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Study of corn stover as a feedstock in the production of biochar-based fertilizers.

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Abstract

The use of chemical fertilizers is necessary to maintain current levels of food production. Nevertheless, their use is associated with greenhouse gas emissions and losses due to leaching, which contribute to global warming and groundwater contamination. As an alternative, biochar-based fertilizers (BBF) have been proposed due to their ability to retain nitrogen within their structure and allow for controlled release. This study evaluated the production of BBF using corn stover (CS) as a raw material through three different routes: i) using the residues from subjecting the CS to anaerobic digestion as a raw material. ii) using CS combined with chicken manure. iii) enriching the biochar resulting from pyrolyzing CS with an ultrasound-assisted urea solution. Additionally, untreated biochar was also used as a control. The enriched biochar showed the best results in terms of nitrogen content at 7.77%. Furthermore, this enriched BBF yielded results most similar to traditional fertilization in growth tests, achieving comparable values for stem and leaf size. Nonetheless, controlled doses of BBF were observed to be necessary, as it can easily lead to over-fertilization at concentrations exceeding 2%. On the other hand, chicken manure-based BBFs can introduce too many minerals into the system due to their high ash content, which is detrimental to plant growth.

Keywords: Agriculture; Biochar; Biofertilizers; Pyrolysis

Highlights:

- Production processes for biochar-based fertilizers were evaluated for the Criollo puya corn variety.
- Several biochar-based fertilizers produced using different methods were characterized.
- The capacity of biochar-based fertilizers to replace traditional fertilizers to promote plant growth was evaluated

1.Introduction

The world population has undergone large increases since the mid-20th century, when the global population was estimated to be close to 2.5 billion. Current measurements point to a population of 8 billion, projected to reach 9.7 billion by 2050 [1]. In the same way, food requirements have increased at the corresponding rate. To satisfy the needs of the population, the large-scale implementation of chemical fertilizers was necessary. The world fertilizer demand for 2022 was estimated by the FAO at 200,919 thousand tons [2]. Nitrogen component is the most demanded component for crops. This element has a fundamental role in completing the biological processes of nitrogen by assisting in protein synthesis, photosynthesis and carbon/nitrogen metabolism [3]. Also increases the volume of biomass generated by the crop and improves fruit flavor and quality. More than 50% of the fertilizers produced worldwide have nitrogen as their main component [4]. Nonetheless, nitrogen application efficiency is usually low in the range of 30 to 50% caused by over-application, low plant density, improper farming practices and weather factors [5].

The use of nitrogen fertilizers also had far-reaching environmental impacts with global consequences. Nitrogen compounds decompose into NH_3 and NH_4^+ which ultimately cause soil acidification. As a result of this phenomenon, microorganism populations are considerably affected, interfering with soil mineralization cycles [6]. Another recurring problem is denitrification processes that result in nitrous oxide (N_2O) emissions causing a negative impact on climate change [7]. Furthermore, about 2% to 10% of unassimilated nitrogen contaminates groundwater due to leaching, which eventually causes eutrophication of water bodies [8]. The constant use of these fertilizers is currently considered a problem with the potential to cause an imbalance in the global earth system. In terms of planetary boundaries, agronomic activities are the main reason why the limit of biogeochemical fluxes is exceeded [9]. The current situation puts the environmental stability of multiple local and global systems under high pressure. Nonetheless, the dependence and need to ensure food security in all countries limits the measures that can be taken in this area. As a contingency measure, several modifications have been proposed for fertilizers and agricultural practices. For instance, controlled-release fertilizers with different types of coatings have been deeply researched in recent years [10]. Nonetheless, its implementation in large agricultural territories is still limited. Regardless of the advances in this field, traditional chemical fertilizers are still predominant in the agricultural sector. There are other proposals for carbon capture and use in agricultural systems with biochar as the centerpiece. Biochar is defined as a solid material that is produced by thermochemical processes using biomass as feedstock [11]. Biochar is mainly composed of carbon and is considered a highly porous material. According to its chemical and physical properties can be used in different processes. In essence, their most important properties are their elemental composition, energy content, fixed carbon, cation exchange capacity, reactivity, etc. Another proposal to take advantage of biochar in the agricultural field is to subject them to a transformation process to produce biochar-based fertilizers (BBF). The main characteristics that these BBF are looking for is to have features such as (i) a high mechanical resistance that allows for greater longevity in the soil; (ii) a large surface area that stimulates better water and nutrient storage in sandy soils and better aeration in clay loam soils; ((iii) a high quantity of macro and micropores that increase aeration and water retention; and finally, (iv) a high nutrient content [12]. BBF have been proposed as a complement to traditional fertilization that also has several environmental benefits. Different research and experiments have shown that biochar has positive effects in retaining nitrogen in the soil. More specifically, Biochar decreases the substrate and energy sources for denitrification and nitrification reactions by the adsorption of soil NH_4^{+}-N and organic matter [13]. Thanks to these mechanisms in the nitrogen cycle, N_2O emissions and leachates are reduced. The production of biochar enriched with fertilizers is classified into direct treatment, pre-treatment or post-treatment according to the stage of the process in which the enrichment is conducted. A diagram of the different routes is shown in **Figure 1.**

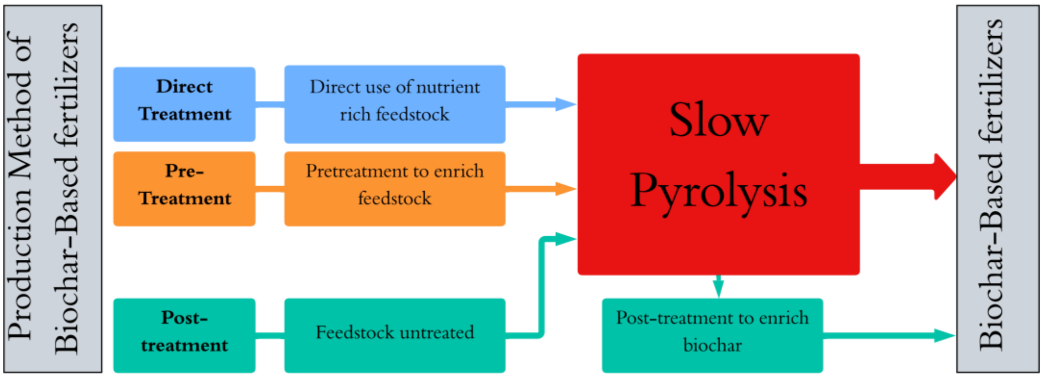


Figure 1. Different methods of production of biochar-based fertilizers

Adapted from Ndoung et al. 2021 [14]

Direct treatment is based on processing nutrient-rich raw materials that can be subjected to thermochemical processes to produce biochar. The resulting biochar has high concentrations of primary nutrients for the crop. Depending on the operating conditions, the enrichment of different elements tends to be achieved. The aim of this study was to test different techniques for synthesizing BBF using lignocellulosic residues from corn as the main raw material. To this end, various approaches to direct treatment, pretreatment, and post-treatment were tested. In addition, the synthesized BBFs were used in growth tests to establish their potential to replace traditional fertilizers and contribute to a circular economy within the corn value chain.

2. Methodology

2.1 Raw Materials

Corn stover (CS) is the main residue generated in corn cultivation. This residue consists mainly of leaves and stalks remaining after harvesting. CS was used as the main raw material in experimental procedures. The CS sample was obtained from Colosó, Sucre, Colombia (9°29′39″N,75°21′09″O). The CS was obtained from yellow corn Criollo puya variety (Zea mays) under a technician cultivation modality. The raw material was dried in the sun until reaching a moisture content of 10% on a dry basis. Then, the samples were milled using a knife mill (Gyratory mill SR200 Gusseisen, Redsch GmbH, Germany) until a particle size of 0.45 mm according to the ASTM 40 Mesh [15].

2.2 Production of biochar-based fertilizers

To evaluate the viability of biochar-based fertilizers from different approaches, four different valorization routes were proposed. Figure 2 presents an overview of the conditions and raw materials used. First, biochar was produced from CS without adding any additional raw materials or additives. The intention of this case was to propose a classic approach where biomass is subjected to slow pyrolysis and biochar is obtained as the main product. 6 grams of CS with a moisture content of less than 10% were placed in a previously calcined porcelain crucible. The crucible was placed in a muffle furnace and subjected to a heating ramp of 10°C/min until reaching a temperature of 550°C. The sample was kept at this temperature for 120 minutes [16]. Throughout the process, a constant flow of nitrogen was supplied to the interior of the muffle furnace to ensure oxygen-free conditions.

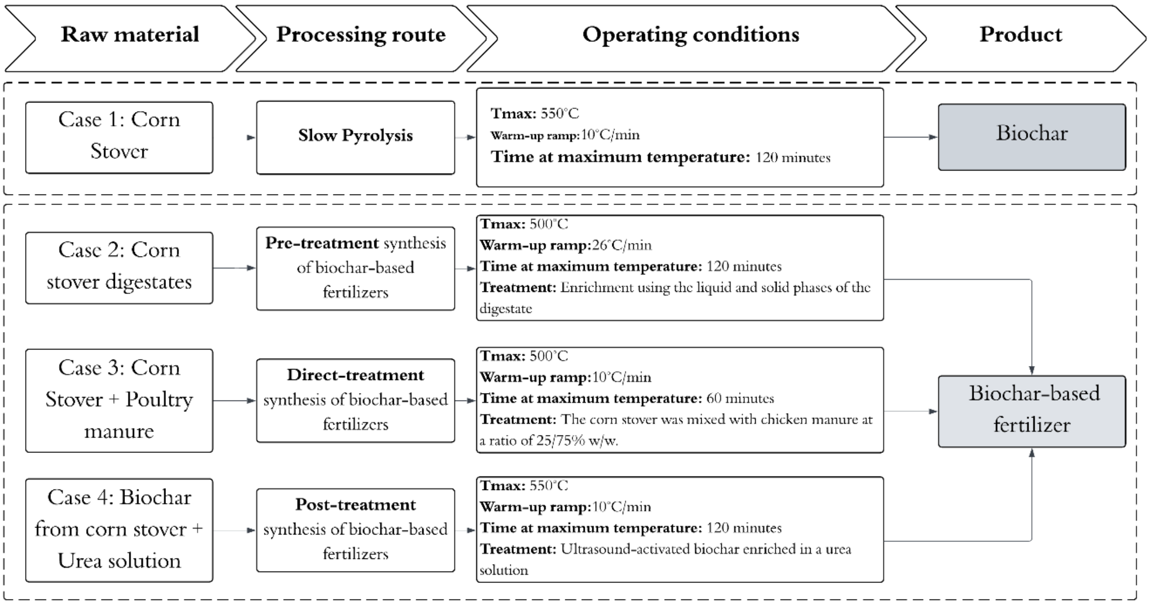


Figure 2. Methodology used for the synthesis of biochar-based fertilizers

The second case proposed the production of biochar-based fertilizers following a pretreatment route. In general, digestates resulting from anaerobic digestion are considered raw materials with moderate nitrogen contents [17]. The solid digestates from the anaerobic digestion of CS were used as raw material to test their capacity to be upgraded to biochar-based fertilizers. The solid phase of the digestate was filtered and dried at 80°C until a constant weight was reached. Six grams of digestate were placed in a previously calcined porcelain crucible. The crucible was placed in a muffle furnace and subjected to a heating ramp of 26.5°C/min until reaching a temperature of 500°C. The sample was kept at this temperature for 120 minutes. A flow of nitrogen was constantly fed into the muffle furnace to ensure an inert atmosphere [18]. Subsequently, the biochar was subjected to a process of impregnation with the liquid phase of the digestate. To do this, the biochar was mixed with the liquid phase in a 1:1 ratio and left in contact for 48 hours. Finally, the resulting biochar-based fertilizers were dried at a temperature of 80°C until they reached a constant weight [19].

The third case proposed the production of biochar-based fertilizers using a mixture of raw materials. CS is a carbon-rich biomass suitable for biochar production. Nonetheless, low nitrogen content limits its use for soil fertilization. Chicken manure is one of the most attractive organic fertilizers because of the positive effects on crop vigor and yield [20]. A biochar-based fertilizer was produced from a 25/75 w/w mixture of CS and chicken manure using a direct treatment. Six grams of the mixture were placed in a pre-calcined porcelain crucible. The crucible was placed in a muffle furnace and subjected to a heating ramp of 10°C/min until a temperature of 500°C was reached. The sample was kept at this temperature for 60 minutes with a constant flow of nitrogen to ensure an inert atmosphere. The chicken manure used was obtained through the company Abonisa. Vereda Cacaos – Mesa de los Santos Piedecuesta, SANTANDER – COLOMBIA (6.85762473478542, -72.98150916083056). The composition of stabilized chicken manure is presented in the following **Table 1**.

Table 1. Composition of chicken manure according to the producer

Component	Content
Total nitrogen (N)	1.5%
Assimilable phosphorus (P2O5)	4%
Water-soluble potassium (K2O)	3.5%
Calcium (CaO)	10%
Total magnesium (MgO)	1.3%
Oxidizable organic carbon	19%
Ratio C/N	16
Ash	29%
Humidity	20%
pH	8.2
Density	0.56g/cm3
Cation exchange capacity	35 meq/100g
Water retention capacity	148%

The fourth case differed from the previous ones in considering a post-treatment approach for the synthesis of biochar-based fertilizers. In this case, the biochar from CS was enriched with a substance with a high nitrogen content after pyrolysis. Urea, being the most widely used element in traditional fertilization, was chosen for enrichment. The biochar from CS was synthesized under the same conditions described for case 1. Subsequently, the biochar was subjected to an activation and enrichment process using ultrasound. The biochar was mixed in a 1:10 w/w ratio with deionized water in an ultrasonic device set at 50W and 30Hz for 45 minutes using the compact lab homogenizer UP-50H. After activation, the biochar was placed in a 2M urea solution in a ratio of 1:10 w/v. The solution was heated to 80°C and mixed at 150 rpm for 2 hours. The samples were then filtered and dried at 60°C until a constant weight was obtained [21]. The urea was obtained from production plant (monómeros colombo-venezolanos) in granular form.

2.3 Growth tests

To determine the potential of BBFs as substitutes for traditional fertilizers, they underwent a characterization process and controlled growth trials First, an elemental analysis was performed on each of the synthesized BBFs to establish the quantity of nitrogen and carbon present in their structure. The elemental analysis was performed on an EMA-502 microanalyzer from Velp Scientifica using a 20 mg sample. This analysis provides information on the BBF's capacity to capture and contribute carbon to the soil. The analysis also indicates the potential nitrogen contribution of the additive in the soil. The second analysis was conducted using the TGA technique. One gram of sample was heated at a rate of 10°/min until reaching a temperature of 850°C. The heating was conducted in an inert nitrogen atmosphere. The aim of this analysis was to test the stability of the synthesized biochar when subjected to extreme conditions. This analysis clearly identified the percentage of biochar remaining in the soil. Finally, these results were complemented with a proximate analysis to establish the fractions of fixed carbon and volatile material in the biochar using the procedure described in the standard. ASTM E872-82 [22]; ASTM D3172 [23] and NREL/TP-510–42622 [24]

Once the BBFs had been characterized, they were used as a substrate in the preparation of soil for cultivation. The objective was to test their ability to replace traditional fertilization. Soil supplemented traditional fertilization and others with BBF fertilization were prepared. A mixture of 2 parts soil and 1 part sand was prepared as a base, to which the substrates were added as shown below:

1. Control System: Mixture 2 parts soil and 1 part sand.
2. Biochar substrate: Mixture of 2 parts soil and 1 part sand + 10% biochar produced by CS pyrolysis.
3. Enriched biochar substrate: Mixture of 2 parts soil and 1 part sand + 10% biochar enriched with urea.

4. Chicken manure substrate: Mixture of 2 parts soil and 1 part sand + 10% biochar produced from chicken manure pyrolysis mixed with CS.
5. Digestate substrate: Mixture of 2 parts soil and 1 part sand + 10% biochar produced from pyrolysis of solid digestate from anaerobic digestion of CS.

The five substrates were subjected to physicochemical analysis to determine pH, nitrogen (N), organic matter (OM or OC), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), aluminum (Al), cation exchange capacity (CEC), iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), boron (B), sulfur (S), soil texture, and electrical conductivity (EC). Soil texture was determined using the Bouyoucos hydrometer method, allowing quantification of sand, silt, and clay fractions and classification according to the USDA textural system. The measured parameters were used to evaluate substrate chemical fertility, nutrient availability, and salinity levels. Micronutrient concentrations were determined to identify potential deficiencies or toxicities, while CEC was used to assess nutrient retention capacity. These analyses were performed to characterize the substrates and to support subsequent evaluation of their agronomic and environmental performance. These analyses were conducted through the company Multilab Agroanalitica SAS Chinchina, Caldas, Colombia. The soil and sand were acquired through the intermediary Los Cerezos Manizales nursery, Caldas, which specializes in seedlings and crops.

Finally, a study to evaluate the impact of using BBFs on corn growth was conducted. To do this, a plastic container was prepared with 200 grams of the substrates, in which a seed of the variety “yellow height” corn was sown. The substrates evaluated were those mentioned above. Also, a second control with 400 mg of urea as fertilizer was included. On the other hand, biochar produced by anaerobic digestion was discarded due to difficulties in producing the necessary quantities. Changes in pH, electrical conductivity, and NPK concentration were monitored daily using a [EC-PH-NPK-12V] 7-in-1 12VDC integrated soil sensor. RENKE. As part of the monitoring, the days of germination, number of leaves, and stem elongation were also registered. Measurements were taken over a period of 30 days. At the end of this period, the resulting biomass was weighed. The response variables that were measured are: i) Maximum leaf length; ii) Leaf weight; iii) Root weight; iv) Stem weight v) Stem length. These tests were conducted with five replicates for each of the substrates mentioned. A random distribution was used to determine the placement of the plants. The same experiment was repeated using additional substrate concentrations of 2% and 5% in all cases. The purpose of this was to evaluate the effect of different doses on plant growth. The measurement data were then subjected to statistical analyses such as the Shapiro-Wilk normality test and Levene’s test for homoscedasticity. The data were statistically analyzed using Hedge's g and Tukey's test.

3. Discussion and Results

3.1 Characterization of the BBF

The yields, elemental and proximate characterization of the different biochars produced are presented in Table 2. Also, Figure 3 shows the synthesized biochar-based fertilizers. The results showed that the main outcome of the BBF synthesis processes was an increase in fixed carbon and elemental carbon at the expense of volatile material loss. The best yields were obtained by BBFs based on chicken manure, but they also had the highest ash content, with values of 69.13%. Also, this chicken manure-based BBF had low nitrogen content, which was lower than the elemental content reported in the technical data sheet for the manure before pyrolysis. This demonstrates nitrogen losses during the pyrolysis process.

A) Biochar produced using corn stover B) Biochar using CS+chicken manure

C) Biochar using digestate D) Biochar enriched with urea

Figure 1. Biochar-based fertilizer synthesis

The high ash content is expected compared to the results reported in the literature, which reports ash values ranging from 23.74% to 37.73% for fresh chicken manure [25], [26] . Nevertheless, this high ash can cause adverse effects on the growing land. Lin et al. 2024 [27] Lui et al. pointed out that ash may provide minerals such as Ca, K, and Mg, but can also cause increases in pH and decrease nutrient uptake by clogging soil pores. High ash content has also been shown to alter the cation exchange capacity and electrical conductivity of the soil, which ultimately causes greater stress on the crop [28].

Table 2. Proximate and elemental analysis of synthesized biochar-based fertilizers

Sample	Yield kg BBF/ kg Raw Mat.	Elemental analysis				Proximate analysis		
		%C	%O	%H	%N	%volatile Matter	%Ash	%Fixed carbon
Corn Stover	-	40.1	53.7	5.69	0.54	83.38±1.01	5.86±0.23	10.18
CS Biochar	0.22±0.105	64.62	32.7	2.37	0.36	13.39±0.49	20.08±1.28	66.53
Digestate Biochar	0.37±0.093	49.5	45.5	1.9	3.14	4.9±3.21	37.55±1.89	57.55
CS+Poultry Manure	0.55±0.056	21.16	76.8	0.79	1.24	26.17±1.59	69.13±4.99	16.28
Enriched biochar	0.30±0.28	61.28	28.1	2.9	7.77	25.11±0.97	18.34±0.71	56.55

The BBFs subjected to the ultrasonic enrichment stage reported the highest amount of elemental nitrogen, achieving an increase from 0.34% in the unenriched biochar to 7.77% after enrichment. The high elemental carbon content achieved by the enriched BBF is another positive result. On the other hand, BBFs synthesized from anaerobic digestion sludge showed intermediate results with a nitrogen content higher than achieved by treatment using chicken manure, but lower than enriched biochar. Notably, the use of sludge also significantly increased the ash content of the resulting BBF, which could influence the factors already discussed. Compared to literature, BBF enrichment has a wide range of expected nitrogen levels. For instance, Castejón-Del Pino et al. 2023 [29] tested different nitrogen sources such as ammonia and urea to enrich biochar using different activation methods. The results of the experiments showed a high range of nitrogen content in the BBF, ranging from 0.68 to 7.02. Compared to this range, all treatments were successful in enriching the biochar with nitrogen, but the ultrasound activation method was more effective than the pretreatment and direct treatment methods.

The range of fixed carbon obtained in the synthesis is highly variable and depends heavily on the raw material and the operating conditions used, resulting in a wide range that can vary from 10% to 80%. [30]. For the BBFs analyzed, the general tendency was to increase the amount of fixed carbon, except for biochar derived from chicken manure, which had the lowest elemental carbon content. A high fixed carbon content is essential for BBF to be stable and provide carbon to the soil at a controlled rate. Moreover, fixed carbon also establishes biochar's capacity to sequester carbon in the long term. [31]. In this regard, CS biochar and enriched biochar have the best results, as they have a higher proportion of fixed carbon and lower ash content. To evaluate the stability of the synthesized BBFs in more detail, **Figure 4** shows the thermogravimetric analysis with the results obtained for untreated CS as a contrast. T

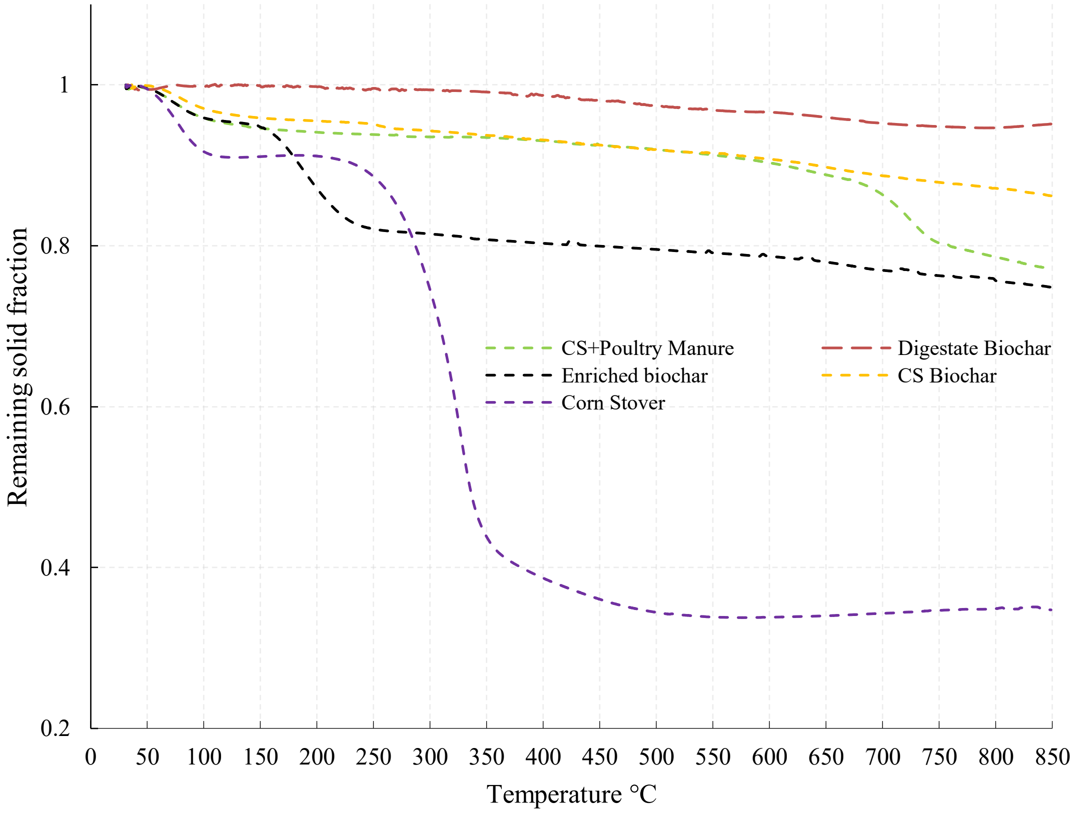
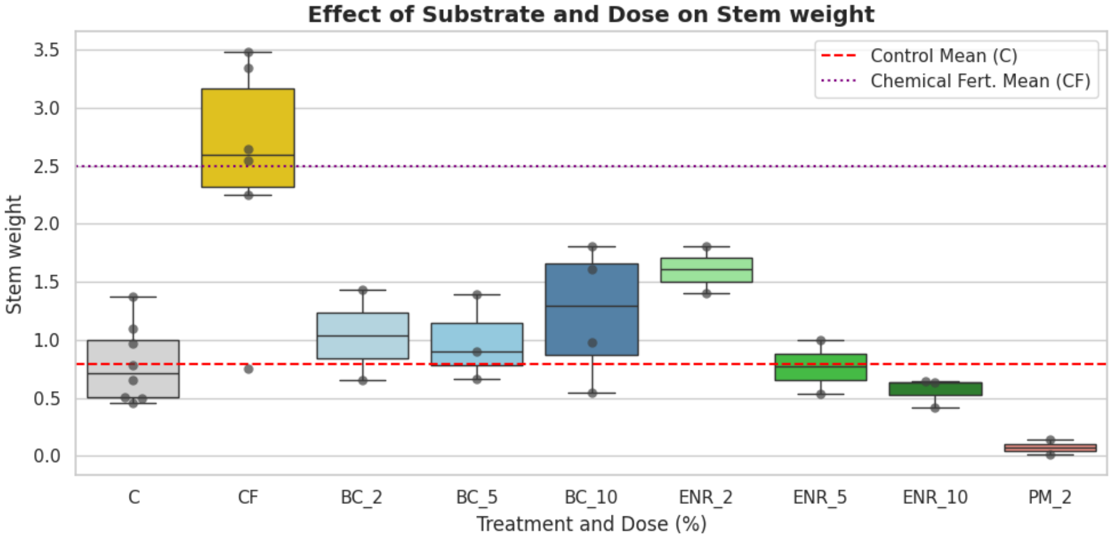


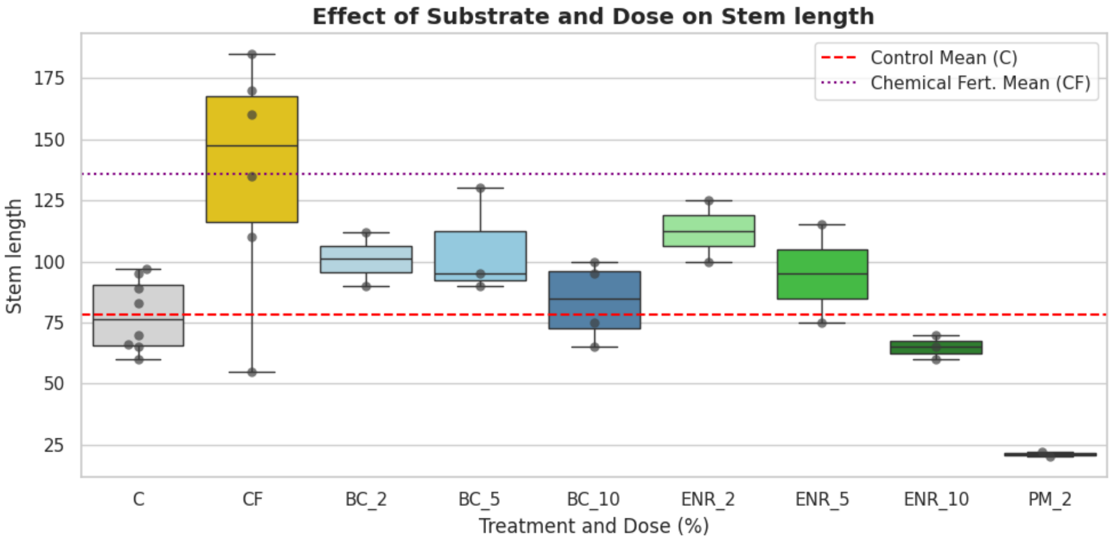
Figure 2. Thermogravimetric analysis (TGA) for corn stover and synthesized BBFs

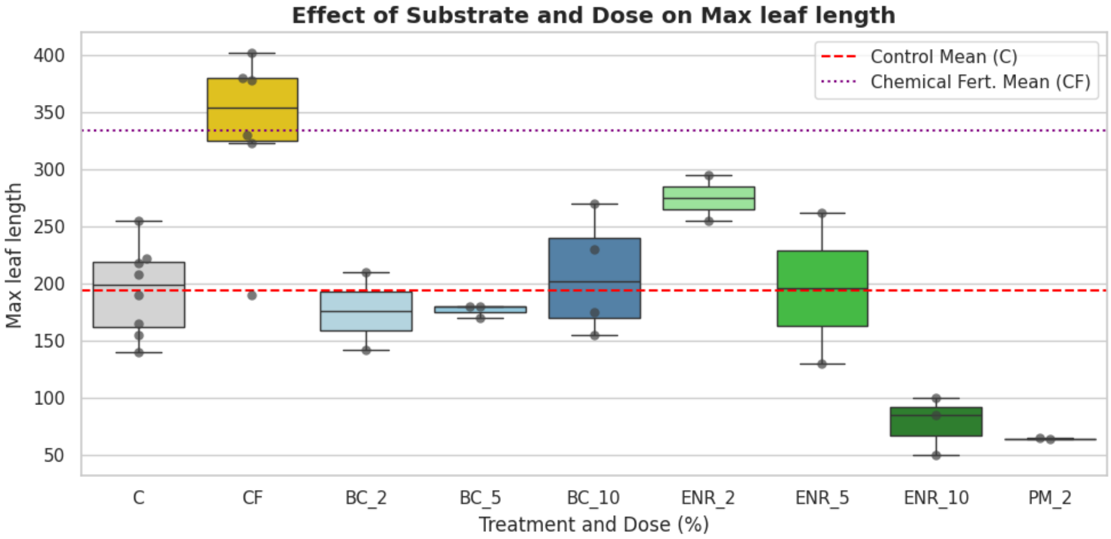
All BBFs showed greater stability compared to unprocessed CS. This showed an initial loss of mass between 50 and 150°C related to the release of moisture and extractives, and a second segment between 250 and 450°C corresponding to the degradation of the lignocellulosic structure. In comparison, BBFs showed a continuous loss of mass throughout the temperature range analyzed. The exception was enriched BBF, which showed a more significant loss of mass between 150 and 250. This difference with the other biochars is presumed to have been caused by the volatilization of nitrogenous components that were absorbed during the enrichment process. Nevertheless, all cases showed that more than 70% of the mass of BBFs remained stable even at extreme temperatures. These results, combined with those already discussed in the elemental and proximal characterizations, preliminarily suggest that these BBFs could be used as a means of carbon sequestration in the medium and long term. Integration with sequestration together with other production processes has positive implications not only because of its contribution to the soil as a source of slow-release carbon, but also because of its ability to compensate for other emissions. Other studies have shown that combining biochar as a CO2 sequestration agent with the production of other products provides the best results in environmental terms [32]. The combined approach of using biochar as a base for BBFs could be an alternative to traditional fertilizers while minimizing the environmental impact of fertilizer production.

3.2 Maize growth tests using BBFs

The analysis of the substrates showed significant differences compared to the control and demonstrated that both the dosage and the type of substrate have a significant impact on plant growth. **Figure A1** shows that there are noticeable variations in leaf and root development among the different specimens. To present the variations more clearly, **Figure 5** shows the average of the response variables compared to the control using a box plot. For all five measured variables, the control treated with traditional fertilizer yielded better results than all other treatments. However, the results for biochar enriched with a 2% dose ranked second and outperformed the unfertilized control. BFF enriched with urea demonstrated potential as a substitute for traditional fertilizer, although it cannot yet compete directly with it. Nevertheless, an inappropriate application rate was found to lead to counterproductive results, as observed with rates of 5% and 10%. In these cases, the measured variables showed, in some instances, worse results than those observed in the control group.




Effect of Substrate and Dose on Stem length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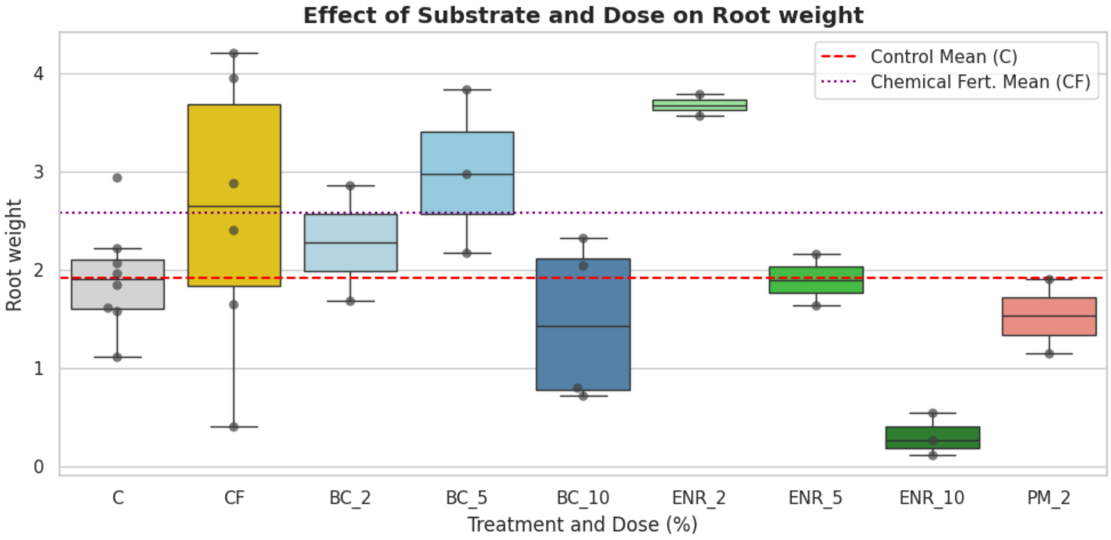
Effect of Substrate and Dose on Root weight

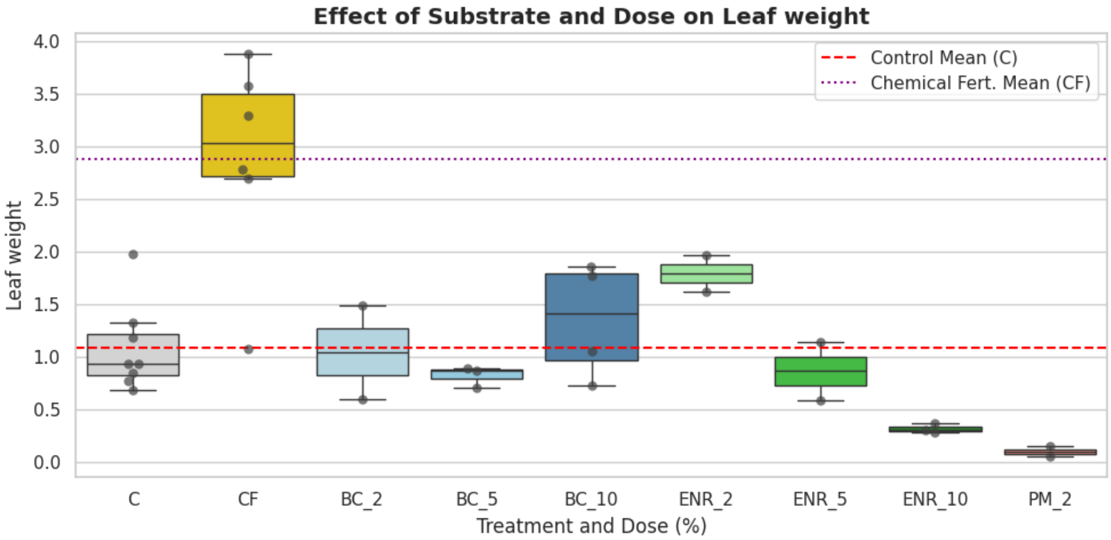

Figure 5. Boxplot graphs for the response variables measured in the growth tests

C: control; CF: Fertilized control; BC: biochar; ENR: Enriched biochar; PM: pyrolyzed chicken manure + corn stover

The use of biochar as a substrate showed results like those of the control group, but compared to the fertilized control, it yielded significantly lower and less competitive results in terms of stimulating plant growth. The results of using pyrolyzed chicken manure as a substrate are another important observation. For the 5% and 10% doses, no germination was observed in any of the plants. Conversely, at a 2% dose, plant growth did occur, but with clearly inferior performance and signs of over-fertilization, as shown in **Figure 6**. The main observations were poor development of both the foliage and root systems, accompanied by yellow spots and signs of burning typical of plant poisoning.

Figure 6. Corn plants showing signs of overfertilization

To obtain more robust conclusions from the observations made, the most statistically robust variables were identified using the Shapiro-Wilk normality test and Levene's test for homoscedasticity. In addition, the results of the overall significance test (ANOVA) and the Kruskal-Wallis H test are presented in Table 3

Table 3. Statistical tests of the response variables analyzed

Variable	$Shapiro_p$	$Levene_p$	$ANOVA_p$	$Kruskal_p$
Stem weight	0.0016	0.3505	0.0002	0.0114
Stem length	0.2048	0.1193	0.0013	0.0286
Max leaf length	0.4132	0.1886	0.0000	0.0063
Root weight	0.4261	0.0825	0.0081	0.0428
Leaf weight	0.0026	0.2012	0.0000	0.0043

According to the statistical analysis, stem length and maximum leaf length are the most robust variables because: 1) they exhibit normality with a Sharpe-Pop value greater than 0.05; 2) they are homoscedastic variables with a Levene's test value greater than 0.05; 3) they show high statistical significance, as indicated by p-values less than 0.05 in the ANOVA and Kruskal-Wallis tests. Given these results, these two variables were used to calculate Hedges' g as a measure of the effect of the different doses and types of substrates used. Other statistical tests, such as a Pearson correlation matrix and principal component analysis, are presented in **Supplementary material.** The calculated Hedges' g values are presented in **Figure 7**. The graph shows that the best results were obtained with the BBF-enriched treatment at a 2% rate and the fertilized control. In contrast, the use of pyrolyzed chicken manure and biochar-enriched treatments at high rates yielded the worst results. Hedges' g reinforces the observations presented in the box plot. In the case of biochar at different doses, it showed mixed results with tall stems but leaf lengths below the control at the 5% and 2% doses.

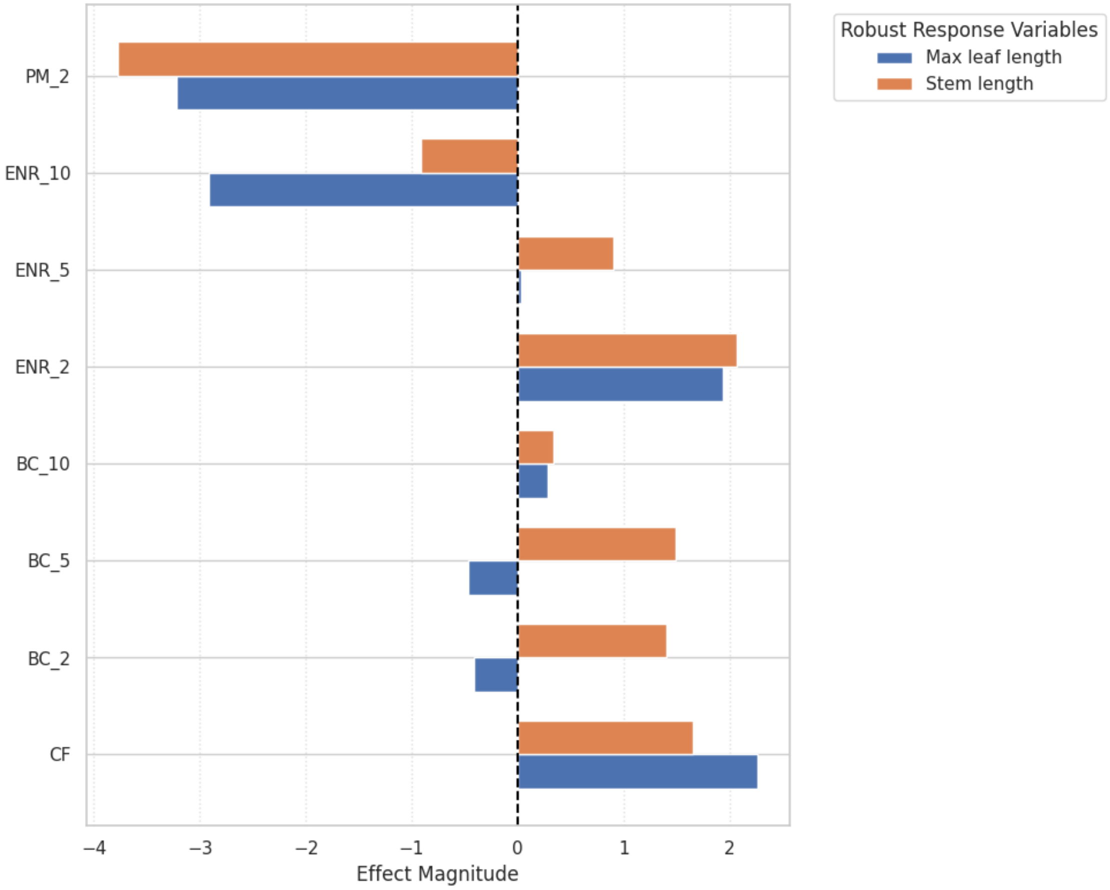

Figure 7. g of hedges for the response variables measured in the growth tests

C: control; CF: Fertilized control; BC: biochar; ENR: Enriched biochar; PM: pyrolyzed chicken manure + corn stover

As an additional test to complement the Hedges' g analysis, Tukey's post-hoc test is also presented in Figure 8. The results presented reinforce the conclusions reached, showing that the highest growth rates were achieved by fertilized control and the 2% biochar-enriched treatment; hence, the statistical tests yield consistent results.

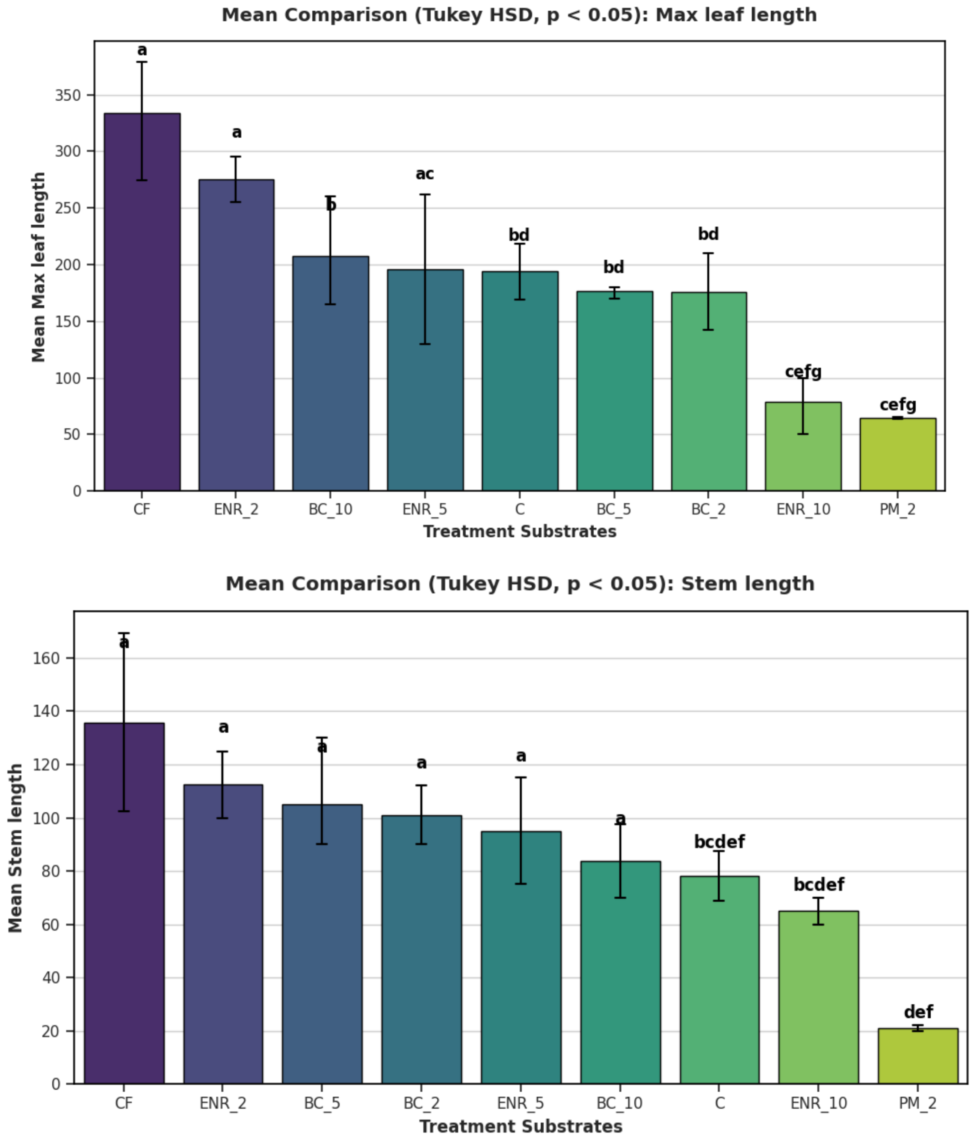

Figure 8. Tukey's statistical analysis of the response variables measured in the growth test

Overall, the results suggest that, except for enriched BBF, other treatments can be rejected as alternatives to traditional fertilizers. According to studies in the literature, yields higher than those achieved with traditional fertilization are possible [33]. In long-term experiments, increased yields have also been observed when using BBFs [34]. Nevertheless, the fact that traditional fertilization often performs slightly better than the use of BBFs is also highlighted [35]. The wide variety of existing techniques for BBFs is the main reason for these variations, as evidenced in this analysis. For the results presented, pre-treatment and direct treatment methods clearly yielded inferior results compared to post-treatment. On the other hand, dosage is one of the most important variables and can completely render the use of BBFs unfeasible. **Figure 9** shows the measurements of conductivity and available NPK ions in the analyzed experiments using a 10% dosage. Figure 9 shows how clearly the application of pyrolyzed chicken manure and enriched biochar can lead to over-fertilization. When compared to the control, the imbalance is evident and is reflected in the signs of over-fertilization described above. Nonetheless, more moderate doses, such as the 2% dose used, can yield results similar to those of conventional fertilization.

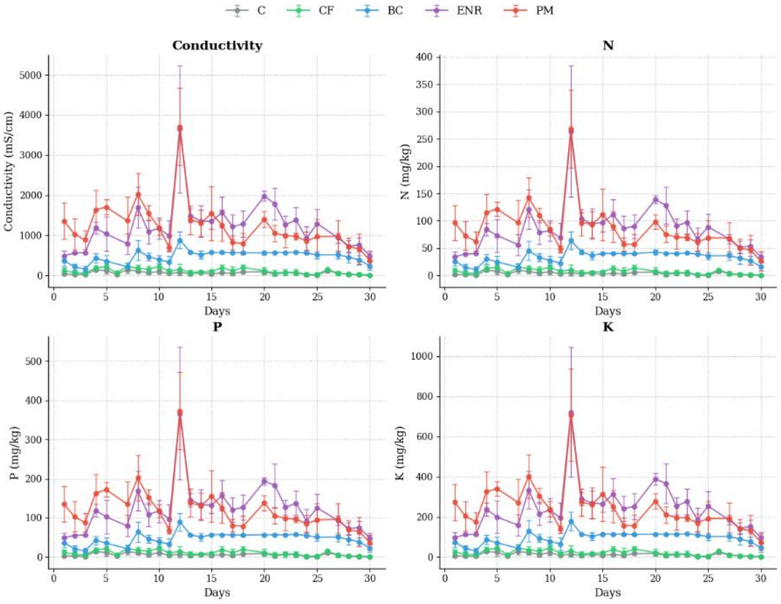

Figure 9. Daily variation in conductivity and ionic availability of N, P, K

Finally, **Table 4** presents the results of the soil characterization using the various substrates at an application rate of 10%. The results reinforce the hypothesis that high doses of BBFs can cause significant imbalances in the soil, which consequently lead to toxic conditions for plants. In the case of fertilization with chicken manure pyrolysate, excessive levels of magnesium, phosphorus, sulfur, and boron were observed. Also, potassium contributions from the BC and PM treatments were found to introduce excessive levels of potassium into the soil. In all cases, soil alkalization was observed, which could also limit nutrient availability.

Table 4. Soil analysis of the substrates evaluated at a 10% dose

Parameter	Optimal range	Control	BC	ENR	PM	Main limitations
pH	5.5–7.0	5.5	7.8	8	7.9	Alkalinity in BC, ENR, PM → reduced nutrient availability
N (%)	0.15–0.30	0.19	0.17	0.2	0.21	Within optimal range
OM (%)	2–5	4.1	3.7	4.3	4.5	Adequate in all samples
K (cmol/kg)	0.2–0.6	0.48	9.13	2.51	10.05	Severe excess → cation imbalance
Ca (cmol/kg)	3–10	2.15	5.09	4.9	6.79	Low in Control
Mg (cmol/kg)	1–3	0.53	1.96	1.65	4.88	Low in Control; excess in PM
Al (cmol/kg)	<1	0.1	0.1	0.1	0.1	No limitation
CEC (cmol/kg)	10–25	12	8	8	11	Low in BC, ENR
P (mg/kg)	10–30	45	104	91	1059	Excess → micronutrient antagonism
Fe (mg/kg)	20–100	168	107	85	84	Elevated in Control
Mn (mg/kg)	5–50	13	15	19	44	Within acceptable range
Zn (mg/kg)	1–5	5.2	13.3	20.1	36.4	Excess → toxicity risk
Cu (mg/kg)	0.2–2	4.2	3.9	4	5.4	Elevated in all samples
S (mg/kg)	10–20	51.7	93.2	3	341.8	Excess; except EB
B (mg/kg)	0.2–1.0	0.71	1.06	0.82	1.61	Elevated in PM and

The high ash content of BBF produced from chicken manure poses a significant limitation to its practical application for introducing minerals into the soil. Furthermore, as discussed, dosage plays a critical role in preventing an imbalance in macronutrients. Since BBFs are structurally more complex and contain more components than urea, it becomes even more important to combine their application with soil remediation measures to prevent soil contamination. While BBFs at appropriate doses can compete with traditional fertilization, ultimately, their application is more complex and riskier if proper precautions are not taken.

4. Conclusion

Corn stover has high potential to serve as a substrate for the synthesis of BBFs; its use in these systems helps the corn value chain reduce the amount of waste generated and promote carbon sequestration. Furthermore, growth trials showed that BBFs could stimulate corn plant growth and compete with chemical fertilizers. However, it was also shown that the application of BBFs is highly likely to be counterproductive depending on soil characteristics and the applied dose. The implementation of BBFs must be accompanied by rigorous field management to avoid over-fertilization.

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Supplementary material

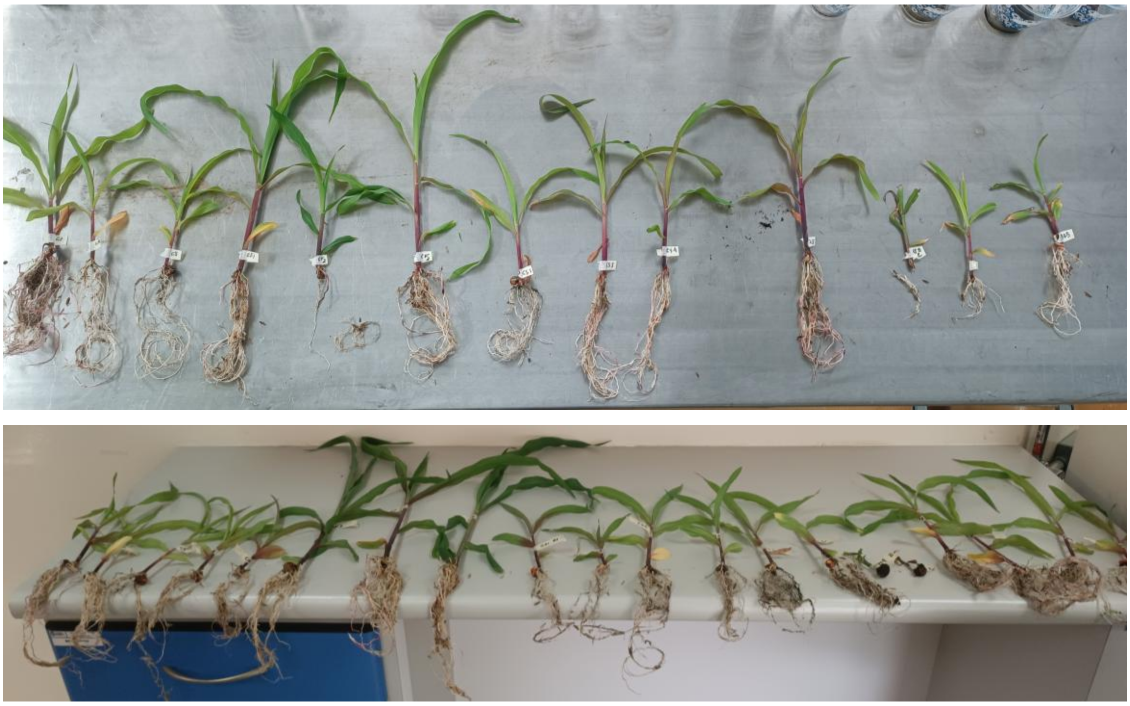


Figure A1. Specimens collected during the growth tests

Table A1. response variables measured in corn growth tests

Dosage	Substrate	Stem weight [g]	Stem length [mm]	Leaf size [mm]	Root weight [g]	Foliar weight [g]
	C3	1.37	83	255	2.07	1.98
	C4	0.65	65	155	1.58	0.93
	C5	0.46	60	165	1.11	0.69
	C6	1.1	97	208	2.94	1.33
	C7	0.97	89	218	2.22	1.18
	C8	0.78	95	222	1.97	0.85
	C9	0.51	70	190	1.85	0.93
	C10	0.5	66	140	1.61	0.77
	CF1	2.64	110	323	2.41	3.29
	CF2	0.75	55	190	0.4	1.08
	CF3	2.25	135	330	1.65	2.78
	CF4	2.54	160	380	2.88	2.7
	CF5	3.48	185	378	3.95	3.57
	CF6	3.34	170	402	4.21	3.88

10%	BC1	0.55	65	175	0.72	0.73
10%	BC2	1.61	95	270	2.05	1.77
10%	BC4	0.98	75	155	0.8	1.05
10%	BC5	1.81	100	230	2.32	1.86
10%	ENR2	0.63	65	50	0.11	0.28
10%	ENR3	0.42	60	100	0.27	0.3
10%	ENR5	0.64	70	85	0.54	0.37
2%	BC1	0.65	90	142	1.69	0.6
2%	BC4	1.43	112	210	2.86	1.49
5%	BC1	0.66	95	170	2.17	0.71
5%	BC2	0.9	90	180	2.98	0.89
5%	BC5	1.39	130	180	3.84	0.87
2%	PM4	0.14	20	65	1.91	0.15
2%	PM5	0.01	22	64	1.15	0.05
2%	ENR1	1.4	100	255	3.57	1.62
2%	ENR2	1.81	125	295	3.79	1.97
5%	ENR4	1	115	262	2.16	1.14
5%	ENR5	0.54	75	130	1.64	0.59

C: control; CF: Fertilized control; BC: biochar; ENR: Enriched biochar; PM: pyrolyzed chicken manure + corn stover

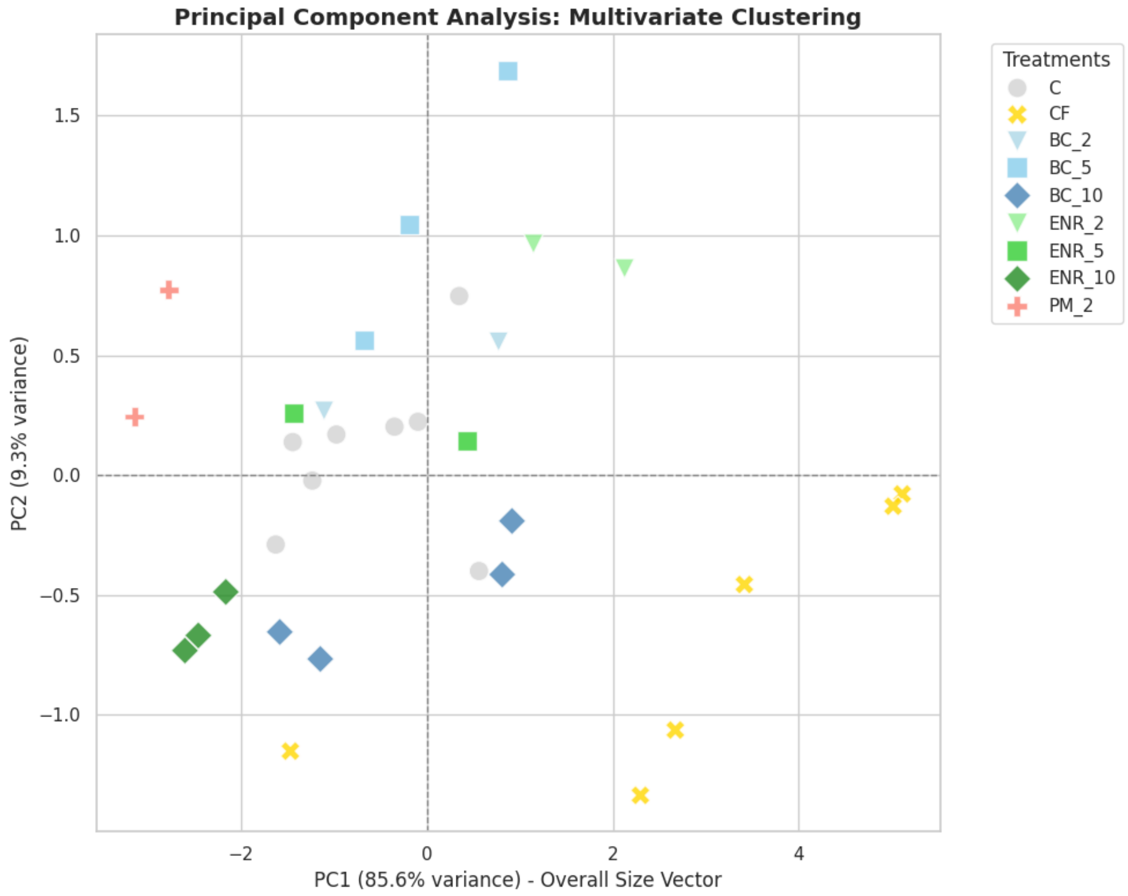
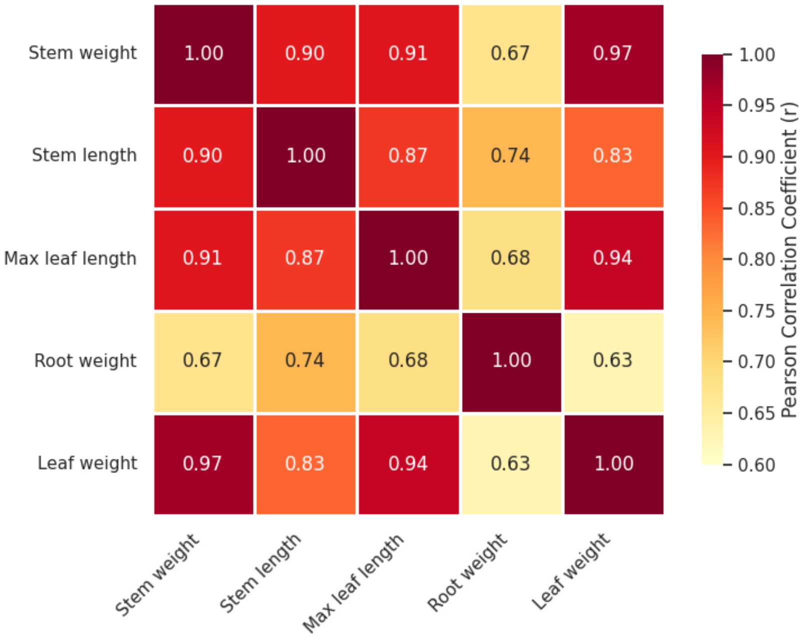


Figure A2 Principal component analysis for the response variables measured in the growth tests



	Stem weight	Stem length	Max leaf length	Root weight	Leaf weight
Stem weight	1.00	0.90	0.91	0.67	0.97
Stem length	0.90	1.00	0.87	0.74	0.83
Max leaf length	0.91	0.87	1.00	0.68	0.94
Root weight	0.67	0.74	0.68	1.00	0.63
Leaf weight	0.97	0.83	0.94	0.63	1.00

Figure A3. Pearson Correlation Matrix Between Response Variables