



HAL
open science

Bio-oil from microalgae: Materials, production, technique, and future

Shams Forruque Ahmed, Sabiha Jannat Rafa, Aanushka Mehjabin, Nuzaba Tasannum, Samiya Ahmed, M Mofijur, Eric Lichtfouse, Fares Almomani, Irfan Anjum Badruddin, Sarfaraz Kamangar

► To cite this version:

Shams Forruque Ahmed, Sabiha Jannat Rafa, Aanushka Mehjabin, Nuzaba Tasannum, Samiya Ahmed, et al.. Bio-oil from microalgae: Materials, production, technique, and future. *Energy Reports*, 2023, 10, pp.3297 - 3314. 10.1016/j.egy.2023.09.068 . hal-04257276

HAL Id: hal-04257276

<https://hal.science/hal-04257276>

Submitted on 31 Oct 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Public Domain

Bio-oil from microalgae: Materials, production, technique, and future

Shams Forruque Ahmed^a, Sabiha Jannat Rafa^a, Aanushka Mehjabin^g, Nuzaba Tasannum^a, Samiya Ahmed^h, M. Mofijur^{b,c}, Eric Lichtfouse^d, Fares Almomani^{e,*}, Irfan Anjum Badruddin^f, Sarfaraz Kamangar^f

^a Science and Math Program, Asian University for Women, Chattogram 4000, Bangladesh

^b Centre for Technology in Water and Wastewater, School of Civil and Environmental Engineering, University of Technology Sydney, Ultimo, NSW 2007, Australia

^c Mechanical Engineering Department, Prince Mohammad Bin Fahd University, Al Khobar 31952, Saudi Arabia

^d Aix Marseille Univ, CNRS, IRD, INRAE, CEREGE, Aix-en-Provence, France

^e Department of Chemical Engineering, Qatar University, Doha, Qatar

^f Mechanical Engineering Department, College of Engineering, King Khalid University, Abha 61421, Saudi Arabia

^g School of Biological Sciences, Georgia Institute of Technology, Atlanta, GA 30332, USA

^h Biological and Biomedical Sciences Department, College of Health and Life sciences, Hamad Bin Khalifa University, Doha, Qatar

ARTICLE INFO

Keywords:

Bio-oil
Microalgae
Pyrolysis
Bio-oil production
Bio-oil upgrading
Biomass

ABSTRACT

Because of its low environmental impact and high production, microalgae bio-oil has quickly become a popular renewable fuel option. The process utilizes microalgae which are readily available in nature to produce an alternative to fossil fuel. Although microalgal bio-oil production mechanisms have been previously reviewed in recent studies, comparatively few of them emphasize the significance of algal bio-oil production through all available bio-oil conversion mechanisms from microalgae. Here we review the available and common bio-oil conversion processes from microalgae, bio-oil upgrading, and the commercial aspects of its utilization. The most efficient route to bio-oil production can be identified by analysing both the biomass feedstock and the final product. For example, pyrolysis can produce high-energy bio-oil, but it also produces large amounts of char and gas. Although hydrothermal liquefaction and gasification are more complex and costly, they have the potential to produce bio-oil with greater consistency. However, the expense of using bio-oil in a commercial context is a major concern. The cost of producing bio-oil from microalgae is typically higher than that of producing conventional fossil fuels. Several factors, including cost, availability, and necessary infrastructure, contribute to the uncertainty of bio-oil's commercial feasibility. With the constant improvements in technology and government support, however, bio-oil has the potential to emerge as a viable alternative to conventional fossil fuels.

1. Introduction

Microalgae-based bio-oil production is a viable and sustainable method to produce renewable energy and sustainable biofuels (Raheem et al., 2018). Due to their high lipid content and rapid development rates, microalgae, a varied collection of microscopic photosynthetic organisms, have emerged as a candidate for bio-oil production (Wang et al., 2022). Compared to conventional oil crops like soybeans and corn, microalgae provide a number of benefits. They may be grown in a number of different environments, including freshwater, saltwater, and wastewater, which helps alleviate the demand for limited farmland and water supplies (Wigmosta et al., 2011). Furthermore, certain strains of microalgae are capable of doubling their biomass in just a few hours,

making them substantially more productive than conventional oil crops (Alam et al., 2012). As a potential feedstock for the production of bio-oil, the popularity of microalgae has risen significantly in recent years (Li et al., 2019). This popularity is due to its many advantageous properties (Sarwer et al., 2022), including its high oil content, fast growth rates, flexible cultivation options, carbon dioxide fixation capabilities, nutrient recycling potential, and potential for co-generation of valuable substances. These advantages recommend microalgae as a viable and long-term resource for producing renewable biofuels. The replacement of fossil fuels with bio-oil has also substantial positive impacts on the environment (Baskar et al., 2019). It is a sustainable and renewable energy choice that reduces the release of greenhouse gases, sulphur, and nitrogen, as well as particle matter, makes use of waste products,

improves energy security, and promotes rural growth. Using bio-oil as a fuel source thus contributes to a sustainable and environmentally friendly future.

Bio-oil must be upgraded in order to be used as a partial or complete transportation fuel replacement (Panwar and Paul, 2021). Bio-oil upgrading is the elimination of nitrogen from algal bio-oil or oxygen from bio-oil (Oasmaa et al., 2021). The deoxygenation is facilitated by the decarbonylation and decarboxylation at a temperature of about 400 °C, while deoxygenation is facilitated through dehydration at a temperature of about 250 °C on catalytic transformations of acetic acid and acetone (Bhoi et al., 2020). By removing oxygen in a two-stage hydro-treatment process, the oil produced during this quick pyrolysis process is upgraded to a stable hydrocarbon oil. Therefore, the mechanism of bio-oil upgrading consists of a series of reactions like decarboxylation, decarbonylation, aromatization, and dehydration, leading to the manufacture of hydrocarbon-rich fuel. Although several researches have been carried out on lignocellulosic biomass pyrolysis, only a handful of papers highlight the importance of algal bio-oil manufacture through pyrolysis. According to (Saber et al., 2016), fast pyrolysis of *Chlorella protothecoides*, a significant algal species, at 500 °C can produce bio-oil with a yield of 57.9% (Li et al., 2019). This bio-oil displays a higher nitrogen and carbon content but a lower content in oxygen compared to wood bio-oil. The bio-oil production using microalgae pyrolysis as the third generation of biofuel is thus a potential method for producing bio-oil as a substitute for fossil fuel. Thermochemical conversion techniques for generating liquid biofuels, such as fast pyrolysis and hydrothermal liquefaction (HTL), have been recognized as the most promising (Zhang et al., 2021). On the other hand, the utilization of these technologies is limited because of the crude bio-oils' poor quality, including high oxygen, high water content and little thermal stability. Therefore, multiple upgrading techniques like hydrotreatment or hydrodeoxygenation have been developed to produce efficient bio-oils via pyrolysis.

Research by Shan Ahamed et al. (2021) offered valuable insight into the processes and techniques used to enhance bio-oil quality. Direct use of such technology, however, is the primary drawback of the research due to its unstable thermodynamic features. Chan et al. (2020) discussed the significance of bio-oil as a highly important product obtained via biomass pyrolysis and highlighted fractionation and extraction as key mechanisms to upgrade bio-oil through the separation of the complex mixture of compounds into discrete fractions and chemicals. Moreover, technological gaps were stated as significant weaknesses in the literature. The gaps, including the mechanisms of microalgae pyrolysis to generate bio-oil, were discussed in the paper. Although many studies have investigated the effectiveness of various methods for extracting bio-oil from microalgae, few have emphasized the importance of algal bio-oil production via all bio-oil conversion routes. This paper thus investigates the available and common bio-oil conversion technologies from microalgae, as well as bio-oil upgrading and the commercial aspects of its use. It highlights how specific steps can be taken so bio-oil can be regarded as an alternative to fossil fuels and how to assist stakeholders like manufacturing industries and climate workers. This research characterizes the immense potential and prospects of bio-oil for future implementation in the oil manufacturing industries as a substitute for fossil fuels, delivering benefits for the industry, consumers, and the environment.

2. Microalgae as a bio-oil feedstock

Microalgae, also known as microphytes, are unicellular plants that are very small. They typically inhabit aquatic and marine habitats (Scott et al., 2010), existing independently or in groups and chains. The structures of these habitats vary according to species, and their size usually ranges between 30 to 400 micrometres (Harun et al., 2014). Microalgae are distinct from larger plants as they lack leaves, branches, and roots. Microalgae have a substantially higher biodiversity than most other plant and crop species, with estimates going as high as 800,000

species (Oncel, 2013). Microalgae are only found in water, thus they do not take up any valuable farmland. They have a high yield and a short growth cycle, and their consumption poses no threat to the food supply for humans (Zhang et al., 2022). Therefore, microalgae are a feasible source of bio-oils that are both environmentally and financially sustainable (Lee et al., 2017). The demand for transportation fuels could be met by biofuels derived from microalgae (Choi et al., 2017).

The advantages of using microalgae as an energy feedstock are numerous. The bio-oil yield relies on the biochemical makeup of the specific microalga and the substituent yields are prioritized as follows: (i) lipids; (ii) proteins; and (iii) carbohydrates. For the production of bio-based fuels, microalgae have been found as a suitable feedstock due to their high lipid levels. Microalgae biorefineries can achieve full biomass utilization by converting all residue into bio-oils after converting lipids into biodiesel (Shahi et al., 2020). The rapid growth rate of microalgae increases their productivity. They also thrive in a salty environment and use atmospheric CO₂ as a source of growth (Jazrawi et al., 2015). Additionally, because they do not contain sulphur, microalgae-derived biofuels are advantageous for the environment in terms of air pollution control (APC) (Sun et al., 2017).

There are several species of microalgae, and they all show potential as a source of bio-oil. Various popular microalgae have been the focus of intense research due to their potential applications. Both *Chlorella vulgaris* and *Nannochloropsis sp.* have shown potential as bio-oil feedstocks; these algae are high in lipid content and can grow quickly in a variety of water conditions. Similarly, the lipid productivity and other distinctive properties of *Scenedesmus sp.*, *Botryococcus braunii*, and *Dunaliella salina* have all been studied. These microalgae species, among others, are being investigated for their potential usefulness in biofuel production; doing so contributes to efforts toward the development of environmentally friendly, renewable energy alternatives. Table 1 summarizes different microalgae species and their advantages and disadvantages.

Due to their distinct properties and prospects for long-term energy sustainability, microalgae have emerged as a highly attractive bio-oil feedstock. The high lipid content of microalgae can be utilized to produce bio-oil by converting sunlight and CO₂ into biomass through photosynthesis (Arun et al., 2022). Advantages over conventional oil crops include their quick development and adaptability to a variety of conditions, such as saline and water wastewater. Cultivating microalgae on non-arable land decreases resource competition (Alam et al., 2012). Microalgal cell lipid extraction can produce bio-oil, which has several potential uses in the chemical, plastics, and fuel industries. After lipids are extracted, the remaining biomass might be used as a byproduct.

Summary: Bio-oil, made from microalgae, is a renewable and clean energy source that could eventually substitute fossil fuels. High production costs, energy-intensive extraction, water use, and scaling up are only some of the difficulties that come with employing microalgae as a bio-oil feedstock. Although microalgae show promise as a useful feedstock for bio-oil production, there is still a need for improvement in terms of cultivation and extraction methods. Although there are still obstacles to overcome, microalgae-based bio-oil production is becoming more efficient and scalable thanks to ongoing research and technical breakthroughs, demonstrating its potential as a sustainable and economically viable alternative to fossil fuels.

3. Conversion techniques for bio-oil production

Biomass derived from microalgae can lead to the conversion of numerous biofuels through two different processes. Firstly, using biochemical processes, microorganisms turn biomass into biofuels, and this conversion can be categorized into four different processes: anaerobic digestion, fermentation of alcohol, photobiological hydrogen production, and transesterification (Azizi et al., 2018). Secondly, thermochemical processes are used to heat and break down biomass with the help of oxygen. In contrast to biological processes, thermochemical techniques can create solid, liquid, and gaseous biofuels (Billar

Table 1

Overview of various microalgae species as a feedstock and their associated advantages and disadvantages.

Microalgae	Lipid	Protein	Carbohydrate	Moisture	Ash content	Advantages	Disadvantages	Ref.
<i>Schizochytrium limacinum</i>	51%	14%	24%	N/A	8.9%	Exhibits high oil or lipid concentrations; ideal for oil synthesis	Expensive equipment cost; high energy consumption	Anand et al. (2017)
<i>Chlamydomonas debaryana</i>	19.9%	59.4%	10.1%	2.7%	7.9%	Produce many heterocyclic compounds due to high protein content	High production of nitrogen-based products; lack of harvesting technology	Ansah et al. (2018)
<i>Chlamydomonas reinhardtii</i>	12.19%	62%	3.28%	N/A	17.96%	High level synthesis; high development rates; endurance and great flexibility	Excessive nitrogen-based compounds were generated due to high protein content	Andrade et al. (2018)
<i>Nannochloropsis gaditana</i>	34.3%	40.3%	12%	N/A	4.5%	The highest concentration of hydrocarbon; great HHV value for bio-oil production	Ash content percentage was higher leading to a high bio-char production rate	Adamczyk and Sajdak (2018)
<i>Nannochloropsis sp</i>	27.8%	36.4%	12.4%	3.14%	8.9%	High protein content; significant bio-oil yield at an ideal temperature of 475 °C	Temperature increase leads to a decrease in bio-char production	Wang et al. (2017)
<i>Chlorella Vulgaris</i>	9%	52.3%	14.5%	4.13%	8%	High protein content; organic compounds in the aqueous phase; aromatic compounds	Hydrothermal liquefaction (HTL) process needs to be evaluated	Khan et al. (2018)
<i>Dunaliella tertiolecta</i>	25%	45.8%	20.6%	4.28%	8.61%	High number of biochemical compositions; high nitrogenous compounds in bio-char	Insufficient quality of yielded bio-oil; bio-char has a very small surface area	Söyler et al. (2017)

et al., 2015). Due to the low energy conversion, prolonged reaction times, and expensive production costs for biochemical conversion procedures, it has been shown that conversion via the thermochemical approach is more beneficial than biochemical processes.

Compared to biological conversion processes, thermochemical transformations occur far more quickly (Kiran Kumar et al., 2018). The

thermochemical method offers a more direct way to generate biofuels than chemical and biological processes. Chemical conversion requires the separation or purification of biomass, transesterification requires a methanol recycling system, and the disposal procedure is complicated due to soap production (Morais et al., 2022). Several days are typically needed to manufacture biofuels via biochemical conversion processes

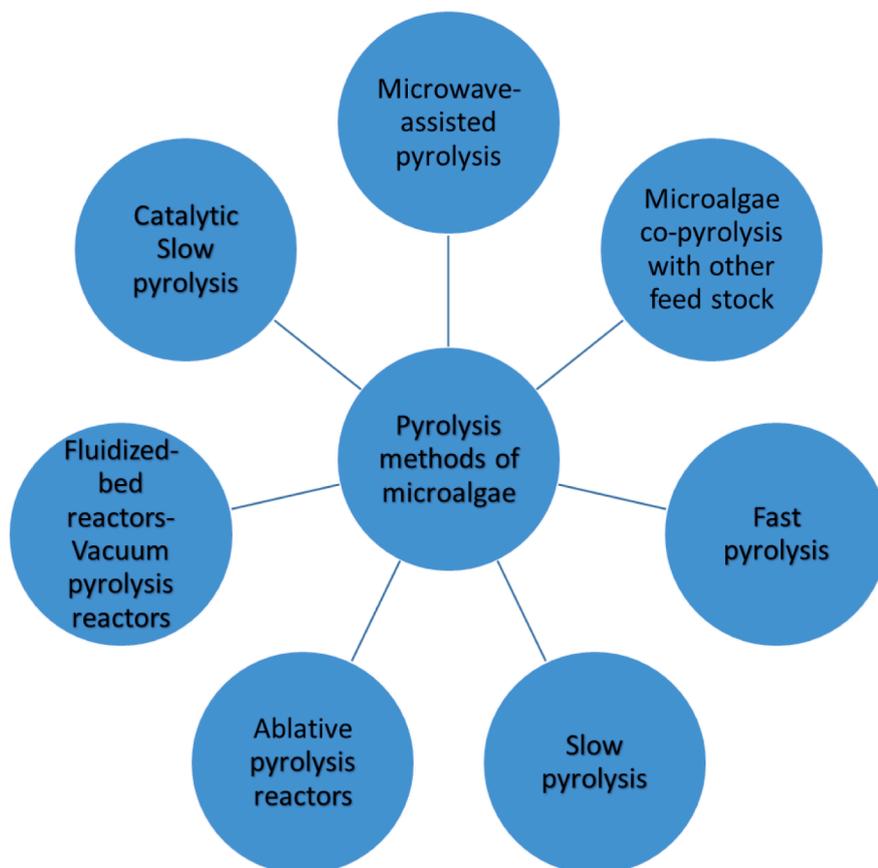


Fig. 1. Different kind of pyrolysis methods.

like fermentation (Chen et al., 2015). In contrast, thermochemical conversion typically does not need chemicals and is accomplished by converting a broad range of feedstocks from biomass and making use of the entire feedstock. The thermochemical technique also requires very little time to produce biofuels. As a result, one important method in processing microalgae into biofuel is the thermochemical conversion process. The four main categories of thermochemical conversion techniques are direct combustion, gasification, hydrothermal liquefaction, and pyrolysis. Hydrothermal liquefaction and pyrolysis are the two most prominent and effective techniques for producing bio-oil (Nagi et al., 2021). Commonly used pyrolysis methods are displayed in Fig. 1.

3.1. Pyrolysis mechanisms of microalgae

Pyrolysis is a thermal breakdown of lignocellulosic derivatives under inert circumstances and in an environment that is oxygen-free (Huang et al., 2016). Microalgal pyrolysis methods involve oxygen-deficient heat decomposition of biomass for producing bio-oil, gas, and char (Ansari and Gaikar, 2019). Drying, devolatilizing, and char production are all steps in the process. Devolatilization releases volatile organic components as gases and vapours while drying removes water from the biomass. Devolatilization results in the generation of bio-oil, the primary product of desire. Bio-oil, gas, and char vary in composition and characteristics based on different factors including pyrolysis temperature, microalgae species, and reactor conditions (Bach and Chen, 2017a). For effective and sustainable bioenergy conversion from microalgae, it is critical to understand and optimize these pyrolysis mechanisms. In recent decades, pyrolysis has shown potential as a promising approach to convert biomass to bio-oil and therefore received increased attention. It is common practice for a pyrolysis system unit to consist of a pyrolysis reactor, a unit for post-pyrolysis processing, and pre-processing equipment for lignocellulosic residues. Fig. 2 depicts a basic pyrolysis unit setup along with its primary outputs.

Pyrolysis is the first step before any sort of thermochemical conversions can take place and is followed by the gasification of char or combustion. In the process of pyrolysis, complex procedures take place including rearrangement reactions, polymerization, fragmentation, decarboxylation, and dehydration. Lipids, carbohydrates, and proteins found in microalgae make them amenable to the pyrolysis process for energy production. As pyrolysis has been proven to be energy and yield efficient, it is considered an economical method for the conversion of algae biomass into fuel (Li et al., 2019). Bio-oil attained through pyrolysis can be utilized in chemical industries in various ways, e.g. as feedstocks and for generating power and heat separately or in combination (Rago et al., 2018). Microalgal pyrolysis is categorized into two main types depending on operating conditions of residence time and rate of heating: slow pyrolysis (usually using 10 °C per minute); and fast pyrolysis (usually needing a temperature over 100 °C per second) (Li

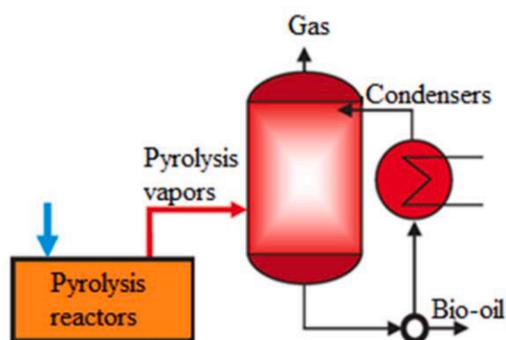


Fig. 2. A simplified flowchart for a pyrolysis unit. Modified from Zaman et al. (2017).

et al., 2019). Though pyrolysis bio-oil shows promise as a feasible source of renewable energy, its features can make it difficult to produce, store, and use.

Pyrolysis oil is a viscous liquid and dark brown. Bio-oil produced using biomass pyrolysis is made up of more than 300 types of compounds including indoles, carbonyls, nitrogenous compounds, polyaromatics, furans, sugars, phenols, alcohols, acids, and hydrocarbons (Li et al., 2019). One significant study aimed to understand the production of bio-oil using microalgae pyrolysis and thermochemical liquefaction methods. In comparison to pyrolysis, they discovered that thermochemical liquefaction used less energy, and char and bio-oil yield was low and relatively high, respectively. The bio-oil also had enhanced fuel characteristics and a higher energy density (Xu et al., 2019). However, Li et al. (2019) highlighted that some specific microalgae behaviours, mechanisms, liquefaction behaviour, and catalytic pyrolysis behaviours are still unknown.

3.1.1. Fast pyrolysis

The purpose of fast pyrolysis is to increase the production of bio-oil which can be conveniently transported or stored due to its low nitrogen and sulphur content. Fast pyrolysis is a systemic process in which biomass is heated to the optimal temperature of pyrolysis before it completely decomposes (Gautam et al., 2017). Rapid cooling of the pyrolysis vapour and very high reaction temperatures and heating rates are characteristics of fast pyrolysis (Ji et al., 2017). In order to generate bio-oil, the maximum temperature must be lower than 500 °C. In rare circumstances, the maximum temperature required to produce biogas is 900 °C (Cieřlik et al., 2015). The prime element that affects liquid production is the heating pace. Another element that affects the generation of bio-oil is the reaction temperature, which should be between 400 °C and 600 °C (Lee et al., 2005).

The fast pyrolysis of dry and crushed *Scenedesmus sp* was demonstrated by Harman-Ware et al. (2013) depending on the sizes of two distinct reactors. During the pyrolysis process, which was conducted at 480 °C, a dynamic pyrolysis-GC/MS tool and an isothermal spouted bed reactor were utilized. The spouted bed reactor produced crude oil with a mean calorific content of 18.4 MJ per kg. According to the outcomes of simulated distillation, a sizeable fraction of the oil corresponded to the heavy gas oil boiling temperature that ranged from 343 °C to 524 °C. The oil produced contained an average of 8.6 wt.% nitrogen and 27.6 wt.% oxygen, with the comparatively high nitrogen level explained by the algae's high protein content. As per the GC-MS data, the oil contained a variety of hydrocarbons and compounds derived through oxygenation and nitrogenating. *Scenedesmus sp* underwent pyrolysis as well as GC-MS to produce principal pyrolysis products.

Anand et al. (2017) conducted a study on *Schizochytrium limacinum*, a microalga enriched in lipids, which underwent fast pyrolysis to assess its potential for producing important compounds and fuel molecules. The alga was differentiated by its value of heat, maximum composition, and elemental makeup. *Schizochytrium limacinum* exhibits high oil or lipid compositions, which makes this chemical ingredient ideal for oil product synthesis via procedures like lipid extraction and transesterification (Chia et al., 2018). However, microalgal lipid content varies significantly based on the microalgal species, from 1.1% to 51%, and is also greatly dependent on the growth stage since lipids can accumulate up to a total content of 90% when more nitrogen gas resources are consumed (Marcilla et al., 2013). The microalgal biomass residual after oil extraction can be used as pyrolysis feedstock instead of being dumped away (Fang et al., 2018).

Lipid, protein, and carbohydrate components were gradually extracted from microalgae *Nannochloropsis sp* by Wang et al. (2017) to analyse the pyrolysis pathway of microalgae. With the exception of a few specific zones, the thermogram metric analysis curve of microalgae was fitted by a single pyrolysis curve comprising protein, carbohydrate, and lipid. Various kinds of pyrolysis processes, such as slow and co-pyrolysis, were used to examine the pyrolysis routes of lipids, protein, and

carbohydrates separately. The percentage of protein components was higher than lipids and carbohydrates. Bio-crude and char yields were shown to be affected by temperature during the pyrolysis process. The bio-crude yield gradually rose between 400 °C and 475 °C, reaching a maximum percentage of 55.2% at 475 °C. The char yield gradually fell from 30.2% to 25% with an increase in pyrolysis temperature. Finally, it was determined that for raw microalgae, 475 °C was the ideal pyrolysis temperature.

The pyrolysis outputs of *N. gaditana* under various pyrolysis conditions were analysed in a study by Adamczyk and Sajdak (2018). Hydrocarbons in the liquid products of pyrolysis of *N. gaditana* indicate its potential use in the production of biofuels. The oil produced from the *N. gaditana* had a reduced oxygen concentration as well as greater higher heating values (HHV) which made it more stable for bio-oil production. The pyrolysis of *N. gaditana*'s biomass could result in the production of biochar with a very high percentage (68%) of ash content.

Söyler et al. (2017) used fast pyrolysis to remove biological components from the solid residue of the microalga *Dunaliella tertiolecta*. The bio-oil yield was at its highest at 45.13 wt.% at 600 °C during pyrolysis, while char attained 29.34 wt.%. The viability of using bio-oil as a biofuel was evaluated and analysed. The study also explained how to evaluate the content and qualities of char as a fertilizer or sorbent for soil restoration. The microalga *D. tertiolecta* can also fast pyrolyse its wastes to generate huge amounts of lipids with a variety of applications, including renewable fuel. Nevertheless, the bio-oil quality produced by fast pyrolysis was insufficient for it to be recommended as fuel without additional improvements such as denitrogenating and deoxygenation. The production of char using fast pyrolysis has been shown to be high in nitrogen as well as other macro elements like calcium, sodium, and potassium, making it appropriate for use in agriculture. Additionally, functional groups of surfaces containing oxygen were also found in char, making it suited for absorbing heavy metals. However, the produced char had a very small surface area, constraining its application as an environmental sorbent for water and soil pollutant absorption.

3.1.2. Slow pyrolysis

Compared to fast pyrolysis, slow pyrolysis results in a much higher biochar yield since it generates less other gaseous and liquid products (Khan et al., 2021). The biomass is disintegrated by slow pyrolysis at different temperatures varying between 400 °C and 500 °C at several stages (Nazem and Tavakoli, 2017). Water content and bond breakage are eliminated first. Lipids, proteins, and carbohydrates are broken down in the second phase due to pyrolysis. Residues high in carbon are created at the last stage. Organic liquid yields ranged between 50 wt.% and 70 wt.% when temperatures were between 450 °C and 550 °C (Gautam et al., 2017). Using 600 °C reaction temperature, conventional pyrolysis yields char, gaseous, and liquid products (Azizi et al., 2018). In general, pyro gas and char yields rise at high and low temperatures, respectively, although the bio-oil yield is directly related to temperature, reaching its optimum value at around 500 °C. However, low-temperature pyrolysis (up to roughly 300 °C) is typically used to produce char at a higher concentration (up to 66%) or, at the very least, to produce char alongside the synthesis of bio-crude oil and pyro gas.

Based on the major product and operating temperature, the slow pyrolysis process is categorized into two main types: carbonization and the conventional method (Bach and Chen, 2017b). Char is the primary by-product of carbonization, and the ideal operating temperature is 400 °C. On the other hand, char, liquid, and gaseous products are produced using the conventional method at a temperature of 600 °C (Gautam and Vinu, 2018). The important influence of temperature on slow pyrolysis is clear from the information above. Zhou et al. (2014) demonstrated that raising the temperature increases the production rate of bio-oil up to an optimal temperature of 500 °C, after which the production yield decreases as the temperature rises. Using a fixed-bed reactor without catalysts, Jamilatun et al. (2017) evaluated the features of slow pyrolysis of *Spirulina platensis* residue and pyrolysis using a thermogravimetric

analyser. 50 grams of SPR were employed as the feedstock for the pyrolysis process in a fixed-bed reactor, with temperatures ranging from 400 °C to 650 °C. The highest bio-oil yield of 25% was generated when the aromatic constituents and phenol increased at 550 °C. Bio-oil showed a high higher heating value (HHV) of 25.70 MJ per kg. However, hydrogen gas, carbon monoxide, and methane dominated gas products may be utilized as the biochar product as they have a large amount of carbon (50.31%) and ash (11.80%) content, leading to the conclusion that they have the potential to be used as an adsorbent and fuel.

The pyrolysis of *Scenedesmus dimorphus* produced the maximum yield of bio-oil, 39.6 wt.%, at temperatures between 300 °C and 600 °C in a study conducted by Bordoloi et al. (2016). The nitrogen yield of the bio-oil and biochars was 10.6 wt.% and 6 wt.%, respectively. The study examined the temperature impact on liquid and solid product yield and chemical compositions using *Scenedesmus dimorphus* microalgae for slow pyrolysis with a fixed-bed reactor and further fractionation utilizing liquid column chromatography. Additionally, the yield included species like amides, indoles, and nitriles. This indicates that a significant amount of the nitrogen used in the procedure was retained. In the present work, *Scenedesmus dimorphus* is shown to be a promising feedstock for the pyrolytic conversion of energy and biomaterials. The limits of cracking, time, and excess heat, in addition to temperature and operating conditions, have made this technique unprofitable in recent years.

3.1.3. Catalytic pyrolysis

Catalytic pyrolysis is the process of converting microalgal biomass into useable products using a catalyst. Typically, catalytic pyrolysis is performed between 300 °C and 600 °C (Jafarian and Tavasoli, 2018). Catalytic pyrolysis produces HHV and bio-oil yields of 20–33 MJ/kg and 19–40 wt.%, respectively (Ansah et al., 2018). Because microalgae derived bio-oil still includes a lot of oxygen, it must be enhanced in order to increase its strength, restrict polymerization and the condensation reaction, and enhance the energy density. Bio-oil generated by catalytic pyrolysis has a greater heating value, lower acidity, and higher aromatic content, suggesting that a higher standard bio-oil can be produced from this process.

In a study by Rahman et al. (2018), *Isochrysis sp.* was pyrolysed through lithium zeolite to generate aliphatic and aromatic compounds. The production of aromatic compounds was almost five times higher during catalytic pyrolysis of Li-LSX zeolite compared to non-catalytic pyrolysis. *Isochrysis sp.* was pyrolysed at 500 °C over the catalyst to produce 29 wt.% bio-oil, containing 34.9 wt.% aliphatic and aromatic compounds in total. The outcome was accomplished through increments and denitrogenating of the pyrolysis products. Increasing the pyrolysis temperature from 400 °C to 500 °C increased bio-oil yield from 20 wt.% to 29 wt.%. Nevertheless, the bio-oil yield dropped to 24 wt.% at 700 °C. This could be caused by the breaking of pyrolysis gases at this temperature. The bio-oil productivity decreased from 30 wt.% to 23 wt.% for the pyrolysis at 500 °C when the catalyst loading was increased from 0.75 g to 4.5 g, however, the yield of gas increased from 34 wt.% to 43 wt.% and the amount of feedstock remained unchanged. This was demonstrated by the extended interaction between pyrolytic gases and the catalyst bed.

Chlamydomonas reinhardtii has various properties that could make it an appealing organism for high level synthesis of biomass, for example, high development rates, same metabolic characteristics, endurance, great flexibility, and it can survive in both light and darkness. A study conducted by Andrade et al. (2018) used multiple methodologies to characterize *Chlamydomonas reinhardtii* and assess its potential as a feedstock for the manufacture of chemicals and fuel. Due to its high protein content, *Chlamydomonas reinhardtii* pyrolysis produced a significant amount of nitrogenous substances. As a result, the compounds derived from oxygenation decreased due to the increase in temperature. Nitrogen containing molecules are reduced in the bio-oil generated by catalytic pyrolysis, indicating that the inclusion of a hydrotalcite

catalyst can enhance the bio-oil quality.

Chlorella vulgaris, one of the most common microalgae, was also studied by Zainan et al. (2018) who used Ni-supported zeolite at temperatures ranging from 300 °C to 600 °C and unique catalyst to feedstock ratios to produce pyrolytic products. Ni-supported zeolite can be produced by ion exchange (IE) and wet impregnation (WI), respectively. In contrast to IE based catalyst, which can work on the reduction of acidic and oxygenated compounds, WI-based catalyst has been found to be able to increase the hydrocarbon ratio while also eliminating nitrogenates. The overall bio-oil yield dropped from 18.97 wt.% to 4.43 wt.% for WI and from 13.06 wt.% to 4.88 wt.% for IE as the loaded catalysts increased. It is expected given that as the catalyst layer's thickness increased, more volatiles were trapped inside its pores, extending secondary reactions and increasing the production of biogas. However, it was found that neither kind of catalyst had any appreciable effects on the yield, rather, they had an effect on the characteristics of the bio-oil. Catalytic pyrolysis is considered a potential thermochemical conversion method for microalgae biomass to enhance bio-oil quality. The optimal pyrolysis temperature for *C. vulgaris* seems to be 500 °C, which produced a significant number of hydrocarbons while releasing fewer acidic and oxygenated compounds into the oil. Ni catalysts can produce more hydrocarbons while producing fewer compounds via the oxygenation mechanism and less acidic chemicals than fast pyrolysis. The quality of the bio-oil is ultimately determined by the catalyst preparation processes, which were highlighted in this study.

Ansah et al. (2018) conducted a study on the pyrolysis of *Chlamydomonas debaryana*, converted through hydrothermal carbonization, in the presence of zeolite as the catalyst. Without using a catalyst, the maximum hydrocarbon content in the category of monoaromatic resulting from the pyrolysis of untreated and treated algae via hydrothermal carbonization were only 11.2% and 12%, respectively, at temperatures of 600 °C. Furthermore, the protein content of microalgae between 14–65.2% is extraordinarily high compared to the 1.1–14.1% range found for macroalgae. Since microalgae biomass has a high protein content, large numbers of heterocycles, like pyrroles and indoles, can be produced as useful chemical synthetics (Ong et al., 2019). However, the concentration of proteins in algal biomass significantly affects the products' nitrogen content. Pyrolysis can either devolatilize

nitrogen-based species or leave them in the resulting bio-oil.

3.1.4. Fluidized-bed reactors

Fluidized-bed reactors combined with effective, adaptable external heating devices can accomplish quick pyrolysis. Sand is usually employed as the solid stage in beds (Fig. 3) because of its high solid density which enables biomass particles to efficiently transport heat (Bordoloi et al., 2016). This convenient, simple, and adaptable technology sweeps the system's by-products by blowing carrier gas, controlling the time period of vapours and solids. After being separated from char in cyclone separators, the carrier gas is compressed in a cooler to isolate the bio-oil (Rahman et al., 2018). In order to generate bio-oil with a desirable quality and yield, char formation in the bed is prevented. However, to achieve the best design, operation, and scale-up, three factors should be taken into consideration. First, a unique design is needed to handle the problems of concentration gradients and transverse temperature related to the utilization of beds in big reactors. Second, a thorough analysis of the hydrodynamics of the biomass and the sand design is essential. Third, biomass with small particle sizes is necessary to obtain high process efficiencies. Further, char development in the fluidized bed must be prevented if bio-crude oil of a desired quality and yield is to be generated.

There are two types of fluid beds: (i) a bubbling fluid bed (BFB), which is a bed of small bubbles that sits at the bottom of a reactor, (ii) a circulating fluid bed (CFB) that uses a cyclone to continuously remove bed material from outside the reactor and recirculate it inside (Rahman et al., 2018). The BFB configuration is frequently utilized for fast pyrolysis of microalgae in which sand is used as a heat carrier where temperature management is quite simple and effective heat transmission to the biomass is affected (Hayes, 2013). The carrier gas flow rate regulates the char and vapour's residence duration. The residence duration of the solid particles is longer than that of the vapours. The sand and the pyrolysis products leave the reactor at the CFB simultaneously (Ding et al., 2016). Cyclones are implemented for the separation of the sand and char particles from the gaseous products, which are then delivered to a combustion chamber prior to recycling the gas into the fluid bed reactor. The sand is heated by the char combustion process and then recycled back into the pyrolysis reactor. However, this reactor

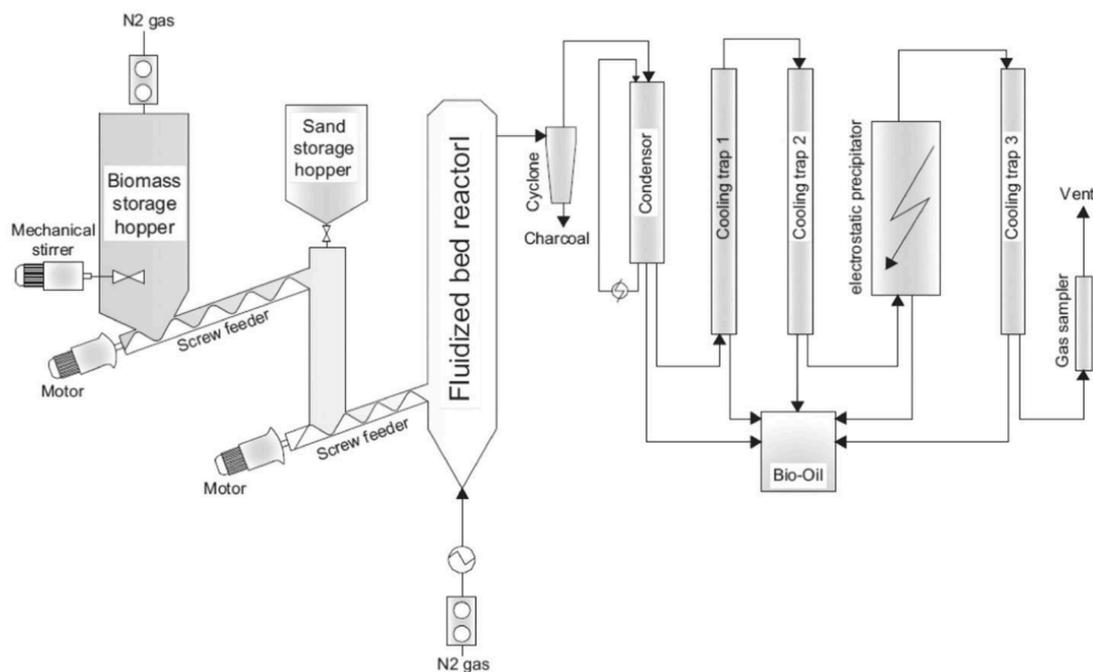


Fig. 3. Diagrammatic representation of fluidized bed reactor for biomass pyrolysis. Reprinted with the permission of Elsevier from Papari and Hawboldt (2015).

arrangement allows for the recycling of solid ash back into the pyrolysis reactor, which may result in an unfavourable ash build-up and reduce the liquid output (Trinh et al., 2013).

The feasibility of recovering nutrients and energy through the pyrolysis of microalgal by-products was investigated by Wang et al. (2013). The biomass of *Chlorella vulgaris* was initially solvent-extracted to recover the lipids and the remains were employed as feedstock for studies involving fast pyrolysis in a fluidized bed reactor at 500 °C. The bio-oil, charcoal, and gas yields were determined as 53 wt.%, 31 wt.%, and 10 wt.%, respectively. A sophisticated combination of aromatic compounds and hydrocarbons, phenols, amines, and other substances with molecular weights varying from 70 to 1200 Da made up the bio-oil made from the *C. vulgaris* remains. Biochar with a high inorganic compound content could be utilized to provide nutrients for crop development. The energy content of the microalgae residual feedstock was made up of 57% bio-oil and 36% biochar, respectively.

Flash pyrolysis was used in a study by Urban et al. (2017) to assess the liquid fuels produced from oleaginous biomass feedstock. The structure and development of a fluidized-bed flash pyrolysis reactor at a laboratory scale allowed for rapid heat transmission to the biomass and a brief vapour residence period. The temperature range used for pyrolysis was between 250–610 °C, and the vapour residence period was 0.2 s–0.3 s. Around 70% of the primary mass and carbon feedstocks were converted into bio-oil at 550 °C or higher. In addition, under these pyrolysis conditions, 90% of the lipid feedstocks were converted into bio-oil. Compared to bio-oil derived from wood, the bio-oil generated in this study had a high carbon, hydrogen, and calorie content, and low oxygen and water content. These findings demonstrate that oleaginous feedstock can be flash pyrolysed to produce bio-oil in high amounts. Table 2 provides an overview of the pyrolysis of microalgae for bio-oil production.

3.1.5. Vacuum pyrolysis reactors

Vacuum pyrolysis reactors follow the principle of converting biomass raw materials in low-pressure environments while maintaining additional conditions of the slow pyrolysis process. Vacuum pyrolysis reactors conduct a semi-fast pyrolysis process which helps with the vapour

dwelling time as well as a comparatively slow transfer of heat and mass to and across the solid biomass (Raza et al., 2021). The vacuum is utilized to remove vapour and help the decomposition to occur at lower temperatures. This fast vapour removal is advantageous and assists in the production of a higher quality bio-oil and porous biochar (Gabhane et al., 2020). Pyrolysis using vacuum reactors generates products that are structurally similar to the original biomolecular chemical arrangements due to the minimization of the secondary degradation reactions enabled by volatilization (Kazemi Shariatb Panahi et al., 2019). After collection, the fragmentation residues are then subjected to condensation and then cut under high atmospheric pressure conditions to reduce high boiling points.

Vacuum pyrolysis reactors self-regulate vapour control, which allows biomass particles to be decomposed simultaneously to the collection of vapour (Kazemi Shariatb Panahi et al., 2019). Further, this process does not need any carrier gasses and can be performed on large biomass particles. Lam et al. (2019) conducted a comparative analysis of microwave vacuum pyrolysis with traditional methods in terms of technological and commercial viability, especially in cases of co-processing. By demonstrating a high rate of heating, a high temperature for processing, a shorter processing time, less electricity consumption, and a large bio-oil yield (84 wt.%), the results indicated that microwave vacuum pyrolysis was advantageous. The produced bio-oil was much cleaner and free of harmful residues. However, the authors did not elaborate on the classification of plastic waste used in this method or investigate which kind of plastic waste is best suited for this method.

Another study conducted by Fan et al. (2018) discussed a method of non-thermal plasma synergistic catalysis (NPSC) that upgrades the vapours from biomass in vacuum pyrolysis reactors in the preparation of biofuel. The results revealed a higher hydrocarbon content in bio-oils and improved physical and chemical properties. However, the approach reduced the overall bio-oil production. Min Ju et al. (2018) analysed the performance analysis of vacuum pyrolysis reactors and the resulting biofuel properties and commercial capacity. Their analysis showed a higher yield and quality of fuel produced from vacuum pyrolysis and the effect of pyrolysis on moisture and oxygen composition. Comparisons with other pyrolysis reactors were not completed, leaving

Table 2
Bio-oil yields from microalgae pyrolysis.

Pyrolysis	Microalgae	Conditions of pyrolysis	Yield of bio-oil (wt.%)	Reference
Fast pyrolysis	<i>Botryococcus braunii</i>	600 °C	65	Piloni et al. (2021)
	<i>C. vulgaris</i>	550 °C	47.7	Sotoudehniakarani et al. (2019)
	<i>Nannochloropsis gaditana</i>	480 °C	20–31	Priharto et al. (2020)
Slow pyrolysis	<i>Spirulina platensis</i>	556 °C	66.04	Rocha et al. (2020)
	<i>Dunaliella salina</i>	500–550 °C	55.4	Yang et al. (2019)
Catalytic pyrolysis	<i>Nannochloropsis sp</i>	400 °C	47.84	Tang et al. (2021)
	<i>Spirulina Platensis</i>	450 °C	43.6	Mo et al. (2020)
	<i>Chlorella sorokiniana</i>	450–550 °C	>40 (ex-situ catalyst); 40 (in-situ catalyst)	Shirazi et al. (2020)
Pyrolysis of microwave-assisted (with catalyst)	<i>Chlorella sp</i>	Microwave power at 600 watts, t = 20 min, CaO catalyst	20.57	Qadariah et al. (2021)
	<i>Chlorella vulgaris</i>	Catalyst TiO ₂	14.74	Chen et al. (2021a)
	<i>Scenedesmus Species</i>	60 °C	20.8 per gm	Mamo and Mekonnen (2020)
Microwave-assisted pyrolysis (without catalyst)	<i>C. vulgaris</i> and <i>N. occulata</i>	300 °C	38 (<i>C. vulgaris</i>)	Tsubaki et al. (2019)
Co-pyrolysis with microwave	<i>Chlorella vulgaris</i>	40% addition of Fe/AC	25.6	Chen et al. (2022)
	<i>Chlorella vulgaris</i>	Optimal avg weight loss, CV:RS = 10:0	19.2, hydrocarbon 20.73	Wei et al. (2023)
Co-pyrolysis without microwave	<i>Nannochloropsis sp. (NS)</i>	Fixed bed reactor	65.17	Tang et al. (2019)

a proper analysis of vacuum pyrolysis's performance incomplete.

3.1.6. Ablative pyrolysis reactors

Ablative pyrolysis reactor systems are suitable for the use of large substances as stock in addition to fine smaller particles which saves the cost of grinding. In this process, the biomass goes through melting and possibly sublimation since it has direct contact with a hot and solid surface. The biomass surface also has a vertical temperature gradient following the creation of a thin layer of reacting solid (Luo et al., 2017). This thin layer then proceeds to the centre of the colder biomass at a fixed rate, so the entire reactive process occurs only in the superficial layer and not across the entire biomass. The rate of reaction is not constricted by the heat movement through the entire particle. In this kind of reactor, the heat moves down away from the scathing plane of the reactor to the biomass, which stays mechanically pressed against the reactor's scorching plane. When the mass is removed, the melted layer evaporates and converts into pyrolysis products. In comparison to other traditional reactors, the reaction rate for ablation is not regulated by the movement of heat along the biomass particles of the biomass (Khuenkaeo et al., 2020; Khuenkaeo and Tippayawong, 2018) which allows the use of larger biomass particles. This kind of reactor does not need an inert gas for maintaining a pyrolytic environment. It needs a vacuum condition or a gas acting as a carrier with a fast flow rate so that pyrolytic products can be removed in a short time.

A study carried out by Wise et al. (2019) discussed fast pyrolysis in an ablative reactor for the transformation of lodgepole pine into vapours. Later on, these vapours are converted to aromatic hydrocarbon following an ex-situ catalytic approach. Results showed that this method is possible to be made portable and an efficient way for alternative energy production even without the need for pre-treatment and movement. Although this process is shown to be environmentally and economically stable, there has not been sufficient comparative analysis with other pyrolysis methods. Auersvald et al. (2020) also studied the possibility of using ablative fast pyrolysis in a mobile unit using cellulosic residues as biomass for transformation into bio-oil. Ablative pyrolysis in a mobile unit not only helps minimize the overall project cost but also the possibility of waste and errors. The advantage of the ablative fast pyrolysis reactor as a mobile application over others was, however, not thoroughly discussed. A comparative analysis performed by Khuenkaeo and Tippayawong (2018) discussed the potential of ablative fast pyrolysis as an eco-friendly method for the conversion of biomass into biofuel. This study used corncob pellets as the biomass and the investigation showed that a good quality of fuel and highly oxygenated hydrocarbons were obtained. The study also found that the required temperature was lower and the yield higher than other methods. The benefit of this method over others in terms of eco-friendliness has not been thoroughly examined in this paper.

3.1.7. Microwave-assisted pyrolysis

The widespread adoption of microwave-assisted pyrolysis (MAP) as a method for producing biofuels from various biomass sources such as macro and microalgae (Hong et al., 2017; Huang et al., 2017), agricultural and forestry waste, and even human waste has contributed to its rising popularity in recent years. Unlike conventional methods of producing thermal energy via thermochemical conversion, MAP generates heat from within the biomass and outwards. The MAP is renowned for its quick processing time, effective heat transfer, low energy consumption, and uniform and selective internal heating. It is also an approach that works well when working with feedstocks that have a high moisture content, unlike some alternatives (Zaker et al., 2019). Microwaves penetrate the feedstock particles in MAP, releasing thermal energy. This causes a temperature gradient from the particles' interior to their exterior, and the volatile compounds are diffusely discharged from the particles' inside to their exterior via low temperature area (Zhang et al., 2020). Since this type of heating is dependent on the interactions between radiation and the feedstock, the production and quality of the

biofuel derived from biomass are also strongly associated with biomass properties (Wang et al., 2015).

The use of a continuous MAP technique to generate biofuel from plastic wastes was reported by Chen et al. (2021b). They studied the results of temperature changes, the composition of plastic content, and fuel yield. Their results showed that greater temperatures caused the generation of more stable hydrocarbons of a light composition. Low energy use throughout the process was also demonstrated. The study lacked in-depth research on the properties of used plastic and a comparison of this technique with other traditional methods. The use of MAP in the case of macroalgae was discussed by Gautam et al. (2019) and the results recorded higher production of carbon monoxide, methane and hydrogen. MAP also had a higher deoxygenation and condensation rate. The major amine in MAP was recorded to be ammonia and heterocyclic nitro compounds. This study focussed on analytical fast pyrolysis and lacked a broader scope of comparison. Zbair et al. (2018) proposed a novel method of utilizing MAP for the fast production of porous carbon. In this method, H₂O₂ (hydrogen peroxide) was used as an activator and almond shells as the biomass. This method showed good potential for removing antibiotics from treatment facilities, however as it was a novel study, further research on commercial viability and wide-scale implementation is needed.

3.1.8. Microalgae co-pyrolysis with other feedstocks

Co-pyrolysis, in which multiple materials are used as feedstock, is a simple and efficient method that has been shown to significantly increase biofuel yield and quality. Several studies have shown that the enhanced biofuel quality is due in large part to the co-pyrolysis collaborative effect on the feedstock (Hassan et al., 2016). The usability of the resulting bio-oil has been demonstrated to increase due to a drop in oxygenated molecules, which in fact has been associated with a prominent collaborative event between the extra reactants and the biomass (Cao et al., 2018; Wu et al., 2020; Yang et al., 2019). Co-pyrolysis that uses substances rich in hydrogen and biomass has been shown to convert waste materials into useable raw resources. This contributes to protecting the environment and recycling resources. Microalgae co-pyrolysis with other compounds has been found to increase aromatics production and biofuel yield (Wang et al., 2016).

Varsha et al. (2021) studied the co-pyrolysis of microalgae, solid waste as well as a mixture of both. The investigation showed microalgae was resistant to thermal heat while solid waste was more sensitive. The data obtained from the co-pyrolysis can be utilized in designing reactors dealing with similar wastes, however this method has not been studied in this paper for other kinds of wastes such as municipal liquid sludge. Aromatic hydrocarbons were processed utilizing HZSM-5 and examined by Qi et al. (2018), who obtained them by the co-pyrolysis of polypropylene and microalgae. The co-pyrolysis showed a collaborative effect in creating aromatic hydrocarbons than if the reaction had been carried out individually. This increased the yield as well as the hydrocarbon production time. This method's sustainability and efficiency were not discussed in light of other methods, so a gap in understanding the best reactor for this case remains.

3.2. Hydrothermal liquefaction

The conversion of biomass from its solid state into the liquid fuels that humans use is not a ready and natural process. Rather, it requires years of geochemical processing or artificial thermochemical or biochemical conversions. Thermochemical conversions happen at a much higher temperature and more rapidly than biochemical conversions (Krishnan et al., 2022). This type of conversion usually improves the biomass by heating it in a pressured and oxygen-deficient system. Hydrothermal or direct liquefaction is one kind of thermochemical conversion which converts biomass to liquid fuels by treating it in a hot, pressured water environment for enough time to breakdown the solid biomass into its liquid components.

The most efficient results in hydrothermal liquefaction are produced at high temperatures and pressures, and the process is based on the principle of reacting biomass with water found in hydrothermal environments (Fig. 4). Many depolymerizing reactions, including hydrolysis, decarboxylation, and dehydration, occur in this process, with the end result being intermediate compounds that are water-soluble (Castello et al., 2018). This method is advantageous due to the sterilizing effects of its components that are biologically active. The subsequent condensation and repolymerization reactions produce biofuel that is insoluble in water. The dependency of this method on specific temperatures and pressures makes it more susceptible to errors and halts the continuous flow process.

3.2.1. Pretreatment

Due to the structure of lignocellulosic feedstock, the process of pretreatment is required to break down the cross-links in the mass so that the accessibility and degradability of fibrils and matrices are enhanced before they are moved into processes such as hydrolysis, fermentation, or digestion in an anaerobic state (Soltanian et al., 2020). An effective pretreatment procedure for microalgae can result in the easier use of constituents for a variety of implementations. Pretreatment methods used on microalgal biomass are usually categorized as mechanical, chemical, thermal, or biological (Sankaran et al., 2020). Chemical pretreatments are most admired due to their low-energy demand, and ease of scalability. Also, it changes the biomass when it comes to the chemical structure and enhances the process of pyrolysis (Nagarajan et al., 2020). The physical qualities of biomass particles, such as size, shape, and density, determine the handling of the material as well as its flowability, which are crucial for sustaining an uninterrupted feeding system (Sivabalan et al., 2021). Along with this, the elemental and proximate analyses, affect the arrangement and pyrolysis products' properties. Even with the innate heterogeneous nature of biomass, many physiochemical and thermal pretreatments help in achieving biomass homogeneity. Homogeneous feedstock materials with unvaried physiochemical properties have a substantial impact on the pyrolysis process and the quality of the end products. Even with their additional costs, pretreatments are beneficial in providing consistent feedstock for power plants (Rezaei et al., 2019).

Lin et al. (2019) assessed the existing hydrothermal pretreatments for hydrolysis and generation of bio-methane and bio-hydrogen from seaweed. Their results showed that the heat released during

pretreatment is crucial in attaining significant energy efficiency. Recovering the heat from pretreatment can increase energy efficiency by a significant amount. The breakdown of micro and macro structures of seaweed has been shown to improve biofuel production. Recovering heat from pretreatment and its viability were not discussed to any great extent. Mahmood et al. (2019) comprehensively discussed the process of selecting and utilizing correct pretreatment processes based on the final products (biofuels, composites, or chemicals) and the biomass best suited for a particular treatment process. Results revealed that reaction time and energy used can be lowered to an extent if assisted by microwave reactors. Further analysis based on this study to understand treatment applications at a commercial level and techno-economic sustainable settings is required.

3.2.2. Hydrothermal liquefaction

Liquid forms of fuel energy are more convenient for many uses, especially for transportation, feeding engines or turbines, and increasing energy density (energy distribution of raw solid biomass is generally lower). This is why there are many thermal, chemical, and biological conversion systems to transform biomass into liquid fuel. Hydrothermal liquefaction (HTL) of biomass is an initial successful thermal conversion technology for the efficient valorization of a range of biomass feedstocks (Castello et al., 2018; Katongtung et al., 2022). It is incredibly flexible when working with feedstock, with the potential to generate lower oxygen levels and work with wet biomass (Gollakota et al., 2018). Hydrothermal liquefaction is based on a principal reaction of biomass or other organic materials with water present under standard hydrothermal conditions. The water in these conditions remains liquid or in a supercritical conformation with high density. Due to the incorporation of a wet reaction setting, HTL is good for damp feedstocks omitting the drying need. During the refining of HTL, the biomass or organic material undergoes many depolymerization reactions, such as hydrolysis, decarboxylation, and dehydration, to obtain water-soluble intermediates. Further repolymerization includes many mechanisms of condensation to form non-water-soluble compounds, including bio-crude and biochar.

Alherbawi et al. (2021) studied the yield of biofuel from manure using hydrothermal liquefaction and the potential upgrade to drop-in fuels. The adoption of this process showed a yield of 37.9% bio-crude and was upgraded to bio-gasoline. This gasoline helps reduce greenhouse gases by almost 7%, showing the sustainability potential of hydrothermal liquefaction. A theoretical framework for the

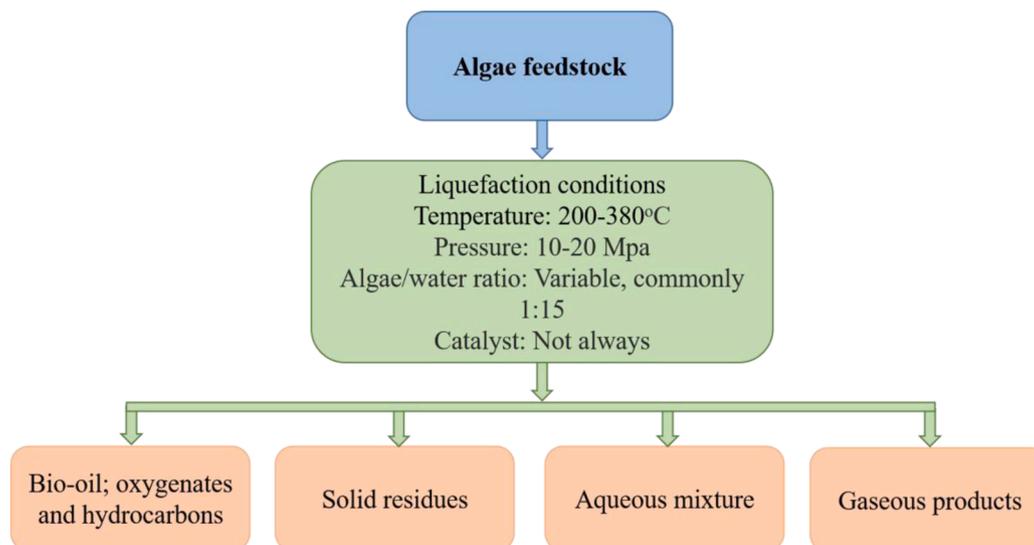


Fig. 4. Flowchart illustrating the hydrothermal liquefaction of algae. Adapted from Galadima and Muraza (2018).

commercialization of this method was discussed but the lack of its implementation does not give a complete picture of the full potential of this route. Masoumi and Dalai (2021) discussed hydrochar, a popular by-product of hydrothermal liquefaction when algae are used as biomass, and assessed the techno-economic aspects and life cycle of algal bio-oil generation through liquefaction oxygenation. This method showed significant enhancements in yield and the environmental effect on the bio-oil production process. Utilizing the by-product of liquefaction improves the sustainability of this method.

Photobioreactors were utilized for the development of the microalgae *Chlorella vulgaris* using hydrothermal liquefaction by Khan et al. (2018) for the subsequent production of bio-crude oil. Microalgae produced 0.93 g per litre of biomass and it was harvested with 250 mg per litre of ferric chloride. The outcomes of laboratory-scale experiments were compared to a model created for the simulation of the hydrothermal liquefaction (HTL) process. While modelling predicted 38% of bio-crude oil formation, laboratory-scale trials produced 30% bio-oil. The generation of bio-oil and other products, such as organic molecules in the aqueous phase, was estimated by the model based on the chemical composition of the microalgae. This also aided in understanding how nitrogenous chemicals are formed. However, to calculate the energy, water, and land requirements for the production of bio-crude oil from microalgae *Chlorella vulgaris* via the HTL approach, a

continuous process must be evaluated.

The study conducted by Durak et al. (2022) investigated how waste process water affected the development of useful- pathogenic fungi and algae. Biomass was obtained from *Ammi visnaga*; catalysts were metal powders of Cu, W, and Fe; fungi included *Trichoderma harzianum*, *Verticillium dahlia*, and *Trichoderma virens*; and algae included *Chlorella minutissima*. In experiments, temperatures of 250, 275, 300, and 325 °C and times of 0, 15, 30, and 45 min were chosen. The techniques of TOC, GC-MS, XRD, and elemental analysis were employed to characterize the sample. Light bio-oil was effectively processed at 300 °C, but heavy bio-oil required 325 °C. In the presence of Fe catalyst, the maximum HHV value of 30.30 MJ/kg was achieved. It was shown that waste process waters promote the growth of beneficial fungi and algae while inhibiting the formation of pathogens.

The thermochemical processes along with their methods, products involved, energy carriers, advantages, and disadvantages are tabulated in Table 3.

Not all conversion mechanisms are suitable for all applications; this relies on aspects including feedstock qualities, process conditions, and the intended end products, among others. Some of the challenges of using these conversion mechanisms to produce bio-oil may be alleviated as research and development continue. The advantages and disadvantages of the conversion mechanisms are tabulated in Table 4.

Table 3
Thermochemical processes and their methodologies, energy carrier, advantages, and disadvantages.

Thermochemical process	Main task	Procedure involved	Main products	Energy carrier	Advantages	Disadvantages	References
Torrefaction	To convert microalgae biomass into energy	In an innocuous or oxygen-deficient environment, micro biomass was progressively heated to a maximal degree of 300 °C	- Solid coal fuel - CO, CO ₂ , H ₂ , CH ₄ , benzene, toluene, and CxHy	- Heat - Electricity	- Moisture content is reduced - Energy density is increased - O/C ratio is reduced - Thermal value is increased - Both the duration and reactivity of processed fuel are enhanced	- Difficult to disintegrate coal - Substantial inorganic matter - High porosity (helps to absorb during preservation)	Ribeiro et al. (2018), Niu et al. (2019) and Cahyanti et al. (2020)
Pyrolysis	To convert biomass into an aqueous phase	In an oxygen-deficient atmosphere, the substance was subjected to extreme temperatures and undergoes physiochemical segregation into separate molecules	Methane, hydrogen, carbon monoxide and carbon dioxide	- Charcoal - Heat - Electricity	- Low-cost, user-friendly method for processing a wide variety of feedstocks - Reduces the volume of waste directed to landfills and mitigates the emission of greenhouse gases - Reduces the chance of water pollution	- There is greater complexity in the product flow than there is in most alternative processes - Since the product gases contain so much CO, they must be treated before being released into the living space	Khuenkao et al. (2020), Wise et al. (2019), Auersvald et al. (2020), Chen et al. (2021b), Gautam et al. (2019) and Varsha et al. (2021)
Gasification	To convert algal biomass into gaseous fuels	Used a regulated supply of oxygen and/or steam to transform organic or fossil-based carbon containing materials with extreme temperatures (>700 °C) without ignition	Carbon monoxide, hydrogen, and carbon dioxide	- Heat - Electricity - Combustion gases	- Suitable for damp biomass - Can be used in commercialization	- In contrast to the updraught gasifier, there is no internal heat transfer - Less effective because of the limited thermal efficiency of gases	Kamble et al. (2019), Shahabuddin et al. (2020), and Hameed et al. (2021)
Liquefaction	Thermochemical conversion of biomass into liquid fuels	The polymer framework was broken down into liquid constituents in a high-temperature pressurized atmosphere for less than 60 min	Bio-oil, biochar, and water-soluble organic compounds	- Heat - Electricity	The aqueous phase, which includes C, N, and P ingredients, can be recycled and used in microalgae cultivation	- High processing constraints - Biocrude with a higher oxygen content relative to its heating value	Sankaran et al. (2020), Lin et al. (2019), and Mahmood et al. (2019)
Hydrothermal	Thermochemical conversion of biomass into biooil or biofuel	The aqueous biomass was heated at extreme pressures to create an energy transporter with a greater capacity	Aldehyde, alcohol, ketone, acetic acid, phenol, fatty acid.	- Heat - Electricity - Charcoal	- Not very energy intensive - Extremely high energy density in comparison to the original component	- Need for highly developed autoclaves - Lack of ability to observe the crystal's formation	Castello et al. (2018), Gollakota et al. (2018), Masoumi and Dalai (2021) and Alherbawi et al. (2021)

Summary: Depending on the characteristics of the biomass feedstock and the desired characteristics of the bio-oil output, the most advantageous conversion method can be determined. For instance, while pyrolysis can yield a high-energy bio-oil, it also creates substantial amounts of char and gas as byproducts. Hydrothermal liquefaction and gasification are more sophisticated and expensive processes, but they can yield a more consistent bio-oil output. While commonly employed for certain feedstocks like vegetable oils and sugars, transesterification and fermentation may not be applicable to all biomass.

4. Upgrading of bio-oil from microalgae

Bio-oil needs to be fine-tuned and upgraded, which is done so the specifications of the product correspond to current transportation infrastructures. The main objective of upgrading is to eliminate oxygen content and reduce the solid content, ageing potential, and viscosity. Upgrading techniques fall into two main categories: physical and chemical upgrading (Sharifzadeh et al., 2019). To meet the fuel

Table 4
Advantages and disadvantages of the conversion mechanisms (pyrolysis, hydrothermal liquefaction and gasification).

Conversion mechanisms	Advantages	Disadvantages
Pyrolysis	<ul style="list-style-type: none"> - Produces stable bio-oil with a high energy density. - Able to process numerous feedstocks, including lignocellulosic biomass. - Bio-oil can be enhanced and utilized as a fossil fuel substitute. - The pyrolysis-produced syngas can be utilized for energy generation. - As a soil amendment, biochar byproducts contribute to carbon sequestration. 	<ul style="list-style-type: none"> - Temperature regulation is crucial for optimum outcomes. - Char can form, which will render the catalyst useless. - There may be a need for additional purification. - Inefficient processes often have large energy demands. - Transporting and managing feedstocks can be difficult.
Hydrothermal liquefaction	<ul style="list-style-type: none"> - Ability to transform wet biomass effectively without drying it first. - Accepts a large variety of feedstocks for processing, such as microalgae and sewage sludge. - Produces a bio-oil of sufficient grade to be used as a direct fuel replacement. - Possibility of recovering nutrients from sewage systems. - It is possible to meet the energy needs of a process with the help of excess or waste heat. 	<ul style="list-style-type: none"> - The cost of operations increases when pressure and temperature are both high. - The product may contain trace amounts of nitrogen and sulphur compounds. - It is possible for catalyst deactivation and reactor fouling to develop. - The transition to an industrial scale might be difficult. - Energy consumption can increase significantly during aqueous phase separation and treatment.
Gasification	<ul style="list-style-type: none"> - Clean and flexible syngas are produced through the efficient combustion of biomass. - Syngas has many potential applications, including electrical and thermal energy production as well as biofuel and chemical production. - Adaptable to a wide range of feedstocks, such as wood and agricultural waste. - The implementation of carbon capture and storage (CCS) techniques could reduce emissions of greenhouse gases. - By replacing fossil fuels with syngas, we can use less of these finite resources. 	<ul style="list-style-type: none"> - Needs precise regulation of operational parameters to produce the required gas composition. - The removal process could become more involved if tar forms. - Ash can cause problems with reactor fouling and gas cleaning. - Gasification plants can have substantial initial investment costs. - Syngas purification requires a gas cleaning system to eliminate contaminants.

standards on which petroleum is based, bio-oils require to be upgraded as the bio-oil generated through hydrothermal liquefaction (HTL) is of low quality compared to petroleum-based fuels. Various methods are developed to upgrade bio-oil, as shown in Fig. 5. These methods include catalytic pyrolysis, emulsification, hydrodeoxygenation, molecular distillation, hydrogenation, catalytic cracking, esterification and supercritical fluids (SCFs) (Baloch et al., 2018).

Biofuels obtained via the process of thermochemical conversion can occur in liquid, gas, or solid. Microalgae properties can be enhanced through torrefaction to make better use of solid fuels. Bio-oil is the main product of the liquefaction process. Biochar and bio-oil can be obtained from the pyrolysis of microalgae. Methane and syngas are the by-products of the microalgae gasification process. Syngas is a combination of carbon monoxide and hydrogen. Torrefaction is a thermochemical conversion technique that improves the calorific value of microalgae by upgrading it (Chen et al., 2015). First, the microalgae undergo thermal degradation at 1 atm in a nitrogen environment or an inert environment at a temperature of around 200–300 °C from several minutes to hours. This process is similar to the pyrolysis process except that pyrolysis occurs at a temperature of about 350–650 °C (Chen et al., 2014).

Microalgae's pyrolytic process with a temperature range of 25–800 °C can be broken down into four stages (Chen et al., 2014b). Stage one is dehydration at a temperature range of 25–200 °C. Stage two is depolymerization, the thermal decomposition of carbohydrates and proteins which leads to the process of cracking with temperatures ranging from 200–430 °C, and decarbonization. Stage three is lipid thermal degradation with temperatures ranging from 430–530 °C. Lastly, stage four involves slow and continuous carbonaceous matters causing a loss of weight within a temperature range of 530–800 °C. Accordingly, during the process of torrefaction microalgae are partially dehydrated and some of their proteins and carbohydrates are partially decomposed, leading to partial carbonization. During pretreatment, duration and temperature play a big role in the torrefaction process. However, temperature impacts the biomass more than duration. The extent of the torrefaction process can be differentiated as severe, mild, and light torrefaction at temperature ranges of 275–300 °C, 235–275 °C, and 200–235 °C, respectively (Chen et al., 2014b). Table 5 lists compositional, elemental analyses and various microalgae heating values.

Maintaining the quality of bio-oil is crucial that can be enhanced by employing refining processes. These processes are utilized to purify the oil, keep it from degrading, and improve its quality so that it can be used in a wide range of applications (Atadashi et al., 2011). Some typical refining processes to improve the quality of bio-oil include filtration, sedimentation, centrifugation, solvent extraction, acid/base treatment, catalytic upgrading, and distillation. Depending on the desired outcomes and parameters, these refining methods can be utilized separately or in combination during the bio-oil refining process (Gupta et al., 2021). The nature of the feedstock, the quality of the final product, and its intended use all play a role in deciding which processing methods to employ.

Bio-oil must be stored and transported properly to maintain its quality, avoid degradation, and allow for safe handling. To prevent oxidation, bio-oil can be kept in storage containers specifically designed for the substance and constructed from nonreactive materials. Maintaining a consistent temperature and avoiding significant fluctuations in temperature are essential for this. The purity of the oil can be preserved through careful handling and filtration (Pinheiro Pires et al., 2019). Important factors include container suitability, leak prevention, and limiting exposure to air and moisture during transit. The quality and safety of bio-oil in storage and during transport are further ensured through compliance with regulations, continuous monitoring, and quality control procedures.

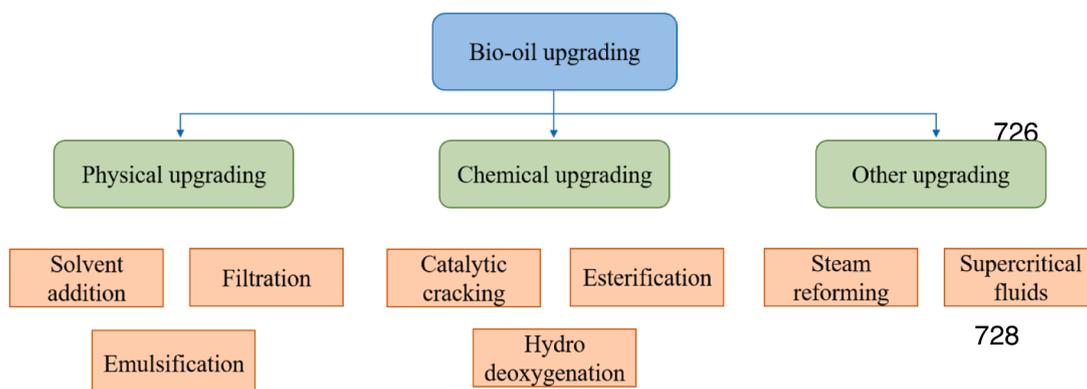


Fig. 5. Bio-oil upgrading methods.

Table 5

Various microalgae and their elemental analysis of carbon, nitrogen, hydrogen, and oxygen, composition of protein and lipid, and heating values.

Microalgae	Elemental analysis (weight %) of carbon	Elemental analysis (weight %) of hydrogen	Elemental analysis (weight %) of nitrogen	Elemental analysis (weight %) of oxygen	Composition (dry-as%) of protein	Composition (dry-as%) of lipid	HHV (MJ kg ⁻¹)	Ref.
<i>Chlorella vulgaris</i> residue	45.04	6.88	9.79	29.42	61.24	5.71	19.44	Wang et al. (2013)
<i>Chlamydomonas</i> sp. Residue of JSC4	–	–	–	–	12.18	6.85	17.41	Chen et al. (2014a)
<i>Nannochloropsis oceanica</i>	50.06	7.46	7.54	34.47	19.1	24.8	21.46	
<i>Nannochloropsis oculata</i>	39.90	5.50	6.20	–	39.00	20.00	16.80	Du et al. (2012)
<i>Chlamydomonas reinhardtii</i> (wild)	52.00	7.40	10.70	29.80	29.80	18.10	23.00	Kebelmann et al. (2013)
<i>Scenedesmus obliquus</i> CNW-N	37.37	5.8	6.82	50.02	30.38	4.66	16.10	Chen et al. (2014b)
<i>Spirulina platensis</i>	45.70	7.71	11.26	25.69	–	–	20.46	Wu et al. (2012)
<i>Arthrospira platensis</i>	36.49	6.12	7.89	49.51	–	–	12.66	Ho et al. (2018)
<i>C. vulgaris</i>	45.66	5.9	9.05	31.95	31.17	13.99	18.77	Phusunti et al. (2018)
<i>Nannochloropsis oceanica</i>	53.98	8.18	8.42	29.42	52.63	1.10	21.02	Zhang et al. (2019)

4.1. Physical upgrading

Some of the methods for the physical upgrading of bio-oil to enhance its quality include filtration, emulsification, and solvent addition. Filtration is a simple and widely employed technique for removing bio-oil of solid particles and char residues. Filters and membranes are utilized to eliminate the contaminants from the oil (Kumar and Strezov, 2021), resulting in a more visible and pure product. A major advantage of hot vapour filtration is that it considerably reduces char and ash levels, hence preventing secondary reactions. Additionally, this filtration method increases the burning rate and reduces the delay in fuel ignition. Emulsification can occur by adding diesel to the oil. The liquid microstructure is modified by ethanol or methanol (polar solvents) addition. This dissolves components that are less soluble eventually stabilizing the ageing process. Other results from this method are a reduction in bio-oil viscosity and homogenization (Sharifzadeh et al., 2019).

Arthrospira platensis (*A. platensis*) has a spiral shape which is usually called spirulina (Böcker et al., 2021). According to historical classification, it is a blue-green alga while phylogenetically it is a cyanobacterium. Böcker et al. (2021) investigated the emulsifying capability of

A. platensis when its proteins were isolated and demonstrated the formation of an interfacial network. Moreover, they hypothesized a mechanistic difference in purification progress. They also found that emulsions with a 20% by volume of medium-chain triglycerides (MCT) oil can potentially be formed by the purification of all extracts at different temperatures. Upon normalizing the concentrations of protein, the isolated fractions and smaller droplets can also be stabilized. While other single cell proteins or proteins of microalgae are purified, the functionality must be improved to counteract biomass loss when other single cell proteins or proteins of microalgae are purified (Böcker et al., 2021).

4.2. Chemical upgrading

Some of the methods for the chemical upgrading of bio-oil to enhance its quality include zeolite cracking, hydrothermal treatment, gasification, steam reforming, esterification, and hydrodeoxygenation (HDO). Instances of how some of these processes help to upgrade microalgal bio-oil are discussed in the following. Zeolite cracking (reverse of hydrotreatment) decreases the distributed components of bio-oil by releasing carbon dioxide in the form of oxygen atoms. This

decreases fuel yield by reducing the need for expensive hydrogens.

Tao et al. (2021) studied mixed microalgal culture's growth and how to efficiently remove nutrients by adding and not adding zeolite in natural conditions in a low concentration. Using microscopy, they found microalgal cells growing on the surface of particles of zeolites. This helped them understand that zeolite has the potential to support the growth of microalgae that has been attached to it. However, when doses of zeolite were added in a higher amount within the reactor, solution turbidity was found to increase rapidly causing the zeolite particles to break down into finer particles. The decrease in light penetration due to the removal of ammonium does not benefit the growth of microalgae. Hence, we can infer that a low dosage of zeolite minimizes the effects of turbidity and functions as a microcarrier to increase the concentration of microalgal biomass. This also helps remove ammonium efficiently.

The application of hydrothermal processing was investigated by Sharifzadeh et al. (2017) for the upgrading of pyrolysis oil using critical water. The results found that within half an hour or less, about 30% of hydroxyl compounds can be deoxygenated using hydrothermal upgrading (HTU) (Sharifzadeh et al., 2019). This makes HTU suitable for first-stage upgrading of bio-oil for a shortened residence time. Additionally, for the production of hydrogen, the product obtained in the aqueous phase of HTU is a suitable feedstock (Sharifzadeh et al., 2015). The water-soluble fractions resulting from the hydrothermal process treatment of microalgae that have been defatted contain effective nutritional sources for the growing of microalgae. The nutrient sources include phosphorus as well as nitrogen (Aida et al., 2017).

Effluents used to cultivate *Chlorella vulgaris* were produced from a process called supercritical water gasification (SCWG) (Nurcahyani and Matsumura, 2021). This was undertaken at 400 °C and 600 °C after which Bristol medium was added. An enhanced growth rate was found for a specific medium with effluent at 600 °C. This study explained why SCWG effluents show more potential for the cultivation of algae rather than effluents from hydrothermal liquefaction. Additionally, this study observed 2.5 times higher accumulation of phosphorus in the algae within SCWG media effluents. From this, they inferred that for the recycling process of nutrients, a mixture of SCWG and *C. vulgaris* can potentially be used.

Summary: The oxygen and substances found in microalgal bio-oil make it inappropriate for direct use in most internal combustion engines. Therefore, bio-oil requires refinement before it can be used as a sustainable fuel. Bio-oil derived from microalgae must be refined before it can be used as a useable fuel. Bio-oil's value and energy density can be increased through the application of various upgrading processes, such as thermal, catalytic, and hydrothermal upgrading, and the usage of bio-refineries, making it a more sustainable and competitive alternative to fossil fuels.

5. Commercial aspects of bio-oil utilization

Bio-oil, produced by methods like pyrolysis and hydrothermal liquefaction, is gaining popularity and attention in the commercial sector. Although bio-oil has demonstrated promising results as a renewable energy source and fossil fuel replacement (Vamvuka, 2011), its commercial deployment is in the early phase. Research and development efforts have centred on making bio-oil production and refining methods more reliable, cost-effective, and high-quality. In order to test its viability and determine whether it might be scaled up, numerous pilot and demonstration facilities have been set up around the world. Potential uses for bio-oil include heat and power generation, as well as being used as a feedstock in bio-refineries for producing goods like biofuels and speciality chemicals. The technical and economic viability, feedstock availability, and the necessity for further optimization of refining and upgrading processes are all challenges that must be overcome (Mirkouei et al., 2017). The economic potential of bio-oil and its incorporation into the larger energy environment as a sustainable and renewable alternative can only be realized with continued research,

investment, and governmental support.

The ability of microalgae to efficiently fix carbon rates and grow at a faster rate than most other algae differentiates them from the rest (Chen et al., 2014b). During their growth and harvest, they show a good ability to capture and store carbon. They are known for various commercial applications, including being assimilated into cosmetics, used as animal fodder, and used to enrich food due to their high nutritional value (Spolaore et al., 2006). Additionally, microalgae are commonly known to have the ability to be mass produced and taken up as a greenhouse gas which is why their potential as feedstock for the production of bio-oil is so great (Chen et al., 2014). Third generation biofuels that used microalgae biomass as feedstock include: biogas obtained from algal biomass that is anaerobically fermented (mainly refers to methane); photosynthetically generated biohydrogen; bioethanol produced from starch; and biodiesel produced from lipids (Gilmour, 2019).

Triacylglycerol (TAG) has been widely researched and is known to be the most promising for the production of biodiesel from the storage of neutral lipids. The simple conversion of fatty acid methyl esters (FAMES) from triacylglycerols (TAGs) in the presence of catalysts such as alkoxides (e.g., sodium methoxide) or alkali metal hydroxides through the process of transesterification makes TAG vital. Methanol can be used in excessive amounts to enhance the reaction in the way we desire. The process of transesterification occurs in a stirred tank, is a continuous process requiring a temperature of 60 °C, and leaves glycerol as the end product which can be taken away by continuous centrifugation. The centrifugation process is useful for lowering the oil's solids, water, and heavy impurity content. By utilizing centrifugal force, heavy contaminants and water can be eliminated from the bio-oil during the centrifugation process. Denser impurities can be removed by centrifuging the mixture and allowing them to settle to the bottom. It has been reported that the transesterification process has a 99% efficiency rate (Gilmour, 2019). FAMES are essentially biodiesel and are used in diesel engines (Knothe, 2005). The very first diesel engine can be dated back to the late 19th century. This continued up until the 1920s after which petroleum-based diesel replaced vegetable oils.

Species of *Chlorella* are grown on a normal medium called Watanabe medium. For these species, biomass has a caloric content of about 18 to 21 kJ g⁻¹. In order to increase the proportion of liquid, cells are grown with a limited amount of nitrogen. The increase of calorific value is about 29 kJ g⁻¹ which equates to a total lipid content of about 63% (w/w). *Chlorella* slurry was incorporated with rapeseed oil esters into a liquid fuel which produced favourable results when tested in a diesel engine. This clearly proved that high-energy neutral lipid algae cells must be extracted in order to reach petroleum diesel's calorie content. The versatility of diesel engines was confirmed through this study. The calorie content of FAMES from microalgae was found to be approximately 38.5 kJ g⁻¹ which is almost 80% of petroleum oil's standard energy (Gilmour, 2019).

Summary: The cost is a major factor in deciding whether or not to use bio-oil in an industrial context. In most cases, the price of making bio-oil from microalgae exceeds the price of making more traditional fossil fuels. Technological improvements, economies of scale, and government subsidies are all reducing the price of bio-oil production. Using bio-refineries to create a wide variety of products—from biofuels to chemicals to materials—can also help bring down the price of bio-oil. The financial viability of bio-oil use is complicated by a number of issues, such as price, supply, and infrastructural needs. However, bio-oil has the ability to emerge as an environmentally friendly and economically viable alternative to traditional fossil fuels, especially with the continuous developments in technology and government assistance.

6. Opportunities and challenges

Bio-oil has a low environmental impact, but producing it from microalgae pyrolysis is challenging and requires the application of cutting-edge technology. Because of its high oxygen content, bio-oil has

qualities that hinder its use as fuel if it is not refined first (Sánchez-Borrego et al., 2021). The use of microalgae pyrolysis for generating bio-oil poses unique challenges, including high acidity, high viscosity, and a low heating value (Lee et al., 2020a). However, these obstacles can be overcome with the help of current technologies applied in an organized way. Therefore, advanced technologies for the pyrolysis of microalgae to produce bio-oil have the potential to improve boiler combustion, stimulate engine and turbine performance, provide transportation fuels, and serve as a renewable feedstock for chemical and material production (Sharifzadeh et al., 2019).

The key challenges of bio-oil production by microalgae pyrolysis lie in the lack of advanced technologies. For instance, intermediate pyrolysis delivers a lower yield which causes a higher proportion of secondary products like char and reaction water (Zainan et al., 2018). Bio-oil fractionation strategies come with multiple challenges. When water and trace amounts of reactive oxygenated molecules and inorganic compounds are present, they combine to form complicated structures that are both acidic and thermally unstable (Kazemi Shariatb Panahi et al., 2019). This presents a challenge in developing the idea of bio-oil refineries. Given that bio-oil is a heterogeneous blend of compounds, there is currently no reliable method for fully characterizing it. This opens the door to new avenues for investigation and the development of useful guidelines for the industry (Dabros et al., 2018). To reduce the amount of time spent processing and the amount of secondary degradation experienced by extremely unstable substances, cutting-edge technologies are necessary (Lee et al., 2020b). Complex processes like hydrodeoxygenation and catalytic cracking also require reliable reactors with optimal settings (Srifa et al., 2019).

In recent years, some inland waters and oceans faced water blooms caused by algae that harmed the environment and endangered the safety of drinking water (Baloch et al., 2018). Species of algae that are often eliminated via ecological and chemical approaches can be useful in the production of bio-oil through pyrolysis. To protect the environment, secondary pollution from algal blooms can be utilized to provide a renewable fuel source (Hu and Gholizadeh, 2020). Bio-oil generated via the pyrolysis process has a yield of about 60%–65% (Dabros et al., 2018). Microalgae pyrolysis also produces bio-oils which can reduce potential greenhouse gas emissions relative to fossil fuels by 60–80% (Saber et al., 2016). Therefore, microalgae are a favourable alternative to harmful fossil fuels because of their high lipid yields, prospective use of poor-quality water in the production process, commercial feasibility, and their productivity potential as a biofuel feedstock.

Summary: Microalgae bio-oil production has the potential for sustainable energy and decreased carbon emissions. However, issues including high cultivation costs, biomass composition, efficient extraction, and sustainable sourcing must be addressed before they can be used widely or beneficial for commercial enterprises. To get over these hurdles and reach the full potential of microalgae-based bio-oil production, continuous research and advances in technology are necessary.

7. Future prospects of bio-oil production from microalgae

Bio-oil production from microalgae has tremendous potential for the long-term efficient use of both energy and materials. Technology, research, and commercialization efforts will continue to improve, and this is what is expected to remedy current issues and drive the sector forward. Improving methods for growing microalgae is one such area. Microalgae productivity is increasing as photobioreactors, closed-loop systems, and genetic engineering approaches are lowering the amount of water and nutrients needed for culture. This makes large-scale production more economically feasible. These advancements may lead to a dramatic rise in the quantity of microalgae biomass available for use in producing bio-oil.

To increase bio-oil production and enhance its quality, researchers are also looking at new extraction and conversion techniques. Energy efficiency, bio-oil stability, and production costs can all be improved by

ongoing efforts to perfect conversion technologies like pyrolysis and hydrothermal liquefaction. The extraction of valuable co-products including proteins, lipids, and carbohydrates from microalgae biomass is facilitated by the integration of these processes with other biorefinery operations. Sustainable and environmentally friendly harvesting procedures are also crucial to the future of microalgae-based bio-oil production. To reduce the dependency on synthetic fertilizers and their associated environmental damage, scientists are investigating the feasibility of using waste and wastewater as nutrient sources. Furthermore, both the benefits of reducing GHG emissions and producing bio-oil can be accomplished by the incorporation of microalgae cultivation with carbon capture and utilization.

Standardized quality control techniques and certification schemes for microalgae-based bio-oil could be established in the future. This would guarantee uniformity in product quality, compatibility with existing infrastructure, and compliance with regulations, allowing it to fit in with the current energy market without any disruptions. As mentioned earlier, the potential for microalgae to be used in bio-oil production is promising. Microalgae-based bio-oil has the potential to become a financially viable and environmentally sustainable alternative to traditional fossil fuels due to ongoing advances in developing methods, conversion technology, sustainability practices, and quality control processes. As a result of its broad use, greenhouse gas emissions might be reduced, energy security could be improved, and a more sustainable and resilient energy future might emerge.

8. Conclusion

This article thoroughly reviewed the main mechanisms of microalgal bio-oil production, as well as its economics, applications, and upgrading. It also discussed the technological advancements, challenges, and prospects of the production mechanisms. The different methods were highlighted alongside the factors affecting the pyrolysis process. The process of microalgae pyrolysis to produce bio-oil uses fewer chemicals and is environmentally friendly. The maximum bio-oil production from microalgae via fast pyrolysis was found to be approximately 60%, despite the current lack of use of advanced technology. The production rate was increased to 72%, with a biochar content of 36%. Bio-oil separation strategies could face numerous challenges including not using advanced technologies which affect upgrading mechanisms and lead to a lower bio-oil yield. However, using the appropriate advanced technology can help overcome such challenges. For instance, implementing extraction and fractionation during upgrading can be used for the efficient conversion of harmful algal bloom into a resource by utilizing the eliminated algae to produce bio-oil by pyrolysis.

The key advantages of this process lie in its advanced use of technology and the mass availability of microalgae. Some other significant issues were identified, such as the production of complicated structures with low thermal stability and pH due to the presence of water and the lack of reactive oxygenated compounds and inorganic compounds in sufficient quantities. These challenges can be tackled using advanced technology, especially regarding extraction and fractionation. As a result, the upgrading process using the pyrolysis of microalgae will face fewer complications. However, the price of producing bio-oil is going to decrease as a result of technological advancements, economies of scale, and government subsidies. The production of chemicals, biofuels, and materials through bio-refineries can also contribute to lowering the cost of bio-oil. This study thus recommends further research to overcome the challenges and introduce highly developed and advanced technologies for microalgae pyrolysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgement

The authors extend their appreciation to the Deanship of Scientific Research at King Khalid University, Saudi Arabia for funding this work through the Small Groups Project under grant number RGP.1/244/44.

Funding

Open Access funding is provided by the Qatar National Library .

References

- Adamczyk, M., Sajdak, M., 2018. Pyrolysis behaviours of microalgae nannochloropsis gaditana. Waste Biomass Valorization 9, 2221–2235. <https://doi.org/10.1007/s12649-017-9996-8>.
- Aida, T.M., Maruta, R., Tanabe, Y., Oshima, M., Nonaka, T., Kujiraoka, H., Kumagai, Y., Ota, M., Suzuki, I., Watanabe, M.M., Imomata, H., Smith, R.L., 2017. Nutrient recycle from defatted microalgae (*Aurantiochytrium*) with hydrothermal treatment for microalgae cultivation. Bioresour. Technol. 228, 186–192. <https://doi.org/10.1016/j.biortech.2016.12.078>.
- Alam, F., Date, A., Rasjadin, R., Mobin, S., Moria, H., Baqui, A., 2012. Biofuel from algae- Is it a viable alternative? Proc. Eng. 49, 221–227.
- Alherbawi, M., Parthasarathy, P., Al-Ansari, T., Mackey, H.R., McKay, G., 2021. Potential of drop-in biofuel production from camel manure by hydrothermal liquefaction and biocrude upgrading: A Qatar case study. Energy 232, 121027. <https://doi.org/10.1016/j.energy.2021.121027>.
- Anand, V., Gautam, R., Vinu, R., 2017. Non-catalytic and catalytic fast pyrolysis of *Schizochytrium limacinum* microalga. Fuel 205, 1–10. <https://doi.org/10.1016/j.fuel.2017.05.049>.
- Andrade, L.A., Batista, F.R.X., Lira, T.S., Barrozo, M.A.S., Vieira, L.G.M., 2018. Characterization and product formation during the catalytic and non-catalytic pyrolysis of the green microalgae *Chlamydomonas reinhardtii*. Renew. Energy 119, 731–740. <https://doi.org/10.1016/j.renene.2017.12.056>.
- Ansah, E., Wang, L., Zhang, B., Shahbazi, A., 2018. Catalytic pyrolysis of raw and hydrothermally carbonized *Chlamydomonas debaryana* microalgae for denitrogenation and production of aromatic hydrocarbons. Fuel 228, 234–242. <https://doi.org/10.1016/j.fuel.2018.04.163>.
- Ansari, K.B., Gaikar, V.G., 2019. Investigating production of hydrocarbon rich bio-oil from grassy biomass using vacuum pyrolysis coupled with online deoxygenation of volatile products over metallic iron. Renew. Energy 130, 305–318.
- Arun, J., Raghu, R., Hanif, S.S.M., Thilak, P.G., Sridhar, D., Nirmala, N., Dawn, S.S., Sivaramakrishnan, R., Chi, N.T.L., Pugazhendhi, A., 2022. A comparative review on photo and mixotrophic mode of algae cultivation: Thermochemical processing of biomass, necessity of bio-oil upgrading, challenges and future roadmaps. Appl. Energy 325, 119808.
- Atadashi, I.M., Aroua, M.K., Aziz, A.R.A., Sulaiman, N.M.N., 2011. Refining technologies for the purification of crude biodiesel. Appl. Energy 88, 4239–4251.
- Auersvald, M., Macek, T., Schulzke, T., Staš, M., šimáček, P., 2020. Influence of biomass type on the composition of bio-oils from ablative fast pyrolysis. J. Anal. Appl. Pyrolysis 150. <https://doi.org/10.1016/j.jaap.2020.104838>.
- Azizi, K., Keshavarz Moraveji, M., Abedini Najafabadi, H., 2018. A review on bio-fuel production from microalgal biomass by using pyrolysis method. Renew. Sustain. Energy Rev. 82, 3046–3059. <https://doi.org/10.1016/j.rser.2017.10.033>.
- Bach, Q.-V., Chen, W.-H., 2017a. Pyrolysis characteristics and kinetics of microalgae via thermogravimetric analysis (TGA): A state-of-the-art review. Bioresour. Technol. 246, 88–100.
- Bach, Q.-V., Chen, W.-H., 2017b. A comprehensive study on pyrolysis kinetics of microalgal biomass. Energy Convers. Manage. 131, 109–116. <https://doi.org/10.1016/j.enconman.2016.10.077>.
- Baloch, H.A., Nizamuddin, S., Siddiqui, M.T.H., Riaz, S., Jatoti, A.S., Dumbre, D.K., Mubarak, N.M., Srinivasan, M.P., Griffin, G.J., 2018. Recent advances in production and upgrading of bio-oil from biomass: A critical overview. J. Environ. Chem. Eng. 6, 5101–5118. <https://doi.org/10.1016/j.jece.2018.07.050>.
- Baskar, G., Kalavathy, G., Aiswarya, R., Selvakumari, I.A., 2019. Advances in bio-oil extraction from nonedible oil seeds and algal biomass. In: Advances in Eco-Fuels for a Sustainable Environment. Elsevier, pp. 187–210.
- Bhoi, P.R., Quedraogo, A.S., Soloiu, V., Quirino, R., 2020. Recent advances on catalysts for improving hydrocarbon compounds in bio-oil of biomass catalytic pyrolysis. Renew. Sustain. Energy Rev. 121, 109676 <https://doi.org/10.1016/j.rser.2019.109676>.
- Billar, P., Sharma, B.K., Kunwar, B., Ross, A.B., 2015. Hydroprocessing of bio-crude from continuous hydrothermal liquefaction of microalgae. Fuel 159, 197–205. <https://doi.org/10.1016/j.fuel.2015.06.077>.
- Böcker, L., Bertsch, P., Wenner, D., Teixeira, S., Bergfreund, J., Eder, S., Fischer, P., Mathys, A., 2021. Effect of *Arthrospira platensis* microalgae protein purification on emulsification mechanism and efficiency. J. Colloid Interface Sci. 584, 344–353. <https://doi.org/10.1016/j.jcis.2020.09.067>.
- Bordoloi, N., Narzari, R., Sut, D., Saikia, R., Chutia, R.S., Katakai, R., 2016. Characterization of bio-oil and its sub-fractions from pyrolysis of *Scenedesmus dimorphus*. Renew. Energy 98, 245–253. <https://doi.org/10.1016/j.renene.2016.03.081>.
- Cahyanti, M.N., Doddapaneni, T.R.K.C., Kikas, T., 2020. Biomass torrefaction: An overview on process parameters, economic and environmental aspects and recent advancements. Bioresour. Technol. 301, 122737 <https://doi.org/10.1016/j.biortech.2020.122737>.
- Cao, B., Xia, Z., Wang, S., Abomohra, A.E.F., Cai, N., Hu, Y., Yuan, C., Qian, L., Liu, L., Liu, X., Li, B., He, Z., Wang, Q., 2018. A study on catalytic co-pyrolysis of cellulose with seaweeds polysaccharides over ZSM-5: Towards high-quality biofuel production. J. Anal. Appl. Pyrolysis 134, 526–535. <https://doi.org/10.1016/j.jaap.2018.07.020>.
- Castello, D., Pedersen, T.H., Rosendahl, L.A., 2018. Continuous hydrothermal liquefaction of biomass: A critical review. Energies 11. <https://doi.org/10.3390/en11113165>.
- Chan, Y.H., Loh, S.K., Chin, B.L.F., Yiin, C.L., How, B.S., Cheah, K.W., Wong, M.K., Loy, A.C.M., Gwee, Y.L., Lo, S.L.Y., Yusup, S., Lam, S.S., 2020. Fractionation and extraction of bio-oil for production of greener fuel and value-added chemicals: Recent advances and future prospects. Chem. Eng. J. 397, 125406 <https://doi.org/10.1016/j.cej.2020.125406>.
- Chen, C., Fan, D., Ling, H., Huang, X., Yang, G., Cai, D., Zhao, J., Bi, Y., 2022. Microwave catalytic co-pyrolysis of *Chlorella vulgaris* and high density polyethylene over activated carbon supported monometallic: Characteristics and bio-oil analysis. Bioresour. Technol. 363, 127881 <https://doi.org/10.1016/j.biortech.2022.127881>.
- Chen, W.-H., Huang, M.-Y., Chang, J.-S., Chen, C.-Y., 2014a. Thermal decomposition dynamics and severity of microalgal residues in torrefaction. Bioresour. Technol. 169, 258–264. <https://doi.org/10.1016/j.biortech.2014.06.086>.
- Chen, W., Lin, B., Huang, M., Chang, J., 2014. Bioresource technology thermochemical conversion of microalgal biomass into biofuels: A review. Bioresour. Technol. <https://doi.org/10.1016/j.biortech.2014.11.050>.
- Chen, W.-H., Lin, B.-J., Huang, M.-Y., Chang, J.-S., 2015. Thermochemical conversion of microalgal biomass into biofuels: A review. Bioresour. Technol. 184, 314–327. <https://doi.org/10.1016/j.biortech.2014.11.050>.
- Chen, C., Qi, Q., Zeng, T., Fan, D., Zhao, J., Qiu, H., Huang, H., 2021a. Effect of compound additive on microwave-assisted pyrolysis characteristics and products of *Chlorella vulgaris*. J. Energy Inst. 98, 188–198. <https://doi.org/10.1016/j.joii.2021.06.019>.
- Chen, W.-H., Wu, Z.-Y., Chang, J.-S., 2014b. Isothermal and non-isothermal torrefaction characteristics and kinetics of microalga *Scenedesmus obliquus* CNW-N. Bioresour. Technol. 155, 245–251. <https://doi.org/10.1016/j.biortech.2013.12.116>.
- Chen, R., Zhang, S., Yang, X., Li, G., Zhou, H., Li, Q., Zhang, Y., 2021b. Thermal behaviour and kinetic study of co-pyrolysis of microalgae with different plastics. Waste Manage. 126, 331–339. <https://doi.org/10.1016/j.wasman.2021.03.001>.
- Chia, S.R., Ong, H.C., Chew, K.W., Show, P.L., Phang, S.-M., Ling, T.C., Nagarajan, D., Lee, D.-J., Chang, J.-S., 2018. Sustainable approaches for algae utilisation in bioenergy production. Renew. Energy 129, 838–852. <https://doi.org/10.1016/j.renene.2017.04.001>.
- Choi, D., Lee, J., Tsang, Y.F., Kim, K.-H., Rinklebe, J., Kwon, E.E., 2017. Modification of hydrothermal liquefaction products from *Arthrospira platensis* by using carbon dioxide. Algal Res. 24, 148–153. <https://doi.org/10.1016/j.algal.2017.03.017>.
- Cieślak, B.M., Namieśnik, J., Konieczka, P., 2015. Review of sewage sludge management: standards, regulations and analytical methods. J. Clean. Prod. 90, 1–15.
- Dabros, T.M.H., Stummann, M.Z., Hoj, M., Jensen, P.A., Grunwaldt, J.D., Gabrielsen, J., Mortensen, P.M., Jensen, A.D., 2018. Transportation fuels from biomass fast pyrolysis, catalytic hydrodeoxygenation, and catalytic fast hydroprocessing. Prog. Energy Combust. Sci. 68, 268–309. <https://doi.org/10.1016/j.pecs.2018.05.002>.
- Ding, Y., Liu, Y., Liu, S., Li, Z., Tan, X., Huang, X., Zeng, G., Zhou, L., Zheng, B., 2016. Biochar to improve soil fertility, A review. Agron. Sustain. Dev. 36, 36. <https://doi.org/10.1007/s13593-016-0372-z>.
- Du, Z., Mohr, M., Ma, X., Cheng, Y., Lin, X., Liu, Y., Zhou, W., Chen, P., Ruan, R., 2012. Hydrothermal pretreatment of microalgae for production of pyrolytic bio-oil with a low nitrogen content. Bioresour. Technol. 120, 13–18. <https://doi.org/10.1016/j.biortech.2012.06.007>.
- Durak, H., Genel, S., Durak, E.D., Özçimen, D., Koçer, A.T., 2022. Hydrothermal liquefaction process of ammi visnaga and a new approach for recycling of the waste process water: cultivation of algae and fungi. Biomass Convers. Bioref. 1–17.
- Fan, Y., Zhao, W., Shao, S., Cai, Y., Chen, Y., Jin, L., 2018. Promotion of the vapors from biomass vacuum pyrolysis for biofuels under non-thermal Plasma Synergistic Catalysis (NPSC) system. Energy 142, 462–472. <https://doi.org/10.1016/j.energy.2017.10.060>.
- Fang, J., Zhan, L., Ok, Y.S., Gao, B., 2018. Minireview of potential applications of hydrochar derived from hydrothermal carbonization of biomass. J. Ind. Eng. Chem. 57, 15–21. <https://doi.org/10.1016/j.jiec.2017.08.026>.
- Gabhane, J.W., Bhanghe, V.P., Patil, P.D., Bankar, S.T., Kumar, S., 2020. Recent trends in biochar production methods and its application as a soil health conditioner: a review. SN Appl. Sci. 2, 1–21. <https://doi.org/10.1007/s42452-020-3121-5>.
- Galadima, A., Muraza, O., 2018. Hydrothermal liquefaction of algae and bio-oil upgrading into liquid fuels: Role of heterogeneous catalysts. Renew. Sustain. Energy Rev. 81, 1037–1048.
- Gautam, R., Shyam, S., Reddy, B.R., Govindaraju, K., Vinu, R., 2019. Microwave-assisted pyrolysis and analytical fast pyrolysis of macroalgae: Product analysis and effect of heating mechanism. Sustain. Energy Fuels. <https://doi.org/10.1039/c9se00162j>.
- Gautam, R., Varma, A.K., Vinu, R., 2017. Apparent kinetics of fast pyrolysis of four different microalgae and product analyses using pyrolysis-FTIR and pyrolysis-GC/

- MS. Energy Fuels 31, 12339–12349. <https://doi.org/10.1021/acs.energyfuels.7b02520>.
- Gautam, R., Vinu, R., 2018. Non-catalytic fast pyrolysis and catalytic fast pyrolysis of nannochloropsis oculata using Co-Mo/ γ -Al₂O₃ catalyst for valuable chemicals. Algal Res. 34, 12–24. <https://doi.org/10.1016/j.algal.2018.06.024>.
- Gilmour, D.J., 2019. Microalgae for biofuel production, pp. 1–30. <https://doi.org/10.1016/bs.aams.2019.10.001>.
- Gollakota, A.R.K., Kishore, N., Gu, S., 2018. A review on hydrothermal liquefaction of biomass. Renew. Sustain. Energy Rev. 81, 1378–1392. <https://doi.org/10.1016/j.rser.2017.05.178>.
- Gupta, S., Mondal, P., Borugadda, V.B., Dalai, A.K., 2021. Advances in upgradation of pyrolysis bio-oil and biochar towards improvement in bio-refinery economics: A comprehensive review. Environ. Technol. Innov. 21, 101276.
- Hameed, Z., Aslam, M., Khan, Z., Maqsood, K., Atabani, A.E., Ghauri, M., Khurram, M.S., Rehan, M., Nizami, A.S., 2021. Gasification of municipal solid waste blends with biomass for energy production and resources recovery: Current status, hybrid technologies and innovative prospects. Renew. Sustain. Energy Rev. 136, 110375 <https://doi.org/10.1016/j.rser.2020.110375>.
- Harman-Ware, A.E., Morgan, T., Wilson, M., Crocker, M., Zhang, J., Liu, K., Stork, J., Debolt, S., 2013. Microalgae as a renewable fuel source: Fast pyrolysis of *Scenedesmus* sp. Renew. Energy 60, 625–632. <https://doi.org/10.1016/j.renene.2013.06.016>.
- Harun, R., Danquah, M.K., Thiruvankadam, S., 2014. Particulate size of microalgal biomass affects hydrolysate properties and bioethanol concentration. Biomed. Res. Int. 2014, 435631 <https://doi.org/10.1155/2014/435631>.
- Hassan, H., Lim, J.K., Hameed, B.H., 2016. Recent progress on biomass co-pyrolysis conversion into high-quality bio-oil. Bioresour. Technol. 221, 645–655. <https://doi.org/10.1016/j.biortech.2016.09.026>.
- Hayes, D.J.M., 2013. In: Triantafyllidis, A.A., Stöcker, M.B.T.-T.R. of C. for the S.P. of B. and B (Eds.), Chapter 2 - Biomass Composition and Its Relevance to Biorefining. Elsevier, Amsterdam, pp. 27–65. <https://doi.org/10.1016/B978-0-444-56330-9.00002-4>.
- Ho, S.-H., Zhang, C., Chen, W.-H., Shen, Y., Chang, J.-S., 2018. Characterization of biomass waste torrefaction under conventional and microwave heating. Bioresour. Technol. 264, 7–16. <https://doi.org/10.1016/j.biortech.2018.05.047>.
- Hong, Y., Chen, W., Luo, X., Pang, C., Lester, E., Wu, T., 2017. Microwave-enhanced pyrolysis of macroalgae and microalgae for syngas production. Bioresour. Technol. 237, 47–56. <https://doi.org/10.1016/j.biortech.2017.02.006>.
- Hu, X., Gholizadeh, M., 2020. Progress of the applications of bio-oil. Renew. Sustain. Energy Rev. 134, 110124 <https://doi.org/10.1016/j.rser.2020.110124>.
- Huang, X., Cao, J.-P., Zhao, X.-Y., Wang, J.-X., Fan, X., Zhao, Y.-P., Wei, X.-Y., 2016. Pyrolysis kinetics of soybean straw using thermogravimetric analysis. Fuel 169, 93–98.
- Huang, F., Tahmasebi, A., Maliutina, K., Yu, J., 2017. Formation of nitrogen-containing compounds during microwave pyrolysis of microalgae: Product distribution and reaction pathways. Bioresour. Technol. 245, 1067–1074. <https://doi.org/10.1016/j.biortech.2017.08.093>.
- Jafari, S., Tavasoli, A., 2018. A comparative study on the quality of bioproducts derived from catalytic pyrolysis of green microalgae *Spirulina* (Arthrospira) plantensis over transition metals supported on HMS-ZSM5 composite. Int. J. Hydrog. Energy 43, 19902–19917. <https://doi.org/10.1016/j.ijhydene.2018.08.171>.
- Jamilatun, S., Budiman, A., Budhijanto, B., Rochmadi, R., 2017. Non-catalytic slow pyrolysis of spirulina plantensis residue for production of liquid biofuel. Int. J. Renew. Energy Res. 7, 1901–1908.
- Jazrawi, C., Biller, P., He, Y., Montoya, A., Ross, A.B., Maschmeyer, T., Haynes, B.S., 2015. Two-stage hydrothermal liquefaction of a high-protein microalga. Algal Res. 8, 15–22. <https://doi.org/10.1016/j.algal.2014.12.010>.
- Ji, C., He, Z., Wang, Q., Xu, G., Wang, S., Xu, Z., Ji, H., 2017. Effect of operating conditions on direct liquefaction of low-lipid microalgae in ethanol-water co-solvent for bio-oil production. Energy Convers. Manage. 141, 155–162. <https://doi.org/10.1016/j.enconman.2016.07.024>.
- Kamble, A.D., Saxena, V.K., Chavan, P.D., Mendhe, V.A., 2019. Co-gasification of coal and biomass an emerging clean energy technology: Status and prospects of development in Indian context. Int. J. Min. Sci. Technol. 29, 171–186. <https://doi.org/10.1016/j.ijmst.2018.03.011>.
- Katongtung, T., Phromphithak, S., Onsree, T., Tippayawong, N., Lauterbach, J., 2022. Bio-oil production from hydrothermal liquefaction of pennisetum purpureum × *Pennisetum typhoides*. Energy Rep. 8, 1170–1176. <https://doi.org/10.1016/j.egyr.2022.07.152>.
- Kazemi Shariati Panahi, H., Tabatabaei, M., Aghbashlo, M., Dehghani, M., Rehan, M., Nizami, A.S., 2019. Recent updates on the production and upgrading of bio-crude oil from microalgae. Bioresour. Technol. Rep. 7, 100216 <https://doi.org/10.1016/j.biteb.2019.100216>.
- Kebelmann, K., Hornung, A., Karsten, U., Griffiths, G., 2013. Intermediate pyrolysis and product identification by TGA and py-GC/MS of green microalgae and their extracted protein and lipid components. Biomass Bioenergy 49, 38–48. <https://doi.org/10.1016/j.biombioe.2012.12.006>.
- Khan, S.A., Ali, I., Naqvi, S.R., Li, K., Mehram, M.T., Khoja, A.H., Alarabi, A.A., Atabani, A.E., 2021. Investigation of slow pyrolysis mechanism and kinetic modeling of *Scenedesmus quadricauda* biomass. J. Anal. Appl. Pyrolysis 158, 105149. <https://doi.org/10.1016/j.jaap.2021.105149>.
- Khan, S., Gholkar, P., Shastri, Y., Shah, N.G., Bhartiya, S., 2018. Hydrothermal liquefaction of chlorella SP for biocrude oil production: Comparison of experimental and modeling results. Int. Agric. Eng. J. 27, 8–16.
- Khuenkaeo, N., MacQueen, B., Onsree, T., Daiya, S., Tippayawong, N., Lauterbach, J., 2020. Bio-oils from vacuum ablative pyrolysis of torrefied tobacco residues. RSC Adv. 10, 34986–34995. <https://doi.org/10.1039/d0ra06014c>.
- Khuenkaeo, N., Tippayawong, N., 2018. Bio-oil production from ablative pyrolysis of corncob pellets in a rotating blade reactor. IOP Conf. Ser. Earth Environ. Sci. 159. <https://doi.org/10.1088/1755-1315/159/1/012037>.
- Kiran Kumar, P., Vijaya Krishna, S., Verma, K., Pooja, K., Bhagawan, D., Srilatha, K., Himabindu, V., 2018. Bio oil production from microalgae via hydrothermal liquefaction technology under subcritical water conditions. J. Microbiol. Methods 153, 108–117. <https://doi.org/10.1016/j.mimet.2018.09.014>.
- Knothe, G., 2005. Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. Fuel Process. Technol. 86, 1059–1070. <https://doi.org/10.1016/j.fuproc.2004.11.002>.
- Krishnan, R.Y., Manikandan, S., Subbaiya, R., Kim, W., Karmegam, N., Govarthanan, M., 2022. Advanced thermochemical conversion of algal biomass to liquid and gaseous biofuels: A comprehensive review of recent advances. Sustain. Energy Technol. Assess. 52, 102211.
- Kumar, R., Strezov, V., 2021. Thermochemical production of bio-oil: A review of downstream processing technologies for bio-oil upgrading, production of hydrogen and high value-added products. Renew. Sustain. Energy Rev. 135, 110152.
- Lam, S.S., Wan Mahari, W.A., Ok, Y.S., Peng, W., Chong, C.T., Ma, N.L., Chase, H.A., Liew, Z., Yusup, S., Kwon, E.E., Tsang, D.C.W., 2019. Microwave vacuum pyrolysis of waste plastic and used cooking oil for simultaneous waste reduction and sustainable energy conversion: Recovery of cleaner liquid fuel and techno-economic analysis. Renew. Sustain. Energy Rev. 115, 109359 <https://doi.org/10.1016/j.rser.2019.109359>.
- Lee, J., Choi, D., Kwon, E.E., Ok, Y.S., 2017. Functional modification of hydrothermal liquefaction products of microalgal biomass using CO₂. Energy 137, 412–418. <https://doi.org/10.1016/j.energy.2017.03.077>.
- Lee, K.-H., Kang, B.-S., Park, Y.-K., Kim, J.-S., 2005. Influence of reaction temperature, pretreatment, and a char removal system on the production of bio-oil from rice straw by fast pyrolysis, using a fluidized bed. Energy Fuels 19, 2179–2184.
- Lee, J., Kwon, E.E., Park, Y.K., 2020a. Recent advances in the catalytic pyrolysis of microalgae. Catal. Today 355, 263–271. <https://doi.org/10.1016/j.cattod.2019.03.010>.
- Lee, X.J., Ong, H.C., Gan, Y.Y., Chen, W.H., Mahlia, T.M.I., 2020b. State of art review on conventional and advanced pyrolysis of macroalgae and microalgae for biochar, bio-oil and bio-syngas production. Energy Convers. Manage. <https://doi.org/10.1016/j.enconman.2020.112707>.
- Li, F., Srivatsa, S.C., Bhattacharya, S., 2019. A review on catalytic pyrolysis of microalgae to high-quality bio-oil with low oxygenate and nitrogenous compounds. Renew. Sustain. Energy Rev. 108, 481–497. <https://doi.org/10.1016/j.rser.2019.03.026>.
- Lin, R., Deng, C., Ding, L., Bose, A., Murphy, J.D., 2019. Improving gaseous biofuel production from seaweed saccharina latissima: The effect of hydrothermal pretreatment on energy efficiency. Energy Convers. Manage. 196, 1385–1394. <https://doi.org/10.1016/j.enconman.2019.06.044>.
- Luo, G., Chandler, D.S., Anjos, L.C.A., Eng, R.J., Jia, P., Resende, F.L.P., 2017. Pyrolysis of whole wood chips and rods in a novel ablative reactor. Fuel 194, 229–238. <https://doi.org/10.1016/j.fuel.2017.01.010>.
- Mahmood, H., Moniruzzaman, M., Iqbal, T., Khan, M.J., 2019. Recent advances in the pretreatment of lignocellulosic biomass for biofuels and value-added products. Curr. Opin. Green Sustain. Chem. 20, 18–24. <https://doi.org/10.1016/j.cogsc.2019.08.001>.
- Mamo, T.T., Mekonnen, Y.S., 2020. Microwave-assisted biodiesel production from microalgae, scenedesmus species, using goat bone-made nano-catalyst. Appl. Biochem. Biotechnol. 190, 1147–1162. <https://doi.org/10.1007/s12010-019-03149-0>.
- Marcilla, A., Catalá, L., García-Quesada, J.C., Valdés, F.J., Hernández, M.R., 2013. A review of thermochemical conversion of microalgae. Renew. Sustain. Energy Rev. 27, 11–19. <https://doi.org/10.1016/j.rser.2013.06.032>.
- Masoumi, S., Dalai, A.K., 2021. Techno-economic and life cycle analysis of biofuel production via hydrothermal liquefaction of microalgae in a methanol-water system and catalytic hydrotreatment using hydrochar as a catalyst support. Biomass Bioenergy 151, 106168. <https://doi.org/10.1016/j.biombioe.2021.106168>.
- Min Ju, Y., Cheol Oh, K., Yol Lee, K., Hyun Kim, D., 2018. Performance analysis of a vacuum pyrolysis system. J. Biosyst. Eng. 43, 14–20.
- Mirkouei, A., Haapala, K.R., Sessions, J., Murthy, G.S., 2017. A review and future directions in techno-economic modeling and optimization of upstream forest biomass to bio-oil supply chains. Renew. Sustain. Energy Rev. 67, 15–35.
- Mo, L., Dai, H., Feng, L., Liu, B., Li, X., Chen, Y., Khan, S., 2020. In-situ catalytic pyrolysis upgradation of microalgae into hydrocarbon rich bio-oil: Effects of nitrogen and carbon dioxide environment. Bioresour. Technol. 314, 123758 <https://doi.org/10.1016/j.biortech.2020.123758>.
- Morais, M.G., Cassuriaga, A.P.A., Cruz, C.G., Moraes, L., Costa, J.A.V., 2022. In: Ngo, H., Guo, W., Pandey, A., Chang, J.-S., Biofuels, Lee, Biochemicals, D.-J.B.T.-B. (Eds.), Chapter1 - Metabolism of Microalgae and Metabolic Engineering for Biomaterial Applications. Elsevier, pp. 1–20. <https://doi.org/10.1016/B978-0-323-96142-4.00010-5>.
- Nagarajan, D., Chang, J.S., Lee, D.J., 2020. Pretreatment of microalgal biomass for efficient biohydrogen production – Recent insights and future perspectives. Bioresour. Technol. 302, 122871 <https://doi.org/10.1016/j.biortech.2020.122871>.
- Nagi, G.K., Minhas, A.K., Gaur, S., Jain, P., Mandal, S., 2021. Integration of algal biofuels with bioremediation coupled industrial commodities towards cost-effectiveness. Front. Energy Res.

- Nazem, M.A., Tavakoli, O., 2017. Bio-oil production from refinery oily sludge using hydrothermal liquefaction technology. *J. Supercrit. Fluids* 127, 33–40. <https://doi.org/10.1016/j.supflu.2017.03.020>.
- Niu, Y., Lv, Y., Lei, Y., Liu, S., Liang, Y., Wang, D., Hui, S., 2019. Biomass torrefaction: properties, applications, challenges, and economy. *Renew. Sustain. Energy Rev.* 115, 109395 <https://doi.org/10.1016/j.rser.2019.109395>.
- Nurchayani, P.R., Matsumura, Y., 2021. Reutilization of algal supercritical water gasification waste for microalgae *Chlorella vulgaris* cultivation. *ACS Omega* 6, 12551–12556. <https://doi.org/10.1021/acsomega.1c00476>.
- Oasmaa, A., Lehto, J., Solantausta, Y., Kallio, S., 2021. Historical review on VTT fast pyrolysis bio-oil production and upgrading. *Energy Fuels* 35. <https://doi.org/10.1021/acs.energyfuels.1c00177>.
- Oncel, S.S., 2013. Microalgae for a macroenergy world. *Renew. Sustain. Energy Rev.* 26, 241–264. <https://doi.org/10.1016/j.rser.2013.05.059>.
- Ong, H.C., Chen, W.H., Farooq, A., Gan, Y.Y., Lee, K.T., Ashokkumar, V., 2019. Catalytic thermochemical conversion of biomass for biofuel production: A comprehensive review. *Renew. Sustain. Energy Rev.* <https://doi.org/10.1016/j.rser.2019.109266>.
- Panwar, N.L., Paul, A.S., 2021. An overview of recent development in bio-oil upgrading and separation techniques. *Environ. Eng. Res.* 26.
- Papari, S., Hawboldt, K., 2015. A review on the pyrolysis of woody biomass to bio-oil: Focus on kinetic models. *Renew. Sustain. Energy Rev.* 52, 1580–1595. <https://doi.org/10.1016/j.rser.2015.07.191>.
- Phusunti, N., Phetwarotai, W., Tekasakul, S., 2018. Effects of torrefaction on physical properties, chemical composition and reactivity of microalgae. *Korean J. Chem. Eng.* 35, 503–510. <https://doi.org/10.1007/s11814-017-0297-5>.
- Piloni, R.V., Daga, I.C., Urcelay, C., Moyano, E.L., 2021. Experimental investigation on fast pyrolysis of freshwater algae, prospects for alternative bio-fuel production. *Algal Res.* 54, 102206 <https://doi.org/10.1016/j.algal.2021.102206>.
- Pinheiro Pires, A.P., Arauzo, J., Fontes, L., Domine, M.E., Fernandez Arroyo, A., Garcia-Perez, M.E., Montoya, J., Chejne, F., Pfromm, P., Garcia-Perez, M., 2019. Challenges and opportunities for bio-oil refining: A review. *Energy Fuels* 33, 4683–4720.
- Priharto, N., Ronsse, F., Prins, W., Carleer, R., Heeres, H.J., 2020. Experimental studies on a two-step fast pyrolysis-catalytic hydrotreatment process for hydrocarbons from microalgae (*Nannochloropsis gaditana* and *Scenedesmus almeriensis*). *Fuel Process. Technol.* 206, 106466 <https://doi.org/10.1016/j.fuproc.2020.106466>.
- Qadriyah, L., Aswie, V., Widjaya, H.V., Aditya, K.H., Mahfud, M., 2021. Microwave-assisted pyrolysis of microalgae in producing bio-oil using CaO catalyst and charcoal as heat absorber. *IOP Conf. Ser. Earth Environ. Sci.* 765. <https://doi.org/10.1088/1755-1315/765/1/012095>.
- Qi, P., Chang, G., Wang, H., Zhang, X., Guo, Q., 2018. Production of aromatic hydrocarbons by catalytic co-pyrolysis of microalgae and polypropylene using HZSM-5. *J. Anal. Appl. Pyrolysis* 136, 178–185. <https://doi.org/10.1016/j.jaap.2018.10.007>.
- Rago, Y.P., Mohee, R., Surroop, D., 2018. A review of thermochemical technologies for the conversion of waste biomass to biofuel and energy in developing countries, pp. 127–143. https://doi.org/10.1007/978-3-319-63612-2_8.
- Raheem, A., Prinsen, P., Vuppalladadiyam, A.K., Zhao, M., Luque, R., 2018. A review on sustainable microalgae based biofuel and bioenergy production: Recent developments. *J. Clean. Prod.* 181, 42–59. <https://doi.org/10.1016/j.jclepro.2018.01.125>.
- Rahman, N.A.A., Fermojo, J., Sanna, A., 2018. Effect of Li-LSX-zeolite on the in-situ catalytic deoxygenation and denitrogenation of *isochrysis* sp. microalgae pyrolysis vapours. *Fuel Process. Technol.* 173, 253–261. <https://doi.org/10.1016/j.fuproc.2018.01.020>.
- Raza, M., Inayat, A., Ahmed, A., Jamil, F., Ghenai, C., Naqvi, S.R., Shanableh, A., Ayoub, M., Waris, A., Park, Y.K., 2021. Progress of the pyrolyzer reactors and advanced technologies for biomass pyrolysis processing. *Sustain* 13, 1–42. <https://doi.org/10.3390/su131911061>.
- Rezaei, H., Yazdanpanah, F., Choon Lim, J., Lau, A., Sokhansanj, S., 2019. Woody feedstock pretreatments to enhance pyrolysis bio-oil quality and produce transportation fuel. *Biomass Bioenergy - Recent Trends Futur. Chall.* <https://doi.org/10.5772/intechopen.81818>.
- Ribeiro, J.M.C., Godina, R., Matias, J.C.de O., Nunes, L.J.R., 2018. Future perspectives of biomass torrefaction: Review of the current state-of-the-art and research development. *Sustain* 10, 1–17. <https://doi.org/10.3390/su10072323>.
- Rocha, K.C., Alonso, C.G., Leal, W.G.O., Schultz, E.L., Andrade, L.A., Ostroski, I.C., 2020. Slow pyrolysis of *Spirulina platensis* for the production of nitrogenous compounds and potential routes for their separation. *Bioresour. Technol.* 313, 123709 <https://doi.org/10.1016/j.biortech.2020.123709>.
- Saber, M., Nakhshiniev, B., Yoshikawa, K., 2016. A review of production and upgrading of algal bio-oil. *Renew. Sustain. Energy Rev.* 58, 918–930. <https://doi.org/10.1016/j.rser.2015.12.342>.
- Sánchez-Borrego, F.J., Álvarez-Mateos, P., García-Martín, J.F., 2021. Biodiesel and other value-added products from bio-oil obtained from agrifood waste. *Processes* 9, 797.
- Sankaran, R., Cruz, R.A.P., Pakalapati, H., Show, P.L., Ling, T.C., Chen, W.-H., Tao, Y., 2020. Recent advances in the pretreatment of microalgal and lignocellulosic biomass: A comprehensive review. *Bioresour. Technol.* 298, 122476.
- Sarwer, A., Hamed, S.M., Osman, A.I., Jamil, F., Al-Muhtaseb, A.H., Alhajeri, N.S., Rooney, D.W., 2022. Algal biomass valorization for biofuel production and carbon sequestration: a review. *Environ. Chem. Lett.* 20, 2797–2851.
- Scott, S.A., Davey, M.P., Dennis, J.S., Horst, I., Howe, C.J., Lea-Smith, D.J., Smith, A.G., 2010. Biodiesel from algae: challenges and prospects. *Curr. Opin. Biotechnol.* 21, 277–286. <https://doi.org/10.1016/j.copbio.2010.03.005>.
- Shahabuddin, M., Alam, M.T., Krishna, B.B., Bhaskar, T., Perkins, G., 2020. A review on the production of renewable aviation fuels from the gasification of biomass and residual wastes. *Bioresour. Technol.* 312, 123596 <https://doi.org/10.1016/j.biortech.2020.123596>.
- Shahi, T., Beheshti, B., Zenouzi, A., Almasi, M., 2020. Bio-oil production from residual biomass of microalgae after lipid extraction: The case of *Dunaliella* Sp. *Biocatal. Agric. Biotechnol.* 23, 101494 <https://doi.org/10.1016/j.bcab.2020.101494>.
- Shan Ahamed, T., Anto, S., Mathimani, T., Brindhadevi, K., Pugazhendhi, A., 2021. Upgrading of bio-oil from thermochemical conversion of various biomass – Mechanism, challenges and opportunities. *Fuel* 287, 119329. <https://doi.org/10.1016/j.fuel.2020.119329>.
- Sharifzadeh, M., Richard, C.J., Liu, K., Hellgardt, K., Chadwick, D., Shah, N., 2015. An integrated process for biomass pyrolysis oil upgrading: A synergistic approach. *Biomass Bioenergy* 76, 108–117. <https://doi.org/10.1016/j.biombioe.2015.03.003>.
- Sharifzadeh, M., Richard, C.J., Shah, N., 2017. Modelling the kinetics of pyrolysis oil hydrothermal upgrading based on the connectivity of oxygen atoms, quantified by 31 P-NMR. *Biomass Bioenergy* 98, 272–290. <https://doi.org/10.1016/j.biombioe.2017.01.022>.
- Sharifzadeh, M., Sadeqzadeh, M., Guo, M., Borhani, T.N., Murthy Konda, N.V.S.N., Garcia, M.C., Wang, L., Hallett, J., Shah, N., 2019. The multi-scale challenges of biomass fast pyrolysis and bio-oil upgrading: Review of the state of art and future research directions. *Prog. Energy Combust. Sci.* 71, 1–80. <https://doi.org/10.1016/j.pecc.2018.10.006>.
- Shirazi, Y., Viamajala, S., Varanasi, S., 2020. In situ and ex situ catalytic pyrolysis of microalgae and integration with pyrolytic fractionation. *Front. Chem.* 8, 1–12. <https://doi.org/10.3389/fchem.2020.00786>.
- Sivabalan, K., Hassan, S., Ya, H., Pasupuleti, J., 2021. A review on the characteristic of biomass and classification of bioenergy through direct combustion and gasification as an alternative power supply. *J. Phys. Conf. Ser.* 1831. <https://doi.org/10.1088/1742-6596/1831/1/012033>.
- Soltanian, S., Aghbashlo, M., Almasi, F., Hosseinzadeh-Bandbafha, H., Nizami, A.S., Ok, Y.S., Lam, S.S., Tabatabaei, M., 2020. A critical review of the effects of pretreatment methods on the exergetic aspects of lignocellulosic biomass. *Energy Convers. Manage.* 212, 112792 <https://doi.org/10.1016/j.enconman.2020.112792>.
- Sotoudehniakarani, F., Alayat, A., McDonald, A.G., 2019. Characterization and comparison of pyrolysis products from fast pyrolysis of commercial *Chlorella vulgaris* and cultivated microalgae. *J. Anal. Appl. Pyrolysis* 139, 258–273. <https://doi.org/10.1016/j.jaap.2019.02.014>.
- Söyler, N., Goldfarb, J.L., Ceylan, S., Saçan, M.T., 2017. Renewable fuels from pyrolysis of *Dunaliella tertiolecta*: An alternative approach to biochemical conversions of microalgae. *Energy* 120, 907–914. <https://doi.org/10.1016/j.energy.2016.11.146>.
- Spolaore, P., Joannis-Cassan, C., Duran, E., Isambert, A., 2006. Commercial applications of microalgae. *J. Biosci. Bioeng.* 101, 87–96. <https://doi.org/10.1263/jbb.2010.87>.
- Srifa, A., Chaiwat, W., Pitakjakkipop, P., Anutrakakda, W., Faungnawakij, K., 2019. In: *Advances in Bio-Oil Production and Upgrading Technologies. Sustainable Bioenergy: Advances and Impacts.* Elsevier Inc. <https://doi.org/10.1016/B978-0-12-817654-2.00006-X>.
- Sun, J., Yang, J., Shi, M., 2017. Review of denitrogenation of algae biocrude produced by hydrothermal liquefaction. *Trans. Tianjin Univ.* 23, 301–314. <https://doi.org/10.1007/s12209-017-0051-4>.
- Tang, Z., Chen, W., Chen, Y., Hu, J., Yang, H., Chen, H., 2021. Preparation of low-nitrogen and high-quality bio-oil from microalgae catalytic pyrolysis with zeolites and activated carbon. *J. Anal. Appl. Pyrolysis* 159, 105182. <https://doi.org/10.1016/j.jaap.2021.105182>.
- Tang, Z., Chen, W., Chen, Y., Yang, H., Chen, H., 2019. Co-pyrolysis of microalgae and plastic: Characteristics and interaction effects. *Bioresour. Technol.* 274, 145–152. <https://doi.org/10.1016/j.biortech.2018.11.083>.
- Tao, R., Bair, R., Pickett, M., Calabria, J.L., Lakaniemi, A.-M., van Hullebusch, E.D., Rintala, J.A., Yeh, D.H., 2021. Low concentration of zeolite to enhance microalgal growth and ammonium removal efficiency in a membrane photobioreactor. *Environ. Technol.* 42, 3863–3876. <https://doi.org/10.1080/09593330.2020.1752813>.
- Trinh, T.N., Jensen, P.A., Sárossy, Z., Dam-Johansen, K., Knudsen, N.O., Sørensen, H.R., Egsgaard, H., 2013. Fast pyrolysis of lignin using a pyrolysis centrifuge reactor. *Energy Fuels* 27, 3802–3810. <https://doi.org/10.1021/ef400527k>.
- Tsubaki, S., Oono, K., Onda, A., Kadono, T., Adachi, M., Mitani, T., 2019. Microwave-assisted solubilization of microalgae in high-temperature ethylene glycol. *Biomass Bioenergy* 130, 105360. <https://doi.org/10.1016/j.biombioe.2019.105360>.
- Urban, B., Shirazi, Y., Maddi, B., Viamajala, S., Varanasi, S., 2017. Flash pyrolysis of oleaginous biomass in a fluidized-bed reactor. *Energy Fuels* 31, 8326–8334. <https://doi.org/10.1021/acs.energyfuels.7b01306>.
- Vamvuka, D., 2011. Bio-oil, solid and gaseous biofuels from biomass pyrolysis processes—an overview. *Int. J. Energy Res.* 35, 835–862.
- Varsha, S.S.V., Vuppalladadiyam, A.K., Shehzad, F., Ghaedi, H., Murugavel, S., Dong, W., Antunes, E., 2021. Co-pyrolysis of microalgae and municipal solid waste: A thermogravimetric study to discern synergy during co-pyrolysis process. *J. Energy Inst.* 94, 29–38. <https://doi.org/10.1016/j.joei.2020.10.010>.
- Wang, Y., Akbarzadeh, A., Chong, L., Du, J., Tahir, N., Awasthi, M.K., 2022. Catalytic pyrolysis of lignocellulosic biomass for bio-oil production: A review. *Chemosphere*, 134181.
- Wang, K., Brown, R.C., Homsy, S., Martinez, L., Sidhu, S.S., 2013. Fast pyrolysis of microalgae remnants in a fluidized bed reactor for bio-oil and biochar production. *Bioresour. Technol.* 127, 494–499. <https://doi.org/10.1016/j.biortech.2012.08.016>.
- Wang, X., Sheng, L., Yang, X., 2017. Pyrolysis characteristics and pathways of protein, lipid and carbohydrate isolated from microalgae *Nannochloropsis* sp. *Bioresour. Technol.* 229, 119–125. <https://doi.org/10.1016/j.biortech.2017.01.018>.

- Wang, N., Tahmasebi, A., Yu, J., Xu, J., Huang, F., Mamaeva, A., 2015. A comparative study of microwave-induced pyrolysis of lignocellulosic and algal biomass. *Bioresour. Technol.* 190, 89–96. <https://doi.org/10.1016/j.biortech.2015.04.038>.
- Wang, X., Zhao, B., Yang, X., 2016. Co-pyrolysis of microalgae and sewage sludge: Biocrude assessment and char yield prediction. *Energy Convers. Manage.* 117, 326–334. <https://doi.org/10.1016/j.enconman.2016.03.013>.
- Wei, D., Chen, C., Huang, X., Zhao, J., Fan, D., Zeng, T., Bi, Y., 2023. Products and pathway analysis of rice straw and *Chlorella vulgaris* by microwave-assisted co-pyrolysis. *J. Energy Inst.*, 101182 <https://doi.org/10.1016/j.joei.2023.101182>.
- Wigmosta, M.S., Coleman, A.M., Skaggs, R.J., Huesemann, M.H., Lane, L.J., 2011. National microalgae biofuel production potential and resource demand. *Water Resour. Res.* 47.
- Wise, H.G., Dichiara, A.B., Resende, F.L.P., 2019. Ex-situ catalytic fast pyrolysis of beetle-killed lodgepole pine in a novel ablative reactor. *Fuel* 241, 933–940. <https://doi.org/10.1016/j.fuel.2018.12.101>.
- Wu, K.-T., Tsai, C.-J., Chen, C.-S., Chen, H.-W., 2012. The characteristics of torrefied microalgae. *Appl. Energy* 100, 52–57. <https://doi.org/10.1016/j.apenergy.2012.03.002>.
- Wu, Q., Wang, Y., Jiang, L., Yang, Q., Ke, L., Peng, Y., Yang, S., Dai, L., Liu, Y., Ruan, R., 2020. Microwave-assisted catalytic upgrading of co-pyrolysis vapor using HZSM-5 and MCM-41 for bio-oil production: Co-feeding of soapstock and straw in a downdraft reactor. *Bioresour. Technol.* 299, 122611 <https://doi.org/10.1016/j.biortech.2019.122611>.
- Xu, Y., Hu, Y., Peng, Y., Yao, L., Dong, Y., Yang, B., Song, R., 2019. Catalytic pyrolysis and liquefaction behavior of microalgae for bio-oil. *Bioresour. Technol.*, 122665 <https://doi.org/10.1016/j.biortech.2019.122665>.
- Yang, C., Li, R., Zhang, B., Qiu, Q., Wang, B., Yang, H., Ding, Y., Wang, C., 2019. Pyrolysis of microalgae: A critical review. *Fuel Process. Technol.* 186, 53–72. <https://doi.org/10.1016/j.fuproc.2018.12.012>.
- Zainan, N.H., Srivatsa, S.C., Li, F., Bhattacharya, S., 2018. Quality of bio-oil from catalytic pyrolysis of microalgae *Chlorella vulgaris*. *Fuel* 223, 12–19. <https://doi.org/10.1016/j.fuel.2018.02.166>.
- Zaker, A., Chen, Z., Wang, X., Zhang, Q., 2019. Microwave-assisted pyrolysis of sewage sludge: A review. *Fuel Process. Technol.* 187, 84–104. <https://doi.org/10.1016/j.fuproc.2018.12.011>.
- Zaman, C.Z., Pal, K., Yehye, W.A., Sagadevan, S., Shah, S.T., Adebisi, G.A., Marlina, E., Rafique, R.F., Johan, R. Bin, 2017. *Pyrolysis: A Sustainable Way to Generate Energy from Waste*. IntechOpen Rijeka, Croatia.
- Zbair, M., Ait Ahsaine, H., Anfar, Z., 2018. Porous carbon by microwave assisted pyrolysis: An effective and low-cost adsorbent for sulfamethoxazole adsorption and optimization using response surface methodology. *J. Clean. Prod.* 202, 571–581. <https://doi.org/10.1016/j.jclepro.2018.08.155>.
- Zhang, Y., Cui, Y., Liu, S., Fan, L., Zhou, N., Peng, P., Wang, Y., Guo, F., Min, M., Cheng, Y., Liu, Y., Lei, H., Chen, P., Li, B., Ruan, R., 2020. Fast microwave-assisted pyrolysis of wastes for biofuels production – A review. *Bioresour. Technol.* 297, 122480 <https://doi.org/10.1016/j.biortech.2019.122480>.
- Zhang, M., Hu, Y., Wang, H., Li, H., Han, X., Zeng, Y., Xu, C.C., 2021. A review of bio-oil upgrading by catalytic hydrotreatment: Advances, challenges, and prospects. *Mol. Catal.* 504, 111438 <https://doi.org/10.1016/j.mcat.2021.111438>.
- Zhang, C., Wang, C., Cao, G., Chen, W.-H., Ho, S.-H., 2019. Comparison and characterization of property variation of microalgal biomass with non-oxidative and oxidative torrefaction. *Fuel* 246, 375–385. <https://doi.org/10.1016/j.fuel.2019.02.139>.
- Zhang, S., Zhang, L., Xu, G., Li, F., Li, X., 2022. A review on biodiesel production from microalgae: Influencing parameters and recent advanced technologies. *Front. Microbiol.* 13, 970028.
- Zhou, H., Wu, C., Onwudili, J.A., Meng, A., Zhang, Y., Williams, P.T., 2014. Polycyclic aromatic hydrocarbon formation from the pyrolysis/gasification of lignin at different reaction conditions. *Energy Fuels* 28, 6371–6379. <https://doi.org/10.1021/ef5013769>.