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Biochar production from slow pyrolysis of biomass under CO_2 atmosphere: A review on the effect of CO_2 medium on biochar production, characterisation, and environmental applications

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Abstract

The replacement of inert gas by CO_2 in pyrolysis has piqued a great deal of interest in recent years due to its numerous positive effects on end products. The reactive nature of CO_2 at higher pyrolysis temperatures (above 700 °C) during pyrolysis improves pyrolytic gas production (H_2, CO, and CH_4) by increasing thermal cracking of tar, inhibiting secondary char formation, and enhancing char gasification, thereby reducing char yield. The existing review articles focus on the impact of CO_2 on tar and gaseous products during pyrolysis, with little information on its impact on biochar production and properties via slow pyrolysis of various organic wastes. Therefore, it is worthwhile to investigate the effect of CO_2 on biochar production during slow pyrolysis for industrial purposes, because CO_2 from flue gas can be used as the pyrolysis gas environment, which can ultimately improve biochar production in terms of economic viability, environmental impact, and modified properties. The goal of this review is to conduct a thorough investigation of the effect of CO_2 atmosphere on slow pyrolysis performance (400–700 °C), with a particular emphasis on biochar yield and properties for environmental and agricultural applications in comparison to inert atmosphere by highlighting the existing challenges and future opportunities.

Key words: Slow pyrolysis; CO_2 atmosphere; biochar yield; biochar properties; agro-environmental applications; biomass

1. Introduction

The rapid expansion of the global population and economy has boosted the transition from non-renewable toward renewable resources. Increasing greenhouse gas (GHG) concentrations in the atmosphere are currently a major concern and carbon dioxide contributes the most to global warming, which has enormous social, environmental, and economic consequences [1, 2]. Therefore, to mitigate the climate issues, a removal of large-scale GHG from the atmosphere is necessary to accomplish the 2021 Glasgow Climate Pact COP26 [3] by keeping alive the 2015 Paris Agreement's goal of limiting the global average temperature rise well below 2 °C with the aim of 1.5 °C [4]. Among the many available negative emissions technologies (NETs), pyrolysis biochar systems are one of the few effective solutions for carbon-negative technology [5]. Biochar produced from the pyrolysis of biomass is an efficient carbon sequestration and GHG emission reduction approach [6].

Biochar is a carbonaceous fine-grained and porous material, produced by thermal decomposition of biomass under oxygen limited conditions [7, 8]. Since the start of the twenty-first century, biochar has been evolved as a prominent research topic in a variety of academic disciplines due to its unique properties, large range of applications, and promising future prospects [9]. Biochar is considered as soil amendment materials that can enhance soil health by retaining nutrients and water and storing carbon [10]. However, their physical, chemical, and biological qualities make biochar an adaptable material that can be utilized in a number of ways [11]. Biochar has a wide range of applications, including heat and electricity generation [9, 12], flue gas purification [13], metallurgical applications [14], use in agricultural [15] and animal husbandry [16], construction material [17], compositing and catalysis [18] and super capacitor electrode [19]. In an effort to reduce greenhouse gas emissions, biochar could be employed as soil supplement to increase soil fertility, enhance plant growth [20], remove or immobilise toxins in soil, water, and air [21].

Slow pyrolysis is considered a promising method for biochar productions among the thermochemical processes [22]. Slow pyrolysis is a thermochemical cracking of organic matters into a wide range of usable products (biochar, bio-oil and producer gas), either in the entire absence of oxidizing agents or with a restricted supply that does not permit gasification to a considerable amount [23, 24]. Each pyrolytic product has its own economic value, product distributions and properties which are highly depended on feedstock type [25] and pyrolysis parameters [26]. New industrial examples of slow pyrolysis focus primarily on biochar synthesis, while also utilizing bio-oil and pyrolytic gas as pyrolysis energy carriers to reach the energetic sustainability [27]. Pyrolysis in general is considered a complex process as it involves both endothermic and exothermic reactions, huge number of factors affecting and wide range of chemical heterogeneity of the feedstocks [22]. Therefore, the optimization of the process parameters, efficiency and products properties are still under investigations and significant efforts have been carried out in the recent past for developing pyrolysis technology to the fully commercial scale. There are numerous methods to improve the usefulness of biochar for desired purposes. Most of the previous lab scale research on slow pyrolysis investigated the effect of feedstock type [6, 28], pyrolysis temperature [29, 30], heating rate [31], pressure [32, 33], and residence time [34, 35] as the main operating variables that affected the char yield and properties, and at the same time an inert gas (mostly nitrogen) has been employed as a pyrolysis medium.

However, on the other hand, CO_2 as a pyrolysis medium has recently been found to affect the biochar yield and properties during the pyrolysis [36-42]. CO_2 pyrolysis has various advantages over traditional pyrolysis, including increased reactivity and conversion of waste feedstocks to pyrolysis products, resulting in greater overall efficiency [43-45]. Recycling and utilizing CO_2 within the pyrolysis process has been proposed as an environmentally friendly and energy-efficient process because it requires no external energy and produces no CO_2 emissions due to its complete recirculation within the integrated pyrolysis process [45].

Available mixed studies showed that pyrolysis in CO_2 led to varying degrees of carbonization, which alter the physicochemical properties of biochar [46, 47]. For example, biochar produced by pyrolysis in CO_2 is more porous and recalcitrant than that produced in N_2. This is significant since pre/post physical/chemical treatment is no longer necessary to tailor the biochar characteristics [42].

Although lab scale studies of CO_2 utilization have been found beneficial for biochar production during slow pyrolysis in terms of its modified physico-chemical properties and thermal efficiency to some extent, however, no boundaries and mechanisms for temperature, heating rate and feedstock type during slow pyrolysis have been defined. In the literature, different behaviour of CO_2 has been reported at various temperatures ranging from 300 to 800 °C for various feedstocks. Therefore, it is critical to distinguish and examine the influence of CO_2 during slow pyrolysis at industrial temperature ranges (400–650 °C) and to investigate the relationship between CO_2 and feedstock type. To the best of author's knowledge, no review study has been found in the literature that offers extensive examinations into the effect of CO_2 atmosphere on biochar productions, mechanisms, and properties during slow pyrolysis. Some review papers in the literature exist that describe the effect of CO_2 on pyrolysis performance, with a greater emphasis on pyrolytic gas and oil rather than biochar [43, 44, 48-50].

Therefore, the purpose of this review is to assess how the CO_2 atmosphere affects the production of biochar using slow pyrolysis at industrial temperatures (400–700 °C). A thorough review of the production, mechanism, and properties of biochar is done based on existing studies, with an emphasis on its environmental and agricultural applications. Furthermore, the motivation of this paper is to fundamentally understand the potential for CO_2 utilization in slow pyrolysis for the production of biochar by utilizing exhaust flue gases or pyrolytic gases to not only make the process feasible, but also to modify the biochar's properties. Lastly, the limitations and future prospects of using CO_2 as a pyrolysis medium are also discussed.

2. Biochar and its potential environmental applications

In this review, only biomass is considered as feedstocks to produce biochar through slow pyrolysis, because they represent social, environmental and economic problems that can be solved through their valorization in second generation biorefinery system. Biochar can be produced from a variety of organic wastes, including municipal organic wastes and agri-industrial residues and its properties are highly dependent on feedstock type and pyrolysis working conditions [51]. Biochar is mostly made up of carbon compounds with traces of hydrogen, oxygen, ash, nitrogen, and sulfur [52]. Through pyrolysis and carbonization, biomass is converted into carbon-rich microporous materials with a well-developed porous structure, a high specific surface area, and a high degree of aromatization [53]. The range of these parameters strongly depends on production conditions and feedstock type, moreover the surface area and total pore volume of biochar can be increased, when a suitable precursor and preferred pyrolysis parameters are chosen [54].

Biochar contains a variety of functional groups, the majority of which are oxygen-containing or alkaline, provide biochar with high absorption, buffering, and ion exchange capacity [55]. High levels of aromatic, alcoholic, phenolic and carboxylic functional groups, and higher carbon contents in biochar increase its stability by increasing its boiling point, making less soluble and resistant to biological and thermochemical degradation [9, 56]. Also, fresh or aged (or partially oxidized) biochar results in different presence of surface functional groups.

The use of biochar in agricultural soils has attracted a lot of interest in the recent past due to its chemical-physical characteristics. The addition of biochar or its composites to soil can modify various soil features, such as physical and chemical composition, microbial activity, soil fertility, and pollution load, and the extent of such effects are closely connected with biochar characteristics [57]. **Fig. 1** highlights the biochar and associated soil properties.

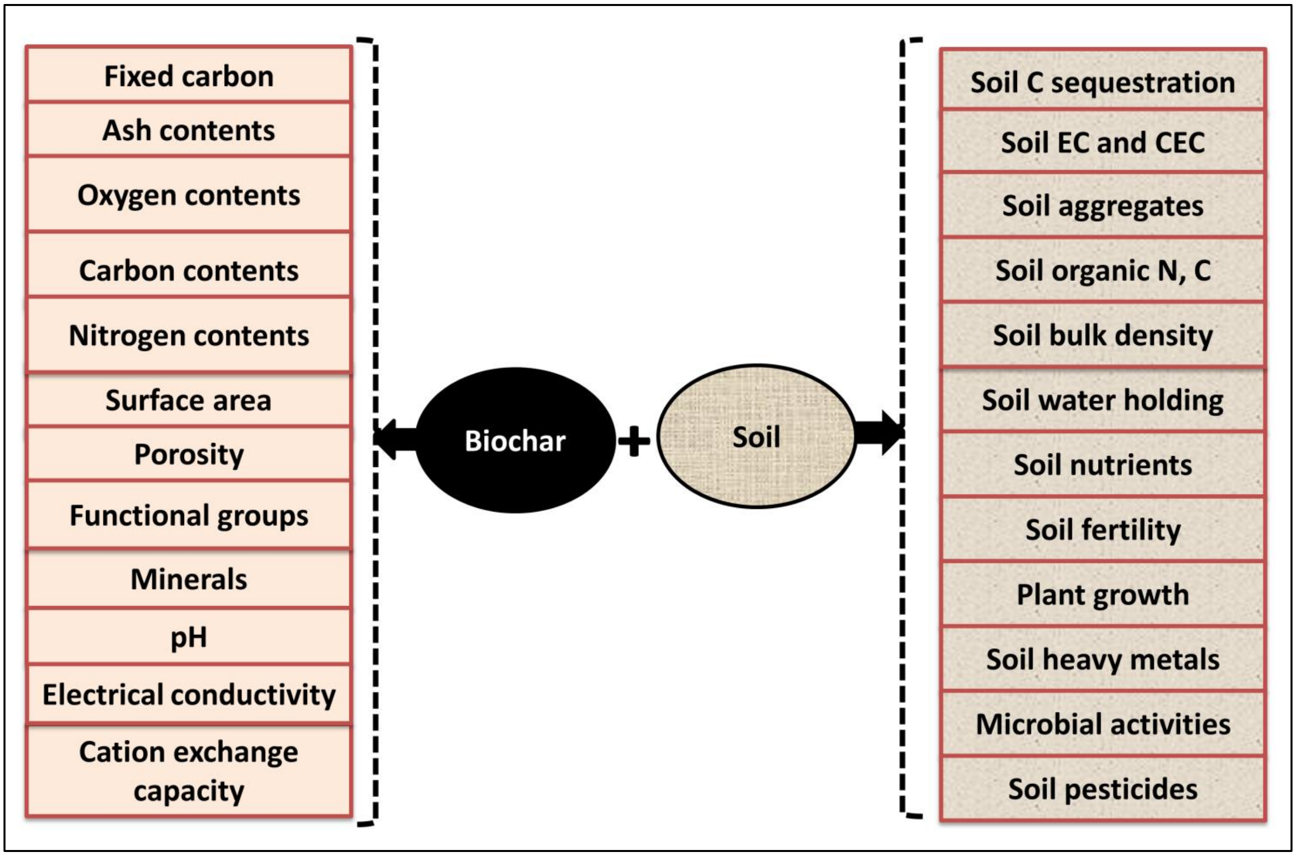

Fig.1. Important properties of biochar with associated soil properties

2.1. Remediation of contaminated soil

The surface area, porosity and functional groups are the important properties of biochar for the removal of heavy metals, organic and inorganic contaminants in the soil. The primary mechanism by which biochar works to remediate soil is adsorption [58]. The biochar adsorption process includes surface complex formation, hydrogen binding, electrostatic attraction, acid-base connection, and pi-pi connections [59-61].

According to Zhang et al [62] research, water hyacinth biochar can successfully adsorb around 90 % of As^{5+}, whereas rice straw biochar had the highest Zn^{2+} adsorption [63]. Such variations in biochar performance may be explained by differences in experimental conditions and feedstock. Moreover, biochar modifications increase its ability to remove heavy metals [64, 65]. Sulphur treated rice husk biochar, for instance, significantly increased the removal of mercury [66]. Biochar addition could also alter the fate of pesticides in the soil due to high pesticide sorption capacity of biochar compared to the original soils. The increased sorption and decreased dissipation of pesticides in the presence of biochar may reduce the risk of environmental contamination and human exposure. Gamiz et al. [67] found that adding biochars (prepared from hardwood species) to the soils successfully adsorbed the Clomazone (CZM) and bispyribac-sodium (BYP) pesticides, that reduce the environmental impact of CMZ and BYP in soil.

Biochar is also considered to reduce the hazardous polycyclic aromatic hydrocarbons (PAHs) in the soil. Addition of wheat straw and sawdust derived biochar showed the significantly reduction of PAHs from petroleum-polluted soil. High molecular weight PAHs with 4-6 rings were much more resistant to biodegradation than low molecular weight PAHs [68].

2.2. Soil carbon sequestration

Carbon sequestration is the storage of carbon in plants, soils, geologic formations, and ocean which explains how organic carbon is assimilated into soils and turned into a long-lived carbon pool that would otherwise be released as CO_2 [69, 70]. Carbon sequestration through biochar has been proposed as method of reducing GHG emissions in the soil through long time storage of carbon. Biochar is thought to sequester carbon primarily through three pathways: 1) biochar itself delivers recalcitrant C into soil; 2) biochar may limit mineralization of native SOC; and 3) biochar increases plant production for atmospheric C capture [71].

Biochar fixed carbon content can be used to predict how long it will last in the soil. High carbon contents are important markers of its aromatic properties, stability against decomposition in soils, and consequently longer carbon retention time in soils amended with biochar [72].

Several studies have been performed to determine how biochar affects soil carbon sequestration [71, 73-75]. For instance, soil organic carbon was encouraged to turn over when carbon from fire was added [76]. On the other side, the biochar addition made from wood sawdust to soil decreased the mineralization of carbon, increasing carbon sequestration [77]. According to Cheng et al. [78] biochar's capability to sequester carbon is attributed to its own carbon content rather than carbon acquired from soil organic matter. Yang et al. [79] investigated that the application of corn residue-derived biochar (30 t ha^{-1}) reduced CH_4 emissions by 132%, increased soil organic carbon sequestration by 16%, and decreased total CO_2 emissions by 18–25% during the first growing season and 19–41% during the second growing season, respectively.

Based on the study of Windeatt et al. [80], considering the global annual production of agricultural products, if all agricultural residues are pyrolyzed into biochar, the biochar yield is estimated to be 3.73×10^{11} kg, and the long term carbon storage potential is equal to 1.5×10^{11} Cy^{-1} (0.55 Pg CO_{2eq} yr^{-1}). Hence, biochar not only sequesters carbon but also reduces soil CO_2 emissions through interaction with the soil. The study of Kan et al. [81] proved that 1.8×10^{3} kg $ha^{-1}y^{-1}$ of biochar, which is equal to 6.97×10^{2} kg ha^{-1} C, can increase soil organic carbon about 4.22×10^{2} kg $ha^{-1}y^{-1}$.

2.3. Soil amendment: fertility and plant growth

Biochar addition to the soils has been found to improve the number of physico-chemical properties of the soil including bulk density, water holding capacity, aggregation, porosity, and hydrophobicity [82, 83]. The applicability of biochar in the soil is regulated by the EU Regulation 2011/2088. In a review study on the effect of biochar on soil’s physical properties, Canqui et al. [84] found that out of 34 tested soils, adding biochar improved wet aggregate stability in 24 soils while having no impact on 10. After biochar application, the proportion of water-stable aggregates increased by 21 % to 226 %, and the mean weight diameter of water-stable aggregates increased by 4 % to 58 %. The biochars produced from slow pyrolysis of biological sludge at 450 °C [85] showed the increase in water-holding capacity from 210.5 g/kg in the raw soil to 234.7, 247.1 and 345.1 g/kg, respectively. Toková et al. [86] discovered that applying 20 t ha^{-1} of biochar produced by slow pyrolysis (at 550 °C for 30 minutes) without fertilizer increased soil porosity by 12 % while decreasing bulk density by 12 %. Furthermore, it has been reported that large biochar particles reduce the bulk density of sandy loam soil more effectively, whereas small biochar particles reduce the bulk density of sandy soil more effectively [87].

The presence of minerals, nutrients, and functional groups gives biochar an alkaline nature that can be used to increase the cation exchange capacity (CEC) of acidic soils and balance the pH [57]. The addition of biochar to soils has also an impact on the metabolic activities of soil microorganisms, which in turn affect the soil quality and plant performance [57, 88]. Studies have revealed that the biochar amendment changed microbial abundance, activity, and community composition, resulting in a more productive microbial community with lower CO_2 and N_2O emissions [89]. In a systemic review highlighting the impact of biochar on soil biota, Pathy et al. [90] concluded that on the soil biota, biochar has both positive and negative effects. Its benefits include shelter for microorganisms, the provision of nutrients to microbes, the modification of microbial habitats, and the alteration of enzymatic activity; however, the use of biochar carries risks such as toxicity of biochar towards microbial population, increased pathogen contaminations, and uncertainty regarding the long-term behavior of biochar.

One of the potential applications of biochar in soil amendment is its positive effects on soil fertility and plant growth [20]. Addition of biochar has been found to improve plant growth by supplying and retaining nutrients by providing either directly nutrients to plants or indirectly by improving the soil environment, thus increasing fertilizer use efficiency [91]. In an eight-year field experiment, Luo et al. [92] that biochar additions significantly influenced the nutrient contents, such as increasing total nitrogen, nitrate nitrogen, ammonium nitrogen, and phosphorus contents in the soil depending on biochar dose and soil type. Yu et al. [20] reviewed the impact of biochar amendment on crop production in problem soils (poor physical, chemical, and biological properties). According to their findings, adding biochar to problem soils is not only an effective but also a cost-effective way to improve their physical, chemical, and biological properties. Biochar has been shown to improve plant growth in multiple defective soils such as soils with physical limitations, acidic soils, alkaline soils, nutrient-deficient soils, salt-affected soils, and metal-contaminated soils. Along with biochar alone, biochar composites also hold out great promise, providing numerous advantages for both agriculture and environmental remediation. Composites made from biochar have a noticeable impact on bulk density and water retention ability.

3. Biochar production through slow pyrolysis

Slow pyrolysis is one of the most utilized approaches to convert number of feedstock materials into biochar, gases, and bio-oils. During slow pyrolysis, the feedstocks are thermally decomposed at temperatures between 300 and 900 °C with little or no oxygen [48], but the industrial applications are normally operating up to 600–650 °C maximum. The degradation of biomass into simple, medium, and longer chain hydrocarbons is turned into liquid, gaseous, and solid products and is separately collected during heating at different temperatures [93]. The process of pyrolysis is often categorized into two types: slow and fast, based on its operational parameters, particularly the heating rate. If it takes significantly longer to heat the feedstock to the peak pyrolysis temperature than the typical reaction time, it is regarded as slow, and vice versa [23]. Slow pyrolysis takes place at lower heating rate (5–10 °C /min) with long vapor residence time (few minutes and a few hours) [25, 94].

Primary and secondary are the two main stages in the slow pyrolysis of biomass. Primary pyrolysis involves the breaks down of biomass into light gases (including CO, CO_2, H_2O, and H_2), tar, char, and mineral ash at relatively low temperatures. Secondary pyrolysis occurs at higher temperatures (>500 °C), where the products of primary pyrolysis, particularly tar, undergo further reactions at higher temperatures and for a longer period of time [95]. During the primary decomposition of biomass, a limited amount of char is produced along with permanent gases and other condensable volatile species, which may then go through heterogeneous secondary decompositions to form more char, condensable volatiles, and permanent gases [96]. The pyrolysis temperature and heating rate are the most important variables influencing yield and the properties of biochar. The effect of pyrolysis temperature and heating rate on biochar yield and properties has been largely investigated in the literature [29, 30, 97-99] and is well understood. A higher pyrolysis temperature and heating rate, produces a lower biochar yield but with a higher proportion of aromatic carbon structures, higher carbon contents and specific surface area which may improve the soil’s physico-chemical characteristics [100]. Numerous studies have shown that the properties of biochar can be altered to satisfy specific requirements, such as improving agro-environmental physicochemical properties, carbon sequestration, or contaminant sorption, typically by managing the pyrolysis temperature and heating rate [34, 97]. Effect of particle size

[101-103] and pressure [104-106] has also been widely investigated in the literature. Pyrolysis atmosphere (medium) is one of the crucial factors that causes changes in the production yield and biochar characteristics e.g., surface area and aromaticity [107]. Several carrier gases (reductive and oxidative) have been employed in the pyrolysis process to investigate their effects on the performance of pyrolytic products these includes CO_2, steam, CO, CH_4, H_2, and mixture of these gases [36-38, 108-110]. It has been discovered that in an impure pyrolysis atmosphere including H_2O, char structure is more developed and disordered (with more carbon active sites), which leads to a greater char reactivity [36]. Pyrolysis of pine sawdust between 400 and 600 °C in H_2 showed a reduction in char yield compared to inert (Ar) atmosphere, demonstrating that H_2 can promote the release of vapors by the reaction of carbon with H_2 at high temperatures which leads to a decrease in char yield [111]. Among all, utilization of CO_2 in pyrolysis has been widely studied due to its potential of energy recovery, positive impacts on products' characteristics and ability to scale up due to the recycling of flue gas [22, 112]. Studies have shown that, CO_2, a weak oxidation agent, in slow pyrolysis increases the CO production, improves the biochar properties, and reduces the net CO_2 emissions [47, 50, 110].

4. Slow pyrolysis in CO_2 atmosphere

Carbon dioxide has been widely used as a pyrolysis medium to enhance the thermal efficiency of pyrolysis because it decomposes the biomass due to its reactive nature at elevated temperatures [50]. Studies in the literature showed the enhanced generation of CO caused by CO_2. Pyrolysis of lignin in CO_2 at higher temperatures (> 550 °C) [113] revealed an increase in the formation of producer gas (H_2 + CO) due to an unknown reaction produced by CO_2 which proceeded concurrently and independently with the dehydrogenation of VOCs (volatile organic carbons), which greatly increased CO production by providing an additional source of C and O.

Jeong et al. [114] found an increased CO production (by a factor of 100) during the pyrolysis of food waste at higher temperature under CO_2 atmosphere. Moreover, studies about tar reduction caused by the addition of CO_2 in pyrolysis have also been done in the literature [115-118]. Briefly, tar reduction is caused by increasing the amount of producer gas through the thermal cracking of VOCs via dehydrogenation; and the direct homogeneous reaction between VOCs and CO_2 via gas phase reactions.

The usefulness of biochar for agronomical applications or adsorbent is currently limited by its physiochemical characteristics which greatly depend on the pyrolysis working conditions. The use of CO_2 in pyrolysis greatly affects the biochar yield and its properties. Yi et al. [119] found during the slow pyrolysis of cellulose, CO_2 significantly improved the secondary condensation reaction, leading to the production of more biochar with a higher C/O ratio and greater thermal stability by encouraging the deoxygenation reactions at all three temperature i.e. 400, 500 and 600 °C. Moreover, by accelerating the deoxygenation and dehydrogenation reactions, CO_2 boosts the carbonization of the aliphatic structures on the surface of the biochar, which increase its aromaticity. CO_2 mainly reacts with groups that have been hydrogenated or oxygenated, producing biochar with a greater specific surface area (maximum up to doubled compared to N_2 pyrolyzed biochar), therefore, enhancing the adsorption capacity of biochar [120]. Biochars prepared form the slow pyrolysis of rice straw under CO_2 [121] showed superior properties for agronomical applications, compared to the one prepared with N_2 pyrolyzed biochars. The improved properties include the thicker walls, more developed pore structures, greater mechanical strength and higher total pore volume and specific surface area. Additionally, compared to N_2, biochars in CO_2 had relatively higher contents of macro-nutrients K, N, and P. During the slow pyrolysis, CO_2 also affects the chemical compositions of the bio-oils; indeed, the bio-oil produced under CO_2 and N_2 atmospheres exhibits differences due to the various reactions that could occur under different atmospheres. According to Lee et al. [122] bio-oil derived from CO_2 slow pyrolysis (400, 500, 600 °C) contained less oxygenated compounds, phenolic compounds, benzene derivatives, and polycyclic aromatic hydrocarbons. This could be because CO_2 inhibits free radical reactions, which stifle cyclization and aromatization reactions, suppressing the formation of those compounds. Similar observations have been reported for the CO_2 slow pyrolysis of banana peel [123] and cattle excreta [124]. Thus, CO_2 can be used to alter the productions and properties of biochar, bio-oil and pyrolytic gas that are necessary for applications, such as surface area, porosity, elemental composition, and chemical functional groups. Consequently, CO_2 slow pyrolysis can be used to create engineered biochar to produce high-value products.

5. Effect of CO_2 on thermal degradations of biomass

To elucidate the interactions between biomass feedstocks and CO_2 during slow pyrolysis, thermogravimetric investigations have been carried out on different feedstocks under CO_2 and N_2 environments including hemicellulose, cellulose, and lignin [125, 126], red seaweed, [40], spent coffee grounds, oak wood, corn stover [126], municipal sludge [127] and microalgal biomass [128].

Fig. 2 (A) depicts the mass loss (TG) and mass loss rate (DTG) curves of hemicellulose, cellulose and lignin under CO_2 environment [125] and with CO_2 atmosphere the decomposition of solid mass was slightly higher compared to N_2 at lower pyrolysis temperatures (300–700 °C), which might be because of the interactions of CO_2 with tars, which hinders the formation of secondary char. For cellulose, the greatest weight loss in a CO_2 atmosphere occurred between 300 and 400 °C (maximum rate of 2.8 wt% /°C at 330 °C). Compared to cellulose, lignin showed a wider temperature range of thermal degradation (200–600 °C) and with a higher solid residual mass (around 38 wt%) under CO_2. Similar findings have been observed by Zhang et al. [129] during the TGA analysis of hemicellulose, cellulose, and lignin. Moreover, the TGA of red seaweed [40], corn stover and oak wood [130] showed nearly the identical mass loss curves in the lower temperature range between 30–600 °C at different heating rates. This finding revealed that CO_2 has a little effect on physical aspects like the onset and end temperatures of biomass thermal breakdown. In a detailed study on the investigation of different biomasses' susceptibility to CO_2-assisted pyrolysis (including microalgae, red seaweed, cellulose, lignin, hemicellulose, spent coffee grounds, corn stover, and oak wood), Lee et al. [126] discovered that all biomasses exhibit a similar thermal degradation rate until 800 °C even at different heating rates proving the minimal impact of CO_2 on physical aspects. Furthermore, despite being thermodynamically favored above 720 °C, the expected Boudouard reaction did not occur, which can be explained by the heterogeneous reaction like slow reaction kinetics between solid phase carbon and gaseous phase of CO_2.

Whereas in **Fig. 2** (B), the TGA of walnut shells under N_2 and CO_2 environments follow the same pattern until 600 °C, specifically with two stages peaks at 280 °C and 340 °C and a slow mass loss stage above 400 °C. However, the effect of CO_2 could be seen at higher temperatures (above 600 °C) where the two peaks at 725 °C and 850 °C represent the char gasification caused by CO_2 [131].

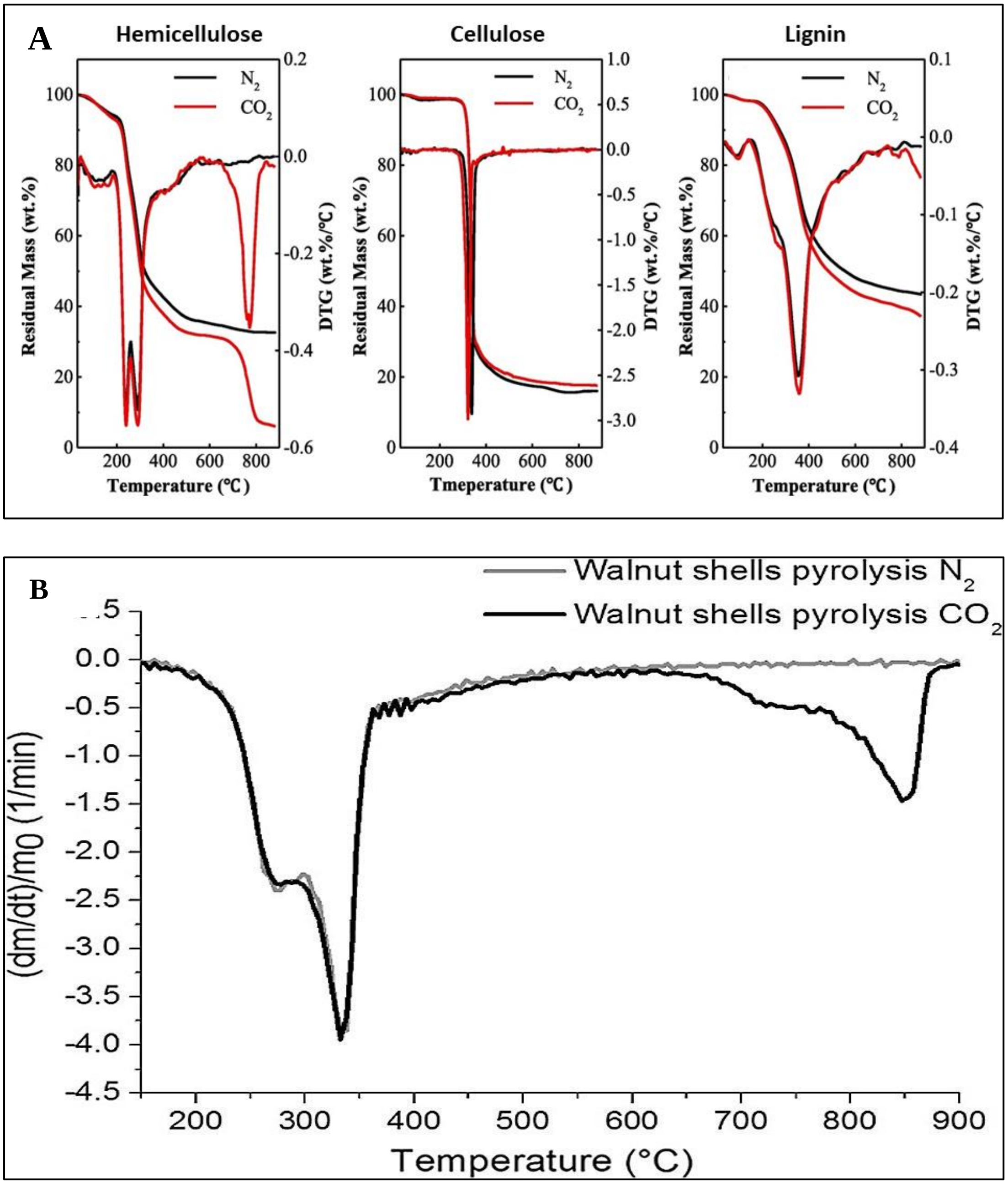

Fig. 2. Thermograms of (A) hemicellulose cellulose and lignin under N_2 and CO_2 [125] and (B) walnut shells under N_2 and CO_2 [131]

When the char comes into contact with CO_2 at higher temperatures (> 700 °C) and for an extended period of time, a Boudouard reaction may occur, which results in the formation of CO

[132]. Based on the above mixed information about the effect of CO_2 on thermal degradation of biomass in TGA, it should be noted that TGA analysis mostly provides the information about the physical aspects of CO_2 but no difference in chemical aspects providing only a limited knowledge of how CO_2 affects biomass pyrolysis.

6. Effect of CO_2 on biochar yield

Table 1 compares the effect of CO_2 environment on biochar yields from the slow pyrolysis of several feedstocks in comparison to inert atmosphere within the temperature range between 300–700 °C. To avoid the effect of the well-known Boudouard reaction (char gasification activates at 720 °C), this work limits the temperature range of slow pyrolysis to 700 °C in order to understand the mechanistic roles of CO_2 during pyrolysis of various feedstocks.

As shown in the **Table 1**, literature study shows the mixed effect of CO_2 on biochar yield during the slow pyrolysis of various feedstocks. Therefore, the influence of CO_2 on biochar yield can be broadly divided into two categories based on the temperature range of slow pyrolysis, one is industrial pyrolysis at medium temperature range (300–600 °C) and the other is higher temperature range (600–800 °C).

Within the temperature range between 400–600 °C, almost all of studies reported that the CO_2 increases the biochar yield [42, 123, 125, 133].

Feedstock type	Pyrolysis Conditions				Biochar yield wt.%	Ref
	Temperature °C	Heating rate °C/min	Residence time min	Environment N_2/CO_2		
Lignin	400	5	-	N_2	56.0	[134]
				CO_2	56.8	
	500	5	-	N_2	52.8	
				CO_2	53.8	
	600	5	-	N_2	49.0	
				CO_2	51.0	
	700	5	-	N_2	47.4	
				CO_2	48.6	
Wheat straw	300	20	20	N_2	54.375	[39]
				CO_2	55.708	
	400	20	20	N_2	40.472	
				CO_2	39.042	
	500	20	20	N_2	35.625	
				CO_2	34.833	

	600	20	20	N_2	35.361	
				CO_2	35.014	
Sawdust	300	5	240	N_2	38.2 ± 0.8	[107]
				CO_2	40.6 ± 1.4	
	700	5	240	N_2	19.4 ± 2.0	
				CO_2	21.3 ± 2.1	
Rice straw	300	5	240	N_2	37.4 ± 0.7	
				CO_2	38.8 ± 1.7	
	700	5	240	N_2	12.3 ± 2.7	
				CO_2	13.3 ± 0.7	
Spent coffee grounds	300	5	240	N_2	46.2 ± 2.9	
				CO_2	48.5 ± 0.8	
	700	5	240	N_2	20.3 ± 0.6	
				CO_2	23.1 ± 0.4	
Oil palm fiber	400	10	30	N_2	37	[135]
				CO_2	36	

	450	10	30	N_2	34	
				CO_2	32.3	
	500	10	30	N_2	32	
				CO_2	32	
Oil palm fiber pellets	400	10	30	N_2	39	
				CO_2	39	
	450	10	30	N_2	34	
				CO_2	35	
	500	10	30	N_2	32.8	
				CO_2	34	
Rice straw	300	20	60	N_2	39.2	[133]
				CO_2	47.0	
	350	20	60	N_2	35.6	
				CO_2	42.0	
	400	20	60	N_2	34.2	

				CO_2	38.0	
	450	20	60	N_2	33.2	
				CO_2	37.0	
Biosolids	400	35	60	N_2	54.7 ± 0.3	[136]
				CO_2	54.1 ± 0.1	
	500	35	60	N_2	50.3 ± 1.5	
				CO_2	47.5 ± 0.5	
	600	35	60	N_2	46.2 ± 0.1	
				CO_2	46.2 ± 0.1	
Banana peel	600	10	-	N_2	36.21	[123]
			-	CO_2	36.84	
Orange peel	690	10	-	N_2	26.087	[137]
				CO_2	27.270	
Oil sludge	600	10	30	N_2	54.43	[138]
				CO_2	50.19	
Bio-oil distillation residue	400	20	30	N_2	44.62	[139]

				CO_2	49.21	
	500	20	30	N_2	36.79	
				CO_2	40.81	
	600	20	30	N_2	33.60	
				CO_2	33.55	
	700	20	30	N_2	31.70	
				CO_2	18.97	
Sewage sludge	700	10	180	N_2	44.4	[140]
				CO_2	40.3	
Rice straw chips	400	20	20	N_2	40.42	[121]
				CO_2	40.35	
	600	20	20	N_2	33.49	
				CO_2	33.17	

Table 1. Effect of CO_2 and N_2 atmospheres on biochar yield from slow pyrolysis of various feedstocks

Study of the slow pyrolysis of hemicellulose, cellulose and lignin under CO_2 atmosphere [125] showed that, compared to nitrogen environment, the biochar yield of all three biomass components under CO_2 atmosphere was slightly higher below 600 °C pyrolysis temperature. At 550 °C, for example, the biochar yield under CO_2 atmosphere was 32 wt% from hemicellulose, 21 wt% from cellulose, and 42 wt% from lignin, whereas at similar conditions, nitrogen atmosphere yielded 26 wt%, 18 wt%, and 38 wt% from hemicellulose, cellulose, and lignin respectively. On the other hand compared to nitrogen, the liquid yield under CO_2 was higher and the gas yield was lower from all lignocellulosic components. The similar trend of increased biochar and liquid yield was observed by Yi et al. [119, 134] during the slow pyrolysis of cellulose and lignin under both atmopsheres at temperature, 400, 500 and 600 °C and Wang et al. [141] during the slow pyrolysis of cellulose at 350 °C.

Thus, based on existing individual studies of slow pyrolysis (300–600 °C) of hemicellulose, cellulose, and lignin, it can be concluded that CO_2 as the atmosphere inhibits the cracking or encourages the secondary condensation of volatiles, facilitating the formation of biochar and bio-oil while inhibiting the formation of gases via cracking or gasification reactions. This could be due to the fact that the high CO_2 partial pressure outside the biomass particle is not favorable to the diffusion of small molecule gas products such as CO_2; as a result, the volatile cracking reaction rate was lowered. Moreover, in the reactor, uncondensed gas and CO_2 could react to produce condensed oil. If CO_2 encourages defragmentation reactions to produce repolymerised products, the production of gas decreases while the yield of biochar increases. Nevertheless, more study and clarification are needed to determine how exactly CO_2, a reactive gas, contributes to the synthesis of biochar and development of volatiles at temperatures below 600 °C. Aside from the individual pyrolytic characteristics of the three components mentioned above, many lignocellulosic biomasses showed a similar trend of increased biochar and liquid products and decreased gaseous products during the slow pyrolysis (under CO_2) within the temperature range of 400 to 600 °C, such as oil palm fiber and its pellets [135], rice straw [107, 133], seed shell and corncob [142], sawdust and spent coffee grounds [107]. Furthermore, similar trend have also been reported for other waste feedstocks such as waste activated sludge [143], municipal sludge [144], bio-oil distillation residue [139]. On the other side, some of the experiments experienced the slight reduction of biochar yield under CO_2 in comparison with N_2 atmosphere, such as wheat straw at 500 °C [39], oil palm fiber at 450 °C [135] and biosolids at 500 °C [136] revealing that, along with temperature and heating rate, influence of CO_2 also depends upon feedstock type and other operating conditions, however, due to a lack of available studies and the minor effect of CO_2 on biochar yield, it is not possible to draw firm conclusions about the feedstock type and CO_2.

Looking on the effect of CO_2 on biochar yield during slow pyrolysis at higher temperature range (600–800 °C), again slow pyrolysis of lignin at 700 °C resulted in higher biochar yield (2.5 % increased) under CO_2 atmosphere compared to N_2 environment [134]. Similar trend of increased biochar yield was observed during the slow pyrolysis at 700 °C for sawdust, rice straw and spent coffee grounds [107] and orange peel [137]. On the contrary, non-lignocellulosic biomass such as bio-oil distillation residue [139] and sewage sludge [140] showed reduced biochar yield under CO_2 atmosphere at 700 °C compared to nitrogen pyrolysis. The possible effects on CO_2 during slow pyrolysis at lower temperature (400–600 °C) and higher temperature (600–800 °C) are highlighted in **Fig. 3.**

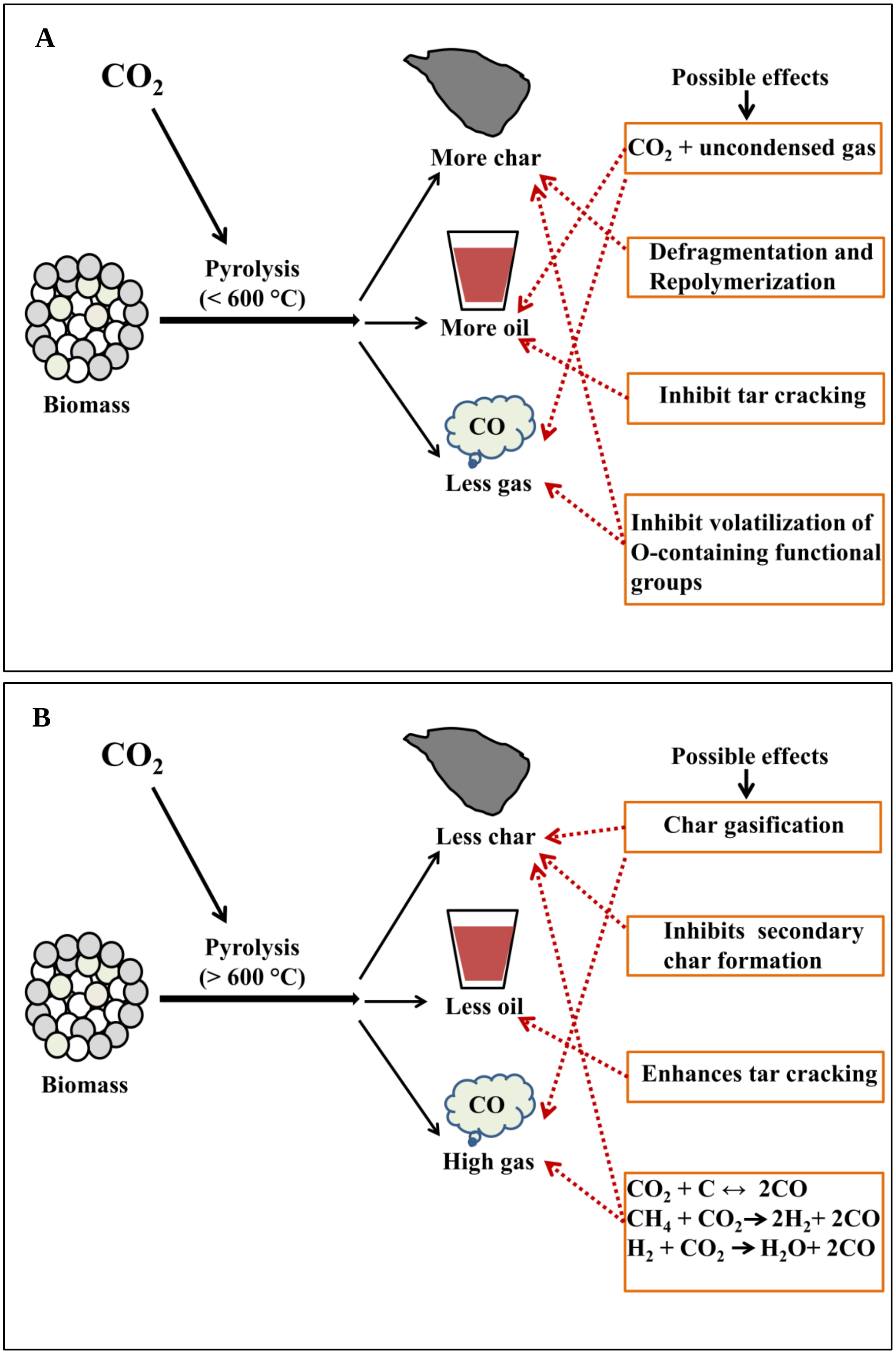

Fig. 3. Possible effects of CO_2 on slow pyrolysis at (A) lower temperature range (300–600 °C) and (B) higher temperature range (600–800°C)

7. Effect of CO_2 on biochar properties

Pyrolysis and/or gasification under CO_2 atmosphere for various biomass feedstocks at higher temperatures (> 700 °C) have been widely studied in the literature [48, 50], and it is well known fact that at higher temperatures, CO_2 causes char gasification, resulting in biochar with higher surface area, porosity, and larger pore sizes due to the reactive nature of CO_2 at elevated temperatures. In this study, we reviewed the chemical, physical, and structural properties of biochar produced by slow pyrolysis in CO_2 and N_2 atmospheres at temperatures ranging from 300 to 700 °C.

7.1. Surface area and porosity

The positive correlation between CO_2 and surface area and porosity of biochar has been reported by several researchers in the literature [42, 115, 121, 142, 145, 146]. **Table 2** compares the specific surface area and pore volume of different biochars produced by slow pyrolysis at various temperatures and heating rates in N_2 and CO_2 atmospheres. Almost all reported studies showed an enhanced specific surface area of biochars under CO_2 in comparison to N_2 pyrolyzed biochars within the temperature range between 400 and 700 °C. The degree of enhancement largely depends on pyrolysis peak temperature and feedstock type.

At pyrolysis temperature of 400 °C, biochar derived from rice straw chips [121] did not show any significant difference in specific surface area, pore volume and pore size between the CO_2 and N_2 atmosphere. On the other hand, non-lignocellulosic biomass such as biosolids [136], municipal sludge [144] and sewage sludge [146] showed slight increase in surface area under CO_2 atmosphere in comparison with N_2 pyrolyzed chars. However, at higher temperature between 500 and 700 °C, utilization of CO_2 significantly increased the specific surface area, pore volume and size. At 500 °C, compared to nitrogen environment, CO_2 resulted in 2.8% of increase of surface area derived from municipal sludge [144] and 71.42% of increased surface area of biochar from biosolids [136]. Moreover, at 550 °C, Salicornia bigelovii derived biochar possessed 12 times greater specific surface area than nitrogen pyrolyzed biochar [147].

To study the influence of CO_2 on surface area and porosity of the developed biochar from the slow pyrolysis of five distinct biomasses, Kim et al. [145] proved that the use of CO_2 in the pyrolysis process increased the surface area and pore volume of biochar. For example, the BET (Brunauer–Emmett–Teller) surface area and total pore volume of oak-wood-derived biochar produced from slow pyrolysis at 680 °C in the CO_2 atmosphere were 463.6 m^2 g^{-1} and 106.5 m^3 g^{-1}, approximately twice as large as the biochar produced in the N_2 atmosphere, which had 231.2 m^2 g^{-1} and 53.1 m^3 g^{-1}, respectively. Lee et al. [115] highlighted the role of CO_2 on the development of pores on the surface of the biochar produced from slow pyrolysis at 700 °C. Biochar possessed higher surface area (93 m^2 g^{-1}) under a CO_2 atmosphere compared to a N_2 atmosphere (85 m^2 g^{-1}). Kim et al [145] studied the influence of CO_2 on the surface properties of biochars produced from the slow pyrolysis of various biomasses (grass, oak wood, cellulose, xylan and lignin) at 680 °C. They observed that the use of CO_2 significantly increased the BET surface area and total pore volume of all biochars except cellulose. Among them, grass showed the highest (223%) increased of surface area compared to N_2 pyrolyzed, followed by oak wood (100%), xylan (18%) and lignin (8%), respectively, revealing the strong dependency on feedstock type. Similarly, biochar produced from the slow pyrolysis of rice husk at 700 °C [110] resulted in more porous biochar with 14% and 11% larger surface area and total pore volume compared to biochar produced under N_2. Similar trend of increased surface area and pore volume of biochar in CO_2 atmosphere during the slow pyrolysis has been reported for various feedstocks including red pepper stalk at 650 °C [42], rice straw at 600 °C [121], municipal solid waste pellets at 700 °C [117], cellulose at 700 °C [119], red seaweed at 700 °C [40], rice straw, spent coffee grounds and sawdust at 700 °C [107].

During pyrolysis under inert environment, when biomass materials are devolatilized, porosity is created in the biochars, producing particles that essentially have a micro-macropore structure. Therefore, devolatilization is the main cause of porous structure and is more intense at higher temperatures, making the char more porous [148]. As reported above, changing the pyrolysis atmosphere from inert to CO_2, results in biochar with increased surface area and porosity during slow pyrolysis at temperatures ranging from 400 to 700 °C, with the profound effect being greater at higher temperatures. Similarly, the majority of studies revealed that CO_2 atmosphere improved the development of porosity in the range of micropores, mesopores, and macropores.

The mechanism of increased surface area and porosity particularly at lower pyrolysis temperature is still not fully understood. According to Lee et al. [115], the heterogeneous reaction between CO_2 and the sample surface may account for the higher surface area in CO_2 atmosphere compared to inert atmosphere. The effect of CO_2 on morphological changes of biochar have been linked to the gasification effect of CO_2 during pyrolysis by several researchers [42, 146], CO_2 as a weak oxidant agent, causes additional formation and release of volatile matters and pores due to oxidation of biochars which ultimately results in modified porosity [110]. However, as reported in section 6, within the temperature range between 400 and 700 °C, biochar yield did not show any major effect under CO_2 which can justify the gasification effect of CO_2 during slow pyrolysis at lower temperature ($\leq$ 700 °C). Moreover, according to Cho et al. [46], the influence of CO_2 would have a hierarchical order; first, the unknown reactions between CO_2 and the volatile organic carbons (VOCs) evolved from the thermal degradation of the sample are triggered, and then CO_2 can selectively trigger the morphological modification of biochar after VOCs are depleted.

Along with temperature, the influence of CO_2 on surface area is also depends on type of feedstocks. At similar pyrolysis conditions cellulose biochar did not show difference in surface area between the two atmopsheres, however, hemicellulose showed the highest increased (18%) surface area followed by lignin (8%) which was further proved from the biochars produced from grass and oak wood [145]. The similar trend could also be observed for spent coffee grounds (SCG), rice straw (RS) and sawdust (SD) [107] where at similar pyrolysis conditions, enhancement of surface area under CO_2 atmosphere was greater for rice straw followed by spent coffee grounds and sawdust due to higher content of hemicellulose and lignin in RS followed by SCG and SD. Therefore it is safe to conclude that biomass contains higher amount hemicellulose and lignin would produce more porous biochar under CO_2 compared to higher cellulose contained biomass.

Feedstock type	Pyrolysis conditions				Surface area (m^2/g)	Total Pore volume (cm^3/ g)	Avg. Pore size (nm)	Ref.
	Temperature (°C)	Residence time (min)	Heating rate (°C/min)	Environment (N_2/CO_2)				
Biosolids	400	60	35	N_2	7.6	0.048	9.76	[136]
				CO_2	11.1	0.060	9.70	
	500	60	35	N_2	17.5	0.071	9.66	
				CO_2	30	0.058	9.38	
	600	60	35	N_2	32	0.058	9.35	
				CO_2	45	0.056	8.80	
Wheat straw (^{15}N content =100%)	300	20	20	N_2	15.27	0.0300	-	[39]
				CO_2	13.41	0.0251	-	
	400	20	20	N_2	39.59	0.0504	-	
				CO_2	23.32	0.0424	-	
	500	20	20	N_2	43.31	0.0549	-	
				CO_2	41.92	0.0486	-	
	600	20	20	N_2	52.68	0.0587	-	
				CO_2	61.87	0.0569	-	

Cellulose	680	6	10	N_2	506.94	1.6679	116.47	[145]
				CO_2	507.53	1.6643	116.61	
Xylan	680	6	10	N_2	340.43	2.0224	78.216	
				CO_2	402.35	1.6324	92.441	
Lignin	680	6	10	N_2	299.97	1.6624	68.918	
				CO_2	325.85	1.6365	74.865	
Grass	680	6	10	N_2	6.5783	1.5114	13.83	
				CO_2	21.253	4.8829	13.545	
Oak wood	680	6	10	N_2	231.15	1.9709	53.108	
				CO_2	463.58	1.9969	106.51	
Pine sawdust briquettes	600	30	20	0% CO_2	313.51	1.461	-	[149]
				10% CO_2	337.67	1.850	-	
				30% CO_2	449.37	1.928	-	
				60% CO_2	465.27	2.031	-	
				100% CO_2	478.81	2.033	-	
Rice straw chips	300	20	20	N_2	1.809	0.00670	14.807	[121]

				CO_2	2.105	0.00957	18.178	
	400	20	20	N_2	4.649	0.0142	12.242	
				CO_2	4.985	0.0146	11.684	
	600	20	20	N_2	10.273	0.0148	5.613	
				CO_2	13.511	0.0158	4.673	
Red pepper stalk	650	-	10	N_2	32.46	0.02	3.79	[42]
				CO_2	109.15	0.09	2.64	
Sewage sludge	650	30	20	N_2	15.0	-	-	[146]
				CO_2	35.0	-	-	
Rice husk	700	-	10	N_2	156.2	0.109	2.7	[110]
				CO_2	178.4	0.121	2.8	
Waste activated sludge	600	40	-	N_2	22.02	0.032	0.93	[143]
				CO_2	19.54	0.024	3.43	
Cellulose	700	-	5	N_2	255.91	0.183	2.86	[119]
				CO_2	269.64	0.2216	3.28	
Rice straw	700	240	5	N_2	327.36	-	-	[107]

				CO_2	393.12	-	-
Spent coffee grounds	700	240	5	N_2	79.91	-	-
				CO_2	86.69	-	-
Sawdust	700	240	5	N_2	541.1	-	-
				CO_2	561.62	-	-

Table 2. Effect of CO_2 and N_2 environments on biochar surface area and pore volume

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7.2. Elemental compositions

Table 3 shows the effect of CO_2 on the elemental compositions of various biochars derived from slow pyrolysis of different biomass feedstocks.

The biochar derived from slow pyrolysis of cellulose under CO_2 atmosphere [119] showed higher carbon content than that produced under N_2 atmosphere at all temperatures (400, 500, and 600 °C), especially at 500 and 600 °C. For example, the carbon content of biochar produced in CO_2 (at 500 °C) was 9.96 % higher while the O content was lower by 36.68 % than that of biochar produced in N_2. Furthermore, biochar produced under CO_2 conditions had higher C/H and C/O ratios than biochar produced under N_2 conditions. This implies that CO_2 is responsible for producing more aromatic and thermally stable biochar. During the slow pyrolysis of hemicellulose, cellulose and lignin [125], it was discovered that for hemicellulose, the O/C ratio of CO_2 derived biochar was lower compared to N_2 derived biochar, indicating that the addition of CO_2 during the slow pyrolysis process is advantageous for the removal of oxygen in bio-char. Cellulose derived biochar under CO_2 atmosphere showed similar H/C and O/C like that of N_2 derived char. The atomic ratio of lignin char varied similarly to that of cellulose; however, the value of O/C in the bio-char under CO_2 was significantly lower than that under N_2. Similar trend of increased carbon contents and reduced O contents was observed during the pyrolysis of pine sawdust briquettes [149] and rice straw [107]. On the contrary several studies showed opposite trend (reduced carbon and increased O contents) in biochar produced under CO_2 atmosphere [42, 121, 135, 136]. Study of the slow pyrolysis of red peeper stalk at 650 °C [42] demonstrated that biochars prepared under CO_2 and N_2 atmosphere had a similar molar H/C ratio indicating that both are similarly aromatic. Nevertheless, the O/C molar ratios of CO_2 biochar (0.10) and nitrogen biochar (0.7) indicate that CO_2 derived biochar is probably more hydrophilic and polar than nitrogen induced biochar. Thus, the effect of CO_2 on elemental compositions is also strongly correlated with the feedstock type.

Feedstock type	Pyrolysis conditions				Ash (%)	C (%)	H (%)	O (%)	N (%)	H/C	O/C	Ref
	Temperature (°C)	Residence time (min)	Heating rate (°C/min)	Environment (N_2/CO_2)								
Pine sawdust briquettes	600	30	20	0% CO_2	3.92	87.81	3.07	7.06	2.06	-	-	[149]
				10% CO_2	4.05	88.92	3.48	5.97	1.63	-	-	
				30% CO_2	4.20	91.13	2.65	4.93	1.29	-	-	
				60% CO_2	4.36	91.91	2.41	4.65	1.03	-	-	
				100% CO_2	5.04	93.51	1.65	3.93	0.92	-	-	
Rice straw chips	300	20	20	N_2	-	45.73	4.08	44.64	1.68	-	-	[121]
				CO_2	-	44.35	3.99	45.56	1.65	-	-	
	400	20	20	N_2	-	48.05	2.71	41.92	1.42	-	-	
				CO_2	-	46.64	2.49	43.03	1.48	-	-	
	600	20	20	N_2	-	47.80	1.24	42.83	1.04	-	-	
				CO_2	-	47.03	1.05	43.67	1.13	-	-	
Cellulose	400	0	5	N_2	-	71.3	3.3	25.4	-	-	-	[119]
				CO_2	-	72.6	3.3	24.1	-	-	-	
	500	0	5	N_2	-	77.3	2.9	19.9	-	-	-	

				CO_2	-	85.0	2.5	12.6	-	-	-	
	600	0	5	N_2	-	79.2	2.8	18.0	-	-	-	
				CO_2	-	86.0	2.5	11.5	-	-	-	
Red peeper stalk	650	-	10	N_2	9.30	86.63	2.42	8.34	2.62			[42]
		-	10	CO_2	11.91	83.85	2.22	11.36	2.56	-	-	
Sawdust	700	240	5	N_2	-	90.6	1.1	3.1	-	-	-	[107]
				CO_2	-	91.0	1.2	3.3	-	-	-	
Rice straw	700	240	5	N_2	-	54.3	0.9	5.1	-	-	-	
				CO_2	-	58.5	0.9	6.3	-	-	-	
Spent coffee grounds	700	240	5	N_2	-	84.0	1.1	4.6	-	-	-	
				CO_2	-	84.1	1.2	5.0	-	-	-	
Biosolids	400	60	35	N_2	53.10	21.44	1.68	20.43	3.34	0.94	0.72	[136]
				CO_2	55.73	20.64	1.44	17.99	3.19	0.83	0.65	
	500	60	35	N_2	62.99	16.29	0.38	17.18	2.63	0.17	0.82	
				CO_2	61.73	14.23	0.27	21.25	2.37	0.23	1.12	
	600	60	35	N_2	64.25	14.18	0.23	18.48	2.02	0.32	0.98	

				CO_2	64.27	13.24	0.24	20.16	2.09	0.21	1.14	
Oil palm fiber	400	30	10	N_2	-	53.57	2.48	42.90	1.06	-	-	[135]
				CO_2	-	53.51	2.75	42.56	1.18	-	-	
	450	30	10	N_2	-	54.37	2.09	42.26	1.28	-	-	
				CO_2	-	53.70	2.45	42.51	1.35	-	-	
	500	30	10	N_2	-	56.85	2.11	39.72	1.33	-	-	
				CO_2	-	55.44	2.28	40.78	1.51	-	-	
Salicornia bigelovii	550	20	20	N_2	20	51.09	2.42	20.91	5.51	0.57	0.31	[147]
				CO_2	18	57.6	2.52	6.26	6.26	0.53	0.2	

Table 3. Effect of CO_2 and N_2 environments on elemental compositions of biochars derived from the slow pyrolysis of various feedstocks

7.3. Ash contents and pH

The influence of CO_2 on ash content, pH, electrical conductivity and nutrients and mineral contents of biochar are shown in **Table 3** and **Table 4**.

At similar pyrolysis conditions, ash contents in biochars produced from CO_2 atmosphere were always higher than those produced in nitrogen atmosphere and is proportional to the pyrolysis temperature [42, 136, 147, 149], indicating the gasification effect of CO_2. However, despite increases in ash content, the pH of biochars produced in CO_2 atmosphere was always lower than that of biochars produced in N_2 atmosphere, as reported by almost all available studies [42, 136, 150], and could be advantageous in terms of using CO_2 to control the acidity/alkalinity of biochar based on applications [42]. For example, at similar pyrolysis circumstances, the pH values of biosolids derived biochar produced in a CO_2 environment were about 2 units lower than those produced in a nitrogen atmosphere [136]. The lower band intensity for -OH groups in CO_2 (compared to N_2) indicated that CO_2 increased the rupture of hydroxyl group. Furthermore, the biochar generated in a CO_2 environment had more ketones and acidic groups at higher temperatures, explaining the biochar's slightly acidic to neutral pH in CO_2 media.

Feedstock type	Pyrolysis conditions				pH	EC (µS cm^{-1})	CEC (cmol kg^{-1})	Ca (mg/kg)	Mg (mg/kg)	Na (mg/kg)	K (mg/kg)	Ref.
	Temperature (°C)	Residence time (min)	Heating rate (°C/min)	Environment (N_2/CO_2)								
Red peeper stalk	650	-	10	N_2	12.19	200	-	-	-	-	-	[42]
		-		CO_2	9.50	110	-	-	-	-	-	
Biosolids	400	60	35	N_2	7.47	72	26.30	-	-	-	-	[136]
				CO_2	6.53	61	28.48	-	-	-	-	
	500			N_2	9.92	167	34.73	-	-	-	-	
				CO_2	7.34	131	33.13	-	-	-	-	
	600			N_2	11.26	406	47.44	-	-	-	-	
				CO_2	8.08	144	36.55	-	-	-	-	
Sewage sludge	500	180	10	N_2	9.4	2300	-	-	-	-	-	[150]
				CO_2	9.2	2500	-	-	-	-	-	
	600			N_2	12.1	4800	-	-	-	-	-	
				CO_2	9.5	1700	-	-	-	-	-	
	700			N_2	2.4	9000	-	-	-	-	-	
				CO_2	9.8	1100	-	-	-	-	-	

Sawdust	300	240	5	N_2	-	-	-	1817.6	238.9	292.2	424.2	[107]
				CO_2	-	-	-	1511.4	193.8	246.2	305.4	
	700			N_2	-	-	-	1628.7	169.9	1251.9	577.2	
				CO_2	-	-	-	2235.4	219.0	316.7	412.1	
Rice straw	300	240	5	N_2	-	-	-	5792.7	2353.8	556.1	15299.0	
				CO_2	-	-	-	5552.1	2382.2	583.1	15235.0	
	700			N_2	-	-	-	10139.3	5214.7	753.8	19127.0	
				CO_2	-	-	-	10269.9	4431.2	1436.7	18203.6	
Spent coffee grounds	300	240	5	N_2	-	-	-	1086.9	1017.5	451.6	7842.8	
				CO_2	-	-	-	1182.2	1010.8	1568.9	8948.1	
	700			N_2	-	-	-	1237.9	753.9	296.4	3590.4	
				CO_2	-	-	-	1088.2	666.8	259.5	3179.2	

Table 4. Effect of CO_2 and N_2 environments on pH, electrical conductivity and nutrient contents of biochars derived from the slow pyrolysis of various feedstocks

7.4. Electrical conductivity and cation exchange capacity

About the effect of CO_2 on electrical conductivity (EC) and cation exchange capacity (CEC) of biochars, only few studies have been found in the literature [42, 136, 150]. Existing studies show that CO_2 significantly reduces the electrical conductivity and cation exchange capacity of biochars when compared to N_2 atmopsheres. Biosolids-derived biochars produced under CO_2 atmosphere had around 100 µS/cm lower EC values than those produced under N_2 atmosphere were connected to lower number of salts (calcite, iron phosphate hydroxide, and magnesium calcite) in CO_2 atmosphere biochars [136]. Similar findings were observed for sewage sludge and red pepper stalk derived biochars [42, 150].

7.5. Nutrients and mineral contents

Utilization of CO_2 has also been found to affect the nutrients and mineral contents in biochar produced from slow pyrolysis. Tan et al. [121] found the slight increment of N and K and P in CO_2 pyrolyzed biochar. For instance, biochar produced under CO_2 atmosphere at 400 °C contained 4.11% N, 0.46% P and 11.40% K, while biochar produced under N_2 atmosphere at similar temperature reached 3.89% N, 0.45% P and 11.38% K, respectively.

Considering nitrogen as a key element in improving soil fertility and plant growth Tan et al. [151] used the ^{15}N tracer method to examine how pyrolysis atmosphere (CO_2 and N_2) affect the distribution of nitrogen in the biomass-biochar-plant system (**Fig. 4**). They found that compared to biochar produced in a N_2 environment, biochar produced through CO_2 pyrolysis resulted in a larger amount of biochar ^{15}N in the soil and plants. It suggests that the biochar produced in a CO_2 atmosphere has a higher concentration of inorganic nitrogen and organic nitrogen which can be quickly converted into $NH4^+$-N and NO_3^--N and therefore improve soil fertility. Furthermore, the higher distribution of ^{15}N in the plants and soil from the biochar indicates that a significant amount of N was released from the biochar at a high rate of N release. As a result, the N in the biochar made in a CO_2 atmosphere has higher release capacity and it can be employed by plants in the soil-plant system more effectively. This might be due to the more volatiles and acid functional groups present in biochar produced under CO_2 atmosphere at lower temperatures, that can release more N-containing nutrients that can be taken and utilized by plants, since the release of N from biochar is strongly affected by the content of volatiles and acid functional groups present in it [152]. Similar findings have been reported by Liu et al. [153] during the investigation of the influence of rice straw derived biochars (produced by slow pyrolysis at 400 °C in N_2 and CO_2 atmospheres) on biochar nitrogen conversion in a 'preparation-application' system, and response of its transportation in plants.

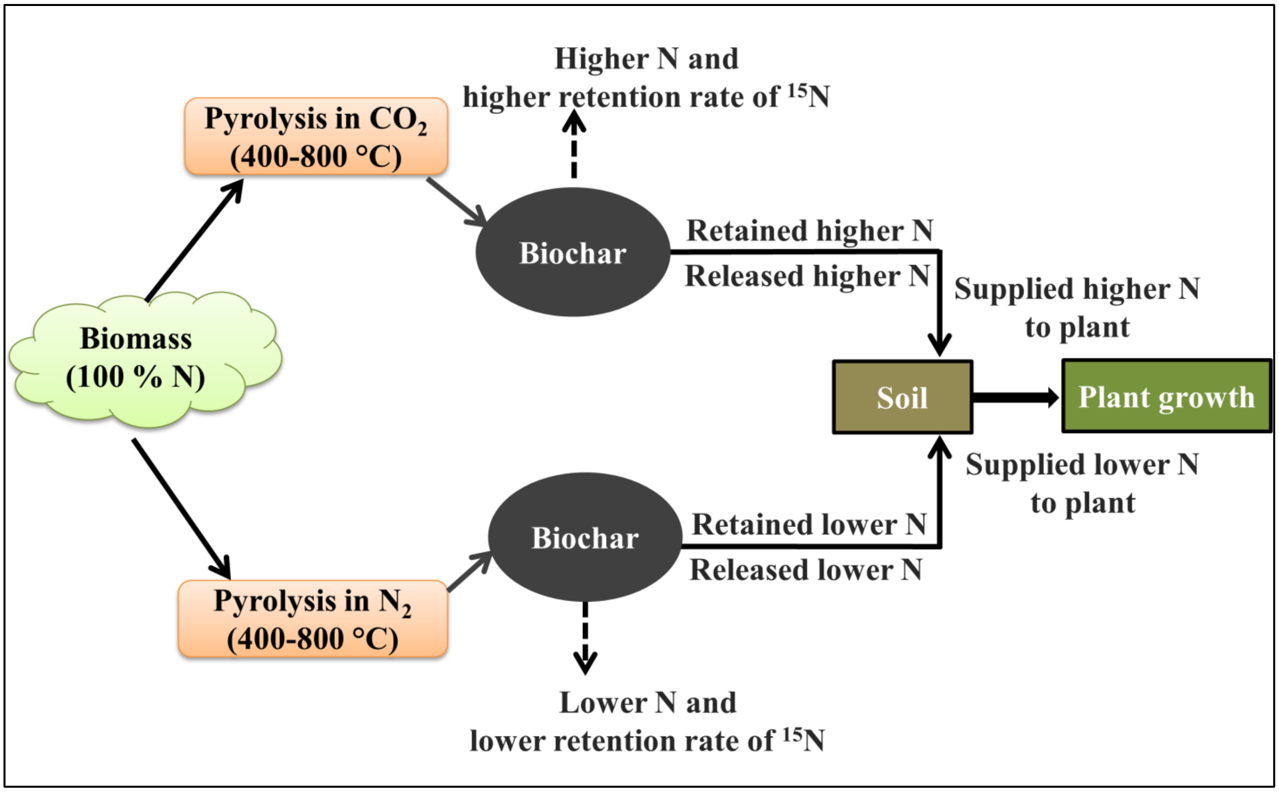

Fig. 4. Performance of CO_2 and N_2 pyrolyzed biochars in soil and plant nitrogen distribution based

7.6. Abiotic aging and biochar stability

In the study of the interaction of biochar stability and abiotic aging, Kim et al. [107] discovered that using CO_2 as a pyrolysis medium produced more stable carbon structures with higher aromatic functional groups compared to N_2 medium. Additionally, the CO_2 produced stable biochar which reduced the leaching of dissolved organic matter (DOM) and arsenic (As) mobility with slightly higher extent than biochar prepared from N_2 atmosphere.

7.7. Surface functional groups

The biochars obtained from slow pyrolysis of cellulose at various temperatures [119] showed that the absorption intensity of the -OH peak in in CO_2 atmosphere at the lower pyrolysis temperatures (400 and 500 °C) were higher in that of N_2 derived biochars. Additionally, the biochar in CO_2 had a higher ratio of –OH–400 °C/-OH –700 °C than the biochar obtained from N_2, indicating that the presence of CO_2 increased the dehydration to a greater extent. Furthermore, the ratio of C=O/C=C for the biochar produced 400 °C in N_2 (0.35) was higher than that in CO_2 (0.14). Therefore, the biochar produced in N_2 was more oxygen-rich, aliphatic, and CO_2 atmosphere clearly enhanced the deoxygenation and aromatization. Aljaziri et al. [147] discovered that Salicornia bigelovii (550 °C) biochar produced through slow pyrolysis in a CO_2 atmosphere contained more polycyclic aromatic compounds than biochar produced through nitrogen environment. FT-IR of the biochar derived from bio-oil distillation residue demonstrated that C=O stretching vibration in CO_2 was more lasting than that in N_2, however, -CH_2 and C-C stretching vibrations demonstrated the opposite trend between both atmopsheres [139]. Lee et al. [42] observed that FT-IR peaks (shown in **Fig. 5**) of biochar produced under CO_2 (BC-C) at 3422 cm^{-1} (-OH) and 1623 cm^{-1} (C=C, C-O) were almost vanished compared to the FTIR spectra of nitrogen induced biochar (BC-N) and was explained by the interaction of CO_2 with base functional groups. Moreover, the BC-C had higher aromatic matter content at 874 cm^{-1} and a lower aliphatic matter content at 2931 cm^{-1}, indicating the stronger aromaticity and lower aliphaticity. Since, aromatic carbon is more persistent than aliphatic carbon under biotic and abiotic oxidation circumstances; the BC-C can be more recalcitrant than the BC-N.

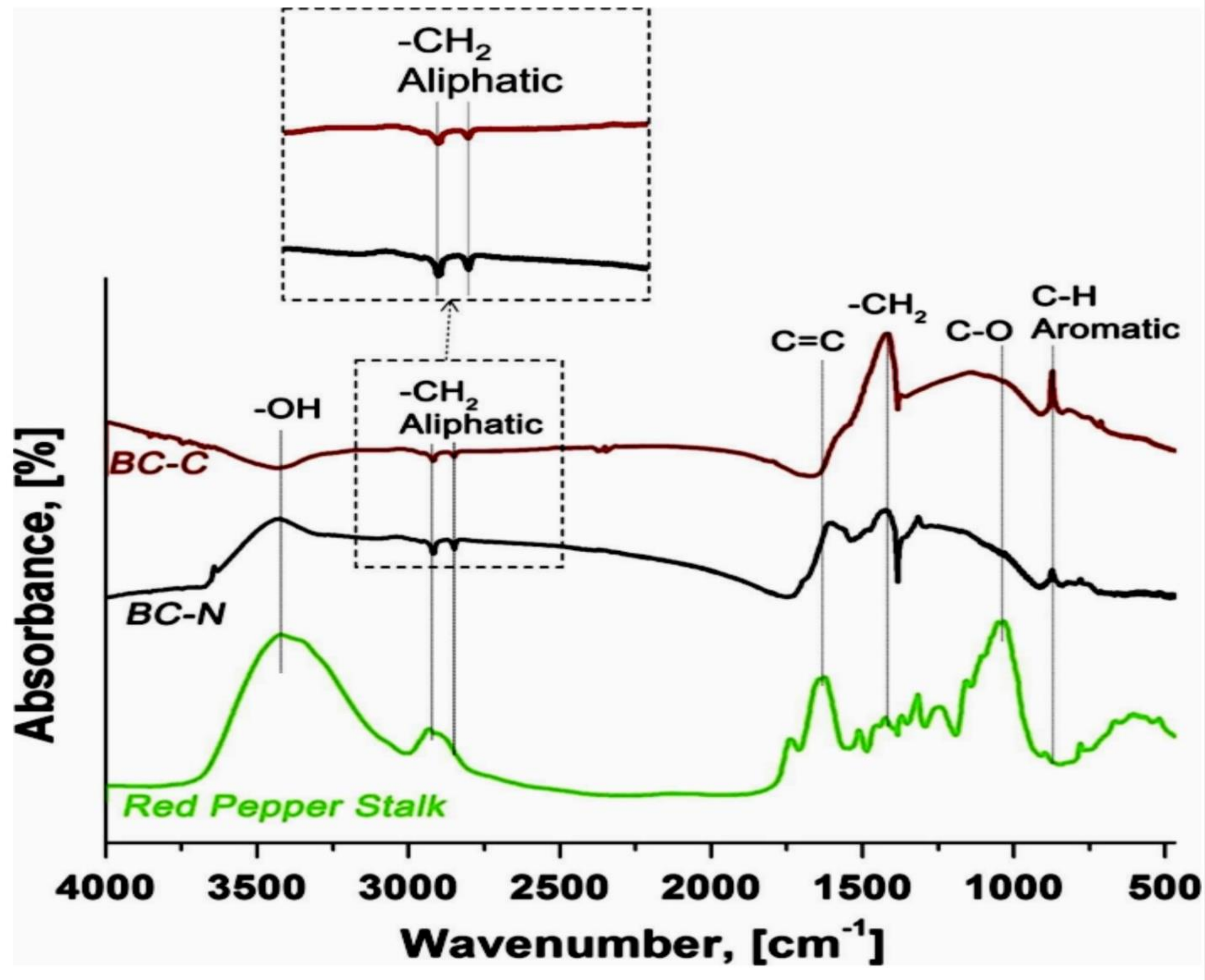

Fig. 5. FT-IR analysis of biochars produced from red pepper stalk under N_2 (BC-N) and CO_2 (BC-C) atmopsheres [42]

8. Limitations and future prospects

The purpose of this study is to comprehensively review the effect of CO_2 atmosphere on biochar productions from slow pyrolysis (400–700 °C) of various biomass and its properties relevant to its environmental applications in comparison with inert (N_2) pyrolysis to serve a positive control. However, due to a lack of studies, the mechanistic role of CO_2 during slow pyrolysis at lower temperatures (400–600 °C) has not yet been fully developed and understood. It has been discovered that CO_2 increases the production of biochar at the aforementioned temperature range, but more research is needed to determine exactly how it contributes to biochar production. Specific surface area and porosity are the two crucial physical characteristics of biochar for its usefulness in environmental applications. Although, it has been discovered in the current study that CO_2 significantly improves the surface area, there was no discernible pattern for porosity. All of the existing studies have used nitrogen adsorption with BET analysis; however, the wide range of pore sizes makes it difficult to accurately characterize the biochar's pore structure and pore size distribution by this method. Therefore, the porosity analysis of CO_2 derived biochars should also use a more precise method, such as mercury porosimetry for better understanding. Additionally, some other crucial biochar characteristics, such as bulk density, skeleton density, aggregate stability, and water holding capacities, have not been studied for the CO_2 atmosphere pyrolysis. Therefore, more study should be done to look into these characteristics, which support the use of biochar as a tool for environmental management and can have both direct and indirect effects on soil systems. Because of its weak oxidizing nature, higher molecular mass, acidic nature, and different thermal diffusivity from nitrogen gas, CO_2 is expected to have a greater impact on these properties. Finally, all of the reported studies were conducted at the lab scale level, where high purity CO_2 was used from cylinders, which is not feasible at large industrial scale. As a result, the utilization of CO_2 from real flue (exhaust) gases should be investigated in order to make the process both economically and environmentally sustainable. Although CO_2 is a major component of flue gases, the presence of other gases such as O_2 and CO may also have an impact on biochar production and properties.

9. Conclusions

Compared to inert (N_2) atmosphere, CO_2 as a pyrolysis medium promotes the biochar production (yield) within the temperature range between 400 and 600 °C for almost all of the biomasses studied, and its susceptibility depends of type of feedstock. The possible mechanisms of biochar formation could be unknown reaction between CO_2 and uncondensed gas, defragmentation and repolymerization processes. As temperature increases from 600 to 700 °C, the yields of biochar slightly decreases might be due to the oxidizing effect of CO_2 at elevated temperatures. The highest increment of biochar yield by CO_2 reported was 19.8% for rice straw derived biochars.

On the other side, it significantly enhances the most of the important biochar characteristics; including surface area and porosity, nutrients and mineral contents, carbon and ash contents, aromaticity, stability and abiotic aging, which could make biochar an ideal candidate for its use in soil amendment. CO_2, as a weak oxidant agent might causes additional formation and release of volatile matter and pores as a result of biochar oxidation, resulting in altered porosity. CO_2 is also found to be negatively correlated with pH, electrical conductivity and cation exchange capacity might be due to acidic nature of CO_2. However, the intensity of these altered properties strongly depends on operating conditions and feedstock type, for example, biomass containing more hemicellulose and lignin was found to produce more porous biochar under CO_2 conditions than biomass containing more cellulose. Thus, CO_2 could be used to modify the physiochemical properties of biochar, such as surface area, porosity, elemental composition, and chemical functional groups for specific applications. Moreover, its utilization from industrial flue gases or recycling within pyrolysis process itself could be the way forward to mitigate the global warming.

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References:

[1] M. Komiyama, A. Aqsha, Y. Uemura, Effect of combustion and nitrogen gas atmospheres on the torrefaction performance of oil palm frond leaves and stems, in: IOP Conference Series: Materials Science and Engineering, IOP Publishing, 2020, pp. 022020.
[2] N.H. Solangi, A. Anjum, F.A. Tanjung, S.A. Mazari, N.M. Mubarak, A review of recent trends and emerging perspectives of ionic liquid membranes for CO2 separation, Journal of Environmental Chemical Engineering, 9 (2021) 105860.
[3] C. Goals, UN Climate Change Conference (COP26) at the SEC—Glasgow 2021, in.
[4] J. Rogelj, M. Den Elzen, N. Höhne, T. Fransen, H. Fekete, H. Winkler, R. Schaeffer, F. Sha, K. Riahi, M. Meinshausen, Paris Agreement climate proposals need a boost to keep warming well below 2 C, Nature, 534 (2016) 631-639.
[5] P.A. Brownsort, Biomass pyrolysis processes: review of scope, control and variability, United Kingdom Biochar Research Centre, London, 1 (2009) 1-39.
[6] L. Leng, H. Huang, An overview of the effect of pyrolysis process parameters on biochar stability, Bioresource technology, 270 (2018) 627-642.
[7] S. Sohi, E. Lopez-Capel, E. Krull, R. Bol, Biochar, climate change and soil: A review to guide future research, CSIRO land and water science report, 5 (2009) 17-31.
[8] P. PREMCHAND, TORREFACTION OF OIL PALM FROND LEAVES AND STEMS UNDER COMBUSTION GAS AND INERT NITROGEN ATMOSPHERES, in, Universiti Teknologi PETRONAS, 2019.
[9] W. Chen, J. Meng, X. Han, Y. Lan, W. Zhang, Past, present, and future of biochar, Biochar, 1 (2019) 75-87.
[10] G. Rahman, M.M. Rahman, M.S. Alam, M.Z. Kamal, H. Mashuk, R. Datta, R.S. Meena, Biochar and organic amendments for sustainable soil carbon and soil health, in: Carbon and nitrogen cycling in soil, Springer, 2020, pp. 45-85.
[11] T.R. Miles, Introduction to the biochar world with a focus on new possible applications, in: Biochar: Emerging applications, IOP Publishing, 2020.
[12] S.S. Qureshi, M. Javed, S. Saeed, R. Abro, S.A. Mazari, N.M. Mubarak, M.T.H. Siddiqui, H.A. Baloch, S. Nizamuddin, Hydrothermal carbonization of oil palm trunk via taguchi method, Korean Journal of Chemical Engineering, 38 (2021) 797-806.
[13] Y. Li, Y. Liu, W. Yang, L. Liu, J. Pan, Adsorption of elemental mercury in flue gas using biomass porous carbons modified by microwave/hydrogen peroxide, Fuel, 291 (2021) 120152.
[14] L. Ye, Z. Peng, L. Wang, A. Anzulevich, I. Bychkov, D. Kalganov, H. Tang, M. Rao, G. Li, T. Jiang, Use of biochar for sustainable ferrous metallurgy, Jom, 71 (2019) 3931-3940.
[15] P. Grutzmacher, A.P. Puga, M.P.S. Bibar, A.R. Coscione, A.P. Packer, C.A. de Andrade, Carbon stability and mitigation of fertilizer induced N2O emissions in soil amended with biochar, Science of the Total Environment, 625 (2018) 1459-1466.
[16] K.Y. Man, K.L. Chow, Y.B. Man, W.Y. Mo, M.H. Wong, Use of biochar as feed supplements for animal farming, Critical Reviews in Environmental Science and Technology, 51 (2021) 187-217.
[17] M. Legan, A.Ž. Gotvajn, K. Zupan, Potential of biochar use in building materials, Journal of Environmental Management, 309 (2022) 114704.
[18] H. Lyu, Q. Zhang, B. Shen, Application of biochar and its composites in catalysis, Chemosphere, 240 (2020) 124842.

[19] J. Kim, C. Park, H. Park, J. Han, J. Lee, S.-K. Kim, Upcycling of cattle manure for simultaneous energy recovery and supercapacitor electrode production, Energy, 258 (2022) 124877.

[20] H. Yu, W. Zou, J. Chen, H. Chen, Z. Yu, J. Huang, H. Tang, X. Wei, B. Gao, Biochar amendment improves crop production in problem soils: A review, Journal of environmental management, 232 (2019) 8-21.

[21] L. Wang, Y.S. Ok, D.C. Tsang, D.S. Alessi, J. Rinklebe, H. Wang, O. Mašek, R. Hou, D. O'Connor, D. Hou, New trends in biochar pyrolysis and modification strategies: feedstock, pyrolysis conditions, sustainability concerns and implications for soil amendment, Soil Use and Management, 36 (2020) 358-386.

[22] G. Greco, C. Di Stasi, F. Rego, B. González, J.J. Manyà, Effects of slow-pyrolysis conditions on the products yields and properties and on exergy efficiency: A comprehensive assessment for wheat straw, Applied Energy, 279 (2020) 115842.

[23] P. Basu, Biomass gasification, pyrolysis and torrefaction: practical design and theory, Academic press, 2018.

[24] A. Selvarajoo, Y.L. Wong, K.S. Khoo, W.-H. Chen, P.L. Show, Biochar production via pyrolysis of citrus peel fruit waste as a potential usage as solid biofuel, Chemosphere, 294 (2022) 133671.

[25] T. Kan, V. Strezov, T.J. Evans, Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters, Renewable and sustainable energy reviews, 57 (2016) 1126-1140.

[26] R.K. Mishra, K. Mohanty, Effect of Process Parameters on the Production of Pyrolytic Products from Biomass Through Pyrolysis, Liquid Biofuels: Fundamentals, Characterization, and Applications, (2021) 231-284.

[27] T.Y. Fahmy, Y. Fahmy, F. Mobarak, M. El-Sakhawy, R.E. Abou-Zeid, Biomass pyrolysis: past, present, and future, Environment, Development and Sustainability, 22 (2020) 17-32.

[28] A.T. Tag, G. Duman, S. Ucar, J. Yanik, Effects of feedstock type and pyrolysis temperature on potential applications of biochar, Journal of Analytical and Applied Pyrolysis, 120 (2016) 200-206.

[29] A.Y. Elnour, A.A. Alghyamah, H.M. Shaikh, A.M. Poulose, S.M. Al-Zahrani, A. Anis, M.I. Al-Wabel, Effect of pyrolysis temperature on biochar microstructural evolution, physicochemical characteristics, and its influence on biochar/polypropylene composites, Applied sciences, 9 (2019) 1149.

[30] A. Tomczyk, Z. Sokołowska, P. Boguta, Biochar physicochemical properties: pyrolysis temperature and feedstock kind effects, Reviews in Environmental Science and Bio/Technology, 19 (2020) 191-215.

[31] C. Li, J.-i. Hayashi, Y. Sun, L. Zhang, S. Zhang, S. Wang, X. Hu, Impact of heating rates on the evolution of function groups of the biochar from lignin pyrolysis, Journal of Analytical and Applied Pyrolysis, 155 (2021) 105031.

[32] J.J. Manyà, F.X. Roca, J.F. Perales, TGA study examining the effect of pressure and peak temperature on biochar yield during pyrolysis of two-phase olive mill waste, Journal of analytical and applied pyrolysis, 103 (2013) 86-95.

[33] N. Mahinpey, P. Murugan, T. Mani, R. Raina, Analysis of bio-oil, biogas, and biochar from pressurized pyrolysis of wheat straw using a tubular reactor, Energy & Fuels, 23 (2009) 2736-2742.

[34] B. Zhao, D. O'Connor, J. Zhang, T. Peng, Z. Shen, D.C. Tsang, D. Hou, Effect of pyrolysis temperature, heating rate, and residence time on rapeseed stem derived biochar, Journal of Cleaner Production, 174 (2018) 977-987.
[35] M.M. Hasan, R. Bachmann, S. Loh, S. Manroshan, S. Ong, Effect of pyrolysis temperature and time on properties of palm kernel shell-based biochar, in: IOP Conference Series: Materials Science and Engineering, IOP Publishing, 2019, pp. 012020.
[36] J. Ouyang, D. Hong, L. Jiang, Z. Li, H. Liu, G. Luo, H. Yao, Effect of CO2 and H2O on char properties. Part 1: pyrolysis char structure and reactivity, Energy & Fuels, 34 (2020) 4243-4250.
[37] B. Xu, M.D. Argyle, X. Shi, A.K. Goroncy, A.H. Rony, G. Tan, M. Fan, Effects of mixture of CO2/CH4 as pyrolysis atmosphere on pine wood pyrolysis products, Renewable Energy, 162 (2020) 1243-1254.
[38] H. Zhang, R. Xiao, D. Wang, G. He, S. Shao, J. Zhang, Z. Zhong, Biomass fast pyrolysis in a fluidized bed reactor under N2, CO2, CO, CH4 and H2 atmospheres, Bioresource technology, 102 (2011) 4258-4264.
[39] Z. Ye, L. Liu, Z. Tan, L. Zhang, Q. Huang, Effects of pyrolysis conditions on migration and distribution of biochar nitrogen in the soil-plant-atmosphere system, Science of The Total Environment, 723 (2020) 138006.
[40] D.-W. Cho, E.E. Kwon, H. Song, Use of carbon dioxide as a reaction medium in the thermo-chemical process for the enhanced generation of syngas and tuning adsorption ability of biochar, Energy Conversion and Management, 117 (2016) 106-114.
[41] D.-W. Cho, E.E. Kwon, G. Kwon, S. Zhang, S.-R. Lee, H. Song, Co-pyrolysis of paper mill sludge and spend coffee ground using CO2 as reaction medium, Journal of CO2 Utilization, 21 (2017) 572-579.
[42] J. Lee, X. Yang, S.-H. Cho, J.-K. Kim, S.S. Lee, D.C. Tsang, Y.S. Ok, E.E. Kwon, Pyrolysis process of agricultural waste using CO2 for waste management, energy recovery, and biochar fabrication, Applied energy, 185 (2017) 214-222.
[43] S.Y. Foong, Y.H. Chan, W.Y. Cheah, N.H. Kamaludin, T.N.B.T. Ibrahim, C. Sonne, W. Peng, P.-L. Show, S.S. Lam, Progress in waste valorization using advanced pyrolysis techniques for hydrogen and gaseous fuel production, Bioresource technology, 320 (2021) 124299.
[44] X. Hu, M. Gholizadeh, Biomass pyrolysis: A review of the process development and challenges from initial researches up to the commercialisation stage, Journal of Energy Chemistry, 39 (2019) 109-143.
[45] S. Kim, J. Byun, H. Park, N. Lee, J. Han, J. Lee, Energy-efficient thermal waste treatment process with no CO2 emission: A case study of waste tea bag, Energy, 241 (2022) 122876.
[46] D.-W. Cho, S.-H. Cho, H. Song, E.E. Kwon, Carbon dioxide assisted sustainability enhancement of pyrolysis of waste biomass: a case study with spent coffee ground, Bioresource technology, 189 (2015) 1-6.
[47] E.E. Kwon, H. Yi, H.-H. Kwon, Energy recovery from microalgal biomass via enhanced thermo-chemical process, Biomass and Bioenergy, 63 (2014) 46-53.
[48] E.E. Kwon, S. Kim, J. Lee, Pyrolysis of waste feedstocks in CO2 for effective energy recovery and waste treatment, Journal of CO2 utilization, 31 (2019) 173-180.
[49] S. Lee, Y.F. Tsang, K.-Y.A. Lin, E.E. Kwon, J. Lee, Employment of biogas as pyrolysis medium and chemical feedstock, Journal of CO2 Utilization, 57 (2022) 101877.

[50] A.M. Parvez, M.T. Afzal, T.G.V. Hebb, M. Schmid, Utilization of CO2 in thermochemical conversion of biomass for enhanced product properties: A review, Journal of CO2 Utilization, 40 (2020) 101217.
[51] J. Wang, S. Wang, Preparation, modification and environmental application of biochar: a review, Journal of Cleaner Production, 227 (2019) 1002-1022.
[52] N.S. Kamarudin, F.A. Dahalan, M. Hasan, O.S. An, N.A. Parmin, N. Ibrahim, M. Hamdzah, N.A.M. Zain, K. Muda, E.A. Wikurendra, Biochar: A Review of its History, Characteristics, Factors that Influence its Yield, Methods of Production, Application in Wastewater Treatment and Recent Development, (2021).
[53] J. Lehmann, S. Joseph, Biochar for environmental management: an introduction, in: Biochar for environmental management, Routledge, 2015, pp. 1-13.
[54] L. Leng, Q. Xiong, L. Yang, H. Li, Y. Zhou, W. Zhang, S. Jiang, H. Li, H. Huang, An overview on engineering the surface area and porosity of biochar, Science of the total Environment, 763 (2021) 144204.
[55] R. Antón-Herrero, C. García-Delgado, M. Alonso-Izquierdo, G. García-Rodríguez, J. Cuevas, E. Eymar, Comparative adsorption of tetracyclines on biochars and stevensite: Looking for the most effective adsorbent, Applied Clay Science, 160 (2018) 162-172.
[56] L. Leng, H. Huang, H. Li, J. Li, W. Zhou, Biochar stability assessment methods: a review, Science of the total environment, 647 (2019) 210-222.
[57] M. Kamali, N. Sweygers, S. Al-Salem, L. Appels, T.M. Aminabhavi, R. Dewil, Biochar for soil applications-sustainability aspects, challenges and future prospects, Chemical Engineering Journal, 428 (2022) 131189.
[58] A.U. Rajapaksha, M. Vithanage, J.E. Lim, M.B.M. Ahmed, M. Zhang, S.S. Lee, Y.S. Ok, Invasive plant-derived biochar inhibits sulfamethazine uptake by lettuce in soil, Chemosphere, 111 (2014) 500-504.
[59] W. Zheng, M. Guo, T. Chow, D.N. Bennett, N. Rajagopalan, Sorption properties of greenwaste biochar for two triazine pesticides, Journal of hazardous materials, 181 (2010) 121-126.
[60] X. Zhang, H. Wang, L. He, K. Lu, A. Sarmah, J. Li, N.S. Bolan, J. Pei, H. Huang, Using biochar for remediation of soils contaminated with heavy metals and organic pollutants, Environmental Science and Pollution Research, 20 (2013) 8472-8483.
[61] L. He, H. Zhong, G. Liu, Z. Dai, P.C. Brookes, J. Xu, Remediation of heavy metal contaminated soils by biochar: Mechanisms, potential risks and applications in China, Environmental pollution, 252 (2019) 846-855.
[62] F. Zhang, X. Wang, J. Xionghui, L. Ma, Efficient arsenate removal by magnetite-modified water hyacinth biochar, Environmental Pollution, 216 (2016) 575-583.
[63] K. Lu, X. Yang, G. Gielen, N. Bolan, Y.S. Ok, N.K. Niazi, S. Xu, G. Yuan, X. Chen, X. Zhang, Effect of bamboo and rice straw biochars on the mobility and redistribution of heavy metals (Cd, Cu, Pb and Zn) in contaminated soil, Journal of environmental management, 186 (2017) 285-292.
[64] S. Wang, J. Wang, Activation of peroxymonosulfate by sludge-derived biochar for the degradation of triclosan in water and wastewater, Chemical Engineering Journal, 356 (2019) 350-358.
[65] Z. Liu, Z. Xu, L. Xu, F. Buyong, T.C. Chay, Z. Li, Y. Cai, B. Hu, Y. Zhu, X. Wang, Modified biochar: Synthesis and mechanism for removal of environmental heavy metals, Carbon Research, 1 (2022) 1-21.

[66] D. O'Connor, T. Peng, G. Li, S. Wang, L. Duan, J. Mulder, G. Cornelissen, Z. Cheng, S. Yang, D. Hou, Sulfur-modified rice husk biochar: a green method for the remediation of mercury contaminated soil, Science of the total environment, 621 (2018) 819-826.

[67] B. Gámiz, P. Velarde, K.A. Spokas, M.C. Hermosín, L. Cox, Biochar soil additions affect herbicide fate: importance of application timing and feedstock species, Journal of agricultural and food chemistry, 65 (2017) 3109-3117.

[68] L. Kong, Y. Gao, Q. Zhou, X. Zhao, Z. Sun, Biochar accelerates PAHs biodegradation in petroleum-polluted soil by biostimulation strategy, Journal of hazardous materials, 343 (2018) 276-284.

[69] A. Gross, T. Bromm, B. Glaser, Soil organic carbon sequestration after biochar application: A global meta-analysis, Agronomy, 11 (2021) 2474.

[70] N.H. Solangi, F. Hussin, A. Anjum, N. Sabzoi, S.A. Mazari, N. Mubarak, M.K. Aroua, M. Siddiqui, S.S. Qureshi, A review of encapsulated ionic liquids for CO2 capture, Journal of Molecular Liquids, (2023) 121266.

[71] J. Yin, L. Zhao, X. Xu, D. Li, H. Qiu, X. Cao, Evaluation of long-term carbon sequestration of biochar in soil with biogeochemical field model, Science of The Total Environment, 822 (2022) 153576.

[72] Y. Kuzyakov, I. Bogomolova, B. Glaser, Biochar stability in soil: decomposition during eight years and transformation as assessed by compound-specific 14C analysis, Soil Biology and Biochemistry, 70 (2014) 229-236.

[73] J. Zhang, X. Zhang, H. Sun, C. Wang, S. Zhou, Carbon sequestration and nutrients improvement meditated by biochar in a 3-year vegetable rotation system, Journal of Soils and Sediments, 22 (2022) 1385-1396.

[74] Y. Luo, Z. Li, H. Xu, X. Xu, H. Qiu, X. Cao, L. Zhao, Development of phosphorus composite biochar for simultaneous enhanced carbon sink and heavy metal immobilization in soil, Science of The Total Environment, 831 (2022) 154845.

[75] G.O. Abagandura, S. Bansal, A. Karsteter, S. Kumar, Soil greenhouse gas emissions, organic carbon and crop yield following pinewood biochar and biochar–manure applications at eroded and depositional landscape positions: A field trial in South Dakota, USA, Soil Use and Management, 38 (2022) 487-502.

[76] D.A. Wardle, M.-C. Nilsson, O. Zackrisson, Fire-derived charcoal causes loss of forest humus, Science, 320 (2008) 629-629.

[77] B. Yousaf, G. Liu, R. Wang, Q. Abbas, M. Imtiaz, R. Liu, Investigating the biochar effects on C-mineralization and sequestration of carbon in soil compared with conventional amendments using the stable isotope (δ13C) approach, Gcb Bioenergy, 9 (2017) 1085-1099.

[78] H. Cheng, P.W. Hill, M.S. Bastami, D.L. Jones, Biochar stimulates the decomposition of simple organic matter and suppresses the decomposition of complex organic matter in a sandy loam soil, GCB Bioenergy, 9 (2017) 1110-1121.

[79] W. Yang, G. Feng, D. Miles, L. Gao, Y. Jia, C. Li, Z. Qu, Impact of biochar on greenhouse gas emissions and soil carbon sequestration in corn grown under drip irrigation with mulching, Science of the Total Environment, 729 (2020) 138752.

[80] J.H. Windeatt, A.B. Ross, P.T. Williams, P.M. Forster, M.A. Nahil, S. Singh, Characteristics of biochars from crop residues: potential for carbon sequestration and soil amendment, Journal of environmental management, 146 (2014) 189-197.

[81] Z.-R. Kan, Q.-Y. Liu, G. Wu, S.-T. Ma, A.L. Virk, J.-Y. Qi, X. Zhao, H.-L. Zhang, Temperature and moisture driven changes in soil carbon sequestration and mineralization under biochar addition, Journal of Cleaner Production, 265 (2020) 121921.

[82] S. Adhikari, W. Timms, M.P. Mahmud, Optimising water holding capacity and hydrophobicity of biochar for soil amendment–A review, Science of The Total Environment, (2022) 158043.

[83] A. Mukherjee, R. Lal, Biochar impacts on soil physical properties and greenhouse gas emissions, Agronomy, 3 (2013) 313-339.

[84] H. Blanco-Canqui, Biochar and soil physical properties, Soil Science Society of America Journal, 81 (2017) 687-711.

[85] A.C. Vilas-Boas, L.A. Tarelho, M. Kamali, T. Hauschild, D.T. Pio, D. Jahanianfard, A.P.D. Gomes, M.A. Matos, Biochar from slow pyrolysis of biological sludge from wastewater treatment: characteristics and effect as soil amendment, Biofuels, Bioproducts and Biorefining, 15 (2021) 1054-1072.

[86] L. Toková, D. Igaz, J. Horák, E. Aydin, Effect of biochar application and re-application on soil bulk density, porosity, saturated hydraulic conductivity, water content and soil water availability in a silty loam Haplic Luvisol, Agronomy, 10 (2020) 1005.

[87] F.G. Verheijen, A. Zhuravel, F.C. Silva, A. Amaro, M. Ben-Hur, J.J. Keizer, The influence of biochar particle size and concentration on bulk density and maximum water holding capacity of sandy vs sandy loam soil in a column experiment, Geoderma, 347 (2019) 194-202.

[88] K.N. Palansooriya, J.T.F. Wong, Y. Hashimoto, L. Huang, J. Rinklebe, S.X. Chang, N. Bolan, H. Wang, Y.S. Ok, Response of microbial communities to biochar-amended soils: a critical review, Biochar, 1 (2019) 3-22.

[89] C. Bamminger, N. Zaiser, P. Zinsser, M. Lamers, C. Kammann, S. Marhan, Effects of biochar, earthworms, and litter addition on soil microbial activity and abundance in a temperate agricultural soil, Biology and Fertility of Soils, 50 (2014) 1189-1200.

[90] A. Pathy, J. Ray, B. Paramasivan, Biochar amendments and its impact on soil biota for sustainable agriculture, Biochar, 2 (2020) 287-305.

[91] T. Purakayastha, T. Bera, D. Bhaduri, B. Sarkar, S. Mandal, P. Wade, S. Kumari, S. Biswas, M. Menon, H. Pathak, A review on biochar modulated soil condition improvements and nutrient dynamics concerning crop yields: Pathways to climate change mitigation and global food security, Chemosphere, 227 (2019) 345-365.

[92] C. Luo, J. Yang, W. Chen, F. Han, Effect of biochar on soil properties on the Loess Plateau: Results from field experiments, Geoderma, 369 (2020) 114323.

[93] K. Jeyasubramanian, B. Thangagiri, A. Sakthivel, J.D. Raja, S. Seenivasan, P. Vallinayagam, D. Madhavan, S.M. Devi, B. Rathika, A complete review on biochar: Production, property, multifaceted applications, interaction mechanism and computational approach, Fuel, 292 (2021) 120243.

[94] S. Al Arni, Comparison of slow and fast pyrolysis for converting biomass into fuel, Renewable Energy, 124 (2018) 197-201.

[95] E. Amini, M.-S. Safdari, J.T. DeYoung, D.R. Weise, T.H. Fletcher, Characterization of pyrolysis products from slow pyrolysis of live and dead vegetation native to the southern United States, Fuel, 235 (2019) 1475-1491.

[96] A. Dieguez-Alonso, A. Anca-Couce, N. Zobel, F. Behrendt, Understanding the primary and secondary slow pyrolysis mechanisms of holocellulose, lignin and wood with laser-induced fluorescence, Fuel, 153 (2015) 102-109.

[97] M. Tripathi, J.N. Sahu, P. Ganesan, Effect of process parameters on production of biochar from biomass waste through pyrolysis: A review, Renewable and Sustainable Energy Reviews, 55 (2016) 467-481.

[98] J. Cheng, S.-C. Hu, G.-T. Sun, Z.-C. Geng, M.-Q. Zhu, The effect of pyrolysis temperature on the characteristics of biochar, pyroligneous acids, and gas prepared from cotton stalk through a polygeneration process, Industrial Crops and Products, 170 (2021) 113690.

[99] H. Huang, N.G. Reddy, X. Huang, P. Chen, P. Wang, Y. Zhang, Y. Huang, P. Lin, A. Garg, Effects of pyrolysis temperature, feedstock type and compaction on water retention of biochar amended soil, Scientific Reports, 11 (2021) 1-19.

[100] J.A. Ippolito, L. Cui, C. Kammann, N. Wrage-Mönnig, J.M. Estavillo, T. Fuertes-Mendizabal, M.L. Cayuela, G. Sigua, J. Novak, K. Spokas, Feedstock choice, pyrolysis temperature and type influence biochar characteristics: a comprehensive meta-data analysis review, Biochar, 2 (2020) 421-438.

[101] J. Encinar, J. Gonzalez, J. Gonzalez, Fixed-bed pyrolysis of Cynara cardunculus L. Product yields and compositions, Fuel Processing Technology, 68 (2000) 209-222.

[102] A. Demirbas, Effects of temperature and particle size on bio-char yield from pyrolysis of agricultural residues, Journal of analytical and applied pyrolysis, 72 (2004) 243-248.

[103] M. Guida, S. Lanaya, F. Laghchioua, Z. Rbihi, A. Hannioui, Production of bio-oil and bio-char from pyrolysis of sawdust wood waste (SWW), Progress in Agricultural Engineering Sciences, 16 (2020) 61-80.

[104] J.J. Manyà, M.A. Ortigosa, S. Laguarta, J.A. Manso, Experimental study on the effect of pyrolysis pressure, peak temperature, and particle size on the potential stability of vine shoots-derived biochar, Fuel, 133 (2014) 163-172.

[105] J.J. Manyà, M. Azuara, J.A. Manso, Biochar production through slow pyrolysis of different biomass materials: Seeking the best operating conditions, Biomass and Bioenergy, 117 (2018) 115-123.

[106] L. Qin, Y. Wu, Z. Hou, E. Jiang, Influence of biomass components, temperature and pressure on the pyrolysis behavior and biochar properties of pine nut shells, Bioresource Technology, 313 (2020) 123682.

[107] H.-B. Kim, J.-G. Kim, T. Kim, D.S. Alessi, K. Baek, Interaction of biochar stability and abiotic aging: Influences of pyrolysis reaction medium and temperature, Chemical Engineering Journal, 411 (2021) 128441.

[108] G. Wang, J. Zhang, W. Chang, R. Li, Y. Li, C. Wang, Structural features and gasification reactivity of biomass chars pyrolyzed in different atmospheres at high temperature, Energy, 147 (2018) 25-35.

[109] M. Yan, S. Zhang, H. Wibowo, N. Grisdanurak, Y. Cai, X. Zhou, E. Kanchanatip, Biochar and pyrolytic gas properties from pyrolysis of simulated municipal solid waste (SMSW) under pyrolytic gas atmosphere, Waste Disposal & Sustainable Energy, 2 (2020) 37-46.

[110] H. Kim, S. Kim, J. Lee, M. Kim, D. Kwon, S. Jung, Pyrolysis of rice husk using CO2 for enhanced energy production and soil amendment, Energy & Environment, (2022) 0958305X221079422.

[111] J.-X. Wang, J.-P. Cao, X.-Y. Zhao, T.-L. Liu, F. Wei, X. Fan, Y.-P. Zhao, X.-Y. Wei, Study on pine sawdust pyrolysis behavior by fast pyrolysis under inert and reductive atmospheres, Journal of Analytical and Applied Pyrolysis, 125 (2017) 279-288.

[112] S. Kim, Y.T. Kim, L.S. Oh, H.J. Kim, J. Lee, Marine waste upcycling—Recovery of nylon monomers from fishing net waste using seashell waste-derived catalysts in a CO 2-mediated thermocatalytic process, Journal of Materials Chemistry A, 10 (2022) 20024-20034.

[113] J. Kim, K.-H. Kim, E.E. Kwon, Enhanced thermal cracking of VOCs evolved from the thermal degradation of lignin using CO2, Energy, 100 (2016) 51-57.

[114] J.-I. Oh, J. Lee, T. Lee, Y.S. Ok, S.-R. Lee, E.E. Kwon, Strategic CO2 utilization for shifting carbon distribution from pyrolytic oil to syngas in pyrolysis of food waste, Journal of CO2 Utilization, 20 (2017) 150-155.

[115] J. Lee, X. Yang, H. Song, Y.S. Ok, E.E. Kwon, Effects of carbon dioxide on pyrolysis of peat, Energy, 120 (2017) 929-936.

[116] J.-M. Jung, S. Kim, J. Lee, J.I. Oh, Y.-E. Choi, E.E. Kwon, Tailoring pyrogenic products from pyrolysis of defatted Euglena gracilis using CO2 as reactive gas medium, Energy, 174 (2019) 184-190.

[117] C. Yue, P. Gao, L. Tang, X. Chen, Effects of N2/CO2 atmosphere on the pyrolysis characteristics for municipal solid waste pellets, Fuel, 315 (2022) 123233.

[118] J. Lee, T. Lee, Y.S. Ok, J.-I. Oh, E.E. Kwon, Using CO2 to mitigate evolution of harmful chemical compounds during thermal degradation of printed circuit boards, Journal of CO2 Utilization, 20 (2017) 66-72.

[119] Z. Yi, C. Li, Q. Li, L. Zhang, S. Zhang, S. Wang, L. Qin, X. Hu, Influence of CO2 atmosphere on property of biochar from pyrolysis of cellulose, Journal of Environmental Chemical Engineering, 10 (2022) 107339.

[120] Y. Shen, D. Ma, X. Ge, CO 2-looping in biomass pyrolysis or gasification, Sustainable energy & fuels, 1 (2017) 1700-1729.

[121] Z. Tan, J. Zou, L. Zhang, Q. Huang, Morphology, pore size distribution, and nutrient characteristics in biochars under different pyrolysis temperatures and atmospheres, Journal of Material Cycles and Waste Management, 20 (2018) 1036-1049.

[122] N. Lee, S. Kim, J. Lee, Valorization of waste tea bags via CO2-assisted pyrolysis, Journal of CO2 Utilization, 44 (2021) 101414.

[123] D. Kwon, S.S. Lee, S. Jung, Y.-K. Park, Y.F. Tsang, E.E. Kwon, CO2 to fuel via pyrolysis of banana peel, Chemical Engineering Journal, 392 (2020) 123774.

[124] S.-R. Lee, J. Lee, T. Lee, S.-H. Cho, J.-I. Oh, H. Kim, D.C. Tsang, E.E. Kwon, Carbon dioxide assisted thermal decomposition of cattle excreta, Science of the Total Environment, 615 (2018) 70-77.

[125] Z. Dong, Z. Liu, X. Zhang, H. Yang, J. Li, S. Xia, Y. Chen, H. Chen, Pyrolytic characteristics of hemicellulose, cellulose and lignin under CO2 atmosphere, Fuel, 256 (2019) 115890.

[126] J. Lee, J.-I. Oh, Y.S. Ok, E.E. Kwon, Study on susceptibility of CO2-assisted pyrolysis of various biomass to CO2, Energy, 137 (2017) 510-517.

[127] Z. Wang, X. Ma, Z. Yao, Q. Yu, Z. Wang, Y. Lin, Study of the pyrolysis of municipal sludge in N2/CO2 atmosphere, Applied Thermal Engineering, 128 (2018) 662-671.

[128] S.-H. Cho, K.-H. Kim, Y.J. Jeon, E.E. Kwon, Pyrolysis of microalgal biomass in carbon dioxide environment, Bioresource Technology, 193 (2015) 185-191.

[129] J. Zhang, T. Chen, J. Wu, J. Wu, Multi-Gaussian-DAEM-reaction model for thermal decompositions of cellulose, hemicellulose and lignin: Comparison of N2 and CO2 atmosphere, Bioresource technology, 166 (2014) 87-95.

[130] D. Choi, S. Jung, Y.J. Jeon, D.H. Moon, E.E. Kwon, Study on carbon rearrangements of CO2 co-feeding pyrolysis of corn stover and oak wood, Journal of CO2 Utilization, 42 (2020) 101320.
[131] O. Senneca, F. Cerciello, S. Heuer, P. Ammendola, Slow pyrolysis of walnut shells in nitrogen and carbon dioxide, Fuel, 225 (2018) 419-425.
[132] F. Sher, S.Z. Iqbal, H. Liu, M. Imran, C.E. Snape, Thermal and kinetic analysis of diverse biomass fuels under different reaction environment: A way forward to renewable energy sources, Energy Conversion and Management, 203 (2020) 112266.
[133] B. Biswas, R. Singh, J. Kumar, R. Singh, P. Gupta, B.B. Krishna, T. Bhaskar, Pyrolysis behavior of rice straw under carbon dioxide for production of bio-oil, Renewable energy, 129 (2018) 686-694.
[134] Z. Yi, C. Li, L. Zhang, S. Zhang, W. Gao, S. Wang, B. Li, X. Hu, Impacts of CO2 atmosphere on property of the biochar from pyrolysis of lignin, Journal of Analytical and Applied Pyrolysis, 167 (2022) 105689.
[135] W.-H. Chen, B.-J. Lin, Characteristics of products from the pyrolysis of oil palm fiber and its pellets in nitrogen and carbon dioxide atmospheres, Energy, 94 (2016) 569-578.
[136] S. Aktar, M.A. Hossain, N. Rathnayake, S. Patel, G. Gasco, A. Mendez, C. de Figueiredo, A. Surapaneni, K. Shah, J. Paz-Ferreiro, Effects of temperature and carrier gas on physico-chemical properties of biochar derived from biosolids, Journal of Analytical and Applied Pyrolysis, 164 (2022) 105542.
[137] D. Kwon, J.-I. Oh, S.S. Lam, D.H. Moon, E.E. Kwon, Orange peel valorization by pyrolysis under the carbon dioxide environment, Bioresource technology, 285 (2019) 121356.
[138] Z. Gong, A. Du, Z. Wang, P. Fang, X. Li, Experimental study on pyrolysis characteristics of oil sludge with a tube furnace reactor, Energy & Fuels, 31 (2017) 8102-8108.
[139] X. Zhu, K. Li, L. Zhang, X. Wu, X. Zhu, Comparative study on the evolution of physicochemical characteristics of biochar produced from bio-oil distillation residue under different induction atmosphere, Energy conversion and management, 157 (2018) 288-293.
[140] M. Kończak, P. Oleszczuk, K. Różyło, Application of different carrying gases and ratio between sewage sludge and willow for engineered (smart) biochar production, Journal of CO2 Utilization, 29 (2019) 20-28.
[141] M. Wang, S.-L. Zhang, P.-G. Duan, Slow pyrolysis of biomass: effects of effective hydrogen-to-carbon atomic ratio of biomass and reaction atmospheres, Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, (2019) 1-14.
[142] D.D. Chun, D. Ni, A. Simson, The effect of inherent inorganics and CO2 co-pyrolysis on biochar production from biowastes and their gasification reactivity, Biomass and Bioenergy, 158 (2022) 106361.
[143] G.R. Mong, W.W.F. Chong, S.A.M. Nor, J.-H. Ng, C.T. Chong, R. Idris, M.C. Chiong, S. Wong, B.B. Nyakuma, Waste-to-BioEnergy pathway for waste activated sludge from food processing industries: An experiment on the valorization potential under CO2 and N2 atmospheres through microwave-induced pyrolysis, Fuel, 323 (2022) 124380.
[144] S. Guo, X. Xiong, D. Che, H. Liu, B. Sun, Effects of sludge pyrolysis temperature and atmosphere on characteristics of biochar and gaseous products, Korean Journal of Chemical Engineering, 38 (2021) 55-63.
[145] Y. Kim, J.-I. Oh, M. Vithanage, Y.-K. Park, J. Lee, E.E. Kwon, Modification of biochar properties using CO2, Chemical Engineering Journal, 372 (2019) 383-389.

[146] C. Jindarom, V. Meeyoo, B. Kitiyanan, T. Rirksomboon, P. Rangsunvigit, Surface characterization and dye adsorptive capacities of char obtained from pyrolysis/gasification of sewage sludge, Chemical Engineering Journal, 133 (2007) 239-246.
[147] J. Aljaziri, R. Gautam, S. Alturkistani, G.M. Fiene, M. Tester, S.M. Sarathy, On the effects of CO2 atmosphere in the pyrolysis of Salicornia bigelovii, Bioresource Technology Reports, 17 (2022) 100950.
[148] P. Fu, S. Hu, J. Xiang, L. Sun, S. Su, J. Wang, Evaluation of the porous structure development of chars from pyrolysis of rice straw: Effects of pyrolysis temperature and heating rate, Journal of Analytical and Applied Pyrolysis, 98 (2012) 177-183.
[149] Z. Liu, F. Zhang, H. Liu, F. Ba, S. Yan, J. Hu, Pyrolysis/gasification of pine sawdust biomass briquettes under carbon dioxide atmosphere: Study on carbon dioxide reduction (utilization) and biochar briquettes physicochemical properties, Bioresource technology, 249 (2018) 983-991.
[150] M. Kończak, P. Oleszczuk, Co-pyrolysis of sewage sludge and biomass in carbon dioxide as a carrier gas affects the total and leachable metals in biochars, Journal of Hazardous Materials, 400 (2020) 123144.
[151] Z. Tan, Z. Ye, L. Zhang, Q. Huang, Application of the 15N tracer method to study the effect of pyrolysis temperature and atmosphere on the distribution of biochar nitrogen in the biomass–biochar-plant system, Science of the Total Environment, 622 (2018) 79-87.
[152] A. Mukherjee, A.R. Zimmerman, Organic carbon and nutrient release from a range of laboratory-produced biochars and biochar–soil mixtures, Geoderma, 193 (2013) 122-130.
[153] L. Liu, Z. Tan, L. Zhang, Q. Huang, Influence of pyrolysis conditions on nitrogen speciation in a biochar ‘preparation-application’process, Journal of the Energy Institute, 91 (2018) 916-926.