



Communication Production of Pelleted Biochar and Its Application as an Amendment in Paddy Condition for Reducing Methane Fluxes

Jin-Ju Yun¹, Jae-Hyuk Park¹, Bharat Sharma Acharya², Jong-Hwan Park³, Ju-Sik Cho^{1,4}, and Se-Won Kang^{1,4,*}

- ¹ Department of Agricultural Chemistry, Sunchon National University, Suncheon 57922, Korea; wlswn6511@hanmail.net (J.-J.Y.); jaehyuk0309@naver.com (J.-H.P.); chojs@scnu.ac.kr (J.-S.C.)
- ² Independent Researcher, Oklahoma City, OK 73106, USA; bikatiaas@gmail.com
- ³ Department of Life Resources Industry, Dong-A University, Busan 49315, Korea; zoqlsqkr@dau.ac.kr
- ⁴ Department of Agricultural Life Sciences & Interdisciplinary Program in IT-Bio Convergence System, Sunchon National University, Suncheon 57922, Korea
- * Correspondence: kangsw@scnu.ac.kr; Tel.: +82-61-750-5192; Fax: +82-61-752-8011

Abstract: The global focus continues with respect to increasing agricultural productivity, such as in paddy soils using inorganic fertilizers. Such practices could adversely affect the agricultural environment by deteriorating soils and increasing greenhouse gas emissions. The aim of this study was to assess the effect of biochar pellet blended with condensed molasses soluble (CMS) on rice productivity, soil quality, and methane (CH₄) emissions in a paddy condition for healthy agricultural ecosystem. This study used a commercial scale pyrolysis system to produce biochar at 600 °C from bamboo. The experiment consisted of three different treatments: control, inorganic fertilizer (IF, N-P-K = 90-45-57 kg ha⁻¹), and biochar pellet (BC_PT, 1000 kg ha⁻¹). Compared to other treatments, the biochar pellet decreased annual CH₄ flux by 15.8–18.8%. The rice grain yield under inorganic fertilizer as conventional rice management was slightly more than applied biochar pellets, despite lower soil chemical properties. However, for long-term paddy management, including environmental protection and rice production, biochar pellets are better suited for maintaining a healthy agricultural ecosystem than conventional practices. Indeed, the application of biochar pellets appears to potentially reduce CH₄ emissions and maintain stable rice productivity through the slow release of nutrients.

Keywords: biochar pellet; condensed molasses soluble; methane; agricultural ecosystem; conventional practices

1. Introduction

Rice is one of the most important food sources globally and is grown on about 11% of the world's arable land [1]. Rice production usually requires more water than other crops since rice is mostly cultivated on puddled soils under anaerobic conditions in paddy fields. Such cultivation system and practice affect both localized and global climate by releasing methane (CH₄) into the atmosphere [2]. CH₄ is a major greenhouse gas with global warming potential that is 25 times higher than carbon dioxide (CO₂), which consequently contributes to climate change. CH₄ in paddy fields is produced by the decomposition of soil organic matter (SOM) by methane producing bacteria under anaerobic conditions and is affected by soil temperature, redox potential and soil characteristics [3]. According to FAO [4], rice is consumed by more than half the world's population, which calls for a production increase by 40% by 2030 to meet the increasing demand of growing population. In particular, rice farming in South Korea is both socially and economically crucial. Therefore, soil and nutrient management practices are necessary to reduce methane emissions, while sustainably increasing agricultural productivity and building resilience to climate change.



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Biochar is a carbon-rich solid material produced by the pyrolysis of biomass in an oxygen-limited environment [5]. Biochar is an excellent tool for reducing greenhouse gases in the atmosphere and is reported to perform well as a soil amendment, improving soil structure and increasing soil fertility and fertilizer use efficiency [6–8]. Specifically, biochar improves soil health and crop production by increasing nutrient cycling, cation exchange, and plant available water. The efficacy may, however, vary with biochar type, rate, production conditions, climate, soil, and management practices. Globally, different biochars are available, depending on the type of biomass used. However, despite these advantages, due to the lower nutrient content compared with inorganic fertilizers, there is limited use of biochar in the continuous production of crops [9]. To address these shortcomings, some researchers have attempted to make pellets by mixing biochar with other organic materials [10,11]. However, our understanding on the effects of biochar pellets in the paddy environment is limited due to shorter study durations and the absence of studies related to CH_4 reduction.

Condensed molasses soluble (CMS), a byproduct of lysine production through molasses fermentation, contains a large amount of organic matter and nitrogen. In addition, CMS contains numerous beneficial ingredients for crops, such as sugars and amino acids, and can be used as a nutrient feeder for soil and plants. Hence, the application of CMS as a biochar pellet binder in terms of efficient recycling of resources and environmental conservation is expected to be advantageous for many agricultural systems.

This study, therefore, focuses on pelleted biochar production with blended with CMS and its impact on rice growth attributes and productivity, soil characteristics and methane emissions in a two-year (2016–2017) field experiment.

2. Materials and Methods

2.1. Raw Materials

Dried bamboo was used as raw feedstock to produce biochar. Biochar production was achieved through pyrolysis at 600 $^{\circ}$ C, for 4 h using anaerobic conditions with an injection of continuous flow of N₂ gas. The yield and pH of bamboo biochar (BB) were 28.8% and 10.1, whereas C, H, O, N, and S of BB were 87.2, 2.79, 9.63, 0.54, and 0.01%, respectively (Table 1).

BET SA *	Yield	лU	Elemental Composition					Molar Ratio			
		рп	С	Н	0	Ν	S	H/C	O/C	(O + N)/C	(O + N + S)/C
$(m^2 g^{-1})$	(%)	(1:10H ₂ O)			(%)						
228	28.8	10.1	87.2	2.79	9.63	0.54	0.01	0.39	0.08	0.09	0.09
	± 2.56 ^a	±0.02	±0.15	± 0.03	±0.13	±0.02	± 0.00	± 0.00	± 0.00	±0.00	± 0.00

Table 1. Biochar characteristics used in this study.

* SA, surface area. ^a Standard deviation.

The soil used for plot cultivation was collected from the paddy area at Suncehon-si, South Korea. The particle size distribution of the collected soil was 34.6% sand, 50.5% silt, and 14.9% clay. The pH and EC of soil were 5.64 and 0.24 dS m⁻¹, respectively, and comprised 5.64 g kg⁻¹ soil organic carbon (SOC), 0.74 g kg⁻¹ total nitrogen (TN), 38.0 mg kg⁻¹ available phosphate (Avail. P₂O₅), 0.09 cmol_c kg⁻¹ K, 4.24 cmol_c kg⁻¹ Ca, 0.44 cmol_c kg⁻¹ Mg, and 5.71 cmol_c kg⁻¹ cation exchange capacity (CEC). The characteristics of condensed molasses soluble (CMS) before the experiment began were as follows: pH 4.43, organic matter (OM) 56.6%, total nitrogen (TN) 6.54%, total phosphorus (TP) 0.18%, and potassium (K) 0.31%.

2.2. Preparation of Biochar Pellet

The biochar produced with pyrolysis was ground in a grinder and a roller and passed through a 200 μ m sieve before the start of the experiment. Ground biochar that passed

through the sieve was selected as soil amendment, and it was further processed by blending with CMS (diluted 10 times with distilled water) as a binder to produce a biochar pellet (BC_PT).

The combination ratio of biochar and binder was 9:1 (w/w), and the size of BC_PT was Ø 0.2 cm. The blended material was completely mixed using an agitator for 10 min. The process of producing the biochar pellet through the extrusion machine by combining biochar and binder is illustrated in Figure 1.



Grinding

Supplement

Extrusion

Production

Figure 1. Manufacturing process of pelleted biochar (BC_PT) using bamboo biochar.

2.3. Experimental Design and Sampling

This experiment was conducted at Sunchon National University, South Korea, in 2016–2017 by applying inorganic fertilizer (IF) and BC_PT to experimental plots (1 m L. \times 1 m W. \times 0.5 m H.). This area is heavily influenced by sea climate but the deviation of annual temperature is not large. The study area has a mean annual precipitation of 1249 mm and mean temperature of 13.4 °C during 2 years (Figure 2). The treatment conditions were divided into three treatments with three replicates each, and a total of 9 plots for each year. Each treatment was separated by a control, inorganic fertilizer (IF, N-P-K = 90-45-57 kg ha⁻¹), and biochar pellet (BC_PT, 1000 kg ha⁻¹) treatments, respectively. BC_PT was applied by hand and plowed into the soil 14 days before rice transplanting.



Figure 2. Mean daily precipitation and air temperature during rice cultivation.

Dongjinbyeo (*Oryza sativa*, Joponica type) was used as the test crop. Rice was transplanted on 25 May 2016 and 24 May 2017 in each plot, with 20 cm space between plots, and harvested on 28 September 2016 and 27 September 2017, respectively. Soil samples in each treatment were collected after rice harvesting. The harvested plant samples were also investigated for growth characteristics including plant height, tiller number, seed per panicle, 1000 seed weight, and grain yield.

2.4. CH_4 Monitoring

A static chamber was used to monitor fluxes of CH_4 . Gas sampling was performed between 10 and 11 a.m. every 7 days using a syringe. The gas sample for CH_4 measurement was collected at 0, 15, and 30 min after chamber closure of the chamber. CH_4 measurements were simultaneously analyzed on a gas chromatograph (GC-2014, Shimadzu) with a flame ionization detector (FID), as described in the GC manual. The temperature of the equipment for gas analysis was controlled at 55 °C for the column, 100 °C for the injector, and 230 °C for the detector in FID. A gas mixture of argon and methane was used as a carrier for CH_4 and flux was calculated by using the following equation:

$$F = \rho \times (V/A) \times (\Delta c/\Delta t) \times (273/T)$$
(1)

where F is CH₄ flux, ρ is CH₄ density, V is the volume of the chamber (m³), A is the area of chamber (m²), $\Delta c/\Delta t$ is the average increase in gas concentration, and T is the 273 + mean temperature in the chamber (°C).

The total CH_4 flux for the entire rice cultivation was computed as described in Kang et al. [3]:

Total CH₄ flux =
$$\sum_{i}^{n} (\text{Ri} \times \text{Di})$$
 (2)

where Ri is rate of CH_4 emission in the sampling interval, Di is number of days in the sampling interval, and *n* is number of sampling intervals.

2.5. Soil Analysis

Soil analysis was performed as described in NIAST [12]. Briefly, after rice harvesting, soil samples were collected from the surface layer (15 cm depth) in each treatment, airdried, and passed through a 2 mm mesh. The chemical properties of the sieved soils were analyzed using different standard methods: soil pH was measured in a soil–water ratio of 1:5 after shaking the mixture for 30 min; organic matter (OM) and total nitrogen (TN) analysis were performed using Tyurin method and Kjeldahl method, respectively; available phosphate (Avail. P_2O_5) was conducted by the Lancaster method; and the exchangeable cations in soil were extracted by 1N-NH₄OAc.

2.6. Statistical Analysis

Statistical analyses of all data were performed using the JMP15 software with SAS (version 14.2). The mean values were measured as an average of three replicates. Each mean value was subjected to one-way analysis of variance (ANOVA) and a comparison of the treatments was performed by applying Tukey's test. The determination of differences among the parameters was performed via two-way ANOVA that included years, treatment conditions, and their interaction.

3. Results

3.1. Rice Production

The overall changes in the rice yield components under biochar and IF treatments were either similar or better in 2017 than in 2016 (Table 2). Generally, the yield components were influenced by the biochar pellet application compared with IF treatments. In 2016, the yield components between pelleted biochar and control plots did not differ in most cases but were significantly higher under pelleted biochar in 2017. Among the rice yield components, the mean values of plant height and tiller number were higher in 2016. In addition, the rice yield components of IF treatment are slightly better than BC_PT treatments in 2016, but no significant differences were observed between the fertilizer and biochar in 2017. Significant interaction effect (year \times treatment) was observed for plant height and 1000 seed weight. Biochar increased the 1000 seed weight in 2017 and both the 1000 seed weight and grain yield in 2017 compared to the control treatment.

Year	Treatment	Plant Height	Tiller Number	Seed per Panicle	1000 Seed Weight	Grain Yield	
		(cm)	(per hill ⁻¹)	(no.)	(g)	$(g m^{-2})$	
2016	Control	$48.6 \pm 3.24 b^{1}$	$6.8\pm0.45b$	$32.8 \pm 1.79 \mathrm{b}$	$23.1\pm0.73b$	$226\pm8.87\mathrm{c}$	
	IF	$54.9 \pm 2.72a$	$8.6\pm0.55a$	$37.2\pm2.17a$	$26.3\pm1.03a$	$272 \pm 4.10a$	
	BC_PT	$49.8\pm1.95b$	$7.4\pm0.55b$	$35.4\pm0.89ab$	$24.4\pm0.79b$	$257\pm3.11b$	
2017	Control	$47.8 \pm 3.00a$	$6.4\pm0.55b$	$32.4 \pm 1.52b$	$22.7\pm0.96\mathrm{b}$	$213\pm6.52b$	
	IF	$52.3\pm3.21a$	$8.2\pm0.45a$	$36.8 \pm 1.64a$	$26.0\pm0.75a$	$270\pm3.56a$	
	BC_PT	$52.4\pm3.33a$	$8.0\pm0.71a$	$36.4\pm0.89a$	$25.8\pm1.19a$	$268\pm3.41a$	
Statistica	ıl analysis ²						
Yea	Year (A)		ns	ns	ns	ns	
Treat	Treatment (B)		***	***	***	***	
А	$A \times B$		ns	ns	***	ns	

Table 2. Rice yield components in paddy soils.

¹ Different letters within the same column indicate significant differences between treatments, as determined by Tukey's test with p < 0.05. ² ns, *, **, and *** denote not significant (ns) and significant differences at the 5, 1, and 0.1% levels, respectively.

3.2. Soil Chemical Characteristics

Soil chemical properties were significantly different among different treatments during rice cultivation (Table 3). However, no interaction effect between year and treatments were observed. In particular, the soil chemical characteristics were relatively better under biochar than control and IF treatments in 2017, as compared to 2016. Interestingly, soil chemical characteristics and rice yield components with biochar application showed a similar tendency. Irrespective of the sampling year, the ranges of soil chemical characteristics after rice harvesting, in treatments without and with biochar are as follows: soil pH between 5.14–5.24 and 5.48–5.51, SOC content between 5.22–5.56 and 5.95–5.97 g kg⁻¹, TN content between 0.67–0.79 and 0.72–0.77 g kg⁻¹, Avail. P₂O₅ content between 28.7–32.8 and 32.2–33.3 mg kg⁻¹, and CEC between 5.48–5.64 and 5.90–5.95 cmol_c kg⁻¹.

Table 3. Soil chemical characteristics after rice harvest.

Year	Treatment	рН	SOC	TN	Avail. P2O5]	Exch. Cations	6 (cmol _c kg ⁻¹)
		(1:5)	(g k	(g ^{−1})	$(mg kg^{-1})$	К	Ca	Mg	CEC
2016	Control	5.17 ±0.05c ¹	5.56 ±0.20b	0.71 ±0.10b	30.6 ±0.39b	$\begin{array}{c} 0.07 \\ \pm 0.00 \mathrm{c} \end{array}$	4.18 ±0.05b	0.41 ±0.02a	5.55 ±0.23b
	IF	5.24 ±0.04b	5.55 ±0.25b	0.76 ±0.17a	31.4 ±0.29ab	$\begin{array}{c} 0.08 \\ \pm 0.00 b \end{array}$	4.22 ±0.07b	$\begin{array}{c} 0.41 \\ \pm 0.02a \end{array}$	5.64 ±0.12b
	BC_PT	$\begin{array}{c} 5.48 \\ \pm 0.02a \end{array}$	5.95 ±0.20a	0.72 ±0.16b	32.2 ±0.87a	$\begin{array}{c} 0.10 \\ \pm 0.00 a \end{array}$	4.42 ±0.07a	$\begin{array}{c} 0.44 \\ \pm 0.01 a \end{array}$	5.90 ±0.06a
2017	Control	5.19 ±0.05b	5.29 ±0.33b	0.67 ±0.09b	28.7 ±1.23b	$\begin{array}{c} 0.07 \\ \pm 0.00 \mathrm{c} \end{array}$	4.15 ±0.10b	0.37 ±0.00b	$5.49 \\ \pm 0.08 \mathrm{b}$
	IF	$5.14 \pm 0.02b$	5.22 ±0.19b	0.79 ±0.16a	32.8 ±1.02a	$\begin{array}{c} 0.08 \\ \pm 0.00 b \end{array}$	$\begin{array}{c} 4.16 \\ \pm 0.02 b \end{array}$	0.40 ±0.03b	$\begin{array}{c} 5.48 \\ \pm 0.15 b \end{array}$
	BC_PT	5.51 ±0.11a	5.97 ±0.23a	0.77 ±0.15a	33.3 ±1.54a	$\begin{array}{c} 0.10 \\ \pm 0.00 a \end{array}$	4.49 ±0.02a	$\begin{array}{c} 0.48 \\ \pm 0.03a \end{array}$	$5.95 \pm 0.11a$
Statistical analysis ²									
Yea Treatr	ar (A) ment (B)	ns ***	ns ***	ns ***	ns ***	ns ***	ns ***	ns ***	ns ***
A × B		ns	ns	ns	ns	ns	ns	ns	ns

¹ Different letters within the same column indicate significant differences between treatments, as determined by Tukey's test with p < 0.05. ² ns, *** denote not significant (ns) and significant differences at the 0.1% levels.

3.3. Changes in CH₄ Emission Rate

The CH₄ emission rate was significantly affected by biochar application and sampling seasons (Figure 3). The CH₄ emission rates rapidly increased with flooding and peaked at around 2 months after rice transplanting between 2016 and 2017. The changes in CH₄ emission patterns were comparable during cropping and fallow seasons. The annual CH₄ flux scale was mostly observed in the rice cropping season, with a lesser effect during the fallow season (Table 4). The CH₄ emission rates in all treatments ranged from 0.65 to 26.8 mg m⁻² hr⁻¹ during the rice cropping season and -0.61 to 3.47 mg m⁻² hr⁻¹ during the fallow season. BC_PT treatment showed comparatively lower CH₄ emission rates, with a mean value of 6.4–6.6 mg m⁻² hr⁻¹ during the rice cropping season, as compared to IF treatments. In the IF treatment, the total CH₄ flux recorded 24.4 g m⁻² during the 2016 rice cropping season. In comparison, the application of biochar pellet significantly reduced CH₄ flux by 5.0 g m⁻² and 3.2 g m⁻² (total flux: 19.4 and 20.1 g m⁻²) during the 2016 and 2017 rice cropping seasons, respectively.



Figure 3. Changes in CH₄ emission rates during rice cropping and fallow seasons. Error bars represent standard deviations (n = 3).

Treatment	Total CH ₄ Flux (g m ⁻²)							
	Rice Cropp	ing Season	Fallow Season	Annual				
	2016	2017	2016–2017					
Control	24.0a *	25.3a	3.67a	53.0a				
IF	24.4a	23.3a	3.48a	51.2a				
BC_PT	19.4b	20.1b	3.59a	43.1b				

Table 4. Total CH₄ flux during rice cropping, fallow, and annual.

* Different letters within the same column indicate significant differences between treatments, as determined by Tukey's test with p < 0.05.

4. Discussion

With global population rise and climate change threatening food production, it is imperative to understand the influence of management practices, such as biochar application, on soil properties, agricultural productivity, and greenhouse gas emissions. This study was largely aimed at investigating the soil and agronomic effects of biochar pellet blended with CMS application under paddy conditions. Many earlier studies on biochar pellets show that organic or inorganic materials mixed with biochar tend to release nutrients slowly and improve soil quality. For example, Kim et al. [5] studied biochar pellets prepared by blending switchgrass-derived biochar, lignin, and fertilizer K and P together and reported that the lignin content and processing temperatures could control the release rate of nutrients. Such pellets are durable, and they produce smaller pore sizes and lower total surface area and pore volume. These properties play important role in slowly releasing nutrients; thereby reducing leaching losses. Indeed, nutrient-rich biochar pellets are believed to be involved in holding nutrients for a longer-period of time due to higher nutrient absorption capacity and high specific surface area [11]. However, chemical properties of the pellets may vary depending on the feedstock elemental composition and pyrolysis temperature. Therefore, for soil application, it is highly recommended to consider soil environmental conditions and pellet properties [6,10].

Studies indicate several benefits of nutrient-rich biochar pellets, including improvements in crop yield. For example, biochar pellets increased the yields of rice [9], tomato [13] and sunflower grain and peppers fruit [14]. Such an increase was associated with improved nutrient availability and soil health and quality. In this study, the application of biochar pellet also played an important role in either maintaining or increasing the rice yield and yield attributing components for two years despite a single application. Importantly, the biochar pellet served as a promising slow-releasing amendment potentially due to its high capacity for nutrients retention and cation exchange.

Short-term and long-term experiments reveal biochar's role in reducing or mitigating CH₄ emissions from soils, particularly from paddy environments [2,15,16]. According to Kang et al. [17], the high specific surface area and lower bulk density of biochar directly affects soil properties and fertility. Mechanisms reducing methane could include sorption of CH₄ to biochar surface and methanotropic CH₄ consumption at oxic/anoxic interface under anoxic conditions [18]. The suppression of CH₄ emission by biochar in this study is on par with some previous studies [19,20]. Wang et al. [21] reported that incorporating biochar into the paddy soil significantly decreased the annual CH₄ emission by 20–51% when compared to the control treatment. Yang et al. [7] reported that increasing the soil pH reduces the methanogen's activity, thereby reducing CH₄ emissions. Liu et al. [22] also reported that CH₄ emissions are reduced when pH increases after biochars are incorporated into the soil. Indeed, biochars have higher pH then the soil, causing liming effects. In our study, significant differences in soil pH were found in all three treatments, with higher pH under biochar for both years. This may have potentially caused reduced CH₄ emissions in the current study.

5. Conclusions

Our field study demonstrates that over a 2-year period, the application of pelleted biochar decreased the annual CH_4 emissions in a rice cropping system by 15.8% than standard fertilizer treatment. In addition, our study indicated that the application of pelleted biochar changes the soil properties, thus resulting in stable rice production. Assessing rice yields showed that inorganic fertilizer treatment resulted in slightly higher production for 2 years than the pelleted biochar treatment. However, in terms of methane reduction and conservation of the paddy environment, the application of pelleted biochar showed an unequivocal benefit to the agroecosystem over inorganic fertilizer treatment. Further long-term studies are, however, required to better understand the effect of pelleted biochar and other factors including microbial activity on CH_4 emission, soil properties, and rice yields.

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