



Review article

Breakdown of biomass for energy applications using microwave pyrolysis: A technological review

Scarlett Allende, Graham Brodie, Mohan V. Jacob*

Electronics Material Lab, College of Science and Engineering, James Cook University, Townsville, QLD, 4811, Australia



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ABSTRACT

The agricultural industry faces a permanent increase in waste generation, which is associated with the fast-growing population. Due to the environmental hazards, there is a paramount demand for generating electricity and value-added products from renewable sources. The selection of the conversion method is crucial to develop an eco-friendly, efficient and economically viable energy application. This manuscript investigates the influencing factors that affect the quality and yield of the biochar, bio-oil and biogas during the microwave pyrolysis process, evaluating the biomass nature and diverse combinations of operating conditions. The by-product yield depends on the intrinsic physicochemical properties of biomass. Feedstock with high lignin content is favourable for biochar production, and the breakdown of cellulose and hemicellulose leads to higher syngas formation. Biomass with high volatile matter concentration promotes the generation of bio-oil and biogas. The pyrolysis system's conditions of input power, microwave heating susceptor, vacuum, reaction temperature, and the processing chamber geometry were influence factors for optimising the energy recovery. Increased input power and microwave susceptor addition lead to high heating rates, which were beneficial for biogas production, but the excess pyrolysis temperature induce a reduction of bio-oil yield.

1. Introduction

Fossil fuel dependence, waste management, greenhouse emissions, and the disposal of several types of waste generated by individuals and industries are crucial issues in the electrical energy sector (Ferrari et al., 2022; Yu et al., 2022b). The conversion of waste into energy is of significant interest because it represents a sustainable and environmentally friendly way of managing waste and also, recovering the energy and thereby contributing to the circular economy (Ferrari et al., 2022; Yu et al., 2022b; Zhao et al., 2022). Renewable energy development is vital to decrease greenhouse gas emissions and increase the reliability of the energy system and energy supply (Sun et al., 2022). Microwave pyrolysis is an attractive method of bioenergy production that allows the replacement of fossil fuels in favour of clean energy applications, like fuel production (biodiesel), heat, electricity, chemicals and other commodities from biowaste materials (Siddique et al., 2022; Sun et al., 2022). Lignocellulosic biomass used in bioenergy production is diverse (Yu et al., 2022b). These include agricultural waste, energy crops, forestry products, urban waste and industrial residue (Cai et al., 2021b; Duarah et al., 2022). Thus, bioenergy offers abundant feedstock to

produce liquid, gas and solid fuels. Unlike other types of renewable energy, the bioenergy source supply is continuous (biomass) and hence is not affected by the intermittency of resources such as solar and wind energy (Li et al., 2022a; Liu et al., 2022).

Biomass waste can be converted into biofuels by two conversion processes, which are thermochemical and biochemical. These bioenergy methods have substantial dissimilarities associated with biomass feedstock, by-products and applications (Shahbeig and Nosrati, 2020; Varjani et al., 2022). Combustion, gasification, and conventional or microwave pyrolysis are thermochemical conversion methods (Karpagam et al., 2021; Von Cossel et al., 2021). Biochemical conversion involves anaerobic digestion and microbial fermentation (García-Depraect et al., 2022; Karpagam et al., 2021). A biochemical process requires biomass pretreatment and is selective (microbes, enzymes and chemicals). However, thermochemical conversion is possible for practically any type of biomass without pretreatment (García-Depraect et al., 2022; Karpagam et al., 2021; Zhao et al., 2022). The thermochemical process has less reaction time and higher productivity than the biochemical technique due to its limited by-products (biological conversion) and long reaction rate (Sun et al., 2022; Yu et al., 2022b). Fig. 1 shows different energy conversion methods, where combustion conversion

* Corresponding author.

E-mail address: Mohan.Jacob@jcu.edu.au (M.V. Jacob).

Nomenclature

Abbreviations:

Dielectric constant (ϵ_r')	permeability of free space (ϵ_0)
dielectric constant of the material (ϵ')	dielectric loss factor of the material (κ'')
dielectric constant of free space (ϵ_0)	surface reflection coefficient of the material (τ)
dielectric loss factor (ϵ_r'')	strength of the electromagnetic field at the surface of the material (E_0 , V/m)
dielectric loss of the material (ϵ'')	wave attenuation factor (β)
conductivity of the material (σ)	convective heat transfer coefficient at the surface of an object (h , W/m K)
microwave frequency (f)	Rayleigh number (Ra_i)
electric loss tangents ($\tan \delta\epsilon$)	Prandtl number (Pr)
magnetic loss tangents ($\tan \delta m$)	thermal conductivity of the fluid (k , W/m °C)
heat generation per unit volume (Q_g)	length of the object being heated (L , metres)
heating rate of the material (HR)	initial temperature of the material (T_i , °C)
electric field (E)	distance from the surface into the core of the material (x , meters)
magnetic field (H)	thermal conductivity of the heated material (k_s , W/m °C)
thermal conductivity (ρ_t);	thermal diffusivity of the heated material (α_s , m ² /s)
specific heat (C_p)	heating time (t , seconds)
angular frequency of the microwave field (ω , rad/s)	speed of light (c , m/s)
	relative dielectric constant of the material (k')

implies the burning of biomass in the presence of oxygen, intending to generate heat and power.

Anaerobic digestion implicates microbial decomposition of organic biomass in an oxygen-free environment by applying an optimal temperature for the microorganism activity (Dhanya et al., 2020; Liu et al., 2022; Zhu et al., 2021). The product obtained from the conversion process is mainly biogas (methane, carbon dioxide, water vapour and lesser concentration of hydrogen sulphide and hydrogen) (Dhanya et al., 2020; Yu et al., 2022b). Fermentation is also a biochemical conversion process in the absence of oxygen, in which organic biomass is broken-down by the action of enzymes (Pishvae et al., 2021; Yu et al., 2022b). Biomass decomposition by fermentation involves a long process time, where the first step is sucrose conversion into fructose and glucose by hydrolysis enzymes (Ghosh et al., 2020; Yu et al., 2022b). Products obtained from the conversion process are alcohol fuels, such as ethanol and lactic acid (Gautam et al., 2019; Pishvae et al., 2021).

The gasification method involves a high-temperature process that allows converting organic biomass into mainly syngas generation in a controlled oxygen environment for energy applications (Yu et al., 2022b; Zhang et al., 2019). Conventional pyrolysis involves a convective heating method that occurs in the absence of an oxidizing agent, where the heating is transferred into the biomass through internal conduction from the surface of the biomass (Li et al., 2022d). The pyrolysis range temperature is between 400 °C and 1200 °C (Rajendran et al., 2019). Conventional heating is conducted using a batch furnace, auger reaction chamber or fixed bed reactor. In contrast, microwave pyrolysis technology is achieved by the thermal decomposition of biomass exposed to electromagnetic heating in the absence of oxygen (Hadiya et al., 2022; Wang et al., 2020). The heating method is material-dependent (feed-stock dielectric properties), in which microwave energy is transferred by the microwave susceptors (biochar or activated carbon) that absorb the microwave radiation and starts to burn the biomass (Prathiba et al.,

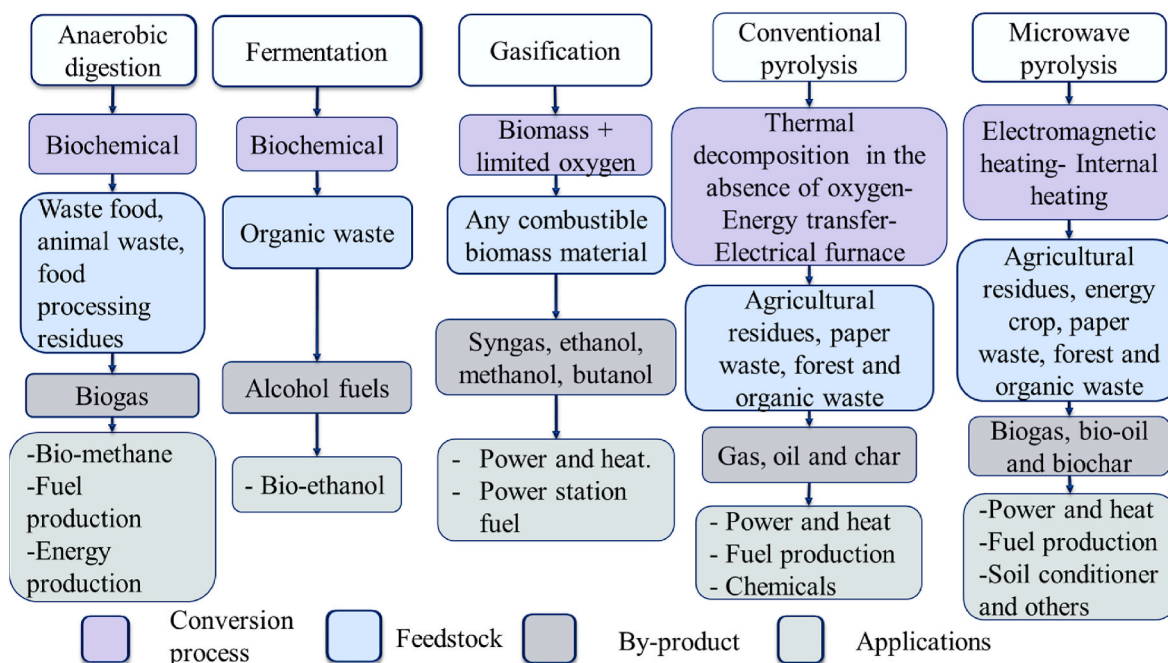


Fig. 1. Biomass conversion process by bioenergy technology (Anca-Couce et al., 2021; Fodah et al., 2022; Hasan et al., 2021; Liu et al., 2022; Sun et al., 2022).

2018; Toscano Miranda et al., 2021). There are beneficial factors associated with the conversion process compared to conventional pyrolysis. For example, microwave heating provides quick start-up, higher heating rates and an efficient heating distribution (Li et al., 2022d; Toscano Miranda et al., 2021; Zhang et al., 2022b). The microwave pyrolysis method is a promising alternative to energy generation due to its high heating efficiency, which can lead to higher yield and quality of the by-products, contributing to increased energy recovery efficiency of the conversion process (Hadiya et al., 2022; Li et al., 2022d; Zhang et al., 2022b). Consequently, the type of conversion method depends on the nature of the biomass, energy applications (the kind of energy obtained), economic factors, environmental standards, operating conditions of the conversion system, and others (Shahbeig and Nosrati, 2020; Toscano Miranda et al., 2021; Varjani et al., 2022).

2. Microwave pyrolysis technology

The pyrolysis concept comprises the thermal degradation of the raw waste in inert atmospheric conditions (absence of oxygen) to obtain gas, liquid and solid products (Foong et al., 2020; Ge et al., 2021; Rajendran et al., 2021). Microwave pyrolysis technology can include three stages. The first stage involves the evaporation of free moisture existing in the biomass. The second phase comprises dehydration, demethylation, and decarboxylation reactions, which are related to the depolymerization and fragmentation process of lignocellulosic compounds. The final stage is secondary reactions associated with repolymerization and recondensation (Foong et al., 2020; Ge et al., 2021).

The pyrolysis process has three relevant factors associated with the pyrolysis operating settings and biomass conditions that depend on the residence time, heating rate, temperature and particle size. The particle size of the sample impacts the intensity and distribution of the microwave irradiation, affecting the uniformity of the dielectric heating on the biomass. Small particle size is favourable to increasing the gaseous phase products (Li et al., 2022c; Suresh et al., 2021). The slow pyrolysis process applies a low operating temperature and long solid residence time (between 5 and 30 min) (Ethaib et al., 2020; Robinson et al., 2015; Suresh et al., 2021; Yaning Zhang et al., 2017; Zhang et al., 2017a). These conditions produce limited bio-oil quality. Alternatively, fast pyrolysis is commonly used for liquid fuel production due to the high heating rate and low solid residence time (Tomczyk et al., 2020; Yaning Zhang et al., 2017). Furthermore, flash technology produces lower thermal stability and oil corrosiveness because of the short residence time and elevated heating rate and temperature (Suresh et al., 2021; Yaning Zhang et al., 2017). The detail of the operating ranges is shown in Table 1.

Diverse studies reported the use of microwave pyrolysis for processing multiple types of waste materials. The configuration of the microwave system depends on biomass conversion, by-product target and energy application. Some work reveals the use of plastic and triglycerides as feedstock for maximising bio-oil production, considering a series of columns and condensers (Wan Mahari et al., 2022). Other research established the conversion of food waste into activated biochar by using microwave heating and CO₂ activation (Yek et al., 2020).

Table 1
Operating parameters by pyrolysis process (Ethaib et al., 2020; Foong et al., 2020; Hasan et al., 2021; Kung et al., 2022).

Pyrolysis classification	Residence time (s)	Heating rate (°K/s)	Particle size (mm)	Temperature (°K)
Slow	450–550	0.1–1	5–50	550–950
Fast	0.5–10	10–200	<1	850–1250
Flash	<0.5	>1000	<0.2	1050–1300

2.1. Microwave pyrolysis principles

Microwave heating is a form of electromagnetic heating, involving the interaction of electromagnetic waves with ionic and dipolar molecules (Ge et al., 2021; Siddique et al., 2022; Yu et al., 2022a). Therefore, the heat is generated within the material rather than external to the heated object, which is the opposite of conventional heating. Commercial microwave systems commonly operate at frequencies of 915 MHz and 2.45 GHz (Lam and Chase, 2012). Nevertheless, microwave heating requires an external microwave energy source to transfer energy to the content through a surface (Ethaib et al., 2020; Ge et al., 2021; Hadiya et al., 2022).

Microwaves have a wavelength range between 10⁻³ and 1 m and photon energy between 1.2 μeV and 1.2 meV. Microwaves are electromagnetic waves with perpendicular electric and magnetic fields, considering a frequency from 300 MHz to 300 GHz (Bartoli et al., 2019; Zamorano Ulloa et al., 2019). Microwave heating comprises two types of interactions between the material and the radiation. The most common interaction involves ion and dipole displacement by the wave's electric field; however, in some ferric materials, the wave magnetic field can interact with magnetic domains or induce eddy currents in the material. The most common interaction is with the electric field (Ge et al., 2021; Hadiya et al., 2022).

To fully understand the behaviour of feedstock material under microwave pyrolysis is crucial to study the volumetric absorption of electromagnetic energy in the heated material. The dissipated power in the feedstock reveals the main difference between conventional and microwave pyrolysis, which is to determine the heating profile (electromagnetic penetration depth) of the feedstock. Equations 1, 2, 3 and 4 (Bartoli et al., 2019) explain the interaction of electric and magnetic fields. Specifically, the relative dielectric constant (ϵ'_r) associated with the dielectric constant of the material (ϵ') and the dielectric constant of free space (ϵ_0). The dielectric loss factor (ϵ''_r) is linked to the dielectric loss of the material (ϵ''), the conductivity of the material (σ), and the microwave frequency (f). The relative magnetic permittivity (μ'_r) is the ratio of the magnetic permeability properties of the material (μ') and the magnetic permeability of the void (μ_0). The magnetic loss (μ''_r) comprises additional factors like the magnetic loss of the material (μ'') (Bartoli et al., 2019).

$$\epsilon'_r = \epsilon' / \epsilon_0 \quad (1)$$

$$\epsilon''_r = (\epsilon'' / \epsilon_0) + \left(\frac{\sigma}{2\pi f \epsilon_0} \right) \quad (2)$$

$$\mu'_r = \mu' / \mu_0 \quad (3)$$

$$\mu''_r = (\mu'' + \mu_0) + \left(\frac{\sigma}{2\pi f \mu_0} \right) \quad (4)$$

Equations 5 (Bartoli et al., 2019) and 6 (Bartoli et al., 2019) describe the electric ($\tan \delta_e$) and magnetic loss tangents ($\tan \delta_m$), both of which represent absorption of the electromagnetic energy. Also, Equations 7 (Bartoli et al., 2019) and 8 (Bartoli et al., 2019) describe heat generation per unit volume (Q_g) and the heating rate of the material (HR), respectively, as the absorbed energy is converted to internal kinetic energy (i.e., heat) in the material. The electric field (E) and magnetic field (H), which are the mutually perpendicular fields of electromagnetic radiation, are related. Furthermore, thermal conductivity (ρ_t) and specific heat (C_p) of the material are related to its heating rate calculation.

$$\tan \delta_e = (\epsilon''_r / \epsilon'_r) \quad (5)$$

$$\tan \delta_m = (\mu''_r / \mu'_r) \quad (6)$$

$$Q_g = \pi f \epsilon_0 \epsilon''_r |E|^2 + \pi f \mu_0 \mu''_r |H|^2 \quad (7)$$

$$HR = Q_s / \rho_t C_p \quad (8)$$

Electromagnetic heating depends on volumetric heating conditions. The dissipated microwave power in the material is an influencer of the thermal diffusion in the heated material (Brodie, 2008; Zamorano Ulloa et al., 2019). Equation 9 describes the involved factors in dissipated microwave power (Brodie, 2008). The factors associated with the dissipated power are; the angular frequency of the microwave field (ω , rad/s), the permeability of free space (ϵ_0), the dielectric loss factor of the material (κ''), the surface reflection coefficient of the material (τ), the strength of the electromagnetic field at the surface of the material (E_0 , V/m), and the wave attenuation factor (β) (Brodie, 2008).

$$q = \frac{\omega \epsilon_0 \kappa'' \tau^2 E_0^2}{2} e^{-2\beta x} \quad (9)$$

The heat from the object, which is interacting with the electromagnetic wave, will also be transferred to the surrounding environment by convection. The convective heat transfer coefficient at the surface of an object (h , W/m K) is described by Equation 10 (Tomar, 2019; Welty; et al., 2007). The convective heat transfer calculation involves; the Rayleigh number (Ra_L), Prandtl number (Pr), the thermal conductivity of the fluid (k , W/m °C), and the characteristic length of the object being heated (L , metres) (Welty; et al., 2007).

$$h = \frac{k}{L} \left\{ 0.825 + \frac{0.387 Ra_L^{1/4}}{\left[1 + \left(\frac{0.492}{Pr} \right)^{9/16} \right]^{4/5}} \right\}^2 \quad (10)$$

The temperature generated inside a semi-infinite material or a material that is many times larger than the penetration depth of the wave due to microwave heating can be calculated by Equation 12 (Brodie, 2008). The associated factors are the initial temperature of the material (T_i , °C), distance from the surface into the core of the material (x , metres), the thermal conductivity of the heated material (k_s , W/m °C), thermal diffusivity of the heated material (α_s , m²/s), and heating time (t , seconds). The propagation factor is described in Equation 11 (Brodie, 2008; J. Tang, 2009), which includes the speed of light (c , m/s) and the relative dielectric constant of the material (κ').

$$\beta = \frac{\omega}{c} \sqrt{\frac{\kappa'}{2} \left[\sqrt{1 + \left(\frac{\kappa''}{\kappa'} \right)^2} - 1 \right]} \quad (11)$$

$$T = \frac{\omega \epsilon_0 \kappa'' \tau^2 E_0^2}{8 k_s \beta^2} \left(e^{4\alpha_s \beta^2 t} - 1 \right) \left[e^{-2\beta x} + \left(\frac{h}{k_s} + 2\beta \right) x \bullet e^{-\frac{x^2}{4\alpha_s t}} \right] + T_i \quad (12)$$

2.2. Difference between conventional and microwave pyrolysis

The difference between conventional and microwave pyrolysis lies in the heating method. Microwave heating is produced from internal sources, meaning that the heat is generated within the biomass, while conventional heating is from the external environment (Ethaiab et al., 2020; Li et al., 2022d; Yu et al., 2022a). Fig. 2 illustrates the heating

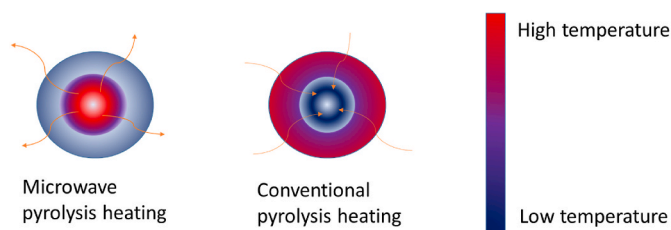


Fig. 2. Comparison between heating mechanisms of microwave and conventional pyrolysis.

mechanism of both technologies. Microwave heating transfers energy, through the interaction of the molecules (agitating dipolar molecules) within the biomass, in a much shorter reaction time than conventional heating (Yu et al., 2022a; Zhang et al., 2022a).

The electromagnetic energy is converted into heat by applying diverse microwave susceptors that absorb the microwave radiation and heat the biomass (Li et al., 2022d; Siddique et al., 2022). Another reason for adding microwave susceptor into the biomass is due to the low dielectric characteristics of the biomass feedstock (i.e., the dry biomass is relatively transparent to microwave radiation), which does not produce a heating effect by itself. Carbon material or water, which has much higher dielectric loss than dry biomass, can be added to the biomass to transform the microwave energy into heat (Ethaiab et al., 2020; Li et al., 2022d; Nhuchhen et al., 2018; Siddique et al., 2022).

The advantages of microwave pyrolysis consist of the transfer of heat energy within the bulk of the material instead of heat transfer from outside to inside and the wide range of biomass materials that can be used (i.e., versatility in biomass processing) (Czajczyńska et al., 2017; Shukla et al., 2019; Yaning Zhang et al., 2017). For example, feedstocks can include agricultural biomass, plastics, tyre residues, and any other type of municipal solid waste. The precise and controlled heating method leads to the rapid and efficient start-up of the microwave system (Hadiya et al., 2022; Wu et al., 2022; Zhang et al., 2020). Microwave pyrolysis has instantaneous volumetric heating and uniform distribution in the energetic coupling. Subsequently, the microwave mechanism provides efficiency in the heating process, saving time, providing better heating distribution and controlling overheating (Hadiya et al., 2022; Siddique et al., 2022; Wu et al., 2022). Fig. 3 shows a comparison of the pyrolysis technologies.

Microwave pyrolysis consists of dielectric heating, in which the absorption of microwave irradiation produces the migration and rotation of ionic and dipolar species, respectively. Then, the mixture of a microwave susceptor with a high dielectric loss factor into the biomass allows for improved heating rates and pyrolysis temperatures (Ellison et al., 2017; Hadiya et al., 2022; Nhuchhen et al., 2018; Yaning Zhang et al., 2017). Table 2 shows the dielectric properties of different microwave susceptors. Carbonaceous materials, like carbon, graphite and SiC, are the most common microwave susceptor used (Ellison et al., 2017; Zhang et al., 2020). The ratio of the microwave susceptor to raw feed stock is a relevant factor in terms of by-product yield. For instance, bio-oil production can increase by adding a higher microwave susceptor ratio. But at the later stage of pyrolysis, rapid excess temperature leads to secondary reactions of the liquid products to form permanent gaseous products (Nhuchhen et al., 2018; Yaning Zhang et al., 2017).

3. Biomass feedstock classification

Cellulose, hemicellulose and lignin are the three main components of biomass. The common term used to identify these three constituents is lignocellulosic (S.Bharathiraja et al., 2017). Cellulose has a crystalline structure and a molecular formula of (C₆H₁₂O₆)_n and exhibits exceptional resistance to acids and alkalis, but hemicellulose and lignin are amorphous (Fermanelli et al., 2020). The lignin component comprises units of phenylpropane and its derivatives, which are bonded 3-dimensionally (Tawaf Ali et al., 2022). The hemicellulose interaction in the biomass is covalently bonded (ester bond) (Fermanelli et al., 2020). In the microwave pyrolysis process, the fibre constituents have different thermochemical stability. For instance, hemicellulose breakdown is faster (from 200 °C to 300 °C) than cellulose (from 300 °C to 400 °C). Nevertheless, lignin is the most heat-resistant due to its gradual decomposition (from 200 °C to 500 °C) (Fermanelli et al., 2020; Ge et al., 2021). In microwave pyrolysis, the thermochemical stability can also depend on the microwave power levels. For example, low power will produce a minor thermal degradation of the lignin component, obtaining biochar with a high heating value (Huang et al., 2016b; Tomczyk et al., 2020).

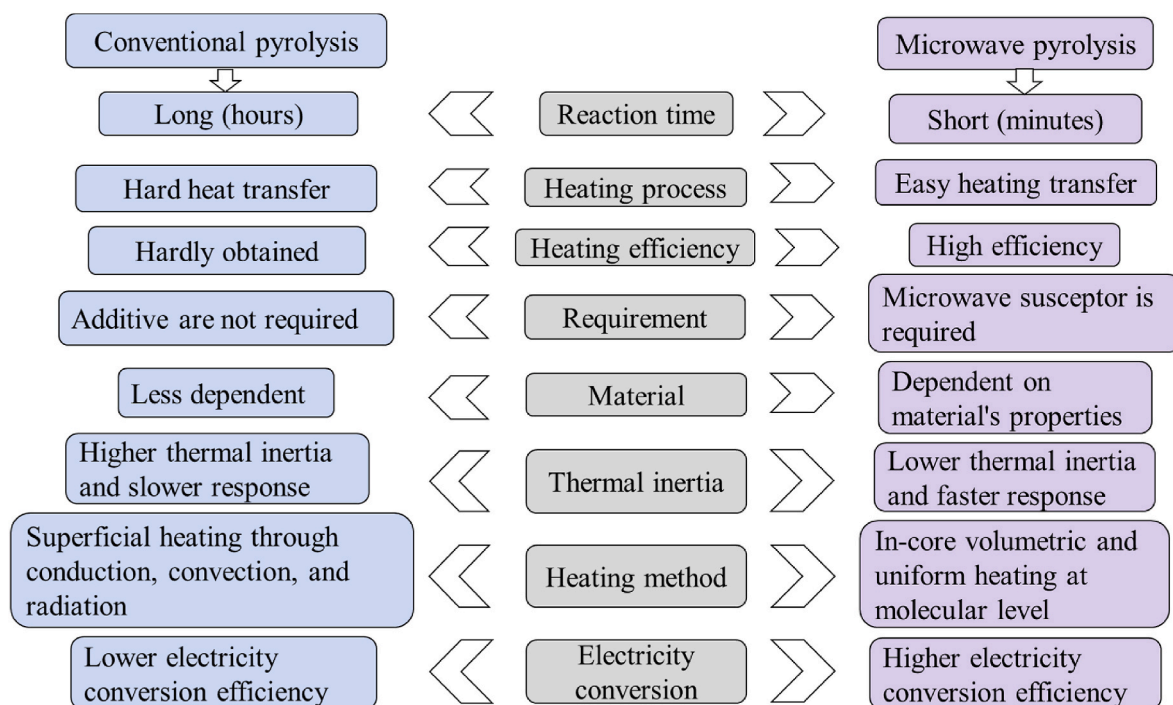


Fig. 3. Difference between conventional and microwave pyrolysis technologies (Siddique et al., 2022; Toscano Miranda et al., 2021; Yanning Zhang et al., 2017; Zi et al., 2019).

Table 2

Dielectric loss tangent of diverse microwave susceptor materials (Ellison et al., 2017; Yanning Zhang et al., 2017; Zhang et al., 2017a; Zhang et al., 2020).

Material	tanδ
Water	0.15
SiC	0.37–1.05
Activated carbon	0.07–0.9
Biochar	0.2–1.04
Graphite	0.03–0.17
Carbon	0.28–0.38
Glycerol-water	0.3
Ethylene glycol	1

Biomass fibre composition varies depending on its nature. The biomass components like lignin, cellulose, and hemicellulose are directly related to the pyrolysis by-product yield (Lin et al., 2015). For example, lignin and hemicellulose influence the cellulose characteristics during the pyrolysis conversion process but not vice versa. Mostly, bio-oil is obtained from the cellulose component, while biochar is derived from lignin (Burhenne et al., 2013; Lin et al., 2015; Tomczyk et al., 2020). Furthermore, lignin content has a significant impact on the carbonization and biochar properties due to its increased carbon and ash content (Tomczyk et al., 2020).

The heating value of biochar is susceptible to the thermal decomposition of lignocellulosic compounds. The heating value of cellulose and hemicellulose is lower than lignin. Therefore, the gradual thermal breakdown of the lignin compound is beneficial for increasing the heating value of biochar (Chen et al., 2021; Ge et al., 2021; Li et al., 2016). Subjecting biomass with high lignin to pyrolysis technologies can improve bio-oil quality (heating value) due to the high heating value of the lignin compound and its steady thermal decomposition. However, there is an increase in its molecular weight and viscosity (Ge et al., 2021; Kan et al., 2016). Table 3 shows a compilation of the fibre composition of different biomass feedstocks. Cotton and banana peel has the highest cellulose (82.7%) and hemicellulose content (48.2%). The cellulose

Table 3

Fibre composition ranges of diverse lignocellulosic biomass.

	Lignin (%)	Cellulose (%)	Hemicellulose (%)	Reference
Olive husk	48.4	24	23.6	Jahirul et al. (2012)
Tea waste	40	30.2	19.9	Jahirul et al. (2012)
Walnut shell	52.3	25.6	22.7	Jahirul et al. (2012)
Almond shell	20.4	50.7	28.9	Jahirul et al. (2012)
Sunflower shell	17	48.4	34.6	Jahirul et al. (2012)
Nutshell	35	27.5	27.5	Jahirul et al. (2012)
Sugarcane	24.353	55.6	23.9	Jayaprakash et al. (2022)
Pineapple leaf	5.35	70.55	18.73	Jayaprakash et al. (2022)
Banana peel	5.55	60.25	48.2	Jayaprakash et al. (2022)
Corn cob	21	28	39	Nozieana et al. (2021)
Rice husk	23	44	19	Senthilkumar et al. (2021)
Coconut	41.23	36.62	0.15	Dungani et al. (2015)
Rice straw	12.65	28.42	23.22	Dungani et al. (2015)
Oil palm	19	65	–	Hao et al. (2018)
Cotton	–	82.7	5.7	Hao et al. (2018)
Kenaf	21.2	53.4	33.9	Hao et al. (2018)
Bamboo	11.9	53.1	35	Shi et al. (2020)
Gumwood	14.4	62.4	23.2	Shi et al. (2020)
Pine	11.2	59.1	29.7	Shi et al. (2020)
Rosewood	24.1	62.9	13	Shi et al. (2020)

percentage suggests that paper is a suitable feedstock to produce a high bio-oil yield. In contrast, walnut shells have 52.3% lignin, which has the potential to generate a higher biochar yield.

3.1. Biomass raw material properties

Usually, raw biomass needs preparation to be used in pyrolysis technology. The mechanical (physical) pre-analysis of the biomass includes moisture content and particle size (Bu et al., 2016; Yaning Zhang et al., 2017). This latter variable involves cutting and grinding the feedstock until the required particle size is obtained; for example, for sugarcane bagasse, the required size of between 0.12 and 0.5 mm (Lin and Chen, 2015). The calculation of the water content biomass is another influencer factor on the yield and quality of the by-products (Ethaiab et al., 2020; Ge et al., 2021; Li et al., 2022c). The following points explain the physicochemical parameters of the biomass.

4. Content of moisture and ash on the biomass

Moisture content is a vital property of biomass, upon which its heating value depends. The standard method for determining moisture involves heating a 1 gm biomass sample in a hot air oven at 110 °C. The moisture content of the biomass can be calculated using Equation 13 (Basu, 2010).

$$\text{Moisture content (\% M)} = \frac{w1 - w2}{w3} * 100 \quad (13)$$

w1 : Weight of the crucible & the air – dried sample (g)

w2 : Weight of the crucible & oven dried sample (g)

w3 : Weight of the air – dried sample (g)

Once the moisture content is obtained, the ash percentage can be estimated by heating the oven-dried product at 575 °C until it attains constant weight (usually over 180 min). This value is the amount of inorganic material in the sample (Sluiter et al., 2008). In most cases, the weight of the residue represents the ash content of the biomass (Basu, 2010; Sluiter et al., 2008):

$$\text{Ash content (wt\%A)} = \frac{\text{Ash mass}}{\text{Initial mass}} * 100 \quad (14)$$

5. Volatile matter, fixed carbon, and high heating value

The following experimental step is to calculate the volatile matter, obtained by the difference between the dried sample exposed at 600 °C and 900 °C for 6 min at each temperature (Basu, 2010, 2013). Equation (15) represents weight loss due to heating:

$$\text{VM (wt\%)} = \left[\frac{\text{moisture mass} - \text{volatile mass}}{\text{initial mass}} \right] * 100 \quad (15)$$

Fixed carbon involves the non-volatile part of carbon content present in the biomass. Carbon content is estimated by the difference between the total biomass weight and the volatile matter, ash, and moisture content of the biomass (Basu, 2010):

$$\text{FC (wt\%)} = 100 - (\% A + \% \text{VM} + \% M) \quad (16)$$

The high heating value (HHV) of the raw biomass is calculated based on the elemental content, such as carbon (C), hydrogen (H), and oxygen (O*). The O* value includes the rest of the elements, such as sulphur and nitrogen. The HHV represents the heat released at the end of the combustion process when water vapour is condensed (Sheng and Azevedo, 2005). Moreover, the low heating value (LHV) implies the formation of gaseous water during combustion (elimination of condensation heat of water) (Özyüğüran et al., 2018). Equations 17 (Sheng and Azevedo, 2005) and 18 (Özyüğüran et al., 2018) estimate the HHV (with more than 90% predictions) and LHV.

$$\text{HHV} \left(\frac{\text{MJ}}{\text{kg}} \right) = -1.3675 + 0.3137 * C + 0.7009 * H + 0.0318 * O^* \quad (17)$$

$$\text{LHV} \left(\frac{\text{MJ}}{\text{kg}} \right) = \text{HHV} - \left[\frac{18.015 * H}{2} + \% \text{Moisture} \right] * 5.85 \quad (18)$$

5.1. Physical and chemical classification of the biomass

The physical and chemical behaviour of the biomass feedstock depends on the previously discussed variables, such as fibre composition, volatile matter, the content of ash and moisture, etcetera (Ge et al., 2021; Li et al., 2022c). Notably, it is possible to get a higher biochar yield in a pyrolysis process when the biomass composition is high in lignin content due to the increased heating value, reaction temperature, and pollutants associated with the lignin presence (Ge et al., 2021; Su et al., 2022a). At the same time, influencing factors linked to the residue conditions can affect biomass product yield. These include density (kg/m³), volatile matter (%), moisture, and ash content (%). For example, high fixed carbon represents a higher biochar yield with a minor portion of hydrogen, oxygen, nitrogen, and sulphur after subtracting the volatile matter, moisture and ash content in the biochar residue (Chen et al., 2015; K. Sarkar, 2015). Similarly, the volatile matter content is a vital parameter for combustion processes, producing high quantities of bio-oil and syngas during pyrolysis (Jahirul et al., 2012; Mierzwa-Hersztek et al., 2019)— the details are described in Fig. 4.

The yield and quality of the by-products are significantly affected by the moisture content of the raw biomass because of the presence of organic compounds. The water content in biomass exists in three forms; water vapour, bound water and a free liquid state (Li et al., 2022c; Tomczyk et al., 2020; Yaning Zhang et al., 2017). Biomass with a high moisture presence decreases the biochar formation but increases the bio-oil yield. Low water content is the optimal condition in biochar production, thereby heat energy and treatment time required during the pyrolysis process is less (Li et al., 2022c; Tomczyk et al., 2020; Tripathi et al., 2016). High moisture in biomass produces a bio-oil with a higher aqueous fraction, lower viscosity and heating value (Ethaiab et al., 2020; Yaning Zhang et al., 2017). On the other hand, since the water has high dielectric properties (high loss tangent factor, tanδ), dry lignocellulosic biomass requires a high percentage of microwave susceptor addition to absorbing the microwave energy due to its low electromagnetic absorbing properties (Supramono et al., 2015; Wu et al., 2019; Yaning Zhang et al., 2017; Zhang et al., 2017a).

The moisture in bio-oil comes from two sources; i) water in the biomass or ii) dehydration reactions generated during the microwave pyrolysis process. The water content of the bio-oil impacts the quality and yield of the bio-oil (Zhang et al., 2017b). High moisture content influences the heat transfer distribution during the conversion process. Moreover, water produces large quantities of condensate water in the liquid phase, generating a higher bio-oil yield, reducing its viscosity, and improving its combustion properties (Jahirul et al., 2012; Nomanbhay et al., 2017; Zhang et al., 2017b). Nonetheless, the high water content in bio-oil contributes to lower heating value, causing ignition delay and reducing combustion rate (Ethaiab et al., 2020; Zhang et al., 2017b).

The raw biomass particle size will influence the yield of by-products using microwave-assisted pyrolysis; for example, a small size implies higher biogas and bio-oil generation. Conversely, larger particle sizes will contribute to higher biochar yield (Leng et al., 2021; Zaman et al., 2018). The main reason for this parameter is that the particle size determines the effect on the reaction time and temperature of the biomass. Small particles are conducive to shifting the pyrolysis process to a lower temperature, generating a quick thermochemical conversion (Leng et al., 2021; Li et al., 2022c). Analogously, the size of the particle is directly related to the liquid yield; the larger the biomass particle, the lower the bio-oil production due to the incomplete decomposition of the kerogen (Nizamuddin et al., 2018).

Fig. 5 displays a collection of different investigations associated with the physical ranges of some feedstock components, considering the

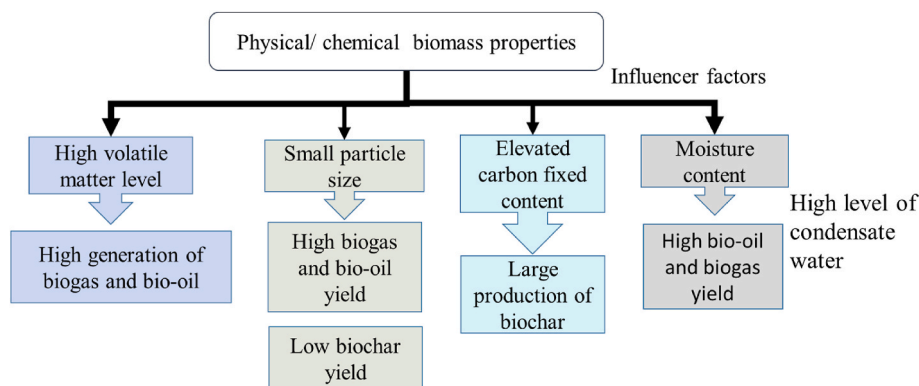


Fig. 4. Factors influencing biomass product yield and generation (Ethaib et al., 2020; Ge et al., 2021; Leng et al., 2021; Su et al., 2022a; Yaning Zhang et al., 2017).

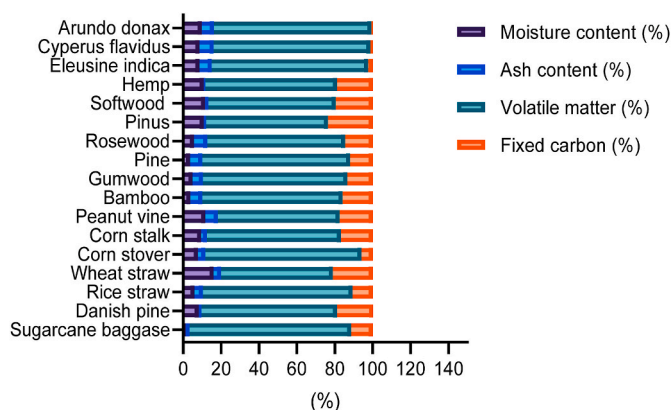


Fig. 5. Biomass feedstock physical analysis (Cong et al., 2018; Huang et al., 2016a; J. Solar et al., 2016; Qu et al., 2011; Shi et al., 2020; Singh, 2019; Wallace et al., 2019).

volatile matter, fixed carbon, moisture, and ash content. Sugarcane bagasse and Arundo donax have high volatile matter content of around 86% and 83%, respectively. Nevertheless, bagasse, bamboo, and pine sources have the lowest moisture levels of between 2% and 4% of the content. Therefore, sugarcane bagasse has considerable potential for producing high-quantity biogas due to its volatile matter content. The high moisture content of wheat straw (16%) and peanut vine (11.58%) promote liquid formation (bio-oil) during microwave pyrolysis with a lower heating value due to the presence of water.

The high calorific value of raw biomass denotes the energy content of the biomass, which is associated with the properties of the feedstock, such as elemental composition and ash content (Lo et al., 2017). Low heating value has been associated with the energy required to vaporise the water generated during fuel combustion. A high heating value considers the heat released in the combustion process, including vapour in the condensed state (Abhijeet et al., 2020). Table 4 shows studies of lignocellulosic feedstock characterisation, including the calorific value and elemental composition. A correlation possibly exists between the elemental composition of the raw biomass and the by-products obtained from microwave-assisted pyrolysis. For example, biochar yield is affected by a significant variation between elementary and average elemental composition. Also, a high hydrogen presence produces higher moisture content. Similarly, the high carbon content of biomass generates more CO₂ production during the thermochemical conversion process (Abhijeet et al., 2020). Ash content represents a vital factor in the energy value of the biomass and by-products due to obstruction of the heat released during the burning of the biomass, causing a reduction in the fuel properties (Allen and Downie, 2020; Aller et al., 2017; Domingues et al., 2017; Rafiq et al., 2016).

6. Microwave pyrolysis by-products analysis

6.1. By-product yield calculation

After completing the microwave pyrolysis procedure, the by-products can be analysed using the yield calculation of bio-oil, biochar and biogas. These values are defined in Equations 19, 20 and 21, respectively (Chen et al., 2008; Lin and Chen, 2015). Specifically, the yield factor is calculated by the ratio between the by-product weight obtained from the conversion process and the raw biomass weight.

$$\text{Liquid yield (wt\%)} = 100 \frac{\text{weight of condensed liquid}}{\text{weight of raw biomass}} \quad (19)$$

$$\text{Solid yield (wt\%)} = 100 \frac{\text{weight of char residue}}{\text{weight of raw biomass}} \quad (20)$$

$$\text{Gas yield (wt\%)} = 100 - (\text{liquid yield} - \text{solid yield}) \quad (21)$$

$$\text{General yield (wt\%)} = \left(\frac{\text{biochar weight} + \text{oil} + \text{gas}}{\text{biomass weight}} \right) * 100 \quad (22)$$

Alternatively, Equations 23, 24 and 25 show the calculation of by-product yields (Lo et al., 2017). The value establishes the relation between the fibre composition of biomass and product performance. The fibre analysis is crucial for determining comparative ranges between the predicted yields and the experimental data. These factors evaluate the effects of the operating parameters on the yield products.

$$\text{Solid yield (wt\%)} = -0.167H - 0.239C + 0.007L + 34 \quad (23)$$

$$\text{Liquid yield (wt\%)} = 0.185H - 0.076C + 0.272L + 34 \quad (24)$$

$$\text{Gas yield (wt\%)} = -0.018H + 0.315C - 0.280L + 31.9 \quad (25)$$

H: Hemicellulose content, wt%

C: Cellulose content, wt%

L: Lignin content, wt%

6.2. Yield and characterisation of the by-products

6.2.1. By-product yield analysis

The operating conditions of the microwave system have a crucial effect on the biochar, bio-oil, and biogas yield. Some influencing factors are input power, microwave susceptor, vacuum pressure system, heating rates, nitrogen flow, and geometry of the processing chamber (Fang et al., 2021; Nizamuddin et al., 2018; Zhang et al., 2017a). For instance, high reaction temperatures and pyrolysis power produce low biochar yield but high biogas yield. A higher heating rate promotes the rapid formation of volatiles, causing secondary reactions of non-condensable gases and converting condensable vapours into permanent gaseous

Table 4
Heating value and elemental composition of raw lignocellulosic biomass.

Biomass	HHV (MJ/kg)	LHV (MJ/kg)	C (wt %)	H (wt %)	N (wt %)	O (wt %)	Reference
Rice straw	16.16	–	45.76	6.22	0.52	47.50	Lo et al. (2017)
Rice straw	–	12.5	35.22	4.57	0.79	34.92	Qu et al. (2011)
Rice husk	15.91	–	43.98	5.94	0.4	49.68	Lo et al. (2017)
Corn Stover	16.82	–	44.92	5.77	0.98	41	Cong et al. (2018)
Corn Stover	17.06	–	49.38	6.52	0.63	43.47	Lo et al. (2017)
Pineapple peel	–	–	43.37	5.83	1.4	49.4	Allende et al. (2023)
Sugarcane bagasse	16.92	–	48.88	6.71	0.27	44.15	Lo et al. (2017)
Sugarcane bagasse	17.32	13.83	41.93	5.47	0.21	53.39	Allende et al. (2022)
Sugarcane peel	17.03	–	46.47	6.23	0.92	46.38	Lo et al. (2017)
Waste coffee grounds	16.78	–	44.89	6.14	0.35	48.62	Lo et al. (2017)
Bamboo leaves	15.75	–	39.98	5.81	1.12	53.09	Lo et al. (2017)
Bamboo	–	6.9	49.9	6.5	6.0	37.0	Shi et al. (2020)
Bamboo	18.07	–	52	5.1	0.4	42.5	Abhijeet et al. (2020)
Gumwood	–	6.7	48.9	6.5	3.5	0.6	Shi et al. (2020)
Pine	–	5.7	49.7	6.6	2.4	40.6	Shi et al. (2020)
Rosewood	–	6.2	54.9	6.6	0.5	37.4	Shi et al. (2020)
Coffee husk	18.5	–	46.41	6.33	2.66	44.51	Setter et al. (2020)
Woody biomass	15.7	–	57.7	7.2	0.3	34.8	(J.Solar et al., 2016)
Kenaf	17.13	–	48.4	6.0	1.0	48.5	Abhijeet et al. (2020)
Reed canary	18.72	–	49.4	42.7	6.3	1.5	Abhijeet et al. (2020)
Miscanthus	18.06	–	49.2	44.2	6.0	1.0	Abhijeet et al. (2020)
Switchgrass	18.54	–	49.7	6.1	0.7	43.4	Abhijeet et al. (2020)
Cornstalk	–	13.6	39.24	4.92	0.81	42.52	Qu et al. (2011)
Peanut vine	–	12.2	35.07	4.89	1.26	40.62	Qu et al. (2011)

products (Dai et al., 2019; Ge et al., 2021; Nizamuddin et al., 2018; Shi et al., 2020; Su et al., 2022a). A longer reaction time is beneficial for biochar and bio-oil yield. A prolonged thermochemical conversion and low power produce enough temperature to complete the pyrolysis process, reducing the secondary breakdown of organic vapours and increasing the release of volatiles for the formation of liquid components (Siddique et al., 2022; Toscano Miranda et al., 2021; Yaning Zhang et al., 2017).

Fig. 6 shows the comparison of by-product yields between both technologies. In comparison to conventional pyrolysis, biogas yield is higher for microwave. Microwave pyrolysis can reach high heating rates

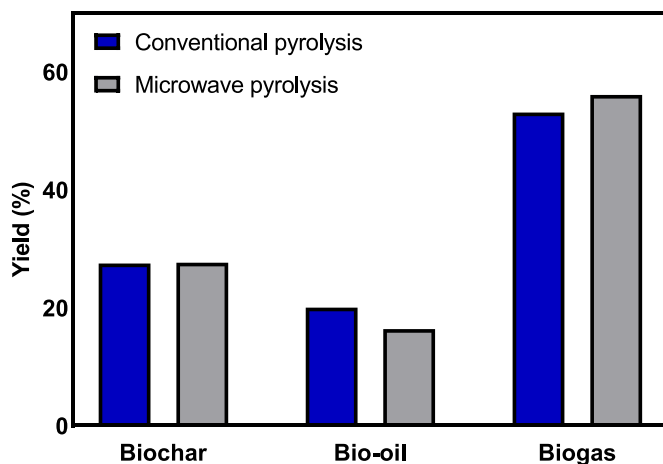


Fig. 6. Comparison of by-product yield between conventional and microwave pyrolysis (Abdelsayed et al., 2019; Dominguez et al., 2007; Ferrera-Lorenzo et al., 2014; Halim and Swithenbank, 2016; K. Shi et al., 2013; Lin and Chen, 2015; Shi et al., 2020; Wu et al., 2014).

faster producing increased biomass devolatilization (promote the biomass molecules interactions), higher breakdown of lignin structure (promote CO formation), favoured the dehydrogenation reactions, and increase the secondary reactions of heavy intermediates and higher biogas fraction (Lin et al., 2022; Liu et al., 2021; Macquarrie et al., 2012; Shi et al., 2020). However, as biogas increased, bio-oil yield decreased (18%) in microwave pyrolysis. This is associated with the secondary reactions of organic non-condensable gases and the devolatilization of biomass generated from the breakdown of intermediate vapours, converting them into syngas compounds (Shi et al., 2020; Yaning Zhang et al., 2017). Biochar yield in microwave pyrolysis is slightly lower than in conventional pyrolysis due to the microwave heating method allowing higher thermal decomposition of the biomass compounds (Gabhane et al., 2020; Zhang et al., 2017a). Furthermore, a microwave reactor can reach a higher carbonization level than conventional pyrolysis, generating a higher graphitic char form (Macquarrie et al., 2012; Shi et al., 2020).

Although the technology and operating conditions are relevant factors in the performance of the by-products, the nature of biomass is also another aspect to consider. The fibre composition of the biomass is influenced by diverse pyrolysis reactions, like depolymerization, dehydration, reformation, and repolymerization (Ansari et al., 2019). The bio-oil and biochar yield is correlated to cellulose and lignin components, respectively. The biomass fibre composition also affects the by-product quality and energy value (Lin et al., 2015; Tomczyk et al., 2020). The devolatilization of cellulose and hemicellulose is favourable for increasing biochar energy value. In contrast, the devolatilization of lignin causes a decreased biochar heating value, but increased biogas (Zhang et al., 2017a). Table 5 presents studies associated with by-product yields obtained in conventional and microwave pyrolysis using different biomass feedstocks and operating conditions. In microwave pyrolysis, the increase in temperature causes a decrease in biochar yield and an increase in biogas formation (Nhuchhen et al., 2018). For instance, the biochar yield generated from coffee hulls biomass decreased by 4%, and biogas increased by 3%. The reason is that increased reaction temperature produces higher devolatilization and decomposition of the biomass, producing a significant mass loss, further volatile release, and gaseous products (Nhuchhen et al., 2018; Shi et al., 2020). However, conventional pyrolysis generated a 33% higher bio-oil yield than microwave pyrolysis using coffee hull biomass. This increased yield fraction is due to the heating method of microwave pyrolysis promoting the conversion of liquid products into non-condensable gases (Jennita Jacqueline et al., 2022; S. Mutsengerere et al., 2019; Toscano

Table 5
By-product yield from conventional and microwave pyrolysis using different biomass.

Biomass	Temp (°C)	Time (min)	Conventional pyrolysis			Microwave pyrolysis			Ref.
			Char wt%	Oil wt%	Gas wt%	Char wt%	Oil wt%	Gas wt%	
Macroalgae	750	60	31	36	34	28	35	37	Ferrera-Lorenzo et al. (2014)
Sugarcane bagasse	550	30	32	53	16	62	22	16	Lin and Chen (2015)
Coffee hulls	800	25	25	12	63	26	9	65	Domínguez et al. (2007)
	1000	25	24	10	67	23	9	69	Domínguez et al. (2007)
Bamboo	600	15	27	12	61	19	8	73	Shi et al. (2020)
Pine	800	15	14	8	77	18	4	79	Shi et al. (2020)
Gumwood	800	15	8	14	78	15	4	81	Shi et al. (2020)
Rosewood	700	15	12	10	78	22	6	72	Shi et al. (2020)
Wood pellets	800	16	23	17	61	22	26	52	Halim and Swithenbank (2016)
Rubberwood	800	16	22	14	70	21	19	60	Halim and Swithenbank (2016)
Wood sawdust	200	18	60	32	9	43	47	10	Wu et al. (2014)
Gumwood	500	30	30	6	65	18	9	73	(K. Shi et al., 2013)
Pinewood + lignite coal	550		50	38	12	43	14	43	Abdelsayed et al. (2019)

Miranda et al., 2021; Yaning Zhang et al., 2017).

6.2.2. Biochar characterisation

The type of pyrolysis technology used influences the yield of biochar. It also influences the elemental composition and surface structure (Li et al., 2022d; Omar and Robinson, 2014; Riva et al., 2021; Sakhiya et al., 2020). For example, microwave pyrolysis produces biochar with a higher heating value than conventional pyrolysis due to the thermal breakdown of biomass compounds with low heating value (cellulose and hemicellulose), whose decomposition is established at the early stages of the pyrolysis reaction. In contrast, the lignin biomass compound has high thermo-resistant properties and a high heating value. Therefore, a gradual thermal decomposition of lignin is beneficial to reaching a high biochar energy value.

Since the heating value is based on the biochar elemental composition, microwave pyrolysis produces a low oxygen range and high carbon and hydrogen content (Fang et al., 2021; Ghesti et al., 2022; Su et al., 2022a; Wu et al., 2022). Some work report that biochar with high carbon content indicates that during biomass pyrolysis was produced the release of volatile matter and the elimination of oxygen-containing groups (Lim et al., 2022). Microwave heating promotes the formation of aromatic compounds and the coalification degree associated with low H/C and low O/C atomic ratio, improving the biochar energy potential (Liu et al., 2021; Raheem et al., 2022). Table 6 shows the comparison of elemental composition and energy value between biochar produced from both pyrolysis technologies.

The surface morphology of biochar generated under the microwave pyrolysis process has higher quality and stability than conventional pyrolysis (Halim and Swithenbank, 2016). Microwave pyrolysis produces biochar with a higher surface area and pore volume, contrary to conventional pyrolysis, which generates biochar with no uniform pores, high cracks, and fissures (Halim and Swithenbank, 2016; M. Waqasa et al., 2018; Shin Ying Foong, 2020). The volumetric heating method of microwave pyrolysis promotes the formation of micropores by the rapid release of volatile matter (volatilization process) leading to clean pore production (Li et al., 2016; Wallace et al., 2019). Table 7 shows an estimation of surface area and pore volume formation generated from

Table 6

Ultimate analysis of biochar generated from conventional and microwave pyrolysis (Brickler et al., 2021; Halim and Swithenbank, 2016; Nzediegwu et al., 2021; Wu et al., 2014).

Element yield (wt%)	Conventional pyrolysis	Microwave pyrolysis
C	~43–87	~36–88
H	~1–6	~0.68–5.76
O	~11–46	~9.75–58
N	~0.3–5	~0.28–3.91
HHV (MJ/kg)	~33–38	~27.1–37.1

Table 7

Comparison of biochar surface area obtained from conventional and microwave pyrolysis (Halim and Swithenbank, 2016; Masek et al., 2013; Mohamed et al., 2016; Nzediegwu et al., 2021).

	Conventional pyrolysis	Microwave pyrolysis
BET Surface Area Analysis (m ² /g)	~0.33–332.96	~1.14–377.56
Pore Volume Analysis (cm ³ /g)	~0.049–1.44	~0.096–2.07

conventional and microwave pyrolysis.

6.2.3. Bio-oil characterisation

Table 8 shows the bio-oil comparison of the ultimate analysis produced from both pyrolysis technologies. Conventional pyrolysis produces a higher bio-oil yield than microwave pyrolysis. However, microwave pyrolysis generates higher bio-oil quality, considering its heating value, elemental analysis, and chemical composition (Halim and Swithenbank, 2016; Huang et al., 2016b; Mohamed et al., 2016; Wu et al., 2014). For instance, bio-oil from microwave pyrolysis has higher carbon but lower oxygen levels. A low oxygen content indicates higher organic functional group decomposition with high oxygen contained. The deoxygenation reactions comprise phenol group reduction, higher stability, and higher heating values (HHV and LHV) (Suriapparao et al., 2020a; Zhao et al., 2021). Moreover, in microwave pyrolysis, the H/C and H/O ratios are slightly higher and lower than in conventional pyrolysis. A low H/C value represents higher aromatic functional groups (Ferrera-Lorenzo et al., 2014; Halim and Swithenbank, 2016). However, exceeding pyrolysis temperatures leads to the breakdown of aromatic groups, generating more aliphatic content (Halim and Swithenbank, 2016; Liu et al., 2021; Nhuchhen et al., 2018).

Bio-oil functional groups are subject to pyrolysis technology and biomass nature. Conventional pyrolysis produces bio-oil with a higher phenol and alkane content, associated with the thermal decomposition of lignin compounds that promotes phenolic group formation

Table 8

Estimation of bio-oil elemental analysis and the heating value obtained from conventional and microwave pyrolysis (Du et al., 2011; Ferrera-Lorenzo et al., 2014; Halim and Swithenbank, 2016; Nhuchhen et al., 2018; Suttibak et al., 2012).

Element yield (wt%)	Conventional pyrolysis	Microwave pyrolysis
C	~45–66	~21–63
H	~6–9	~6–11
O	~13–45	~20–70
N	~0.1–9.5	~0.01–9
H/C	~0.1–0.2	~0.1–0.38
H/O	~0.2–0.6	~0.11–0.32
HHV (MJ/kg)	~21.8–26	~10–28

(Ferrera-Lorenzo et al., 2014; Zhao et al., 2021). In contrast, microwave pyrolysis generates bio-oil with higher aromatic compounds due to higher cracking reactions of phenols leading to benzene conversion (Ghesti et al., 2022; Suriapparao et al., 2020b, 2022; Zhao et al., 2021). Moreover, the increased pyrolysis temperature (over 500 °C) in a shorter reaction time induces the further breakdown of phenols, reducing phenol groups and increasing aromatic hydrocarbons content (Halim and Swithenbank, 2016; Khuenkaeo et al., 2021; Zhao et al., 2021). Alcohol and methylene content increases at elevated pyrolysis temperatures, but alkanes are decreased (Khuenkaeo et al., 2021; Liu et al., 2021).

6.2.4. Biogas characterisation

The principal chemical composition of biogas from microwave pyrolysis is H₂ and CO; however, conventional pyrolysis is predominated by the generation of CH₄ and CO₂. Microwave heating promotes the breakdown of methoxy (lignin form) and biochar self-gasification, causing increased CO and decreased CO₂ generation. The high heating rate reached during the microwave pyrolysis process contributes to large H₂ formation by the dehydrogenation and secondary reactions, which involves converting heavy intermediate compounds (condensable gases) into a permanent gaseous fraction (Lin et al., 2022, 2023; Sahoo and Remya, 2022; Shi et al., 2020; Su et al., 2022a, 2022b).

Table 9 shows the comparison of biogas yield between conventional and microwave pyrolysis techniques. Available data substantiates that conventional pyrolysis can produce 9% higher CO₂ than microwave heating. On the other hand, microwave pyrolysis exhibits a considerable increase in hydrogen (~19–52 vol%) and syngas (~54–81 vol% CO, H₂, CO₂) generation than conventional heating. Increased pyrolysis temperature (600 °C to 900 °C) and prolonged residence time promote the breakdown of bio-oil (secondary reactions) and the volatile release from the biomass, causing more gaseous products (Ferrera-Lorenzo et al., 2014; Halim and Swithenbank, 2016; Liu et al., 2021; Shi et al., 2020). Then, higher syngas production makes microwave pyrolysis a better alternative for improving biogas heating value (Sharma et al., 2020; Su et al., 2022a, 2022b).

7. Comparison and analysis of energy balance

The biochar calorific value (MJ/kg) can be studied by its ultimate analysis. Equation 26 (Qian et al., 2020) shows the relationship between the factors associated with carbon, hydrogen and oxygen content (%).

$$HHV(MJ/kg) = 33.2C + 176.6H - 17.7O + 0.702 \quad (26)$$

The high heating value (HHV) of bio-oil can be estimated by its elemental composition. The determination of the HHV is obtained by the correlation between the carbon, oxygen, sulphur and hydrogen content (%). The factors related are illustrated in Equation 27 (Riaz et al., 2016).

$$HHV(MJ/kg) = (34C + 124.3H + 6.3N + 19.3S - 9.8O) / (100) \quad (27)$$

The relevance of the heating value of biogas released during pyrolysis is represented by the gas composition, mainly for the concentration of four gases: hydrogen (H₂), methane (CH₄), carbon monoxide (CO) and ethyne (C₂H₂). The lower heating value (LHV, MJ/m³) of biogas is

Table 9

Gaseous fraction of microwave and conventional pyrolysis (Ferrera-Lorenzo et al., 2014; Halim and Swithenbank, 2016; Liu et al., 2021; Shi et al., 2020).

Composition	Vol (%)	
	Conventional pyrolysis	Microwave pyrolysis
CO ₂	~3.2–36	~13–31
CH ₄	~13–23	~1–15
CO	~18–67.1	~23–44
H ₂	~0.8–24	~19–52
Syngas	~41–68	~54–81

calculated by Equation 28 (Kazim, 2017; Moghadam et al., 2014).

$$LHV \left(\frac{MJ}{m^3} \right) = \frac{107.98 H_2 + 126.36 CO + 358.18 CH_4 + 56 C_2H_2}{1000} \quad (28)$$

Equation 34 shows the calculation of the by-product energy obtained through their heating value (HV, MJ/kg), the mass of the biomass sample (M, kg) and yields (%). Then, the total energy output achieved in the microwave pyrolysis process involves the energy value of biochar (Echar), bio-oil (Eoil) and biogas (Egas) (Jesus et al., 2018). The energy conversion efficiency can be obtained by Equation 31 (Suriapparao et al., 2015), considering the ratio between the total energy achieved from the three by-products and the electrical consumption of the microwave pyrolysis system.

$$By-product E(MJ) = HV \left(\frac{MJ}{kg} \right) * M (kg) * yield (%) \quad (29)$$

$$Total output E (MJ) = (Echar + Eoil + Egas) \quad (30)$$

$$Energy recovered (%) = \frac{Total output energy}{electrical consumption} * 100 \quad (31)$$

Since the energy recovery of pyrolysis depends on the by-products of energy and energy system consumption, microwave pyrolysis produces slightly higher output energy (Hansirisawat and Srinophakun, 2020; Shi et al., 2020). Table 10 shows a compilation of energy by-products generated from both pyrolysis technologies. Studies demonstrated that microwave pyrolysis has output energy (~7.2–22.1 MJ) higher than conventional heating (~2%), considering the same total input energy by applying an identical pyrolysis temperature and reaction time. The biogas energy efficiency in microwave heating is ~16% higher than conventional pyrolysis. The increased total efficiency in microwave pyrolysis is attributed to its increased biogas energy value (high H₂ formation and low CO₂ content), reaching higher energy efficiency than conventional heating (Shi et al., 2020; Su et al., 2022a; Zhou et al., 2021). Microwave heating achieves higher efficiency than slow pyrolysis due to low energy consumption during the biomass conversion process (Hansirisawat and Srinophakun, 2020; Shi et al., 2020).

8. Application of microwave pyrolysis by-products

Other biomass conversion methods offer a limited application of by-products, mainly due to the restricted number of feedstock materials that can be processed and the target product obtained from the technology method. Microwave pyrolysis has several advantages over other bioenergy methods that involve the versatility of biomass uses and the simultaneous generation of char, oil and gas in shorter reaction time. Microwave pyrolysis generates biochar with a higher surface area than conventional heating, whose property is crucial for developing modified/activated biochar (Allende et al., 2023; Selvam S and Paramasivan, 2022). In terms of electricity generation, microwave pyrolysis provides two pathways mechanisms - by using biogas in a gas turbine or applying bio-oil upgraded in an engine. However, combustion, gasification and anaerobic digestion offer only one by-product to produce electricity by using steam, gas and biogas in the turbine, fuel cell and engine, respectively (Ifeanyi Michael Smarte et al., 2022).

Table 10

Energy efficiency of conventional and microwave pyrolysis (Ferrera-Lorenzo et al., 2014; Shi et al., 2020; Xiqiang Zhao et al., 2011).

	MJ	
	Conventional pyrolysis	Microwave pyrolysis
Char	~1.1–7.83	~1.3–7.1
Oil	~0.3–9.3	~0.19–8.6
Gas	~4.6–6.28	~5.6–7.3
Total output energy	~7.6–21.83	~7.2–22.1

The by-products generated from microwave pyrolysis of lignocellulosic biomass have diverse applications in the industrial sector (Su et al., 2022a; Xin et al., 2021; Xue et al., 2021; Zi et al., 2019), as shown in Fig. 7. Biochar products present higher mineral content and elemental carbon composition due to the nature of the original feed material (Mierzwa-Hersztek et al., 2019). Thus, biochar is an excellent resource for producing pellet conversion, activated carbon, soil conditioner, carbon nanofilaments, solid additives, and others (Shukla et al., 2019; Su et al., 2022a; Xin et al., 2021; Xue et al., 2021). Recent research reveals that biochar is an excellent additive that improves the properties of construction materials, especially mechanical strength and other relevant physical properties (Rossignolo et al., 2017). Interestingly, the integration of aluminium-siliceous material in concrete increases its strength, durability, performance, and porosity (Xu et al., 2019).

The electrochemical sensors development, based on biochar use, has gained relevance due to its significant electrocatalytic potential. The biochar activation consists of chemical activation before the pyrolysis process, considering biomass soaking into KOH, ZnCl₂, HNO₃ or H₂SO₄ (Cheng et al., 2017; Monticelli, 2020). The biomass chemical treatment and the pyrolysis process improve biochar porous structure, electron transfer, and ion insertion (Allende et al., 2023). Once the biochar is pyrolysed, the modified biochar is applied in the electrode fabrication by drop-casting (in a carbon glassy carbon electrode) or carbon paste (Cheng et al., 2017; Monticelli, 2020; Sudha et al., 2019). The sustainable electrode can be used for different analytes detection, like dopamine, oxalic acid, nitrite, and uric acid (Monticelli, 2020; Sudha et al., 2019; Teo et al., 2019).

Some bio-oil uses comprise fuel combustion, power generation (stationary diesel engine), chemical production, transportation fuel, binders for pelletizing, etc. (Hu and Gholizadeh, 2020; Li et al., 2022b; Zeng et al., 2022). However, bio-oil often contains unstable chemical compounds that require upgrading for its application as fuel due to the viscosity and oxygen, water, and nitrogen presence. Previous factors lead to bio-oil with low heating value and decreased thermal and chemical variability (Hussain et al., 2018; Li et al., 2021; Su et al., 2022a). The purification process involves the separation of the bio-oil from the raw product to obtain better quality and performance as a fuel (Bu et al., 2016; Su et al., 2022a). Some purification techniques are.

- The solvent addition (with a high heating value) in the bio-oil, causes a physical-chemical reaction between the solvent and the bio-oil components, increasing the heating value and decreasing viscosity. The standard solutions are ethyl acetate, acetone, methanol, and ethanol (Hu and Gholizadeh, 2020; Li et al., 2022b; Liu et al., 2014).
- Emulsification with other fuels, like diesel or biodiesel integration, improves ignition properties, although this represents some

problems with heating values, corrosion and cetane number (Cai et al., 2021a). This last property indicates the ignition quality of diesel fuel (VenkataMohan et al., 2019).

- Esterification involves a reversible conversion, where it is possible to obtain methyl ester or biodiesel. The process entails the reaction between the bio-oil and alcohol (methanol or ethanol) in the presence of an acid catalyst (HZSM-5 or aluminium silicate) at a lower temperature than the boiling point of the alcohol (60 °C) (Hansen et al., 2020; Hu and Gholizadeh, 2020; Li et al., 2022b).
- Supercritical fluid means a fluid at pressure and temperature above a critical point that can dissolve the liquid. Some common solvents include ethanol, methanol and water (Bu et al., 2016).
- Hydrotreating reduces the concentration of oxygen, nitrogen, and sulphur in the form of water and H₂S (Hansen et al., 2020). This method requires removing the oxygen as water by adding hydrogen at high pressure in a catalytic process. Conventional catalysts are CoMo-based and NiMo-based, intended to remove O, N and S (Bu et al., 2016; Hansen et al., 2020; Huber et al., 2006; Kumar and Strezov, 2021). Hydrocracking is a method that uses high temperature (310 °C–275 °C) and pressure (10–20 MPa) in a catalytic cracking process in the presence of hydrogen gas, which involves the conversion of polymeric components into small fragments (Hansen et al., 2020; K. Tanneru and H. Steele, 2015; Li et al., 2022b; P.M. Mortensen et al., 2011).
- The extraction of valuable chemicals from the mixture also qualifies as an oil purification method. There are diverse separation processes, for example, through the absorption by acetone as a solvent, distillation techniques and fractionation of the oil (Bu et al., 2016; Li et al., 2022b).

Biogas application comprises combustible gas production, like hydrogen (H₂), acetylene (C₂H₂), methane (CH₄), ethylene (C₂H₄), ethane (C₂H₆), and carbon monoxide (CO) and some minority content of carbon dioxide and pollutants. The biogas produced from microwave pyrolysis had high hydrogen and carbon monoxide content, which allows the synthesis of gases, such as ammonia. As a result, biogas applications include the direct firing of boilers (without flue gas treatment), and gas turbines or engines for electricity generation (Abanades et al., 2022; Khan et al., 2021; Mulu et al., 2021). Fuel production is possible through steam reforming, which is the production of syngas (a reaction between hydrocarbon and water), whose objective is hydrogen generation (Bu et al., 2016; Mahari et al., 2018). Furthermore, microwave pyrolysis in a vacuum environment will generate more condensation volatiles, allowing bio-oil formation (Mahari et al., 2018).

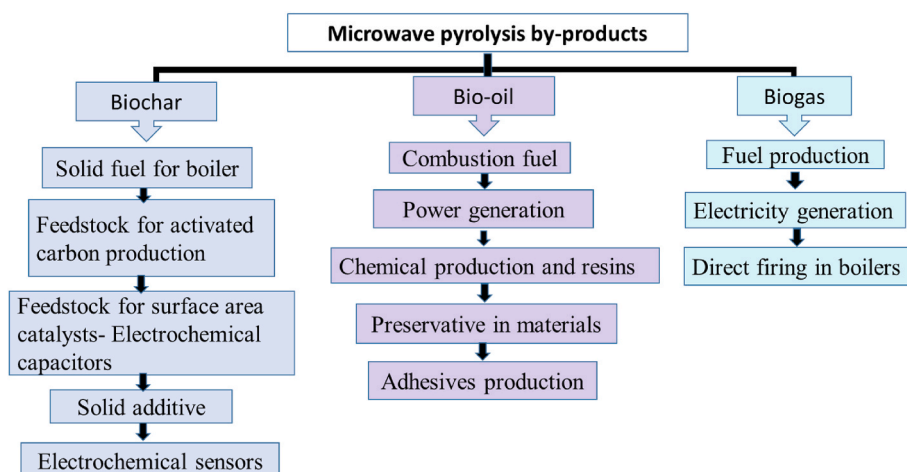


Fig. 7. Applications of microwave pyrolysis by-products (Bu et al., 2016; Fernandez et al., 2011; Undri et al., 2011; Xu et al., 2019).

9. Microwave pyrolysis economic analysis

Microwave pyrolysis development is crucial for sustainable benefits associated with energy independence, CO₂ mitigation, and the reduction of agricultural residues. Nevertheless, the economic factor of pyrolysis technology is challenging due to the highly competitive cost of fossil fuels (Inayat et al., 2022; Li et al., 2022c; Mulu et al., 2021). Additionally, multiple variable costs (V.C) are associated with financial viability and operating parameters, like technology method, biomass storage, plant size (operating scale), feedstock (represents 23–30% of the variable cost), maintenance (17–24% of the V.C), grinding (7–9% of the V.C), and transportation (5–7% of the V.C) (Hansirisawat and Srinophakun, 2020; Mullaney et al., 2002).

The economic analysis is determined considering the energy balance of the conversion process that involves the relationship between the energy consumed by the microwave pyrolysis and the energy generated from the by-products (biogas, bio-oil and biochar). Microwave energy demand depends on system conditions; for example, microwave vacuum pyrolysis or microwave pyrolysis process in a nitrogen environment. The energy consumption of both microwave pyrolysis conditions is obtained by Equations 32 and 33 (Lam et al., 2019; Yang et al., 2018).

$$E_{MP\text{system}}(kWh) = [A + B + C]X D \quad (32)$$

A = Microwave power (W)

B = Thermocouple (W)

C = Vacuum power (W)

D = Reaction time (hr)

$$E_{MP\text{system_N2environment}}(kWh) = [A + B]X D \quad (33)$$

Microwave pyrolysis system design, biomass state, and optimal operating conditions are relevant to determine its techno-economic viability and efficiency. The optimal microwave pyrolysis system design decreases the microwave heating loss, improves the energy conversion process and enhances by-product quality and yield (Inayat et al., 2022; Lam et al., 2019). For instance, using biogas as a fuel with high hydrogen content could be enough to self-supply the system (Xiqiang Zhao et al., 2011). Table 11 shows the operating cost comparison of both pyrolysis technologies. Biomass conversion based on small-scale microwave pyrolysis technology can be economically convenient (Beneroso et al., 2017; Wang et al., 2015). The economic viability lies in the low biomass cost, transportation, high returns (economic benefits for biomass producers), and accessible operating technology (Bu et al., 2016; Wang et al., 2015). Additional work is required to understand the economic viability of scaled-up systems, and the level of scaling achievable.

10. Conclusion

This work revealed the influential parameters on the energy recovery of the breakdown of biomass using the microwave-assisted pyrolysis method. Microwave heating is a promising alternative for biomass conversion due to its high efficiency and fast heat transfer capacity. The energy conversion of biomass feedstock using microwave pyrolysis is a feasible method that allows excellent yield on the by-products. The conditions and nature of biomass, microwave power, microwave susceptor and reaction time are some influencing factors that are essential to determine the quality and yield of the bio-oil, biochar, and biogas. For instance, pre-treatment of the biomass, high-water content, and particle size produces a higher bio-oil and biogas yield. The operating conditions of microwave pyrolysis, such as input power, heating rate, and microwave susceptor also influence the outcomes. By modifying these parameters to optimal ranges, the by-product yield can be optimised to

Table 11

Estimation of the techno-economic analysis of conventional and microwave pyrolysis (Badger et al., 2011; Lam et al., 2019; Wang et al., 2015; Yahya et al., 2021).

Item	US \$/yr	
	Conventional pyrolysis	Microwave pyrolysis
Capital costs		
Capital investment	110,000	208,000
Others costs	265,000	74,300
	375,000	282,300
Operating costs		
Feedstock	124,500–1,460,000	124,500–1,460,000
Electricity	38,880–104,869	8640
Labour cost	270,000	12,000
Maintenance	40,000–91551	10,000
Insurance	39,539	4000
	1,239,439	826,890

obtain a higher energy production potential and improved elemental composition.

The optimisation of the by-products and their quality is varied based on the operating conditions of the microwave pyrolysis system. High microwave susceptor addition and high microwave power cause more volatilization of larger molecules and the rapid release of small molecules, generating low biochar yield and non-uniform modification in its structure. Low temperature and longer reaction time are the optimal biochar conditions to obtain a higher BET surface area, adsorption efficiency and micropore volume. The combination of high power and microwave susceptor contributes to the thermal breakdown of heavy hydrocarbon and facilitates the formation of volatiles from the biomass, generating more gaseous fraction. Moderate microwave power and low microwave susceptor are beneficial for producing bio-oil with higher aromatic content. These factors are relevant to fully understanding the challenges that face energy recovery of a microwave pyrolysis system.

Credit author statement

S. Allende: investigation, data curation, methodology, writing of original draft, conceptualized, designed and performed the study. G. Brodie and M. Jacob: work supervision, the guidance of paper framework, conducted the study, data validation, writing review, and editing. All authors read, edited, and approved the final draft.

Declaration of competing interest

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

Data availability

Data will be made available on request.

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