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Research Paper

Study on the effects of carbon dioxide atmosphere on the production of biochar derived from slow pyrolysis of organic agro-urban waste

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ABSTRACT

Slow pyrolysis, a widely recognized thermochemical technique, is employed to produce biochar usually under inert atmospheres. Recently, there is a growing interest in utilizing CO₂ as a carrier gas during pyrolysis as an alternative to inert atmospheres, aiming to modify the resulting pyrolytic products and make them suitable for different applications. This study investigated and compared the impact of CO₂ atmosphere with N₂ on pyrolysis of food waste, rice husk, and grape tree branches waste via slow pyrolysis at temperatures of 400, 500, and 600 °C at 5 and 15 °C/min for 1 h, to evaluate biochar production and its properties. The results demonstrate that CO₂ atmosphere increased the biochar yield for all feedstocks and significantly influenced the physicochemical properties of biochar. Compared to N₂, CO₂-derived biochar exhibited less volatile matter, higher carbon content, lower O/H and O/C molar ratios and enhanced textural properties. This study highlighted the potential of utilizing CO₂ for biochar production and tailoring biochar properties for specific applications and the findings contribute to the establishment of sustainable and efficient waste management systems and the production of value-added biochar products.

1. Introduction

Waste valorisation has gained prominence in academic and policy discussions to tackle the issue of climate change and to maximize the potential environmental, economic, and social benefits (Chen et al., 2020). Among the various organic wastes, food waste (FW) is emerging as a problem that can contaminate water and land while also contributing to greenhouse gas emissions (Carmona-Cabello et al., 2020). There are limited studies available on the use of FW feedstock due to its diverse composition which requires a wide range of process temperature (Bonga et al., 2020).

On the other hand, substantial quantities of agricultural waste are produced as a byproduct of farming and processing operations, including waste from grape plants (GW) and rice husks (RH) (Bushra and Remya, 2020). There are few viable uses for agricultural waste; the majority are used to make fuel pellets or as livestock bedding, with the majority being frequently incinerated, adding to the growing carbon footprint (Rowan et al., 2022). The conversion of these agro-food wastes

into biochar is an effective technique for their management. Biochar, a pyrogenic biomass product, has emerged as a crucial component for sustainable development approaches aimed at carbon neutralization, agricultural and environmental management (Qin et al., 2022). Biochar is primarily composed of carbons, with trivial amounts of hydrogen, oxygen, nitrogen, sulphur, and ash (Jha et al., 2022). Biochar is typically produced via pyrolysis, which transforms biomass into porous material with a higher carbon content, greater specific surface area, a higher aromaticity, and a diversity of functional groups (Rawat et al., 2023). Slow pyrolysis, which thermally decomposes biomass at temperatures ranging from 300 to 900 °C, is a common method for producing biochar in inert conditions. However, in industrial practices, working temperatures often range from 600 to 650 °C (Cusenza et al., 2021). Nonetheless, biochar's final usage and attributes are heavily reliant on manufacturing conditions and feedstock type (Cai et al., 2021). The biochar's production and its physicochemical characteristics are influenced by several factors, with temperature ((Tomczyk et al., 2020) and heating rate (Tripathi et al., 2016; Zhao et al., 2018) having the most impact and

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have been largely investigated (Chaves Fernandes et al., 2020; Pickering et al., 2011).

The effect of the pyrolysis medium on biochar characteristics is scarcely researched, with much of the literature focused on biochar formation in a nitrogen inert gas environment. Among the different carrier gases, utilizing CO₂ in pyrolysis as an alternative to pure inert atmospheres has recently received particular attention (Pilon and Lavoie, 2013; Liu et al., 2023). The utilization of CO₂ from residual gases into the pyrolysis has the potential to benefit both the economy and the environment. It should be noted, however, that CO₂ is anticipated to have a major effect on the characteristics of pyrolytic products. This is because it has a weaker oxidizing and acidic nature, a higher molecular mass, and a distinct thermal diffusivity than N₂ (Kwon et al., 2019; Parvez et al., 2020). The existing literature on CO₂ pyrolysis has predominantly focused on examining its impact on bio-oil and syngas production at higher temperatures and reported that the increased CO generation, as well as reduced tar and char yields caused by CO₂. This impact is due to an unknown CO₂-induced reaction that takes place independently along with the dehydrogenation of volatile organic carbons. The CO₂ acts as an additional carbon and oxygen provider, contributing to the significant increase in CO production (Jung et al., 2019; Kang et al., 2022; Kim et al., 2016) due to the gasification of CO₂ with carbon (Kwon et al., 2014; Lee et al., 2017c) and increasing total gas yield (Yue et al., 2022). The use of CO₂ as a carrier gas for biochar production via slow pyrolysis within an industrial temperature range has not been thoroughly researched, and information is scarce with only few studies (Tan et al., 2018; Yi et al., 2022a). Available studies reported the mixed effects of adding CO₂ to pyrolysis on biochar (400–600 °C). For example, some studies reported that CO₂ increased the biochar yield (Biswas et al., 2018; Lee et al., 2017b), while others found that it decreased the biochar yield (Jindarom et al., 2007; Zhang et al., 2011) and some reported no discernible difference (Kwon et al., 2015) in contrast to inert N₂ atmosphere. On the other side, CO₂ has been found to significantly affect textural properties of biochar (Chun et al., 2022; Jindarom et al., 2007; Tan et al., 2018).

Based on the abovementioned background, there is a clear research gap regarding the behaviour of CO₂ under different pyrolysis temperatures and heating rates, its impact on various feedstocks under industrial slow pyrolysis conditions, and its effect on a wide range of physico-chemical characteristics of biochar (elemental and proximate, pH, surface functional groups) that are relevant for agricultural and environmental applications. To address these research gaps and develop a more sustainable biochar production platform, the current study focused on biochar production from three feedstocks, namely, FW, RH, and GW, in a CO₂ environment employing a fixed bed batch reactor operated at different temperatures (400, 500, and 600 °C) and the heating rates (5 and 15 °C/min) in comparison with N₂. A detailed analysis was conducted to examine the impacts of CO₂ on a wide variety of biochar formation and its properties, considering varied feedstocks, temperatures, and heating rates. The novelty of this study arises from its thorough investigations of previously overlooked area of biochar research. This study contributes to a better comprehension of the synergistic interactions between CO₂ and biochar production by introducing an innovative concept of employing CO₂ as a medium in the sustainable production of biochar for agricultural and environmental purpose.

2. Materials and methods

2.1. Sample preparation

Three feedstocks were selected according to their origin and availability. One feedstock came from the urban context; the food waste (FW) mostly consisted of cooked pasta, and the other two came from the agricultural context; the rice husk (RH) and grape tree branches waste (GW). The FW was collected from the canteen of Polytechnic of Turin

(Italy), while the RH and GW were provided by the company Ecopack (Piobesi, Italy). The FW sample was homogenized with a mixer and oven dried at 102 °C prior to slow pyrolysis to reduce the moisture content from 64.7 wt% to 1.62 wt%, whereas RH and GW were used in their received forms. The elemental and proximate compositions of FW, RH, and GW are listed in Table 1.

2.2. Pyrolysis experimental procedure

The biochar was produced via slow pyrolysis using a fixed-bed pyrolysis reactor with a capacity of 1L as depicted in Fig. 1. The reactor setup consisted of a stainless-steel chamber equipped with an electric heater and two thermocouples placed at different depths within the reactor. The CO₂ and N₂ gases were kept in the gas supply unit and were controlled at a flow rate of 500 mL/min via mass flow rate controller to create the pyrolysis environment. A condenser was connected at the reactor outlet to collect liquid products, while the permanent gases were collected in a Tedlar gas bag (500 mL) connected to the condenser outlet.

First, 8 to 10 g of feedstock was manually put into the reactor. Prior to heating, N₂ or CO₂ was purged at a flow rate of 500 mL/min for 30 min to establish an inert or CO₂ environment inside the reactor. The reactor was then heated using an automatic proportional-integral-derivative (PID) controlled electric heater, gradually reaching the pre-determined pyrolysis temperature (400, 500, 600 °C) with the heating rate of 5 or 15 °C/min. After reaching the desired temperature, the reaction time (60 min) was started, and a gas bag was connected to the condenser's outlet. Once the reaction time was completed, the heater was switched off and the reactor was left to cool down to ambient temperature. The biochar was then manually removed from the reactor. The liquid product was recovered from the condenser by washing it with ethyl acetate and subsequently separated from the bio-oil using a rotary vacuum evaporator. The biochar was weighed and sealed in an airtight container for characterization. The weight of the liquid products was calculated by the difference of the weight between the condenser before and after experiments. The weight of the non-condensable gas was calculated by subtracting the mass of the biochar and liquid products from the initial mass of the feedstock. The solid yield (Y_m), liquid yield (Y_l) and gas yield (Y_g) were calculated by using the following equations:

$$Y_m(\text{wt}\%) = \frac{m_b}{m_i} \times 100 \quad (1)$$

$$Y_l(\text{wt}\%) = \frac{m_l}{m_i} \times 100 \quad (2)$$

$$Y_g(\text{wt}\%) = 100 - Y_m - Y_l \quad (3)$$

Table 1
Proximate and elemental analysis of feedstocks.

	Food waste (FW)	Rice husk (RH)	Grape waste (GW)
Proximate analysis (wt. %)			
Moisture ^a	1.62	6.90	4.90
Ash ^a	2.42	13.93	2.98
Volatile matter ^a	79.06	72.11	84.37
Fixed carbon ^b	16.90	7.06	7.75
Elemental analysis (wt. %)			
Carbon ^a	40.81	42.99	48.30
Hydrogen ^a	6.45	4.09	5.50
Nitrogen ^a	2.24	1.79	3.55
Sulphur ^a	1.56	0.35	0.21
Oxygen ^b	48.93	50.79	42.43
H/C	1.90	1.14	1.37
O/C	0.90	0.89	0.66
C/N	21.26	28.02	15.87

^a Dry basis.

^b By difference.

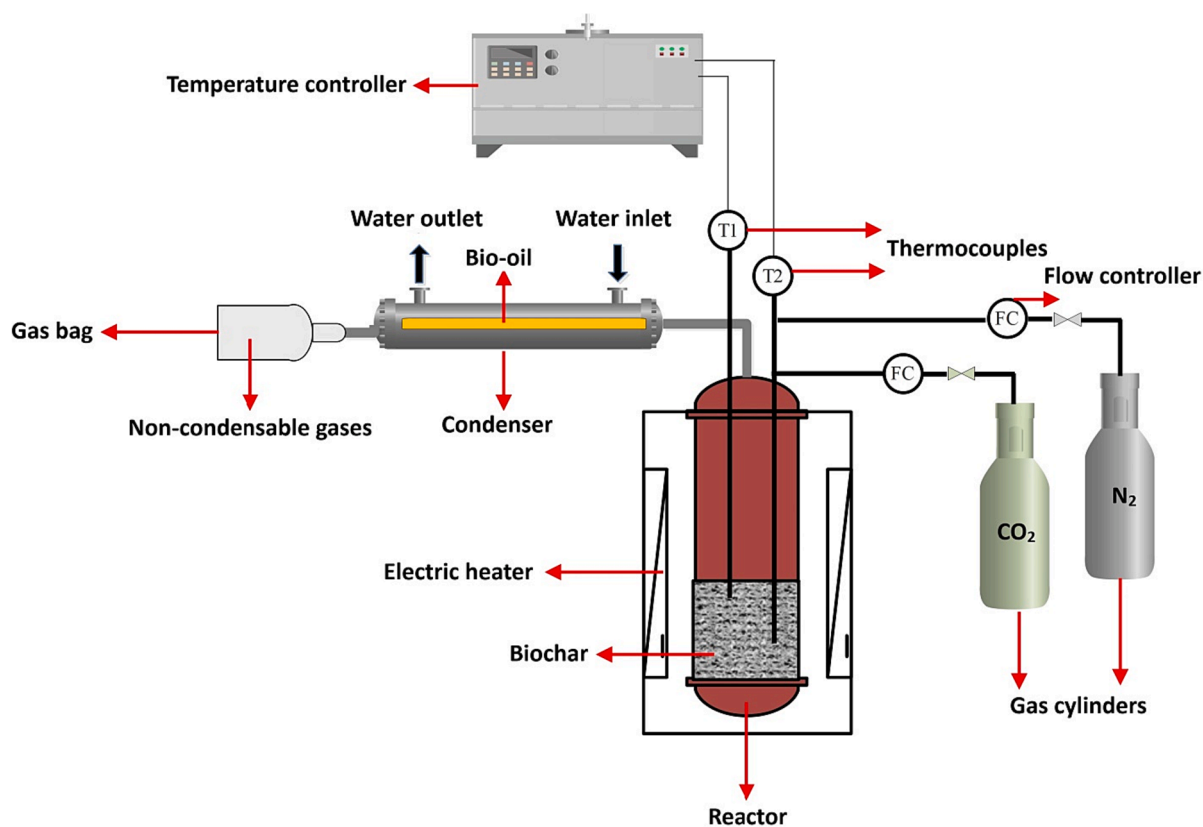


Fig. 1. Schematic diagram of reactor setup.

where m_i indicates the mass of biomass feedstock, while m_b , m_l and m_g represent the mass of biochar, liquid and gas, respectively. All the experiments and characterization analyses were carried out in triplicate.

2.3. Characterisations and analysis

2.3.1. Thermogravimetric analysis of feedstock

The weight changes and rate of weight changes in a biomass feedstock were measured using a thermogravimetric analyser (TGA/SDTA851e) as a function of temperature in a non-isothermal manner. TGA experiments were conducted on samples weighing approximately 20–25 mg, with an argon flow rate of 50 mL/min. The maximum temperature reached during the analysis was 800 °C, and the typical heating rate used was 5 and 15 °C/min to mimic the heating conditions of the laboratory-scale pyrolysis experiments. Each TGA run commenced with a 5 min isothermal hold at 105 °C to ensure that the analysis began with a dry sample.

2.3.1.1. Characterisations of biochar. Thermogravimetric analysis (TGA/SDTA851e) was utilized to perform the proximate analysis of both feedstocks and biochars. For moisture content (MC) determination, approximately 10 to 12 mg of the sample was heated from ambient temperature to 105 °C at a rate of 10 °C/min, followed by a 5 min hold at 105 °C. The temperature was then increased to 900 °C (by 15 °C/min) and kept for 7 min to eliminate volatile matter (VM). The ash content was determined by slowly heating a dried sample at 600 °C in an air atmosphere for two hours. Finally, the fixed carbon (FC) content was calculated by difference as shown in equation (4).

$$FC(\%) = 100\% - (MC\% + AC\% + VM\%) \quad (4)$$

The elemental compositions i.e., carbon (C), nitrogen (N), hydrogen (H), and sulphur (S) contents of biomass/biochar were determined by a

CHNS analyser (Elemental Cube, Germany) through combustion at 950 °C and the weight percentage of oxygen was calculated by difference. The functional groups on the surface of biochar were analysed by F-TIR Spectrophotometer Equinox 55 by Bruker with an MCT (Mercury Cadmium Telluride) within the wavenumber range of 4000 to 400 cm^{-1} . The biochar's specific surface area and total pore volume were measured using the N_2 adsorption method on a BET analyser (Micromeritics TriStar II 3020). Prior to BET analysis, the degassing of samples was carried out under vacuum for 2 h at 300 °C. The samples were then cooled in a liquid nitrogen bath at -196 °C for analysis. A field-emission scanning electron microscope (FESEM; S-4300, Hitachi, Japan) was used to examine the biochar's morphology by sputtering the samples with a thin layer of Pt for one minute prior to image development. The pH of the biochar was measured using a digital pH meter (PH50 XS + DHS, GEASS S.r.L.), employing a biochar/water suspension ratio of 1:20 after 30 min of mechanical shaking.

3. Results and discussion

3.1. Characterisations of feedstock

The proximate and elemental analysis results for the three feedstocks (FW, RH, and GW) used in the production of biochar through slow pyrolysis are shown in Table 1. Dried FW demonstrated a higher FC content (16.90%) and S (1.56%) while lower AC (2.42%), and C (40.81%). RH had a higher AC (13.93%) and O (50.79%), and GW exhibited higher VM (84.37%) and C contents (48.30%). Additionally, the different S contents of the three feedstocks can be seen, with FW having the highest S content at 1.56% while RH and GW have the lowest S contents at 0.35% and 0.21%, respectively. The content of S in different kinds of biomass varies significantly. Typically, agricultural waste contains lower S content as shown in RH and GW. However, the higher S content in FW could be attributed to sulphur-containing ingredients in FW like animal

proteins, plant proteins and vegetables (Zhang et al., 2023) in mixed and cooked food waste used in this study. These results are relatively comparable with the literature (KOÓS, 2014; Shen and Fu, 2018; Zacharof, 2017). These differences in composition can impact the pyrolytic performance and the properties of the resulting biochar. Understanding these compositional variations is crucial for selecting appropriate feedstocks and optimizing the biochar production process for specific

applications i.e., soil amendment, carbon sequestration, and environmental remediation (Adhikari et al., 2022; Bonga et al., 2020). Fig. 2 depicts the thermogravimetry (TG) and derivative thermogravimetry (DTG) curves of the three feedstocks analysed under a N₂ atmosphere at the heating rate of 5 °C/min (the TGA and DTG of feedstocks carried out at heating rate of 15 °C/min is shown in Figure S1). It is important to note that the TGA analyses were not conducted under a CO₂ atmosphere

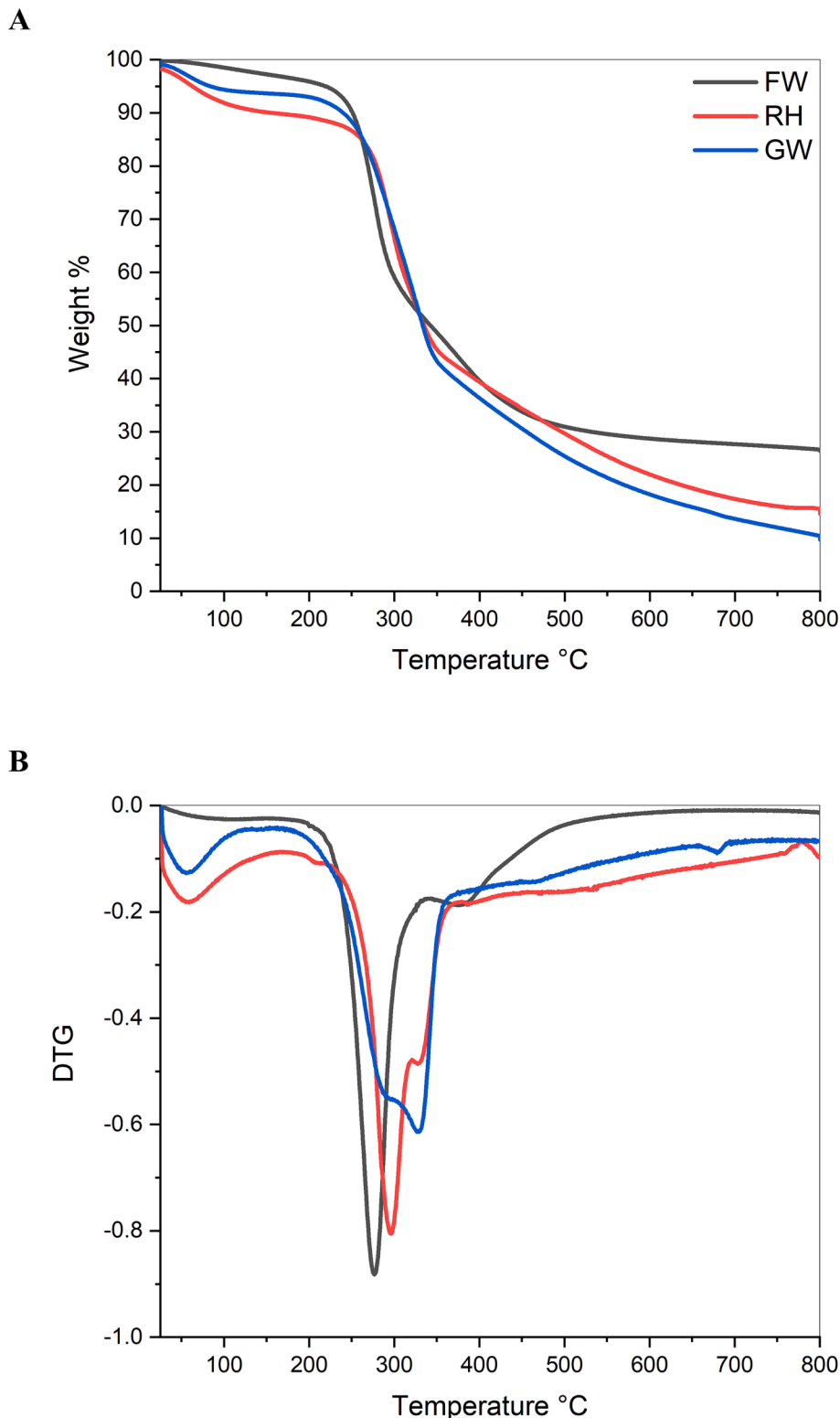


Fig. 2. TGA (A) and DTG (B) curves of FW, RH and GW at heating rate of 5 °C/min.

in this study because majority of the previous studies demonstrated that changing medium from inert to CO₂ in TGA had minimal influence on the physical properties, specifically the onset and end temperatures, of thermal decomposition process for various biomass samples (Lee et al., 2017a; Premchand et al., 2023).

As shown in Fig. 2 A, overall GW showed the highest weight loss (88%), followed by RH (80%) and GW (70%) and it could be because of proximate and compositional differences. Moreover, the feedstocks' weight loss exhibited three distinct stages. The initial stage, from room temperature to 200 °C, showed a weight loss of around 10% attributed to evaporation and dehydration, releasing water and light volatiles. The second stage, between 200 and 500 °C, exhibited significant thermal degradation, resulting in a weight loss of approximately 60 to 65%. This degradation primarily stemmed from hemicellulose, cellulose, and lignin (Cho et al., 2015). The third stage occurred between 500 and 800 °C, with a marginal decrease in weight attributed to the thermal decomposition of heavier components (PREMCHAND, 2019). Similar stages of biomass decomposition can be clearly seen in the DTG curves (Fig. 2 B). Based on preliminary TGA results, pyrolysis temperatures of 400, 500, and 600 °C were chosen for the experiments in the fixed bed reactor.

3.2. Effect of CO₂ on pyrolysis product's distributions

The yields of biochar, liquid, and gas obtained from different feedstocks (FW, RH, and GW) under varying pyrolysis conditions, including temperatures (400, 500, and 600 °C), atmospheres (N₂ and CO₂), and heating rates (5 and 15 °C/min) are depicted in Fig. 3. Overall, these findings reveal a consistent pattern where the biochar yield gradually decreases, while the liquid and gas yields increase as the pyrolysis temperatures and heating rates are elevated. This trend is well understood and frequently reported in the literature, and it is attributed to the accelerated break down of organic matter, condensation, and polymerization reactions at elevated temperatures (Aktar et al., 2022; Jha et al., 2022). Similar trend of decreasing biochar yield with increasing temperature was found by (Rodriguez et al., 2021) from the co-pyrolysis of industrial and agricultural wastes. Fig. 3A depicts the yield of biochar from the pyrolysis of FW, RH and GW at different temperatures, and heating rates under CO₂ and N₂ atmosphere. Overall, CO₂ atmosphere led to increased biochar yield across all three temperatures (400, 500, and 600 °C) as well as heating rates (5 and 15 °C/min) with expense of liquid or gas yield, compared to N₂ atmospheres. However, upon examining the effect of CO₂ at different temperatures in comparison to N₂, it was observed that at lower pyrolysis temperatures (400–500 °C), CO₂ led to a higher biochar yield compared to the yield at 600 °C. For instance, at 400 °C, the utilization of the CO₂ atmosphere resulted in a significant rise increase in biochar yield, with a percentage increase of approximately 4.84% for RH. In contrast, at 600 °C, the increase in biochar yield by CO₂ was only 0.1%. This biochar yield trend was also observed for FW and GW. Similar results have been observed for lignin (Yi et al., 2022b), cellulose (Yi et al., 2022a), sawdust (Kim et al., 2021), and rice straw (Biswas et al., 2018) as shown in Table S1. The results indicate that CO₂ could be used to enhance the biochar yield and for that moderate temperature (400–500 °C) is favourable.

On the other hand, the atmosphere of CO₂ has demonstrated a significant influence on the liquid and gas yields (compared to biochar), as depicted in Fig. 3B and 3C. Notably, these effects exhibit a dependence on the type of feedstock employed. For lignocellulosic biomass (RH and GW) the atmosphere of CO₂ increased in the liquid yield, while concurrently decreasing the gas yield. For FW, however, the relationship was observed to be inverse, with the CO₂ atmosphere leading to decrease the liquid yield while increase the gas production. These findings underscore the pronounced influence of both the feedstock type and the atmospheric conditions, emphasizing the need for careful consideration of these factors in the optimization of pyrolysis processes for various biomass sources. Overall, for RH and GW feedstocks, the presence of a

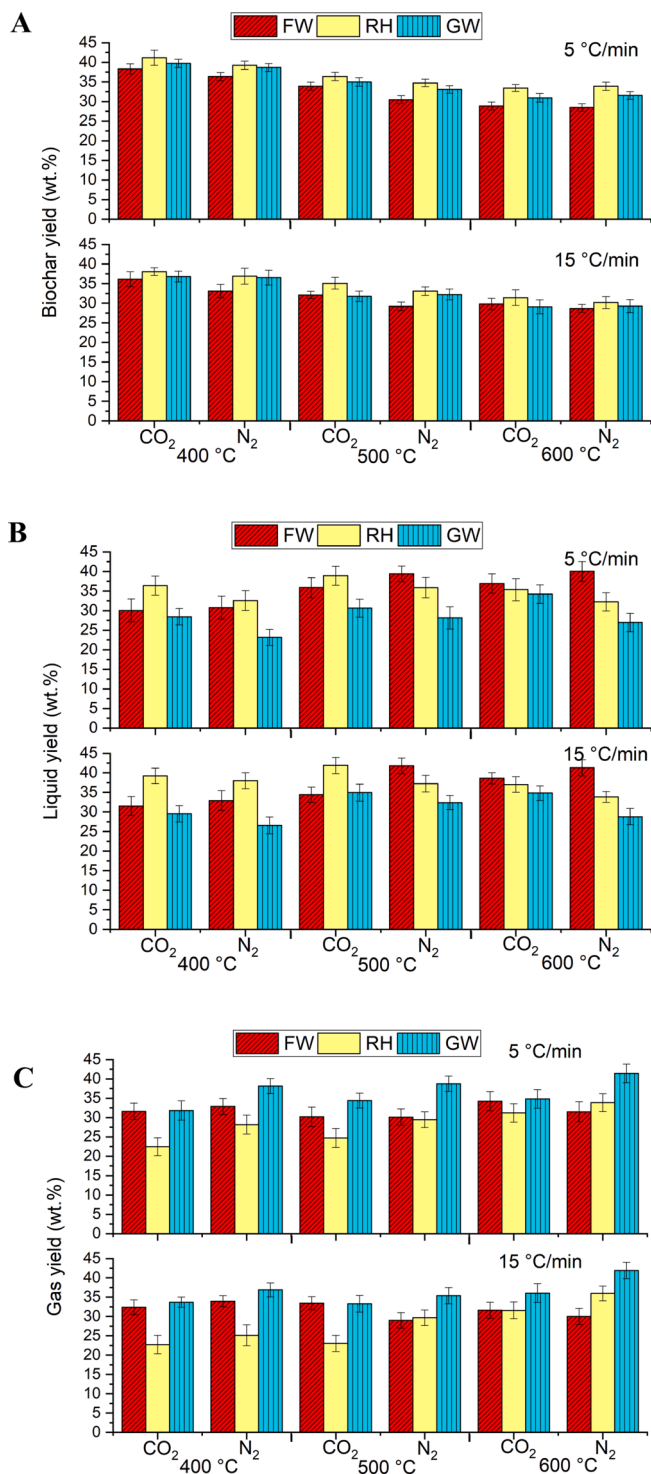


Fig. 3. Yields of biochar (A), liquid (B), and gas (C) from the pyrolysis of FW, RH and GW under CO₂ and N₂ atmospheres.

CO₂ atmosphere resulted in an increase in both the biochar and liquid yields, accompanied by a decrease in the gas yield. For RH, the CO₂ atmosphere resulted in a maximum increase in liquid yield of 12.47% at 500 °C temperature with 15 °C/min heating rate. In the case of GW, the maximum increase in liquid yield induced by the CO₂ atmosphere was 26.76% at a 600 °C of pyrolytic temperature with heating rate of 5 °C/min. There could be several possible explanations for this observation. The presence of CO₂ may have inhibited the cracking process or promoted secondary condensation of volatile compounds, which could have

facilitated the generation of biochar and bio-oil while inhibiting gas production via gasification or cracking reactions (Yi et al., 2022b). Additionally, it is also possible that CO₂ reacted with the uncondensed gas, leading to the formation of condensed oil or CO₂ may have accelerated defragmentation reactions, producing compounds that were then repolymerized to produce biochar (Biswas et al., 2018). The trend aligns with earlier research findings for lignin (Yi et al., 2022b), cellulose (Yi et al., 2022a), sawdust rice straw and spent coffee grounds (Kim et al., 2021).

For FW, the CO₂ atmosphere led to an increase in the biochar and gas yields, while simultaneously reducing the liquid yield. The maximum gas yield was observed at a pyrolytic temperature of 500 °C and a heating rate of 15 °C/min, where the gas yield increased by a factor of 1.154 % by CO₂ in comparison with N₂. This implies that in CO₂ environment, the carbon in the food waste transformed from liquids to gases. In other words, the presence of CO₂ aided in the breakdown of macromolecules (i.e., those that can condense) into lighter molecules (i.e., permanent gases) (Lee et al., 2020; Lin et al., 2020).

3.3. Effect of CO₂ on biochar properties

3.3.1. Proximate analysis

The proximate analysis has significant importance for understanding the agro-environmental related characteristics of biochar. The VM content of biochar refers to its level of thermal alteration, and this characteristic has a direct impact on the dynamics of carbon and nitrogen in soil (Maaz et al., 2021). In general, biochars with high VM

content may not be suitable as soil amendments due to their potential to stimulate microbial activity and temporarily immobilize plant-available nitrogen (N) (Deenik et al., 2009). On the other hand, higher AC can indicate a rich mineral composition, which may be beneficial for improving soil nutrient levels and higher FC suggests the biochar's stability and resistance to further decomposition (Leng et al., 2019). Table 2 indicates the proximate analysis of biochars generated from different feedstocks at different temperature levels and heating rates under both atmospheric conditions. Overall, regardless of the atmosphere, the VM content generally decreases while the AC and FC contents increase with the rising of pyrolysis temperature as well as heating rate. For example, for FW, the VM contents decreased from 23.55% to 13.75% as the temperature rose from 400 to 600 °C at a heating rate of 5 °C/min under N₂ atmosphere. Concurrently, the AC increased from 10.22% to 14.57%, and the FC contents increased from 55.58% to 68.93%. Similarly, for GW biochar under a CO₂ atmosphere, the VM contents decreased from 25.89% to 9.11%, AC increased from 10.06% to 12.96% and FC contents increased from 63.16 to 77.18% by increasing temperature from 400 to 600 °C at a heating rate of 15 °C/min under CO₂ atmosphere. The RH followed the same pattern. The increase in AC with temperature could be due to organic matter decomposition leaving the non-volatile mineral components through the expulsion of volatile organic products. At higher pyrolysis temperatures, the labile carbon present in volatile matter can undergo transformation into a more resilient form, thereby leading to an increase in the FC contents (Aktar et al., 2022; Komiyama et al., 2020). On the effect of pyrolysis atmosphere, as shown in Table 1, biochars produced under CO₂ pyrolysis

Table 2
Ph, proximate (wt%) and elemental (wt%) analyses of biochars.

Feedstock	Biochar	pH	Ash ^a	Volatile matter ^a	Fixed Carbon ^b	Carbon ^a	Hydrogen ^a	Nitrogen ^a	Sulphur ^a	Oxygen ^b	H/C	O/C	
Food waste	400–5-C	7.45	11.82	28.99	59.19	70.99	3.84	4.92	0.74	19.51	0.65	0.21	
	400–5-N	7.69	10.22	30.62	59.16	66.06	4.11	4.94	0.34	24.55	0.75	0.28	
	500–5-C	8.30	12.68	18.42	68.90	71.09	2.27	5.15	0.23	21.26	0.38	0.22	
	500–5-N	8.41	12.42	18.72	68.86	72.64	2.77	4.78	0.30	19.46	0.46	0.20	
	600–5-C	8.40	13.17	21.79	65.04	75.87	2.21	4.89	0.68	16.35	0.35	0.16	
	600–5-N	9.03	14.57	22.59	62.84	74.17	2.26	4.82	0.28	18.47	0.37	0.19	
	400–15-C	7.79	10.77	35.85	53.38	72.58	3.97	5.14	0.37	17.94	0.66	0.18	
	400–15-N	7.86	14.61	37.46	47.93	71.82	4.24	5.15	0.83	17.96	0.71	0.19	
	500–15-C	8.16	12.96	20.69	66.35	74.7	2.98	5.08	0.15	17.09	0.48	0.17	
	500–15-N	8.44	11.99	23.50	64.51	72.83	3.07	4.97	0.27	18.86	0.51	0.19	
	600–15-C	8.48	14.51	24.39	61.10	76.18	2.22	4.84	0.11	16.65	0.35	0.16	
	600–15-N	8.70	16.29	27.16	56.55	76.49	2.21	4.62	0.37	16.31	0.35	0.16	
	Rice husk	400–5-C	7.84	14.12	35.53	50.35	57.43	3.13	1.56	0.19	37.69	0.65	0.49
		400–5-N	7.94	13.25	37.36	49.39	54.46	2.43	1.55	0.66	37.90	0.53	0.52
		500–5-C	8.23	23.43	19.05	57.52	59.22	2.37	1.55	0.17	36.70	0.48	0.46
500–5-N		8.32	26.74	18.46	54.80	60.00	2.61	1.55	0.16	35.68	0.52	0.45	
600–5-C		9.34	29.46	17.15	53.39	68.30	1.73	1.35	0.23	28.4	0.30	0.31	
600–5-N		9.72	32.39	17.36	50.25	64.00	1.90	1.35	0.22	28.52	0.36	0.33	
400–15-C		7.48	20.18	26.68	53.14	65.89	3.30	2.01	0.02	28.78	0.60	0.33	
400–15-N		7.95	22.43	28.37	49.20	63.81	3.63	1.43	0.02	31.11	0.68	0.37	
500–15-C		8.45	24.45	28.68	46.87	69.5	2.98	1.98	0.08	25.46	0.51	0.27	
500–15-N		8.27	28.46	28.94	42.60	67.30	2.61	1.55	0.16	27.35	0.55	0.30	
600–15-C		8.84	33.45	15.08	51.47	74.09	2.09	1.68	0.12	22.02	0.34	0.22	
600–15-N		9.68	34.36	15.45	50.19	72.00	1.90	1.35	0.22	24.52	0.32	0.26	
Grape waste		400–5-C	5.89	9.36	26.60	64.04	56.33	6.17	1.13	0.09	36.28	1.31	0.48
		400–5-N	5.92	8.12	28.54	63.34	50.75	6.40	1.18	0.09	38.40	1.51	0.57
		500–5-C	7.22	11.43	15.81	72.76	68.00	5.59	1.04	0.14	25.23	0.99	0.28
	500–5-N	7.23	10.98	15.03	73.99	64.80	5.80	1.08	0.14	38.40	1.07	0.44	
	600–5-C	7.69	11.05	10.04	78.91	74.22	4.92	0.96	0.29	19.61	0.80	0.20	
	600–5-N	7.87	12.74	10.74	76.52	69.08	5.10	1.00	0.30	38.4	0.89	0.42	
	400–15-C	6.08	10.06	25.89	64.05	63.05	6.63	1.69	0.02	28.61	1.26	0.34	
	400–15-N	6.12	9.12	27.07	63.81	56.80	6.88	1.76	0.02	34.54	1.45	0.46	
	500–15-C	7.42	12.47	14.03	73.50	72.00	5.79	1.49	0.12	20.61	0.96	0.21	
	500–15-N	7.57	11.04	16.73	72.23	68.80	6.00	1.55	0.12	23.53	1.05	0.26	
	600–15-C	7.72	12.96	9.11	77.93	73.42	5.30	1.36	0.25	19.66	0.87	0.20	
	600–15-N	7.95	12.89	9.77	77.34	70.80	5.50	1.42	0.26	38.40	0.93	0.41	

5 and 15 represent heating rate in °C/min.

C and N represent pyrolysis atmosphere CO₂ and N₂.

^a Dry basis; ^b By difference.

generally exhibited lower VM contents and higher FC contents compared to biochars produced under N_2 pyrolysis, with few exceptions. The AC, on the other hand, did not follow a consistent trend. However, at lower pyrolysis temperatures, the use of CO_2 resulted in higher AC in the biochars, while at elevated temperatures, N_2 produced higher AC. For example, when RH was pyrolyzed at 500 °C under N_2 atmosphere, the resulting biochar had an AC of 26.74%, VM content of 18.46%, and FC content of 54.80%. In contrast, under similar conditions but with CO_2 atmosphere, the biochar had an AC of 23.43%, VM content of 19.05%, and FC content of 57.52%. In the literature (Table S1), only a few studies have presented the effect of CO_2 on proximate analysis of biochar. Aktar et al., (Aktar et al., 2022) did not find any major difference on AC and FC for biosolid derived biochars, however, the VM was significantly affected by CO_2 being lowered compared to N_2 pyrolysis. The same trend of increasing AC and FC contents while decreasing VM contents under CO_2 atmosphere was reported for biochar derived from pine sawdust briquettes (Liu et al., 2018). The lower VM content in biochar produced from CO_2 atmosphere observed in this study is likely because of CO_2 suppressing the release of volatile organic compounds (VOC) during pyrolysis. CO_2 can act as a diluent gas, reducing the volatility of organic compounds and favouring their transformation into more stable carbonaceous structures. Higher FC contents may result from the presence of CO_2 , which can cause the conversion of labile carbon compounds into more stable carbon structures, increasing the proportion of FC in the biochar. Overall, the influence of CO_2 during pyrolysis promotes the production of biochar by favouring carbonization reactions, reducing the removal of volatile matter, and enhancing the formation of stable carbon structures.

3.3.2. Elemental analysis

Elemental analysis of biochar (C, H, N, S, and O) provides critical information about its nutrient dynamics, carbon sequestration potential, environmental impact, biochar characterization, and quality control (Bushra and Remya, 2020; Sun et al., 2021). Moreover, biochar's H/C and O/C molar ratios are crucial factors of its stability, carbon sequestration capability, nutrient retention and availability, and impact on soil structure (Abagandura et al., 2022). Understanding these ratios allows for informed selection and application of biochars in agro-environmental practices, facilitating their optimal utilization for sustainable agriculture and soil management. Lower H/C and O/C ratio biochars generally possess higher thermal stability, which makes them more resistant to deterioration and breakdown in the soil. Because of its stability, biochar can benefit long-term carbon sequestration (Ghani et al., 2013). Moreover, biochar with lower H/C and O/C ratios are generally associated with higher surface area and cation exchange capacity (CEC), which enhances the biochar's capacity to retain and exchange essential plant nutrients (Tag et al., 2016). Elemental analysis of all the biochars is listed in Table 2. Overall, the elemental compositions of biochars were significantly influenced by pyrolysis temperature. The increase in temperature from 400 to 600 °C significantly increased the carbon contents from 57.43 to 68.30% for RH biochar under CO_2 pyrolysis, and from 66.06% to 74.17% for FW biochar pyrolyzed under N_2 atmosphere, on the contrary it significantly reduced H and O contents. GW biochar followed the same trend. It has been suggested that raising the pyrolysis temperature aids in the elimination of O and H by removing volatile substances, undergoing thermal breakdown processes, and carbonizing the remaining carbon-dense compounds (Yi et al., 2022b).

Looking on the effect of pyrolysis atmosphere, as shown in Table 2, CO_2 significantly increased all biochars' carbon contents relative to the N_2 atmosphere while decreasing their hydrogen and oxygen contents. For example, biochar produced from GW at 500 °C and 5 °C/min under N_2 atmosphere contained 64.8% of C, 5.8% of hydrogen and 38.4% of oxygen, while at similar conditions, CO_2 pyrolysis resulted in biochar with 68% of carbon, 5.59% of hydrogen and 25.23% of oxygen, respectively.

The CO_2 aided pyrolysis affects the reaction pathways and thermodynamics during the decomposition of biomass. It promotes carbonization, facilitates the removal of hydrogen and oxygen through reactions and inhibits secondary reactions that could increase the hydrogen and oxygen contents. As a result, pyrolysis in a CO_2 atmosphere tends to yield biochar with lower H/C and O/C ratio compared to pyrolysis in a nitrogen atmosphere (Kim et al., 2021; Yi et al., 2022b). This indicates that the presence of CO_2 during pyrolysis results in the biochar with a greater level of aromatic compounds and enhanced thermal stability. This trend is consistent with earlier studies conducted under the presence of CO_2 (Kim et al., 2021; Yi et al., 2022a; Yi et al., 2022b).

3.3.3. Ash and pH

The pH of biochar influences soil chemical properties, nutrient availability, microbial activity, and overall soil health and plays a crucial role in influencing soil pH when biochar is applied to agricultural or remediation systems (Bushra and Remya, 2020; Sun et al., 2021). pH and ash contents of all the biochars are listed in Table 2. As mentioned earlier, CO_2 as a reaction atmosphere increased the ashes in the biochars and the ash contents and pH are positively correlated since it mostly contains inorganic mineral contents (Komiya et al., 2020). In this study, all the biochars, except for the one produced from GW at 400 °C (pH 5.89–5.92), were found to be alkaline. An interesting observation in this study was that despite the biochars having higher ash content under a CO_2 atmosphere, the pH of the biochar (CO_2 medium) was consistently lower than that of biochar produced under an N_2 atmosphere and could be beneficial in terms of regulating the acidity or alkalinity of biochar according to specific application requirements (Lee et al., 2017b).

Pyrolysis under a CO_2 atmosphere may induce different chemical reactions compared to N_2 atmospheres. These reactions can lead to the formation of acidic compounds or alteration of the biochar's chemical composition, affecting its pH (Parvez et al., 2020; Premchand et al., 2023). The similar observations of decrease of pH under CO_2 pyrolysis were reported by different authors (Aktar et al., 2022; Kończak and Oleszczuk, 2020; Lee et al., 2017b) as reported in Table S1.

3.3.4. Specific surface area and porosity

The textural properties are the primary characteristics of biochar and play a crucial role in the adsorption-based removal of heavy metals, inorganic contaminants, and organic pollutants from soil (Premchand et al., 2023).

The pore volume (PV) and surface area (SA) of biochars produced from various feedstocks and various pyrolytic conditions are shown in Fig. 4. Irrespective of the atmospheric conditions, the pyrolysis temperature showed to exert a significant influence on the textural properties of the resulting biochar. An increase in temperature was observed to enhance both the SA and PV of the biochar. For example, increasing the pyrolysis temperature from 400 to 600 °C (5 °C/min in a N_2 atmosphere) increased the SA of RH biochar 5.3 times, FW biochar 3.8 times, and GW biochar 5.7 times. Similarly, the PV increased 1.3 times for RH, 1.3 times for FW, and about 3 times for GW.

Similar trends were observed for CO_2 atmosphere. In terms of heating rate, it was observed that a higher heating rate of 15 °C/min resulted in biochar with a relatively greater PV and SA than lower heating rate (5 °C/min). It is well known that the increase in both pyrolysis temperature and heating rate could accelerate the thermal breakdown of organic compounds, the elimination of VM, and the subsequent formation of pores and voids which ultimately contribute to an expansion in the SA and PV of the resulting biochar (Aktar et al., 2022; Biswas et al., 2018; Fu et al., 2023).

Between the atmospheres, it was observed that the introduction of CO_2 led to biochar with a significantly higher SA and PV than N_2 atmosphere, with this difference being particularly apparent at higher temperatures, (i.e., 600 °C). For instance, under N_2 atmosphere (600 °C and 15 °C/min), the SA and PV of RH derived biochar reached 55.7013

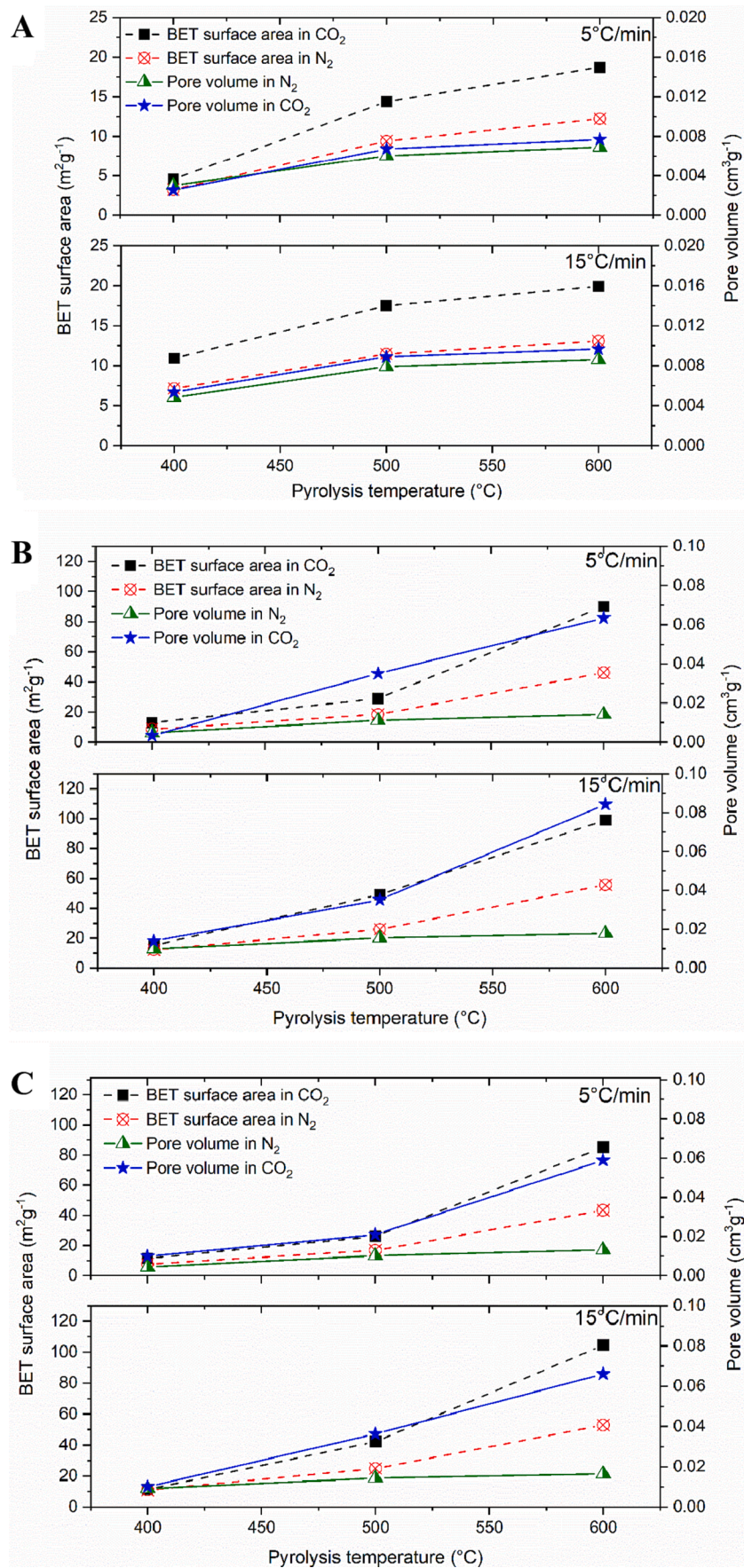


Fig. 4. Specific surface area and pore volume of biochars derived from pyrolysis of (A) FW, (B) RH and (C) GW.

m²/g and 0.0178 cm³/g, FW biochar were 13.0756 m²/g and 0.0086 cm³/g, and GW biochar showed 52.8760 m²/g and of 0.0164 cm³/g. In contrast, under CO₂ atmosphere (similar temperature and heating rate), the resulting biochars demonstrated significantly higher PV and SA. For example, RH derived biochar exhibited a SA of 141.0356 m²/g and a PV of 0.0843 cm³/g, FW biochar displayed a SA of 19.9140 m²/g and a PV of 0.0097 cm³/g, and GW derived biochar showed a SA of 104.5600 m²/g and a PV of 0.0661 cm³/g, respectively. CO₂ increased the SA and porosity of the resultant biochars, is frequently reported in the literature (Table S1) for a different feedstock including red pepper stalk (Lee et al., 2017b), rice straw (Tan et al., 2018), sewage sludge (Jindarom et al., 2007), and biosolids (Aktar et al., 2022).

Several factors can be attributed to the observed increase in SA and PV of biochar under CO₂ environments. One well-known mechanism is the role of CO₂ as a gasification agent. During pyrolysis, CO₂ can react with the carbonaceous material, facilitating gasification and releasing extra VM, resulting in more porous structural biochar (Parvez et al., 2020; Premchand et al., 2023). However, this mechanism does not seem

to fit here due to the increased amount of biochar yields as well as carbons in the resulting biochars. Therefore, another possible mechanism would be the influence of CO₂ atmosphere on carbonization process. The presence of CO₂ can alter the chemical reactions and kinetics of pyrolysis by enhancing the disintegration of organic compounds and facilitate the formation of smaller carbonaceous fragments, which contribute to the increased development of mesopores and micropores (Premchand et al., 2023; Yi et al., 2022a; Yue et al., 2022). Moreover, the interaction between carbon and CO₂ could promote the formation of porous structures within the biochar, increasing its SA and porosity. Furthermore, the morphologies of biochars obtained from RH and GW at 600 °C under N₂ and CO₂ atmospheres are shown in Fig. 5. Biochars produced under a CO₂ atmosphere exhibited more destructive morphology with increased porosity and larger pores. Obviously, as mentioned above, CO₂ as an atmosphere can interact in a certain way during the pyrolysis, like enhancing the decomposition of organic compounds, leading to the formation of smaller carbonaceous fragments which contribute to the observed destructive morphology and increased

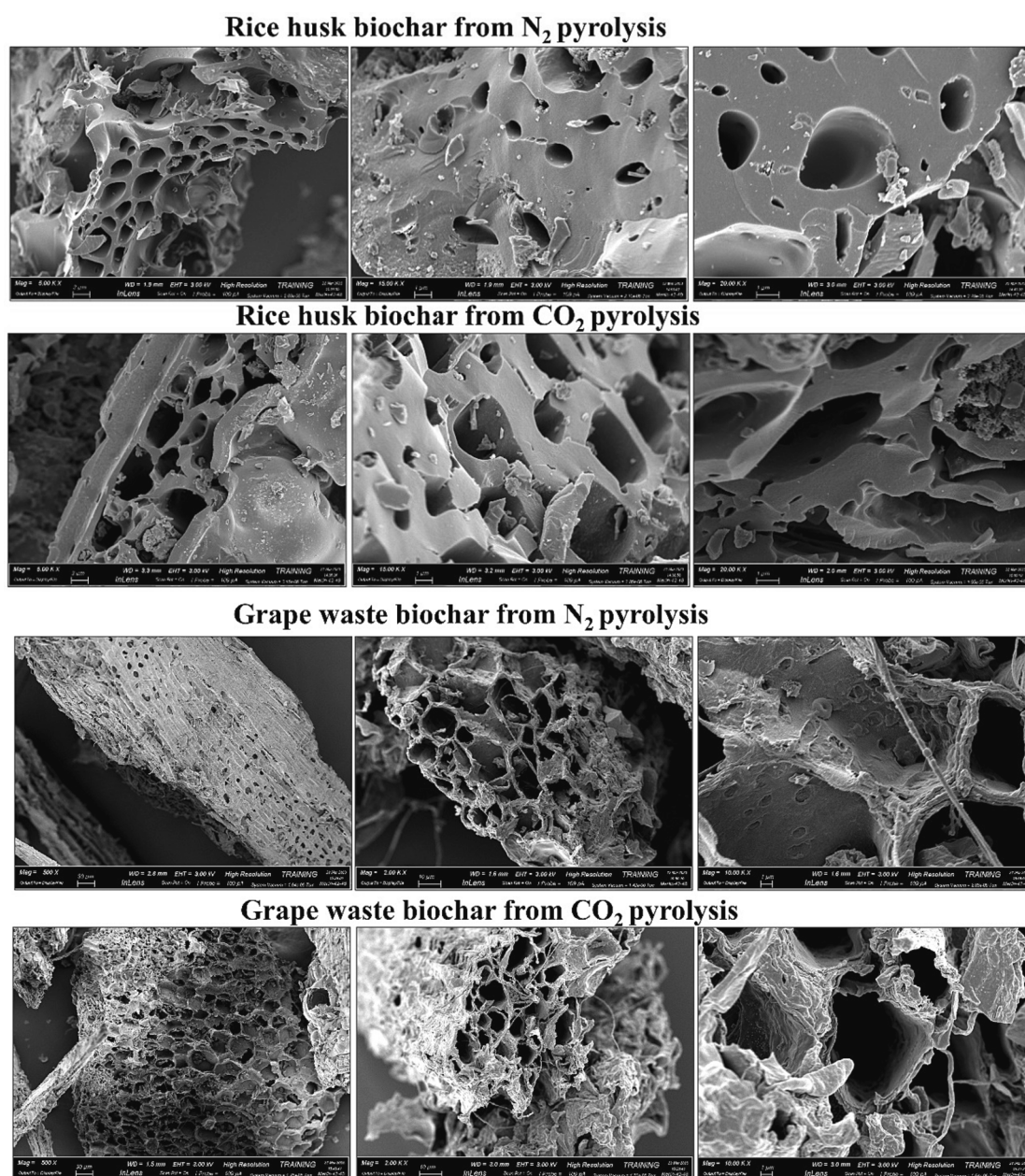


Fig. 5. FE-SEM images of RH and GW biochars under N₂ and CO₂ pyrolysis.

porosity. Overall, the presence of CO₂ during pyrolysis influences the chemical reactions and kinetics, enhances the decomposition of organic compounds, acts as a carbon source for reorganization, promotes the formation of porous structures, and facilitates the re-condensation and reorganization of carbon compounds. These combined effects contribute to increased carbon content, SA, and porosity of the resulting biochar. The larger SA and improved porosity of CO₂-derived biochar creates a larger matrix for possible adsorption of soil elements such as nutrients, heavy metals, and organic compounds. This increased adsorption capacity has broad implications for soil quality and plant nutrition. Thus, CO₂-derived biochar has the potential to boost nutrient availability to plants by effectively adsorbing and conserving key nutrients, enabling healthier growth and greater agricultural yields.

3.3.5. FT-IR analysis

Functional groups in biochar play important roles in its agro-environmental applications such as influencing nutrient retention and release, cation exchange capacity, soil pH and microbial interactions (Kamali et al., 2022; Premchand et al., 2023). Fig. 6 indicates the FT-IR patterns of biochars produced from three different feedstocks using different pyrolysis conditions. The weak and broad intensity of a band between the wavenumber 3400–3700 cm⁻¹ (FW), representing the stretching vibration of hydroxyl (–OH) functionalities, was found either weak or vanished completely which is attributed to the decomposition of larger amounts of free hydroxyl groups and relative hydroxyl groups causing the decrease in their presence (Aktar et al., 2022; Zhang et al., 2021). The absorbance bands observed in biochars at 2800–3000 cm⁻¹,

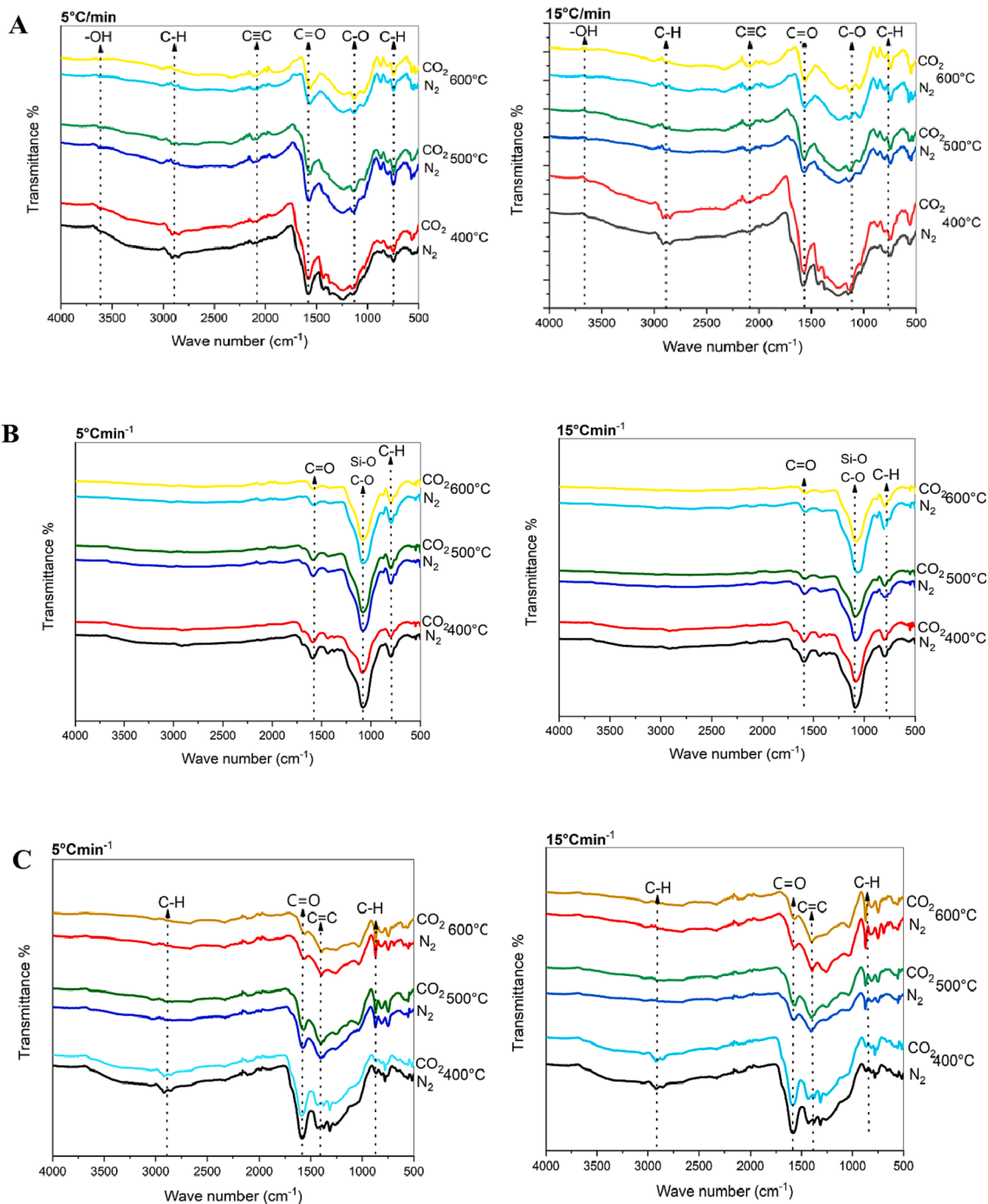


Fig. 6. FT-IR spectra of biochars from FW (A), RH (B) and GW (C).

which correspond to aliphatic CH_n groups (stretching of C–H bonds), showed a significant reduction, and nearly disappeared at higher pyrolysis temperatures and could be attributed to the increased levels of dehydration and aromatization occurring during the pyrolysis process (Kim et al., 2021; Tang et al., 2022). Furthermore, the absorbance peaks identified between 1300 and 1680 cm⁻¹ were attributed to C = O stretch indicating the presence of aldehydes, aromatic C = C stretching from the aromatic ring (Lee et al., 2017b; Yi et al., 2022b). The peak detected at 950–1246 cm⁻¹ was associated to the stretching of C–OH, C–O and C–O–C functional groups (Komiya et al., 2020). The functional groups in the biochar were not notably altered by the type of atmosphere. All the functional groups found in the N₂ pyrolyzed biochars were also present in the CO₂ pyrolyzed biochar, however, upon careful examination, it was found that the intensities of oxygen functional groups in CO₂ atmosphere were relatively lower compared to N₂ pyrolyzed biochar's. Overall, the pyrolysis temperature showed significant effect on biochar functionalities followed by heating rate and atmosphere.

4. Conclusions

The slow pyrolysis of food waste, rice husk, and grape waste was investigated in a fixed bed pyrolyzer in CO₂ and N₂ atmospheres. The findings underscore the significant influence of the choice of reaction medium on the pyrolysis product yields and the resulting biochar properties. Notably, under CO₂ environment, biochar yields increased consistently across all feedstock types, with the most pronounced effects occurring at moderate temperatures between 400 and 500 °C. At higher temperatures (600 °C), the differences between the two atmospheres became less distinct. On the other hand, the use of CO₂ as the reaction medium significantly altered the physicochemical properties of the resulting biochar, including changes to the elemental and proximate compositions, acidity/alkalinity profiles, and surface properties. These findings show that adding CO₂ during slow pyrolysis can modify the properties of biochar for specific applications. This study demonstrates the dual benefits of using CO₂ in this context, producing biochar with improved agro-environmental properties while also promoting more sustainable waste management practices.

Declaration of Competing Interest

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

Data availability

Data will be made available on request.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.wasman.2023.10.035>.

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