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# Materials, fuels, upgrading, economy, and life cycle assessment of the pyrolysis of algal and lignocellulosic biomass: a review

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## Abstract

Climate change issues are calling for advanced methods to produce materials and fuels in a carbon-neutral and circular way. For instance, biomass pyrolysis has been intensely investigated during the last years. Here we review the pyrolysis of algal and lignocellulosic biomass with focus on pyrolysis products and mechanisms, oil upgrading, combining pyrolysis and anaerobic digestion, economy, and life cycle assessment. Products include oil, gas, and biochar. Upgrading techniques comprise hot vapor filtration, solvent addition, emulsification, esterification and transesterification, hydrotreatment, steam reforming, and the use of supercritical fluids. We examined the economic viability in terms of profitability, internal rate of return, return on investment, carbon removal service, product pricing, and net present value. We also reviewed 20 recent studies of life cycle assessment. We found that the pyrolysis method highly influenced product yield, ranging from 9.07 to 40.59% for oil, from 10.1 to 41.25% for biochar, and from 11.93 to 28.16% for syngas. Feedstock type, pyrolytic temperature, heating rate, and reaction retention time were the main factors controlling the distribution of pyrolysis products. Pyrolysis mechanisms include bond breaking, cracking, polymerization and re-polymerization, and fragmentation. Biochar from residual forestry could sequester 2.74 tons of carbon dioxide equivalent per ton biochar when applied to the soil and has thus the potential to remove 0.2–2.75 gigatons of atmospheric carbon dioxide annually. The generation of biochar and bio-oil from the pyrolysis process is estimated to be economically feasible.

**Keywords** Biomass · Pyrolysis · Product distribution · Pyrolysis upgrading · Economic and life cycle assessment · Pyrolysis integration

## Introduction

The increased use of fossil fuels worldwide over the past few decades has resulted in many environmental challenges, including the emissions of greenhouse gases. Additionally,

the volatility of fossil fuel prices and the gradual depletion of fossil resources have detrimental effects on the global economy. As a result, producing carbon-neutral and low-emission fuels from renewable energy sources such as biomass has grown in importance as a replacement for traditional fossil fuels. Using biomass resources can help mitigate environmental damage, promote economic stability, and secure a more sustainable future. With an estimated 100 billion tons of biomass produced each year globally, biomass resources are plentiful and have a wide range of uses. As the only renewable carbon-based resource, biomass has the potential to produce heat, electricity, fuel, chemicals, and other products (Farghali et al. 2022a; Osman et al. 2021). Specifically, biomass energy is one of the greatest renewable energy sources in the world, accounting for 77.4% of all renewable energy sources and 10.4% of the world's total primary energy supply (Farghali et al. 2022b). Therefore, the

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The views and opinions expressed in this review do not necessarily reflect those of the European Commission or the Special EU Programmes Body (SEUPB).

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sustainable and efficient use of biomass resources is crucial for reducing the environmental impacts of energy production. Biomass characteristics are crucial in this regard, as shown in Fig. 1.

Biomass pyrolysis is one of the thermochemical processes that has gained the most interest, as it offers a potential way for processing different types of biomasses into fuels and chemicals. Thus, in this review, we explore the distribution of pyrolytic products in biomass pyrolysis as well as the mechanistic pathways that govern the process to optimize efficiency and product properties. In addition, we evaluate the economic viability of the process and investigate the potential benefits of integrating pyrolysis with anaerobic digestion and algae cultivation. In addition, we review 20 published life cycle assessment studies between 2020 and 2022 to highlight methodological approaches and key findings.

## Lignocellulose biomass

### Biomass opportunities in sustainability

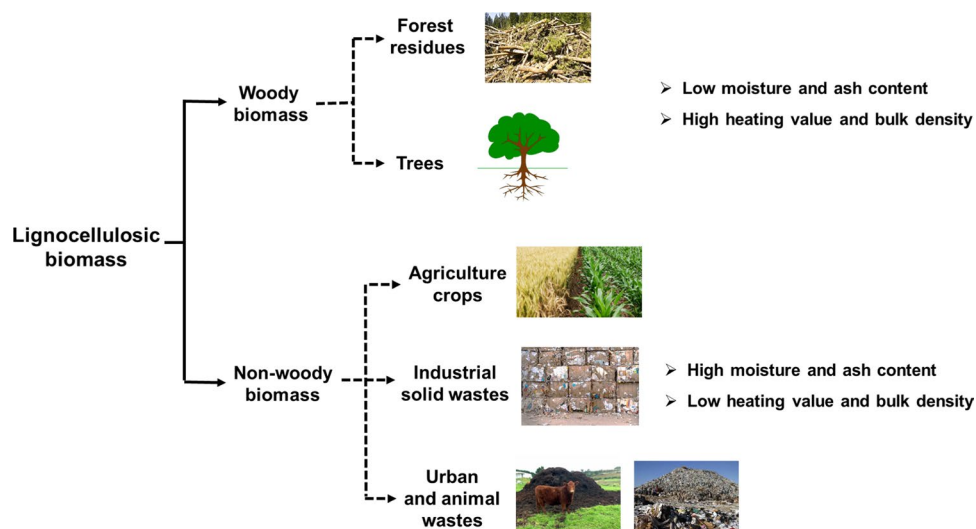
Biomass can be transformed into fuels and chemicals through various techniques, including biochemical and thermochemical ones. Methane and alcohol are frequently produced by biochemical processes, including digestion (aerobic and anaerobic), fermentation, and others (Farghali et al. 2022b; Osman et al. 2022a). Additionally, biomass is frequently converted through thermochemical processes such as pyrolysis, gasification, combustion, hydrothermal liquefaction, and hydrothermal carbonization. However, the potential for biomass production and the resulting renewable bioenergy varies among countries and is influenced by geography, resource availability, biodiversity, technology,

and economy. By 2050, biomass has the potential to provide 3000 terawatt hours of electricity and could save 1.3 billion tons of carbon dioxide equivalent emissions per year. However, it is essential to note that bioenergy production also generates emissions, with each terawatt hour of energy produced resulting in 472.89 kilotons of carbon dioxide (Antar et al. 2021).

Pyrolysis is one of the thermochemical processes that has received the most attention because it offers a promising method for converting various forms of biomass into fuels and chemicals through the thermal degradation of organic molecules in the absence of oxygen. Organic materials are pyrolyzed to produce three main products: solid carbon (biochar), liquid (bio-oil), and non-condensable volatiles (syngas). The process relies on various factors, including temperature, reaction time, heating rate, pressure, feedstock composition, and moisture content, affecting the reactions' efficiency and product distribution yield. The degradation of the critical components of biomass, such as hydrogen and oxygen bonds, occurs within a temperature range of 350–800 °C.

Additionally, using various feedstocks and process conditions can significantly affect the properties of the final products and their potential applications (Gahane et al. 2022; Mukherjee et al. 2022). The reaction mechanisms of biomass pyrolysis include main and subsequent steps, such as dehydration, devolatilization, decomposition, cracking, and polymerization (Al-Rumaihi et al. 2022; Mukherjee et al. 2022; Makavana et al. 2020). Therefore, understanding the product distribution and the mechanistic pathways of biochar, bio-oil, and syngas, which are the products of pyrolysis, is crucial for optimizing the pyrolysis process and making it more efficient. By studying these pathways, researchers can identify the key factors that affect product yields and develop strategies to improve the process. This

**Fig. 1** Lignocellulosic biomass origin is categorized as wood-based and other biomass types. Wood-based biomass contains low ash and moisture content, high heating value, and high bulk density. Hence, these attributes also influence the pathway of the pyrolysis process and product distribution



knowledge can also aid in developing new applications for the products such as bio-oil as an alternative to fossil fuels and biochar as a soil amendment and carbon sequestration tool.

Pyrolysis has received significant attention as a carbon-negative energy process due to its ability to convert biomass into biofuels, materials, and chemicals while recycling and storing carbon in the biochar. The pyrolysis process can combine bioenergy generation with carbon removal, making it a sustainable and environmentally friendly method for producing energy. While pyrolysis is a promising process for treating agro-food wastes, it has some limitations, particularly when handling higher moisture-containing wastes. This can reduce the efficiency of the system. To overcome these limitations, researchers have proposed coupling the pyrolysis process with other techniques, such as anaerobic digestion or microalgal cultivation. This integrated approach can compensate for the shortcomings of each process, achieve a net-zero waste concept, recover bioenergy from digestate, utilize waste, upgrade the biogas produced, and promote a circular economy (Tayibi et al. 2021a; Monlau et al. 2015). This could lead to more efficient and sustainable ways of treating agro-food wastes and recovering their energy (Farghali et al. 2022b; Farghali et al. 2022c).

Economic analysis of the pyrolysis process involves evaluating its costs and revenues and determining whether it is economically viable. The main factors considered in an economic analysis of pyrolysis include the cost of the feedstock, the cost of the equipment and facilities required for the process, the operating costs such as labor, energy, and maintenance, and the revenue generated from the sale of the products. It is important to note that the price of fossil fuels, government policies and regulations, and the availability of subsidies and incentives also influence the economic viability of pyrolysis. Fawzy et al. (2022) proposed using pyrolytic plants for carbon removal services in addition to conventional biochar sales. They found that a pyrolytic plant that processes 6.5 tons/hour of olive tree pruning residue can permanently remove 24,450 tons of carbon dioxide equivalent from the atmosphere annually. The internal rate of return achieved was approximately 22% with the combined revenue from both carbon removal service (EUR 110/ton CO<sub>2</sub> equivalent) and biochar sales (EUR 350/ton), with a net present value of approximately €3 million and a discounted payback period of 8 years at a 15% cost of capital. However, Haeldermans et al. (2020) proposed a different approach, suggesting a much higher minimum selling price for biochar when electricity sales and carbon removal are involved. Thus, economic analysis results vary depending on the different feedstock, technology, location, and economic conditions. The price of fossil fuels, government policies

and regulations, and the availability of subsidies and incentives also influence the economic viability of pyrolysis.

Life cycle assessment evaluates a product's or process's environmental impact throughout its entire life cycle. In the case of biomass pyrolysis, the life cycle can assess the environmental impacts of feedstock production, pyrolysis process, product use, and end-of-life. The results of the life cycle assessment can identify key environmental impacts of the process and opportunities for improvement, such as reducing energy consumption, emissions, and waste generation and using products in a more sustainable way, such as the potential utilization of biochar as a carbon sequestration tool and bio-oil as a renewable energy source. In this study, we aim to investigate the distribution of products and techniques for upgrading bio-oil to improve its quality and value. We also examine the integration of pyrolysis with other processes, such as anaerobic digestion and algae cultivation, to enhance the negative carbon footprint and provide additional benefits. Additionally, we conduct an economic evaluation and life cycle assessment to evaluate the sustainability and feasibility of the process. The results of this study can be used to optimize the pyrolysis process and make it more efficient, sustainable, and economically viable.

## Lignocellulose biomass composition and processing

Biomass contains a substance called lignocellulose, which is commonly made from organic materials. This material is the first step in turning biomass into value-added products (Abhijeet et al. 2020). Lignocellulosic biomass consists of a composite structure of complex compounds such as lignocellulose with a lower quantity of hydrocarbons or lipids and inorganic ash. Therefore, lignocellulosic biomass controls the mechanism of thermal pyrolytic degradation and products in various ways. Lignocellulosic biomass is generally sorted under two types: woody and non-woody materials (Wang et al. 2020a), and includes a variety of compounds like herbaceous and agricultural residues, forest residues, and agro-industrial wastes. The rest of the biomass resources incorporate aquatic plants, animals and human wastes, food manufacturing, processing remains, and organic fractions of municipal solid wastes. According to the nature of the feedstock, the lignocellulosic biomass exhibits various characteristics, including moisture and ash content, bulk density, and calorific value, as shown in Fig. 1.

The primary benefit of lignocellulosic biomass is its environmentally friendly composition, comprising low sulfur and nitrogen content and low carbon dioxide emitted into the atmosphere. Consequently, recent research is shedding light on carbon originating from wastes from agriculture, forest, and manufacturing to produce products with enriched value and implement renewable energy with valuable and feasible resources (Amenaghawon et al. 2021). The three

main components of lignocellulosic biomass are cellulose (32–45%), hemicellulose (19–25%), and lignin (14–26%), which are regarded as binding substances. Cellulose is thought to be the primary support that gives the cell walls their structure (Mukherjee et al. 2022). The interconnections between lignocellulosic compounds, such as covalent and hydrogen bonds, revealed a remarkable effect on pyrolysis features and product distribution as a sequence of various thermal degradation pathways through the pyrolysis process.

Cellulose is a homopolymer of D-glucose, which is insoluble in water under normal conditions. Cellulose is recognized to be employed in producing paper, textiles, biofuels, and binding composite materials (Tursi 2019). Cellulose is a crystallized structure due to hydrogen, strongly bonded with cellulose polymer molecules. The distribution of cellulose highly depends on the type of biomass. For example, wood-based material contains cellulose ranging from 38 to 55%,

turfs from 20 to 35%, switchgrass nearly 40%, and rice husk around 36%. Hemicellulose is a heteropolymer composite that benefits food packaging, healthcare, and animal food. Unlike cellulose, hemicellulose is naturally non-crystalline and easily dissolved in water with high reactivity compared to cellulose (Amenaghawon et al. 2021; Magagula et al. 2022).

Lignin is a heteropolymer formed by connected phenylpropane monomers producing larger molecular structures. The decomposition temperature of lignin is higher in wood and strongly hydrophobic compared to cellulose and hemicellulose. Lignin is utilized in making adhesive materials and bioenergetic compounds (Verdini et al. 2022). Table 1 shows various biomass feedstocks with lignocellulosic components. Some organic materials with low molecular weight are entitled extractive contents in biomass. The extractives contain terpenes, high oil, fatty acids, fats, waxes, and

**Table 1** Composition of different lignocellulosic biomass in terms of cellulose, hemicellulose, and lignin as they are not uniformly present within cell walls. The structure and quantity of these plant cell wall

components differ based on species, tissues, and maturity of the plant cell wall

Feedstock	Cellulose (weight%)	Hemicellulose (weight%)	Lignin (weight%)	Reference
<i>Forrest feedstock (hard and soft woods)</i>				
Bamboo pulp	68.00	20.00	12.00	Hidayati et al. (2019)
Eucalypt wood	41.60	19.6	27.00	Chen et al. (2020)
Oak	41.78	24.8	27.43	Ghavidel et al. (2020)
Spruce	42.11	32.20	26.06	Čabalová et al. (2021)
Birchwood	39.30	28.00	23.20	Przybysz Buzala et al. (2019)
Poplar	42–49	16–23	21–29	Zhang et al. (2020)
<i>Agricultural feedstock</i>				
Rice husk	35.00	19.00	22.00	Shahi et al. (2021)
Rice straw	40–50	20–30	10–18	Yan et al. (2021)
Wheat straw	52.40	18.20	18.80	Yu et al. (2021)
Sugarcane straw	32–44	24–30	12–36	Lopez-Velazquez et al. (2021)
Corn stover	41.05	31.39	6.34	Wang et al. (2019a)
Sunflower stalks	35–45	5–10	3–5	Zhang et al. (2021)
Palm kernel shell	29.70	47.70	53.40	Baffour-Awuah et al. (2021)
Walnut shell	25–50	20–40	10–35	Jovičić et al. (2022)
Cotton stalks	58.50	14.40	21.50	Bano et al. (2019)
Coconut fiber	36–50	30–46	10–20	Thinkohkaew et al. (2020)
Spent coffee grounds	59.2–62.94	5–10	19.8–26.5	Park et al. (2021a)
Oat hull	23.00	35.00	25.00	Schmitz et al. (2021)
Acai seed	53.20	12.30	22.3	Barros et al. (2021)
Barley straw	35.40	28.70	13.10	Raud et al. (2021)
Olive leaves	5.70	3.80	39.6	Espeso et al. (2021)
<i>Grassy feedstock</i>				
Switchgrass	32–45	21–31	12–28	Wang et al. (2020a)
<i>Eichhornia crassipes</i>	17.6	40.2	7.2	Tran et al. (2021)
Miscanthus	40–53	18–26	20–26	Xu et al. (2020a)
Reed	61	27	12	Li et al. (2019a)

\*Some total feedstock composition is not 100% as other components are not considered in the table

alcohol (Yuan et al. 2021; Devi et al. 2022). Extractives are considered part of combustible organic compounds that enhance the heat content of fuel material.

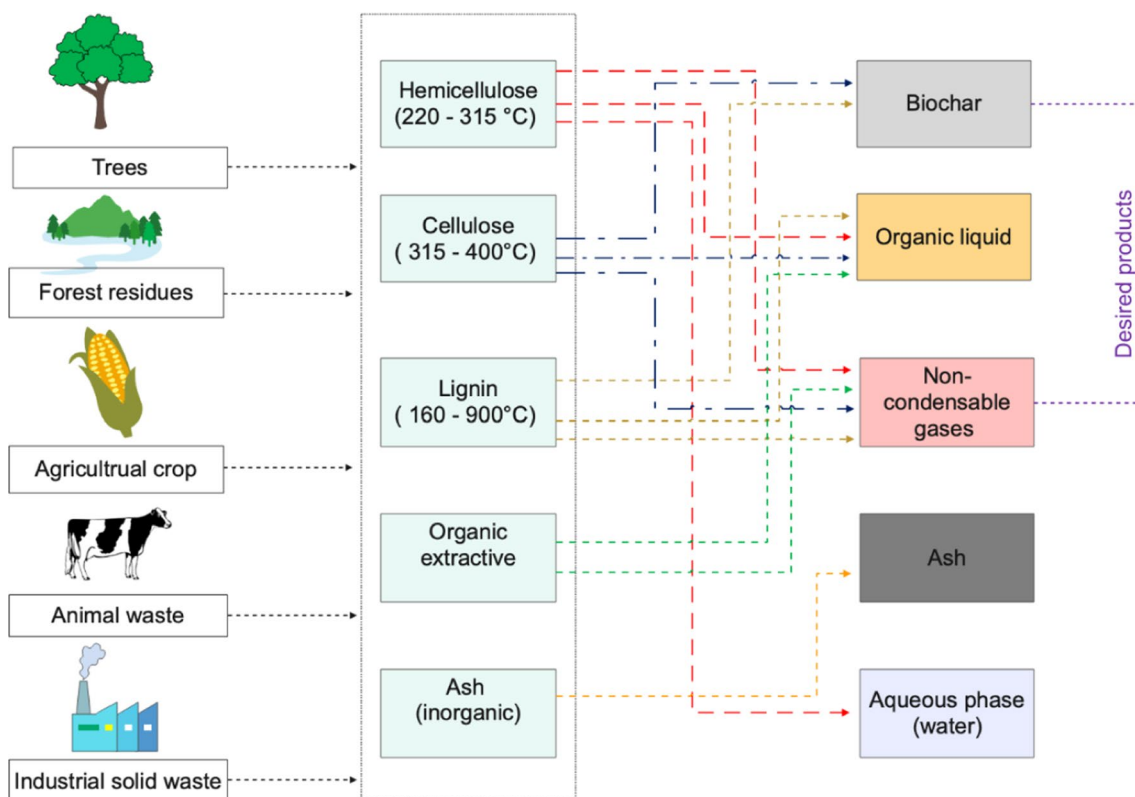
### Degradation of lignocellulosic biomass and products distribution

The pyrolysis process, also known as devolatilization, is the thermal degradation of biomass at high temperatures in an inert or partially inert atmosphere into liquid bio-oil, solid biochar, and pyrolytic gas. To maximize the yields of either bio-oil or biochar, three basic categories of biomass pyrolysis—slow, fast, and flash pyrolysis—can be distinguished based on the heating rate and residence time. Several factors influence the biomass pyrolysis procedure, yields, and product characteristics. These include the type of biomass used, the physical, chemical, and biological pretreatment processes carried out, the reaction environment, temperature, heating rate, and vapor residence time (Kan et al. 2016).

The principal competitive reactions during biomass degradation include dehydrogenation, depolymerization, and fragmentation (Kan et al. 2016). These reactions generally are classified into essential and auxiliary reactions. The primary reaction trajectory includes dehydration and

the charring process, where different chemical bonds in the polymers within the biomass are broken during heating, causing the release of volatile chemicals and rearrangement reactions in the matrix of the residue. Afterward, the secondary reactions of cracking or recombination can occur when the released volatile intermediates achieved through primary reactions are unstable at the reactor temperature.

The variance in biomass composition, which is made up of three primary polymers (hemicelluloses, cellulose, and lignin), also influences the complexity of the finished product. Hemicellulose is usually the first to degrade, then cellulose, and finally lignin which requires a vast temperature scale (Gao et al. 2022). Feedstocks that contain high concentrations of nutrients like animal manure, can form biochar with excessive nutrient content. Generically, remarkable char yield is achieved from feedstocks containing significant ash content. Previous studies revealed that cellulose and hemicellulose are most likely to produce volatile products through pyrolysis. At the same time, lignin is the essential source of biochar production based on lignin's highly aromatic structure, which enhances biochar yields (Deshavath et al. 2019). Figure 2 displays a schematic



**Fig. 2** Lignocellulosic biomass degradation pathways. Lignocellulosic biomass degrades independently at a wide range of temperatures, producing target products, and byproducts. Therefore, selecting a particular biomass feedstock may have a meaningful impact on the final product yield

pattern of lignocellulosic thermal degradation and production of required byproducts through the pyrolysis process.

Cellulose has a significant effect on maximizing bio-oil yield production but leads to minor char and gas production. The effect of cellulose on bio-oil strongly relies on decomposition stages. During the 150–300 °C, cellulose polymers undergo dehydration to char and water, decompose to levoglucosan, the chief component derived from cellulose, and finally crack to secondary tar. Breakdown of levoglucosan occurs at 300–390 °C, where various condensable volatile components are formed during levoglucosan decomposition (Tran et al. 2021; Pang et al. 2021). The result of biomass with high hemicellulose composition is greater syngas production with a reduction in bio-oil and biochar yield (Zadeh et al. 2020). Chemicals associated with cracked monosaccharide rings at low temperatures in hemicellulose, such as methoxy, acetyl groups, and a carboxylic acid, break down into carbon dioxide, methanol, formic acid, and acetic acid. The shatter of the mentioned substituents during pyrolysis causes considerable gaseous product yield.

Further decomposition occurs at nearly 240 °C where monomer chains are volatile and rapid polymerization occurs. The unsettled intermediates created are subjected to dehydration, crash, and secondary reactions to form an extra amount of carbon dioxide, water, and carbon monoxide. At a temperature higher than 300 °C, additional methyl substituents are turned into methane by the demethylation process. A remarkable quantity of carbon dioxide, carbon monoxide, methane, and hydrogen is generated from hemicellulose pyrolysis. Therefore, the pyrolysis of the predominant hemicellulose feedstock would contribute directly to syngas products.

## Pyrolysis of lignocellulosic biomass

Thermochemical processes such as pyrolysis are currently employed to convert biomass to biofuels. Compared with other techniques, such as bio-chemicals, the thermochemical method is preferable to produce biofuels as they have shorter operating times and lower capital costs compared to the different biochemical pathways, which require the separation of biomass components (Sankaran et al. 2020).

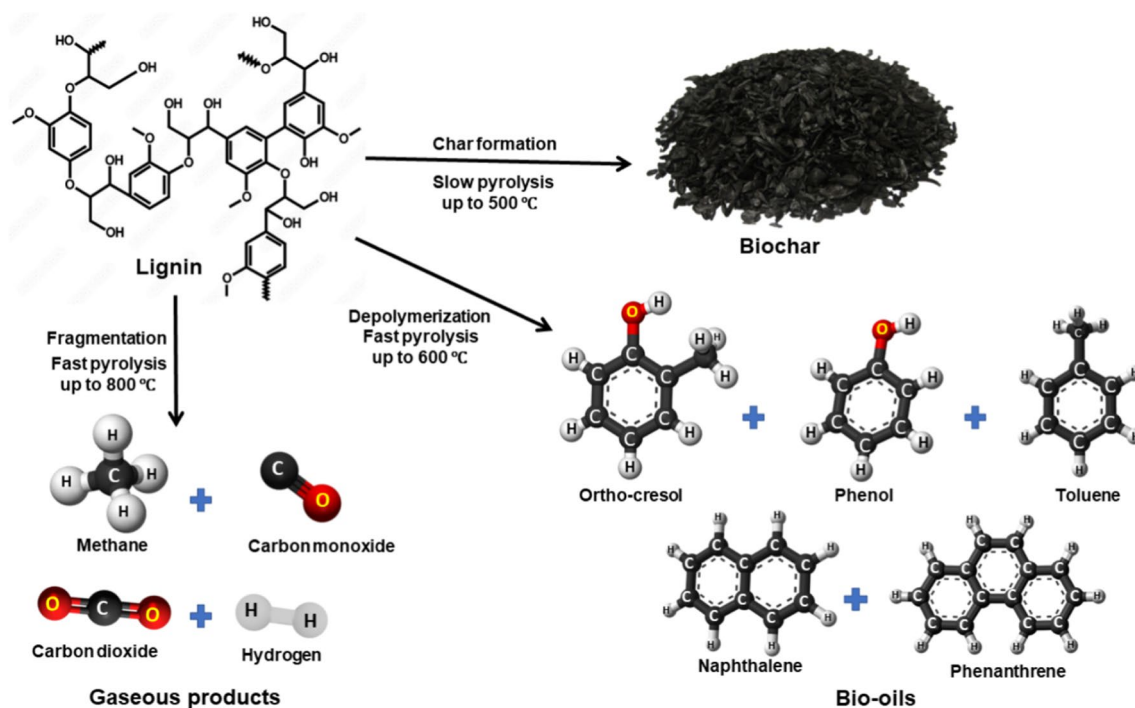
Lignocellulosic pyrolysis is a temperature-absorbing operation that involves the breakdown of the biomass's organic fraction, mostly into biochar, bio-oil, and syngas (Elgarahy et al. 2021). The degradation is a multi-step complex process that occurs under controlled temperature ranges and without air and oxygen under atmospheric pressure conditions (Chen et al. 2021a). Long-chain hydrocarbons that form the structure are degraded under suitable pyrolysis conditions in lignocellulosic biomass. Moreover,

the thermal decomposition rate and residual biomass stage depend highly on feedstock composition, pyrolytic temperatures, and other factors, such as heating rate and residence time (Mukherjee et al. 2022).

Generically, a process based on pyrolysis has two main mechanisms, primary and secondary. The primary reactions involve bond breaking that results in the synthesis of biochar (Elyounssi et al. 2012), bio-oils through the process of de-polymerization (Collard et al. 2012), and gaseous products in a fragmentation step (Lu et al. 2011), as shown in Fig. 3. The leading technique comprises chemical bonds that break down reactions and emit light components inside the reactor subjected to heat. Furthermore, more reactions are developed and considered part of the side mechanism (Al-Rumaihi et al. 2022). On the other hand, the subsequent reactions of these products, like cracking and re-polymerization, are classified as secondary reactions (Van de Velden et al. 2010; Wei et al. 2006). The first stage of thermal degradation forms benzene that bonds to create solid biochar residue with organic matter proceeding to decompose up to 800 °C. When decomposed, organic matter is comprised of long polymeric chains, which de-polymerize organic matter into monomers.

Consequently, products such as water, synthesis gas, condensable vapors, and other volatile compounds are released through a primary mechanism (Osman et al. 2021), while in a different technique, the unstable compounds are cracked or re-joined for restructuring. Cracking involves breaking down the compounds to form elements with lower molecular weights, whereas in recombination, volatile compounds with higher molecular weights in addition to developing secondary char in some circumstances (Pang et al. 2021). The feedstock's humidity is vital to the pyrolysis process as a noticeable amount of moisture will be a major key to enhancing the production of liquid byproducts. On the other hand, lower moistness will promote ash/char production rather than bio-oil (Eke et al. 2020).

Pyrolysis at slower heating rates and temperatures lower than 450 °C will promote a higher biochar yield. In contrast, a slightly faster heating rate with intermediate temperatures will escalate bio-oil outputs. Based on the latter conditions of operating pyrolysis parameter, biomass pyrolysis is categorized into the following subclasses: slow or conventional pyrolysis (Cong et al. 2022), fast pyrolysis (Hu et al. 2022), intermediate pyrolysis (Yang et al. 2017), and flash pyrolysis (Nzihou et al. 2019). Moreover, other technologies are recently utilized, such as microwave-assisted pyrolysis (Iturbides et al. 2022), catalytic-based pyrolysis (Qiu et al. 2022), catalytic hydro-pyrolysis (Nguyen et al. 2016), and hydro-catalytic pyrolysis (Kawale and Kishore 2021) to optimize the products



**Fig. 3** Stages of lignin pyrolysis. Char formation occurs at a temperature of up to 500 °C through slow pyrolysis. De-polymerization of the biomass material at around 600 °C produces bio-oils through fast pyrolysis, with common examples including phenol, toluene, and

naphthalene. Fragmentation of biomass material into gaseous products such as hydrogen, methane, carbon monoxide, and carbon dioxide occurs at high temperatures (800 °C) through fast pyrolysis

yields. Table 2 demonstrates modern works on lignocellulosic biomass in various pyrolysis methods with product distribution.

## Biomass product distribution analysis and mechanistic insights

Pyrolysis is a thermal treatment process that occurs in the absence of oxygen or limited oxygen conditions at temperatures ranging from 250 to 900 °C. This process is distinct from the traditional combustion of organic materials, which occurs in the presence of atmospheric oxygen and produces carbon dioxide and water vapor (Wang et al. 2020b). Pyrolysis has several benefits compared to other treatment methods, including its eco-friendliness, the ability to use a variety of feedstock materials, the potential to minimize environmental pollution, and the production of a wide range of valuable products (Hasan et al. 2021). These products can be classified into solid, liquid, and gaseous categories, depending on factors such as type of feedstock, pyrolysis temperature, heating rate, and reaction time (Cha et al. 2016). Generally, solid products, including biochar, are more prevalent at lower temperatures (below 500 °C). In comparison, higher temperatures decrease the biochar yield and increase the yields of other liquids, such as bio-oil and

tar products like levoglucosan, and gaseous products, such as hydrogen, methane, and carbon monoxide (Collard and Blin 2014). Thus, a thorough understanding of the pyrolysis process and the distribution of its products is of great importance and will be thoroughly discussed in this section.

## Biochar

Char is the product of biomass pyrolysis in solid carbonaceous form. Based on biomass structure and pyrolysis conditions, char can have different chemical and physical properties. Biochar is fine-grained charcoal. Unlike biomass feedstock, biochar has unique features such as high surface area, high porosity, catalytic activity, and physicochemical stability, which promotes char utilization as a catalyst during the pyrolysis process (Sahoo et al. 2021). Moreover, biochar is implemented as a carbon amendment in the soil to prevent carbon emission to the atmosphere by decreasing oxidation and reduction of feedstock, which considers a mitigation strategy for greenhouse gases. Char is also utilized for wastewater treatment by adsorbing different pollutants (Awasthi et al. 2020; Wang et al. 2020c).

Biochar is synthesized from various biomass feedstocks including crop and agricultural residues with high lignin content that are subjected to thermal decomposition. Char yield is enhanced when biomass undergoes longer residence



**Table 2** Product yields of pyrolysis of lignocellulosic biomass. Bio-oil was mainly produced from feedstock with high cellulose content, which was subjected to slow pyrolysis at intermediate temperatures. Feedstocks with nearly equal cellulose and hemicellulose approached relatively uniform distribution between bio-oil and biochar under low residence time and intermediate temperature

Lignocellulosic feedstock	Pyrolysis type	Process variables	Desired outcome (wet weight)	Reference
<i>Camellia oleifera</i> shell	Microwave-assisted pyrolysis	Temperature: 500 °C Residence time: 20 min	Bio-oil yield: 37.30–40.27% With the diffusion of bio-char and bio-gas products	Dai et al. (2019)
Corn cob	Fast pyrolysis	Temperature: 500 °C Residence time: 20 s Heating rate: (10, 20, 40, 80 °C/min)	Biochar yield: 10.1–25.8% Anhydrosugar and levoglucosan byproducts as the primary product	Jiang et al. (2019)
<i>Quercus rubra</i> (red oak) wood chips	Autothermal/partial oxidative pyrolysis	Temperature: 500 °C Residence time: 0.7 s	Bio-oil composition change compared to conventional fast pyrolysis	Peterson et al. (2020)
Beechwood	Catalytic fast pyrolysis	Catalyst: Aluminosilicate zeolites and mesoporous aluminosilicate	Bio-oil yield: 9.07–23.37% Water yield: 31.92–43.09% Gas yield: 18.11–22.34% Biochar yield: 24.57–26.60%	Ratnasari et al. (2018)
	Thermal pyrolysis	Temperature: 500 °C Residence time: 30 min	Bio-oil yield: 28.43% Water yield: 28.87% Gas yield: 11.93% Biochar yield: 30.77%	
Rice straw	Slow pyrolysis	Temperature: 500 °C Residence time: 3 h	Bio-oil yield: 40.59% Biochar: 31.25% Synthesis gas yield: 28.16%	Sakhiya et al. (2020)
Banana pseudo-stem	Fast pyrolysis	Temperature: 500 °C Residence time: 0.9 s	Biochar: 41.25% Bio-oil yield: 36.50% Synthesis gas yield: 21.16%	Taib et al. (2021)
Brewer's spent grain	Intermediate pyrolysis	Temperature: 500 °C Residence time: 3 min	Synthesis gas yield: 21.16% Bio-oil yield: 36.50% Biochar: 31.25%	Bieniek et al. (2022)

time and moderate temperature. On the other hand, lower residence time and higher temperatures decrease biochar yield. Biochar comprises carbon, hydrogen, oxygen, nitrogen, sulfur, and ash. Biochar is typically produced as a main product of slow pyrolysis. However, the temperature is crucial in defining the main and byproducts from various pyrolysis technologies (Panwar et al. 2019). Higher biochar yields are produced through slow pyrolysis when the lignocellulosic feedstock has a larger particle size and higher

content of lignin and ash. Consequently, the feedstock type, reaction environment, and operating conditions impact biochar production and composition—Table 3 lists various biochar compositions based on feedstock and temperature range.

According to a recent study (Yuan et al. 2020), three factors can provide insight into the characteristics of the resulting biochar. These include the formation of free radicals, which are produced by breaking covalent bonds and are most

**Table 3** Biochar compositions based on biomass type and temperatures. Biomass produces biochar with various carbon, hydrogen, oxygen, nitrogen, and ash contents. The best biochar yields require proper substrate selection and temperature optimization

Feedstock	Process temperature (°C)	Biochar properties (%)					Reference
		Carbon	Nitrogen	Hydrogen	Oxygen	Ash	
Animal dung	800	27.78	1.67	3.98	20.3	34.00	Zhou et al. (2020a)
Bamboo	500–900	54.49	0.19	6.15	37.1	Not reported	Tong et al. (2020)
Banana peel	600	67.50	0.36	Not reported	16.70	22.58	Bong et al. (2022)
Crop residues	600	50.00	Not reported	1.50	6.00	35.00	Hong et al. (2020)
<i>Samanea saman</i> seeds	400–700	62.66	3.45	2.06	31.83	13.18	Mishra et al. (2020a)
<i>Madhuca indica</i> seeds	450–550	60.27	3.19	2.27	34.27	Not reported	Mishra et al. (2020b)

concentrated at temperatures between 400 and 500 °C. The second factor is the amount of oxygen-containing functional groups, which can indicate biochar production efficiency and decrease at low temperatures, indicating a high carbon content and biochar yield (Zhao et al. 2016). At temperatures above 600 °C, carbon content decreases due to breaking carbon–carbon bonds (Yu et al. 2019). The third factor is the microcrystallinity of graphite crystals, which increases with increasing reaction temperature. While biochar yield decreases with increasing pyrolysis temperature, the surface area tends to increase (Sakhiya et al. 2021). Therefore, the choice of pyrolysis conditions can be based on the desired properties of the resulting biochar and the intended application. Biochar has a wide range of potential applications, including adsorption. It is a support material in catalytic and photocatalytic processes for degrading various organic pollutants, such as dyes and pharmaceuticals. (Hosny et al. 2022a; Eltaweil et al. 2022; Hosny et al. 2022b).

Heating rates that are balanced between slow and fast are referred to as intermediate pyrolysis. Intermediate pyrolysis produces a wide range of products and can be used in the coproduction of bio-oil, biochar, and syngas. However, biochar produced by intermediate pyrolysis is less than that produced by slow pyrolysis due to a higher heating rate maintained at a temperature range of 450–550 °C, which stimulates high molecular weight tar and inhibits the formation of bio-oil and syngas (Mukherjee et al. 2022).

## Bio-oil

Bio-oils, which are in the form of a dark-brownish organic liquid resulting from biomass pyrolysis, are sustainable, cost-effective, and efficient fuel sources, including bio-ethanol and bio-diesel (Martínez et al. 2014). Bio-oils have several advantages compared to fossil fuels, including low emissions of nitrogen and sulfur oxides and compatibility with a wide range of equipment (Terry et al. 2021). Bio-oil comprises oxygenated compounds, which cause high thermal instability and lower heating value, making bio-oil unsuitable for engines (Hu and Gholizadeh 2019).

As the pyrolysis temperature and/or heating rate increases, there is a shift from solid products like biochar to liquid products like bio-oils. This conversion typically begins at low temperatures through the breaking of weak bonds and continues at higher temperatures, around 500 °C or above (Collard and Blin 2014), through a process called de-polymerization, in which linkages within the polymer structures, such as ester, phenolic, and non-phenolic ether bonds that are broken at low temperatures and more persistent condensed biphenyl bonds within the lignin structure that are broken at high temperatures, are broken down into constituent monomers (Chio et al. 2019). The amount of these monomers, which are condensable at room temperature

(Mullen and Boateng 2011), increases with increasing pyrolysis temperature due to the cleavage of carbon–carbon side-chain bonds (Kawamoto 2017). These monomers are typically stable in liquid form. Still, under certain conditions, such as the limited availability of hydrogen donors, they may re-polymerize to form oligomers and polymers that are different from the original depolymerized polymers (Bay-erbach and Meier 2009). These re-polymerized compounds are more resistant to further de-polymerization due to the formation of resistant condensed linkages (Kawamoto 2017).

The overall constitution of bio-oil is water as well as a variety of organic compounds like ketones, aldehydes, acids, furans, phenols, alcohols, ethers, esters, sugars, alkenes, nitrogen, and oxygen. Bio-oil can be regarded as a multiphase microemulsion where oligomers produce aerosols. Therefore, bio-oil stability is affected and quickly aging, leading to water accumulation, increasing viscosity, and phase separation. Consequently, bio-oil must be treated before being utilized as engine fuel (Machado et al. 2022). For example, the pyrolysis should be fast with a high heating rate of 100–200 °C/second or higher, the residence time should be short, typically less than two seconds, and the formed biochar should be rapidly separated using gas–solid separation techniques such as cyclones, and the vapors should be cooled to prevent secondary cracking (Van de Velden et al. 2010; Li et al. 2019a). Additionally, water should be controlled by drying the biomass before pyrolysis to avoid reducing the bio-oil quality (Rover et al. 2019). Under these conditions, the bio-oil yield is expected to be between 50 and 70% (Fahmy et al. 2020). If the heating rate is further increased through flash pyrolysis, the yield can be higher, ranging from 75 to 80% (Kan et al. 2016).

Many factors, like the type of biomass feedstock, heating rate, residence time, feedstock particle size, and temperature, influence bio-oil characteristics. Table 4 shows bio-oil characteristics produced from different biomass feedstocks. Biomass with major cellulose content promotes the yield of bio-oil products, whereas higher lignin content contributes to bio-oil reduction (Zhang et al. 2019a).

Unlike petroleum fuels, the water content in bio-oil from wood pyrolysis acts as a microemulsion and cannot be extracted by physical techniques. Moisture in bio-oil is measured via Karl Fischer volumetric titration according to ASTM standard E 203. Residual carbon solids are measured via ASTM D4530 or ASTM D189. Sulfur content can be detected via ASTM standard D5453-09 or EN ISO 20846, which is recommended (Hu and Gholizadeh 2019). For chlorine detection, no precise technique exists. ASTM standard D 4052 is usually utilized to determine the density of petroleum fuels at 15 °C via a digital density meter. For bio-oil density measurement, the same method is implemented. Other vital properties of bio-oil are viscosity and the pour point that controls the pumping process.

**Table 4** Composition of bio-oil from several biomass feedstocks at various temperatures. The elemental analysis is necessary to ascertain the bio-oil's carbon, hydrogen, oxygen, and nitrogen, as the entire content is directly proportional to reaction temperature

Feedstock	Process temperature (°C)	Bio-oil properties (%)				Reference
		Carbon	Nitrogen	Hydrogen	Oxygen	
Spirulina microalgae	300	45.73	1.27	5.96	47.04	Xu et al. (2020b)
Rice husk	300	41.90	Not reported	8.3	49.80	
Delonix regia	500–700	50.62–58.32	1.06–1.28	6.93–7.65	32.75–41.34	Kawale and Kishore (2020)
Sawdust	400	68.550	0.110	7.176	22.219	Cao et al. (2019)
Spent coffee grounds	500	70.00	3.8	9.00	16.9	Park et al. (2021a)
Water hyacinth	450	59.77	0.235	8.98	30.8	Wauton and Ogbeide (2021)
Palm shell	250–300	76.4	9.8	11.8	0.3	Qureshi et al. (2021)
<i>Madhuca longifolia</i> seeds	500	67.32	2.33	8.12	21.34	Mishra et al. (2020b)

The highest kinematic viscosity of bio-oil is measured at 20 centistokes at 40 °C (Machado et al. 2022). The pour point of bio-oil can be measured according to ASTM standard D 97 (van Schalkwyk et al. 2020).

Physical adjustment of lignocellulosic biomass feedstock before introducing pyrolysis facilitates feeding to pyrolysis reactors. Grinding or milling biomass into smaller particles enhances mass and heat transfer during pyrolysis and promotes uniform temperature distribution across particles, maximizing bio-oil by suppressing char formation and secondary cracking reactions of vapors. Due to biomass's poor heat conductivity, larger biomass particles result in the incomplete transformation to bio-oil because of heat transfer limitations, decreasing pyrolysis efficiency (Qureshi et al. 2021).

### Pyrolytic gas

Gases produced from the pyrolysis of lignocellulosic biomass are mainly composed of carbon dioxide, carbon monoxide, hydrogen, methane, ethane, ethylene, propane, sulfur oxides, nitrogen oxides, and ammonia (Hu and Gholizadeh 2019). Carbon monoxide and carbon dioxide are formed initially from the decomposition process and the conversion of carbonyl and carboxyl groups—light hydrocarbons released from the breakdown of weak methoxy and methylene bonds. Hydrogen is formed by degrading carbon-hydrogen groups and aromatics (Mishra et al. 2020a). Van de Velden et al. (2010) reported that forming various incondensable gaseous products, such as methane, carbon dioxide, and syngas (a mixture of hydrogen and carbon monoxide), involves breaking covalent bonds through a process called fragmentation. This fragmentation occurs at pyrolysis temperatures of 700–800 °C or higher (Lu et al. 2011; Zaini et al. 2021) and can break bonds within polymers or monomers. The distribution of products resulting from fragmentation is influenced mainly by factors such as biomass particle size, heating rate, residence time, reactor temperature, and

pressure (Zhang et al. 2022). Fragmentation can also lead to the formation of short-chain organic molecules that are condensable at room temperatures, such as ethane (C<sub>2</sub>H<sub>6</sub>) and ethene (C<sub>2</sub>H<sub>4</sub>) (Krumm et al. 2016; Al Arni 2018). Another mechanism contributing to the formation of low molecular weight volatile compounds is cracking, a secondary reaction similar to fragmentation (Caposciutti et al. 2019).

Optimization of gaseous products produced during pyrolysis can be achieved through high reaction temperatures (up to 1000 °C), small particle sizes biomass such as wood chips, and catalysts to improve process efficiency (Dufour et al. 2009; Gong et al. 2020). For example, sodium zirconate derived from dental waste has been used as a catalyst to enhance hydrogen production from various biomass sources, including municipal sludge (Wang et al. 2019b). Reactions that can be involved in forming gaseous products during pyrolysis include carbon–oxygen reactions, carbon–water reactions, hydrogenation, water–gas shift reaction, and the methanation reaction (Pecha and Garcia-Perez 2020).

On the other hand, Hong et al. (2020) reported that larger particle sizes boost the production of gaseous products due to the high heat transfer during the pyrolysis process, which means a longer distance from a hot surface to the cold core of the particle. This obstructs the heat transfer process; hence, the temperature gradient enhances the generation of gaseous products. However, smaller particle sizes influence the composition of gas products as smaller sizes increase component cracking, forming more hydrogen and carbon monoxide with less carbon dioxide.

Pyrolysis gas production is also boosted by subjecting biomass inside the reactor with longer residence time as biomass is a breakdown of biochar and part of liquids in secondary reactions to produce volatile gases (Safdari et al. 2019). Lower heating rates enhance pyrolytic gas yields in fast and intermediate pyrolysis with relatively higher temperatures. However, a heating rate increase can improve gas yield due to the biomass feedstock type. Moisture content also contributes to the pyrolytic gas output. High water

content boosts the separation of water-soluble components from the gas phase, leading to a remarkable reduction of pyrolysis gas yield (Elgarahy et al. 2021; Li et al. 2019a). Figure 4 illustrates product distribution in slow, fast, intermediate, and flash pyrolysis.

Temperature is a major factor in deciding gas yield. Generally, more gas products are formed when secondary cracking reactions take place at high pyrolytic temperatures. Furthermore, the volume fractions of each component in the gas mixture are not increased simultaneously due to different changes in the change rate of individual gas (Fernandez et al. 2022). Table 5 lists recent experimental studies that show the influence of temperature on pyrolytic gas fraction distribution.

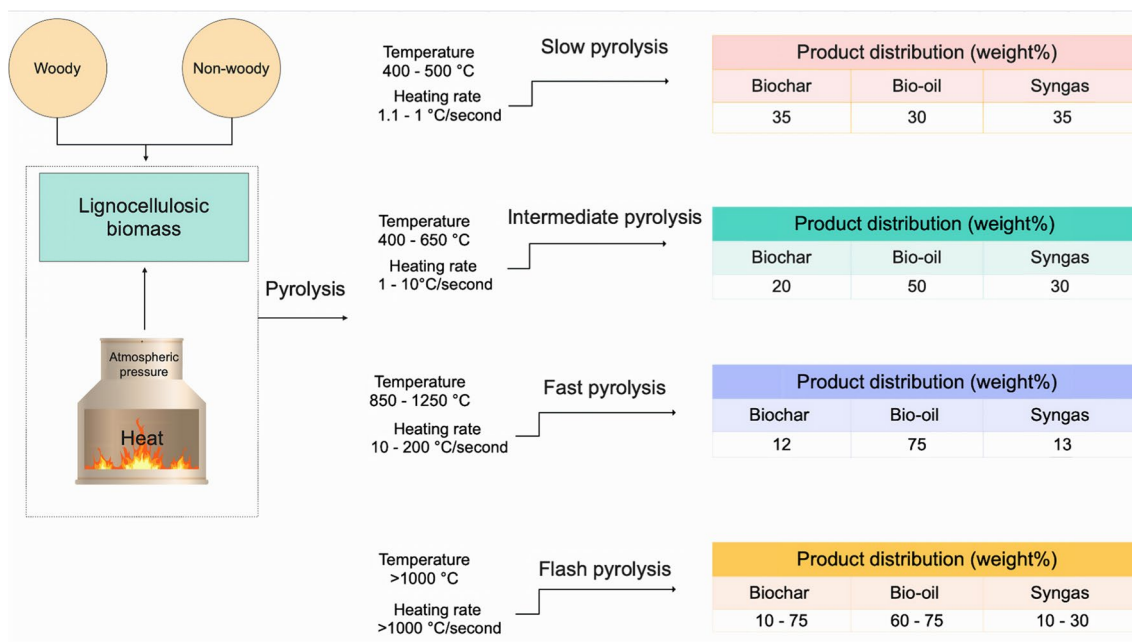
### Pyrolytic temperature influence on product distribution

Temperature is considered an essential and crucial key factor in the pyrolysis process. Management of temperature gradient is vital owing to its strong influence on pyrolysis product distribution. Increasing temperatures lower char yield due to the secondary and parallel reactions that occur to enhance the formation of other products like bio-oil and more degradation of biochar, resulting in the production of more pyrolysis gases at temperatures higher than 600 °C (Almutairi et al. 2022). Carbon dioxide was the dominant product at 250 °C, while at 350 °C, quantities of carbon monoxide were

found to be 25.43% in the gas product and slightly increased to 29.44% at 450 °C temperature. Light hydrocarbon gas production occurred as the temperature increased further to 650 °C. Reaction temperature variation during slow pyrolysis, as compared to other process conditions, was found to have a significant impact on the production of biochar from rice husk (Vieira et al. 2020). The biochar yield was found to be maximum at 300 and 400 °C, or around 65.8% and 59.1%, respectively, when exhausted grape marc was subjected to biomass pyrolysis temperatures of 300 °C to 700 °C. However, at temperatures of 500 °C and 700 °C, biochar yield significantly decreased, with 33.8% for the former and 30.9% for the latter (Ferjani et al. 2019).

A recent study was carried out on cellulose, hemicellulose, and lignin, the three major components of lignocellulosic biomass, to determine the effect of reaction temperature on the behavior of pyrolytic product distribution. The experimental work included a wide range of temperatures in a fixed-bed reactor and a high-purity nitrogen environment with temperatures ranging from 400 to 800 °C. Results showed that a moderate temperature (450–700 °C) is the most suitable for bio-oil production for hemicellulose, cellulose, and lignin feedstocks. On the contrary, higher temperatures produced more gaseous products (Chen et al. 2022).

A study by Makavana et al. (2020) demonstrated the influence of temperature on the pyrolysis of cotton stalks. Results revealed that increasing pyrolytic temperature reduced the biochar yield owing to many primary decompositions or



**Fig. 4** Distribution of products from various pyrolysis mechanisms. Compared to other pyrolysis types, intermediate pyrolysis produces a wide range of products and can thus be used in the co-production

of biochar, bio-oil, and syngas. On the other hand, oil production is maximized via rapid cooling and controlled residence time for the secondary cracking reactions to repress syngas production

**Table 5** Gaseous products obtained at various operating temperatures during the pyrolysis process for different feedstocks. The gaseous products can be categorized into combustible and non-combustible components. The gaseous profile demonstrated an increase of combustible products proportionally with pyrolytic temperature, unlike non-combustible gases reduced with higher temperatures. Carbon monoxide was reduced as temperature increased, which may increase gas heating values

Feedstock	Tem-perature (°C)	Gas composition (wet weight %)										Reference		
		Carbon monoxide	Carbon dioxide	Hydrogen	Methane	Ethylene	Ethane	Propylene	Propane	Butane	Oxygen		Nitrogen	
Spent coffee waste	400	32.87	62.97	1.40	1.78	0.28	0.17	Not reported	0.12	0.41	Not reported	Not reported	Not reported	Ly et al. (2022)
	420	31.14	61.23	1.57	3.66	0.42	0.77	Not reported	0.5	0.71	Not reported	Not reported	Not reported	
	440	25.79	50.62	4.22	11.6	1.61	2.15	Not reported	1.81	2.21	Not reported	Not reported	Not reported	
	460	26.81	55.06	2.56	9.02	1.29	1.89	Not reported	1.65	1.72	Not reported	Not reported	Not reported	
	480	27.54	59.12	2.04	6.03	1.06	1.42	Not reported	1.31	1.48	Not reported	Not reported	Not reported	
Wood pellets	500	29.29	60.22	1.76	4.73	0.95	1.12	Not reported	0.86	1.07	Not reported	Not reported	Not reported	
	600	47.00	15.00	14.5	16.00	Not reported	7.50	Not reported	Not reported	Not reported	Not reported	Not reported	Not reported	Santamaria et al. (2021)
	700	43.00	18.00	17.00	16.00	Not reported	6.00	Not reported	Not reported	Not reported	Not reported	Not reported	Not reported	
Anaerobic sludge	800	37.00	21.00	23.00	14.00	Not reported	5.00	Not reported	Not reported	Not reported	Not reported	Not reported	Not reported	
	400	5.70	34.30	2.30	5.90	0.80	1.40	Not reported	0.50	Not reported	Not reported	Not reported	Not reported	Hanif et al. (2019)
	500	15.10	34.30	2.30	10.90	1.50	2.60	Not reported	0.70	Not reported	Not reported	Not reported	Not reported	
	600	9.40	21.00	17.10	23.10	1.40	4.20	Not reported	0.70	Not reported	Not reported	Not reported	Not reported	
Rape straw	600	27.00	58.00	15.00	Not reported	Not reported	Not reported	Not reported	Not reported	Not reported	Not reported	Not reported	Not reported	Bulmău et al. (2019)
	700	28.00	51.00	21.00	Not reported	Not reported	Not reported	Not reported	Not reported	Not reported	Not reported	Not reported	Not reported	
	800	18.00	47.00	35.00	Not reported	Not reported	Not reported	Not reported	Not reported	Not reported	Not reported	Not reported	Not reported	

secondary degradation of the char residues. They also noted that the escalation of biochar yields at lower temperatures indicates partial pyrolysis of the feedstock, whereas bio-oil and gaseous product yields soared dramatically. Recent steam pyrolysis experiments on pinewood at temperatures ranging from 500 to 800 °C were carried out on a bench-scale plant. The study's outcome revealed that the highest bio-oil yield was obtained at 500 °C, and when the temperature increased, a higher gas yield was achieved. In contrast, bio-oil and biochar were reduced significantly (Fernandez et al. 2022).

Simple kinetic modeling was implemented to predict the effect of pyrolytic temperature using a wide range of temperatures from 200 to 1000 °C for grass biomass as feedstock. The results showed that operational temperature significantly impacted product yields; for example, when temperature increased, biochar yield decreased, while bio-oil and synthesis gas increased (Abhijeet et al. 2020). Experimental work was performed by Hanif et al. (2019) to elucidate the relation between temperature and pyrolysis of anaerobic sludge. The work's outcome showed that remarkable biochar reduction was detected when the temperature increased. Moreover, yields of bio-oil and gas products increased as temperature increased incrementally. Table 6 lists recent studies

conducted to demonstrate the influence of temperature on product distribution.

## Summary

The decomposition products of lignocellulosic biomass via pyrolysis are categorized into bio-oil, syngas, and biochar. The distribution of these products significantly depends on the composition of feedstock introduced to the reactor. Bio-oil is the most dominant product from cellulosic biomass pyrolysis, with adjacent syngas and lower biochar. Similar behavior is obtained from hemicellulosic-based biomass but with relatively lower yields than cellulosic-based materials. On the other hand, biochar is a superior product from lignin-rich biomass with traces of syngas, which may be considered a byproduct.

The type of pyrolysis, heating rate, and residence time are crucial contributors to determining the kind of pyrolysis products. The pyrolysis residence time is prolonged with a slower heating rate to obtain the maximum amount of biochar. Bio-oil is produced via lower residence time and faster heating rate.

Pyrolytic temperature is the most critical factor that controls several outcomes, such as product distribution,

**Table 6** The distribution of pyrolysis products is remarkably controlled via various parameters such as lignocellulosic feedstock type, pyrolytic temperature, heating rate, and reaction retention time. Slow pyrolysis produced biochar as the desired product by lower residence

time and moderate pyrolytic temperature. On the contrary, biooil was desired product from fast pyrolysis by increasing the heating rate with a wide range of temperatures. Bio-oil and syngas yields are boosted through fast pyrolysis compared to slow pyrolysis

Feedstock	Temperature (°C)	Pyrolysis mechanism	Pyrolysis conditions	Product distribution (weight%)					Reference
				Biochar	Bio-oil	Gas	Aqueous	Losses	
Anaerobic sludge	400	Slow pyrolysis	Heat rate: 5.5 °C /min	68.00	2.00	1.00	12.00	17.00	Hanif et al. (2019)
	500			43.00	6.00	5.00	28.00	18.00	
	600			44.00	7.00	5.00	24.00	20.00	
Pinewood	500	Fast pyrolysis	Residence time: 20 s	15.00	73.00	12.00	Not reported	Not reported	Fernandez et al. (2022)
	600			12.00	64.00	24.00	Not reported	Not reported	
	700			10.00	50.00	40.00	Not reported	Not reported	
	800			9.00	27.00	64.00	Not reported	Not reported	
Palm fiber	300	Slow pyrolysis	Heat rate: 5 °C /min	55.00	0.00	45.00	Not reported	Not reported	Selvarajoo and Oochit (2020)
	500			30.00	14.00	56.00	Not reported	Not reported	
	700			28.00	29.00	43.00	Not reported	Not reported	
	900			27.00	7.00	66.00	Not reported	Not reported	
Wood pellets	200	Slow pyrolysis	Residence time: 240 min	64.80	11.80	23.40	Not reported	Not reported	Santamaria et al. (2021)
	300			44.20	14.20	41.60	Not reported	Not reported	
	400			37.20	16.60	46.20	Not reported	Not reported	
	500			34.00	19.00	47.80	Not reported	Not reported	
Oat straw	300	Slow pyrolysis	Heat rate: 10 °C /min	48.00	39.00	13.00	Not reported	Not reported	Mlonka-Mędrala et al. (2021)
	400			38.00	48.00	14.00	Not reported	Not reported	
	500			35.00	50.00	15.00	Not reported	Not reported	
	600			27.00	57.00	16.00	Not reported	Not reported	

syngas composition, and volumetric flow rate. Increasing temperature is vital to obtain syngas with considerable flow rates with reduced biochar. Temperature highly impacted combustible and non-combustible gas yield within syngas products, where the combustible gases boosted as the temperature increased.

## Bio-oil upgrading techniques

To address the limitations of bio-oil, physical and chemical approaches have been used for upgrading. These approaches aim to reduce the water content and acidity that contribute to bio-oil corrosiveness and improve its stability by decreasing the oxygen and solid phase content and reducing its viscosity. A high hydrogen/carbon ratio and good combustion performance are essential qualities that should be present in high-grade bio-oil. Figure 5 illustrates the main techniques for upgrading bio-oil, including physical and chemical methods.

### Hot vapor filtration

Bio-oil contains a high percentage of ash and alkali content that negatively impacts its quality, molecular weight, and viscosity (Wang et al. 2016a). Hot vapor filtration has been used as an upgrading technique to reduce bio-oil ash content

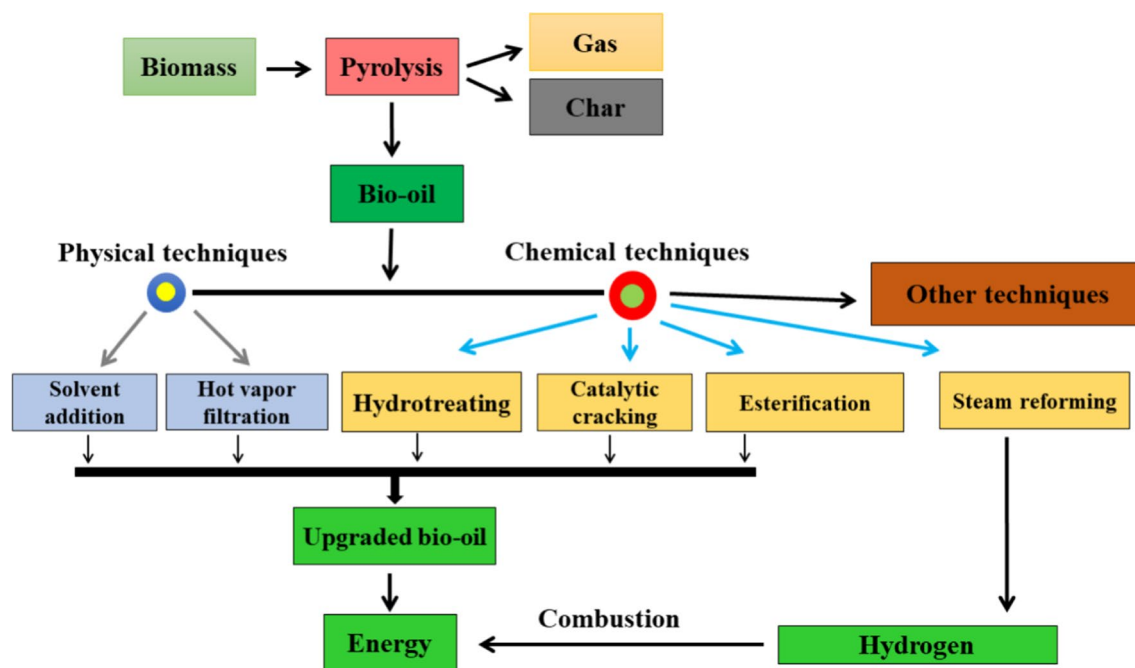
to below 0.01% and alkali concentration to 10 ppm. This process involves filtering vapor at a high temperature of over 250 °C (Pawar et al. 2020).

Two types of filters can be used in this process: bag-type (conventional) filters, which are unsuitable for high temperatures, and candle-shaped filters, with one end for capturing vapor and the other closed (Krutof and Hawboldt 2018). The type of filter used can significantly affect the properties of the resulting bio-oil. Ceramic filters have been shown to produce bio-oil with low alkali and solid content and low iron content. However, hot vapor filtration has some limitations, including a low bio-oil yield, increased iron content, and the need for self-cleaning filters (Baldwin and Feik 2013).

In conclusion, hot vapor filtration is an effective physical upgrading technique for reducing bio-oil's alkali and ash content. However, it can be costly and has a low bio-oil yield.

### Solvent addition

Solvent addition is widely utilized for enhancing bio-oil quality by increasing its heating value and improving its viscosity and homogeneity. This technique involves using polar solvents, including ethanol, isopropanol, furfural, and methanol, which have been shown to be effective in improving bio-oil properties (Oasmaa and Kuoppala 2003). It has been demonstrated that the immediate use of polar solvents



**Fig. 5** Techniques used to upgrade bio-oil, including physical and chemical methods. Physical processes include solvent addition and hot vapor filtration, while chemical techniques include hydrotreating, catalytic cracking, esterification, and steam reforming. These

approaches can result in upgraded oil with varying quality depending on the method used. Steam reforming can also produce renewable and clean hydrogen

following the pyrolysis process can enhance the bio-oil's stability and heating value. Solvent addition also helps to prevent phase separation, leading to an improved homogeneity of the bio-oil (Czernik et al. 2002). The solvent addition process has also been found to inhibit polymerization through chemical interactions between bio-oil and alcohol solvents, such as esterification and acetalization.

In comparing the effects of methanol, isopropanol, and ethanol on bio-oil upgrading, it was found that ethanol improved the heating value more than the other two solvents. In contrast, methanol increased bio-oil's acidity, stability, and viscosity more effectively than isopropanol and ethanol (Oasmaa et al. 2004). Another study found that increasing the proportion of methanol from 3 to 15 wet weight% led to improved bio-oil stability and viscosity that may be attributed to changes in bio-oil structure, the inhibition of chain reactions, and physical dilution (Chen et al. 2014; Mei et al. 2019). Additionally, increasing methanol dosage above 6 wet weight% was found to increase the pH of upgraded bio-oil over time, likely due to methanol's ability to inhibit H<sup>+</sup> activity (Mei et al. 2019; Kim et al. 2012a). However, the solvent addition process has some drawbacks, including a decrease in flash points and the complexity of the mechanism (Panwar and Paul 2021).

In summary, solvent addition is a valuable technique for upgrading bio-oil by improving its heating value, viscosity, and homogeneity. Alcohol solvents, particularly methanol, are commonly used for this purpose and have been shown to increase bio-oil's acidity, stability, and viscosity. Ethanol, on the other hand, is more effective at increasing the heating value of bio-oil. However, it should be noted that this technique also has the potential to decrease the flash point of bio-oil.

## Emulsification

Emulsification is a simple physical method for upgrading bio-oil by mixing it with petroleum fuels such as diesel. Since bio-oil and diesel fuel have low miscibility, the emulsification process typically involves the use of surfactants (e.g., Atlox 4914 and Span 80) or co-surfactants (e.g., ethanol and methanol) to facilitate the mixing (Bridgwater 2012). Surfactants have a polar, hydrophilic head and a non-polar, lipophilic tail. During the emulsification process, the polar bio-oil connects to the head of the surfactant, while the tail attaches to the nonpolar diesel fuel (Zhang and Wu 2017).

Physical methods, such as sonication and stirring, can significantly improve the stability of the emulsification process and the quality of the upgraded bio-oil. The stability of the emulsion is also influenced by factors including the ratio of bio-oil to diesel, the concentration of surfactant,

temperature, mixing time, and stirring rate—stable emulsification results in the production of high-grade bio-oil with long-term stability (Zhang et al. 2018; Abismail et al. 1999).

While surfactants can facilitate the blending of bio-oil and diesel fuel, they also increase the risk of corrosion in engines and require high levels of Energy. On the other hand, emulsification has several advantages, including producing bio-oil with excellent ignition properties, calorific value, and low water content (Leng et al. 2018; Lin et al. 2016). Despite these benefits, emulsification also has some significant drawbacks, such as the high energy requirements and the high cost of surfactants.

In conclusion, the emulsification technique is widely used for upgrading bio-oil due to its ability to produce bio-oil with desirable characteristics such as high ignition performance, calorific value, and low water content, but these benefits must be weighed against the energy and cost demands of the process.

## Esterification

Esterification is a process for upgrading bio-oil by converting it to esters using alcohols and catalysts. This technique produces bio-oil with low density, acidity, water content, and high heating value (Wang et al. 2010a; Wang et al. 2010b). The esterification process involves adding ethanol or methanol to form esters under specific conditions, such as initial pressure of 5 MPa, a temperature of 300–350 °C, and a stirring rate of 360 rpm.

The bio-oil produced through the esterification upgrading process consists of two phases: a light soluble oil and a heavy insoluble oil. It has been found that catalytic esterification significantly reduces the oxygen content and acidity of bio-oil (Milina et al. 2014). Various acid catalysts have been used in the esterification of bio-oil, including liquid-phase catalysts such as sulfuric, hydrochloric, and citric acid, and solid-phase catalysts such as zeolite, resin, and aluminum silicate (Milina et al. 2014; Zhang et al. 2006).

In summary, esterification is a technique for converting bio-oil to esters using alcohols, which results in upgraded bio-oil with low viscosity, high stability, high calorific value, and high intensity. However, the yield of bio-oil through this process is not exceptionally high.

## Catalytic cracking

Catalytic cracking is a process that involves the removal of oxygen in the form of water, carbon dioxide, and carbon monoxide, improving the properties of bio-oil, such as acidity, viscosity, water content, and calorific value (Yang et al. 2015). This process can be carried out at normal pressure in fluidized or fixed bed reactors and is often catalyzed by



HZSM-5, a catalyst known for its high reactivity, selectivity, porous structure, and high acidity.

Sunarno et al. (2018) studied the kinetics of bio-oil catalytic cracking using silica-alumina as a catalyst. The catalytic cracking was conducted in a fixed bed reactor at temperatures of 450–600 °C and with catalyst lengths of 1–4 cm. The optimal catalytic cracking condition was found at 500 °C with a 1 cm catalyst length. The concentration of the produced bio-oil was found to decrease with increasing process temperature and catalyst length, likely due to the deoxygenation of oxygen functional groups in bio-oil. It is worth noting that the bio-oil produced through catalytic cracking is classified as a low-grade bio-oil and that the short lifetime of the catalyst is a limitation of this technique (Ogunkoya et al. 2015).

In summary, catalytic cracking is a chemical upgrading method that aims to reduce the oxygen content of bio-oil, improving its acidity, viscosity, and water content. However, the short lifetime of the catalyst used in this process is a significant drawback.

## Hydrotreatment

Bio-oil produced through biomass pyrolysis typically contains high levels of oxygen, up to 35–40 wet weight% (Hansen et al. 2020), and comprises around 300 oxygen-containing compounds (Han et al. 2016). The oxygen content of bio-oil is a major factor in determining its viscosity, and in being suitable for use as a fuel, the total oxygen content should not exceed 5% (wet weight) (Elliott 2007). Hydrodeoxygenation is a process that aims to remove oxygen from bio-oil while overcoming the limitations of catalytic cracking. This process involves a series of reactions, including hydrocracking, dehydration, decarboxylation, polymerization, and hydrogenolysis (Saidi et al. 2014). Hydrodeoxygenation produces bio-oil with a high hydrogen/carbon ratio and high grade. It can also increase the hydrogen on the catalyst surface to protect it from coke deposition (Mortensen et al. 2011; De et al. 2015).

Hydrogenation is a form of hydrotreatment that can improve the quality and stability of bio-oil by reducing the levels of aldehydes and organic acids, which contribute to the corrosiveness and acidity of bio-oil. It also increases the hydrogen content of bio-oil, improving its fuel quality (Khosravanipour Mostafazadeh et al. 2018). Interestingly, hydrogenation enhances bio-oil quality without altering its boiling range due to its non-damaging nature (Panwar and Paul 2021).

Overall, hydrotreatment is a promising upgrading technique that can reduce the viscosity and oxygen content of bio-oil and improve its heating value. However, it has some drawbacks, including low yield and high levels of

char, coke, and tar in bio-oil, which can poison the catalyst used in the process.

## Steam reforming

Steam reforming is an advanced upgrading method that aims to produce upgraded bio-oil and clean, renewable hydrogen (Gollakota et al. 2016). The upgrading of bio-oil through steam reforming involves the conversion of bio-oil to syngas, which is reformed into synthetic fuel through the Fischer–Tropsch process. At the same time, pure hydrogen is generated through the water gas shift reaction (Wright et al. 2010a; Sharifzadeh et al. 2015). It has been found that the yield of hydrogen through steam reforming decreases significantly in the presence of high oxygen content in bio-oil. In contrast, high hydrogen content directly increases hydrogen yield (Trane et al. 2012).

Notably, the steam reforming technique requires a higher temperature (> 800 °C) than the other upgrading techniques (Mei et al. 2016). In addition, the amount of carbon deposition on the catalyst surface is relatively high, reaching 15% of the initial carbon content, which reduces the lifetime and reusability of the catalyst and is a major challenge in this upgrading process (Chan et al. 2016). Lan et al. found that coke formation on the catalyst surface occurred at 650 °C but that raising the temperature to 950 °C reduced the amount of coke on the catalyst surface, possibly due to the reaction between the deposited coke and absorbent steam (Lan et al. 2014).

Overall, steam reforming is a method for producing clean, renewable hydrogen. However, it has several drawbacks, including low reusability and lifetime of the catalyst, the need for higher temperatures than other upgrading methods, and high cost.

## Supercritical fluids

The use of supercritical fluids for upgrading bio-oil has gained popularity due to their ability to improve bio-oil's caloric values and viscosity. Supercritical fluids are substances that become supercritical when the temperature and pressure of the mixture or compound exceed their critical point. These fluids have properties that are intermediate between gases and liquids (Jessop and Leitner 2008).

Supercritical fluids, particularly organic solvents such as acetone (Liu and Zhang 2008; Li et al. 2019b), ethanol (Xiu et al. 2010; Shafaghat et al. 2019), n-hexanol (Guzmán-Albores et al. 2021), 1,4 dioxane (Mazaheri et al. 2010; Wu et al. 2019a), and propanol (Park et al. 2021b), have been used in supercritical fluid technology to improve the quality of bio-oil (Xiu and Shahbazi 2012). While water is the most commonly used supercritical fluid, it has limitations

that prevent it from being used as a solvent for biomass liquefaction, including the production of viscous bio-oil with high oxygen content and low production of water-insoluble bio-oil.

The supercritical fluid technique is environmentally friendly and operates at low temperatures and pressures. Still, it is not economically feasible for large-scale use due to the high cost of solvents. Researchers have therefore explored alternative, cost-effective solvents such as crude glycerol, which has shown promising results in biomass conversion to bio-oil (Nomanbhay et al. 2018; Forero et al. 2022).

Overall, supercritical fluids offer the potential to improve the calorific value and reduce the acidity and viscosity of bio-oil, but the high cost of solvents is a significant limitation.

### Transesterification

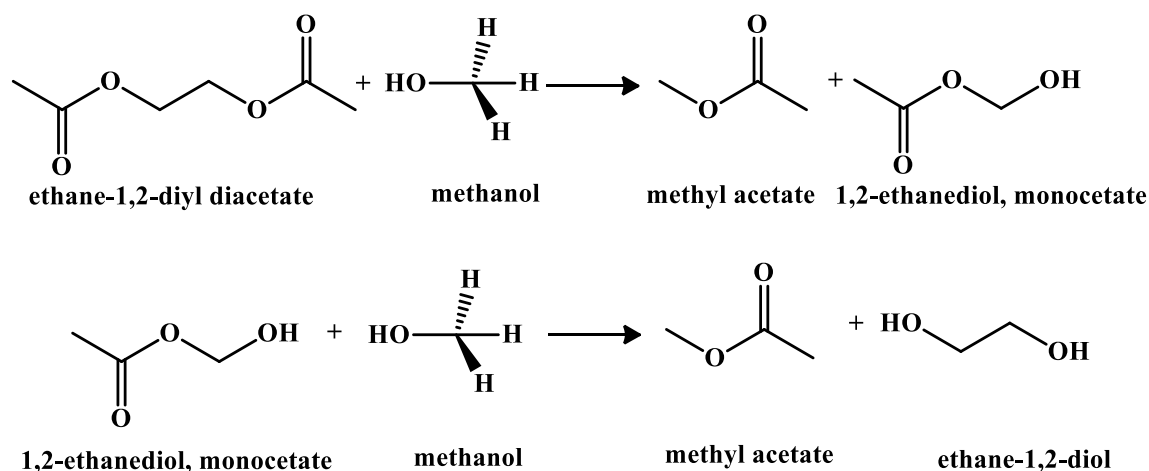
Transesterification is an upgrading technique that aims to reduce the water content and viscosity and increase the pH of bio-oil. It involves a substitution reaction in which the long chain in the ester is replaced with a smaller one, as shown in Fig. 6 (Hu et al. 2012). Nevertheless, using large amounts of alcohol can lead to environmental issues due to water pollution (Milina et al. 2014; Ciddor et al. 2015). The biodiesel produced via this method has excellent combustion efficiency, low sulfur content, and high cetane value (Leung et al. 2010). It is important to note that while esterification produces esters as the final product, transesterification uses esters as a reactant and produces a treated ester as the final product.

Overall, transesterification differs from esterification in its reactants, final product, and advantages and disadvantages, as listed in Table 7. It effectively reduces the viscosity and water content of bio-oil but may have negative environmental impacts due to the use of alcohol.

### Role of biochar in achieving a negative carbon footprint

Carbon-negative energy is an approach that combines energy production with zero net carbon emissions. Wide adaptation of carbon-negative energy will lead to a carbon-negative economy where economic activity removes carbon dioxide instead of adding carbon dioxide to the atmosphere. In this regard, thermochemical methods can be applied with carbon removal to accomplish carbon-negative energy.

Pyrolysis is a thermochemical process that received significant attention as a carbon-negative energy process. Plants usually utilize biological photosynthesis to fix atmospheric carbon as an energy source. Biomass can be converted thermochemically into biofuels, materials, or chemicals. In particular, the feedstock's carbon can be recycled and stored in the environment as biochar. This way, pyrolysis can combine bioenergy generation with carbon removal to achieve carbon-negative energy. Approximately 1.2–1.5 billion tons of biomass in the USA will be accessible at roughly \$60/ton by 2040 (Brown 2021). Therefore, the thermochemical process of biomass can annually remove 0.2–2.75 gigatons of atmospheric carbon dioxide, assuming carbon content at 47% of the biomass. Additionally, biochar is a stable form of carbon and can remain stable for more than 1000 years in the environment (Farghali et al. 2022b). Crop residues converted



**Fig. 6** Transesterification of ester-containing bio-oil. Transesterification entails the substitution of a shorter chain ester for the long chain ester. Through transesterification, 1,2-ethanediol diacetate is con-

verted to methyl acetate; in addition, 1,2-ethanediol monoacetate is converted to 1,2-ethanediol. Transesterification yields biodiesel with good combustion properties

**Table 7** Benefits and drawbacks of several bio-oil upgrading techniques. Bi-oil has been improved using a variety of processes, including transesterification, solvent addition, emulsification, esterification, catalytic cracking, hydrothermal and supercritical treatment, hot water filtering, and esterification. There is no perfect technique to improve bio-oil. The benefits and drawbacks of each method are also present

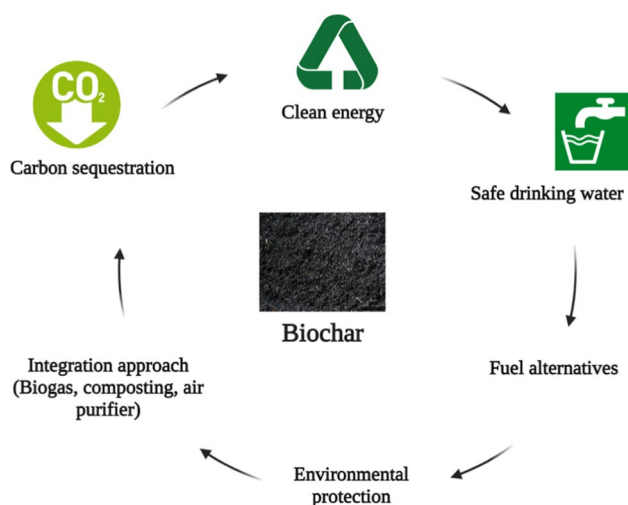
Upgrading approach	Advantage	Disadvantage
Hot vapor filtration	Reduce ash percent (0.01%) Reduce alkali concentration (10 ppm)	Low bio-oil yield High iron content Require self-cleaning filters
Solvent addition	Increase heating value Improve the bio-oil homogeneity Enhance the bio-oil stability	Decline the flash point The mechanism difficulty
Emulsification	Improve ignition specifics Enhance calorific value Decrease water content	Require high energy Corrosion problem High cost of surfactant
Esterification	Enhance stability Decline viscosity Reduce oxygen and water contents Increase density Increase calorific value	Low yield Poor performance
Catalytic cracking	Remove oxygen content Enhance the bio-oil specification: acidity, calorific value, viscosity, and water content	The short lifetime of the catalyst Production of bio-oil with a low grade
Hydrotreatment	Decrease oxygen amounts Increase heating value Decrease viscosity Produce high-grade bio-oil	Require high pressure High cost Low yield
Steam reforming	Production of hydrogen	The short lifetime of the catalyst Low reusability of the catalyst High cost Need high temperature (800 °C)
Supercritical fluids	Decrease acidity Increase calorific value Decrease viscosity Proceed at low pressure and temperature	Solvent's high cost
Transesterification	Decline water content Decline viscosity Raise pH Good combustion performance Low sulfur content	Environmental issue

into biochar can provide several benefits for humans and the environment, as shown in Fig. 7.

Pyrolysis conditions such as temperature and residence time can impact product properties, distribution, and the carbon footprint of subsequent products. For instance, Thers et al. (2019) examined the role of biomass pyrolysis with subsequent soil amendment in optimizing greenhouse gas emissions from oilseed rape cultivation. Pyrolysis of oilseed rape straw at 400 °C and 800 °C resulted in –392 and –429 kg carbon dioxide equivalent, respectively. The greenhouse gas emissions were decreased by 73–83% in the biochar-converted biomass compared with the control due to improved carbon sequestration. Similarly, Cheng et al. (2020) found that the biochar generated from agriculture residues at temperatures between 400 and 700 °C offset carbon emissions of 200–470 kg carbon dioxide equivalent per ton of biomass. Gong et al. (2021) indicated that the intermediate pyrolysis of rice straw and slow pyrolysis of corn stover could offset carbon dioxide by 1.636- and 1.839-ton

carbon dioxide equivalent per ton of biomass, respectively. The pyrolysis conditions also affect bio-oil and syngas production (Matuščík et al. 2020). Thus, carbon dioxide sequestration is related to the type of pyrolysis and biomass.

In addition, pyrolysis equipment affects biochar's efficiency, yield, and properties. Large-scale pyrolysis plants usually achieve higher productivity with better co-product energy offsets. In contrast, small-scale reactors are generally unstable, of lower production, labor- and effort-intensive systems, and mainly experience particulate emissions that cause air pollution. For example, Mohammadi et al. (2016) exhibited carbon footprints of 3.85- and 1.11-kg carbon dioxide equivalent per kg of milled rice for drum ovens and pyrolytic cook-stove, respectively. However, Mohammadi et al. (2017) found negative global warming potentials of –229, –318, and –360 kg of carbon dioxide equivalent per ton of dry rice husk for brick kiln, stove, and large-scale pyrolysis plants, respectively. Therefore, more sophisticated pyrolysis equipment maximizes environmental benefits



**Fig. 7** Benefits offered from the conversion of crop residues into biochar. Clean and affordable energy to communities, carbon fuel alternatives, safe drinking water, security, livelihood, carbon sequestration, and environmental protection are consequences of biochar generation from biomass. CO<sub>2</sub> refers to carbon dioxide

by reducing carbon dioxide emissions. Thus, selecting an appropriate pyrolysis technology is critical in developing areas.

Lefebvre et al. (2021) estimated the greenhouse gas removal potential of biochar converted from sugarcane residues. The authors found that slow pyrolysis of sugarcane residues could sequester  $6.3 \pm 0.5$ -ton carbon dioxide equivalent per hectare per year, comparable to 36 million tons of carbon dioxide equivalent per year and  $1.64 \pm 0.11$ -ton carbon dioxide equivalent per ton biochar. These benefits arise mainly from the carbon stored as biochar in the soil. Similarly, Muñoz et al. (2017) identified a biochar-soil system in reducing greenhouse gas emissions from agricultural and forestry biomass pyrolyzed at 300–500 °C. They found that biochar produced from residual forestry biomass at 500 °C could sequester 2.74-ton carbon dioxide equivalent per ton biochar when applied to the soil. Robb and Dargusch (2018) estimated the carbon footprint of biochar from oil palm waste applied to the crops at  $-691$  kg carbon dioxide equivalent per ton of biochar and  $-286$  carbon dioxide equivalent per ton of biochar when replaced the chemical fertilizers over 100 years.

Additionally, Yang et al. (2021) reported that 921.30 kg of carbon dioxide equivalent could be removed by converting 1 ton of crop residues into biochar. Llorach-Massana et al. (2017) found a carbon sink between 21- and 155- kg of carbon dioxide equivalent per ton of biochar produced from tomato plant residues. Additionally, Fawzy et al. (2022) estimated that one ton of biochar could permanently remove approximately 2.68 tons of carbon dioxide equivalent from the atmosphere, corresponding to 3.26 tons of carbon

dioxide equivalent per hour and 24.45-kilo tons of carbon dioxide equivalent annual removal. The biochar added to soil could sequester approximately 376.11 million tons of carbon dioxide equivalent and aid in retaining 1.66 million tons of soil nutrients (Anand et al. 2022). The crop residues could produce 373 million tons of biochar and sequester 150 million tons of carbon dioxide equivalent per year in soils (Windeatt et al. 2014). Several agro-residues can be utilized in the pyrolysis process, as shown in Table 8. The crop-derived residues are appropriate feedstocks for biochar generation and carbon sequestration and are eco-friendly.

Variations in feedstock and pyrolysis conditions primarily result in various biochar properties, which is a significant challenge. For instance, the higher ash content in herbaceous biomass produces lower-fixed carbon biochar than woody biomass (Brewer et al. 2014; Jafri et al. 2018), lowering its carbon sequestration capability/unit mass. Biochar formed at shorter residence time, and lower temperatures contain more labile carbon and volatile matter (Bakshi et al. 2018), rapidly mineralizing soils and not contributing to long-standing carbon sequestration. On the other hand, high pyrolysis temperature generates biochar with a significantly improved specific surface area, porosity, high pH, and carbon and ash content but with low cation exchange capacity values and volatile matter content (Tomczyk et al. 2020) because of organic matter decomposition. Biochars from animal litter and solid waste demonstrate lower surface areas, carbon content, volatile matter, and high cation exchange capacity than wood biomass and crop residue, even at greater pyrolysis temperatures (Tomczyk et al. 2020). This is because of variations in cellulose, lignin content, and biomass's moisture content. Therefore, biochar physicochemical properties define its application as an additive to improve soil quality and biochar carbon sequestration potential.

In conclusion, the pyrolysis process is identified as a negative emissions technology that can generate energy and achieve zero net carbon emissions. Biomass can be utilized in pyrolysis to accomplish the negative emissions concept. For example, agriculture residues can embody approximately 2.74-ton carbon dioxide equivalent/ton biochar at 500 °C. Hence, net carbon sequestration, global warming reduction potential, and greenhouse gas reduction potential can be a sequence of the pyrolysis process.

## Integrating pyrolysis and anaerobic digestion

Rapid global population growth, climate change, energy demands, and vast waste induced several environmental and economic concerns. Urbanization and industrialization make up approximately 80% of energy demands covered by fossil fuels such as coal, petroleum products, and natural gas

**Table 8** Role of pyrolysis in achieving negative carbon emissions from various biomass feedstocks. Several crop residues, including oil palm waste, corn, oilseed, tomato, straw, rice husk, and other lignocellulose, can be used as substrates for pyrolysis. Biomass can be pyrolyzed at a temperature between 280 and 740 °C to produce various carbon sequestration efficiency depending on the type of feedstock, pyrolysis and application condition, crop and soil type, and chemical fertilizer replacement

Environmental category	Carbon emission impact	Pyrolysis reactor	Pyrolysis temperature	Feedstocks	References
Carbon footprint	−691 kg carbon dioxide equivalent when used to affect crop production, and −286 kg carbon dioxide equivalent when utilized to substitute fertilizer	Pyrolysis reactor	280 °C	Oil palm waste	Robb and Dargusch (2018)
Global warming potential	−0.24 to −0.787-ton carbon dioxide equivalent for combustion, −0.386 to −0.933-ton carbon dioxide equivalent for soil improvement	Pilot-scale reactor	400 °C, 10 min	Corn stover	Righi et al. (2016)
Greenhouse gas emission	Contributions of −392 and −429 kg carbon dioxide equivalent at biochar formed at 400 °C and 800 °C, respectively	Pyrolysis plant	400 °C and 800 °C	Oilseed rape	Thers et al. (2019)
Global warming potential	−921.30 kg carbon dioxide equivalent	Pyrolysis plant	Not mentioned	Crop residues	Yang et al. (2021)
Global warming potential	−4.46 kg carbon dioxide equivalent	Fluidized bed reactor	450 °C	Oil palm empty fruit bunch	Chan et al. (2016)
Global warming potential	−200 to −470 kg carbon dioxide equivalent /ton biomass	Auger-based reactor	400 °C, 550 °C, and 700 °C	Crop residues and woody wastes	Cheng et al. (2020)
Carbon footprint	Carbon removal of 21–155 kg carbon dioxide equivalent	Pilot-scale	350–400 °C	Tomato plant residues	Llorach-Massana et al. (2017)
Global warming potential	−1.06-ton carbon dioxide equivalent	Pyrolysis	Not mentioned	Straw	Clare et al. (2015)
Global warming potential	−1.101, −1.143, and −1.636-ton carbon dioxide equivalent under slow, fast, and intermediate pyrolysis, respectively	Fluidized bed for slow pyrolysis	400–550 °C	Rice straw	Gong et al. (2021)
Global warming potential	−1.122, −1.748, and −1.839-ton carbon dioxide equivalent for intermediate, fast, and slow pyrolysis, respectively	Fluidized bed for fast pyrolysis	400–550 °C	Corn stover	Gong et al. (2021)
Greenhouse gas reduction potential	Total greenhouse gas reduction potential 1.41 gigatons carbon dioxide equivalent, estimated from Chinese crop residues source in 2012	Not mentioned	Not mentioned	Crop residue	Dai et al. (2020)
Global warming potential	−0.62 kg carbon dioxide equivalent	Rotary kiln, centralized pyrolysis system	550 °C	Crop straw	Yang et al. (2020)

Table 8 (continued)

Environmental category	Carbon emission impact	Pyrolysis reactor	Pyrolysis temperature	Feedstocks	References
Global warming potential	-130 kg carbon dioxide equivalent	Mobile pyrolysis units	Not mentioned	Olive solid pellet waste	El Hanandeh (2015)
Global warming potential	0.988 kg carbon dioxide equivalent	Modeled pyrolysis reactor	600 °C for 15 min	Empty fruit bunches and oil palm kernel shell	Mo et al. (2022)
Global warming potential	-5.5 kg carbon dioxide equivalent	Fast pyrolysis reactor	740 °C	Orange peel waste	Negro et al. (2017)
Global warming potential	-229 kg, -318 kg, and -360 kg carbon dioxide equivalent for a brick kiln, stove, and BigChar 2200 unit, respectively	Brick kiln, stove, and BigChar 2200 unit	400 to 650 °C	Rice husk	Mohammadi et al. (2017)
Net carbon sequestration	0.141 to 0.217-ton carbon dioxide equivalent for the portable systems 0.204-ton carbon dioxide equivalent for the centralized system	Portable systems, Centralized plant	Not mentioned	Agricultural residues	Thakkar et al. (2016)
Global warming potential	-6.3 ± 0.5-ton carbon dioxide equivalent/hectare/year, -36 megaton carbon dioxide equivalent/year	Industrial slow pyrolyzer	550 °C	Sugarcane residues	Lefebvre et al. (2021)
Global warming potential	-2.59 to -2.74 (at 500 °C) ton carbon dioxide equivalent/ton biochar	Pilot-scale pyrolyzer	300, 400, and 500 °C	Agricultural and residual forestry biomass	Muñoz et al. (2017)

(Madadi Avargani et al. 2022). Fossil fuels usually generate carbon dioxide that increased from 6 gigatons in 1950 to 34.81 gigatons in 2020, responsible for approximately 90% of the total carbon dioxide emissions (Farghali et al. 2022b; Osman et al. 2022b). Increased carbon dioxide emissions resulted in several disasters, including climate change, global warming, environmental pollution, ecosystem imbalance, and human and livestock disorders. For instance, climate changes affect the frequency and strength of storms, floods, droughts, and heatwaves, with subsequent physical and mental health disorders (Hrabok et al. 2020; Agha-Kouchak et al. 2020). In 2018, the world witnessed more than 300 cases of climatic-related natural disasters affecting 68 million people. About \$131.7 billion in financial damages were reported, of which wildfires, floods, droughts, and storms, represented 93%. Water, food, infrastructure, human health, and the ecosystem have been identified as the most susceptible to climate crises. Climate change also alters crop yields and causes infectious disease distribution (Farghali et al. 2022b). Therefore, climate change mitigation is urgently required to protect humans and all living beings from the worst of these consequences.

One available option could be accomplished through net-zero waste and sustainable energy transition, where wastes can generate renewable bioenergy to meet energy demands (Farghali et al. 2022b). Several valorization processes have been used to treat biomass/wastes, such as pyrolysis, hydrothermal carbonization, anaerobic digestion, landfilling, and composting (Peng et al. 2023). Nevertheless, most conventional waste valorization systems have several disadvantages and limitations, such as water and soil contamination, climate change, and pollution (Duan et al. 2021; Gaska et al. 2021).

The anaerobic digestion process is a promising biotechnology that can aid in solving the current energy crisis by using waste and nutrient recovery without impacting the ecosystem (Farghali et al. 2022b; Farghali et al. 2021). A biogas system application in each nation could limit global warming to 2 °C. It might decrease greenhouse gas emissions by 3.3–4.4 billion tons of carbon dioxide equivalent, accounting for 13% of global emissions (Farghali et al. 2022b). Bioenergy generation from the anaerobic digestion process can generate approximately 14,000 terra watt-hours energy, accounting for 9% of primary energy consumed or about 32% of coal utilized globally (Farghali et al. 2022b).

Research has been conducted to enhance biogas generation using various feedstocks (Lu et al. 2022; Farghali et al. 2020; Ap et al. 2021). However, approximately 10–40% (weight/weight) of agro/food waste is utilized for biogas generation, while the residual digestate portion remains undegraded. The unutilized digestate is a byproduct rich in nutrients and is used as fertilizer to enhance soil fertility. Nevertheless, improper uses of digestate, besides digestate's

solid organic and inorganic contents, moisture, microbial residue, and fiber, may pollute water, cause unpleasant odors, and cause environmental pollution from the residual greenhouse gas emissions (Lamolnara et al. 2022). On the other hand, the cleaning and purifying of raw biogas from hydrogen sulfide, carbon dioxide, ammonia, vapor, and silica to high biomethane content comparable to natural gas is another issue facing the anaerobic digestion process (Khan et al. 2021). In addition, other challenges still need to be solved, including system instability, long retention times, the lower calorific value of biogas, the generation of low-quality digestate, and difficulties in the biodegradation of high-fiber feedstock.

The pyrolysis process can offer benefits such as eco-friendly nature and system controls. Additionally, the produced biochar has superior characteristics to unprocessed digestate to improve the crops and be utilized for raw biogas cleaning (Farghali et al. 2022b). However, using the pyrolysis process alone to treat agro-food wastes has limitations, such as difficulties in treating higher moisture-containing wastes, which reduces the system's efficiency. Therefore, coupling the anaerobic digestion process with pyrolysis corresponds to each other, compensating for the shortcomings of individual techniques (Tayibi et al. 2021a; Monlau et al. 2015). An integrated approach can achieve a net-zero waste concept, recover bioenergy from digestate, utilize waste, upgrade the biogas produced, and promote a circular economy (Farghali et al. 2022b; Farghali et al. 2022c).

Generally, three essential scenarios have been implemented in integrating the anaerobic digestion process with the pyrolysis process: First, utilizing the liquified and gasified pyrolyzed fractions as feedstocks for the anaerobic digestion process "upstream upgrading." Second, converting the solid recalcitrant digestate from the anaerobic digester in the pyrolysis process "downstream valorization process." Ultimately, cycling systems include downstream and upstream approaches.

The integrated approach has many benefits, including (i) treatment of large quantities of biomass, where readily degradable products are sent to anaerobic digestion, whereas harsh biodegradable (straw, wood, and solid digestate fraction) are utilized via pyrolysis. (ii) Avoiding pretreatment for anaerobic digestion units as pyrolysis could manage the dry and inadequately degradable feedstocks. (iii) In situ and ex situ biogas upgrad and purification of biogas using biochar addition into the anaerobic digestion system. (iv) The in situ or ex situ syngas upgrad via the biological methanation process, and (v) the beneficial uses of digestate with biochar for agronomic optimization (Tayibi et al. 2021b).

## Upstream integration system

In this integration approach, the pyrolyzed biomass/wastes served as feedstocks for the anaerobic digester. The input feedstock, the byproduct of the pyrolysis process, could be bio-oil, syngas, or biochar. Uses of biochar in anaerobic digestion are extensively studied in the literature, either to control anaerobic digestion inhibitors, to enhance and purify biogas from hydrogen sulfide, to upgrade the raw biogas through the removal of carbon dioxide (Farghali et al. 2022b), or as a mean to increase the agronomic value of the digestate (Farghali et al. 2022b; Tayibi et al. 2021b).

This section focuses on the valorization of bio-oil and syngas through an integrated approach. Bio-oils are known as pyrolysis fluids, pyrolysis oils, pyroligneous acids, and bio-petroleum (Drugkar et al. 2022). A liquid fraction from the pyrolysis process comprises about 400 different functional groups in two components: an organic bottom bio-oil of 15–30% weight/weight and an aqueous bio-oil part of 70–85% weight/weight. The aqueous phase consists of water, water-soluble substances (volatile fatty acids, sugars of C<sub>2</sub>–C<sub>6</sub> structure, oligomers), and little soluble substrates mainly in the form of furans and phenols (Tayibi et al. 2021b; Drugkar et al. 2022; Álvarez-Chávez et al. 2019). Bio-oil has a low heating value, high ammonia–nitrogen, and high water content. Thus, using aqueous bio-oil in anaerobic digestion has gained recent awareness (Torri and Fabbri 2014; Seyedi et al. 2019; Hübner and Mumme 2015), as shown in Table 9.

Torri and Fabbri (2014) use pyrolysis bio-oil from corn stalks as feedstock for an anaerobic test underlining biological inhibition. They reported methane generation corresponding to 65% of the theoretical value after adding bio-oil at 5 g/liter digester/day in a semi-continuous system. Likewise, Hübner and Mumme (2015) investigated the biomethane generation of various aqueous pyrolysis liquor produced from solid digestates at 330–530 °C, which were added to batch systems at four chemical oxygen demand-based dosages of 3, 6, 12, and 30 g/liter. The pyrolyzed liquor at 330 °C produced the highest methane outcome of 199.1 L/kilogram chemical oxygen demand, corresponding to 56.9% chemical oxygen demand removal, followed by the 430 °C pyrolyzed liquor. Most volatile organic carbons, such as phenol, furfural, catechol, levoglucosan, and guaiacol, in the pyrolysis liquor, were reduced below the detection limit. The authors emphasized the meaning of integrated pyrolysis and anaerobic digestion in the valorization of digestate and pyrolysis liquors.

Some authors reported inhibitory effects after utilizing pyrolysis liquids in anaerobic digestion. For example, Seyedi et al. (2019) explored various liquid toxicity derived from pyrolysis at 800 °C to anaerobically digested waste-activated municipal water and primary sludge. The authors

found methanogenic toxicity after using the aqueous pyrolysis liquid digester at loading rates higher than 0.5 g/chemical oxygen demand. The toxicity was attributed to organic byproducts of 2,5-dimethoxybenzyl alcohol, 3,5-dimethoxy-4-hydroxybenzaldehyde, cresol, benzene, phenols, ethylbenzene, xylenes, styrene, pyridine, and benzonitrile, but not attributed to ammonia–nitrogen concentration. However, Yu et al. (2020) examined the influence of diluted aqueous pyrolysis liquid 5–100 times on the anaerobic digestion of swine manure. They found an improvement in the methanogenic capacity by 22.98% in the digester supplied with 50% diluted aqueous pyrolysis liquid compared to the control. The *Methanosarcina* and *Methanobrevibacter* dominated microbial communities and biodegraded volatile fatty acids, maximizing the biomethane yield.

Additionally, Yue et al. (2019) explored the impact of sewage sludge pyrolysis liquid on batch anaerobic digestion of cow manure. They found that adding sewage sludge pyrolysis liquid produced at 550 °C increased biomethane yield by 128.7% compared to the group without addition. The sewage sludge pyrolysis liquid-rich trace elements promoted microbes' growth and contributed to the decomposition of toxic organic compounds, hence being an economical and reliable alternative for waste valorization.

Few studies have determined the effect of an upstream integration system in a continuous anaerobic fermentation system. Torri et al. (2020) indicated that continuous anaerobic digestion of aqueous pyrolysis liquid derived from pine wood in an up-flow anaerobic sludge bed reactor resulted in a 52% biodegradation of the chemical oxygen demand of the aqueous pyrolysis liquid at an organic loading rate of 1.5 g chemical oxygen demand/liter/day. This helps guide more research to develop aqueous pyrolysis liquid in continuous anaerobic fermentation to increase its feasibility on a large scale.

Apart from bio-oil, syngas has the potential to be upgraded into biomethane (Schwede et al. 2017; Paniagua et al. 2022), as listed in Table 10. The composition of syngas varies according to the organic waste composition and its producing conditions. Parameters, including reactor configuration, production time, temperature, and feedstock moisture content, influence the syngas composition (Aryal et al. 2021; Cerone et al. 2020).

Biological biomethanation is the method that converts syngas to biomethane via methanogenic microorganisms metabolism at temperature ranges of 35–75 °C (Paniagua et al. 2022). The biological methanation of syngas can occur via the conversion of carbon monoxides, carbon dioxides, and hydrogen into methane using different routes harbored by archaea and bacteria, as shown in Fig. 8. Acetate and hydrogen/carbon dioxide pathways are common in the biological syngas methanation. The biological conversion of carbon dioxides to methane with a hydrogen-assisted

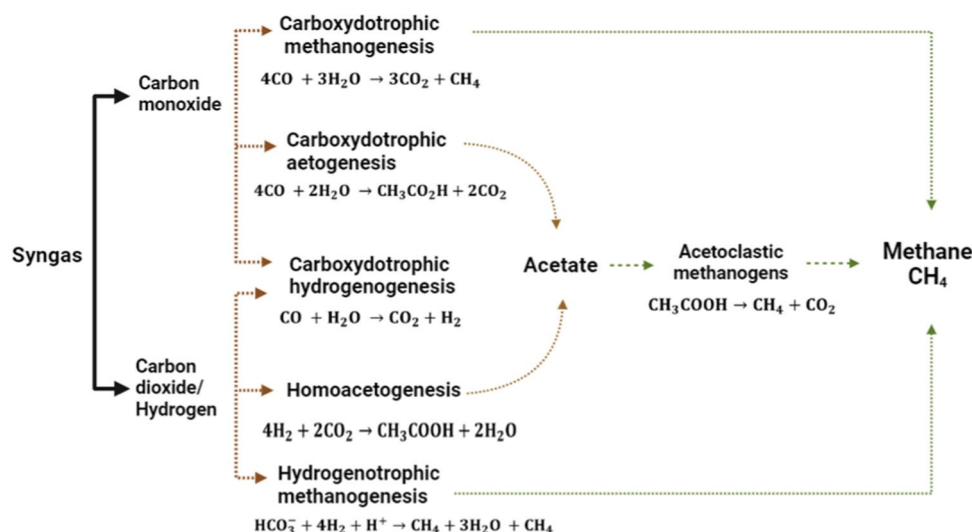


**Table 9** Effect of adding aqueous pyrolysis liquid from various lignocellulosic biomass on methane production and organic biodegradation. Different pyrolysis conditions and reactors are used to produce bio-oils applied as feedstock for the anaerobic digestion system. Such integration generated an improved biomethane yield of up to 128.7% compared to the control non-supplemented digester. In addition, the organic matter was degraded by approximately 63%

Biomass	Reactor and condition	Digestion temperature and period	Pyrolysis condition	Loading rate	Methane yield	Organic degradation effect	Reference
Cornstalk	Batch, 100-ml syringe	40 °C, 225 days	Fixed bed pyrolysis (intermediate) at 400 °C for 10 min	35 g chemical oxygen demand /liter Food/microorganism: 0.6	126-L methane/kilogram bio-oils	34% chemical oxygen demand removal	Torri and Fabbri (2014)
Digestate of cow manure and maize (4:3)	Batch, 100-ml syringe (20-ml effective volume),	40.5 °C, 49 days	Pyrolysis at 330–530 °C for 45 ± 15 min	0.129 to 49.1 g chemical oxygen demand/liter	199.1 ± 18.5-L methane/kilogram chemical oxygen demand	56.9%, 55.4%, and 36.9% of chemical oxygen demand removal	Hübner and Mumme (2015)
Pinewood (softwood)	Continuous up-flow reactor	40 °C, 79 days	Pyrolysis at 400 °C for 30 min	1.25 g chemical oxygen demand /liter/day Hydraulic retention time: 80 days	34% of fed chemical oxygen demand	Not detected	Torri et al. (2020)
Swine manure	Batch, 500- milliliter serum bottle	35 °C, 67 days	Commercially obtained from the pyrolysis process	Diluted 5–100 times with pure water	22.98% improvement at 50-time dilution	About 63% volatile solids reduction	Yu et al. (2020)
Rice straw and reed straw	Glass bottle of 0.5 L	55 °C	Pyrolysis at 350 °C, 450 °C and 550 °C for 30 min	10 g/digester	57.5%, 71.6%, and 128.7% increase in the cumulative methane yield, respectively	Not detected	Yue et al. (2019)

**Table 10** Syngas biomethanation. Mixtures of syngas, including hydrogen, carbon dioxide, carbon monoxide, and others used as feedstock gas for anaerobic digestion system. The final methane obtained ranged between 49 and 96.0%. Continuous stirred-tank reactor configuration utilized syngas in a lower aspect than the tickling bed reactor and bubble column

Culture	Reactor	Feed syngas composition (%)	Volume (liter)	pH	Temperature (°C)	Final methane composition (%)	Methane yield (mole methane/mole syngas)	Reference
Co-culture <i>Methanobacterium thermoautotrophicus</i> and <i>Carboxydothermus hydrogenoformans</i>	Continuous stirred-tank reactor	Hydrogen/carbon dioxide (66.6/33.3)	1.5	7.2	65	70.0	Not mentioned	Diender et al. (2018)
Anaerobic-digester sludge	Continuous stirred-tank reactor	Hydrogen/carbon dioxide/methane/nitrogen (80/20/0/14.7)	9.5	8.1	55	49.0	0.16	Voelklein et al. (2019)
Anaerobic-digester sludge	Continuous stirred-tank reactor	Hydrogen/carbon dioxide/methane/nitrogen (54/14/32/0)	9.5	8.1	55	61.0	0.22	Voelklein et al. (2019)
Mixed microbes (waste-water treatment plant anaerobic sludges)	Tickling bed reactor	Hydrogen/carbon dioxide/carbon monoxide/nitrogen (45/25/25/10)	0.18	7.0	37	67.0	Not mentioned	Asimakopoulos et al. (2020)
Mixed microbes (waste-water treatment plant anaerobic sludges)	Tickling bed reactor	Hydrogen/carbon dioxide/carbon monoxide/nitrogen (45/25/25/10)	0.18	7.0	60	86.0	Not mentioned	Asimakopoulos et al. (2020)
<i>Methanobacterium formicum</i> , <i>Pseudomonas</i> sp. and Peptococcaceae	Tickling bed reactor	Hydrogen/carbon dioxide/methane/nitrogen (62/15/23/0)	0.8	7.1	54	96.0	Not mentioned	Ghofrani-Isfahani et al. (2022)
Biogas plant digester ( <i>Methanobacterium thermoautotrophicus</i> and <i>Clostridia</i> sp.)	Tickling bed reactor	Carbon dioxide/methane/nitrogen (15/23/65)	1.2	8.0	52	66.0	Not mentioned	Kougiaris et al. (2017)
Microbes ( <i>Methanobacterium thermoautotrophicus</i> and <i>Clostridia</i> sp.)	Bubble column	Carbon dioxide/methane/nitrogen (15/23/65)	1.4	8.0	52	73.0	Not mentioned	Kougiaris et al. (2017)
Mixed anaerobic culture enriched with hydrogenotrophic methanogens	Bubble column	Hydrogen/carbon dioxide/methane/nitrogen (65/17.5/0/17.5)	0.29	7.5	52	67.1	0.18	Sieborg et al. (2020)
Mixed anaerobic culture enriched with hydrogenotrophic methanogens	Bubble column	Hydrogen/carbon dioxide/methane/nitrogen (62/15/23/0)	1.0	8.3	54	95.1	0.25	Porté et al. (2019)
Anaerobic-digester sludge ( <i>Coprothermobacter</i> and <i>Methanobacterium</i> )	Bubble column	Hydrogen/carbon dioxide (4.2 ratios)	22.0	7.5	55	94.0	Not mentioned	Laguillaumie et al. (2022)



**Fig. 8** Biomethanation of syngas into methane. The syngas biological methanation can occur via converting carbon monoxides, carbon dioxides, and hydrogen into methane using different archaea and bacteria. Carbon monoxides can be converted into carbon dioxides or acetate using methanogens and acetogenic microbes. The carbon

dioxides and hydrogen can be converted into acetate by carboxydrotrophic hydrogenogenesis and hydrogenotrophic methanogens. Acetoclastic methanogens furtherly utilize acetate in methane.  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{CH}_3\text{COOH}$  refer to carbon monoxide, hydrogen, water, carbon dioxide, methane, and acetic acid, respectively

pathway is a well-known process for ex situ and in situ biogas upgrading (Farghali et al. 2022b).

The conversion of syngas into acetate through the utilization of microorganisms, such as members of the genera *Eubacterium*, *Acetobacterium*, *Clostridium*, and *Sporomusa*, is a well-documented process in the literature (Novak et al. 2021; Renaudie et al. 2022). These microorganisms, commonly referred to as acetogens, can utilize hydrogen and carbon monoxide in the syngas to produce acetate as a metabolic byproduct. Subsequently, the acetate produced is utilized by acetoclastic methanogens, such as *Methanosarcina barkeri*, to generate methane through the process of acetoclastic methanogenesis (Renaudie et al. 2022; Novak et al. 2021). This pathway represents a critical step in converting syngas into methane, a valuable energy source.

An alternative pathway for syngas methanation is the conversion of carbon monoxide to hydrogen and carbon dioxide through carboxydrotrophic hydrogenogenesis (Paniagua et al. 2022). This reaction is facilitated by microorganisms, including *Thermincola*, *Rhodospirillum*, *Desulfotomaculum*, *Caboxydocella*, *Carboxydotherrmus*, and *Moorella* (Kato et al. 2021; Liu et al. 2020). Then the reaction is completed by hydrogenotrophic methanogenesis.

The utilization of acetic acid in the process of methanogenesis can occur through two pathways: acetoclastic methanogens or syntrophic acetate-oxidizing bacteria. Whether one pathway or the other is used depends on the availability of different compounds, such as formate or hydrogen, in the system. In the case of acetoclastic methanogens, acetic acid

is converted directly into methane (Paniagua et al. 2022; Dyksma et al. 2020). On the other hand, syntrophic acetate-oxidizing bacteria oxidize acetic acid into carbon dioxide and hydrogen, which is then utilized by hydrogenotrophic methanogens to produce methane. This latter pathway has been considered particularly important under thermophilic fermentation conditions (Paniagua et al. 2022).

Compared to chemical compounds, the utilization of microorganisms makes the biological conversion process less vulnerable to feed gas impurities and more eco-friendly (Ba et al. 2020). Therefore, adopting the biological syngas conversion into biomethane has attracted significant attention. Multiple strategies can be implemented to upgrade syngas molecules, including carbon monoxides and carbon dioxides, into biomethane using hydrogen in syngas as an electron donor. Methane can be generated from non-converted carbon dioxides using conventional biogas scrubbing or by methanation of carbon dioxides with hydrogen addition (Farghali et al. 2022b).

The biological conversion of syngas to biomethane is still in its infancy and has several limitations. For example, poor hydrogen and carbon monoxide solubilities limit the mass transfer of the gas and the microbial biomass (Schwede et al. 2017; Thema et al. 2019). In contrast, carbon dioxide is about 23 times more soluble than hydrogen in an aqueous medium (Götz et al. 2016). Schwede et al. (2017) examined the methanogenic archaea immobilization onto biochar to enhance the biomethanation process. They found that about 50% of the syngas components were converted to methane during the first

24 h; however, carbon monoxide was almost utilized for acetate/formate formation rather than the methanogenesis pathway. Afterward, methane production decreased due to increased carbon monoxide partial pressure that caused methanogenesis inhibition. Figueras et al. (2021) explored the effect of 4 bars of pressure on the syngas-liquid transfer in a 10-L continuous stirred tank reactor at 55 °C. The authors found that a syngas mixture of 40% carbon monoxide, 40% hydrogen, and 20% carbon dioxide was successfully biomethanated at 6.8 mmol biomethane per liter reactor with 97% carbon monoxide and 98% of hydrogen bioconversion rates.

pH is among the limiting factors affecting microorganisms' activity and syngas biomethanation (Li et al. 2022). The neutral pH of 7 is optimum for syngas biomethanation. However, the existence of hydrogen in the reaction would react with carbon dioxides rather than carbon monoxide, resulting in a higher pH value and suppressing the activity of carbon monoxide utilizing microbes (Li et al. 2020).

### Cycling downstream and upstream integrated approaches

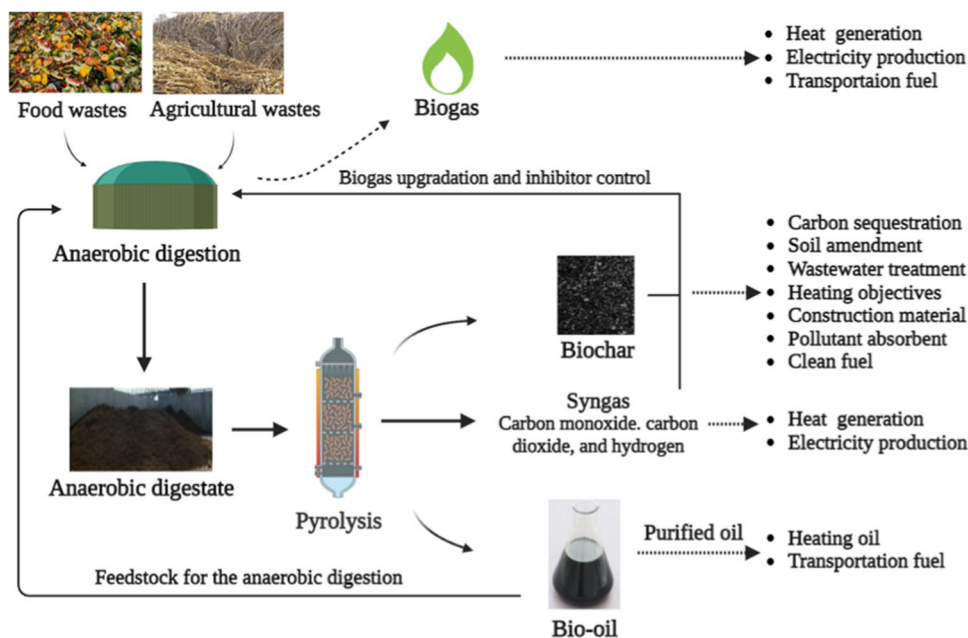
The anaerobic digestion-downstream-upstream pyrolysis is a system in which the raw feedstocks are introduced to the biogas plants to generate biogas and the digestate. After that, the produced digestate is utilized through the pyrolysis process to produce energy, biochar, and bio-oil—the pyrolysis product are then introduced into the biogas plants as co-supplements, as shown in Fig. 9.

In the standard anaerobic fermentation process, the produced digestate, rich in nutrients, is used as organic fertilizer

to enhance crop and soil properties. However, the direct application of fertilizer into soils has several drawbacks, such as greenhouse gas emissions, high transportation costs, and storage difficulties. Such an integrated approach reduces greenhouse gas emissions and improves waste recycling and the bioenergy potential of a biogas system. Balsari et al. (2013) reported that 1 megawatt of electricity produced from a biogas plant generates about 100 tons of digestate per day, having 30% and about 40% of total solid content and organic particulate, respectively, which is considerable amounts to be utilized in pyrolysis. However, the produced digestate contains high moisture contents, which limits the direct use of raw digestate in pyrolysis; hence removing the water from the digestate is essential before the pyrolysis process. Excess water in the digestate can be removed by mechanical dewatering, followed by thermal drying, which can be supplied by surplus heat of hot gases from the pyrolysis reactor. In a pyrolysis reactor, the solid digestate is pyrolyzed to biochar, bio-oil, and syngas which then would be utilized in the integrated system.

On the other hand, raw biogas from the anaerobic fermentation process needs to be purified and upgraded for subsequent use. Therefore, biochar formed from pyrolyzed digestate may be further applied to enhance methane production and remove carbon dioxide, ammonia, hydrogen sulfide, and siloxanes impurities (Farghali et al. 2022b; Nguyen et al. 2021). The unique physicochemical properties of biochar, including porosity, cation exchange capacity, specific surface area, redox traits, the existence of functional groups, electrical conductivity, aromaticity, and pH, can help to improve the anaerobic digestion process (Kumar et al. 2021). Additionally, biochar can be used in various areas,

**Fig. 9** The combined effect between pyrolysis and anaerobic digestion utilizing biochar, bio-oil, and syngas as primary elements. An anaerobic digestion system involves the digestion of biomass and wastes in the cycling downstream and upstream integrated approaches. After that, solid digestate is pyrolyzed to produce utilizing biochar, bio-oil, and syngas. The pyrolysis byproducts are further used as either co-feedstock or additives to stabilize, improve, purify, or upgrade biogas and soil amendment



**Table 11** Impact of biochar supplementation on the biomethane yield produced from the anaerobic digestion process. Biochar produced from various biomass and wastes can be introduced into an anaerobic digestion system. Amendment of biochar could result in a 4–94% enhancement in methane yield

Feedstock for anaerobic fermentation	Biochar production	Anaerobic fermentation temperature	Improvement effect on methane (%)	Reference
Chicken manure	Fruitwood (5% of total solids)	Mesophilic (35 °C)	69	Pan et al. (2019)
Dry chicken manure	Wood (5% on total solids)	Mesophilic (35 °C)	12	Ma et al. (2019)
Sewage sludge	Corn straw (28 g/liter)	Mesophilic (35 °C)	57	Zhang et al. 2019b
Food waste	Phosphate-laden (10 g/liter)	Mesophilic (37 °C)	94	Rezaeitavabe et al. (2020)
Waste activated sludge	Sludge biochar (10 g/liter)	Mesophilic (37 °C)	4	Wu et al. (2019b)
Food waste-sludge co-digestion	Wheat straw (10 g/liter)	Mesophilic (35 °C)	24	Kaur et al. (2020)
Diary manure	Manure (10 g/liter)	Psychrophilic (20 °C), mesophilic (35 °C), and thermophilic (55 °C)	28 32 36	Jang et al. 2018
Food waste	Pinewood (15 g/liter)	Mesophilic (35 °C)	47	Sugiarto et al. (2021)
Poultry litter	Wood (1:1 feedstock to biochar)	Mesophilic (37 °C)	32	Indren et al. (2020)
Food waste	Wood (5 g/liter)	Thermophilic (55 °C)	18	Lim et al. (2020)
Hydrothermal pretreated waste-activated sludge	Corn straw (10 g/liter)	Mesophilic (37 °C)	24	Shi et al. (2021)

including carbon sequestration, water treatment, animal feed, composting, microbial fuel cells, construction, soil remediation, and energy storage. Table 11 lists the potential role of biochar from different feedstocks in the anaerobic fermentation process.

Studies have shown that adding biochar to the anaerobic digestion process improved methane yield and enhanced system stability. For instance, Zhang et al. (2019b) have examined the effect of nine biochar types obtained from corn straw on the anaerobic fermentation process. They reported a 57% increase in methane yield. Similarly, biochar can remove biogas impurities; for example, Farghali et al. (2022b) reported that biochar shows excellent adsorption capacity toward hydrogen sulfide and carbon dioxide. The authors reviewed that the adsorption capacity for hydrogen sulfide and carbon dioxide was 53–652 mg/gram and 18.2–470 mg/gram, respectively. They mentioned that physical sorption is the pathway for carbon dioxide sequestration, whereas chemical sorption is mainly for hydrogen sulfide.

Another benefit of an integrated system is utilizing the aqueous bio-oil and syngas with the substrate to enhance biomethane yield and recover energy, as mentioned in the previous section.

In conclusion, using the pyrolysis or anaerobic digestion process as a sole process has several limitations and disadvantages. However, integrating pyrolysis with anaerobic digestion could overcome each restriction and increase the product yield with better characteristics. The integration can be in the form of upstream or downstream or cyclic upstream and downstream. Upstream integration is widely studied,

and downstream integration is scarce; however, cyclic upstream and downstream are still in its infancy, particularly at a larger scale. Thus, downstream and cyclic integration approaches are recommended for future studies.

## Energy derived from algal biomass pyrolysis

The industrial development of biomass-based biofuels has become a worldwide mandate due to their economic, political, and environmental influences. Algae-based biofuels contribute to net-zero dioxide emission and play a key role in minimizing carbon footprint through carbon capture and storage methods (Onyeaka et al. 2021). Microalgae-based biofuels have shown potential to resolve the global climate change crisis; their sustainability and renewability make them a promising candidate to fulfill the rising energy demand worldwide. Algal biomass (micro- and macroalgae) are rich sources of carbohydrates, lipids, and proteins which could be converted to various biofuel forms contingent on the conversion technique (Hamed et al. 2020a). For instance, algal biomass can be converted to biodiesel via transesterification (Hamed et al. 2022a), bio-methane using anaerobic digestion (Farghali et al. 2021; Prajapati et al. 2013), bioethanol through fermentation processes, or into bio-oil and hydrogen using thermochemical conversion (Pourkarimi et al. 2019). The thermochemical conversion technology offers a more straightforward pathway to producing biofuels than chemical and biochemical processes.

Pyrolysis is one of the most attractive and promising techniques of thermochemical conversion methods. This method involves the complete thermal decomposition of biomasses, in the absence of oxygen, to produce solid (biochar), liquid (bio-oil), and gaseous (non-condensable gases) biofuels (Das et al. 2021). The quality and yield of pyrolysis derivatives mainly depend on the operating parameters such as biomass properties, temperature, heating rate, pressure, and presence of catalysts (Pourkarimi et al. 2019). Among the feedstock materials used in the pyrolysis process, algae are the most promising source of biomass compared to other feedstocks due to their outstanding biomass production, high growth rate, and simple input nutrients required for their cultivation (Das et al. 2021). In addition, microalgae are stable in their bio-oils compared to those from lignocellulosic biomass (Suali and Sarbatly 2012). Studies on *Spirulina* sp. and *Chlorella* spp. have been done extensively to produce high bio-oil yield. Algae biomass is rich in carbohydrates, proteins, and lipids. The decomposition of carbohydrates and proteins occurs at a temperature below 400 °C, but lipids decomposition occurs at a temperature above 550 °C during the pyrolysis process (Pourkarimi et al. 2019). Raising the heating temperature of the biomass to 600 °C increases the secondary cracking processes, which breaks up more significant molecular weight hydrocarbons into smaller ones. As a result, the amount of produced bio-oil progressively declines (Maguyon and Capareda 2013). On the other hand, the slow heating of the biomass leads to volatiles releasing from the reactor, decreasing product yield. However, high algal biomass moisture content necessitates a drying step before the biomass pyrolysis process, which requires greater heating energy consumption (Suganya et al. 2016). Macroalgae (seaweeds) have also been considered as a potential pyrolysis feedstock. Several studies have been made on red macroalgae such as *Gracilaria gracilis* and *Porphyria* sp. (Bae et al. 2011; Francavilla et al. 2015) and brown algal species as *Sargassum* sp. and *Saccharina japonica* sp. (Kim et al. 2012b; Kim et al. 2013).

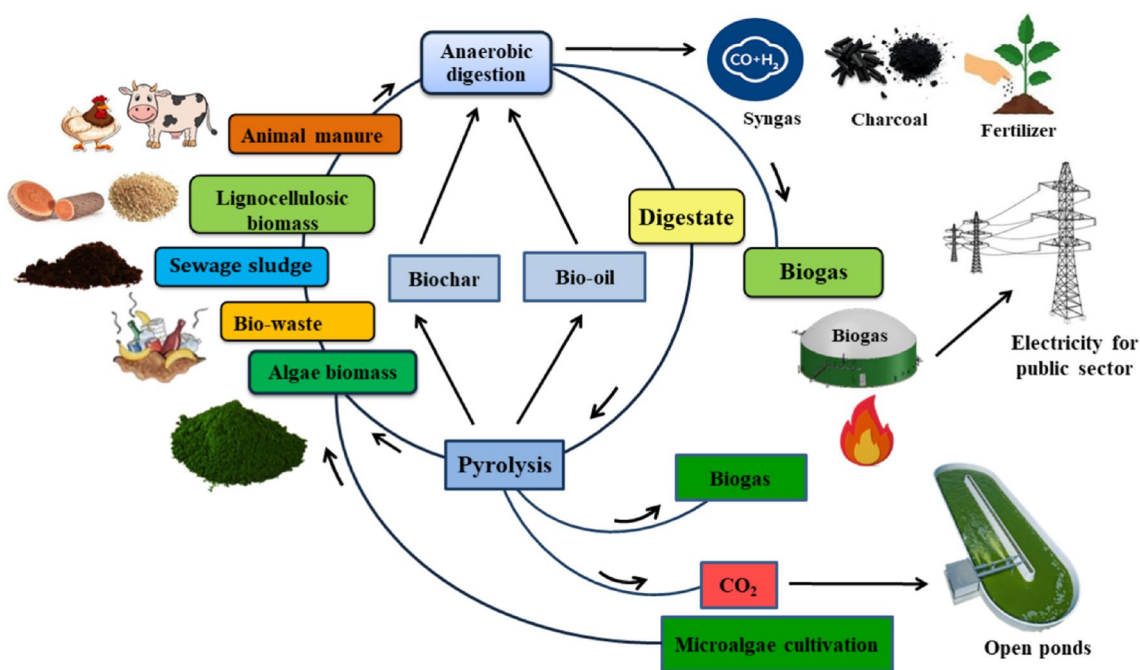
Recently, the concept of the synergic effect induced by the co-pyrolysis of algae biomass with organic waste feedstocks is seen as a cost-effective and eco-friendly approach, attracting the interest of environmental scientists. For instance, Chen et al. (2018a) conducted a study on the co-pyrolysis of *Chlorella vulgaris* biomass with kitchen waste and *Chlorella vulgaris* biomass with coal (Chen et al. 2012). The co-pyrolysis of microalgae and sewage sludge (Wang et al. 2016b) and co-pyrolysis of microalgae with municipal solid waste (Varsha et al. 2021) are considered a cost-effective strategy and reduce waste and an alternative fuel resource. Additionally, co-pyrolysis efficiently avoids the disadvantages of individual sludge pyrolysis and increases the pyrolysis stability of sewage

sludge due to the higher heating value of the added microalgae (Wang et al. 2016b). Co-pyrolysis of marine microalga biomass, *Dunaliella salina*, with different plastics promoted microalgae pyrolysis. They decreased the solid residues owing to the hydrogenation reaction between the unsaturated products generated by plastics and biochar (Chen et al. 2021b). Therefore, developing an influential industry based on the co-pyrolysis of microalgae biomass with plastics or other organic wastes would help solve several environmental issues, resulting in zero waste and achieving positive net energy from biomass.

## Integrating pyrolysis with algae cultivation for emission reduction

The thermochemical conversion of biomass feedstock, including pyrolysis, resulted in the production of gaseous fraction comprised of hydrogen, carbon monoxide, carbon dioxide, nitrogen, methane, ethene, ethane, and others. Combination and concentration of these gases rely on biomass type and the operating conditions of the pyrolysis process (Das et al. 2021). The slow pyrolysis of six different microalgae biomass, *Tetraselmis chui*, *Chlorella vulgaris*, *Chlorella*-like strain, *Chaetoceros muelleri*, *Dunaliella tertiolecta*, and *Synechococcus* sp. yielded gaseous fractions comprised of carbon monoxide, carbon dioxide, methane, ethene, ethane, and hydrogen with estimated concentrations of 20%, 25%, 22%, 14%, 13%, and 18% of biomass weight, respectively (Grierson et al. 2009).

The pyrolytic gases of hydrogen, carbon monoxide, and methane are usually transformed into heating energy or electricity for the public system, as shown in Fig. 10. Purging carbon dioxide into microalgae cultivation systems is considered a reasonable technology to maintain the overall energy conversion process with negative net carbon dioxide emission, a phenomenon known as bioenergy with carbon capture and storage (Zhao et al. 2017). Since microalgae have a high ability to use excessive atmospheric carbon dioxide for biomass proliferation, microalgae are considered a potential tool for global carbon sequestration and promising biomass feedstock for diverse industries and bioproducts, including biodiesel, biogas, biohydrogen, bioethanol, and bioplastic (Hamed et al. 2020a; Abdul-Latif et al. 2020; Hassan et al. 2012; Yu et al. 2018; Hassan et al. 2021). Furthermore, microalgae, particularly green species, have a high potential to grow under stressful environmental conditions of contaminated water with emerging contaminants (Hamed et al. 2022b; Hamed et al. 2020b; Hamed et al. 2021; Hamed et al. 2022c) and industrial wastewater (Hamed et al. 2022a).



**Fig. 10** Coupling biomass pyrolysis and anaerobic digestion processes is an eco-friendly and cost-effective method. This integration results in zero waste, improved energy recovery, and achieved positive net energy from biomass. Pyrolysis of lignocellulosic feedstocks, algae biomass, food bio-waste, sewage sludge, and animal manure

produces gas fraction, biochar, and bio-oil. Gases, including methane and hydrogen, are used for energy production. The biochar and bio-oil added to solid digestate, followed by anaerobic digestion, leads to the upgrading of liquids and syngas into biogas and favors biomethanation on the one hand

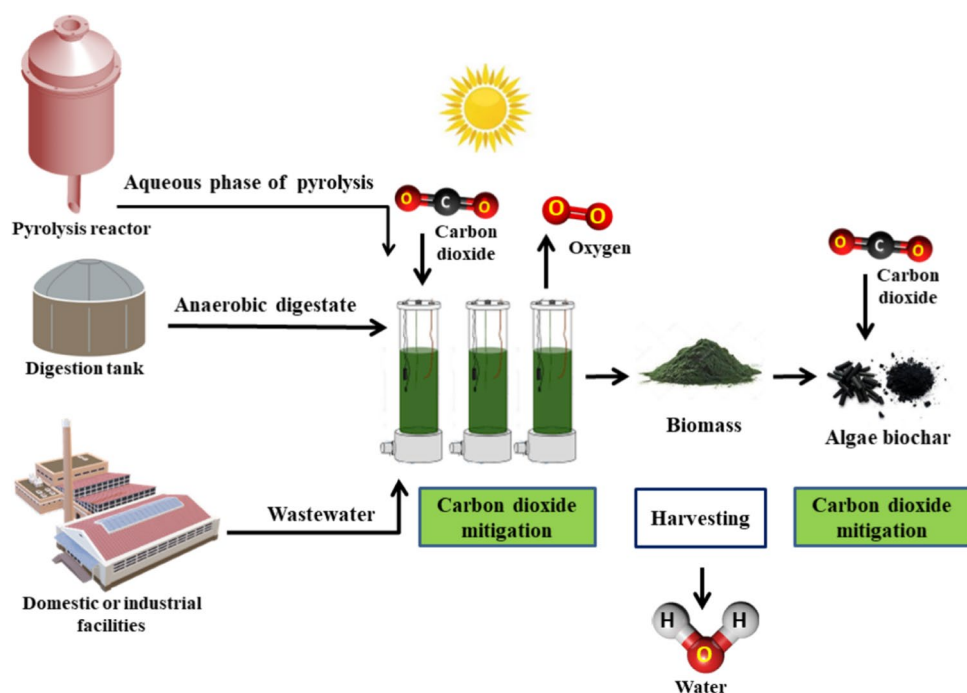
*Chlorella vulgaris* FSP-E showed a high ability to utilize a 7.5% carbon dioxide supply in a growth medium, showing a biomass yield of 7.63 g per liter and productivity of 0.65 g per liter per day at day 13 of cultivation (Yu et al. 2018). The pyrolysis of the obtained microalgal biomass in a fixed-bed reactor yielded 26.9% biochar content with a high heating value of 23.42 megajoules per kilogram. Therefore, the integrated application of algae cultivation for carbon dioxide sequestration resulting from the pyrolysis process and biomass-derived energy production is a realistic and reasonable solution for a sustainable environment (Yu et al. 2018; Hamed et al. 2017). Furthermore, the aqueous phase of pyrolysis is rich in acetic acid, which is employed in fermentation processes using yeast (Lian et al. 2012) and microalgae cultivation (Liang et al. 2013). For instance, the aqueous phase of pyrolysis was used for propagation and lipid-based biofuel production using a heterotrophic microalga *Chlamydomonas reinhardtii* (Liang et al. 2013).

On the other hand, the pyrolysis of anaerobic digestion products (solid digestate) efficiently upgrades them into fuels (char, bio-oil, syngas) and materials (soil fertilizer, sorbent, functionalized materials). Also, using carbon dioxide for microalgae cultivation can maintain the overall energy conversion process with negative net carbon dioxide

emissions. CO and H<sub>2</sub> refer to carbon monoxide and hydrogen, respectively.

The cultivation of mixotrophic microalgae such as *Chlorella* spp. and *Scenedesmus* spp. on the agricultural anaerobic digestate has been extensively discussed by Tawfik et al. (2022). This approach is a promising solution for nutrient recovery and pollutant removal and achieves maximum valorization of digestate. Furthermore, it provides a renewable resource of biomass that could be used for many biorefineries, including biochar production, biofuel, and achieving reasonable carbon sequestration levels, as illustrated in Fig. 11.

In terms of biomass productivity, microalgae are the most prolific biological system. Algal species are an excellent alternative for creating a sustainable ecosystem since they develop quickly and have greater photosynthetic efficiency than terrestrial plants. They might also be grown in open ponds or photobioreactors, reducing the need for arable land. The role of converting algal biomass into biochar as a carbon sequestration tool that could maintain stable carbon for a longer-time scale has also been studied by (Yu et al. 2018). Moreover, algal biochar is rich in nutrients, showing a high ability to exchange ions. Therefore, it has been suggested as an efficient biofertilizer for sustainable agriculture technology (Mona et al. 2021). Thus, coupling pyrolysis with microalgae cultivation significantly decreases carbon dioxide emission, maximizes energy recovery, achieves net



**Fig. 11** Propagation of mixotrophic microalgae on an aqueous phase of pyrolysis, agricultural anaerobic digestate, and wastewater is a cost-effective and eco-friendly strategy. This approach will help nutrient recovery and pollutant removal and achieve maximum valorization of digestate and pyrolysis derivatives. The high photosynthetic efficiency and prolific growth rate of microalgae accelerate the rates of carbon dioxide sequestration from the environment, besides releas-

ing more oxygen to the ambient atmosphere. Furthermore, algae biomass-derived biochar can achieve further carbon sequestration levels. Coupling the pyrolysis and anaerobic digestion industries with microalgae cultivation decreases carbon dioxide emission, maximizes energy recovery, achieves net zero waste, and provides multiple high-energy carriers and bioproducts

zero waste, and provides multiple high-energy carriers and bioproducts.

### Economic analysis of the pyrolysis process

The economic viability of a particular technology is typically affected by technology commercialization. The pyrolytic conversion of biomass to biochar is challenging regarding its economic viability, as merely countable economic-based studies with limited findings have been published in the past years. Meanwhile, the high disparities among the published studies in feedstocks employed and reaction conditions further aggravated the difficulties in analyzing the economic perspective of biomass pyrolysis. On top of these, the economic values of biochar are often beyond the computable monetary value, particularly with biochar's essential role in assisting the development of regional small- and medium-sized industries with limited access to energy. For instance, the lignocellulosic waste from these industries serves as promising feedstocks for biochar conversion, enabling extra energy income in conjecture to the reduced waste treatment costs.

From a narrower perspective, the pyrolysis economic index depends on several factors, including sourcing of raw materials, type of processes, operation conditions, biochar yield, utility, miscellaneous costs, and others. It is acknowledged that employing mixed feedstocks offers a lower financial burden to the company. This can be accounted for a large variety of biomass, which promises facile transportation from nearby regions with lower logistic expenses (Oasmaa et al. 2010). Meanwhile, it should also note that the profitability of the slow/intermediate pyrolytic process largely depends on the biochar yields, given that solid phase product presents the most considerable portion in the product spectrum. Most researchers conduct biomass pyrolysis at a medium–high temperature elevated at a slow rate under an anoxic environment, aiming to retain most carbon species in the resultant solid residue to optimize the solid yield. In the sense of application, while biochar serves as a known fuel source, it could also be used in soil amendment for the betterment of agronomics. This, together with the limited supply of biochar, is the reason for its high selling price, thereby boosting the faith of researchers toward slow/intermediate pyrolytic technologies. Representatively, Wrobel-Tobiszewska et al. (2015) indicated positive profitability of converting *Eucalyptus* plant residues to biochar in Tasmania.



Biochar price and yield significantly affect annual profit, but applying a batch klin with an average capacity of 1 ton/hour generated \$179,000 annually. This was credited to considering biochar production and sales and the cost-saving upon integrating biochar into forestry activity (fertilizer, energy).

A more detailed economic study by Liu et al. (2022) also indicated a similar output, despite the different biomass feedstocks applied. Based on their experimental results, the highest biochar yields of 53.27% and 41.20% could be obtained from pyrolyzing rice straw and sugarcane bagasse, respectively, with a biomass feed rate of 200 kg/hour under 400 °C. Extending from here, the Aspen Plus simulation gives rough estimations of the production costs, i.e., \$0.79/kg and \$0.93/kg for rice straw and sugarcane bagasse-derived biochars, respectively, after considering expenses from raw materials, energy, human, land, and equipment. However, these are higher than empty fruit bunch-biochar, estimated to be \$0.533/kg based on Harsono et al. (2013). Significantly, these results were mainly generated over industrial equipment, offering high reliability and industrial relevance. Figure 12 shows the flow of biochar production using empty fruit bunch biomass, where the energy recovered from the slow pyrolysis process, in the form of heat, will be used to sustain the drying process. Through the existing facilities capable of processing 20 tons of empty fruit bunch/day, the energy demand for biochar production was found to be negative, i.e., biochar's energy content is higher than the energy required in the production process. Meanwhile, the internal rate of return (IRR) and return on investment (ROI) of biochar production from empty fruit bunch were computed as 8.96% and 17.58%, respectively, giving rise to a moderate economic viability with a payback period of 10 years.

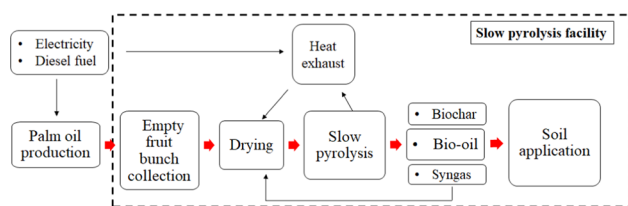
Interestingly, Fawzy et al. (2022) suggested an alternative income source for pyrolytic plants, via carbon removal service, in addition to conventional biochar sales. Based on their life cycle analysis, 24,450 tons of carbon dioxide

equivalent (tCO<sub>2</sub>e) can be permanently removed from the atmosphere yearly over a pyrolytic plant that processes 6.5 tons/hour of olive tree pruning residue. Under an assumed feedstock cost of \$45/ton, the carbon removal incentive at €206.59 /tCO<sub>2</sub>e ensures a good internal rate of return of up to 15%. Intuitively, the combined revenue from both carbon removal service and biochar sales promises an even higher internal rate of return of 22.35% under a base case considering minimum selling prices of €110/tCO<sub>2</sub>e removed and €350/ton biochar. Significantly, a profitable net present value of approximately €3 million was projected in such a case, along with a discounted payback period of 8 years.

Meanwhile, Haelderms et al. (2020) suggested a much higher minimum selling price in cases involving electricity sales rather than carbon removal. Their investigation considered a plant with hourly biochar production of 3 tons, which is expected to cost €14.46 million and €6.164 million for capital and yearly operational investments, respectively. By varying the feedstocks from coffee husks, medium density fiberboard, palm date fronds, AB wood waste, tree bark, and olive stones, a minimum biochar selling price ranged from €436 to 863/ton is required to ensure the profitability of the plant. Meanwhile, the payback period is highly influenced by different biochar feedstocks, as shown in Table 12. The expenses associated with feedstocks and capital investment, the unit price of biochar and subsidiary products (carbon dioxide removal or electricity), and biochar yield are critical aspects for the profitability of biochar plants.

Unlike conventional plants, Bergman et al. (2022) evaluated the economic potential of two portable pyrolytic systems operated in continuous and batch modes, aiming to reduce the logistic costs in biochar production. Such systems are particularly suitable for forest operations usually associated with heavy transportation loads. The continuous system, named biochar solution incorporated (Fig. 13), consists of a downdraft gasifier where the ground biomass is loaded from the top, and the resultant biochar is removed continuously from the bottom. A blower will also be installed to accelerate the air through the gasifier, ramping up the biochar production from forest residue. The capacity of such a system could reach up to 267 kg/hour; however, offering biochar production of only 35 kg/hour.

Meanwhile, the batch system, air-curtain burner (Fig. 13), entails a relatively simple operation: the biomass would be loaded and incinerated in the designated box for biochar production. A diesel-powered fan would be used for air circulation for better biochar yield. In a standard operation that lasts 1 h, 536 kg of biochar could be attained from one ton of forest residue, with no pre-processing required. Upon comparing, though the upfront cost for an air-curtain burner (\$703,283) is slightly lower than that of a biochar solution incorporated (\$764,899), it demanded a nearly doubled operating cost of \$436,696/year. However, considering



**Fig. 12** Process flow for the conversion to the derivation of empty fruit bunch to biochar, subsequently applied in soil modification. In brief, the empty fruit bunch left over after palm fruit removal would be subjected to a drying process before the slow pyrolysis process. The resulting product consists mainly of biochar, which can be used for soil amendment. The byproducts from this process include bio-oil and syngas, where the latter would be applied to the empty fruit bunch drying process together with the recovered heat from the pyrolysis unit. Adapted from Harsono et al. (2013)

**Table 12** Economic analysis of biochar and bio-oil derived from various biomass feedstocks. Using multiple analytical and software techniques, the generation of biochar and bio-oil from the pyrolysis process is estimated to be economically feasible. Profitability, internal rate of return, return on investment, carbon removal service, product pricing, net present value, and other metrics are used to assess the economic impact. The production cost, service fee, capital investment, operating cost, labor cost, and other expenses associated with biochar and bio-oil are also considered

Biomass	Capacity	Analytical approach/software	Findings	Reference
<i>Biochar production</i>				
<i>Eucalyptus</i> plant residues	Batch pyrolyzer with an average capacity of 1 ton/hour	Manual theoretical calculation	Profitability: up to \$179,000/year	Wrobel-Tobiszewska et al. (2015)
Rice straw	200 kg/hour	Aspen Plus	Production cost: \$0.79/kg biochar	Liu et al. (2022)
Sugarcane bagasse	200 kg/hour	Aspen Plus	Production cost: \$0.93/kg biochar	Liu et al. (2022)
Empty fruit bunch	20 tons/day	Practical evaluation using industrial-scale facilities	Internal rate of return: 8.96% Return on investment: 17.58% Payback period: 10 years Selling price: \$0.533/kg biochar	Harsono et al. (2013)
Olive tree pruning residue	6.5 tons/hour	Invest in excel 4.0 Volt	Carbon removal service alone with feedstock cost of €45/ton: Internal rate of return: 15% Service charge: €206.59/ton carbon dioxide removed Carbon removal service and biochar selling: Internal rate of return: 22.35% Net present value: €3 million Payback period: 8 years Biochar price: €350/ton Carbon removal service: 110/ton carbon dioxide equivalent	Fawzy et al. (2022)
Coffee husks, medium-density fiberboard, palm date fronds, AB wood waste, tree bark, olive stones	3 tons biochar/hour (production)	Manual theoretical calculation	Capital investment: €14.46 million Operational cost: €6.164 million /year Minimum selling prices of biochar from different feedstocks: Coffee husks: €436.48/ton (payback period: 11.47 year) Medium-density fiberboard: €572.61/ton (payback period: 17.2 years) Palm date fronds: €891.46/ton (payback period: > 20 years) AB wood: €562.33/ton (payback period: 16.81 years) Tree bark: €494.36/ton (payback period: 10.64 years) Olive stones: €863.75/ton (payback period: > 20 years)	Haeldermans et al. (2020)
Forest residue	267 kg/hour (biochar solution incorporated)	Manual theoretical calculation	Biochar solution incorporated system: Capital cost: \$764,899 Operational cost: \$223,284/year Minimum selling price for biochar: \$1674–1909/ton	Bergman et al. (2022)

Table 12 (continued)

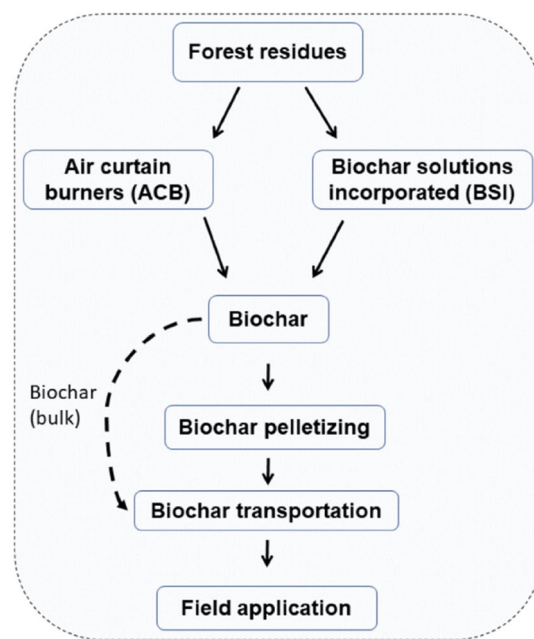
Biomass	Capacity	Analytical approach/software	Findings	Reference
Forest residue	1 ton/hour (air-curtain burner)	Manual theoretical calculation	Air-curtain burner system: Capital cost: \$703,283 Operational cost: \$436,696/year Minimum selling price for biochar: \$528–1051/ton	Bergman et al. (2022)
Municipal solid waste	5 tons/hour (integrated with combined heat and power)	Manual theoretical calculation	Capital cost: £27.64 million Levelized cost of electricity: £0.063/kilowatt-hour internal rate of return: 2.6–10.1% with a selling price of £0.1054/kilowatt-hour -£0.1541/kilowatt-hour	Yang et al. (2018a)
Sludge	3577 tons/year (biochar production)	Manual theoretical calculation	Total cost: €1.214 million/year (inclusive of annualized capital cost, labor cost, fuel cost, and revenue from bio-oil sales) Break-even price: €339.5/ton biochar (fluctuates between €300–387)	Zimmer et al. (2022)
<i>Bio-oil production</i>				
Empty fruit bunch	400 tons/day	Four-level economic potential	Return on investment: 21.69% Payback period: 3.58 years Profit: \$5.41 million/year	Do and Lim (2016)
Rice husk	40 tons/hour	Aspen Plus	Internal rate of return: 13% Payback period: 6 years Profitable revenue: 20% of production cost	Do and Lim (2016)
Rice husk	1000 tons/day	Laboratory-scale experiment and Aspen Plus	Optimum bio-oil yield: 38.4% Least selling price for bio-oil is \$0.55/liter	Wang and Jan (2018)
Rice husk	0.3–1000 kg/hour	Fortran	Production costs for non-catalytically treated oil: \$0.18–18.73/kg; for catalytically treated oil: \$0.56–37.66/kg Note that low capacity comes with a higher unit cost	Islam and Ani 2000
Corn cob	96.5 tons/hour	Aspen HYSYS	Energy recovery from biomass: 72.7% Minimum bio-oil price: \$1.47–2.01/gasoline gallon equivalent (estimated based on corn cob price of \$50–70/ton) Payback period: 6–11 years	Brigagão et al. (2019)

Table 12 (continued)

Biomass	Capacity	Analytical approach/software	Findings	Reference
Sugarcane bagasse	10 tons/hour	Aspen Plus	Capital cost: \$52.5 million Operating cost: \$6.16 million/year Minimum selling price: \$1.10–1.28/liter	Ramirez and Rainey (2019)
Sugarcane bagasse	100 tons/hour	Aspen Plus	Annualized capital cost: £37.5 million/year Operation cost: £35 million/year Energy production cost: £12.5/giga-joule Internal rate of return and Return on investment: 8–9% Payback period: > 10 years	Michailos et al. (2017)
Forest residue	2000 tons/day	A combined approach of laboratory-scale experiment and Aspen Plus simulation	Capital cost: \$427 million Operation cost: \$154 million/year Minimum selling price: \$1.65 million/liter (based on 30-year project life)	Carrasco et al. (2017)
Forest residue	338–2549 tons/day	Aspen Plus	Capital cost: \$104.4–507 million Operating cost: \$9.36–62.31 million/year Minimum selling price for internal rate of return of 10–22% Crude bio-oil: \$0.27–0.75/liter Upgraded bio-oil: \$0.78–1.35/liter	van Schalkwyk et al. (2020)
Wheat straw, corn cob, sawdust	100 kg/hour (mobile system); 4000 kg/hour (fixed system)	Aspen Plus	Mobile system: Capital cost: ¥0.86 million/100 kg-capacity Operating cost: ¥0.28 Mmillion/100 kg-capacity Payback period: 6 years Fixed system: Capacity cost: ¥0.66 million/100 kg-capacity Operating cost: ¥0.55 million/100 kg-capacity Payback period: 7 years	Chen et al. (2018b)

Table 12 (continued)

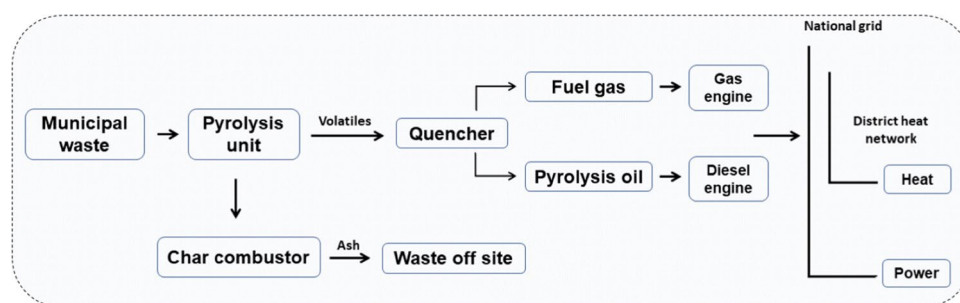
Biomass	Capacity	Analytical approach/software	Findings	Reference
Clean pine, tulip poplar, hybrid poplar, corn stover, switchgrass, oriented strand board, as well as their mixtures with different compositions	2000 tons/day	Aspen Plus	<p>Capital cost: \$528–569 million</p> <p>Material cost: \$64.64–109.67/ton</p> <p>Minimum selling price: \$3.7–5.1/gasoline gallon equivalent</p> <p>Cost contributor:</p> <p>Capital-related costs: 30–40% (taxes, capital depreciation, and return on investment)</p> <p>Biomass feedstock: 30%</p> <p>Catalyst: 13–18% (for hydrotreating process)</p> <p>Labor costs: 12–15%</p>	Meyer et al. (2020)



**Fig. 13** Portable systems for biochar derivation from forest residue. Air-curtain burner (ACB) and biochar solutions incorporated (BSI) systems exhibited considerable potential for biochar production. The resultant biochar would either undergo pelletization for facilitated transportation or be directly transported to the field in bulk form. Adapted from Bergman et al. (2022)

the high productivity of the air-curtain burner, the resultant minimum selling price for its biochar is estimated to be only \$528–1051/ton. On the other hand, biochar from carbon dioxide needed to be sold at \$1674–1909/ton for a profitable scenario. From the perspective of carbon dioxide removal, the air-curtain burner system also stands out with its removal ranging from 750 to 1016 kg carbon dioxide equivalent/ton biochar, thereby promising much higher hidden profits than the biochar solution incorporated system (306–444 kg carbon dioxide equivalent/ton).

Rather than operating alone, integrating a pyrolytic system into a combined heat and power plant may also yield rewarding returns. According to Yang et al. (2018a), an integrated plant that processes 5 tons of municipal solid waste per hour requires a capital investment of £27.64 million. Stabilized operation from this plant (Fig. 14) offers biochar, bio-oil, and combustible gases in the product spectrums, where biochar would mainly employ in fueling the pyrolyzer and supporting the district heat network. Bio-oil and combustible gases, on the other hand, will be adopted in power generation over diesel and gas engines, respectively. As a result, the levelized cost of electricity was calculated at £0.063/kilowatt-hour; therefore, its sales to industrial and domestic users (£0.1054/kilowatt-hour and £0.1541/kilowatt-hour) promise a reasonable internal rate of return of 2.6% and 10.1%, respectively.



**Fig. 14** Combined heat and power plant integrated with a municipal solid waste pyrolytic system. Municipal solid waste will be fed into the pyrolysis unit to produce char and volatile fuels. The char would be subjected to combustion, where the heat could be used to support the pyrolysis operation. On the other hand, the combustible fuels

would be quenched to separate the condensable fraction (oil) from the fuel gas. Gas and diesel engines will then combust these fuels, generating power and heat to support municipal activities. Adapted from Yang et al. (2018a)

Significantly, biomass drying is indispensable before the pyrolytic treatment; however, it often incurs substantial costs that result in high operating expenses. In this regard, Zimmer et al. (2022) provided an exciting horizon for operational cost reduction in pyrolytic processes. The authors proposed the integration of solar drying for biomass pre-processing, further justified with a significant cost reduction of 5–34% compared to conventional belt drying. The vast variation could be attributed to the solar irradiation levels at different longitudinal locations. In brief, the total cost for a base case plant with biochar production of 3577 tons/year from sludge is expected to be €1.214 million/year, with an assumption that the plant is operated at Concepción of Chile (annual average solar irradiation of 222.90 W/m<sup>2</sup>). This gives rise to the break-even price of €339.5 for every ton of biochar. Shifting operational location (varied solar irradiation), resizing the area of the solar dryer, or scaling the production may influence the biochar production economy to a different extent, fluctuating the break-even price to €300–387/ton.

Considering the similarities in nature, bio-oil generation from biomass may also provide some insightful perspectives on the economy of biochar production. Typically, the bio-oil yield remains the primary determinant of the process's economic feasibility. In this aspect, Yang et al. (2018b) provided helpful insight on increasing fuel (char and bio-oil) yield over carbon dioxide-mediated biomass pyrolysis process for a more profitable operation. Meanwhile, the catalyst also plays an integral part in the economic index of bio-oil production. It is known that bio-oil derived from a catalytic process exhibits milder corrosivity (less acidic) than a non-catalytic counterpart, thereby enabling facile and safer production and storage. These characteristics favor the scaling up of the process, considering lower costs are needed to cater to the corrosiveness and safety issues for bio-oil production.

Based on the literature, the economic analysis of biomass-derived bio-oil can be broadly categorized into two

categories: those investigated over theoretical calculations or engineering simulation software (Aspen Plus, CHAMCAD, PRO II) and those that employ a combined approach of laboratory-scale experiment and software. Do and Lim (2016) evaluated the economic value of empty fruit bunch pyrolysis using a manually calculated four-level economic potential approach. Results indicate that the pyrolytic processing of empty fruit bunch promises greater economic potential than bioconversion and gasification processes with a higher return on investment and a lower payback period. At level 4 economic potential analysis, a pyrolytic plant with a throughput of 400 tons of empty fruit bunch/day is estimated to generate \$5.41 million/year, enabling a return on investment of 21.69% and a payback period of 3.58 years. Further increasing the capacity of the plant could realize even better economic performance; however, it comes with higher risk too. Similar positive results were also obtained by Ji et al. (2017), despite the different raw materials of rice husk adopted in their investigation. Based on their Aspen Plus-simulated outputs, a bio-oil derivation plant with a feeding rate of 40 tons of rice husk/hour demands a total project investment of 26.143 million local currency in China. As for the production cost, each ton of pyrolytic liquid fuel is estimated to cost ¥1748 (¥ is the Chinese Yuan), permitting a profitable revenue of 20% and an internal rate of return of 13% in the business. As a result, the corresponding payback period was estimated to be 6 years, indicating high economic feasibility for this plant. While adopting the same feedstock of rice husk, Wang and Jan (2018) employed a hybrid approach involving both experimental and simulation frameworks to evaluate the techno-economical index for bio-oil derivation. The laboratory-scale fluidized bed pyrolytic reaction is experimentally realized in an optimum bio-oil yield of 38.4 weight percent at 400–450 °C, with 45 L/minute carrier gas and rice husk of 21.3 g per feeding time. As for the economic study, the Aspen Plus

simulation displayed that 75% of the operating costs were attributed to the utilities such as electricity, heating, and cooling during bio-oil production. The raw material, rice husk, is regarded as waste in the location of study (Taiwan), thereby only accounting for 20% of the operating costs (transportation). For a plant that processes 1000 tons of rice husk daily, the produced bio-oil must be marketed at least at \$0.55/liter to ensure profitable revenue. Such price is, in fact, well-fallen in the typical range of \$0.11–0.65/liter for the production cost of biomass-derived bio-oil (Wright et al. 2010b).

In another study involving the thermochemical conversion of corn cob to energy, Brigagão et al. (2019) evaluated the economic viability of the pyrolytic route using Aspen HYSYS. Their results indicated a high energy recovery of 79% over the pyrolytic pathway. Economically, bio-oil sales promise an annual profit of \$21.01 million, enabling a short payback period of 6 years for a plant operated at 96.5-ton corn cob/hour. However, it should be noted that the obtained results are susceptible to raw material cost (corn cob), whereby a longer payback period of 11 years may be required if that increases from \$50/ton to \$70/ton. This will concurrently elevate the least selling price of bio-oil from \$1.47/gasoline-gallon equivalent to \$2.01/gasoline-gallon equivalent. Meanwhile, the conversion of sugarcane bagasse to bio-oil was economically evaluated, too, by Ramirez and Rainey (2019) and Michailos et al. (2017). In the former case, a pyrolytic plant running at 10 tons/hour was modeled, which was estimated to incur a \$52.05 million capital cost.

The expected operational expenses amounted to \$6.16 million/year, demanding a minimum selling price of \$1.19/liter for bio-oil to attain a profitable regime. Note that such an estimated price is highly dependent on the conversion rate of biomass and could fluctuate in the range of \$1.10–1.28/liter. Compared to the above range of \$0.11–0.65/liter, sugarcane bagasse is deemed a less competitive raw material for bio-oil production. This is also agreed upon by Michailos et al. (2017), which reveals the superiority of the Fischer-Tropsch route over the pyrolysis process. Significantly, the hydroprocessing unit was identified as the significant financial block in the fast pyrolysis of sugarcane bagasse, leading to high capital (annualized), operation, and energy production costs of £37.5 million/year, £35 million/year, and £12.5/gigajoule, respectively. These give rise to an internal rate of return and return on investment of 8–9%, requiring a long payback period of more than 10 years.

In addition to sugarcane bagasse, pyrolysis of forest residue also appeared challenging from a commercialization perspective. Carrasco et al. (2017) indicated a less favorable minimum selling price of \$1.65/liter for the bio-oil derived from forest residues. Significantly, such a price was attained based on a pyrolytic plant with a throughput of 2000 tons/day, which requires an upfront cost of \$427 million for plant

building. Regarding bio-oil production, raw materials, catalysts, utilities, maintenance, and overhead costs are significant expenses, which amounted to a total operating cost of \$154 million/year and other miscellaneous fees. Interestingly, van Schalkwyk et al. (2020) presented much lower minimum selling prices upon investigating a more detailed pyrolytic study on forest residues. In brief, they studied eight catalytic/non-catalytic (four each) forest residue pyrolysis scenarios with varied capacity (338–2549 tons/day) and sourcing radius (100–300 km). Based on the analysis, cases with non-catalytic processes appear more energy-efficient, with their higher average efficiency recorded at 62.3%. On the other hand, catalytic cases were reported in only 55%. As for the total capital investment, big variations (\$104.4–507 million) were observed amongst these plants, primarily due to their differences in processing capacity and sourcing distances. In contrast, an apparent trend was observed in total operating costs, where those of catalytic plants (\$18.05–126.18 million/year) are generally higher than those of non-catalytic plants (\$9.36–62.31 million/year). With a pre-assumed internal rate of return of 10%, the minimum selling price of crude and upgraded bio-oil should be fixed at \$0.27/liter and \$0.78/liter, respectively, with a throughput of 2549 tons/day. By adjusting the internal rate of return to 22%, such prices increased to \$0.75/liter and \$1.35/liter, respectively. The constantly higher price of upgraded bio-oil has arisen from its higher operating cost and lower yields of liquid and solid products.

Interestingly, Chen et al. (2018b) compared the economic feasibility of a mobile pyrolytic system of a 100 kg/hour capacity and a fixed pyrolytic plant of 4000 kg/hour in China. While adopting the same biomass mixture of wheat straw, corn cob, and sawdust, the mobile pyrolytic system required a higher total investment of ¥0.86 million per 100 kg-capacity, compared to ¥0.66 million for a fixed system. However, the former scenario is bestowed with a significantly lower production cost of ¥0.28 million/100 kg-capacity, thereby promising a better economic index for long-term operation. With the sale of bio-oil and biochar at prices of ¥1250/ton and ¥1200/ton, respectively, the mobile system would be profitable starting from the 6<sup>th</sup> year of operation, while the fixed system, with its almost doubled production cost of ¥0.55 million/100 kg-capacity, required longer payback period of 7 years. In this regard, a mobile pyrolytic system may emerge as an alternative for biomass energy recovery.

While the mode of operation significantly impacts the economic index of the pyrolytic process, the type of bio-oil precursor should also play a significant part in this. This can be evidenced by the recent study of Meyer et al. (2020) that explored the economic feasibility of bio-oil production from different biomass feedstocks. Clean pine, tulip poplar, hybrid poplar, corn stover, switchgrass, oriented strand board, and

different mixtures were subjected to pyrolytic treatment over the same pyrolytic system. Slight modifications were needed for a diverse sample, thereby contributing to a slight variation of fixed capital investment for each piece (\$528–569 million). Other notable differences, including material costs (\$64.64–109.67/ton), processing energy demand, and fuel product yield, can further affect the economics of each sample. As a result, the estimated minimum selling price for the investigated samples falls in the range of \$3.7–5.1/gasoline gallon equivalent, mainly due to capital-related (30–40%), feedstock (30%), catalyst (13–18%), and labor costs (12–15%). In particular, biomass mixture with an 8:2 ratio of clean pine and oriented strand board presented the most economic-promising pyrolytic operation, as a result of its low material costs and high fuel yield.

Recent critical studies related to the economic analysis of biomass pyrolysis are listed in Table 12. Most economic evaluations were conducted using simulation software or manual calculations, but the factors considered varied across different studies. For this reason, considerable variations in terms of capital and production costs can be noticed among these studies. While particular agreement on the commercialization of biomass pyrolysis has yet to be attained among researchers, several rules of thumb provide fairly accurate cost estimation for future implementation. Firstly, it is noted that fuel (biochar and bio-oil) yields serve as the prime descriptor for the economic index of biomass pyrolysis, with an absolute positive correlation regardless of the raw material employed. Also, plants with larger capacities usually promise lower average production expenses, but that comes with more prominent risks and, sometimes, higher hidden costs too. Also, raw feedstock costs must be considered. Though waste biomass could be obtained at no cost, the transportation fees incurred should not be overlooked during economic evaluation. While considering all these abovementioned factors, the determined financial index of biomass pyrolysis should be compared against that of fossil energy to provide a more direct intuition on its viability as a replacement.

## Life cycle assessment of biomass pyrolysis

Using biomass pyrolysis to produce bio-oil and biochar can reduce the environmental impacts due to the use of fossil fuels. For instance, liquid fuels from agricultural/forestry biomass residues can be an alternative energy source and mitigate climate change, which is associated with consuming fossil energy resources. However, it is crucial to assess the advantages of employing biomass pyrolysis using practical, scientific, and reliable tools (Alcazar-Ruiz et al. 2022). It has been determined that life cycle assessment is a thorough evaluation method for determining environmental

consequences along the whole production chain (Al-Mawali et al. 2021).

Assessing the sustainability of biomass pyrolysis is a complex process because there are a variety of pyrolytic processes, such as slow pyrolysis, fast pyrolysis, catalytic pyrolysis; operational constraints; start-up and shut-down of plants; products and co-products involved. Hence, conducting a life cycle assessment of the biomass pyrolysis chain is imperative to elicit environmental sustainability. To that goal, this section summarizes life cycle assessment strategies used in recent research. The Web of Science database was searched using the keywords "biomass," "pyrolysis," "life cycle assessment," and "environmental impact assessment" to find relevant articles. In the current study, the 20 most comprehensive papers that were published between 2020 and 2022 were chosen for examination.

Life cycle assessment is a widely recognized method for assessing the potential environmental impacts of systems and has been applied to various pyrolysis systems (Azzi et al. 2021). It offers data-driven information to decision-makers for making sustainable choices. According to ISO 14040 and ISO 14044, life cycle assessment is divided into four phases: (i) goal and scope definition, (ii) life cycle inventory analysis, (iii) environmental impacts assessment, and (iv) life cycle interpretation. Herein, we analyzed 20 life cycle assessment studies published from 2020 to 2022 on biomass pyrolysis, as in Table 13. These reports explored a variety of biomass feedstocks, geographic areas, life cycle tools, and inventories.

## Goal

Defining the goal, scope, and precise purpose, aim, and objectives for a life cycle assessment is essential to put the results in context. It also includes functional unit definition, linked with product functions rather than physical products. Functional units allow the comparison of different life cycle assessment studies.

The reviewed literature used different functional units to present the respective findings, including biomass used as feedstock at the inlet of the pyrolysis plant (Yang et al. 2021; Brassard et al. 2021; Bora et al. 2020; Ramos and Ferreira 2022); bioenergy produced (Alcazar-Ruiz et al. 2022; Im-Orb and Arpornwichanop 2020; Battle et al. 2020; Cruz et al. 2020; Cusenza et al. 2021; Moreno et al. 2022; Ringsred et al. 2021; Mehta et al. 2022; Lan et al. 2021); quantity of biochemicals after the completion of processing (Thompson et al. 2021; Wang et al. 2020d; Zhou et al. 2020b); quantity of bio-fuel and biochar produced (Fawzy et al. 2022; Ramos and Ferreira 2022); and lastly, one year of operation of pyrolysis plant (Papageorgiou et al. 2021).

The system boundaries in the life cycle assessment studies govern which processes are considered when computing



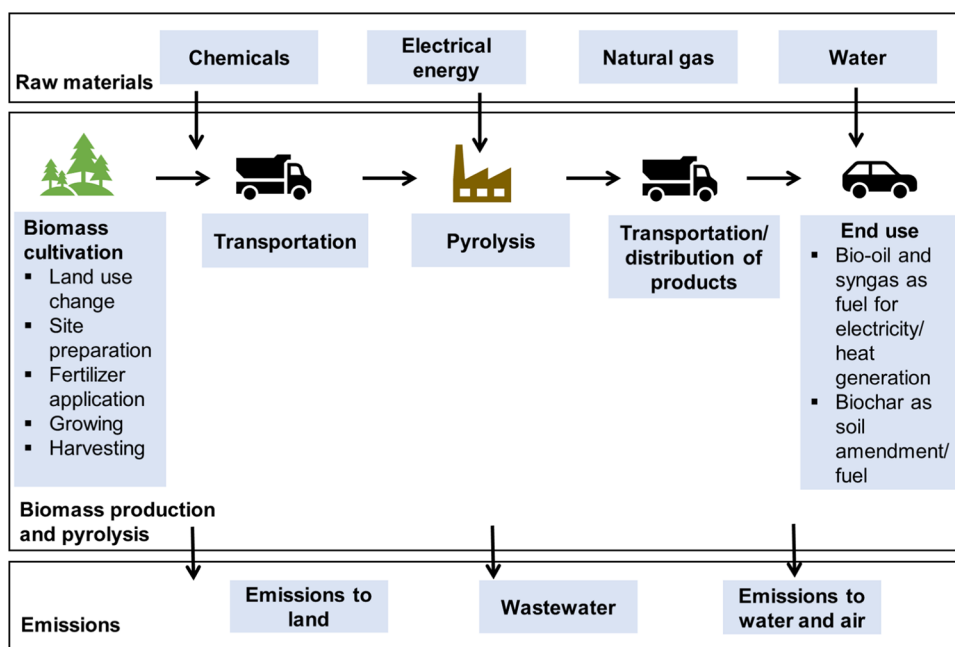
**Table 13** Characteristics of the reviewed studies focused on the life cycle assessment of biomass pyrolysis. The studies were categorized according to the geographical span of the feedstock used and various feedstocks and biomass pyrolysis processes. Additionally, the type of functional unit and life cycle assessment tools and database were also noted. LCA refers to the life cycle assessment

County	Functional unit	Feedstock	Process	Main product	LCA tools	Database	Reference
Thailand	1 kg of methanol produced	Rice straw	Integrated biomass pyrolysis, gasification and methanol synthesis	Methanol	LCSoft version 6.1 Aspen Engineering 8.4	Aspen Plus	Im-Orb and Arpornwichanop (2020)
USA	1 MJ of biofuel produced	Pine residues	Fast pyrolysis followed by combustion	Gasoline and diesel	Aspen Plus	Ecoinvent, GREET (Greenhouse gases, Regulated Emissions, and Energy Use in Transportation)	Lan et al. (2020)
USA	1 MJ of bio-oil produced	Forest residues	Fast pyrolysis and fast catalytic pyrolysis comparison	Biodiesel	Aspen Plus GaBi 9	GaBi 9 LCA	Spatari et al. (2020)
France	1000 kg of dry biomass as feedstock	Forest residues	Pyrolysis	Biochar, bio-oil, and non-condensable gases	SimaPro 9.0	Ecoinvent 3	Brassard et al. (2021)
China	1000 kg of crop residues as input	Crop residues	Slow pyrolysis	Biochar and biofuel	GaBi 8.7	National development and reform commission	Yang et al. (2021)
USA	1000 kg of wet poultry litter as input	Poultry litter	Comparison of fast pyrolysis and slow pyrolysis	Biofuel and biochar	Not available	Ecoinvent 3	Bora et al. (2020)
Spain	1 MJ of output energy as bio-oil	Almond shell, pistachio shell, olive stone, olive pomace, olive branch, and olive leaf	Fast pyrolysis	Bio-oil	SimaPro 9.1.1.1	Ecoinvent	Alcazar-Ruiz et al. (2022)
Brazil	1 MJ of output energy	Palm oil mill residues	Biorefinery integrated with fast pyrolysis followed by transesterification	Bio-oil and biochar	SimaPro 8	Ecoinvent	Battle et al. (2020)
Spain	1 MJ of output energy	Lignocellulosic biomass	Coprocessing of bio-oil in fluid catalytic cracking and hydrocracking units and the co-gasification of pyrolysis char (coproduced with bio-oil) with coke	Propane, butane, kerosene	SimaPro 8.5	Ecoinvent	Cruz et al. (2020)

Table 13 (continued)

County	Functional unit	Feedstock	Process	Main product	LCA tools	Database	Reference
Italy	1 MJ of output energy	Olive tree prunings Olive pomace Lemon peel Orange peel	Slow pyrolysis	Biochar	Aspen Plus	Ecoinvent 3.6	Cusenza et al. (2021)
USA	1 MJ of output energy	Guayule bagasse	Pyrolysis at 500 °C	Gasoline, jet fuel and diesel	Aspen Plus	Ecoinvent 3.4 and the United States Life Cycle Inventory database	Moreno et al. (2022)
Sweden	1 year of the operation of the pyrolysis plant	Wood waste	Pyrolysis with feedstock as 800 kg/hour dry wood and 1250 ton/year biochar	Biochar for soil remediation, heat for district heating	Brightway2 and Activity Browser	Not available	Papageorgiou et al. (2021)
Portugal	1 kg of two-phase olive pomace feedstock	Olive pomace	Slow pyrolysis at 500 °C	Biochar as a soil amendment and bio-oil	SimaPro	Ecoinvent	Ramos and Ferreira (2022)
Canada	1 MJ of bio-jet fuel produced	Forest residues	Fast pyrolysis followed by hydrotreatment	Biojet fuel	GHGenius model 4.03a	British Columbia regional data	Ringsred et al. (2021)
Cuba	1 kg of bio-oil produced	Sugarcane residues	Pyrolysis at 500 °C	Biochar, bio-oil, and non-condensable gases	SimaPro v8.1	Ecoinvent v2.1	Rodriguez-Machin et al. (2021)
Southern Idaho, USA	1 ton of furfural produced	Sugar beet pulp	Pyrolysis at 550 °C	Biochar and furfural	OpenLCA	Literature based	Thompson et al. (2021)
Shaanxi province, China	1 kg of levoglucosan produced	Cotton straw	Fast pyrolysis	Levoglucosan	GaBi	Ecoinvent 2.6	Wang et al. (2020d)
China	1 kg of biochar-modified bio-asphalt produced	Comparison of chopped waste wood and pig manure as feedstock	Pyrolysis at 450 °C	Biochar modified bio-asphalt	Not available	Eurobitume	Zhou et al. (2020b)
Northern Ireland	1 MJ of bioenergy produced	Grass silage and livestock manure	Anaerobic digestion followed by pyrolysis at 500 °C	Biochar and bio-oil	SimaPro	Ecoinvent	Mehta et al. (2022)
UK	1000 kg of biochar produced	Olive tree pruning residue	Pyrolysis at 650 °C	Biochar	SimaPro	Ecoinvent	Fawzy et al. (2022)

**Fig. 15** General system boundary for assessing the life cycle of biomass pyrolysis: (i) biomass cultivation: carbon emissions from land use, use of marginal and/or forest land, fertilizer application, and growing of biomass and harvesting; (ii) transportation of produced biomass for pyrolysis and further processing: transportation mode and distances can vary depending on the geography of the region; (iii) pyrolysis at various temperatures and possible further biorefining process to produce products of different quality; (iv) transportation and distribution of products; (v) end use of products such as for electricity, or as biodiesel for cars/jet engines, or use of biochar as soil amendment material



environmental impacts. Figure 15 shows the generalized crucial phases of biomass pyrolysis: (i) carbon emissions from land usage, utilization of marginal and/or forest land, fertilizer use, biomass production, and harvesting; (ii) transportation of produced biomass for pyrolysis and further processing: transportation mode and distances can vary depending on the geography of the region; (iii) pyrolysis at various temperatures and possible further biorefining process to produce products of different quality; (iv) transportation and distribution of products; (v) end use of products such as for electricity, or as biodiesel for cars/jet engines, or use of biochar as soil amendment material. Both functional unit and system boundary can lead to variation in the environmental impacts calculated for the life cycle of a particular product and process.

### Life cycle inventory analysis

Inventory analysis entails the compilation and quantification of the inputs and outputs for products. This includes raw material needs, energy input, air emissions, wastewater production, solid waste generation, and emissions to land. Journal articles, experimental techniques, and information on the energy consumption of equipment can all be used to prepare material and energy flows. Table 13 shows some of the databases for conducting inventory analysis, including, Ecoinvent, GREET (Greenhouse gases, Regulated Emissions, and Energy use in Transportation), and the United States Life Cycle Inventory database.

### Environmental impacts assessment††

Key environmental impacts are quantified in this step of life cycle assessment and allocated among different environmental categories based on the functional unit, system boundary, modeled systems, and decision-makers' requirements. For example, life cycle environmental impacts can be presented as global warming or climate change potential, including greenhouse gas emissions generally expressed as kg carbon dioxide equivalent (kg CO<sub>2</sub> equivalent). Unless otherwise stated, global warming potential in this review refers to greenhouse gas emissions for a time horizon of 100 years. Depletion of minerals, clay, and peat is referred to as abiotic depletion (kg antimony equivalent). The depletion of fossil deposits is connected to abiotic depletion (fossil fuels, measured in MJ). Ozone layer depletion accounts for emissions of ozone layer-depleting substances (kg trichlorofluoromethane equivalent).

When evaluating the ecotoxicity potential (kg 1,4 dichlorobenzene equivalent or cumulative toxic units), the three different categories are used to consider harm to freshwater, terrestrial, and marine sources during the whole production process. Emissions of reactive molecules harmful to ecosystems and human health are called photochemical oxidation (kg non-methane volatile organic compounds equivalent). The acidifying compounds released into the environment causing acidification are measured in kg sulfur dioxide equivalent. Urban, agricultural, and natural land change is classified as land use (m<sup>2</sup>). Water usage throughout pyrolysis is known as water depletion (m<sup>3</sup>).

The emission of PM<sub>2.5</sub> (particulate matter with a diameter of less than 2.5 μm) and/or PM<sub>10</sub> (particulate matter

with a diameter of more than 10 mm) is related to the creation of particulate matter (PM<sub>2.5</sub> equivalent and/or PM<sub>10</sub> equivalent). The impact of releasing excessive nutrients is known as eutrophication (kg phosphate equivalent). The energy from ionizing radiation (kg Uranium-235 equivalent) is transferred into bodily tissue, which may interfere with molecular structure.

Finally, human toxicity (carcinogens, measured in kilograms of 1,4-dichlorobenzene equivalents or cumulative toxic units) is a measure of the potential harm posed by a unit of a chemical known to cause cancer when emitted into the environment. It is based on a compound's inherent toxicity and possible dose. Non-carcinogenic chemical release, dosages, and exposure are related to non-carcinogenic human toxicity (expressed as kg 1,4 dichlorobenzene equivalent or cumulative toxic units) (Table 14).

To improve the overall environmental performance of the biomass pyrolysis process, this stage of the life cycle assessment involves identifying the phases or processes and drawing conclusions that can be enhanced in the life cycle chain. This stage may also include the presentation and communication of results to stakeholders.

## Key points

A thorough evaluation of 20 life cycle assessment studies, including methodologies and findings, along with key observations was carried out in this work. No two studies were found to be exactly alike, regardless of how close the geographic scope or biomass feedstock considered was. This illustrates that life cycle assessment practitioners and decision-makers need to consider particular processes modeled in the research to determine the approaches toward environmental sustainability, climate change mitigation, and energy efficiency of biomass pyrolysis processes.

The net energy ratio, the ratio of the total process output to input energy, was also provided (Pleanjai and Gheewala 2009) to show the energy efficiency of the pyrolysis system. Mehta et al. (2022) computed the net energy ratio to evaluate the usability of pyrolysis to produce alternative energy sources as 7.3 when livestock manure and underutilized grass silage were used as feedstock for anaerobic digestion followed by pyrolysis. Im-Orb and Arpornwichanop (2020) presented the energy efficiency of the pyrolysis system.

Land usage, which could result from the alteration of natural land, an agricultural area, and urban land, is generally acknowledged as a problematic issue in the production of biofuels. Therefore, almost all the reviewed studies focused on using residues or biomass waste as feedstocks. Waste-to-energy pathways for biomass can mitigate the use of land, fertilizers, and water for the agriculture of energy crops. However, it is crucial to note that life cycle assessment studies should consider the carbon temporal effects

for woody biomass with a much longer growth cycle than annual crops or perennial biomass, such as in the study by Lan et al. (2021).

Pyrolysis is primarily used for sustainable bio-oil and biochar production. However, biorefining of pyrolysis products, i.e., bio-oil and biochar, can help in advanced sustainable material development/chemical recovery. In a similar vein, the life cycle impacts of the production of methanol (Im-Orb and Arpornwichanop 2020), levoglucosan (Wang et al. 2020d), and biochar-modified bio-asphalt (Zhou et al. 2020a) were also evaluated.

## Summary

We conducted a thorough critical analysis of 20 life cycle assessment studies published from 2020 to 2022, including methodology and findings, to understand the most current developments in assessing environmental consequences associated with the production of biofuels. The essential methods and key findings observed were: (i) using waste materials as feedstocks can lead to more eco-friendly energy sources by avoiding environmental harm caused by land and water use during the cultivation of energy crops, and (ii) pyrolysis is mainly used for producing sustainable bio-oil and biochar. However, biorefining pyrolysis products (bio-oil and biochar) can help in advanced sustainable material development/chemical recovery.

## Conclusion

Biomass pyrolysis is a promising technology for converting biomass into various valuable products such as biochar, bio-oil, and gaseous products. Our results showed that the product distribution and properties depend on several factors, including the pyrolytic temperature. The mechanistic pathways that govern the product distribution in biomass pyrolysis were also analyzed, providing a deeper understanding of the process and allowing for better control over the product properties. Additionally, upgrading bio-oil using several processes and integrating pyrolysis with other processes, such as anaerobic digestion, algae cultivation, and others, can help to improve the overall process efficiency and achieve an enhanced negative carbon footprint. Moreover, economic evaluation and life cycle assessment of commercial biomass pyrolysis showed the sustainability and feasibility of the process.

Optimizing biomass pyrolysis necessitates a comprehensive understanding of various factors, including selecting appropriate standard operating conditions for specific biomasses. Further research at a large scale is required to address this issue thoroughly. Additionally, a deeper

**Table 14** Analysis of environmental impacts and key findings from the life cycle assessment studies. This review focuses on analyzing the 20 most complete biomass pyrolysis life cycle assessment studies published from 2020 to 2022. CO<sub>2</sub> and SO<sub>2</sub> refer to carbon dioxide and sulfur dioxide, respectively

Environmental impacts considered	Findings	Reference
Energy efficiency and potential environmental impact	The study analyzed the life cycle impacts of methanol generation using rice straws as feedstock. In addition, potential environmental impact was represented by the average indirect effects of the mass and energy emissions on the environment. The highest energy efficiency value, the percentage of output energy to the sum of input and biomass energy, was 61.2%.	Im-Orb and Arpornwichanop (2020)
Global warming potential (static) and dynamic time-based global warming potential	This study compared traditional static global warming potential and time-based analysis. A carbon temporal effect analysis was performed to explore the impacts of carbon sequestration and emissions at different times for using blended pine residues and switchgrass to produce biochar. The study found that if biochar was utilized as a soil amendment, the carbon intensity was 19.0 to 19.7 g CO <sub>2</sub> equivalent/MJ in the static method and 29.6 to 43.4 g CO <sub>2</sub> equivalent/MJ in the time-based approach. The study highlights that the temporal lag causes the possibility for pine residue-derived biofuels to reduce greenhouse gas emissions to a lesser extent than what would be expected under a typical assumption of carbon neutrality, which takes the effects of carbon sequestration and emissions as static.	Lan et al. (2020)
Life cycle greenhouse gas emissions	This study computed the life cycle of greenhouse gas emissions for the production of 1 MJ of bio-oil produced as: Catalytic fast pyrolysis = - 72 to 32 g CO <sub>2</sub> equivalent Fast pyrolysis = 8 to 13 g CO <sub>2</sub> equivalent	Spatari et al. (2020)
Climate change, human toxicity (carcinogens), ozone layer depletion, freshwater eutrophication, terrestrial, mineral resource use, freshwater acidification, photochemical ozone formation, water scarcity, human toxicity (non-carcinogens), terrestrial eutrophication, respiratory inorganics, marine eutrophication, freshwater ecotoxicity, ionizing radiation, land use, and resource use (energy carriers)	With 1000 kg of feedstock as a functional unit, this study compared using primary forestry residues for pyrolysis to the business-as-usual of no use. It concluded that pyrolysis could positively impact the environment in ten out of sixteen categories. Climate change potential = 906 kg CO <sub>2</sub> equivalent during pyrolysis Climate change potential = 1750 kg CO <sub>2</sub> equivalent during no use	Brassard et al. (2021)
Global warming, ozone layer depletion, abiotic depletion, human toxicity, freshwater ecotoxicity, marine ecotoxicity, terrestrial ecotoxicity, photochemical oxidant formation, acidification, and eutrophication	The study used life cycle assessment to evaluate biochar's potential for carbon sequestration using crop residue in China. A country-level biochar system's annual carbon sequestration potential was estimated at 0.5 × 10 <sup>12</sup> kg CO <sub>2</sub> equivalent, accounting for 4.50% of China's total greenhouse gas emissions Global warming potential = - 5 × 10 <sup>14</sup> g CO <sub>2</sub> equivalent for biochar life cycle Abiotic depletion potential = 4.5 × 10 <sup>7</sup> g antimony equivalent for biochar life cycle	Yang et al. (2021)
Endpoint indicators: ecosystem quality, human health, resource depletion and climate change potential	This study calculated 15 mid-point indicators for using fast and slow pyrolysis to convert poultry litter to fuel and biochar in the USA. Climate change potential for slow pyrolysis = 658 kg CO <sub>2</sub> equivalent/ton of poultry litter Climate change potential for slow pyrolysis = 978 kg CO <sub>2</sub> equivalent/ton of poultry litter Climate change potential for spreading on fields = 1410 kg CO <sub>2</sub> equivalent/ton of poultry litter	Bora et al. (2020)

Table 14 (continued)

Environmental impacts considered	Findings	Reference
Global warming, ozone depletion, photochemical oxidation formation—humans, photochemical oxidation formation potential (ecosystems), terrestrial acidification, freshwater eutrophication, marine eutrophication potential, human toxicity potential (cancer), human toxicity potential (non-cancer), fossil fuel potential, and water consumption potential	This study used different biomass sources to produce bio-oil, including almond shells, pistachio shells, olive stone, olive pomace, olive branch, and olive leaf Global warming potential = $-0.070$ to $0.616$ kg CO <sub>2</sub> equivalent/MJ of bio-oil produced	Alcazar-Ruiz et al. (2022)
Net energy ratio	The net energy ratio for the biorefinery that combined fast pyrolysis with transesterification for producing 1 MJ of bio-oil was 2.1.17 Other environmental impacts were shown as only relative % rather than the values and are not summarized here	Battle et al. (2020)
Abiotic depletion (elements), abiotic depletion (fossil fuels), global warming, ozone layer, acidification, eutrophication	This study focused on the post-processing of bio-oil and biochar produced during pyrolysis. It considered the co-processing of bio-oil (from the pyrolysis of lignocellulosic biomass) in fluid catalytic cracking and hydrocracking units and the co-gasification of pyrolysis char (coproduced with bio-oil) with coke Abiotic depletion of fossil fuels = 1.09 to 1.16 MJ/MJ of bioenergy produced Global warming potential = $1.16 \times 10^{-2}$ to $1.42 \times 10^{-2}$ kg CO <sub>2</sub> equivalent/MJ of bioenergy produced	Cruz et al. (2020)
Cumulative energy demand, global warming potential, human toxicity (carcinogens), human toxicity (non-carcinogens), ozone layer depletion, particulate matter formation, ionizing radiation, acidification, photochemical oxidant formation, terrestrial eutrophication, marine and freshwater eutrophication, ecotoxicity, and abiotic depletion	The study compared the slow pyrolysis processing of olive tree prunings, olive pomace, lemon peel, and orange peel to produce biochar that could generate 1 MJ of thermal energy (functional unit) after combustion based on the ILCD 2011 midpoint method. The study highlights that the biomass type affects the pyrolysis process's environmental impacts under the examined conditions more than the peak pyrolysis temperature Cumulative energy demand = 80.5 to 108.0 MJ Global warming potential = 4.73 to 6.32 kg CO <sub>2</sub> equivalent Ozone layer depletion potential = $6.75 \times 10^{-7}$ to $8.98 \times 10^{-7}$ kg CFC-11 equivalent	Cusenza et al. (2021)
Acidification, ecotoxicity, eutrophication, global warming, carcinogenic, non-carcinogenic, ozone depletion, ozone formation, resource depletion, respiratory effects	Acidification potential = 0.003 to 0.005 mol H <sup>+</sup> equivalent This study focused on the use of guayule bagasse for the production of bioenergy. The environmental impacts of the production of 1 MJ of bioenergy were quantified as follows: Acidification potential = $1.24 \times 10^{-3}$ kg SO <sub>2</sub> equivalent Global warming potential = $3.12 \times 10^{-2}$ kg CO <sub>2</sub> equivalent Ozone layer depletion potential = $2.17 \times 10^{-8}$ kg trichlorofluoromethane equivalent	Moreno et al. (2022)

Table 14 (continued)

Environmental impacts considered	Findings	Reference
Climate change, freshwater, and terrestrial acidification, marine eutrophication, freshwater eutrophication, terrestrial eutrophication, ionizing radiation, ozone layer depletion, photochemical ozone creation, respiratory effects, fossils, land use, minerals and metals	<p>This study investigated wood waste pyrolysis products, i.e., heat for the district and biochar for soil remediation. The study concluded that biochar-based remediation is more environmentally friendly but energy-consuming than the conventional 'dig and dump' technique. By using a functional unit for 1 year of the operation of a pyrolysis plant with feedstock as 800 kg/hour dry wood, environmental impacts were recorded as</p> <p>Climate change potential for conventional remediation = 1.01 kilotons CO<sub>2</sub> equivalent</p> <p>Climate change potential for on-site biochar remediation = - a 2.31 kilotons CO<sub>2</sub> equivalent</p> <p>Fossils for conventional remediation = 17.5 TJ</p> <p>Fossils for on-site biochar remediation = 26.1 TJ</p> <p>Freshwater and terrestrial acidification potential for conventional remediation = 25,300 mol H<sup>+</sup> equivalent</p> <p>Freshwater and terrestrial acidification potential for on-site biochar remediation = 5960 mol H<sup>+</sup> equivalent</p>	Papageorgiou et al. (2021)
Fossil fuel depletion, particulate matter formation, photochemical oxidation, climate change, ozone depletion, human toxicity, terrestrial acidification, marine eutrophication, freshwater eutrophication	<p>The study analyzed using olive pomace and grape marc for the production of biochar as soil amendment material and bio-oil via pyrolysis at 500 °C</p>	Ramos and Ferreira (2022)
Greenhouse gas emissions	<p>In this study, the life-cycle study model compares a 100 million liters-per-year enhanced pyrolysis oil factory employing British Columbia pellet and forest residual feedstocks at three locations in British Columbia, Canada. The greenhouse gas emissions were 69 to 71% lower than the conventional fossil jet fuels, depending on the region, and woody biomass feedstock pyrolyzed</p>	Ringsred et al. (2021)
Human health (carcinogens), human health (respiratory organics and inorganics), climate change, radiation, ozone layer, ecotoxicity, acidification, eutrophication, land use, minerals, and fossil fuels	<p>The study used four different feedstocks for producing biochar and bio-oil: (i) raw sugarcane bagasse, (ii) raw sugarcane trash and acid-leached, (iii) sugarcane bagasse, and (iv) sugarcane trash. The study analyzed environmental impacts as eco-points and concluded that sugarcane bagasse showed 0.75 eco-points for the fossil fuels category</p>	Rodríguez-Machin et al. (2021)
Global warming potential	<p>The global warming potential was observed as 282 kg CO<sub>2</sub> equivalent/metric ton of furfural produced via pyrolysis using sugarcane beet pulp as feedstock</p>	Thompson et al. (2021)
Global warming potential, ozone depletion, acidification, eutrophication, ecotoxicity, resource depletion, human health (carcinogenic), Human health (non-carcinogenic), photochemical ozone formation, respiratory effects	<p>This study observed that the global warming potential of bio-based levoglucosan was 2 times lower than that of traditional ones. For the production of 1 kg of levoglucosan using cotton straw biomass, environmental impacts were recorded as:</p> <p>Global warming potential = 4.57 kg CO<sub>2</sub> equivalent</p> <p>Resource depletion = 5.52 MJ surplus</p> <p>Human toxicity (carcinogens) = 5.76 × 10<sup>-7</sup> cumulative toxicity units</p> <p>Human toxicity (non-carcinogens) = 9.46 × 10<sup>-7</sup> cumulative toxicity units</p>	Wang et al. (2020d)

Table 14 (continued)

Environmental impacts considered	Findings	Reference
Energy consumption, global warming potential	Waste wood and pig manure were used to prepare biochar-modified bio-asphalt Energy consumption for 1 kg of biochar-modified bio-asphalt = 1622.5 MJ when pig manure is used as feedstock	Zhou et al. (2020b)
Net energy ratio, energy output, acidification, eutrophication, ammonia emissions	This study computed the life cycle impacts of using livestock manure and underutilized grass silage for anaerobic digestion followed by pyrolysis. The net energy ratio was observed as 7.3. Furthermore, global warming potential was recorded as - 50 g CO <sub>2</sub> equivalent/MJ of bioenergy produced	Mehta et al. (2022)
Global warming potential	This study presented the findings for the life cycle impacts of industrial biochar production using olive prunings as feedstocks. It demonstrated that per ton of biochar produced and used, 2.68 tons of CO <sub>2</sub> equivalent are permanently removed from the atmosphere	Fawzy et al. (2022)

investigation into the mechanistic pathway of converting biomass to desired byproducts is necessary. Biorefining of pyrolysis products (bio-oil and biochar) can lead to the development of sustainable materials and chemical recovery processes. Furthermore, the inclusion of the potential climate change impacts of biochar in the assessment of the pyrolysis process is crucial for the successful commercialization of the process, as it can result in additional economic benefits and cost-effectiveness.

The economic viability of pyrolytic conversion of biomass to biochar remains a significant challenge, as the literature on this topic is limited and often inconsistent. Factors such as variations in feedstocks and reaction conditions further complicate the analysis of the economic perspective of biomass pyrolysis. Additionally, the economic benefits of biochar are not always quantifiable, particularly in terms of its potential to support the growth of small and medium-sized industries with limited access to energy. For example, using waste as feedstocks for biochar conversion generates additional income through energy production and reduces the cost of waste treatment. To extend the process of commercialization and sustainability, understanding life cycle assessment is essential for mitigating environmental impacts related to biomass pyrolysis.

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## Declarations

**Conflict of interest** The authors have not disclosed any competing interests.

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