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PII: S0960-8524(22)01756-4
DOI: https://doi.org/10.1016/j.biortech.2022.128423
Reference: BITE 128423

To appear in: *Bioresource Technology*

Received Date: 25 September 2022
Revised Date: 27 November 2022
Accepted Date: 28 November 2022

Please cite this article as: Li, Y., Gupta, R., Zhang, Q., You, S., Review of Biochar Production via Crop Residue Pyrolysis: Development and Perspectives, *Bioresource Technology* (2022), doi: https://doi.org/10.1016/j.biortech.2022.128423

Review of Biochar Production via Crop Residue Pyrolysis: Development and Perspectives

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Submitted to ***Bioresource Technology***
November 2022

Abstract

Worldwide surge in crop residue generation has necessitated developing strategies for their sustainable disposal. Pyrolysis has been widely adopted to convert crop residue into biochar with bio-oil and gas being two co-products. The review adopts a whole system philosophy and systematically summarises up-to-date knowledge of crop residue pyrolysis processes, influential factors, and biochar applications. Essential process design tools for biochar production e.g., cost-benefit analysis, life cycle assessment, and machine learning methods are also reviewed, which has often been overlooked in prior reviews Important aspects include (a) correlating techno-economics of biochar production with crop residue compositions, (b) process operating conditions and management strategies, (c) biochar applications includes soil amendment, fuel displacement, catalytic usage, etc. (d) data-driven modelling techniques, (e) properties of biochar, and (f) climate change mitigation. Overall, the review will support the development of application-oriented process pipelines for crop residue-based biochar.

Keywords: Agricultural waste; Resource Recovery; Sustainable Development; Machine Learning; Compositions

1. Introduction

A plethora of crop residues are produced globally per year (5280 mega tonnes in 2020-21) (Shinde et al. 2022), which require significant disposal efforts. Typical treatment techniques for crop residues include composting and open combustion, which are featured by emissions of air pollutants (e.g., H_2S, SO_2, and NH_3) and limited resource utilisation efficiency (Alhazmi and Loy, 2021; Chungcharoen and Srisang, 2020). Recent research has focused on developing new technologies for environment-friendly bioresource recovery from crop residues towards achieving global net-zero goals.

Crop residues can be converted to various value-added products via thermochemical or thermophysical treatments. Among them, pyrolysis is a thermochemical process that involves heating of carbon-rich materials (e.g., crop residues, municipal solid waste) in an inert atmosphere to generate biochar, bio-oil, and gas as value-added products (Li et al. 2022). There are six major types of pyrolysis technologies: fast pyrolysis, flash pyrolysis, slow pyrolysis, vacuum pyrolysis, hydro-pyrolysis, and microwave pyrolysis (MWP). These technologies are differed by their heating rate, pyrolysis temperature, residence time, reaction environments, and heating methods. In general, the proportions of value-added products generated by pyrolysis technologies are different (Ippolito et al. 2020). For example, the fast, flash, and vacuum pyrolysis processes favour the production of bio-oil, while hydro-pyrolysis mainly produces gas under high pressure and hydrogen atmosphere (Liu et al. 2020; Yousaf et al. 2021). Among these technologies, slow pyrolysis and MWP are regarded as promising technologies that favour biochar production (Liu et al. 2021; Nzediegwu et al. 2021).

Biochar, being a carbon-rich material has been utilized in a wide variety of applications due to important characteristics such as specific surface area (SSA), pore volume (PV), gross calorific value (GCV), surface functional groups, cation exchange capacity (CEC), and structural stability (Wang and Wang, 2019). It has the potential for carbon sequestration by effectively removing carbon from the atmospheric carbon cycle and transferring it to long-term storage in the soil (Li and You, 2022). Biochar can be used as an adsorbent to remove water and air pollutants. Catalytic usage of biochar includes a wide range of industrial applications such as biodiesel production, gas production, and microbial fuel cell (MFC) electrodes (Lee et al. 2017). The performance of biochar in these applications and associated environmental impacts is contingent upon the physicochemical properties of biochar that are closely related to pyrolysis process conditions (e.g., pyrolysis temperature, heating rate, residence time, pressure, inert gas flow rate, and particle size) and the composition of feedstocks (Li et al. 2019; Sun et al. 2017). The socio-economic and environmental benefits (or drawbacks) of a biochar production technology are strongly interlinked with the selection of feedstock, operating conditions, reactor specifications, and targeted applications, which necessitates adopting a whole-system approach for rapid process design and optimization.

There have been numerous reviews on biochar production from agricultural residues in recent years, as summarized in Table 1. Compared to the existing reviews, this work adopts a whole-system approach and gathers up-to-date knowledge on the pyrolysis processes, influential factors, and biochar application as well as associated process design methods (e.g., cost-benefit analysis (CBA), life cycle assessment (LCA), and machine learning (ML)-based modelling) that are related to the design of biochar production. Specifically, this review summarises recent knowledge on the composition of crop residues, six major types of pyrolysis technologies, influences of process factors, and new biochar applications and implications.

The article is structured as follows. Section 2 presents the effects of various crop residues composition on biochar production. Also, various pyrolysis reactions are discussed in Section 3 according to the technical characteristics along with the reaction environment. Subsequently, Section 4 comprehensively analyses the pyrolysis process parameters coupled with the corresponding influences on biochar yield and properties. Then, the advanced biochar applications and implications are critically reviewed in Section 5, including bio-product trade-off issues, biochar stability vs. yield, LCA, CBA, ML models, and the latest biochar applications. Finally, the areas for future improvements are recommended based on the conclusive findings.

2. Crop residues

The composition of feedstocks plays a vital role in biochar production and determines the final product characteristics and quality (Tomczyk et al. 2020). Compared to woody biomass and organic waste (e.g., manure, sewage sludge, and compost), crop residues feature low ash contents, high calorific values, and few voids (Ji et al. 2022). A wide variety of crop residues can be utilized as feedstock for pyrolysis-based biochar production (See Table 2). Proximate, ultimate, and lignocellulosic are the three main compositional metrics for crop residues. The proximate composition of biomass includes fixed carbon (FC), volatile matter (VM), ash, and moisture content (MC). For most crop residue feedstocks, FC, VM, ash, and MC content are in the ranges of 3-26%, 65-90%,1-15%, and 0-10%, respectively (see Table 2). The VM content and the yield of biochar are more sensitive to pyrolysis temperature, whilst the feedstock type influences the FC and ash contents of biochar more than pyrolysis temperature. Among them, ash and VM contents are critical factors for biochar when utilized for soil amendment applications (Usman et al. 2015), whilst biochar with a high ash content shows great potential as a catalyst for thermal conversion technologies. Nevertheless, a high ash content of biochar may be undesirable for adsorption-related applications, since it can limit the accessibility of adsorption sites on biochar surface and a high ash content often reduces the micropore surface area. Generally, crop residues have lower ash contents than organic waste, which leads to higher SSA and porosity in crop residues-based biochar (Leng et al. 2021). The FC content of biochar is a key parameter in assessing its stability and potential for sequestering atmospheric carbon. Moreover, MC can significantly affect harvest, transport, storage, and biochar production (Alhazmi and Loy, 2021). Intuitively, a lower value of MC is favourable for transportation and storage purposes due to significant volume reduction and is generally good for achieving higher energy efficiency for pyrolysis.

Another important compositional aspect is the ultimate composition, which includes carbon (C), hydrogen (H), oxygen (O), nitrogen (N), and sulphur (S). Among all these elements, C has the highest proportion in most biomass followed by O and H, accounting for 40-65%, 25-50%, and 5-10%, respectively (See Table 2). Besides, the negligible amount of S and N in raw agricultural biomass indicates that limited toxic gases (H_2S and N_2O) are emitted during the pyrolysis process. The C content of biochar is variable depending on the types of feedstocks, and crop residues-based biochar generally has a higher C content than organic wastes such as manure and sewage sludge (Ji et al. 2022). It was reported that higher C and O contents in feedstocks could result in higher yields and the net calorific value of biochar (Leng and Huang, 2018). The H/C and O/C ratios in produced biochar determine its stability, aromaticity, and polarity. The decrease in H/C and O/C ratios is in accordance with the high aromaticity and low polarity of biochar, suggesting that the biochar has excellent resistance to microbial decomposition, making it a strong contender in the MFC industry (Liew et al. 2022). The N content of biochar is a critical factor for its fertilizer application. A high content of macromolecular amino acids and proteins in the feedstock will result in a high nitrogen content in biochar. Among crop residues, woody biomass and organic wastes, the N content of crop residues is normally higher than woody biomass and lower than organic wastes (Pariyar et al. 2020).

The structural composition of crop residues is quantified by lignin, cellulose, and hemicellulose (L-C-H) contents, which strongly regulate biochar yields and properties. In general, the L-C-H of agricultural biomass is in the range of 9-27%, 28-47%, and 11-39%, respectively (Liu et al. 2018; Shariff and Noor, 2016). They decompose in the temperature range of 200 to 500°C, 300 to 380°C, and 200 to 300°C, respectively (Liu et al. 2018). The degradation of L-C-H with increasing pyrolysis temperature leads to an increase in gas yields (e.g., CO, CO_2, CH_4, and H_2), indicating a decrease in biochar yields. Meanwhile, the pyrolysis rate generally increases when cellulose and hemicellulose contents are higher than lignin, which results in high bio-oil and low biochar yields (Bhattacharjee and Biswas, 2019). However, The SSA and porosity of biochar are generally higher if there is a higher lignin content in feedstock (Leng et al. 2021).

3. Pyrolysis technologies

Based on the choice of crop residue feedstock for pyrolysis, appropriate pyrolysis technology must be selected for optimal biochar production in terms of (e.g., process efficiency, economics, environmental impacts, etc). This review focuses on six major types of pyrolysis technologies: fast, slow, flash, vacuum, MWP, and hydro pyrolysis depending on operation conditions.

3.1. Slow pyrolysis

Slow pyrolysis is operated at a relatively low heating rate (0.1 to 1 °C/s) and long residence time (300 to 7200 s), while having pyrolysis temperature in the range of 300 to 700 °C (Li and You, 2022). The low heating rate reduces secondary pyrolysis and thermal cracking of biomass, favouring biochar formation as the main product (Tan et al. 2021). Biswas et al. (2017) carried out slow pyrolysis experiments for four types of crop residues that were converted to bio-products. In the experiments, the pyrolysis temperature was within the range of 300-450 °C, while the residence time and heating rate were kept constant (residence time = 3600 s and heating rate = 0.33 °C/s). Among four feedstocks (corn cob, rice straw, rice husk, and wheat straw), rice husk achieved the highest biochar yield (43.3%) at 300 °C. Furthermore, the biochar yield decreased from 43.3% to 35.0% when the pyrolysis temperature increased from 300 to 450°C. Zhang et al. (2020) utilized slow pyrolysis of crop residues such as wheat, corn, rape, and rice straws to produce biochar. The associated pyrolysis temperature was varied within the range of 300-600 °C, while the heating rate and residence time were fixed at 0.17 °C/s and 3600 s. For the different types of feedstocks, the effects of pyrolysis temperature on biochar yield were similar, and the biochar yield decreased for higher values of pyrolysis temperature. For instance, the highest biochar yield was 51.4% from rice straw at 300°C, while the lowest biochar was 27.32% at 600 °C from rape straw.

3.2. Microwave pyrolysis

MWP is an emerging technology for efficient biomass conversion into value-added bio-products. Unlike conventional pyrolysis (CP), the heating energy is supplied via microwaves that penetrate the feedstocks, and cause their internal molecules to vibrate i.e., phononic oscillations non-intrusively (Ethaib et al. 2020). The MWP parameters that significantly influence product yields and characteristics include microwave power, amount and concentration of microwave absorber, initial MC, purge gas flow rate, and residence time (Morgan et al. 2017).

There have been several studies to assess the influences of parametric changes toward the efficacy of MWP-based processes. For instance, canola and wheat straws were pyrolysed under variable pyrolysis temperatures (300, 400, and 500 °C) with a microwave frequency of 2.45 GHz (Nzediegwu et al. 2021). As the pyrolysis temperature increased, the biochar yield decreased while the thermal stability of the derived biochar increased. Besides, the biochar produced at 500°C was more favourable for use as a soil conditioner with the highest carbon stability, while the biochar prepared at 300°C showed the greatest affinity for inorganic and polar organic pollutants due to its highest polarity, which could be used as an adsorbent. This suggests that by tuning the MWP parameters, the resultant biochar can be tuned for a bespoke application. Li et al. (2022) proposed a new approach by combining conventional pre-pyrolysis with MWP to produce biochar from the cotton stalk. Experiments were conducted within a pyrolysis temperature range of 250-450 °C while lowering the ramp-up time from 124 to 20 s (compared to MWP). This is synergetic to increase the heating rate in the case of CP processes. By adopting this strategy, the biochar yield was increased from 21% to 33% (compared to MWP) with a high carbon content (>70%). The biochar produced from MWP is also featured by a higher specific area and adsorption ability than the derived from CP. According to the latest study, where the corn stalk was irradiated for 600 s within a power range of 100-600 W, the maximum SSA of the produced biochar was 325.2 m^2g^{-1}, which could adsorb aromatic hydrocarbons (e.g., 54.75 mg/g benzene and 48.73 mg/g o-xylene) (Xiang et al. 2022).

3.3. Other types of pyrolysis

3.3.1. Fast and flash pyrolysis

Fast pyrolysis is featured a high heating rate (10-200 °C/s), during which biomass is prone to be converted to liquid products over biochar formation (Liu et al. 2020). The pyrolysis temperature is within the range of 500-1200°C, at which thermal cracking occurs, and the residence time is controlled within the range of 0.5-10s to reduce char formation (Ghysels et al. 2019; Tripathi et al. 2016). Flash pyrolysis being a variation of fast pyrolysis has a higher heating rate (> 1000 °C/s) and pyrolysis temperature (> 900°C) (Li et al. 2013). The high heating rate combined with the high pyrolysis temperature and short residence time (< 1s) result in high bio-oil and low biochar yields. Both fast and flash pyrolysis are unfavourable for biochar production. Although fast and flash pyrolysis do not favour biochar formation, the biochar formed by these methods has higher SSA than that derived through slow pyrolysis. Due to the shrinking of the solid matrix at higher temperatures, the larger pores of the biochar become smaller, thereby increasing the SSA of biochar and the availability of diffusion and reaction sites (Mendonça et al. 2017).

3.3.2. Vacuum pyrolysis

Vacuum pyrolysis utilises a reactor operating in a sub-atmospheric pressure regime to thermally degrade the feedstock in the absence of oxygen. The pressure, pyrolysis temperature, and heating rate were reported to be in the ranges of 0.01-0.20 MPa, 300-700°C, and 0.1-1°C/s, respectively (dos Santos et al. 2019; Gabhane et al. 2020). Due to the inhibition of secondary degradation, which is essential for biochar production, the vacuum pyrolysis reaction tends to produce high yields of bio-oil (Yousaf et al. 2021). This is attributed to the disproportionate removal of VM at a higher temperature, generating higher levels of heating and thus higher levels of biomass decomposition. For vacuum pyrolysis, raising the pyrolysis temperature lowers the biochar yield which is synergistic with other types of pyrolysis (Lam et al. 2019).

3.3.3. Hydro-pyrolysis

Hydro-pyrolysis is with a high-pressure hydrogen atmospheric condition within the reactor for the process. The process parameters for hydro-pyrolysis are generally in the following ranges: pressure = 10-17 MPa, pyrolysis temperature = 350-600 °C, heating rate = 10-300 °C/s, and residence time > 60 s (Oh et al. 2021). It was reported that the technology under a high-pressure hydrogen atmospheric condition could increase the yields of gas and aromatic hydrocarbons by 19% and 57% when compared with CP operating at an inert atmosphere condition (Zhang et al. 2018). High hydrogen pressure synergistically increases the biochar yield and reduces the yield of tar and light aromatics through secondary reactions. According to Wang and Song (2018), the co-loading of Zinc (Zn) and Gallium (Ga) in hydro-pyrolysis significantly increased the aromatic hydrocarbon yield by 37.4%. However, due to the presence of oxygenated compounds (e.g., acids and aldehydes), the produced bio-oil cannot be directly used as a transportation fuel. Therefore, it needs to be further upgraded by e.g., hydrotreating, incurring additional process complexity and costs and making hydro-pyrolysis a less-popular standalone technology (Kong et al. 2020).

4. Effects of pyrolysis process attributes

The prior discussion on various pyrolysis technologies indicated that the selection of optimal process parameters is required for application-specific biochar production. Essential parameters that dictate the yield and quality of biochar are pyrolysis temperature, particle size of feedstock, residence time, heating rate, gas flow rate, reactor pressure, reactor design, and catalyst usage. The quality of biochar is usually assessed in terms of the chemical (elemental composition) and physical properties (SSA and PV) of the biochar (see Tables 4 and 5).

4.1. Effects of pyrolysis temperature

4.1.1. Biochar properties

The H/C and O/C ratios in produced biochar affect its stability and aromaticity. It was found that the C content in biochar increased when the pyrolysis temperature increased. A further increase in pyrolysis temperature resulted in fewer H- and O-containing functional groups due to dehydration and deoxygenation (Zhou et al. 2021). The increase in the C content and decrease in the H content resulted in a decrease of H/C, implying a more stable structure of biochar. In addition, the content of molten aromatic ring structures in biochar increased with pyrolysis temperature, while that of unstable non-aromatic ring structures tended to decrease (Zheng et al. 2020).

The PV and SSA increased with increasing temperature, especially when the temperature was raised to above 550 °C. This is due to the release of VM from the feedstock. The biochar produced from *Symphytum officinale L* achieved the highest SSA and PV, being 273.8 m^2g^{-1} and 0.243 cm^3g^{-1}, respectively, when the pyrolysis temperature was 750 °C. Higher pyrolysis temperature conditions created more cracks or pores on the surface of biochar, resulting in greater porosity (Du et al. 2019).

4.1.2. Biochar yield

Pyrolysis temperature largely dictates biochar yields which generally decrease at elevated temperatures due to an increase in the primary decomposition of organic matter present in crop residues. Secondary decomposition of biochar residues (charring and shedding) can also contribute to lower biochar yields by producing bio-oil. It was observed that the biochar yield from straw and corn stalk pellets decreased significantly as temperature increased (Yang et al. 2021). According to Zhang et al. (2020), the yield of straw-based (i.e., wheat, corn, rape, and rice straw) biochar decreased significantly with increasing pyrolysis temperature. A more stable downward trend in the biochar yield was observed when temperatures exceeded 400 °C. Another study showed the effect of pyrolysis temperature on the yield of biochar produced from *Symphytum officinale* L. For the pyrolysis temperature range of 350-750 °C, the biochar yield gradually decreased with increasing pyrolysis temperature (Du et al. 2019).

4.2. Effects of heating rate

4.2.1. Biochar properties

The heating rate also critically affects the PV and SSA of biochar. It was shown that the SSA of biochar prepared from rapeseed stem increased from 295.9 m^2g^{-1} to 384.1 m^2g^{-1} when the heating rate of the process increased from 1 °C/min to 20 °C/min (Zhao et al. 2018). It was due to that a higher heating rate condition caused a larger extent of thermal decomposition. Furthermore, low heating rate conditions can facilitate the retention of structural complexity and avoid thermal cracking of biomass (Li et al. 2020).

The ultimate composition of biochar can be affected by the heating rate. Li et al. (2021) analysed the ultimate composition of biochar prepared from a lignin feedstock. Under different heating rate conditions (5, 10, 15, 20 °C/min) of pyrolysis, the elemental contents of biochar varied at the same temperatures. The heating rate was varied from 5 °C/min to 20 °C/min and the pyrolysis temperature was kept at 700 °C. The C content of biochar decreased from 94% to 85.4%, and the H content varied from 1.2% to 1.5%. It indicated that the H/C ratio increased as the heating rate increased, with a decrease in biochar stability.

4.2.2. Biochar yield

Under low heating rate conditions, the secondary decomposition of biomass is minimised, ultimately increasing the biochar yield. In contrast, large amounts of liquid and VM are produced at high heating rate conditions, resulting in lower biochar yields (Yaashikaa et al. 2019). Tripathi et al. (2016) investigated the effects of heating rate on biochar production from safflower seeds, *Ferula orientalis L* and *Charthamus tinctorius L*. The biochar yield decreased when the heating rate was increased from 30 °C/min to 50 °C/min at different temperatures between 400-600°C. Zhao et al. (2018) analysed the effects of heating rate on biochar production from rapeseed. As the heating rate was increased from 1 °C/min to 5 °C/min, the yield first showed a positive correlation with the rate, and the highest yield (27%) was achieved at 5 °C/min. Increasing the heating rate to above 5 °C/min reduced the biochar production and resulted in high yields of by-products due to the enhanced decomposition of organic matter and the production and release of carbon-rich vapour.

4.3. Effect of particle size

4.3.1. Biochar properties

The particle size of feedstock usually affects biochar's physical properties rather than elemental properties and controls the heat and mass transfer rate during the process. For instance, the SSA area of biochar increased from 5.2 to 51.1 m^2g^{-1} while the porosity of biochar marginally decreased when the feedstock particle size decreased from 1 to 0.053 mm (Fazeli Sangani et al. 2020). Besides, it was also reported that the CEC and anion exchange capacity (AEC) of biochar increased when particle size decreased from 0.25 mm to 0.053 mm (Fazeli Sangani et al. 2020; Liao and Thomas, 2019). According to Chen et al. (2017), finer feedstock-derived biochar is suitable to be applied for soil amendment, due to the higher degree of particle destruction and subsequent release of nutrients into the soil.

4.3.2. Biochar yield

The particle size of feedstock also influences biochar yield. Larger biomass particles can result in longer contact time between vapour phase species and char layer, leading to a higher probability of secondary reactions and subsequent formation of additional biochar through repolymerization (Tripathi et al. 2016). This hypothesis is supported by findings in the literature where the biochar yield increased from 31.2% to 38.6% when the particle size of rice husk increased from 0.07 mm to 2.00 mm with 500 °C pyrolysis temperature (Abbas et al. 2018). Another study by Hong et al. (2020) also showed a similar biochar yield trend regarding particle size: the biochar yield increased from 69.8% to 73.9% when the particle size of cotton stalk increased from 0.07 mm to 1.7 mm.

4.4 Effect of residence time

4.4.1. Biochar properties

The residence time could affect biochar's ultimate composition. Abbas et al. (2018) analysed the effects of residence time on the biochar produced from rice husk. The C content increased from 63.28% to 70.89% and H content slightly decreased from 4.87% to 2.09% when the residence time increased from 30 min to 90 min at 500 °C. Accordingly, the H/C ratio decreased from 0.924 to 0.354, indicating a more stable structure of biochar.

The effects of residence time on biochar properties have been determined alongside other influential parameters such as pyrolysis temperature, feedstock type, and heating rate (Tomczyk et al. 2020). The effect of residence time on biochar production is also linked with other dominant parameters. More research is needed to unveil the contribution of residence time towards biochar characteristics independently.

4.4.2. Biochar yield

The residence time is recommended to be within the range of 5-90 min for biochar production via slow pyrolysis (Zhang et al. 2020). It was shown that increasing the residence time from 10 to 100 min decreased the biochar yield from 29.6% to 28.6% (Zhao et al. 2018). For a *what-if* scenario analysis on residence time, Sun et al. (2017) increased the residence time from 0.5 h to 24 h with a constant pyrolysis temperature of 300 °C and wheat straw as the feedstock. The study showed that the biochar yield drastically decreased from 58.2% (residence time =

0.5 h) to 18.8% (residence time = 24 h), while the FC and ash contents of biochar increased from 28.3% to 44.4%, and from 8.6% to 9.8%, respectively. This was because longer residence time enabled further decomposition of feedstock that converted biochar into the two co-products (i.e. bio-oil and gas).

4.5. Effect of other parameters

4.5.1. Gas type and flow rate

The gas flow rate through the pyrolysis reactor affects the contact time between the primary vapour and biochar, therefore affecting the degree of secondary char formation. Moderate to high levels of vapours are formed during the pyrolysis of biomass. If not removed, the vapours will participate in secondary reactions, changing the composition and yield of biochar. Low gas flow rates favour higher biochar yields and are favourable on slow pyrolysis, while higher gas flow rates are used for fast pyrolysis to effectively strip out the vapour once it has been formed. For example, it was shown that biochar yield decreased from 24.4% to 22.6% when the nitrogen flow rate was increased from 1.2 L/min to 4.5 L/min (Tripathi et al. 2016).

Pathomrotsakun et al. (2020) applied a low CO_2 flow (flow rate = 50 ml/min) in their process, where the corresponding optimal values of residence time and pyrolysis temperature were 30 min and 300°C. The H/C and O/C ratios, higher heating value (HHV), and energy yields of the resulting biochar were 0.94 and 0.14, 31.12 MJ/kg, and 48.04%, respectively. This work suggested that CO_2 can be used as a substitute for nitrogen, which has the potential to improve the environmental footprint of biochar production by integrating it with a CO_2 source. Sessa et al. (2021) investigated the impacts of four different types of inert gases (helium, nitrogen, argon, and CO_2) on biochar production. The scenario with CO_2 as the inert gas achieved the highest yield and best quality of biochar. When the flow rate was 0.1 L/min, the biochar yield reached 41.2% in a CO_2 environment, higher than the other types of inert gas (i.e., helium, nitrogen, and argon).

4.5.2. Pressure

Except for hydro-pyrolysis, all other types of pyrolysis are carried out under an inert environment. High pressure can extend the residence time of pyrolysis vapours, increasing the decomposition rate (Li et al. 2020). Also, it was reported that biochar yields increased with increasing pressure. Melligan et al. (2011) showed a slight increase in the biochar yield obtained from *Miscanthus x giganteus*, when the pressure increased from 0 to 12 bar with a temperature condition of below 800°C. It should be noted that pyrolysis at high-pressure conditions requires more stringent reactor design and thus higher construction or capital costs. Also, high pressures conditions require high maintenance costs for the operation of pyrolysis reactors.

4.5.3. Reactor selection

Large-scale biochar production has stringent requirements on continuous production and quality control, which is contingent upon pyrolysis reactor design and operation (Arabiourrutia et al. 2020). Figure 1 shows six types of popularly used pyrolysis reactors: (a) fixed bed, (b) earthen kiln, (c) rotary kiln, (d) fluidised bed, (e) auger reactor, (f) spouted bed (Zhu et al. 2022). The fixed bed pyrolysis reactor typically consists of a fixed bed with heating, a gas collector, a liquid condenser, and a temperature controller. It has several typical features such as operation under batch regime, easy design, and high adaptability for various feedstock particle sizes. However, it also has some drawbacks, such as heat transfer limitations and challenges for continuous operation (Vieira et al. 2020). A fluidised bed reactor is typically suitable for the condition of high heating rate, short residence time, and continuous operation. Nevertheless, the drawbacks of this type of reactor include complex design and operation (high costs) and fine-sized feedstocks requirement (< 0.08mm) (Polin et al. 2019). The earthen kiln is a traditional type of biochar production design, with difficult-to-control operating parameters, long residence time, and a low production conversion efficiency (Garcia-Nunez et al. 2017).

The indirect-heating pyrolysis technology has been applied to a rotary kiln, which could perform in a continuous mode without a heat carrier. However, its poor heat transfer efficiency and gas-solid contact limit the catalyst application for higher process performance (Hu et al. 2022). An auger reactor has similar advantages to a rotary kiln, but its mechanical drive often leads to high energy consumption (Campuzano et al. 2019). The spouted bed reactor is characterised by high heat transfer rates and gas-solid contact. It does not have a strict requirement on particle size, thus reducing the requirement for feedstock grinding. The main product of spouted bed pyrolysis is bio-oil, and only produces a small amount of biochar (Zhu et al. 2022).

4.5.4. Catalyst

The use of catalyst can affect the relative distribution of the pyrolysis products. The catalysts used for pyrolysis can be divided into two types: primary and secondary. Primary catalysts are those that are mixed with biomass prior to pyrolysis, while secondary catalysts are not mixed with biomass but are kept in a secondary reactor downstream of the main pyrolysis reactor (Tripathi et al. 2016). Typical catalysts that have been used in biomass pyrolysis processes include alkaline catalysts (e.g., KOH, NaOH, K_2CO_3, and Na_2CO_3), metal oxides (e.g., Fe_2O_3, Al_2O_3, ZnO, CaO and TiO_2) and activated carbon (AC) (Chen et al. 2020). It was found that increasing the proportion of catalyst raised the temperature and reduced the time required to reach the desired pyrolysis temperature. Moreover, the additional catalyst increased the biochar yield. During the process, the catalyst promoted a stable C structure of biochar and prevented further char pyrolysis, thus promoting biochar production (Tripathi et al. 2016).

5. Emerging topics on biochar production

Various emerging aspects of biochar production are critically reviewed, including (a) biochar, bio-oil, and gas nexus, (b) balance between yield and stability, (c) climate change mitigation and LCA, (d) economics of pyrolysis and biochar data-driven modelling of biochar production via pyrolysis, and (f) emerging applications of biochar. A summary of these aspects and associated research works are provided in Table 6.

5.1. Biochar, bio-oil, and gas nexus

There exists a trade-off between the three pyrolysis products: biochar, bio-oil and gas. Optimal pyrolysis production should match the relative yields of the products with the purpose of production with the consideration of economics and environmental footprints. For a system mainly configured for biochar production, appropriate production of bio-oil and/or gas has the potential to improve the economics of the system (You et al. 2022). It is important to adopt a nexus perspective upon the design of pyrolysis production. As shown above, the relative yields of the products depend on the types of feedstocks and pyrolysis process conditions and design. Accordingly, a technology that favours the accurate control of the yields will be desirable for optimisation. MWP serves as a candidate technology that has the potential to support technology innovation towards accurately controlling the relative production of biochar, bio-oil, and gas. A large pool of literature has focused on analysing bio-oil and gas production from MWP. For example, Li et al. (2022) studied the production of combined MWP and CP processing (MCCP) of cotton stalk under 11 different pyrolysis temperatures. Figure 2a shows the yield distribution of the three products under the different temperature scenarios. M-1 referred to MWP with 1 g microwave absorbent (biochar) under 600W without pre-heating. For A-(250-450) and A-(250-450)-1, 250-450 referred to preheat temperatures and A-(250-450)-1 referred to MWP under the preheat condition. M-1 had the lowest biochar yield and achieved the most gas production. A-250-1 had the highest biochar yield among all scenarios. The MCCP technology was most favourable for biochar production, while the MWP technology had the highest gas yield. Preheating has played a significant role in biochar production. The highest biochar yield of 34.1% was achieved at 250 °C and the highest bio-oil yield was 50.2% when it was at the first stage of 450 °C.

Mohmoud Fodah et al. (2021) studied biochar and bio-oil production from corn stover via MWP cooperated with catalysis. Figure 2c compared product distribution from catalytic MWP and non-catalytic MWP in the power range of 500-700W. In the non-catalytic case, a significant decrease in biochar yield and an increase in gas yield were observed when the power increased from 500 W to 900 W. The addition of Na_2CO_3 catalyst improved the bio-oil and gas yield, reducing the biochar yield. It was due to the increased heating rate and pyrolysis temperature resulting from introducing Na_2CO_3, which facilitated the increase of gas and bio-oil production. Cen et al. (2019) investigated the influences of wash pre-treatment on biomass pyrolysis polygeneration. The pyrolysis experiment was carried out at pyrolysis temperature = 550°C and heating rate = 10°C/min. The rice straw showed the highest biochar yield (38%). The aqueous phase bio-oil (APBO) washing rice straw (Bio-RS) showed the highest gas yield (35%) as shown in Figure 2d. The bio-oil did not show significant changes under different wash pre-treatment conditions.

5.2. Balance between biochar yield and stability

Biochar C content recalcitrance and biochar stability have played a critical role in carbon sequestration. Biochar stability can be considered by the proportion of initial carbon remaining after oxidation treatment and can be determined by the mass of stable carbon remaining in the biochar residue after oxidation. Numerous challenges exist to reconciling the trade-offs between biochar stability and yield (Leng et al. 2019).

The degree of aromaticity and aromatic condensation are two essential evaluation metrics that dictate the stability of biochar (Xu et al. 2021). The unsaturation or aromaticity of biochar can be assessed according to biochar elemental ratios (H/C and O/C)(Zhang et al. 2022). Han et al. (2018) conducted pyrolysis of rice straw at 250-600°C. H/C and O/C ratios were employed to analyse the biochar stability. The H/C and O/C ratios of biochar decreased from 0.87 to 0.34 and 0.36 to 0.13 with the increasing pyrolysis temperature. The increase in pyrolysis temperature led to a trend towards greater carbonisation with more poly-aromatic content, which promoted biochar stability. Vendra Singh et al. (2020) studied the trade-offs between yield and stability of biochar derived from rice straw pyrolysis with pyrolysis temperature between 300-600°C. The H/C and O/C ratios increased from 0.52 to 0.23 and from 0.15 to 0.07, indicating an improvement in biochar stability. On the other hand, the biochar yield decreased from 38.23% to 27.14%, with pyrolysis temperature increasing from 300-600°C. Leng and Huang, (2018) summarised that long residence temperature, slow heating rate, high pressures, biomass feedstocks with high lignin contents, and large particle size would be preferred for biochar yield and stability, and it would also contribute to improved carbon sequestration ability by biochar.

5.3. Climate change mitigation and life cycle assessment

LCA is a tool routinely used to assess the environmental impacts of biochar production via pyrolysis processes. It adopts a whole lifecycle perspective and typically includes processes ranging from raw material extraction and pyrolysis production to waste disposal and recycling. Figure 3 illustrates the typical elements considered during the LCA of pyrolysis and biochar production processes.

Alhashimi and Aktas (2017) applied LCA to compare the environmental impacts of biochar and activated carbon (AC). Especially, long-distance transportation (i.e., nation to nation) was included as part of the biochar/AC developments analysed. The global warming potential (GWP) for biochar and AC were −0.9 kg CO_2-eq/kg and 6.6 kg CO_2-eq/kg, respectively. This work revealed cumulative energy demands for biochar and AC production processes were 6.1 MJ/kg and 97 MJ/kg, respectively. Kozyatnyk et al. (2020) evaluated the environmental footprints of biochar application as a carbonaceous water treatment adsorbent using the approach of LCA. The end-of-life stages were considered in this study including incineration, landfill, and regeneration, and biochar, hydrochar, and AC were the three primary materials assessed. It was shown that combining biochar and hydrochar with regeneration could be an environmentally feasible option to replace AC. The production of sorbents was the most significant GWP contributor within the framework of the LCA study. Therefore, increasing the sorption capacity of sorbents would offer economic and environmental benefits since higher sorption capacities reduced the use of sorbents.

Lefebvre et al. (2021) evaluated GHG emissions of two crop residue utilisation scenarios which are sugarcane residue combustion for heat and power generation and pyrolysis for biochar production. It was shown that sugarcane residue biochar could sequester 36 mega tonnes CO_2-eq/year. Most of the GHG emission was contributed by compensating for the energy deficit caused by pyrolysis. This biochar scenario led to a 23% reduction in the total amount of GHG. Azzi et al. (2019) carried out an LCA study for large-scale biochar production for negative emission. This work compared the climate impact of biomass pyrolysis with biomass combustion. The main applications were energy and power applications, and the potential as a fertiliser additive was also explored. In total, five scenarios were explored, including agricultural application, carbon sequestration, electricity substitution, heat substitution, and transport fuel substitution which had a GWP were -1300 kg CO_2-eq/ton, -1100 kg CO_2-eq/ton, -335 kg CO_2-eq/ton, -60 kg CO_2-eq/ton and 240 kg CO_2-eq/ton in 2040, respectively. This study suggested that LCA helps to design biochar systems with the comparison of the GHG emission trade-offs among various possible applications.

5.4. Economics of pyrolysis and biochar

Despite significant environmental benefits, the current market scenario suggests that biochar applications are prohibitively expensive and economically inviable. This is associated with the high capital costs of pyrolysis plants and low incentives offered by government bodies for achieving carbon-negativity (Rajabi Hamedani et al. 2019). Techno-economic analysis (or CBA) has commonly been used to explore various *what-if* scenarios from improved economics.

For example, Haeldermans et al. (2020) compared biochar production from CP and MWP through techno-economic assessment. Minimum prices ranged from US$454/ton to US$871/ton for CP-biochar and US$588/ton to US$1020/ton for MWP-biochar (based on a EUR/US$ currency exchange rate of 1.04). CP is a simplified and developed technology that makes it more affordable. However, it was mentioned that MWP-biochar had greater quality and better technical feasibility than CP-based biochar. Moreover, biochar price per ton was a critical evaluation criterion for biochar production plants and strongly depended on the government carbon tax.

The economics of biochar production systems has been assessed with respect to raw material or feedstock used, the conversion technology employed, carbon sequestration subsidies and carbon credits reflecting the social value of GHG emission reductions. Implementing smart farming practices could increase crop yields and improve the economic situation of farmers while reducing the adverse effects of climate change (Haeldermans et al. 2020). Compared to inorganic fertilisers, biochar has a long-term capacity for agricultural improvement in the economic aspect. When biochar was used in combination with plant growth-promoting rhizobacteria and N-P-K fertiliser, the wheat crop's grain yield and economic results were significantly increased. An increase in grain yield from 4.54 ton/ha to 4.70 ton/ha resulted to a rise of net benefit from 293 US$/ha to 438 US$/ha (i.e., 50% relative incrment), respectively (Ijaz et al. 2019). This indicated the potential opportunistic benefit from the use of biochar could be an important contributor to the profitability of biochar production.

5.5. Data-driven modelling of pyrolysis-derived biochar

To ensure an accurate whole-system analysis of biochar production from crop residues, generalizable modelling of pyrolysis processes is essential. ML-assisted prediction of biochar yield and composition has gradually become an important tool in recent years. Popular ML approaches evidenced in the biochar modelling literature include Random Forest (RF), Support

Vector Machine (SVM), eXtreme Gradient Boosting (XGB), Adaptive Neuro-Fuzzy Inference System (ANFIS), and Multi-Layer Perceptron Neural Network (MLP-NN).

Zhu et al. (2019) developed an RF-based model to predict biochar yield and C content. 245 datasets of biochar yield and 128 datasets of C content were collected in this study. The highest Coefficients of determination (R^2) were 0.855 and 0.848 for biochar yield and C content prediction. In an effort by Pathy et al. (2020), an XGB model was developed based on 91 datasets considering ultimate composition and elemental composition ratios as input data. However, only one output (biochar yield) was included in this study. The model performance was only evaluated by R^2, which was 0.844. the MLP-NN prediction model was employed by Khan et al. (2022) for biochar yield production, where neural networks were coupled with metaheuristic models. R^2 and RMSE of biochar yield prediction were 0.93 and 1.74. Recently, Li et al. (2022) developed a comprehensive ML-assisted predictive model for biochar yield and composition (FC, VM, ash, C, H, O, N). This study applied MLP-NN and ANFIS, which predicted biochar production from pyrolysis based on 226 datasets. The R^2 values for each of the output variable was biochar yield = 0.96, FC = 0.9, VM = 0.9, ash = 0.94, C = 0.92, H = 0.86, O = 0.88 and N = 0.88. Additionally, feature importance analysis revealed a high dependence of biochar yield and composition on pyrolysis temperature, ash content, and N content. Overall, the data-driven models for biochar production can be used in parallel with LCA and CBA models to develop a better understanding from a whole-system perspective.

5.6. Applications of biochar

Process operating conditions and reactor designs are required to be manipulated to meet the specific requirements of biochar applications with the consideration of economics and environmental implications. An overview of different application areas (e.g., energy, agriculture, and chemical) of crop residue-derived biochar is given and Figure 4 presents the conversion pathway from crop residue into various biochar applications.

Chakraborty et al. (2020) suggested that biochar could be an alternative material to substitute electrodes, cathode catalysts, and proton exchange membranes (PEM) in MFC applications. MFC can convert the energy captured in the chemical bonds of organic compounds into electrical energy while using wastewater as a substrate. Biochar has the potential to be used as an electrode material for MFC and a cathode catalyst. According to Cao et al. (2016), the biochar-based electrode was low-priced compared to commercial electrodes. The material cost of N/Fe-C was about $0.03-0.08/g, which is a thousand times lower than a commercial platinum electrode. However, several issues remain to be tackled prior to practical deployments, such as process efficiency improvement, biochar quality control, and effective biochar applications.

Kant Bhatia et al. (2021) reported that biochar can be used as a catalyst for the transesterification of oils for biodiesel production. Biodiesel is considered as a favourable fuel because of its high energy density and presence of C14-C20 long carbon chain fatty acids. The porous structure of biochar allows easy access of reactants to the active site to facilitate the transesterification process, and biochar's hydrophobic surface helps remove unwanted products generated during catalytic reactions. Behera et al. (2020) analysed the efficiency of acidified biochar catalysts for transesterification. The peanut shell was pyrolyzed under three pyrolysis temperatures (300, 400, and 600°C), among which biochar produced at pyrolysis temperature = 400 °C had the highest catalytic efficiency. The optimal values of biochar's SSA and pore size were 6.61 m^2g^{-1} and 2.98 nm, at which the highest biodiesel yield was achieved (94.94%). Akinfalabi et al. (2020) applied biochar as a catalyst for biodiesel production. The biochar produced from sugarcane bagasse achieved optimal properties when the pyrolysis temperature was 300 °C: the SSA was 310 m^2g^{-1}, and the pore size was 3.92 nm. The conditions for the highest biodiesel production (98.6%) were 1.5 h reaction time, 60 °C, and 2 wt.%

catalyst loading. Acidified biochar catalysts can reduce processing costs and the environmental impact of corrosive chemicals.

Biochar also has great potential for environmental management in various applications. For example, Qu et al. (2020) analysed the effect of agricultural composting using biochar combined with gypsum. The results showed that the application reduced composting duration, nitrogen and carbon losses, and potential ecological hazards. Biochar mixed with gypsum improved compost quality and nutrient retention. In another study, Vamvuka et al. (2020) investigated the suitability of mixing biochar with solid waste for agricultural soil applications. The following physicochemical properties were obtained from the biochar produced from grape husks at 500 °C: pH = 9.7, electrical conductivity (EC) = 15.3 mS/cm, CEC = 205.2 mmol/kg, PV = 0.12 cm^3g^{-1}, average pore size = 4.53 nm and SSA = 0.9 m^2g^{-1}. For all combinations of composts biochar and soil, alkali and alkaline earth metals showed the greatest solubility. Consequently, it increased the pH of the extracts and thus reduced the leachability of heavy metals Cr, Cu, Zr and Sr. In this study, heavy metals concentrations were reduced by 40%-95%.

6. Research needs and future direction

The critical review of biochar production from crop residue pyrolysis revealed extensive developmental efforts during the past decade focusing on biochar yield and property optimization, modelling, and applications. Nevertheless, significant future efforts are necessary for application-specific system efficiency improvement. Specifically, existing research for crop residue-biochar systems is mainly conducted at the laboratory or pilot scale. This indicates a lack of process-level understanding and parametric interplay of industrial-scale pyrolysis plants for which gas recovery remains a challenge. Although the influences of process parameters on biochar yield and stability have been extensively researched, the environmental impacts of other constituent chemicals (e.g., K, P, micronutrients, and toxic/inhibitory compounds) have not been quantified, indicating an opportunity for holistic LCA framework development. Furthermore, the LCA and process optimization frameworks require rapid prediction models, where ML-assisted predictive modelling for a wide range of biochar constituents can offer significant reduction in computational complexity. In the future, ML models should include particle size and gaseous environment types as input features, while considering HHV of biochar and inhibitory compounds as the predicted variables. Although biochar has the potential to displace several chemicals in agricultural and industrial sectors, the current business models do not offer significant government incentives to support the high capital expenditure needs for setting up production plants. Therefore, application-scpefic techno-economic analysis must be extensively conducted in the future, while assessing various business models to support policymaking decisions.

7. Conclusions

This review investigated the influences of different crop-residue feedstock and pyrolysis reaction conditions on the properties and yield of biochar. Moreover, state-of-art biochar production and application were summarised including advanced approaches associated with the trade-off of the different products of pyrolysis processes. Meantime, the use of LCA and economic analysis for evaluating the environmental benefit and economic feasibility of biochar applications was also analysed. ML-assisted modelling is becoming an effective approach supporting biochar production prediction which is important for the optimal design and deployment of biochar systems.

Declaration of Competing Interests

As Siming You, a [co-]author on this paper, is an editorial board member of *Bioresource Technology*, he was blinded to this paper during review, and the paper was independently handled by Samir Kumar Khanal as editor.

Acknowledgement

The authors would like to acknowledge the financial support from the UK Engineering and Physical Sciences Research Council (EPSRC) Programme Grant (EP/V030515/1). Siming You would like to thank the financial support from the Royal Society Research Grant (RGS\R1\211358) and International Exchange Scheme (EC\NSFC\211175). Rohit Gupta gratefully acknowledges the Royal Society Newton International Fellowship (NIF\R1\211013).

All data supporting this study are provided in full in the paper.

Table 1. Past reviews on biochar production for agricultural residues.

No.	Highlights and Scope	Reference
1	Reviewed the different biochar production techniques. Also, the effects of various process parameters on the biochar production were discussed.	Tripathi et al. (2016)
2	Focused on biochar production technologies and application for soil management. It mainly reported the different reaction processes and the potential of biochar for soil applications.	Gabhane et al. (2020)
3	Reviewed the management of crop residues and biochar application benefits for climate change mitigation in India. Impact of slow pyrolysis parameters on biochar production were discussed.	Anand et al. (2022)
4	A comprehensive study on LCA of pyrolysis processes for the sustainable production of biochar from crop residues. Various cases of LCA methodologies and impact categories were reviewed.	Zhu et al. (2022)
5	Reviewed MWP of biomass and produced biochar characteristics, which mainly focused on biochar yield and properties. A comparison of MWP and other pyrolysis was carried out.	Li et al. (2016)
6	Slow pyrolysis and fast pyrolysis on quality biochar were reviewed. The effects of feedstock composition and various process parameters on biochar production were also discussed.	Tan et al. (2021)
7	The relationship between physicochemical properties and applications of biochar was analysed. The future research requirements for biochar preparation and applications were proposed.	Li et al. (2020)
8	Reviewed biochar production from different blended feedstocks for the adsorption of organic and inorganic pollutants	Ahmed and Hameed, (2020)

Table 2. The proximate and ultimate analysis of various crop-based biomass (db: dry basis).

Feedstock	FC (% db.)	VM (% db.)	Ash (% db.)	MC (% db.)	C (% db.)	H (% db.)	O (% db.)	N (% db.)	S (% db.)	Reference(s)
Corncob	12.45	82.38	5.04	0	47.4	5.8	50.1	0.6	0.1	Wang et al. (2022)
Corn stalk	14.68	82.42	2.91	0	43.6	5.8	49.4	1.1	0.1	Wang et al. (2022)
Corn stover	8.93	82.21	8.86	0	43.28	5.92	39.32	1.96	0.66	He et al. (2018)
Sugarcane bagasse	8.87	81.23	2.51	7.39	49.26	5.26	44.95	0.43	0.1	Ahmed et al. (2018)
Coconut shell	11.10	75.50	3.20	10.10	64.23	6.89	27.61	0.77	0.50	Rout et al. (2016)
Coconut fiber	11.10	80.85	8.05	0	47.75	5.61	45.51	0.90	0.23	Rout et al. (2016)
Wheat straw	9.93	80.7	9.37	0	42.95	5.64	40.51	0.76	0.78	He et al. (2018)
Rice husk	11.44	73.41	15.14	0.01	41.92	6.34	-	1.85	0.47	Biswas et al. (2017)
Rice straw	10.06	76.87	13.07	0	40.06	5.47	40.23	0.69	0.48	Hong et al. (2020)
Rape stalk	7.49	86.09	6.42	0	43.92	5.92	42.54	0.49	0.71	He et al. (2018)
Cassava stem	16.07	81.51	2.42	0	44.47	5.82	48.88	0.01	0.83	Shariff and Noor, (2016)
Cassava rhizome	9.08	83.64	7.28	0	41.78	5.97	51.07	0.26	0.92	Shariff and Noor, (2016)
Cotton stalk	10.17	82.38	7.45	0	43.95	5.81	41.12	1.12	0.56	Hong et al. (2020)
Banana leaves	16.92	84.82	6.72	0	43.50	6.20	42.30	0.80	0.90	Sellin et al. (2016)
Sugarcane straw	3.22	87.61	9.17	3.12	41.88	5.87	41.72	0.47	-	dos Reis Ferreira et al. (2018)
Barley straw	11.83	78.8	6.43	2.94	45.41	6.1	46.21	1.18	-	Ahmed and Hameed, (2018)
Flax straw	11.4	81.3	2.9	4.4	44.4	6.7	46.5	1.4	1.2	Mukhambet et al. (2022)
Maize cobs	25.51	72.95	1.54	0	46.92	6.08	44.86	0.61	-	Intani et al. (2016)
Maize husk	22.79	74.24	2.97	0	44.96	6.02	45.57	0.48	-	Intani et al. (2016)
Maize leaves	22.73	67.78	9.49	0	43.68	5.82	39.88	1.06	0.06	Intani et al. (2016)

Table 3. Different types of pyrolysis processes and associated reaction parameters.

Technology	Fast	Slow	MWP	Flash	Vacuum	Hydro
Pressure (Mpa)	0.1	0.1	5-20	0.1	0.01-0.20	10-17
Residence time (s)	0.5-10	300-7200	<30	<1	<1	60-120
Heating rate (°C/s)	10-200	0.1-1	0.5-2	>1000	0.1-1	10-300
Pyrolysis temperature (°C)	500-1200	300-600	300-700	900-1300	300-700	350-600
Gaseous environment	Inert	Inert	Inert	Inert	Inert atmosphere under vacuum	Hydrogen
Reference(s)	Ghysels et al. (2019); Liu et al. (2020); Tripathi et al. (2016)	Biswas et al. (2017); Li and You, (2022); Tan et al. (2021); Tripathi et al. (2016); Zhang et al. (2020)	Foong et al. (2021); Li et al. (2022); Nzediegwu et al. (2021)	Li et al. (2013); Sekar et al. (2021); Tripathi et al. (2016)	dos Santos et al. (2019); Garca-Pèrez et al. (2002); Lam et al. (2019); Yousaf et al. (2021)	Kong et al. (2020); Oh et al. (2021); Wang and Song, (2018); Zhang et al. (2018)

Table 4. The properties and yields of biochar are influenced by pyrolysis temperature.

Feedstocks	Temperature (°C)	Yield (wt.%)	C (wt.%)	H (wt.%)	O (wt.%)	N (wt.%)	SSA (m^2g^{-1})	PV (cm^3g^{-1})	Reference
Rice straw	350-650	8.8-41.9	39.75-50.44	1.73-3.55	14.07-14.70	0.71-0.91	2.90-14.33	0.024-0.100	Yang et al. (2021)
Rice straw	300-600	32.8-51.4	56.42-61.30	0.12-2.95	5.71-17.73	1.90-2.15	-	-	Zhang et al. (2020)
Canola stalk	350-650	8.7-34	41.66-61.87	1.86-3.42	35.41-37.36	0.93-1.96	1.15-7.94	0.005-0.017	Yang et al. (2021)
Wheat straw	300-600	31.6-47	61.48-67.39	0.52-2.73	7.35-19.61	1.10-1.40	-	-	Zhang et al. (2020)
Corn stalk	300-600	30-43.3	58.04-63.93	1.65-4.28	9.33-18.79	2.11-2.75	-	-	Zhang et al. (2020)
Corn straw	300-600	30.9-45.9	61.20-67.48	0.18-3.68	8.98-17.39	2.12-2.93	-	-	Zhang et al. (2020)
Rape straw	300-600	29.3-44.3	61.80-67.85	0.18-3.54	7.89-17.95	0.90-10.02	-	-	Zhang et al. (2020)
Symphytum officinale L	350-750	37-48.4	33.56-41.08	0.93-2.73	7.48-10.72	1.52-1.87	11.54-273.8	0.021-0.243	Du et al. (2019)

Table 5. Effects of pyrolysis process parameters on biochar yield for different crop-residues.

	Particle size (mm)	Pyrolysis temperature (°C)	Residence time (s)	Heating rate (°C/s)	Reaction environment	Biochar yield (wt.%)	Reference
Rice husk	2.5-10	300-500	1800,3600, 5400,7200	0.1,0.16, 0.33	Media: Nitrogen with synthetic air Flow rate: 0.1 L/min Reactor: Stainless steel bed	33.7-51.3	Fazeli Sangani et al. (2020)
Rice straw	0.42-0.62	550	600	0.1	Media: Nitrogen Flow rate: 0.3 L/min Reactor: Stainless steel bed reactor	37.9	Cen et al. (2019)
Palm kernel shell	0.5-2	500	3600	0.1	Media: Nitrogen Flow rate: 0.05 L/min Reactor: Stainless steel bed	37.7	Lee et al. (2017),
Empty fruit bunch	0.5-2	500	3600	0.1	Media: Nitrogen, Flow rate: 0.05 L/min Reactor: Stainless steel bed	35.1	Lee et al. (2017)
Symphytum officinale	<0.15	350-750	3600	0.1	Media: Nitrogen Reactor: Stainless steel bed reactor	37-48.4	Du et al. (2019)
Rice straw	<0.84	300-600	3600	0.17	Media: Nitrogen Flow rate: 0.1 L/min Reactor: Stainless steel bed reactor	32.6-52	Zhang et al. (2020)
Wheat straw	<0.84	300-600	3600	0.1	Media: Nitrogen Flow rate: 0.1 L/min Reactor: Steel bed reactor with tube furnace	31.6-47	Zhang et al. (2020)
Corn straw	<0.84	300-600	3600	0.1	Media: Nitrogen Flow rate: 0.1 L/min Reactor: Steel bed reactor with tube furnace	30.9-45.8	Zhang et al. (2020)
Rape straw	<0.84	300-600	3600	0.1	Media: Nitrogen Flow rate: 0.1 L/min	29.3-44.3	Zhang et al. (2020)

					Reactor: Steel bed reactor with tube furnace		
Corn stalk	5	300-800	3600	0.1	Media: Nitrogen Flow rate: 0.1 L/min Reactor: Steel bed reactor with tube furnace	30-43.3	Xie et al. (2021)
Rapeseed stem	10-20	200-700	600,1200, 2400,3600, 4800	0.1,0.16,0.25, 0.33	Media: Nitrogen Flow rate: 0.3 L/min Reactor: Steel bed reactor with muffle furnace	18.3-80	Zhao et al. (2018)
Maize cobs	2	300-600	1800,3600,5400	0.1,0.16,0.25	Media: Nitrogen Reactor: Steel batch reactor	22-33.8	Intani et al. (2016)
Maize husk	2	300-600	1800,3600,5400	0.1,0.16,0.25	Media: Nitrogen Reactor: Steel batch reactor	21.7-30.7	Intani et al. (2016)
Maize leaves	2	300-600	1800,3600, 5400	0.1,0.16,0.25	Media: Nitrogen Reactor: Steel batch reactor	25.7-38.3	Intani et al. (2016)
Cotton stalk	0.62-0.82	250-450	7200	0.33	Media: Nitrogen, Flow rate: 0.1 L/min Reactor: Horizontal tubular furnace	20-26.5	Li et al. (2022)

1 **Table 6.** Overview of state-of-art in biochar production studies with respect to Section 5.

Topic	Highlights	Reference(s)
Biochar, bio-oil, and gas nexus	MWP coupled with conventional pre-pyrolysis for stalks treatment. Conventional pre-heating enhanced the MWP performance of stalks.	Li et al. (2022)
Biochar, bio-oil, and gas nexus	The most desirable process for biochar production was slow pyrolysis. MWP could offer a balance product distribution in biochar, oil and gas.	Li et al. (2016)
Biochar, bio-oil, and gas nexus	Two-step microwave-assisted processes were used to prepare magnetic porous biochar. MWP biochar had a higher surface area and pore volume than CP biochar.	Qu et al. (2021)
Biochar, bio-oil, and gas nexus	Effects of microwave power and sodium carbonate catalyst were investigated. The catalyst increased the bio-oil and gas yield.	Mohmoud Fodah et al. (2021)
Biochar, bio-oil, and gas nexus	APBO washing pre-treatment increased bio-oil yield. APBO washing has a better improvement effect on pyrolysis products than acid washing.	Cen et al. (2019)
Balance between yield vs. stability	Pyrolysis temperature was the dominant processing parameter to biochar stability. Both biochar yield and stability were decisive to carbon sequestration potential. Elemental and proximate analysis, and biochar structure analysis were methods for measuring biochar stability.	Leng et al., (2019); Leng and Huang, (2018)
Balance between yield vs. stability	Aromaticity determined thermal stability while surface area was critical for chemical stability.	Xu et al. (2021)
Balance between yield vs. stability	Pyrolysis process parameters had an impact on the stability and yield of biochar. The unsaturation or aromaticity of biochar can be assessed by the H/C or O/C ratios.	Zhang et al. (2022)
Climate change mitigation and LCA	Average energy demands were 6.1 MJ/kg biochar and 97 MJ/kg AC. Biochar had lower environmental impacts than AC even after transportation stage.	Alhashimi and Aktas, (2017)
Climate change mitigation and LCA	LCA of biochar application as carbonaceous water treatment adsorbents. Combining biochar and hydrochar with regeneration was desirable to replace AC.	Kozyatnyk et al. (2020)
Climate change mitigation and LCA	Most GHG was contributed by covering the energy deficit caused by pyrolysis.	Lefebvre et al. (2021)
Economics of pyrolysis and biochar	Biochar price was between US$454 and US$871 per tonne for CP. Biochar price was between US$588 and US$1020 per tonne for MWP.	Haeldermans et al. (2020)

Economics of pyrolysis and biochar	Compared to inorganic fertilisers, biochar had a long-term capacity for agricultural improvement. The grain yield and net benefit increased from 4.54-4.70 ton/ha and 293-438 US$/ha.	Ijaz et al. (2019)
Data-driven modelling of pyrolysis-derived biochar	Random forest showed good prediction ability for biochar yield and carbon contents. The highest R^2 were 0.855 and 0.848 for biochar yield and C content prediction.	Zhu et al. (2019)
Data-driven modelling of pyrolysis-derived biochar	XGB model showed good prediction ability for biochar yield. The prediction accuracy achieved 0.844 as R^2.	Pathy et al. (2020)
Data-driven modelling of pyrolysis-derived biochar	MLP-NN and ANFIS were employed to predict biochar yield and composition. Statistical analysis of various feedstock and biochar properties is performed. The prediction accuracy achieved 0.964 for biochar yield.	Li et al. (2022)
Applications of biochar	Comprehensive description and analysis of different biochar applications in MFC. Biochar has the potential as an electrode material for MFC and as a cathode catalyst and contributes to PEM applications.	Chakraborty et al. (2020)
Applications of biochar	Biochar is also used as a catalyst for biodiesel and hydrogen production. Biochar can be utilized for electrode preparation used in MFC.	Kant Bhatia et al. (2021)
Applications of biochar	The addition of biochar combined with gypsum shortened composting time. Applying biochar reduces the composting duration and nitrogen and carbon losses, and potential ecological hazards.	Qu et al. (2020)
Applications of biochar	Waste sugarcane bagasse-based acidic catalyst was synthesized. Biochar produced from sugarcane bagasse archived optimal conditions when the pyrolysis temperature is 400°C.	Akinfalabi et al. (2020)
Applications of biochar	The suitability of biochar mixed with solid waste for agricultural soil applications was investigated. The application of biochar to the soil decreased the concentration of heavy metals in leachate by 40-95%.	Vamvuka et al. (2020)

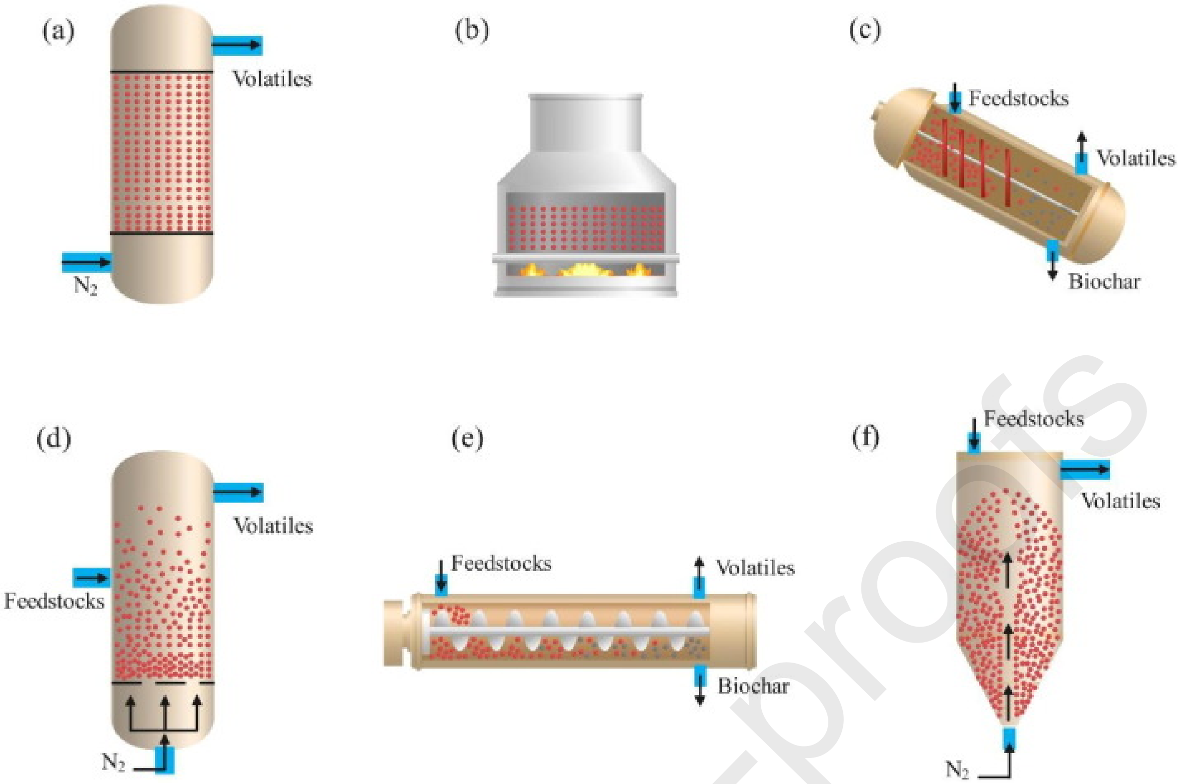

Figure 1. Reactors for biochar production: (a) fixed bed, (b) earthen kiln, (c) rotary kiln, (d) fluidized bed, (e) auger reactor, and (f) spouted bed. Reproduced from the literature (Zhu et al. 2022).

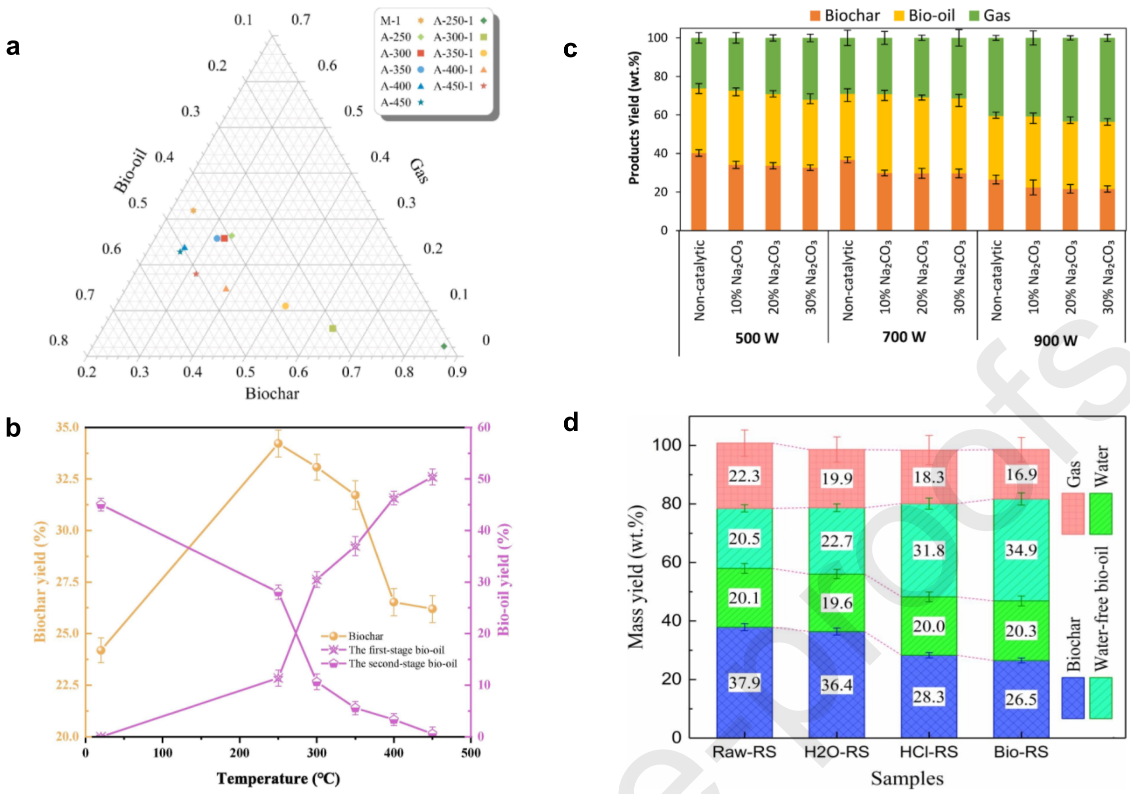

Figure 2. (a) The product distributions of different scenarios (Li et al. 2022). (b) The trend of biochar and bio-oil yields with respect to pyrolysis temperature (Li et al. 2022). (c) The product distribution from catalytic and non-catalytic MWP: the yield of biochar, bio-oil, and gas (Mohmoud Fodah et al. 2021). (d) The product distribution from the processes with different pre-treatment methods (Cen et al. 2019).

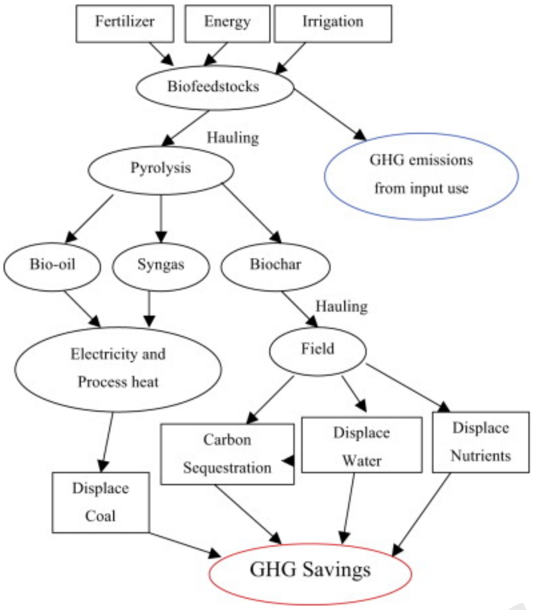

Figure 3. Main elements considered in LCA of biochar production. Reproduced from the literature (Kung et al. 2015).

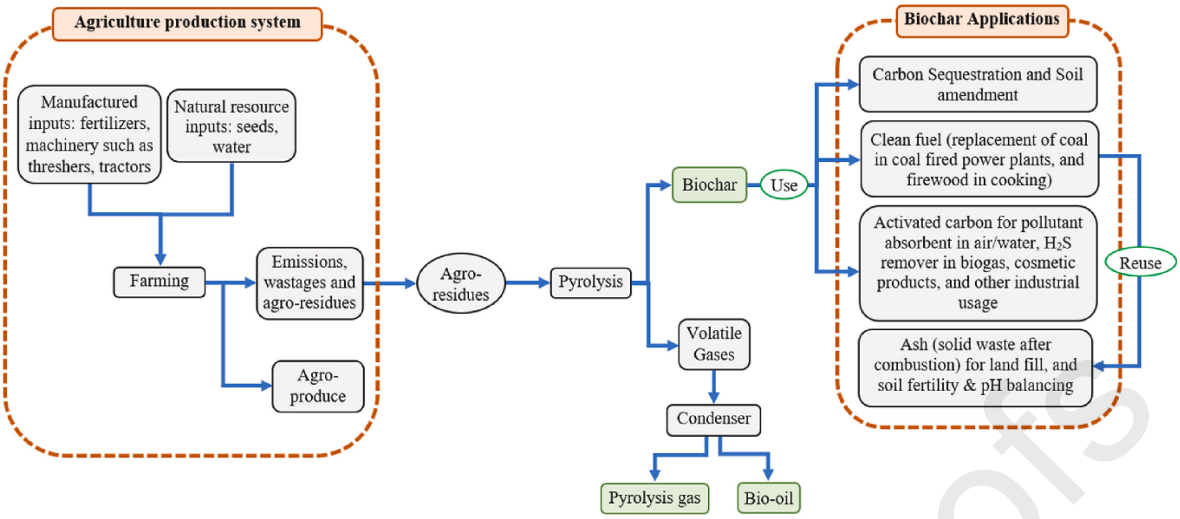

Figure 4. Conversion pathway from crop residue to various applications of biochar. Reproduced from the literature (Anand et al. 2022).

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- Crop residue-derived biochar production reduces global warming potential
- The feedstock composition and pyrolysis temperature strongly regulate biochar yields
- Slow pyrolysis and microwave-assisted pyrolysis suitable for biochar production
- Physical and chemical properties of biochar are critically discussed
- The concept of biochar, bio-oil, and gas nexus is important for sustainability