

Lower biochar yield in pyrolysis and gasification method compared to conventional method might be due to removal of volatile substances from the feedstocks at higher production temperature (650°C). High temperature induced removal of volatile matters, alkali and alkaline earth metals (AAEM) from feedstocks leading to expansion of biochar specific surface area was documented in earlier studies [1], [2]. Significant correlation between production temperature with volatile matter ($r = -0.923$ at $p < 0.01$) and specific surface area ($r = 0.940$ at $p < 0.01$) of biochars in our experiment also supports it. Similarly, higher ash content in biochars obtained from pyrolysis and gasification method is in agreement with the earlier findings of Rafiq et al. [3]. They observed greater ash content in corn stover biochar when produced in a slow pyrolysis process with higher temperature (500°C) compared to lower pyrolysis temperature (300°C). Lower labile carbon and higher fixed carbon content in pyrolyzed and gasified biochars compared to conventionally produced biochars confirms greater stabilization and polymerization of organic compounds under higher production temperature [4], [5]. Additionally, lower H/C and O/C ratio of pyrolyzed biochars (WCP) proves the loss of volatile and oxygenated hydrocarbons under higher pyrolysis temperature leading to formation of fixed carbons and aromatic structures [6]. This accumulated fixed carbon attributed to energy density as documented by higher calorific value of the biochars obtained from pyrolysis and gasification method. Strong positive correlation ($r = 0.834$) of calorific value with fixed carbon (at $p < 0.05$ level) also support this. Furthermore, documented higher fixed carbon and calorific value in biochars produced from mixed wood chips than the tea pruning litter supports the earlier findings of Bruun et al. [7] and Suliman et al. [8] who observed higher fixed carbon in wood based biochars than that of loose biomass and sewage sludge based biochars.

Recorded higher pH of high temperature produced biochars might be due to the destruction of acidic functional groups while preserving alkaline earth elements and easily soluble salts making the biochar alkaline in nature. Our findings are in agreement with the earlier reports of Uras et al. [9]. Observed greater surface alkalinity of tea pruning litter biochars (produced under pyrolysis and gasification methods) confirms that biochar surface alkalinity is influenced by both feedstock and production temperature [10]. Recorded non-similar surface functional groups (FTIR, Figure 4.1) in the studied biochars proves that both pyrolysis condition as well as nature of feedstock significantly influence the biochar surface functionality [11].

Differences in surface functionality in turn regulates the surface acidity or alkalinity of biochars [8]. Presence of higher functional groups in tea pruning litter based biochars (from FTIR study) may be the reason of documented its greater surface alkalinity compared to mixed wood chips. Higher surface alkalinity and pH dependent charges of tea pruning litter biochars may be one of the reasons of observed greater CEC of tea pruning litter biochars [12]. Moreover, higher elemental content in tea pruning litter biomass also contributed to greater pH, EC and cation exchange capacity (CEC) of the biochars derived from it. Higher doses of applied inorganic fertilizers in tea crop may be the reasons of recorded greater elemental content in tea pruning litter biomass compared to mixed wood chips. Use of pesticides and weedicides in tea cultivation may be another reason of recorded greater PAHs content in tea pruning litter biochars compared to mixed wood chips. This is in consistent with the earlier observation where native chemical compounds and PAHs in feedstock had the contribution to concentrations of PAHs in biochars [13], [14]. Cellulose, hemicellulos and lignin content of the feedstock along with production temperature determines the PAHs content in biochars [15]. Documented greater fixed carbon in mixed wood chips than tea pruning litter was corroborated by the higher lignin in it [16]. Similar reports on lower PAH containing biochars was documented when lignin rich feedstocks were used [15]. Our result of lower PAHs in biochars produced from mixed wood chips than tea pruning litter also support this. Superior adsorption capacity of the gasification based biochars is due to greater pore spaces and specific surface area [17]. Similar reports on higher biochar specific surface area and pore spaces were documented under optimal regulation of oxygen during the production process [18]. Higher availability of oxygen during the production process provides extra oxygen to burn the biomass leading to higher carbon (as CO₂) loss [19]. Thus, reduced aromatic carbon structure in biochar leads to distorted or reduced pore structures and specific surface area of the biochars as documented from conventional method. Additionally, rise in pH and specific surface area of biochars increased the adsorption sites for heavy metal [20], [21]. Significant positive correlation of adsorption potential of biochars with pH and specific surface area ($r = 0.870, 0.740$, respectively at $p < 0.05$) demonstrates the relationship between specified parameters as previously documented by Wani et al. [22]. Higher porosity and specific surface area of gasification and pyrolysis made biochars as confirmed from BET analysis also support the same. In contrast, lower porosity and specific surface area of

conventionally made biochars (WCC and TLC) are responsible for poor water holding capacity [23]. Positive correlation between specific surface area and water holding capacity along with the SEM images supports the finding. Absence of sulphur in all the tested biochars is a positive quality as there will be no sulphur emission on burning [24]. Therefore, the studied biochars with higher calorific value (especially pyrolysis and gasification biochars) could be alternative sources of clean energy [25]. Both pH and EC are the two key factors to specify the suitable application of biochar as soil amendment [26]. Positive correlation of production temperature with the pH and EC of the biochars ascertains the applicability of gasified and pyrolyzed biochars in acidic soils of Assam. Our findings on higher surface alkalinity of pyrolysis biochars (both TLP and WCP) indicates their possible use as soil pH regulator. Moreover, the alkaline property of biochars possess the potency to immobilize heavy metals making them unavailable for crops as heavy metals are much soluble in acidic soil solutions. Recalcitrant nature of the produced biochars (as documented by R50 value) of WCP, WCG, TLP, WCC and TLG biochars (O/C ratio ≤ 0.2) confirm long time stability in soil upto 1000 years [27]. Whereas, abundance in elemental concentration and minimal degradation nature of TLC biochar might be helpful as instant source of plant nutrients [28].

Significant influence of the studied biochars on seed germination and seedling growth of both the (mustard and french bean) crops might be due to biochar mediated alterations in soil pH, WHC, SOC and elemental contents [29], [30]. Improved germination parameters (germination percentage, germination index and vigor index) of both the seeds under application of the tested biochars at 10 t ha^{-1} can be attributed to the better water holding capacity of the applied biochars, which in turn increased soil moisture retention capacity required for seed germination. Previous studies documented inhibition or reduction in seed germination due to both high acidity and basicity [31]. In our experiment, alkaline nature of the tested biochars improved the soil pH (5.90 upto 7.7) and led to better germination performance of the tested seeds at 10 t ha^{-1} application rate. The ideal pH for mustard germination of mustard and is near neutral (pH 7) and french bean germination is 6 to 6.5 [32], [33]. Soil acidity lessens the seedling growth by hindering plant uptake of nutrients [34]. Nevertheless, the documented higher germination percentage of bean (10.21%) and mustard seeds (15.56%) under application of TLC biochar (10 t ha^{-1}) can be attributed to its minimal degradation property (lower R50 value). This facilitated quickly to neutralise the soil

acidity and improve soil nutrient dynamics. High alkalinity, presence of heavy metals, PAHs, and other hazardous chemicals in the biochars may be the cause of the observed lower seed germination when applied at higher doses (20 t ha^{-1}). The discharge of more toxic compounds into soil solution may hampers seed germination [35]. While, biochar at lower application dose (10 t ha^{-1}), the negative impacts of toxic compounds were less to give adverse impact on seed germination. Moreover, biochar induced positive influence on soil property under lower application rate supported the seeds to overcome the repressing impacts of toxic compounds. Our results on presence of PAHs and heavy metals in the produced biochars also support this. Similarly, Uslu et al. [36] also documented higher seed germination at lower application rate of biochar which declined with increasing the application dose. Observed higher negative impact of biochar (at 20 t ha^{-1} application rate) on germination of mustard seeds might be due to the smaller seed size and plant specific properties [37]. Thus, biochar induced impact on seed germination is specific to plant species and seed size as seeds smaller in size are more susceptible to injury during germination [38], [36], [39]. Regardless of the seed type, the highest decline in seed germination under application of 20 t ha^{-1} of TLC biochar may be due to the greater level of phytotoxicity caused by the presence of more heavy metals and PAHs in it.

Increased soil organic carbon content under application of the tested soil amendments might be due to improvement on soil physical and chemical properties that offered a sustainable environment for the soil microbial community leading to increase SOC content [40]. Higher increment in SOC content from addition of 10 t ha^{-1} of biochar was also documented earlier [41], [42]. Maximum upsurge in SOC content under biochar application compared to FYM can be attributed to the higher content of fixed carbon in biochars compared to FYM [43], [44]. Improved water holding capacity, available carbon and soil nutrients from biochar application also confirm the same. Moreover, observed condensed aromatic carbon in biochars enhanced the chemically resistant SOC fractions (HAC and FAC) in soil [6]. Whereas, higher content of labile carbon in FYM increased soil carbon mineralization leading to consequent loss of HAC and FAC fractions. Additionally, the calculated higher value of HAC:FAC ratio under addition of biochar (10 t ha^{-1}) confirmed hike in SOC quality and long-term sequestration of C [45]. Our result on improved soil MBC from FYM treated plots compared to biochar is due to existence of inherent microorganisms and higher labile

carbon in FYM that encouraged better microbial growth and amplified the soil MBC content [46], [47]. However, higher MBC noted under application of biochar at 10 t ha⁻¹ might be due to higher specific surface area and porous nature of biochars that provided suitable environment for soil biota [48]. Moreover, improved water holding capacity in biochar treated soil stimulated the microbial growth [49]. Similar to soil MBC, documented highest soil bacterial count (log cfu g⁻¹ soil) under FYM application (10 t ha⁻¹) can be ascribed to the higher readily available carbon sources for bacterial growth and the inherent community of bacteria in it. This increased bacterial community in FYM treated plots also attributed to the higher activities of soil enzymes (urease, phosphatase and dehydrogenase) than the biochar added plots. Improved soil biota in presence of higher labile organic matter in FYM treated plots in turn increased the nutritional demand (particularly nitrogen and phosphorus) and thus enhanced production of urease and phosphatase enzymes. In contrast, the recalcitrant nature of biochar decelerated the process of biological carbon mineralization and enzymatic activities [50]. Recorded higher enzymatic activities under application of conventionally produced biochars than the biochars produced from gasification and pyrolysis methods in our experiment confirm the same.

Application of tested biochars significantly increased soil WHC and reduced soil BD. The inverse relation of soil BD and WHC is well known in literatures [51]. Reduced BD in biochar amended soil compared to other organic fertilizers have described by earlier researchers [52]. Moreover, observed significant positive correlation between the BD of tested biochars with the BD of biochar treated soil also confirm it. The recorded lower soil BD in 10 t ha⁻¹ of biochar added plots is responsible for higher plant root biomass since lower BD alleviate the soil compaction making it easier for roots to grow [53]. Besides, higher increment in WHC under biochar application provided sufficient availability of moisture for plant uptake.

Increased soil pH in biochar added plots and reduction of the same under application of inorganic fertilizers (at recommended dose) can be attributed to the basic nature and liming effect of biochars [54]. Whereas, application of inorganic fertilizers (more particularly ammonium based) releases H⁺ ions in soil when each molecule of ammonia nitrified to nitrate and increased soil acidity [55]. Significant positive correlation between pH of both biochar and biochar treated soil indicates biochar as a sustainable approach to reduce soil acidity. Similarly, recorded hike in soil EC and

CEC in biochar treated plots compared to control and inorganically fertilized plots might be due to leaching of existing elements (K, Ca, Mg, Na and P) [56] from biochars making them accessible for plant adsorption [57]. Significantly higher nutrient content in biochar applied soils (highest under application of tea pruning litter biochars) can be attributed to availability of the same in biochars. Similarly, higher nutrient content was documented in tea pruning litter biomass compared to wood chips. This might be due to higher nutrient demand of tea crop and its maintenance under abundant supply of fertilizers [58]. Irrespective of production methods, the documented higher heavy metals in soil under application of tea pruning litter biochars can also be related to the use of chemical fertilizers, pesticides and weedicides during tea cultivation. Apart from inorganically fertilized plots, recorded higher soil available form of N, P, and K under mixed application of biochar (5 t ha⁻¹) with inorganic fertilizers (50% of recommended dose) suggests the possible reduction in inorganic fertilizer doses in crop cultivation with the addition of biochar. Moreover, the slow mineralization rate of biochar in soil will act as long-term nutrient source for plant. Higher surface adsorption of biochar will help in adsorption of soil available N into its pores, lessening the likelihoods of N leaching and surface run off [59]. Earlier researchers [4], [58] documented similar long-term benefits of biochar as soil amendment on elemental content, and surface adsorption.

Improved soil properties from biochar addition correspondingly enhanced the photosynthesis and transpiration rate in both the tested crops. Similar report on biochar induced nourishment during the whole crop growing period compared to inorganic NPK fertilizers was documented [60]. Observed higher plant dry biomass yield (both root and shoots) and seed yield under application of biochars also confirm it. Recorded highest mustard and french bean yield under addition of tea pruning litter biochar can be attributed to the greater nutrient content and SOC of the same.

In our study, reduction in N₂O flux under treatment TLC10 than control from mustard (up to 45%) and bean field (up to 51%) might be due to lower availability of NO₃-N (upto 39.31% and 37.28% in mustard and French bean field, respectively). This might be because of adsorption of NO₃-N on biochar surfaces. Production of N₂O in soil is controlled by both nitrification and denitrification processes where nitrate serves as a substrate for the denitrifying bacteria [61], [62], [63]. Documented higher contribution of inorganic nitrogen fertilizer (IF) towards N₂O emission might be due

to corresponding increase of nitrification and denitrification processes under higher substrate ($\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$) availability [64], [65]. Recorded higher $\text{NH}_4\text{-N}$ and urease activity in inorganically fertilized plots also support it. Similarly, rise in soil urease activity, $\text{NO}_3\text{-N}$ from co-application of FYM and inorganically fertilized plots revealed rapid mineralization of nitrogen and carbon enhanced the N_2O emission [66]. Moreover, rise in soil pH under biochar application improved activity of N_2O reductase enzyme and thus helped in formation of N_2 instead of N_2O [67]. Maximum activity of enzyme nitrate reductase was documented at pH range of 6.5 to 7.5 [68]. Therefore, the hike in soil pH (mustard field from 5.90 to 6.63; french bean field from 5.93 to 6.57) under biochar addition enhanced the activity of N_2O reductase enzyme resulting lower production and emission of N_2O .

Furthermore, recorded higher transpiration rates (12.02% and 10.00% hike in mustard and french bean, respectively) during flowering stage of both the crops can be related to documented higher N_2O flux at that period, since N_2O emission takes place via transpiration pool [69]. Similar findings of hike in N_2O emission at reproductive stage (due to elevated levels of metabolic activity during flowering or reproductive stage) were reported from different varieties of wheat and rice [70], [69]. Increased availability of N, $\text{NO}_3\text{-N}$ and urease activity in inorganically fertilized plots (NPKR) were the reasons of observed profuse growth of fresh plant biomass and rise in transpiration rate, which in turn led to higher N_2O emission. Similar results on above ground plant biomass induced rise in GHGs transport from soil to atmosphere due to the corresponding hike of internal spaces in plants were documented by earlier scientists [70], [71].

CO_2 effluxes were significantly affected by the applied treatments due to enhanced mineralization of readily available soil organics at the early phases of the crop (seedling and vegetative stages) growth. Documented higher readily available carbon source and CO_2 efflux in FYM applied plots (at 10 t ha^{-1}) reflects the findings of Malav et al. [72], Parkin et al. [73]. They explained that readily available organic matter and consequent rise in soil microbial respiration increase soil CO_2 production. Abundant bacterial growth as documented in the form of higher bacterial colony count in FYM treated plots (10 t ha^{-1}) may be the reason of higher CO_2 emission. Whereas, lower CO_2 efflux from biochar treatment (10 t ha^{-1}) displays the improved carbon sequestration potential of biochars. Recorded higher fractions of fixed carbon (HAC, FAC and HAC:FAC ratio) in biochar treated plots supports the findings.

Several earlier studies also observed significant correlation between carbon equivalent emission (CEE) of N₂O with global warming potential (GWP) which are in support with our results [74], [75]. Application of inorganic chemical fertilizers directly associated to the increased CEE and thus with GWP. Additionally, estimated AEI demonstrated the advantageous effects of the studied biochars on reduction of GWP in both the crop fields.

Salient findings:

- Tea pruning litter is a potential feedstock for biochar production.
- Conventional biochar production method yielded highest biochar compared to gasification and pyrolysis techniques and exhibited positive impacts on soil health, crop growth and reduced the emission of soil N₂O and CO₂ soon after its application.
- Whereas, gasification and pyrolysis method yielded biochars with higher recalcitrance potential which correspondingly increased the soil carbon.
- Seed germination percentage increased under application of TLC biochar at 10 t ha⁻¹ dose, whereas, increasing the application dose to 20 t ha⁻¹ significantly reduce the same.
- All of the investigated biochars have the ability to reduce CO₂ and N₂O emissions and are beneficial for plant growth when employed as soil amendments.
- Higher specific surface area, recalcitrance potential and adsorption capacity of the gasification and pyrolysis based biochars have greater potential to sequester soil carbon. Thus, providing long term benefits as soil amendment.
- Calculated amendment effect index (AEI) shows significant impacts of applied treatments on recorded cumulative N₂O and CO₂ flux.
- In our study, conventionally made tea pruning litter biochar (TLC) was found to be most beneficial for mustard and french bean growth and seed yield.
- Co-application of biochar with FYM or biochar with inorganic fertilizer is an environmentally sustainable approach. Practicing it could reduce GHGs emission, cut the quantity use of inorganic fertilizers without compromising the crop yield and soil health.

- In our investigation, biochar was found to be more effective than FYM in acidic soils of Assam, India to improve crop yield and soil quality while reducing N₂O emissions.

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