Optimization of Biochar Production from Spent Activated Carbon for Anaerobic Biodegradation Enhancement

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Abstract. In this study, effects of temperatures (117-683°C) and heating rates (1.9-23.1 °C/min) on pH and specific surface area (SSA) of biochar produced from the pyrolysis of spent activated carbon (SAC) were investigated. Experiments were designed based on the Central Composite Design (CCD) technique. Results showed that the highest pH and SSA of 11.24 and 998 m^2/g were obtained under the temperature and heating rate of 683°C and 12.5 °C/min, respectively. These pH and SSA values were found to be 28% and 18% higher than those of the unprocessed SAC. The pH and SSA values achieved were found to be in the same range as those capable of increasing biogas production from different feedstocks in the literature.

1 Introduction

Since the year 2014, there has been an increasing trend towards using biochar to improve the efficiency of anaerobic digestion (AD). Biochar is a carbon-based material capable of absorbing toxins in anaerobic digestion systems [1]. It also has a porous structure that allows microorganisms to grow [2]. Previous research indicated that when the appropriate amount of biochar was utilized, the addition of biochar can help increase the efficiency of biogas production by improving system stability and enhances microorganism growth [1, 3, 4].

In Thailand, many industrial enterprises have used activated carbon in their water supply production. After exhausted, the spent activated carbon (SAC) needs to be disposed of in accordance with the Department of Industrial Works regulations, which can be a considerable financial burden for the factory. Thanks to its high specific surface area, porosity and necessary surface functionalization [5], the activated carbon has the potential to be used to increase the efficiency of the biogas production process. Regeneration of the spent activated carbon, therefore, offers an opportunity to reuse industrial waste and is in line with the Bio-Circular-Green Economic (BCG) model craved by the Thai government. Biochar produced from the spent activated carbon is expected to be superior to those produced from the raw biomass in terms of its electrical conductivity, absorbency, and specific surface area. These characteristics of biochar have been reported to improve the anaerobic digestion process by a) increasing the pH buffer capacity, b) increasing the microbial surface area, c) stimulating diet, and d) absorbing potentially toxic compounds [6].

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Biochar can be produced by thermochemical processes, namely pyrolysis, gasification, and hydrothermal carbonization [7]. All three processes have differences in temperature, hold time, and heating rate. Of all processes, pyrolysis - a heating process in the absence of oxygen [2], is considered as the most efficient ones [7]. The typical temperature for pyrolysis to produce biochar is in the range of 300–900°C which was found to affect biochar properties and yield. The specific surface area (SSA) and pH of the biochar increased as the pyrolysis temperature increased. In addition, faster heating rate and pyrolysis volatilization speed helped raise the SSA and pH of biochar [8]. Nevertheless, effects of temperature and heating rate on biochar characteristics, i.e. SSA and pH, depended on different factors, such as ranges of temperature and heating rate and biomass characteristics. Ahmad et al., reported that biochar produced from peanut shells at temperatures of 300 and 700°C had pH of 7.8 and 10.6 and a SSA of 3.1 m^2/g and 448.2 m^2/g, respectively [9]. However, under similar temperatures, the SSAs obtained from poultry litter (3.9 m^2/g and 50.9 m^2/g at 350 and 700°C, respectively) were much lesser, especially at the higher temperature, while pHs were in the same range (pH = 8.7 and 10.3 at 350 and 700°C, respectively) as those reported by Cantrell et al. [10]. As SSA and pH have been reported to be among the most significant factors facilitating anaerobic digestion, it is, therefore, essential to determine the suitable temperature and heating rate specifically for each biomass so that the maximum SSA and pH can be obtained.

This work aimed to determine the suitable temperature and heating rate for biochar production from the spent activated carbon. The biochar was prepared under pyrolysis conditions at temperatures and heating rates of 117-683°C and 1.9-23.1 °C/min. Experiments were designed using the Central Composite Design (CCD) with SSA and pH as the response. Characteristics of produced biochar were also compared to those used for anaerobic digestion enhancement in the literature.

2 Materials and methods

2.1 Biochar preparation

Samples of SAC were obtained from a beverage factory in Lampang, Thailand. To prepare biochar, SAC was placed in a crucible and pyrolyzed in a furnace at the temperature and heating rate determined by Response Surface Methodology (RSM) and Central Composite Design (CCD) (Table 1). To ensure complete oxygen elimination, nitrogen gas at the flow rate of 150 mL/min was injected into the furnace chamber throughout the process. The temperature was raised at the desired heating rate until reaching the pre-determined level and held at that temperature for 2 h before cooling. The prepared biochar samples were, then, homogenized and sieved before characterization. The biochar samples with sizes of <1.70-0.60 mm were taken to measure pH, while those with sizes of <0.15 mm were used to determine the SSA.

2.2 Experimental design

Experiments were designed based on the CCD technique using Minitab 21 software. Levels of temperature and heating rate studied are presented in Table 1. The pH and SSA were used as the response of the experiment. Experiments at each condition were done in duplicate, while those at center points (Level 0 in Table 1) were conducted in three replications. In total, there were 22 experiments conducted in this study. In addition, pH and SSA of the unprocessed SAC were measured in duplicate and referred to as the control sample.

2.3 Analytical methods

The pH of biochar was measured using a pH meter (F-71(LAQUA), HORIBA Advanced Techno Co., Ltd., Kyoto, Japan) at a biochar to deionized water ratio of 1:10 (*w/v*). Before measuring the pH, the biochar sample was mixed and stirred for 5 minutes [11]. The Brunauer-Emmett-Teller (BET) (Autosorb 1 MP, Anton Paar QuantaTec Inc., Florida, USA) method with nitrogen gas was applied to identify the SSA.

Table 1. Factors and factor levels designed by the CCD experiment.

Factors	Units	Level				
		$-\alpha$	-1	0	+1	$+\alpha$
Temperature	°C	117	200	400	600	683
Heating rate	°C/min	1.9	5	12.5	20	23.1

3 Results and Discussion

Effects of temperatures and heating rates on biochar characteristics, i.e. pH and SSA, using SAC as a feedstock can be described as follows:

3.1 pH

When pyrolysis was performed at temperatures ranging from 117 to 400°C, pH was found to be in the range of 7.78–9.48 (Fig. 1a). At temperatures higher than 600°C, pH was greater than 10. The highest pH (11.24) was 28% higher than that of the control sample and obtained under the temperature and heating rate of 683°C and 12.5 °C /min. It was found that pH of the biochar produced from SAC increased significantly with the increase of temperature (*p* = 0.000). While pH of biochar was found to be increased with the increase of temperatures, maximum pH was detected at the heating rate of 12.5 °C /min, which was in the middle of the studied range. At the temperature ≥ 683°C, the highest level of pH could be attained when the heating rate was ≥10°C /min (Fig. 1a). From the multiple regression analysis of the experimental data (Table 2), pH of the biochar could be predicted using Equation (1), which combined all significant independent variables in terms of uncoded (real) values.

Table 2. Regression analysis of pH from biochar production from SAC.

Term	Standard error coefficient	*T*-value	*p*-value*
Constant	0.064	144.16	0.000
A-Temperature	0.039	29.93	0.000
B-Heating rate	0.039	5.71	0.000
A^2	0.047	3.54	0.003
B^2	0.047	-0.94	0.361
AB	0.055	1.04	0.315
R-squared = 98.34% Adjust *R-squared* = 97.82%			

**p*-values are presented as the rounded number to three decimal places.

$$pH = 7.152 - 0.002297Temperature + 0.02971Heating\ rate + 0.000004(Temperature)^2 \quad (1)$$

where pH = pH of biochar, Temperature = pyrolysis temperature, °C and Heating rate = pyrolysis heating rate, °C/min.

The alkalinity and pH of biochar increased linearly as the pyrolysis temperature was raised [1]. Biochar alkalinity is caused by the conversion of carbon dioxide (CO_2) to bicarbonate (HCO_3^-) or carbonate (CO_3^{2-}). At high alkalinity level, pH of the biochar is increased [12]. Increase of biochar's pHs at higher temperatures found in this current study was in line with those reported in previous works using different types of raw materials. Kończak et al. [13] reported that biochar production from sewage sludge at temperature of 500, 600 and 700°C with heating rate 10 °C/min had pH of 9.4, 12.1 and 12.4 and a SSA of 69.7 m^2/g, 75.5 m^2/g and 89.2 m^2/g, respectively. Likewise, Liu et al. [14] reported that biochar from branch of pecan tree had pH of 6.1 and 10.2 under pyrolysis temperatures of 300 and 600°C, respectively. While the structural alkalinities of biochar were reported to be influenced by the heating rate; the faster heating rate, the higher alkalinities [15], the highest pH of biochar from SAC was detected at the middle point (12.5 °C/min) of studied heating rate range (1.9-23.1 °C/min). It was possible that, under pyrolysis conditions, conversion of CO_2 to HCO_3^- or CO_3^{2-} for SAC was already completed at the heating rate of 12.5 °C/min. Similar results were found when heating rates from 10-50 °C/min did not have a significant effect on pH for the pyrolysis of safflower seed press cake [16]. It needs to be mentioned, however, that prediction of biochar alkalinity using only pyrolysis parameters might not be straightforward as biochar alkalinity could arise from complex interactions during production [17]. Level of pH achieved from SAC in this current studied was within the range found to enhance AD. Wei et al. reported increase of cumulative methane production (by 8.6–17.8%) from the primary sludge with the addition of biochar (produced from the pyrolysis of corn stover at 600°C) having pH of 10.1 ± 0.4. It was reported that the pH of the biochar-added reactor was 8.1–8.7, which was higher than that of the non-biochar added one (pH = 7.3) [4]. The addition of biochar significantly helped to reduce the methane production lag time and enhance methane production rate with increasing organic load [18].

3.2 Specific surface area

The range of SSA obtained was between 790-998 m^2/g (Fig. 1b). The highest SSA (998 m^2/g) was derived under a temperature and heating rate of 683°C and 12.5 °C/min. This SSA was found to be 18% higher than that of the control sample. While SSA was found to be increased significantly with increased temperature ($p = 0.004$), the heating rate did not significantly affect SSA ($p = 0.470$). From the multiple regression analysis of the experimental data (Table 3), SSA of the biochar could be calculated using Equation (2).

Table 3. Regression analysis of SSA from biochar production from SAC.

Term	Standard error coefficient	*T*-value	*p*-value*
Constant	16.0	52.81	0.000
A-Temperature	9.81	3.33	0.004
B-Heating rate	9.81	0.74	0.470
A^2	11.7	2.87	0.011
B^2	11.7	-0.13	0.895
AB	13.9	-0.11	0.911
R-squared = 56.71%			
Adjust *R-squared* = 43.18%			

*****p-values are presented as the rounded number to three decimal places.

$$\begin{aligned} SSA &= 893.6 - 0.495 Temperature + 2.08 Heating\ rate + 0.000840(Temperature)^2 \\ &- 0.028(Heating\ rate)^2 - 0.00105(Temperature)(Heating\ rate) \end{aligned} \quad (2)$$

where SSA = Specific surface area, m^2/g and Temperature = pyrolysis temperature, °C

It needs to be stated that to increase the R^2 level of the model, all terms needed to be included in Equation (2). Unlike that of pH, accuracy of the model for SSA prediction did not as high. This variation was partly contributed by higher degree of deviation of SSA obtained from the duplicated samples. The degradation of organic matter and the formation of micropores caused an increase in SSA and porosity when the pyrolysis temperature was increased [8]. Higher pyrolysis temperatures enhanced the formation of micropores by reducing volatile matter, which increased pore volume and SSA [14]. Chatterjee et al. [19] reported that biochar feedstock and pyrolysis temperature had significant effects on surface area when biochar obtained from corn stover at temperature of 500 and 600 °C had SSAs of 96 m^2/g and 284 m^2/g, respectively. On the other hand, the heating rate had a significant effect on the biochar produced from fast pyrolysis (Temperature at 600-1,000°C, heating rate 10-1,000 °C/min and hold time 0.5-5 s.) [20]. However, low heating rates (5-20 °C/min) resulted in slow volatile matter release, which caused a higher volatile matter composition in biochar [21]. At high heating rates (> 1000 °C/min), biochar had lower surface area due to fast depolymerization at the surface of biochar produced from banana pseudo-stem at 500°C from slow pyrolysis and fast pyrolysis (SSA = 1.078 m^2/g and 0.638 m^2/g, respectively) [21]. Insignificant effects of the heating rate on SSA found in this current study could partly be the result of low heating rates utilized.

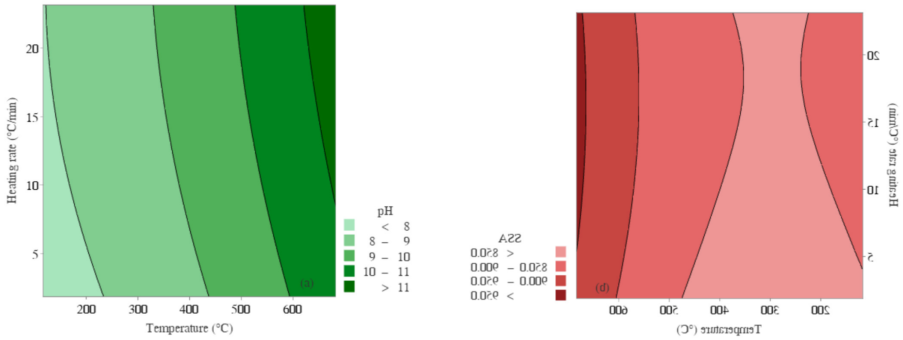

Fig. 1. Contour Plot of pH (a) and SSA (b) versus temperature and heating rate.

3.3 Comparisons of biochar characteristics for AD improvement

Enhancement of AD by biochar addition has been reported in previous studies (Table 4). Compared to those achieved from different types of biomass used as the raw material for biochar production, maximum pH and SSA of biochar produced from SAC in this current study were noticeably more superior. As both pH and SSA are among the most important characteristics for AD enhancement, biochar produced from SAC could be expected to have positive effects on AD performance. Considering that the temperature and heating rate required for SAC were in the similar ranges as those used for other types of biomass, SAC could be regarded as the high potential raw material for producing biochar needed for AD facilitation.

Table 4. Application of biochar for AD system.

Biomass	Pyrolysis Temperature (°C)	Heating rate (°C/min)	pH	Specific surface area (m^2/g)	Biochar dosage	Substrate	AD performance	Ref.
Corn stover	600	-	10.1	302.6	1.82 g/g TS	Sewage sludge	- Methane production increased 8.6-17.8%	[4]
Sycamore sawdust	550	10	9.5	276.67	4% of TS	Waste water and swine manure	- Maximum methane production was 217.99 mg/g VS	[22]
Cow manure	500	1.7	8.5	112.6	10 g/L	Beer lees	- Maximum methane production 456.8 mg/g VS - Short lag time	[23]
Fruit wood	550	-	9.8	211	5%TSS	Dry chicken manure	- Increase of 12% methane production	[24]

Cotton wood	700	-	10.1	13.97	8 g/L	Corn-stalk	- Microbial abundance had increase	[25]
Cattle manure	550	-	10.4	3.28	5%	Rape straw	- Biogas yield and average methane content increased obviously	[26]
Spent Activated Carbon	683	12.5	11.2	998	-	-	-	This study

4 Conclusion

Biochar preparation from the pyrolysis of SAC was investigated in this study. The maximum pH (11.24) and SSA (998 m^2/g) of biochar were achieved at high temperatures (683°C) and a moderate heating rate (12.5 °C/min). Temperature was found to significantly affect pH and SSA whereas effects of increased heating rate on pH was less pronounced and even not significantly detected for SSA. Characteristics of produced biochar from SAC were expected to enhance AD performance, which is the main focus of further studies.

References

1. W. Zhao, H. Yang, S. He, Q. Zhao, L. Wei, Bioresour Technol, A review of biochar in anaerobic digestion to improve biogas production: Performances, mechanisms and economic assessments, **341**, 125797, (2021)
2. Z. B. Khalid, M. N. I. Siddique, A. Nayeem, T. M. Adyel, S. B. Ismail, M. Z. Ibrahim, J Environ Chem Eng, Biochar application as sustainable precursors for enhanced anaerobic digestion: A systematic review (4), **9**, (2021)
3. M. Indren, C. H. Birzer, S. P. Kidd, T. Hall, P. R. Medwell, Biomass Bioenergy, Effect of wood biochar dosage and re-use on high-solids anaerobic digestion of chicken litter, **144**, (2021)
4. W. Wei, W. Guo, H. H. Ngo, G. Mannina, D. Wang, X. Chen, et al., Bioresour Technol, Enhanced high-quality biomethane production from anaerobic digestion of primary sludge by corn stover biochar, **306**, 123159, (2020)
5. O. S. Nille, A. S. Patil, R. D. Waghmare, V. M. Naik, D. B. Gunjal, G. B. Kolekar, et al. *Chapter 11 - Valorization of tea waste for multifaceted applications: a step toward green and sustainable development*. In: Bhat R, Valorization of Agri-Food Wastes and By-Products, Academic Press, 2021, 219-236, (2021)
6. D. Kalantzis, I. Daskaloudis, T. Lacoere, A. S. Stasinakis, D. F. Lekkas, J. De Vrieze, et al., Bioresour Technol, Granular activated carbon stimulates biogas production in pilot-scale anaerobic digester treating agro-industrial wastewater, **376**, 128908, (2023)

7. P. R. Yaashikaa, P. S. Kumar, S. Varjani, A. Saravanan, Biotechnol Rep, A critical review on the biochar production techniques, characterization, stability and applications for circular bioeconomy, **28**, e00570, (2020)
8. A. Tomczyk, Z. Sokołowska, P. Boguta, Rev Environ Sci Bio/Technol, Biochar physicochemical properties: pyrolysis temperature and feedstock kind effects (1), **19**, 191-215, (2020)
9. M. Ahmad, S. S. Lee, X. Dou, D. Mohan, J.-K. Sung, J. E. Yang, et al., Bioresour Technol, Effects of pyrolysis temperature on soybean stover- and peanut shell-derived biochar properties and TCE adsorption in water, **118**, 536-544, (2012)
10. K. B. Cantrell, P. G. Hunt, M. Uchimiya, J. M. Novak, K. S. Ro, Bioresour Technol, Impact of pyrolysis temperature and manure source on physicochemical characteristics of biochar, **107**, 419-428, (2012)
11. H. Liu, X. Wang, Y. Fang, W. Lai, S. Xu, E. Lichtfouse, Renewable Energy, Enhancing thermophilic anaerobic co-digestion of sewage sludge and food waste with biogas residue biochar, **188**, 465-475, (2022)
12. A. R. Salehiyoun, H. Zilouei, M. Safari, F. Di Maria, S. H. Samadi, O. Norouzi, Renewable Energy, An investigation for improving dry anaerobic digestion of municipal solid wastes by adding biochar derived from gasification of wood pellets, **186**, 1-9, (2022)
13. M. Kończak, P. Oleszczuk, K. Różyło, J CO2 Util, Application of different carrying gases and ratio between sewage sludge and willow for engineered (smart) biochar production, **29**, 20-28, (2019)
14. Z. Liu, M. Jia, Q. Li, S. Lu, D. Zhou, L. Feng, et al., Ind Crops Prod, Comparative analysis of the properties of biochars produced from different pecan feedstocks and pyrolysis temperatures, **197**, 116638, (2023)
15. C. Nzediegwu, M. Arshad, A. Ulah, M. A. Naeth, S. X. Chang, Bioresour Technol, Fuel, thermal and surface properties of microwave-pyrolyzed biochars depend on feedstock type and pyrolysis temperature, **320**, 124282, (2021)
16. D. Angın, Bioresour Technol, Effect of pyrolysis temperature and heating rate on biochar obtained from pyrolysis of safflower seed press cake, **128**, 593-597, (2013)
17. R. B. Fidel, D. A. Laird, M. L. Thompson, M. Lawrinenko, Chemosphere, Characterization and quantification of biochar alkalinity, **167**, 367-373, (2017)
18. J.-T. He, N. Yao, Z.-Y. Sun, F. Li, H.-Q. Cai, L.-F. Jin, et al., Ind Crops Prod, Improved biogas production from tobacco processing waste via biochar- assisted thermophilic anaerobic digestion, **202**, 117038, (2023)
19. R. Chatterjee, B. Sajjadi, W.-Y. Chen, D. L. Mattern, N. Hammer, V. Raman, et al., Front Energy Res, Effect of Pyrolysis Temperature on PhysicoChemical Properties and Acoustic-Based Amination of Biochar for Efficient CO2 Adsorption, **8**, (2020)
20. H. Tan, C. T. Lee, P. Y. Ong, K. Y. Wong, C. P. C. Bong, C. Li, et al., IOP Conference Series: Materials Science and Engineering, A Review On The Comparison Between Slow Pyrolysis And Fast Pyrolysis On The Quality Of Lignocellulosic And Lignin-Based Biochar (1), **1051**, 012075, (2021)

21. N. Abdullah, R. Mohd Taib, N. S. Mohamad Aziz, M. R. Omar, N. Md Disa, Heliyon, Banana pseudo-stem biochar derived from slow and fast pyrolysis process (1), **9**, e12940, (2023)
22. B. Jiang, Y. Lin, Y. Lun, Z. Xu, Int J Environ Sci Technol, Optimization of methane production in a swine manure–rice straw anaerobic co-digestion process with sycamore sawdust biochar application (8), **18**, 2197-2208, (2020)
23. C. Sun, F. Liu, Z. Song, J. Wang, Y. Li, Y. Pan, et al., Bioresour Technol, Feasibility of dry anaerobic digestion of beer lees for methane production and biochar enhanced performance at mesophilic and thermophilic temperature, **276**, 65-73, (2019)
24. J. Ma, J. Pan, L. Qiu, Q. Wang, Z. Zhang, Bioresour Technol, Biochar triggering multipath methanogenesis and subdued propionic acid accumulation during semi-continuous anaerobic digestion, **293**, 122026, (2019)
25. R. Shen, Y. Jing, J. Feng, L. Zhao, Z. Yao, J. Yu, et al., Bioresour Technol, Simultaneous carbon dioxide reduction and enhancement of methane production in biogas via anaerobic digestion of cornstalk in continuous stirred-tank reactors: The influences of biochar, environmental parameters, and microorganisms, **319**, 124146, (2021)
26. Y. Xin, W. Liu, C. Chen, D. Wang, BioResources, Effect of biochar on methane production and structural characteristics in the anaerobic digestion (AD) of rape straw (4), **17**, 5632-5644, (2022)