than when microalgae were grown under nutrient repletion (Belotti et al. 2014).

Residual microalgae biomass, such as residues after the extraction of lipids or high-value compounds, can also be processed by pyrolysis in a biorefinery approach. For instance, the fast pyrolysis of *C. vulgaris* remnants resulted in a 53% bio-oil yield, with a high heating value of

24.6 MJ kg^{-1} (Wang et al. 2013). In a different approach, the residual biomass of *Haematococcus pluvialis* after astaxanthin extraction was subjected to pyrolysis at 600 °C, resulting in a bio-oil yield of 26.58% (Gong et al. 2020).

Bio-oil obtained from microalgae pyrolysis has some drawbacks such as high contents of oxygen and nitrogen compounds, which may limit its application as transportation fuel (Babich et al. 2011). Oxygenates such as aldehydes, ketones, acids and phenols reduce the energy content and stability of bio-oil as compared to conventional fuels, and an increased acidity can cause corrosion problems. Furthermore, pyrolysis of protein-rich microalgae biomass leads to nitrogen-containing compounds such as amines, amides, pyridines, pyrroles, pyrazoles, pyrazines, polyheteroaromatics, nitriles, imidazoles and indoles (Andrade et al. 2018), which are undesirable in biofuels due to their potential to release atmospheric pollutants such as NOx gases during combustion processes (Zainan et al. 2015).

Catalytic pyrolysis has great potential to reduce oxygen and nitrogen containing compounds, leading to an increase in the hydrocarbon ratio and the HVV of the produced bio-oil. An extensive review of different catalysts applied to microalgal biomass by Lee et al. (2020) and Li et al. (2019a) has been provided. Metal-loaded zeolites, particularly with nickel and palladium, have been identified as the most efficient catalysts for upgrading microalgal bio-oil by decreasing the nitrogen and oxygen contents and producing significant petrochemicals such as aromatics and olefins. For example, protein-rich *Arthrospira* spp. has been shown to produce bio-oil with a lower oxygen content compared to lignocellulosic biomass after catalytic pyrolysis over H-ZSM5 (23) (Chagas et al. 2016). Besides, *C. vulgaris* catalytic pyrolysis using nitrogen supported zeolites (Si/Al = 30) produced bio-oil with high hydrocarbon content and fewer oxygenated and acidic compounds compared to non-catalytic pyrolysis (Zainan et al. 2018). Meanwhile, *Nannochloropsis* sp. catalytic pyrolysis using zeolite (HY) resulted in low nitrogen content (1.25 wt%) and high monocyclic aromatic yield, although the bio-oil yield (38.3%) was lower than that without catalyst (58.1%) (Tang et al. 2021).

However, the fuel properties of bio-oil are still inferior to those of fossil fuels, which limits their direct use. Therefore, upgrading processes are necessary. Various techniques can be employed for this purpose, including chemical processes such as catalytic esterification, hydrothermal liquefaction, hydrodeoxygenation and catalytic hydroprocessing, as well as physical processes like hot vapor filtration, solvent addition and emulsion formation (Xiu and Shahbazi 2012; Saber et al. 2016; Sharifzadeh et al. 2019). While upgrading can render bio-oil suitable for use as biofuel, the process involves additional steps, chemicals, and equipment, which incurs additional costs (Sorunmu et al. 2020).

Bio-oil has potential applications beyond biofuels, such as the extraction of valuable green chemicals. For instance, liquid–liquid extraction can be used to extract phenols that can serve as raw materials for developing bio-based antioxidants, resins, and additives (Shah et al. 2017). Furthermore, chemicals derived from bio-oil can be used in various industries, including surfactants, biodegradable polymers, preservatives, liquid smoke, resin precursors, adhesives, fertilizer additives, pharmaceuticals and flavoring agents in food (Xiu and Shahbazi 2012). However, the commercialization of these products from bio-oil requires further investigation into the economic aspects of separation and refining techniques.

Pyrolytic gas

There are differences between pyrolytic gas and anaerobic biogas in terms of their production process and composition. Pyrolytic gas is produced by the thermal decomposition of biomass and consists mainly of hydrogen and carbon monoxide (Chen et al. 2017). Conversely, anaerobic biogas is generated by bacterial decomposition of organic matter under anaerobic conditions, primarily composed of methane and carbon dioxide (Costa et al. 2022). In addition, obtaining gas through the pyrolysis process is considered a more cost-effective and sustainable approach of producing energy compared to biochemical methods (Hämäläinen et al. 2022). Pyrolysis decomposes all biomass through the application of heat, which is not possible in anaerobic digestion due to the presence of recalcitrant materials. Moreover, pyrolysis generates high calorific biofuels, while stabilizing heavy metals, reducing organic contaminants, and eliminating pathogenic microorganisms (Yuan et al. 2013).

Flash pyrolysis is a process that generates higher gas yields compared to other processes. This method uses elevated temperatures (≥ 1000 °C s^{-1}) and short residence times of pyrolytic vapors (< 2 s) (Lee et al. 2020). Fluidized bed or entrained flow reactors are the most commonly used for pyrolytic gas production, and small particle size biomass (< 0.1 mm) is recommended to achieve rapid heating rates and complete biomass (Yu et al. 2018a). During microalgae pyrolysis, the main gases produced are CO_2 (50–65%), H_2 (10–9%), CO (10–19%), and light hydrocarbons, predominantly CH_4 (10%) (Du et al. 2011; Bach and Chen 2017; Chen et al. 2017; Maliutina et al. 2017; Azizi et al. 2020). The formation of these gases results from the cracking of carbonyl and carboxyl groups in carbohydrates and proteins, which produce CO_2, ether bonds and carbonyl groups generating CO, polycondensation and demethoxylation reactions that form H_2 and CH_4, respectively. Scission and cyclization reactions of long-chain fatty acids also produce other gases (Chen et al. 2017).

The primary application for gas produced via pyrolysis is thermal and electrical energy generation. Additionally, H_2 and CO can serve as raw materials for the synthesis of hydrocarbons through thermochemical pathways, such as the Fischer–Tropsch process (Chen et al. 2017), and are the primary components of pyrolytic gas/syngas (Hong et al. 2017) (Fig. 2). Factors such as biomass composition, type of pyrolysis process used, temperature, pressure, residence time of pyrolytic gases, heating rate, and reactor type all impact the yield and composition of pyrolysis products — biochar, bio-oil and pyrolytic gas (Table 2).

Temperature is one of the most impacting parameters in the yield of pyrolysis products. Pyrolytic gas production increases at higher temperatures. For instance, in the pyrolysis of *Nannochloropsis* the gas yield was approximately 47, 49 and 57% at temperatures of 400, 500 and 600 °C, respectively (Aysu and Sanna 2015). Similarly, non-catalytic pyrolysis of *S. platensis* in a fixed bed reactor had the highest gas yield at a temperature of 700 °C (29.67%); while at lower temperatures (400 and 500 °C), higher yields of biochar (40%) and bio-oil (34.49%), were obtained (Jafarian and Tavasoli 2018).

The composition of pyrolytic gas is also affected by the process temperature. At lower temperatures (400–500 °C), CO_2 is the primary product. This is due to the cracking and reformation of carbonyl (C = O) and carboxyl (COO^-) containing molecules from microalgae biomass, which are mainly carbohydrates and proteins (Jie et al. 2008). However, as the temperature increases (600–800 °C), CO_2 production decreases while H_2, CH_4, and CO production increases. H_2 production has been attributed to intermediate dehydrogenation reactions and secondary cracking of carbohydrates, proteins and lipids contained in the biomass (Sanchez-Silva et al. 2012; Yuan et al. 2015). CH_4 release is mainly provided by the final chain fission reactions of long-chain aliphatic acids and long-chain N-containing compounds in lipids and proteins (Vinu and Broadbelt 2012; Chen et al. 2016). CO is mainly formed by the cracking of the ether bond (C–O–C) and the C = O groups (Yang et al. 2007). The temperature increase also causes scission and cyclization reactions of long-chain fatty acids, generating small hydrocarbons such as C_2 (Vinu and Broadbelt 2012; Chen et al. 2016).

The compounds present in microalgae biomass have a significant impact on pyrolytic gas composition. For instance, *S. platensis* (50—70% protein) and

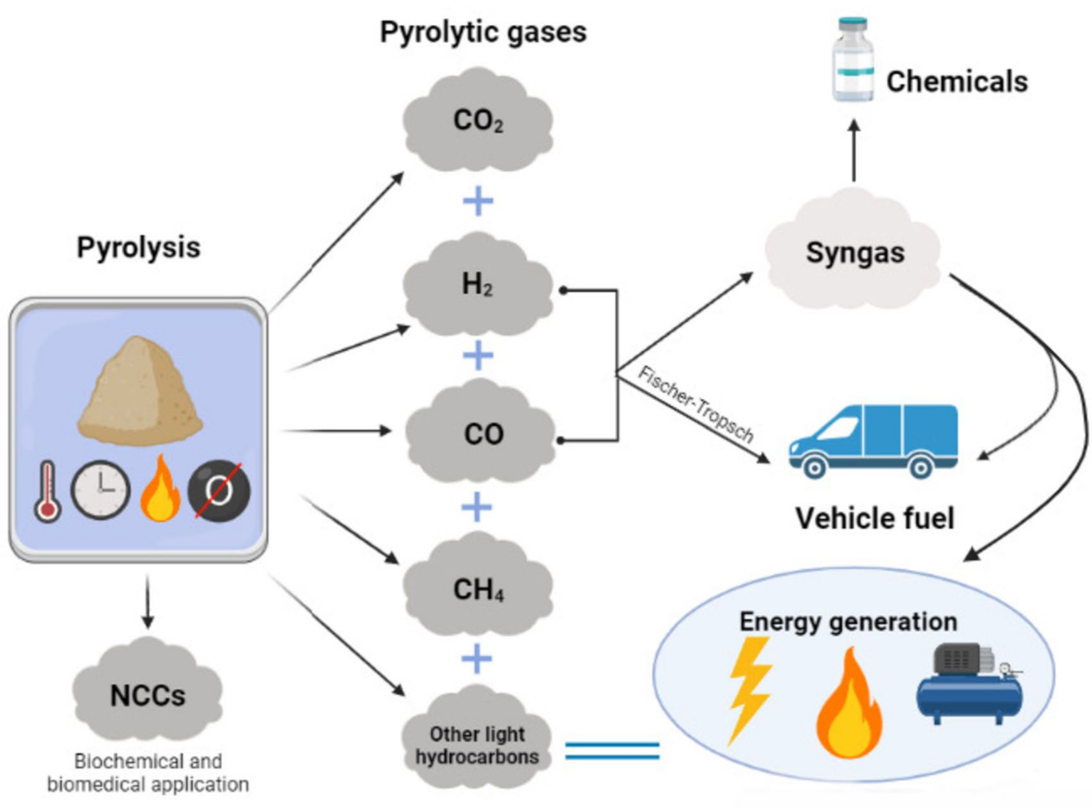

Fig. 2 Applications of gas produced by pyrolysis

Table 2 Influential factors on yield and composition of pyrolytic gas from microalgal pyrolysis

Microalgae	Pyrolysis type	Process feature	Reactor	T (°C)	Heating rate	Residence. time (s)	Pyrolytic gas (%)	Gas composition	Reference
Nannochloropsis sp.	Catalytic pyrolysis	$MgCe/ZrO_2$ catalyst; N_2_15 mL min^{-1}	Fixed-bed reactor	600	50 °C min^{-1}	4.2	61.23	About 40% N in gas	Aysu et al. (2017)
Nannochloropsis	Fast pyrolysis	N_2—100 mL min^{-1}	Spouted-bed reactor	500	15 °C min^{-1}	ND	12	H_2 (19%); CH_4 (2,5%); CO (20%); CO_2 (50%);	Azizi et al. (2020)
Tetraselmis	Fast pyrolysis	N_2—100 mL min^{-1}	Spouted-bed reactor	500	15 °C min^{-1}	ND	13	H_2 (10%); CH_4 (10%); Co (10%); CO_2 (65%);	
Isochrysis galbana	Fast pyrolysis	N_2—100 mL min^{-1}	Spouted-bed reactor	500	15 °C min^{-1}	ND	12.5	H_2 (16%); CH_4 (9%); CO (15%); CO_2 (55%);	
Scenedesmus almeriensis	Microwave-assisted pyrolysis	Microwave power 950 W	Quartz reactor	800	ND	ND	57.5	H_2 (48%); CO (40%); CH_4 (5%); CO_2 (5%);	Beneroso et al. (2013)
Spirulina platensis	Fast pyrolysis	Ar – 200 mL min^{-1}	Fixed-bed reactor	800	10—25 °C s^{-1}	ND	25	CO_2 (21 mL g^{-1}); H_2 (90 mL g^{-1}); CH_4 (90 mL g^{-1}); CO (90 mL g^{-1});	Chen et al. (2017)
Nannochloropsis sp.	Fast pyrolysis	Ar – 200 mL min^{-1}	Fixed-bed reactor	800	10—25 °C s^{-1}	ND	32.18	CO_2 (31 mL g^{-1}); H_2 (75 mL g^{-1}); CH_4 (90 mL g^{-1}); CO (122 mL g^{-1});	
Chlorella sp.	Microwave-assisted pyrolysis	Microwave power 1250 W	Quartz reactor	627	30 °C min^{-1}	20 min	35	H_2 (30%); CH_4 (27%); CO_2 (22%); CO (20%);	Du et al. (2011)
Spirulina	Microwave-assisted pyrolysis	Microwave power	Cylindrical quartz reactor 3 kW	700	140 °C min^{-1} reduced to about 30 °C min^{-1}	30 min	83.7	CH_4 (14%); CO_2 (5%); CO (49%); H_2 (31%);	Hong et al. (2017)
Chlorella	Microwave-assisted pyrolysis	Microwave power 3 kW	Cylindrical quartz reactor	400	140 °C min^{-1} reduced to about 30 °C min^{-1}	30 min	84	CH_4 (15%); CO_2 (18%); CO (22%); H_2 (31%);	
Spirulina *(Arthrospira) platensis*	Catalytic pyrolysis	Ce/HMS-ZSM5 catalyst	Dual-bed pyrolysis reactor	700	1°C min^{-1}	6 h	29.65	CH_4 (4 mmol g^{-1}); CO_2 (5 mmol g^{-1}); CO (3 mmol g^{-1}); H_2 (2.5 mmol g^{-1});	Jafarian and Tavasoli (2018)

Table 2 (continued)

Microalgae	Pyrolysis type	Process feature	Reactor	T (°C)	Heating rate	Residence. time (s)	Pyrolytic gas (%)	Gas composition	Reference
Chlorella vulgaris	Pressurized entrained-flow pyrolysis	Pressure 0.1 MPa	Entrained-flow pyrolysis	900	ND	5 – 6 s	23.87	CH_4 (15%); CO_2 (18%); CO (22%); H_2 (88,01%);	Maliutina et al. (2018a)
Chlorella vulgaris	Conventional pyrolysis	N_2 (100 mL min^{-1})	Fixed-bed reactor	900	10 °C min^{-1}	ND	58.29	CH_4 (22%); CO_2 (28%); CO (22%); H_2 (28%);	Yuan et al. (2015)
*Corncob	Conventional pyrolysis	N_2 (100 mL min^{-1})	Fixed-bed reactor	800	10 °C min^{-1}	ND	41.43	CH_4 (37%); CO_2 (24%); CO (4%); H_2 (32%);	
Chlorella vulgaris	Flash pyrolysis	N_2 atmosphere	Entrained-flow pyrolysis	900	ND	5 – 6 s	29.09	CH_4 (2%); CO_2 (5%); CO (42%); H_2 (40%);	Maliutina et al. (2017)
*Palm kernel shell	Flash pyrolysis	N_2 atmosphere	Entrained-flow pyrolysis	900	10^4–10^5 °C s^{-1}	5 – 6 s	31.78	CH_4 (12%); CO_2 (10%); CO (50%); H_2 (26%);	

ND not described; *Lignocellulosic biomass

Nannochloropsis (20- 40% protein) produce large amounts of H_2 and CH_4 through dehydrocyclization and demethoxylation, respectively, of protein molecules. *Nannochloropsis* sp. also resulted in higher production of C_2 due to its high content of long-chain fatty acids. In contrast, *Enteromorpha prolifera*, which has C–O–C and C = O groups primarily in carbohydrates (51.4%), produced greater amounts of CO than the other mentioned microalgae (Chen et al. 2017).

Microalgae can have high nitrogen contents (more than 10%) (Huang et al. 2017) compared to other lignocellulosic materials (approximately 1%) (Cavalaglio et al. 2020). Thus, microalgae are suitable for producing nitrogen-containing compounds (NCCs) via pyrolysis. Primary and secondary pyrolysis reactions can generate products such as indole, pyridine, quinolines, amides, and nitriles, which have diverse biochemical and biomedical applications (Yu et al. 2018a). The operating pressure can influence the distribution of nitrogen in the pyrolysis products as high pressures favor the accumulation of NCCs in the pyrolytic gas. For instance, the pyrolysis of *C. vulgaris* at pressures greater than 2.0 MPa promoted the transfer of nitrogen-containing compounds, mainly NH_3 and HCN, to the gas phase. However, lower pressures (0.1 and 1.0 MPa) led to nitrogen retention in bio-oil and biochar, respectively (Maliutina et al. 2018b).

Catalytic pyrolysis uses catalysts to promote or prevent reactions as deoxygenation, deamination and denitrogenation. This makes it possible to control the nitrogen content, concentration, and selectivity of NCCs. For instance, Wang et al. (2021) found that combining lanthanum ferrite perovskite ($LaFeO_3$) and a hydrogen atmosphere (H_2) during *S. platensis* pyrolysis led to the transfer of fuel nitrogen to the gas phase. This modified atmosphere was created using catalytic pyrolysis, and the resulting gaseous product showed a nitrogen fuel content of 51%. In contrast, when the same pyrolysis was conducted without a catalyst or in a normal atmosphere, NH_3 production led to only approximately 33.5% nitrogen accumulation in the fuel.

By adjusting the process parameters, it is possible to induce pyrolysis and generate a higher yield of pyrolytic gas. Using auxiliary technologies can also help upgrading hydrogen and gaseous fuel production. Selecting the right microalgae is essential in this process, as biomass with a higher carbohydrate content facilitates the generation of pyrolytic gas (Hong et al. 2017).

Advanced types of pyrolysis, such as catalytic, microwave, vacuum, solar, carbon dioxide, and co-pyrolysis, are being researched and improved to increase the yield of pyrolytic gas, reduce the reaction temperature, and increase the concentration of H_2 in the product (Foong et al. 2021). However, raising the levels of H_2 in the pyrolytic gas can also be achieved through simpler techniques, such as controlling the process pressure. For instance, in *C. vulgaris* entrained flow pressurized pyrolysis, the H_2 concentration reached 88% in syngas at 900 °C and 4 MPa (Maliutina et al. 2018a).

Additionally, the pyrolysis process is sustainable, flexible, and can yield multiple products. The pyrolytic gas/syngas produced through pyrolysis can be used directly as a raw material for boilers, engines, and turbines without any upgrading process. However, pyrolytic gas production is often overlooked. Although there are many microalgae pyrolysis studies, most of them focus on bio-oil or biochar production, likely because microalgae are generally rich in proteins, which results in a low yield of the gaseous fraction.

Biochar

Biochar is a carbon-rich solid produced by a reductive thermal processing, or pyrolysis, of various biomasses (Ahmad et al. 2014). Slow pyrolysis is the primary method used to produce biochar, while other forms of pyrolysis may generate it as a byproduct (Fakayode et al. 2020; Lee et al. 2020). Biochar is a stable carbonaceous material with a high carbon content and a long half-life, which means that it slows down the release of CO_2 into the atmosphere. Instead, CO_2 is gradually returned to the environment through processes such as decomposition, combustion, and consumption (Fakayode et al. 2020; Lee et al. 2020). The properties of biochar, such as mineral content, organic carbon, surface functional groups and pore structure, are influenced by the type of biomass used and the operational conditions during pyrolysis (Fakayode et al. 2020).

Microalgae are considered potential candidates for biochar production due to their sustainable and renewable nature. Table 3 shows the production conditions, yield and composition of biochar produced by different microalgae in different conditions. Azizi et al. (2020), used 3 different microalgae species for fast pyrolysis in a conical spouted bed reactor, and obtained a higher volatile content with *Isochrysis galbana* biomass, which also resulted in a lower biochar yield compared to that obtained for *Nanochloropsis* and *Tetraselmis*. However, the produced biochar composition was similar for all microalgae. The lower the applied temperatures the highest biochar yields were obtained. Jafarian and Tavasoli (2018) studied the pyrolysis of *S. plantensis* in temperatures varying from 400 to 700 °C and obtained the highest yield at 400 °C with a residence time of 30 min and a heating rate of 10 °C min^{-1} (40%).

Microalgae can sequester carbon, thereby reducing atmospheric CO_2 levels in the presence of sunlight during biomass production (Cheah et al. 2015; Suganya et al. 2016). The conversion of microalgal biomass into biochar with high carbon content can be seen as a strategy for capturing and storing carbon, representing a sustainable long-term solution for reducing greenhouse gas accumulation in the atmosphere (Heilmann et al. 2010). Yu et al. (2018b) demonstrated that the production of *C. vulgaris* FSP-E and production of biochar from its biomass through slow pyrolysis could be a sustainable technology for carbon sequestration and microalgal biorefinery. The biomass cultured in 2.5% CO_2 produced a biochar yield of 27% and showed potential for application as an alternative coal for energy production due to a HHV of 23.4 MJ kg^{-1}, which is similar to the calorific value of coal. As a fuel, biochar has potential usage in direct combustion since it emits lower quantities of CO_2 and presents similar or higher energy content to fossil fuels (Lee et al. 2020).

The usage of biochar is diverse due to its availability of functional groups, inert nature, as well as its capability of sequestering liquid or gas molecules (Lee et al. 2020). Biochar can be used as a fertilizer or soil agent due to its high nitrogen and mineral contents (phosphorus, iron, calcium, magnesium), and can also be used to retain water resources in plantations (Lee et al. 2020). Due to the material's high porosity, it can also be used as an absorbent material (Bordoloi et al. 2016; Moon et al 2023). Moreover, biochar has been attracting attention for wastewater treatment due to its properties such as pore structure, elevated specific surface area, and hydrophobicity (Sekar et al. 2021).

Microalgal biomass can be used for the production of biochar after the extraction of products like lipids, making this application even more sustainable under a biorefinery process. Amin and Chetpattananondh (2019) studied the slow pyrolysis of *Chlorella* sp. BC-450 residue after extraction with methanol/hexane of a fraction rich in lipids and pigments in a fixed bed reactor and obtained a high surface area biochar (266 m^3 g^{-1}) rich in ash and O-functional groups indicating its suitability for heavy metal adsorption. Wang et al. (2013) produced biochar from *C. vulgaris* remnants after lipids extraction through fast pyrolysis and obtained a product rich in inorganic compounds (potassium, phosphorous, and nitrogen), suggesting that it may be suitable to be used as a fertilizer (Table 3).

Water and wastewater treatment is an emerging application of biochar due to its exceptional sorption capacity for both inorganic and organic compounds. This sorption capacity is attributed to biochar's properties such as high surface area and pore volume, organic carbon content, mineral components, and diverse functional groups. These characteristics make biochar an efficient tool for removing organic contaminants such as dyes, phenols, polycyclic aromatic hydrocarbons, pesticides, and antibiotics, as well as inorganic contaminants, including heavy metals and nitrates, from wastewater (Xiang et al. 2020).

The removal of heavy metals from wastewater by biochar is attributed to various mechanisms such as electrostatic attraction between heavy metals and the biochar's surface; ionic exchange between heavy metals and alkaline or alkaline earth metals or protons on the biochar's surface; complexation with a domain rich in π electrons

Table 3 Pyrolysis conditions and biochar yields for different microalgae species

Biomass	Pyrolysis type	Reactor	T (°C)	Heating rate	Residence Time	Yield (%)	Biochar composition	Reference
Chlorella sorokiniana	Slow pyrolysis	Fixed bed	500	5 °C min^{-1}	-	31.2	-	Pena et al. (2023)
Tetraselmis	Fast pyrolysis	Conical spouted bed	500	15 °C min^{-1}	-	30.0	C (71.8%); H (3.6%); N (10.5%); O (14,0%); Ash (62.5%)	Azizi et al. (2020)
Isochrysis galbana						21.0	C (72.4%); H (3.4%); N (11.2%); O (13.0%); Ash (68.8%)	
Nannochloropisis						30.0	C (72.4%); H (4.5%); N (11.5%); O (11.7%); Ash (75.0%)	
Chlorella sp. BC-450 residue	Slow pyrolysis	Tube furnance	450	10 °C min^{-1}	60 min	45.0	C (17.2%); H (5.8%); N (3.2%); O (29.7%); Ash (43.0%)	Amin and Chetpattananondh (2019)
Spirulina platensis	Slow pyrolysis	Dual- bed	400	100 °C min^{-1}	30 min	40.0	-	Jafarian and Tavasoli (2018)
Chlorella vulgaris FSP-E	Slow pyrolysis	Fixed-bed	500	10 °C min^{-1}	30 min	27.0	C (61.3%) H (3.5%) N (9.8%) O (11.9%) Ash (13.4%)	Yu et al. (2018b)
Chlorella vulgaris residue	Fast pyrolysis	Fluidized-bed	500	-	-	31.0	C (61.9%) H (3.9%) N (9.4%) O (4.9%) Ash (19.9%)	Wang et al. (2013)

or surface functional groups; and co-precipitation to form insoluble compounds (Tan et al. 2015; Moon et al 2023). Organic compounds can also be removed using microalgal biochar through sorption mechanisms such as pore filling, hydrophobic effect, electrostatic interaction, and hydrogen bonding.

Although biochar exhibits properties similar to activated carbon, its heterogeneity makes sorption more complex, particularly in situations involving ionic force, pH, or the presence of organic matter. Therefore, parameters and operation conditions for large-scale installation are still limited (Wang et al. 2020). Activated carbon can be modified to improve its adsorption capabilities for wastewater treatment (Azam et al. 2022). Following a similar approach, iron-impregnated biochar demonstrated greater efficiency for the treatment of wastewater contaminated with glyphosate compared to unmodified biochar (Zaparoli et al. 2023).

Other application of biochar could be the manufacturing of nanoparticles with sensor properties. Pena et al. (2023) produced biochar from *C. sorokiniana* through slow pyrolysis, aiming to apply the product to sinter carbon dots, nanoparticles with relevant electronic and optical properties that have gained attention in recent years due to numerous application areas, such as catalysis, diagnosis, and drug sensing, bioimaging and toxic metal sensors (Pb^{2+}, Cu^{2+}, Cd^{2+}, and Ni^{2+}) for detection in aqueous medium (Table 3).

Compared to cellulosic biomass of higher plants, microalgal biochar has a lower carbon content, surface area and cation exchange capacity. However, its pH, ash content, nitrogen and inorganic nutrient content are alkaline which make it an effective soil pH corrector for increasing agricultural crop productivity (Yang et al. 2019). The addition of biochar can also improve the quality of compost as an agricultural fertilizer. Biochar-added compost offers advantages by improving the physicochemical properties of the compost, reducing toxic compounds and gas emissions. These improvements are achieved through abiotic interaction (Sun et al. 2020) and microbial activities (Kammann et al. 2015; Godlewska et al. 2017). Indeed, biochar can fill the space between the solid compost materials and reduce heat losses, while creating a proper habitat for microbial activity, resulting in faster heat generation and degradation of organic compounds (Czekała et al. 2016). Moreover, higher temperatures during composting can be more efficient at eliminating pathogens (Casini et al. 2021). Biochar can also affect the compost's pH in various ways. During the thermophilic phase, biochar addition can lower the pH due to the production of acids from the decomposition of organic matter, induced by higher microbial activity. During the mesophilic and maturation phases, however, the pH can be higher, possibly because of the absorption of accumulated ammonia by the biochar (Sun et al. 2020). Furthermore, the alkaline and alkaline earth compounds in biochar can generate a buffer effect that minimizes acidification during the thermophilic phase, resulting in higher pH values for the biochar-added compost (Sánchez-Monedero et al. 2019; Sun et al. 2020).

The use of biochar in agricultural crops is also associated with changes in the physico-chemical properties of compost, resulting in intensive abiotic oxidation and microbial activities (Godlewska et al. 2017). These changes include an increase in acid functional groups and alterations in the profile of minerals and metals. Microbial metabolism is responsible for the decomposition of organic matter, and the addition of biochar in the compost can improve this process by modifying the porous structure and apparent density of the compost, thus providing oxygen for aerobic microorganisms (Sánchez-Monedero et al. 2019). Additionally, the decomposition of organic matter can generate inhibitory molecules, such as NH_3, H_2S, NH_4^+, and SO_4^{2-}, which can be absorbed by the biochar, making the compost more efficient (Vandecasteele et al. 2016; Sun et al. 2020).

Biochar can reduce the mobility and availability of heavy metals and aromatic polycyclic hydrocarbons for agricultural crops (Ignatowicz 2017) through physical absorption, precipitation, electrostatic interaction, and ion exchange (Sun et al. 2020). Furthermore, biochar can be considered a reservoir of macronutrients (sodium, potassium, calcium, magnesium, sulfur, phosphorus) and micronutrients (iron, zinc, manganese, copper). Thus, due to a high capacity of absorption, the use of biochar in compost can increase the total amount of macronutrients and micronutrients liberated in the final product, with water, or after the neutralization by organic and inorganic acids, improving the nutritional value of the final product as an organic fertilizer (Sun et al. 2019, 2020).

Future prospects, economics and challenges

Waste effluents treatment is a costly process, with millions of dollars spent annually, and the demand for sustainable alternatives such as microalgae wastewater treatment is increasing (Morais et al. 2021). Conventional treatments have negative impacts, particularly in relation to the emission of greenhouse gases. In contrast, microalgal systems are advantageous due to their low emission of greenhouse gases and their ability to produce a biomass rich in compounds that can be used to obtain biofuels and other products (Arashiro et al. 2018, 2020). Pyrolysis, a process that is not as well-known or studied as other microalgal biomass processing methods for biofuel production, is a promising alternative for downstream processing in microalgal biorefinery processes. In just one step, three commercially valuable bioproducts can be obtained: bio-oil, biochar, and pyrolytic gas. Even if a preliminary treatment of the biomass for the initial extraction of other compounds is required, the remaining biomass can still be pyrolyzed for further use. Products from pyrolysis processing can also be used to maintain the system itself within a circular bioeconomy concept.

There are several ways to reduce costs in the microalgal biorefinery process, such as developing new reactors and implementing pre-treatment of microalgal biomass. To improve the sustainability of the process and further reduce costs, it is also necessary to optimize the cultivation conditions, refine techniques for extracting bioproducts, and explore the reuse of co-products. Microalgae cultivation costs currently account for around 65% of the total cost of biofuel production, but this figure can be significantly reduced through the integration of effluent treatment and carbon capture. Although cost-effective microalgal biofuels are still in development, research into the processing of biomass as a feedstock for biofuels is crucial for overcoming the current economic constraints of the process (Aliyu et al. 2021).

The efficiency of conversion of microalgal biomass into biodiesel through transesterification can reach up to 92%, depending on the quality and quantity of the lipids in the biomass. The estimated production costs range from 0.96 to 3.69 US$ L^{-1} (Table 4). In comparison, fuel derived from petroleum ranges from 0.43 to 0.44 US$ L^{-1} (Aliyu et al. 2021). The lowest production cost for biodiesel was achieved through a process that involved lipid extraction, fermentation, distillation, hydrodeoxygenation, and the use of CO_2 from anaerobic digestion (Dutta et al. 2016). The highest production cost was US$3.46 for the oil extraction stage alone, with the biodiesel produced from it having a value of US$3.69. This system used hydroprocessing to extract the

Table 4 Comparison of estimated production costs for three different biofuels produced from microalgal biomass

Microalgae Fuel	Production method	Conversion efficiency (MJ_{fuel} $MJ_{feedstock}^{-1}$, dry)	Estimated costs (US$ L^{-1})	Reference
Biodiesel	Transesterification	92%	0.96—3.69	Aliyu et al. (2021)
Biocrude	Hydrothermal liquefation	32%	0.95—23.96	Ranganathan and Savithri (2019) Richardson et al. (2014)
Bio-oil	Pyrolysis	50%	0.41—0.61	Orfield et al. (2014), Xin et al. (2018)

solvent used for lipid extraction and incorporated recirculation of dehydrated cells for the cultivation of microalgae in bioreactors (Batan et al. 2016).

In terms of biocrude production, it has been observed that integrating microalgae production with effluent treatment and using digestate from anaerobic digestion while obtaining the fuel via hydrothermal liquefaction can result in lower estimated production costs (US$0.95) (Ranganathan and Savithri 2019). Conversely, cultivations without nutrient reuse had production costs ranging from US$16.92 to US$23.96 (Richardson et al. 2014).

The biofuel with the lowest estimated production cost was bio-oil, which is the main product of pyrolysis (Table 4). When microalgae cultivation is integrated with effluent and flue gas treatment, the estimated production cost is US$0.61 (Orfield et al. 2014). By using microwave-assisted pyrolysis and defatted microalgal biomass, the estimated cost is reduced to US$0.49 (Xin et al. 2016) and by using the whole microalgae, the cost further decreases to US$0.41 (Xin et al. 2018).

Co-products derived from the pyrolysis of bio-oil and biochar can increase revenue. Studies conducted within an integrated biorefinery framework have shown that the multifaceted use of biochar as a solid fuel, adsorbent, catalyst, and fertilizer can significantly enhance the economic performance of the process. The application of biochar as a solid fuel with a selling price of US$50 per tonne contributes approximately 2.8% of the total revenue generated from the process (Winjobi et al. 2016). By converting biochar to activated carbon, its selling price can be increased to US$1188 per tonne, increasing its contribution to 51.11% of total revenue (Kuppens et al. 2015).

One of the significant advantages of microalgae cultivation is its versatility in applications. The cultivation process is well-suited for various forms of microorganisms, media, and cultivation methods, making it a versatile research field. To further improve the economic and environmental sustainability of microalgal production, research should explore new ways to leverage this versatility. Biorefinery processes offer a promising solution as they are cost-effective, cyclical, and generate little to no waste, while producing multiple compounds in a single process. Therefore, identifying how different methods can be linked and how each process can facilitate the next step is crucial to fully utilize the potential of microalgae in sustainable biorefinery applications.

Microalgae-based biofuel production presents both economic challenges and opportunities. Traditional waste effluent treatment processes incur significant annual costs, motivating the search for sustainable alternatives like microalgae wastewater treatment. This method not only reduces greenhouse gas emissions but also yields valuable biomass. Of particular interest is pyrolysis and to enhance its economic viability, strategies involve optimizing cultivation conditions, refining bioproduct extraction methods, and exploring co-product reuse. Developing cost-effective microalgal biofuels remains essential for overcoming economic constraints.

Conclusion

This study investigated the potential of pyrolysis for valorizing microalgae biomass produced from wastewater treatment. The review showed that pyrolysis can be used to produce a variety of valuable products, including biochar, bio-oil, and pyrolytic gas (syngas). The composition of the products is influenced by the type of microalgae used, the operating conditions of the pyrolysis process, and the presence of contaminants in the biomass. However, the following challenges need to be addressed before pyrolysis can be widely adopted for the valorization of microalgae biomass: (i) high energy requirements, (ii) process optimization, and (iii) potential to produce harmful emissions. Despite this, pyrolysis appears a promising technology with potential to make a significant contribution to the sustainable development of bioeconomy. Future research should address these challenges and study the effect of different microalgae species and strains, operating conditions, contaminants, economic feasibility, and develop new pyrolysis technologies. In this manner, the pyrolysis process could be optimized, and the yield and quality of products improved, thereby promoting the valorization of microalgal biomass via pyrolysis.

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Declarations

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