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Characterization of Corncob Biochar Produced through the Gasification Process for Application as Soil Amendment

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ABSTRACT

Corn cob (CC) produces the highest amount of solid waste from the agriculture sector globally because cob is slow to decompose. Conversion of the CC into carbonaceous material obtained from thermal decomposition of biomass called 'biochar' will be of great value. Biochar is considered a beneficial soil amendment for its role in improving soil physical, chemical and biological properties, that help in enhancing crop productivity. However, the biochar properties depend on the method of biochar production as well as the feedstock. Hence, the assessment of characteristics of biochar produced from cobs using the gasification process is critical. In this study corn cob biochar (CCB) produced from the gasification (800 °C) process is subject to proximate, ultimate and physiochemical analysis for assessing the characters desirable for using biochar as a soil amendment. High ash content (38.02 wt%) and fixed carbon content (31.83 wt%), O/C (0.389), H/C (0.071), low bulk density (0.55 g cc^{-1}), high water holding capacity (124.29%), alkaline pH (10.2), and low CEC (2.72 μS^{-1}) and presence of traces of major and micronutrients, indicate that the CCB can be useful for soil amendment of agricultural soils.

Keywords: Corncob biochar, Gasification, Characterization, Soil amendment

AGRICULTURE makes a significant contribution to the Indian economy and the livelihood of the majority of the population. In different agro-ecological regions of India, a wide range of crops are cultivated across the vast majority of land with a significant quantity of crop residue (non-economical plant parts) left in the field after harvest. Despite using large quantities of agriculture residues as cattle feed, animal bedding, cooking fuel, organic manure, etc., nearly 234 million tonnes / year (30%) is available as surplus. This huge amount of crop residues can still be utilized economically (Devi *et al*., 2017). Energy being the most critical input of all sectors, utilizing excess crop residue has received significant attention in the production of biofuels. The high percentage of agriculture resources produced globally is inefficiently recycled (Billa *et al*., 2019). Burning plant-derived biomass has increased for coal production, but it has serious implications on the environment and human health. Therefore, modified methods are used to increase the efficiency of producing higher-grade fuels (Mark *et al*., 2018).

Waste generated in the food processing from crops such as corncob, rice husk, straws are a potential source of feedstock to produce biochar (Billa *et al*., 2019). Among these crops, corn produces a huge amount of cobs as solid waste and the disposal of cobs is a real concern because it is difficult to decompose naturally. Therefore, conversion of the corn cob to biochar is an efficient way of disposal. Corn is emerging as one of the major crops cultivated because of its wide utility and easy to cultivate under varied climatic conditions (Kuntoji and Subbarayappa, 2021). In India corn is the 3rd most important food crop after wheat and rice. Since corn production is about 2.90 million metric tonnes, so is the corncob waste generated (Rekha and Saravanathamizhan, 2020). There is a high ratio between corn grain and corn cob (100:18) which leads to the accumulation of large amounts of cob globally (Keszthelyi *et al.,* 2009). At present corn cob generated during the processing of corn does not find any specific use hence disposed either in landfills or subject to burning. Thus, it can be a potential feedstock for energy generation. In the process of energy generation, various by-products such as syngas, biochar and bio-oil are produced and these by-products can be resources that can be used in gasification systems for energy production.

Biochar (BC) is the carbonaceous material obtained from the direct thermal decomposition of biomass. It is an eco-friendly solid material obtained from the pyrolysis or gasification of biomass in absence of oxygen (Rohitha *et al.*, 2021 and Billa *et al.*, 2019). In gasification major product is syngas followed by bio-oil and biochar. Here the biomass is burnt at a temperature of more than 700 °C. The stable organic carbon content, large specific surface area and negative surface charge are the characters of biochar widely recognized as beneficial as an amendment that increases productivity by improving soil physical, chemical and biological properties (Igalavithana *et al.*, 2016 and Tian *et al.,* 2018) in soils that are severely depleted. The application of biochar has led to water quality improvements with increased nutrients and made available for plant utilization in those soils (Steiner *et al*., 2010). Preventing the leaching of nutrients is considered another crucial role of biochar in soils, in addition to enhancing the soil quality, carbon in biochar is highly resistant to degradation, which is an important characteristic for C sequestration in soil (Hansen *et al.,* 2015). Biochar properties, however, depend on the feedstock (*i.e.,* elemental composition, moisture, lignin, cellulose, hemicelluloses and inorganic compounds) and thermal conversion conditions (Alexis *et al.,* 2007). Hence, the characterization of biochar is essential prior to its application.

The detailed biochar characterization before any applications is significant to determine the relationship between nature and operating conditions with the physicochemical properties of biochar as well as the soil conditions, to evaluate the suitability of biochar to optimize its use. The International Biochar Initiative (IBI) documented the 'standard product definition and product testing guidelines for biochar that is used in soil' (IBI, 2015). IBI strictly advises that biochar be characterized before utilizing it as a soil amendment. The present study investigates the corn cob biochar produced from the gasification (800 °C) for its properties to explore its potential for use.

MATERIAL AND METHODS

Biochar and Corncob

The corncob biochar preparation (CCB) was carried out according to the standard procedures and standard methods as described by International Biochar Initiative (IBI). The corncob biochar was procured from Arsta Eco Pvt. Ltd., Tiptur, Karnataka, which manufactures CC using gasification process at 800 °C. The biochar was sieved using two mm pore sieve and stored in an airtight poly bag after drying at room temperature for further analysis. The cob of corn cultivated at UAS, GKVK farm is used for comparative analysis.

Biochar Characterization

Various properties of CCB and CC analyzed are presented in Fig. 1. The proximate analysis of CC and CCB includes moisture content, volatile / mobile matter, and ash was analyzed by ASTM D1762-84 method (2013) using a muffle furnace. The resident matter / fixed carbon content was calculated using the formula given by Enders *et al.* (2012) The ultimate analysis which includes Carbon and Nitrogen was determined by CHNS/O analyzer (PerkinElmer, Series II, India), Hydrogen and Oxygen estimated using formula followed by Siddiqui *et al.* (2018). Phosphorus was estimated by spectrophotometer by vanadomolybdate yellow colour method. Other nutrients such as Potassium, Boron, Calcium, Copper, Iron, Magnesium, Sodium, Zinc were analyzed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) (Spectra Genesis, Germany). The physical properties of CCB such as bulk density, maximum water holding capacity, pore space and volume of expansion was carried out with Keen's cup method. The chemical properties such as pH and electrical conductivity were analyzed using a combined water analyzer (Systronics -371, India). Cation Exchange Capacity (CEC) was estimated by the acetate method.

Data Analysis

Data analysis was done using Microsoft Excel 2019, and XLStat 2019.

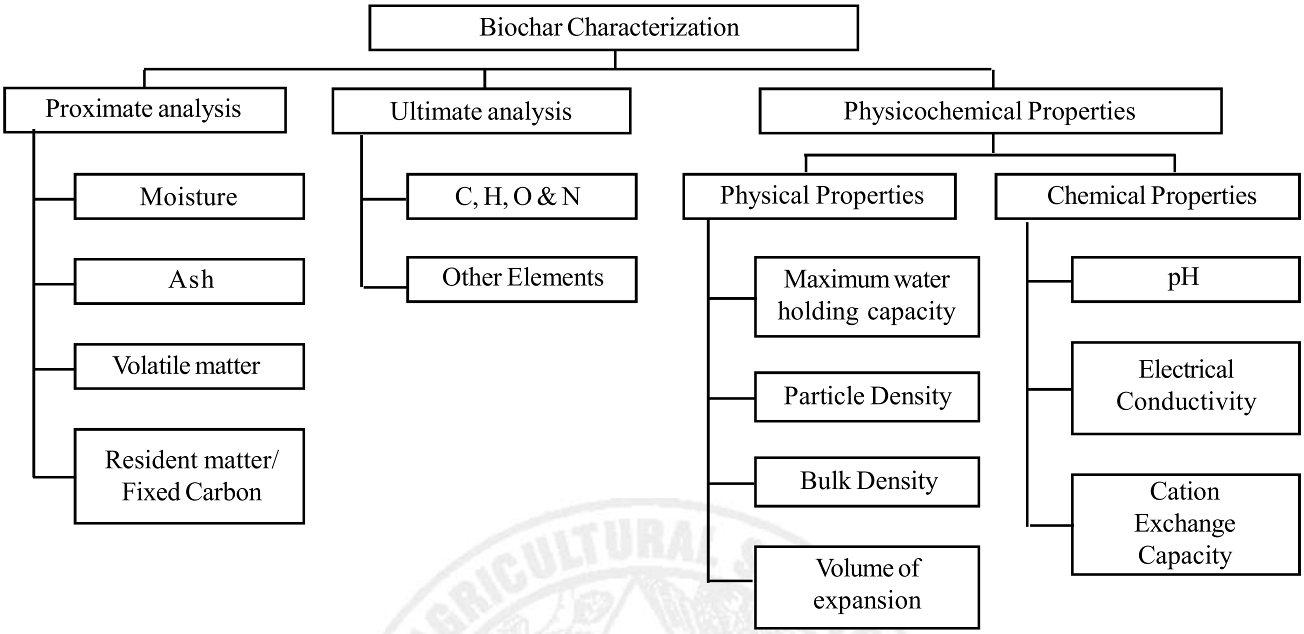

Fig 1 : Graphical overview of CCB characterization

RESULTS AND DISCUSSION

Proximate Analysis of Corncob (CC) and Corncob Biochar (CCB)

Corncob is subject to the proximate analysis to estimate the moisture content (M), volatile matter / mobile matter (VM), fixed carbon / resident matter (FC) and ash content (A) (Table 1). The moisture content of CC is 2.55 wt% which is in the acceptable range for the gasification process. The low moisture content of the feedstock is desirable (Shariff *et al*., 2016). After gasification, the moisture content has reduced to 1.35wt%. Similarly, the volatile matter in CC (84.78 wt %) has reduced to 28.80 wt% in CCB, while ash content (7.73 wt%) has increased to 38.02 wt% in CCB and fixed carbon content has increased from 4.94 wt% in CC to 31.83 wt% in CCB. The volatile matter to fixed carbon ratio of CC and CCB is 17.16 and 28.80 wt%, respectively. The volatile matter to fixed carbon ratio of CCB is 0.90. The findings are comparable with earlier reports (Gupta *et al.,* 2017), where with the increase in temperature in cassava biochar, cassava rhizome biochar and corncob biochar produced by pyrolysis, ash content and fixed carbon is found to increase but moisture content and volatile matter have decreased. The increase in pyrolysis temperature enhances the loss of organic compounds resulting in high ash content in the biochar (Wang *et al.,* 2013) which is evident from the negative relationship seen between carbon content and the ash content (Table 3). The fixed carbon (It is the carbon that remained after evaporation of volatile substances) is dependent on the volatile matter in the feedstock (Paethanom *et al.,* 2012). The volatile matter in the feedstock will be transformed into gases during the thermo-conversion process. The volatile matter is forcibly expelled out of the biochar and expulsion depends on the temperature of the gasification process. Hence, the temperature to which the feedstock is

TABLE 1

Proximate analysis for various parameters in Corncob and Corncob biochar on a dry weight basis

Characteristics	Corn cob (wt %)	Corn cob biochar (wt %)
Moisture (M)	2.55	1.35
Volatile matter / mobile matter (VM)	84.78	28.80
Ash (A)	7.73	38.02
Fixed carbon / Resident matter (FC)	4.94	31.83

exposed in the process of biochar production determines the amount of biochar obtained. The fixed carbon content of biochar obtained therefore depends on the composition of the feedstock (Gupta *et al.,* 2017).

Ultimate Analysis of CC and CCB

The ultimate analysis was conducted to measure the elemental composition (C, H, O, N, P, K, Ca, Mg, Na, Fe, B, Cu, Mn, Zn) of CC and CCB [Fig. 2 (a, b, c)]. Different molecular ratios H/C, O/C, and (O+N)/C were also compared. These ratios are important to consider CCB as a soil amendment. A slight increase in carbon content was observed in CCB (44.08 %) from CC (43.07 %) [Fig. 2(a)]. The findings are comparable with Gupta *et al.* (2017). The increase in C content might be due to dehydration which resulted in the release of OH- functional groups. The H, O and N content of CCB (2.99, 17.38 and 0.72%, respectively) is found to decrease compared to CC (7.40, 49.22, and 0.76%, respectively) [Fig. 2(a)] which might be because of cracking of Nitrile groups which are likely to occur at the higher temperature used in the gasification process (Tian *et al*., 2013). However, N showed a positive correlation with the C content (Table 3) indicating a slight increase in both nutrient contents. The O/C, H/C, and (O+N)/C ratios for CCB are 0.389, 0.071, and 0.405. But the decline in the H/C ratio is attributed to carbonization and aromatization. The decrease in O/C and (O+N)/C ratio are due to a decrease in the hydrophilic nature of biochar (Stefaniuk and Oleszczuk, 2015). Further, if the O/C value is <0.4 and the H/C ratio is <0.6, the biochar is considered suitable for carbon sequestration and soil amendment (Anupam *et al.,* 2015). Thus, CCB produced through the gasification process is suitable for soil application. The oxygen showed a positive effect on the volatile matter content in the CCB (Table 3) suggesting, after the gasification, the oxygen and volatile matter content decreases in the CCB.

Available nutrients (both macro and micro) in biochar are important considerations in utilizing biochar for agricultural applications. The nutrient availability depends on biochar feedstock and production conditions (Igalavithana *et al.,* 2016). As shown in [Fig. 2(c)], Fe, P, K, Ca, Na and Mg, were present in the CCB. At 800 °C temperature of gasification carried out in the present study, the Fe, K, Ca and Mg content is found to increase in CCB (173.34, 121.77, 89.43, and 28.68 ppm, respectively) compared to CC (65.40, 89.16, 13.45 and 10.45 ppm, respectively). The P and Na content have decreased in CCB (142.20 and 43.10 ppm, respectively) when compared to CC (300.33 and 47.46 ppm, respectively) similar trends were reported earlier (Intani *et al.,* 2018). The decrease in P and Na is due to volatilization loss. Similarly, the Fe content has increased. The traces of Ni and Cr (1.11and 2.28 ppm) might have come from the walls of the reactor. At high temperature, due to corrosion, a few cations might migrate to biochar (Intani *et al.,* 2018). Apart from this few nutrients such as B, Cu, Mn, and Zn are also found in minute quantity in CCB (0.79, 0.57, 2.44, 0.73 ppm, respectively) this can be beneficial since they are required by the plants in micro quantities. The potassium content is found to positively correlate with manganese and phosphorus, sodium and hydrogen, while copper with carbon and nitrogen were negatively correlated (Table 3).

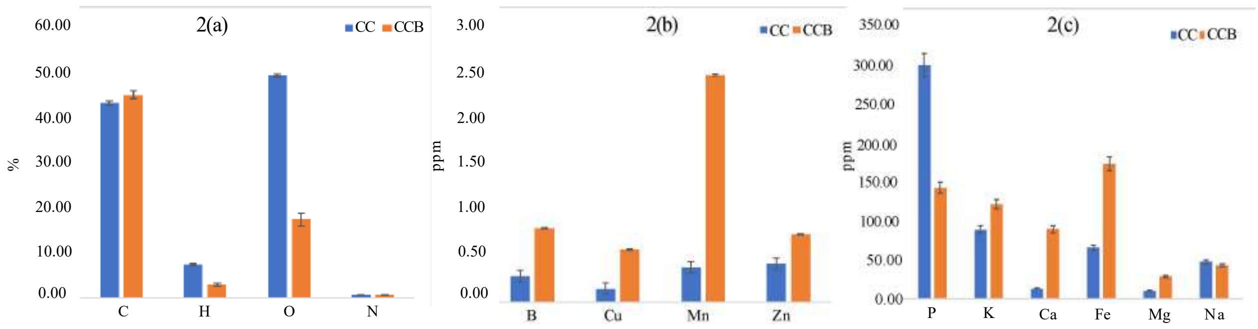

Fig. 2 : Ultimate analysis of CC and CCB

TABLE 2

Quantification of various physico-chemical parameters of CC and CCB

Samples	Physical Properties					Chemical Properties		
	BD ($g\ cc^{-1}$)	PD ($g\ cc^{-1}$)	MWHC (%)	PS (%)	VE (%)	pH	EC (μS^{-1})	CEC ($meq.100\ g^{-1}$)
CC	1.34	2.44	60.25	40.95	9.25	6.8	1.25	16.05
CCB	0.57	1.35	124.49	57.60	11.77	10.2	2.72	28.30

BD- Bulk Density, PD-Particle Density, MWHC-Maximum Water Holding Capacity, Pore Space-PS, VE-Volume of expansion, EC- Electrical conductivity, CEC- Cation Exchange Capacity

Physicochemical Properties of CC and CCB

Physical properties such as bulk density (BD), particle density (PD), pore space (PS), maximum water holding capacity (MWHC), volume of expansion (VE); and other associated properties such as pH, electrical conductivity (EC), cation exchange capacity (CEC) of CC and CCB are presented in Table 2.

The bulk density and particle density were 0.57 and 1.35 g cc^{-1} and 1.34 and 2.44 g cc^{-1} in CCB and CC, respectively. The particle density is found positively correlated with the bulk density (Table 3) suggesting the linear relationship with these two parameters (Anonymous, 2008). Brewer *et al.* (2014) in a study estimated the BD values of biochars produced from different feedstock ranging from 0.25 to 0.6 g cc^{-1}. Oberlin (2002) also reported a similar particle density. Due to higher temperature bulk density and particle density decreases because of the development of new pores (Brewer *et al.*, 2014) due to loss of some of the volatile chemicals impregnated in the tissue of the feedstock.

Further, CCB recorded 57.60, 11.25 per cent pore space and volume of expansion while it was 40.95 and 9.25 per cent, respectively in CC. The increase in porosity with temperature is because of the progressive removal of volatiles from pores (Chan and Xu, 2009). The pore space and volume of expansion are positively related with particle density and bulk density, respectively and particle density inversely related with MWHC (Table 3) is due to bulk density which correlated positively with the pore space (Anonymous, 2008). The CCB recorded (124.49 %) maximum water holding capacity (MWHC) compared to CC (60.25%). A similar observation is reported by Jeyaseeli and Samuel (2010) in coir pith biochar that has helped in higher water holding capacity. The MWHC inversely correlated with the particle density and bulk density (Table 3). The lower bulk density, pore space,and also surface area contribute towards increasing water holding capacity. (Anonymous, 2008 and Jeyaseeli & Samuel, 2010). The boron content in CCB negatively correlated with bulk density, particle densit and pore space and positively with MWHC (Table 3) because, boron being a mineral that affects the BD, PD resulting in increasing the MWHC (Anonymous, 2021).

The pH of biochar is an essential property used to study pH-dependent phenomena in environmental, agricultural, and biological sciences. The pH of CCB was found to be 10.2 suggesting that, CCB is alkaline in nature. The pH of CCB is positively correlated with the Mg (Table 3) suggesting Mg has a role in regulating the pH of biochar. To a large extent, the ash content determines the EC and pH of the biochar and the levels of alkaline elements (*e.g.,* Na, K, Ca and Mg) are most likely responsible for increasing pH and EC (Singh *et al.,* 2010).

Plant growth, soil microbial communities and soil physical properties (*e.g.,* the structure and hydraulic conductivity) thereby indirectly influencing soil nutrient cycling (Wang *et al.,* 2015). The cation exchange capacity of the CCB increased to 28.30 g cc^{-1} from 16.05 g cc-1 seen in CC. The increase in CEC mainly depends on the cations such as K, Mg, Na and Ca

TABLE 3
Correlation coefficient of the properties of the CCB

		Proximate analysis				Ultimate analysis														Physcal properties					Chemical properties		
	Variables	M	VM	A	FC	C	H	O	N	P	K	Ca	Fe	Mg	Na	B	Cu	Mn	Zn	BD	PD	MWHC	PS	VE	pH	EC	CEC
Proximate analysis	M	1																									
	VM	-0.273	1																								
	A	0.411	-0.162	1																							
	FC	-0.272	-0.352	-0.866	1																						
Ultimate analysis	C	-0.424	0.561	-0.751	0.429	1																					
	H	-0.118	0.726	-0.706	0.295	0.798	1																				
	O	-0.081	0.980	-0.136	-0.370	0.529	0.766	1																			
	N	-0.138	0.427	-0.483	0.239	0.897	0.612	0.440	1																		
	P	0.175	0.006	-0.712	0.661	0.455	0.606	0.091	0.395	1																	
	K	0.142	-0.007	-0.470	0.441	0.124	0.402	0.055	0.021	0.876	1																
	Ca	-0.049	-0.015	0.780	-0.723	-0.371	-0.614	-0.075	-0.117	-0.605	-0.382	1															
	Fe	-0.530	-0.227	-0.585	0.679	0.254	0.074	-0.318	-0.028	-0.039	-0.240	-0.587	1														
	Mg	-0.185	-0.145	-0.506	0.554	0.672	0.205	-0.160	0.807	0.436	0.084	-0.083	0.179	1													
	Na	-0.219	0.685	-0.707	0.319	0.616	0.933	0.701	0.313	0.568	0.500	-0.676	0.164	-0.055	1												
	B	0.373	0.544	0.203	-0.478	0.404	0.377	0.632	0.677	0.024	-0.181	0.261	-0.591	0.270	0.080	1											
	Cu	0.187	-0.571	0.365	-0.056	-0.842	-0.607	-0569	-0.945	-0.374	-0.128	-0.080	0.260	-0.689	-0.342	-0.722	1										
	Mn	0.016	-0.387	-0.396	0.569	-0.229	0.029	-0.370	-0.433	0.612	0.815	-0.451	0.142	-0.143	0.268	-0.699	0.401	1									
	Zn	-0.150	0.618	-0.119	-0.200	0.549	0.470	0.610	0.522	-0.306	-0.614	-0.155	0.239	0.102	0.299	0.558	-0.410	-0.782	1								
Physcal properties	BD	-0.174	-0.525	-0.496	0.738	-0.175	-0.068	-0.549	-0.421	0.483	0.603	-0.520	-0.467	-0.024	0.170	-0.860	0.475	0.931	-0.678	1							
	PD	-0.275	-0.582	-0.295	0.581	-0.340	-0.298	-0.644	-0.570	0.252	0.464	-0.278	0.426	-0.122	-0.027	-0.943	0.581	0.868	-0.752	0.956	1						
	MWHC	0.379	0.573	-0.046	-0.259	0.528	0.587	0.679	0.697	0.127	-0.185	-0.122	-0.298	0.246	0.310	0.912	-0.642	-0.637	0.740	-0.739	-0.903	1					
	PS	-0.367	-0.582	-0.007	0.313	-0.505	-0.549	-0.682	-0.686	-0.069	0.232	0.060	0.322	-0.229	-0.270	-0.929	0.641	0.682	-0.751	0.783	0.931	-0.998	1				
	VE	0.043	-0.306	-0.742	0.851	0.157	0.356	-0.259	-0.062	0.786	0.716	-0834	0.436	0.155	0.480	-0.522	0.182	0.835	-0.396	0.855	0.666	-0.281	0.346	1			
Chemical properties	pH	-0.320	-0.466	-0.433	0.662	0.403	-0.121	-0.525	0.484	0.298	0.047	-0.032	0.375	0.899	-0.276	-0.135	-0.352	0.065	-0.166	0.266	0.246	-0.177	0.190	0.242	1		
	EC	-0.232	-0.029	-0.021	0.040	0.417	-0.094	-0.081	0.574	-0.369	-0.732	0.179	0.334	0.610	-0.355	0.364	-0.399	-0.762	0.627	-0.516	-0.494	0.383	-0.405	-0.440	0.540	1	
	CEC	0.067	0.005	-0.296	0.274	0.155	0.252	0.039	0.172	0.763	0.907	-0.012	-0.456	0.266	0.271	-0.003	-0.344	0.620	-0.652	0.391	0.321	-0.166	0.193	0.429	0.213	-0.560	1

M-Moisture, VM- Volatile matter, A -Ash, FC-Fixed carbon, C- Carbon, H- Hydrogen, O-Oxygen, N-Nitrogen, P-Phosphorus, K-Potassium, B- Boron, Ca-Calcium, Cu-Copper, Fe-Iron, Mg-Magnesium, Na-Sodium, Zn-Zinc, BD- Bulk Density, PD-Particle Density, MWHC-Maximum Water Holding Capacity, Pore Space-PS, VE-Volume of expansion, EC- Electrical conductivity, CEC- Cation Exchange Capacity present in the CCB. The acidic functional groups present on biochar surfaces contribute to its CEC (Cheng *et al.,* 2008). Thus, K is positively correlated with CEC (Table 3).

Based on the proximate, ultimate, and physicochemical analysis of the biochar produced through the gasification process of corn cob at 800°C, it can be concluded that the CC can be converted into biochar and used as a soil amendment of cultivable soils. Converting CC into biochar and applying it to soil is not only effective in improving soil health and crop productivity but can also help to dispose of the non-decomposable waste in an environmental friendly manner.

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