EFFECTIVE OF BIOCHAR PREPARED FROM RICE HUSK TO GREENHOUSE GAS EMISSIONS

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ARTICLE INFO **ABSTRACT** This study aims to evaluate the efficiency of biochar prepared from Received: 04/5/2022 rice husks (O. Sativa L., OM5451) to greenhouse gas (CH₄ and N₂O) Revised: 29/5/2022 emissions. Rice husk biochar was produced by pyrolysis method (700°C) by a kiln - VMF 165. The treatments were randomly assigned Published: 30/5/2022 and 4 replicates for each treatment. This study showed that rice husk biochar at 20 tons ha⁻¹ reduced CH₄ and N₂O emissions were 15.99%, **KEYWORDS** 48.47% better than of 10 tons ha⁻¹ and 5 tons ha⁻¹ were 13.01%, Biochar 5.58% and 37.70%, 33.00%, respectively. In conclusion, the addition of rice husk biochar into the paddy soil can reduce greenhouse gas CH_4 emissions. The effectiveness of reducing total greenhouse gas Greenhouse gas emissions of the treatment with 20 tons ha⁻¹ was highest. N_2O Rice husk

ẢNH HƯỞNG CỦA THAN SINH HỌC ĐƯỢC CHẾ TẠO TỪ TRẦU ĐẾN SỰ PHÁT THẢI KHÍ NHÀ KÍNH

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THÔNG TIN BÀI BÁO	TÓM TẮT				
Ngày nhận bài: 04/5/2022	Mục tiêu của nghiên cứu này là đánh giá ảnh hưởng của than sinh				
Ngày hoàn thiện: 29/5/2022	học được chế tạo từ trấu (O. sativa L., OM5451) đến sự phát thải khí nhà kính (CH ₄ and N ₂ O). Than sinh học trấu được chế tạo bằng				
Ngày đăng: 30/5/2022	phương pháp nhiệt phân ở nhiệt độ 700°C bằng máy - VMF 165. Các				
	nghiệm thức được bố trí hoàn toàn ngẫu nhiên với 4 lần lặp lại cho				
TỪ KHÓA	mỗi nghiệm thức. Kết quả nghiên cứu được trình bày rằng than sinh				
CH ₄	- học trấu ở 20 tấn ha-1 giảm phát thải CH ₄ và N ₂ O lần lượt là 15,99%,				
$C\Pi_4$	48,47% tốt hơn so với 10 tấn ha-1 và 5 tấn ha-1 lần lượt là 13,01%,				
Khí nhà kính	5,58% và 37,70%, 33,00 %. Kết luận, bổ sung than sinh học trấu vào				
N_2O	đất trồng lúa có tác dụng giảm phát thải khí nhà kính. Hiệu quả giảm				
Than sinh học	phát thải khí nhà kính của nghiệm thức bổ sung than sinh học trấu 20 tấn ha-1 là tốt nhất.				
Trấu					

DOI: https://doi.org/10.34238/tnu-jst.5940

227(07): 114 - 122

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1. Introduction

CH₄ is produced when organic materials decompose in oxygen-deprived conditions, notably from fermentative digestion by ruminant livestock, from stored manure, and rice is grown under flooded conditions [1]. N₂O is generated by the microbial transformation of nitrogen in soils and manures and is often enhanced where available nitrogen (N) exceeds plant requirements, especially under wet conditions [2], [3].

Paddy field is an important source of methane (CH₄) and nitrous oxide (N₂O) [4] and contributes to 10.5% of total CH₄ emissions and 7-11% of soil N₂O emissions [5]. Methane and nitrous oxide are two important greenhouse gases playing a key role in global warming and the global warming potential of CH₄ and N₂O is 25 and 298 times greater than that of carbon dioxide of unit mass at 100 years scale [6]. The atmospheric concentration of CH₄ and N₂O is 722 ppb and 270 ppb in 1750 and 1803 ppb and 324 ppb in 2011 and maintains a 0.6% and 0.2 - 0.3% rise speed annually [5]. Therefore, formulations of appropriate strategies for the mitigation of these gases are required.

Biochar, which is a byproduct from pyrolysis of any kind of biomass, has received attention recently for its potential to mitigate climate change if we are to apply it to agricultural soil. However, the effects of biochar application on greenhouse gas emissions are difficult to be generalized because we do not fully understand the mechanisms of how biochar influences soil functions [7]. Biochar is believed to improve soil fertility and sequester carbon (C) into the soil to mitigate climate change [8]. Published results suggest that biochar may play a significant role in reducing greenhouse gas (GHG) emissions from upland agricultural soils, reducing pesticide and nutrient leaching loss, improving soil fertility, and boosting crop yield and plant growth. However, the mechanisms responsible for reduced GHG emissions in biochar-amended soils are still not clear [9]. Liu et al. [9] showed that biochar was reduced CH₄ and CO₂ emissions from paddy soils. In contrast, Knoblauch et al. [10] reported no significant changes in CH₄ production from a caloric Fluvisol amended with biochar. Another study showed that biochar amendment significantly reduced total indirect CO₂ while increasing CH₄ emissions from paddy soil [11]. To date, it appears that amounts of CH4 emissions will depend on the physical and chemical properties of the biochar, the type of the soil, the microbiological circumstances, and the water and fertilizer management [12], [13]. Considering these situations, this study was set up with the objective was to evaluate the efficiency by biochar prepared from rice husks (O. Sativa L., OM5451) to CH₄ and N₂O emissions on alternating wetting and drying paddy soil.

2. Materials and methods

2.1. Time and place of the experiment

The experiment was arranged from June to August 2021 at the net house of the Faculty of Environment and Natural Resources, Can Tho University.

2.2. Materials

Paddy soil used for the experiment was collected from a depth of 0-15 cm at Hau Giang Province, Vietnam (sand 1.51%, meat land 35.89%, clay 62.6%). Soil had following characteristics: pH ($\rm H_2O$) 5.6, total nitrogen (TN) 0.181%, total phosphate (TP) 0.097%, total kali (TK) 1.64%.

The rice husks were collected at Hau Giang province, Vietnam. Then they were pyrolysis by a furnace (VMF 165, Yamada Denki, Tokyo, Japan). First, the rice husks were loaded into the center of the furnace with crucibles, nitrogen gas was pumped into the furnace at a flow rate of 3 L min⁻¹ for 30 min to remove the air from inside of the furnace. Second, the furnace temperature was increased from room temperature to 700°C at a heating rate of 10°C min⁻¹. The temperature

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was held at the desired temperature for 2h, and then it was allowed to cool down to room temperature. Physical characteristics of rice husk biochar showed in Table 1.

Table 1. Characteristics of the biochar derived from the pyrolyzed rice husk

Yield	рН ^а	EC ^a	CECa	Moisturea	Fixed carbon ^a	VM/FCb	C/N
(%)		(µS cm ⁻¹)	(cmolc kg ⁻¹)	(wt.%db)	(wt.%db)		
35.9	9.53	92.0	23.98	3.6	43.1	0.35	106.89

a - Values are the average of triplicates.

Origin: [14]

Plastic pots (diameter 26 cm and height 22 cm) in triplicate were filled with about 5.5 kg soil. Gas samples were collected into a vacuum sealed 14 mL vial to measure CH₄ and N₂O using a gas chromatograph (Model SRI 8610C, USA). The chamber design rectangular (26 cm length x 26 cm width x 93 cm height).

All treatments received the same chemical fertilizer rate of 80 kg N (urea), 40 kg P_2O_5 , and 40 kg K_2O per ha applied in three split doses, where 20% N, 20% P₂O₅, and 50% K₂O were applied on the 12 DAS, 40% N, 40% K₂O and 50 % K₂O were applied on the 25 DAS and 40% N and 50% P₂O₅ were applied on the 40 DAS.

The water level management according to the method of alternating wetting and dry. After sowing for 4 - 5 days, maintain a water level of about 2 - 3 cm. There is a water squeeze in the middle of the crop (day 27 - 34 and 15 days before harvest).

2.3. Treatments design

The treatments were randomly assigned and 4 replicates for each treatment. Five types of treatments in triplicate were selected as (Tre1) Soil; (Tre2) Control: Soil and chemical fertilizer (AS); (Tre3) Soil and biochar (5 tons/ha) with AS; (Tre4) Soil and biochar (10 tons/ha) with AS; (Tre5) Soil and biochar (20 tons/ha) with AS. Throughout the entire crop period, gas sampling was done weekly by close chamber method at the interval of 0, 10, and 20 min in pre-evacuated vacuum vials, and then analyzed for CH₄ and N₂O using gas chromatographs.

2.4. Flux calculations

Flux calculations for each of the N_2O or CH_4 were based on the assumption that there was a linear increase in N_2O or CH_4 concentration with time in the closed chambers from sampling time 0 to 20 min. The change in N_2O or CH_4 concentrations per unit time was estimated from the slope of the line obtained by plotting for each N_2O or CH_4 concentration in the headspace of the chamber versus the sampling time. The gas fluxes (N_2O or CH_4) were calculated using the following equation given by Trinh et al. [16]:

$$F = \left(\frac{\Delta C}{\Delta t}\right) x \left(\frac{v}{A}\right) x \left(\frac{M}{V}\right) x \left(\frac{P}{P_0}\right) x \left(\frac{273}{T_{\mathrm{kelvin}}}\right)$$

Where F is the gas flux (μ g N₂O-N m⁻² h⁻¹ or mg CH₄-C m⁻² h⁻¹), Δ C is the change in the concentration of the gas of interest in the time interval Dt, v the chamber volume (L), A the soil surface area (m²), M the molecular mass of the gas of interest (i.e. N in N₂O = 28 g N mol⁻¹ and C in CH₄ = 12 g C mol⁻¹), V the molecular volume occupied by 1 mol of the gas (L mol⁻¹) at standard temperature and pressure, P the barometric pressure (mbar), P₀ the standard pressure (1013 mbar) and T the average temperature inside the chamber during the deployment time.

The cumulative CH_4 or N_2O emissions were calculated using the linear trapezoid formula Trinh et al. [15] as follows:

The cumulative flux of
$$CH_4$$
 or N_2O

$$= (t_b - t_a)x \frac{F_{ta} + F_{tb}}{2} + (t_c - t_b)x \frac{F_{tb} + F_{tc}}{2} + \dots + (t_n - t_x)x \frac{F_{tn} + F_{tx}}{2}$$

b - Volatile matter/fixed carbon ratio.

where t_a , t_b and t_c are the dates of the first, second and third sampling, t_n is the date of the last sampling and t_x is the date before the last sampling. F_{ta} , F_{tb} , F_{tc} , F_{tx} , and F_{tn} are the fluxes of the gas of interest at the t_a , t_b , t_c , t_x and t_n sampling day.

The global warming potential (GWP) was calculated according to Equation:

GWP (kg CO_{2-eq} ha⁻¹) = 25×CH₄ (kg ha⁻¹) + 298 × N₂O (kg ha⁻¹)

2.5. Data analysis

SPSS 16.0 software was used for one and two way ANOVA at the significance level $\alpha = 0.05$; Using the Duncan post-test method at 95% confidence level to test the difference between types of biochar added.

3. Results and discussions

3.1. CH₄ emissions

Application of biochar reduced CH₄ emissions from the paddy soil substantially rice husk biochar amendment (Fig. 1). The amount of biochar added to the paddy soil was closely related to the amount of CH₄ emission reduction. Chemically fertilized rice fields were higher CH₄ emissions than non-chemical fertilizers.

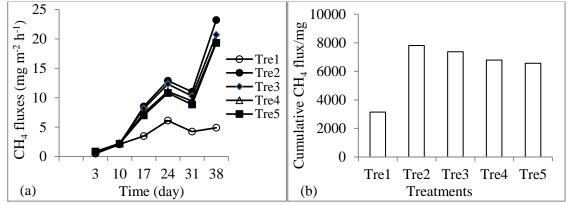


Fig. 1. (a). *CH*₄ *flux rates*; **(b).** *Cumulative CH*₄ *flux*

The results of monitoring the CH₄ emission rate of the treatments during the experiment ranged from 0.493 ± 0.058 to 23.217 ± 0.353 mg CH₄ m⁻² h⁻¹. The CH₄ emission rates of the treatments shown in Fig. 1a are divided into 3 main stages. Phase 3 - 10 DAS (day after sowing) CH₄ emission rate tends to increase slightly. At 3 DAS, the emission rates of the treatments were low ranged from 0.493 ± 0.058 to 0.826 ± 0.04 mg CH₄ m⁻² h⁻¹, at 10 DAS the CH₄ emission increased in all treatments ranged from 2.069 ± 0.97 to $2,260 \pm 0.092$ mg CH₄ m⁻² h⁻¹. CH₄ emission rate during this period did not differ statistically significantly between treatments (p > 0.05). The emission rate of the treatments was low at 3-10 DAS because the oxygen content in the soil was still high or it could be due to the low number of methanogenesis bacteria, so the ability to metabolize organic matter in low soil, so the amount of CH₄ gas was produced poorly. In the period 10 - 31 DAS, at this stage, the environment was completely anaerobic and the CH₄ emission of the treatments increased, except for the Tre2 treatment (without biochar; with chemical fertilizers) increased sharply. At the time of 17 - 31 DAS, the emission rates of the treatments (Tre1, Tre3, Tre4, Tre5) ranged from 3.484 ± 0.041 to 12.311 ± 0.04 mg CH₄ m⁻² h⁻¹, except for treatment Tre2 at the time of 17-24 DAS has a strong increase ranged from $8,523 \pm$ $0.082 - 12.895 \pm 0.078$ mg CH₄ m⁻² h⁻¹. At this stage, the roots develop to form a capillary system that promotes the emission of CH4, in addition, the water level in the experimental pots was flooded continuously and for a long time, creating anaerobic conditions in the soil, making the CH₄ emission increase compared with the previous period. But then all treatments decreased

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on day 31 DAS ranged from 4.242 ± 0.103 to 11.019 ± 0.111 mg CH₄ m⁻² h⁻¹. This can be explained because, from 27 to 34 days after sowing, this was the time to squeeze water in pots, so oxygen infiltrates into the soil, leading to limited methanogenesis of methanogenic bacteria, so the amount of CH₄ gas produced is reduced. In the period 31 - 38 DAS, the emission rate of the treatments increased sharply again, ranging from 4.242 ± 0.103 to 23.217 ± 0.353 mg CH₄ m⁻² h⁻¹. The control treatment (Tre2) had the highest emission with an emission rate of 23.217 ± 0.353 mg CH₄ m⁻² h⁻¹ which was significantly different (p ≤ 0.05) compared with the other treatments. This was the phase of the most intense emissions due to the decomposition of organic matter and the anaerobic environment. According to Dubey [16], the amount of CH₄ produced depends mainly on the organic matter content in soil and the methanogenesis bacteria decomposition. Therefore, in the condition of wetlands and the availability of readily degradable organic matter in the soil, it will be very favorable for the growth of methanogenesis bacteria, which will promote the emission of CH₄ strongly. This result is similar to the studies of Liu et al. [17], Yoo and Kang [18], Feng, et al. [19], and Qian et al. [20].

The control treatment (Tre2) has the highest total CH_4 emission which could be explained by the long-term submerged conditions and high soil organic content (with chemical fertilizers). Therefore, the anaerobic digestion processes of methanogenesis bacteria take place strongly and quickly, forming many products such as acetate, CO_2 , H_2 , promoting the production of much CH_4 in a short time [21] but this process was not hindered or the gas produced was not adsorbed, so the amount of CH_4 generated in the control treatment was the highest compared to other treatments with biochar added. As for the treatments (Tre3, Tre4, Tre5), although fertilized like control treatment (Tre2) because of the biochar, it hinders the activity of methanogenesis bacteria, thereby reducing the CH_4 emission rate or maybe the decrease of CH_4 emission is due to the "biofilter" function of CH_4 oxidizing bacteria with the presence of biochar in the anoxic rhizosphere, they reduce the amount of CH_4 that can penetrate the plant parenchyma to escape [19]. As for the treatment (Tre1) without chemical fertilizers, the CH_4 emission rate was the lowest 4.902 ± 0.02 mg CH_4 m⁻² h⁻¹, the difference was statistically significant (p ≤ 0.05) compared with other treatments.

The cumulative CH₄ emissions during the experimental period of the treatments ranged from 3145.90 - 7809.65 mg CH₄ ha⁻¹ (Fig. 1b). In which the Tre1 treatment (without biochar and without chemical fertilizers) had the lowest cumulative CH₄ emissions 3145.90 mg CH₄ ha⁻¹, the difference was statistically significant (p ≤ 0.05) compared with other treatments. The Tre2 treatment (without biochar; with chemical fertilizers) had the highest cumulative CH₄ emissions 7809.65 mg CH₄ ha⁻¹. For treatments with soil amended by biochar (Tre3, Tre4, Tre5) cumulative CH₄ emissions are lower than the control treatment (Tre2). The CH₄ emission reduction efficiency of the treatments Tre3, Tre4, Tre5 were 5.58%, 13.01%, and 15.99% respectively, as compared to the control treatment (Tre2), this result was similar to the study of some studies by Yoo and Kang [18] và Cai, et al. [22]. However, compared with other studies, the CH₄ emission reduction efficiency of this study was lower, such as Liu et al. [17] CH₄ emissions from the paddy soil amended with bamboo char and straw char at a high rate were reduced by 51.1% and 91.2% respectively, as compared to the control soil without biochar. This difference can be explained by the type of char and the amount of char of the two experiments were the difference, and especially, the difference in the experimental layout, one in the laboratory and one in the net house.

3.2. N₂O emissions

Application of biochar reduced N_2O emissions from the paddy soil substantially rice husk biochar amendment (Fig. 2). The amount of biochar added to the paddy soil was closely related to the amount of N_2O emission reduction. Chemically fertilized rice fields were higher N_2O emissions than non-chemical fertilizers. The difference was statistically significant ($p \le 0.05$).

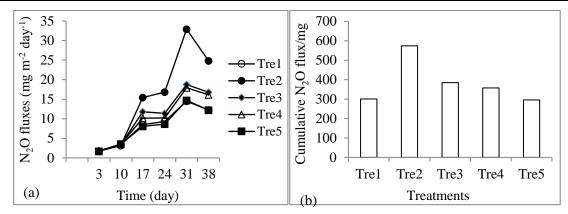


Fig. 2. (a). N2O flux rates; (b). Cumulative N2O flux

The results of monitoring the N2O emission rate of the treatments during the experiment ranged from 1.687 \pm 0.007 to 44.067 \pm 0.019 mg N₂O m⁻² day⁻¹. The N₂O emission rates of the treatments shown in Fig. 2a are divided into 3 main stages. Phase 3 - 10 DAS (day after sowing) N₂O emission rate tends to increase slightly. At 3 DAS, the emission rates of the treatments were low ranged from 1.687 ± 0.007 to 1.872 ± 0.007 mg N_2O m⁻² day⁻¹, at 10 DAS the N_2O emission increased in all treatments ranged from 3.159 ± 0.004 to 3.531 ± 0.005 mg N₂O m⁻² h⁻¹. N₂O emission rate during this period did not differ statistically significantly between treatments (p > 0.05). The emission rate of the treatments was low at 3 - 10 DAS. This may be due to the small number of nitrogen-metabolizing bacteria, so the ability to metabolize nitrogen in the soil was low, therefore the amount of N₂O gas produced was low. In the period 10 - 31 DAS, at this stage, the environment was rich in nutrients because the soil was supplemented with nitrogen fertilizers on days 12 and 25 after sowing, so the N2O emission rate of the treatments increased, except for the control treatment (Tre2) was a strong increase. At the time of 17 - 31 DAS, the emission rates of the treatments (Tre1, Tre3, Tre4, Tre5) ranged from 8.046 ± 0.006 to 18.751 ± 0.009 mg N_2O m^{-2} day⁻¹, except for control treatment (Tre2) which was a strong increase ranging from 15.444 \pm 0.013 to 32.921 ± 0.02 mg N₂O m⁻² day⁻¹ and reached the highest N₂O emission rate on day 31 DAS was 32.921 ± 0 , $02 \text{ mg N}_2\text{O m}^{-2} \text{ day}^{-1}$. This can be explained because, in the period from 27 to 34 days after sowing, this was the time to squeeze water in pots, so the amount of oxygen in the soil was a high increase, creating favorable conditions for bacteria to convert nitrogen into N₂O, therefore emission rate was a strong increase. In the period 31 - 38 DAS, the emission rate of the treatments strongly decreases at 38 DAS, ranging from $12.183 \pm 0.013 - 24.816 \pm 0.043$ mg N₂O m⁻² day⁻¹. During the experiment, the control treatment (Tre2) had the highest emission rate ranging from 32.921 ± 0.02 mg N_2O m⁻² day⁻¹, the difference was statistically significant (p \leq 0.05) compared with other treatments. According to Wang et al. [23] reported that decreased N₂O emissions were mainly resulting from the increase of soil pH caused by the addition of biochar. Biochar application could potentially inhibit the activity of reductase involved in the conversion of nitrite and nitrate to nitrous oxide [24]. Alternating wetting and drying cycles that permit nitrification to progress, and water-filled pore space above about 60%, but below saturation, contribute to the greatest potential for N₂O emissions [25]. The presence of biochar could catalyze N₂O reduction to N₂ as an end-product by acting as an electron shuttle. By increasing the pore volume and size and altering surface functional groups, activation of biochar may affect its pH-buffer capacity, specific chemical toxins, metal complexes, and precipitation products resulting from its addition to soil. All these very likely processes are not clearly understood and thus warrant further investigation [26]. This result is similar to the study of Yang et al. [5] and Qian, et al. [20].

The cumulative N_2O emissions during the experimental period of the treatments ranged from 295.72 - 573.83 mg N_2O ha⁻¹ (Fig. 2b). In which the Tre1 treatment (without biochar and without

chemical fertilizers) and Tre5 had the lowest cumulative N_2O emissions such as 300.882 mg N_2O ha⁻¹, 295.72 mg N_2O ha⁻¹, respectively, the difference was statistically significant ($p \le 0.05$) compared with other treatments. The Tre2 treatment (without biochar; with chemical fertilizers) had the highest cumulative N_2O emissions 8484.45 mg N_2O ha⁻¹. For treatments with soil amended by biochar (Tre3, Tre4, Tre5) cumulative N_2O emissions are lower than the control treatment (Tre2). The N_2O emission reduction efficiency of the treatments Tre3, Tre4, Tre5 were 33.00%, 37.70%, and 48.47% respectively, as compared to the control treatment (Tre2), this result was similar to the study of some studies by Fungo, et al. [26] biochar reduced N_2O emission by 10 - 41%. The cumulative N_2O emissions decreased by 58.0% and 43.1% following 20 and 40 t ha⁻¹ biochar amendment [5]. Biochar reduced N_2O emissions by 10 - 90% in 14 different agricultural soils [27]. Biochar application decreased cumulative N_2O (52 - 84%) emissions compared to a corresponding treatment without biochar after urea and nitrate fertilizer application [28].

3.3. Total greenhouse gas emissions (converted to CO₂ equivalent)

The results of total greenhouse gas emissions (CH₄ and N₂O) after 38 days of the experiment were calculated and converted to CO₂ equivalent (CO_{2-eq}) (Fig. 3). Total CO_{2-eq} emission in the control treatment (without biochar but with chemical fertilizers) (3831.12 kg CO₂-eq ha-1) was the highest, the difference was statistically significant ($p \le 0.05$) compared to treatments with biochar (Tre3, Tre4, Tre5) and without biochar and without chemical fertilizer (Tre1). Treatments (Tre1, Tre3, Tre4 and Tre5) had total CO_{2-eq} emissions of 1731.20 kg CO_{2-eq} ha⁻¹, 2989.10 kg CO_{2-eq} ha⁻¹, 2763.89 kg CO_{2-eq} ha⁻¹ and 2463.86 kg CO_{2-eq} ha⁻¹, respectively. Between these treatments were statistically significant ($p \le 0.05$). Treatment (Tre5) had a lower total CO_{2-eq} emission than treatments (Tre3 and Tre4) (Fig. 4). Treatment (Tre1) (without chemical fertilizers and biochar) had the lowest total emissions 1731.20 kg CO_{2-eq} ha⁻¹.

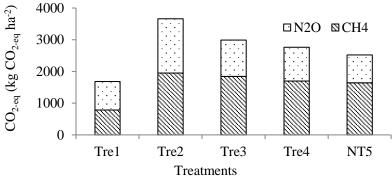


Fig. 3. Total greenhouse gas emissions (CO_{2-eq})

Experimental results showed that growing rice with chemical fertilizers contributes to an increase in greenhouse gas emissions compared with no fertilizer application. Rice husk biochar supplementation was effective in reducing total greenhouse gas emissions compared with no biochar addition to soil. The effectiveness of reducing total greenhouse gas emissions of the treatments (Tre3, Tre4, and Tre5) were 21.98%, 27.86%, and 35.69%, respectively, compared with the control treatment (Tre2). The effectiveness of reducing total greenhouse gas emissions of the treatment with 20 tons ha-1 (rice husk biochar) was highest at 35.69%.

4. Conclusions

This result showed that rice husk biochar at 20 tons ha⁻¹ reduced CH₄ and N₂O emissions were 15.99%, 48.47% better than of 10 tons ha⁻¹ and 5 tons ha⁻¹ were 13.01%, 5.58% and 37.70%, 33.00%, respectively. Growing rice with chemical fertilizers contributes to an increase in greenhouse gas emissions compared with no fertilizer application. Rice husk biochar

supplementation was effective in reducing total greenhouse gas emissions compared with no biochar addition to soil. The effectiveness of reducing total greenhouse gas emissions of the treatments (Tre3, Tre4, and Tre5) were 21.98%, 27.86%, and 35.69%, respectively, compared with the control treatment (Tre2). The effectiveness of reducing total greenhouse gas emissions of the treatment with 20 tons ha⁻¹ (rice husk biochar) was highest.

Acknowledgment

The authors would like to acknowledge Dr. Taro Ueda and Dr. Hiroshi Asakura at Nagasaki University for their technical and equipment support in the EDX measurements and proximate analysis. This study was funded in part by the E7 Project "Building capacity for Can Tho University to be an excellent institution of education, scientific research and technology transfer" of JICA.

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