

**Corn Stover Biochar Enhances Anaerobic Digestion of Primary Sludge for
Producing High-Quality Biomethane**

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Abstract

Previous work has demonstrated that biochar was effective in enhancing anaerobic methane production from waste activated sludge (WAS). In wastewater treatment plants (WWTPs), primary sludge (PS) as the other major sludge stream is generally mixed with WAS and digested simultaneously in the anaerobic digester. However, the effects of biochar on the performance of PS anaerobic digestion have never been documented. This study conducted batch and continuous anaerobic digestion tests to reveal whether PS and WAS could be jointly anaerobically digested with corn stover biochar addition in WWTPs. Dosing biochar (1.82, 2.55 and 3.06 g/g TS) in PS digester improved the high-quality of methane generated with content increasing from 67.5% to 81.3-87.3% and enhanced methane production by 8.6-17.8%. Model-based analysis indicated that biochar addition accelerated the PS hydrolysis and methane production and enhanced methane potential of PS. The mechanistic studies showed that biochar enhanced process stability provided by strong buffering capacity and alleviated NH_3 inhibition. In addition, biochar increased the electrical conductance of the sludge, which probably facilitated direct interspecies electron transfer between syntrophic partners. In continuous test over 116 days, the VS destruction in the biochar-dosed digester increased by 14.9%, resulting in a 14% reduction in the volume of digested sludge for final disposal. This work suggests that biochar technology should be implemented on the mixture of WAS and PS to maximize the energy recovery and sludge reduction from the two sludge streams.

Keywords: Biochar; primary sludge; anaerobic digestion; methane; volatile solids destruction

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47 **1. Introduction**

48 Wastewater carries a lot of chemical energy, which is partly consumed by municipal and
49 industrial wastewater treatment plants (WWTPs). In Australia, the energy in wastewater
50 is equivalent to ~150 kWh/PE/year, but only 1/6 the amount of energy is consumed via
51 WWTPs (Lazarova et al., 2012). Excess sludge is substantially generated in WWTPs.
52 This means that a substantial amount of energy is transferred into the sludge. The average
53 sludge production in global reaches to 20-40 kg/PE/year (PE: population equivalent) (Xie
54 et al., 2016). The transfer and disposal of sludge is costly (e.g., \$30-150 per wet ton in
55 Australia), representing 40-60% of the total operating expenses of a WWTP (Low et al.,
56 2000; Semblante et al., 2014). In order to ensure WWTPs' continuous and regular task,
57 therefore, the effective technique for energy recover and sludge reduction is extremely
58 vital and urgent.

59

60 Anaerobic digestion is a common sludge treatment method adopted by global WWTPs,
61 producing biogas from sludge to recover energy, thereby achieving sludge reduction
62 (Appels et al., 2011; Yin et al., 2018). Biogas is a renewable energy source with great
63 potential to generate heat and power. However, the energy recovery via anaerobic
64 digestion is typically only 5-7% of the energy available in the wastewater due to the slow
65 hydrolysis rate and poor biochemical methane potential of sludge (Appels et al., 2008;
66 Wang et al., 2013). To maximize energy recovery and sludge reduction, various sludge
67 treatment technologies like physical (Muller et al., 2003), chemical (Doğan and Sanin,
68 2003; Wang et al., 2014) and biological methods (Ge et al., 2010; Roman et al., 2006;

Song et al., 2004) have been proposed. Biogas generated from sludge anaerobic digestion based on these treatment technologies typically includes CH₄ with 50-70%, CO₂ with 30-50% and other gas (e.g., H₂S) with trace amounts. However, Onsite utilization of biogas for heat and power generation requires high quality methane with the content more than 96% (Petersson and Wellinger, 2009). The biogas upgrading and cleanup process for the removal of CO₂ and other gas impurities is costly, results in the limiting use of biogas from anaerobic digestion (Shen et al., 2015a).

Biochar is a solid carbonaceous residue, derived from thermochemical processing of carbon-rich biomass under oxygen limited conditions (Ni et al., 2019). It has been proven to be effective in increasing the methane production rate by 15-86% and enhancing the methane production by 10-13% in anaerobic digestion of solid waste (Fagbohunge et al., 2016; Luo et al., 2015; Shen et al., 2016; Sunyoto et al., 2016). The performance depended on the biochar characteristics. Recent studies using batch and continuous tests in Shen et al. 2015b and 2017 demonstrated that corn stover biochar increased methane production from waste activated sludge (WAS), suggesting that corn stover biochar would enhance WAS reduction (i.e., volatile solids (VS) destruction) during anaerobic digestion. Moreover, corn stover biochar could produce high-quality methane from WAS via in-situ CO₂ removal. However, the existing WWTPs typically produce two sludge streams, primary sludge (PS) and WAS, which are commonly mixed and fed in the anaerobic digester. The PS are rich in fatty acids, while WAS mainly contain biomass and extracellular polymeric substances (Carrère et al., 2010; Foladori et al., 2010). It was found that the different sludge properties have significant impact on the efficiency of

treatment techniques. For example, although the pre-treatment technology with free nitrous acid (FNA) (1.0-2.0 mg $\text{HNO}_2\text{-N/L}$, 24 h) was effective in enhancing methane production from WAS by 20-50% (Wang et al., 2013; Wei et al., 2018; Zhang et al., 2015), it decreased methane production from PS under the same pre-treatment and digestion conditions. This indicated that FNA approach should be solely employed to pretreat WAS for enhancing the methane production instead of the two sludge streams. On the contrary, the feasibility studies showed that zero valent iron (ZVI) addition method had the capacity in enhancing methane production from both WAS and PS (Feng et al., 2014; Wei et al., 2018), suggesting that ZVI could be dosed in the anaerobic digester with the mixture of WAS and PS to maximize methane production. Therefore, what happened to PS anaerobic digestion with biochar addition needs to be explored, which will determine whether biochar could be dosed in the anaerobic digester with the mixture of WAS and PS to enhance the performance of anaerobic digestion in WWTPs.

This study evaluated the feasibility of enhancing VS destruction of PS and improving methane content by biochar-dosed technology for the first time. By using batch biochemical methane potential (BMP) tests, the effectiveness of biochar addition was investigated in terms of methane content and production. The mechanisms of biochar were explored based on the model analysis and the change of sludge characteristics before and after anaerobic digestion. Finally, continuous anaerobic digesters were operated to assess the effect of biochar on VS destruction of PS.

2. Materials and methods

2.1. Sludge and biochar preparation

The PS used in this study was collected from the primary sedimentation tank of a local WWTP. The anaerobically digested sludge (ADS) used as the inoculum was harvested from the thermophilic anaerobic digester in the same WWTP. This digester receiving the mixture of PS and WAS was operated with a sludge retention time (SRT) of 15 d at 55 ± 1 °C. The main characteristics of PS and ADS were listed in SI Table S1. The corn stover biochar was prepared according to the method described in Shen et al. 2015b. Briefly, the corn stover was crushed to a particle size of < 2.3 mm in diameter and then pyrolyzed with nitrogen at approximately 600 °C for 2 h in kilns. The biochar produced was cooled, weighed and stored in a desiccator for later use. The Table 1 presented the properties of the produced corn stover biochar, which were similar with the biochar used in Shen et al. 2015b. All biochar used in this study refer to the corn stover biochar.

(Approximate position for Table 1)

2.2. Biochemical methane potential (BMP) experiments design

The effects of biochar addition on the anaerobic digestion of PS were performed by BMP tests, as detailed in our previous studies (Wei et al., 2019). Each serum bottle (160 mL) was fed by PS (30 mL) and ADS (70 mL) with their VS ratio of 2.0 ± 0.1 . Shen et al. 2015b have found that 1.82-3.06 g/g TS of biochar-dosed could increase both methane content and production from WAS, therefore, the corresponding levels of prepared biochar (i.e., 0, 1.82, 2.55 and 3.06 g/g TS) were dosed in the serum bottle, respectively. Each bottle was flushed with N₂, tightly sealed that maintains anaerobic condition, and

then placed in a thermophilic incubating shaker ($55 \pm 1^\circ\text{C}$) until the cumulative biogas volume remains unchanged. A blank test was carried out to eliminate interference of ADS for biogas production. The cumulative biogas production from PS anaerobic digestion was calculated by subtracting the value in the blank test. Three parallel experiments were conducted for each BMP test. The volume and content of biogas produced from each bottle during the whole BMP period were monitored for determining the methane production (recorded as $\text{mL CH}_4/\text{g VS}$). In addition, the pH value, total alkalinity (TA), ammonia nitrogen ($\text{NH}_3\text{-N}$) and conductivity of sludge via anaerobic digestion were measured according the methods in section 2.4.

2.3. Continuous anaerobic digesters setup and operation

The two continuous anaerobic digesters were operated in order to scale up anaerobic process from shake flasks digesters and provide a long-term evaluation. More importantly, continuous operation allow direct measurement of VS destruction, based on which the reduced sludge volume using biochar technology were determined.

Two identical 1.8-L stirred anaerobic reactors (working volume 1.5 L) were set up, as shown in Fig. 1. Each digester was added by ADS and PS with VS ratio of 2:1 and placed in an incubator ($55 \pm 1^\circ\text{C}$) after oxygen removal. The pH in each digester was recorded by pH meter and the biogas production rate was monitored using gas flow-meter. For the initial operation stage, the two reactors are operated under the same condition. The 100 mL of digestate was manually withdrawn from the reactor every day and 100 mL of PS was replenished, resulting in a SRT of 15 days. Until these two digesters reached the

stable and convergence performance in terms of daily methane production and VS destruction, the experimental stage was started. One digester as control group was operated as before, while the other as experimental group was fed by PS with biochar. Specially, the 1.82 g/g TS of biochar was dosed in the experimental reactor at the beginning of experimental stage. Afterwards, the 0.12 g/g TS of biochar was supplemented every day. Other operation conditions were the same as the control group. Two anaerobic reactors were continuously operated for 116 days. The VS concentrations of the PS and digestate as well as the daily methane production from each digester were regularly measured with the method described in section 2.4.

(Approximate position for Fig. 1)

2.4. Analytical methods

2.4.1. Chemical determination

The TS, VS, TCOD and SCOD were determined according to Standard Methods (APHA, 2012). The TA and NH₃-N were analyzed using Hach test kits (Hach, Loveland, CO). The volume of biogas from BMP bottle was measured using a manometer, based on the pressure increase in the headspace volume at 25°C and 1 atm. The content of biogas from BMP bottle and continuous digester was recorded by a gas chromatograph equipped with a thermal conductivity detector (GC-TCD, Lunan 6890). The product of the biogas volume and methane content is equal to the methane production. The organic contents (C, H, O and N) in biochar were determined using elemental analyzer (Carlo-Erba NA-1500). The metal elements in biochar were measured by the ICP-OES (PE Optima 5300 DV,

USA). According to the Brunauer-Emmett-Teller (BET) method, the N₂ adsorption-desorption isotherms were performed to analyze the surface area, the total pore volume and the average diameter of pores.

2.4.2. Modeling analysis

In order to investigate the kinetics and potential of methane production from PS anaerobic digestion with and without biochar addition, three parameters (i.e., the maximum methane production rate (P , mL CH₄/g VS/d), the hydrolysis rate (k , d⁻¹) and biochemical methane potential (B , mL CH₄/g VS)) were evaluated based on the experimental methane production curves.

The modified Gompertz equation as expressed in Eq. (1) was applied to fit the experimental data to estimate the maximum methane production rate (P) (Yin et al., 2018) using the software program OriginPro (version 8.0).

$$Y_t = Y_0 \times \exp \left(-\exp \left(\frac{P \times e}{Y_0} \times (\lambda - t) + 1 \right) \right) \quad (1)$$

where Y_t (mL/g VS) is the cumulative methane production at time t ; Y_0 (mL/g VS) is the maximum methane production; P (mL CH₄/g VS/d) is the maximum methane production rate; e is 2.71828 and λ (d) is the lag-phase time.

The hydrolysis rate (k) and biochemical methane potential (B) were evaluated based on the one-substrate model as expressed in Eq. (2) using a modified version of Aquasim 2.1d, as detailed in Batstone et al. 2009. Two parameters were got until the residual sum of squares between the experimental data and fitted data is minimized.

$$B_t = B \times (1 - \exp(-kt)) \quad (2)$$

2.4.3. Conductivity measurement

The conductivity of the suspended sludge from BMP bottles with and without biochar addition after anaerobic digestion was measured according the method detailed in Zhao et al. 2016. Briefly, the sludge sample was collected after centrifugation and wash with 0.1 mol/L of NaCl. Two gold electrodes were placed on the glass and separated by 0.5 mm gap, which was covered by the sludge sample. Then an electrochemical workstation generated -0.3~0.3 V voltage. The electric current generated from each voltage was recorded to obtain current-voltage curve. The conductivity (σ , S/m) of the sludge sample was calculated by Eq. (3):

$$\sigma = \frac{L}{R \times S} \quad (3)$$

where R (Ω) is the reciprocal of the slope in the current-voltage curve; L (m) is the gap width; S (m^2) is the gap cross-sectional area.

3. Results

3.1. Effects of biochar on the methane content and production from anaerobic digestion of primary sludge

The BMP tests with biochar addition (i.e., 0, 1.82, 2.55 and 3.06 g/g TS) was performed to evaluate the impacts of biochar on methane content and production from PS during anaerobic digestion.

The cumulative biogas productions from PS in all tests throughout the BMP tests period

230 were reported in Fig. 2A. The whole test were terminated on Day 41 when the cumulative
 231 biogas production stopped rising in each test. Without the biochar addition, the
 232 cumulative biogas production from PS over the entire digestion period was 321 ± 5 mL
 233 (mean \pm standard deviation). In contrast, the biochar addition inhibited the biogas
 234 production from PS and the increased biochar dosage resulted in the decreased biogas
 235 production. At the highest dosage of biochar with 3.06 g/g-TS, the cumulative biogas
 236 production was 269 ± 4 mL, representing a significant ($P = 1.39\text{E-}07$) decrease of $16.2 \pm$
 237 0.1% compared to that without biochar addition. However, the methane content (%) in
 238 each test with biochar was higher ($P = 6.31\text{E-}07$, $1.94\text{E-}07$ and $5.52\text{E-}08$) than that of no-
 239 biochar dosage (Fig. 2B). The methane content (%) with biochar addition started from
 240 above 92.1% on Day 1 and dropped gradually, while it with no-biochar dosage gradually
 241 increased from 43.9%, and thereafter reached the steady state. At the dosages of 1.82,
 242 2.55 and 3.06 g/g TS, the methane content (%) over the 41 days' BMP test period was
 243 $81.3 \pm 0.8\%$, $84.1 \pm 1.3\%$, $87.3 \pm 2.0\%$, respectively, as compared to that of no-biochar
 244 dosage ($67.5 \pm 2.6\%$). The cumulative methane production from PS showed a contrary
 245 tendency with the biogas production (Fig. 2C). The biochar addition was effective in
 246 enhancing the methane production during anaerobic digestion of PS, but the cumulative
 247 methane production decreased with the increase of biochar dosage. The maximal methane
 248 productions from PS with adding 1.82, 2.55 and 3.06 g/g TS of biochar was 397 ± 7 , 377
 249 ± 3 and 366 ± 6 mL/g VS, representing the relative increases of $17.8 \pm 0.1\%$, $11.9 \pm 0.1\%$
 250 and $8.6 \pm 0.1\%$, respectively. The above results indicated that the biochar addition
 251 decreased the biogas production during anaerobic digestion of PS, but increased the
 252 methane content and production, which was likely attributed to the CO₂ adsorption and

mineralization. As seen in Fig. 2D, the cumulative CO₂ production from PS without biochar addition throughout the test period was 98 ± 2 mL. However, biochar addition decreased CO₂ amount in biogas. The CO₂ amount in biogas over the entire digestion period decreased from 52 ± 1 mL to 39 ± 1 mL with respect to the increasing biochar dosage from 1.82 g/g TS to 2.55 g/g TS and then further significantly decreased to 29 ± 2 mL with increasing biochar dosage to 3.06 g/g TS. It revealed that the biochar-added digesters achieved CO₂ removal of 46.9-70.4%.

(Approximate position for Fig. 2)

3.2. Model based analysis

The maximum methane production rate (P), the hydrolysis rate (k) and biochemical methane potential (B) of PS in all cases were determined based on model fitting to further investigate the function of biochar.

The simulated methane production curves by the modified Gompertz model and one-substrate model were shown in SI Fig. S1, which showed that both models captured the experimental data well with high fitting degrees ($R^2 > 0.94$ in all tests). Table 2 summarized the estimated P , k and B of PS in the digesters with different biochar dosages. In general, biochar addition increased P , k and B of PS in the digesters. The P , k and B of PS in the digesters without biochar addition was 69.9 ± 2.2 mL CH₄/g VS/d, 0.31 ± 0.01 d⁻¹ and 328 ± 4 mL CH₄/g VS, respectively. The highest increase was achieved at 1.82 g/g TS biochar added, being approximately $53.8 \pm 0.1\%$ ($P = 0.001$),

64.5 \pm 0.1% ($P = 0.001$) and 13.7 \pm 0.1% ($P = 0.0004$), respectively. The decreased P , k and B were observed with biochar dosage continued to increase to 2.55 and 3.06 g/g TS. These results indicated that biochar at the studied dosages (i.e., 1.82, 2.55 and 3.06 g/g TS) was effective in speeding up methane production and improving the hydrolysis and methane potential of PS in the digester, but the biochar dosage was negatively correlated to their performance, which were in accordance with the results observed in Fig. 1C. This could result from the toxicity of biochar at the higher concentration. It was reported that the thermophilic temperature in digester could conduce to the leaching and dissolution of potassium, calcium and even heavy metals from biochar (Shen et al., 2015b), which may exert the adverse impacts on the anaerobic digestion (Chen et al., 2008).

(Approximate position for Table 2)

3.3. Sludge and digestate characteristics

The initial and final characteristics of sludge in anaerobic digester with the different biochar dosage were compared and the results were shown in Fig. 3. The initial pH (i.e., 8.1-8.7) of sludge in the digester without biochar dosed was 7.3 ± 0.2 , whereas the slightly alkaline pH in the biochar-dosed digesters was observed (see Fig. 3A). Alkaline pH condition has been demonstrated to facilitate sludge hydrolysis and increase the short-chain fatty acids (SCFAs) production (Yuan et al., 2006; Zhang et al., 2010). The model analysis results above also indicated that the greater hydrolysis of PS in the biochar-dosed digesters. After digestion, total alkalinity (TA) of all digesters increased after anaerobic digestion and all biochar-dosed digesters provide higher alkalinity ranging

from 3530 to 4680 (mg/L CaCO₃) (see Fig. 3B). This was probably because the slightly alkaline pH in the biochar-dosed digester was effective in converting CO₂ produced to carbonate/bicarbonate, which could further react with calcium content in the biochar to generate calcium carbonate. The final pH values in all biochar-dosed digesters were lower than the initial pH but still in a desired range for methanation (see Fig. 3A), which supported the alkalinity results as the high alkalinity meant the strong buffering capacity. This would contribute to prevent pH drop resulting from the organic acids produced, thereby maintaining stability for anaerobic digestion.

It is well known that the organic nitrogen-compounds in sludge are degraded via anaerobic digestion to generate ammonium (NH₄⁺-N). As seen in Fig. 3C, the ammonia nitrogen (NH₃-N) concentration in no biochar-dosed digester increased by 60.9 ± 0.1% after anaerobic digestion due to NH₃-NH₄⁺ equilibrium. Nakakubo et al. 2008 demonstrated that ammonia had the great inhibitory effect on the activities of microbes involved in sludge anaerobic digestion. The slightly alkaline pH in the biochar-dosed digester would facilitate the NH₃-NH₄⁺ equilibrium towards NH₃ formation (Wei et al. 2017), which was unfavourable for anaerobic digestion. However, the NH₃-N concentrations in biochar-dosed digesters after anaerobic digestion were lower than that in no biochar-dosed digester, which was likely attributed to the NH₃ adsorption by biochar. This suggested that biochar could mitigate ammonia inhibition, thereby enhancing the performance of anaerobic digestion. The conductivities of the sludge after anaerobic digestion in each case were determined (see Fig. 3D). Results showed that

biochar at the studied dosages drastically improved the sludge conductivity by 0.75-1.25 times, which might due to the metals (e.g., Ca) content in biochar.

(Approximate position for Fig. 3)

3.4. Overall performance of continuous anaerobic digesters with primary sludge with biochar addition

The continuous anaerobic reactors with and without biochar dosed were operated to investigate the effects of biochar on VS destruction of PS. Fig. 4 presented the VS destruction with daily methane production in the control and experimental digester during initial and the experimental stage. In the initial stage (Day 1-41), two digesters were operated without biochar dosed. On Day 25, both digesters reached stable and performances. The average VS destruction of PS in the two systems from Day 25 to Day 41 (i.e. over 1 HRT after stable) was $61.7 \pm 1.3\%$ and $60.9 \pm 0.4\%$ ($P = 0.37$). Corresponding, the similar ($P = 0.94$) daily methane productions (694 ± 17 and 695 ± 12 mL/d) in the two digesters were observed. This indicated that the two systems reached convergence performance.

(Approximate position for Fig. 4)

During the experimental stage (Day 41-116), one digester as experimental group was dosed 1.82 g/g TS of biochar. The VS destruction in the experimental group gradually exceeded that in the control group from Day 41 to Day 68 and then remained stable.

There is a similar trend in daily methane production profile. For the control group, the average VS destruction of PS from Day 68 to Day 116 was $61.7 \pm 1.0\%$. In contrast, VS destruction in the experimental group was $70.9 \pm 0.9\%$. Biochar addition significantly ($P = 0.0003$) enhanced VS destruction of PS by $14.9 \pm 0.2\%$. Aligning with VS destruction data, the daily methane production in the experimental group from Day 68 to Day 116 was $13.8 \pm 0.1\%$ higher than that in the control. Based on the VS destruction results, PS anaerobic digestion with 1.82 g/g TS of biochar added was estimated to decrease the volume of waste sludge by 14% (see SI for calculation details).

4. Discussion

This work revealed for the first time that anaerobic digestion of primary sludge (PS) by dosing corn stover biochar can combine the benefits of higher high-quality methane production and greater VS destruction to maximize energy recovery and sludge reduction, which was experimentally demonstrated by batch and continuous anaerobic digestion tests.

The biochar-addition technology applied increased the methane content in biogas from 67.5% to 81.3-87.3% and enhanced methane production from PS by 8.6-17.8%. The characterization results showed that biochar used in this study is highly porous ($0.11 \text{ cm}^3/\text{g}$) and has the large surface area ($302.6 \text{ m}^2/\text{g}$), which would favour the capture of CO_2 produced in digester. In particular, the high concentrations of alkaline earth metals (e.g., Ca, K and Mg) in biochar would promote the CO_2 removal from biogas via mineralization (Smith et al., 2014). Overall, the biochar-added digesters achieved CO_2

removal of 46.9-70.4%, which substantially reduced energy/cost intensive biogas cleanup and upgrading for obtaining high high-quality methane. Model analysis demonstrated that biochar addition accelerated PS hydrolysis and methane production and enhanced methane potential of PS, which suggested that a shorter hydraulic retention time or a smaller anaerobic digester with biochar dosed would achieve the similar methane production as that without biochar added, thereby greatly reducing the cost for sludge treatment (Ge et al., 2010). The more methane production observed in the biochar-dosed digester was mainly due to the strong buffering capacity, ammonia inhibition mitigation and the high conductivity, as shown in Fig. 3. Previous studies (Barua and Dhar, 2017; Morita et al., 2011; Summers et al., 2010) have shown that direct interspecies electron transfer (DIET) between exoelectrogenic/fermentative bacteria and electrotrophic methanogen could accelerate the methane production from organic compounds during anaerobic digestion. Liu et al. 2012 reported that activated carbon can function as an electron conduit to promote DIET between syntrophic partners. Considering the higher electrical conductivity and the faster methane production rate in the biochar-dosed digesters (Fig. 2C and Fig. 3D), the biochar will probably facilitate DIET to improve methane production. However, this warrants further investigations. In addition, biochar dosage was an important parameter for this technology. The methane production from PS decreased with the increase of biochar dosage from 1.82 g/g TS to 2.55-3.06 g/g TS. It was likely due to the increased leaching and dissolution of potassium, calcium and even heavy metals from biochar, resulting in the toxicity. The enhanced VS destruction by 14.9% in the continuous anaerobic digesters with 1.82 g/g TS biochar dosed indicated the reduced sludge volume by 14%, which translates to lower costs for sludge disposal.

390

391 More importantly, WAS is the other major sludge stream in existing WWTPs, which is
392 also generally treated by anaerobic digestion. The previous studies (Shen et al. 2015b and
393 2017) demonstrated that corn stover biochar was effective in increasing methane
394 production from WAS. Therefore, as shown in Fig. 5, this study suggested that corn
395 stover biochar could be dosed in an anaerobic digester with the mixture of WAS and PS
396 to enhance anaerobic digestion instead of separate anaerobic treatment in WWTPs,
397 remarkably reducing the treatment cost. Furthermore, sludge anaerobic digestion with
398 corn stover biochar dosed is an integrated process based on waste control by waste. Using
399 waste corn stover as raw materials, the cost of biochar production is only associated with
400 the machinery and heating, approximately \$4 per gigajoule. No additional treatment is
401 required for the biochar in the digestate, which could function as fertilizer for soil and
402 reduce the mobility and bioavailability of toxic chemicals in contaminated soil. Therefore,
403 this technology attains double effects in technology and economy.

404

405 (Approximate position for Fig. 5)

406

407 **5. Conclusions**

408 This study evaluated the feasibility of enhancing anaerobic digestion of PS by dosing
409 corn stover biochar based on batch BMP tests and continuously operated anaerobic
410 digesters. The main conclusions are as follow:

- The addition of biochar at 1.82 -3.06 g/g TS enhanced methane production from PS by 8.6-17.8% and increased the methane content in biogas from 67.5% to 81.3-87.3% with the CO₂ removal of 46.9-70.4%.
- Biochar increased the maximum methane production rate (P), the hydrolysis rate (k) and biochemical methane potential (B) of PS.
- The addition of biochar provided the strong buffering capacity, alleviated NH₃ inhibition and increased conductivity of the sludge.
- In the continuous biochar-dosed anaerobic digester, the VS destruction increased by 14.9% with the 14% reduced volume of digested sludge for final disposal.
- Biochar technology should implemented on the mixture of WAS and PS to maximize the energy recovery and sludge reduction from the two sludge streams.

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Table 1 - Main characteristics of corn stover biochar used in this study.

Analysis	Contents	Corn stover biochar
Chemical	pH	10.1 ± 0.4^d
	C ^a	55.31 ± 0.50
	H ^a	0.29 ± 0.03
	N ^a	0.52 ± 0.06
	O ^a	0.21 ± 0.03
	H/C ^b	0.063 ± 0.012
	O/C ^b	0.003 ± 0.0001
	N/C ^b	0.008 ± 0.0001
	Total Na ^c	1.2 ± 0.3
	Total K ^c	58.4 ± 1.2
	Total Si ^c	66.8 ± 1.7
	Total Ca ^c	12.2 ± 0.8
	Total Al ^c	9.1 ± 0.9
	Total Mg ^c	9.8 ± 1.2
Physical	Total Fe ^c	5.1 ± 0.6
	Total Ti ^c	0.9 ± 0.1
	Surface area (m ² /g)	302.6 ± 9.1
	Total pore volume (cm ³ /g)	0.11 ± 0.01
	Average diameter of pores (nm)	5.9 ± 0.3

579 ^a Indicate weight percentage (wt%);

580 ^b Indicate molar ratio;

581 ^c Indicate mg/g;

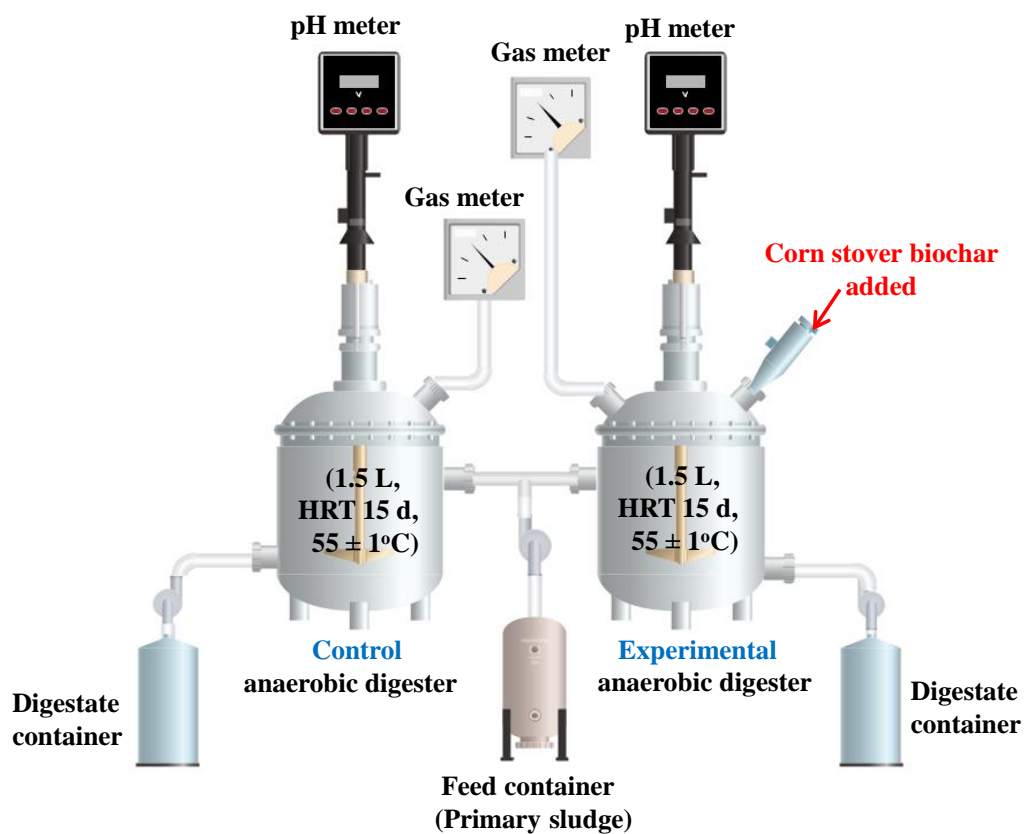
582 ^d Indicate standard deviations.

Table 2 - Estimated the maximum methane production rate (P), the hydrolysis rate (k) and biochemical methane potential (B) of PS in anaerobic digester with different biochar dosage based on model analysis.

Biochar	Parameters		
	P (mL CH ₄ /g VS/d)	k (d ⁻¹)	B (mL CH ₄ /g VS)
0 g/g TS	69.9 ± 2.2 ^a	0.31 ± 0.01	328 ± 4
1.82 g/g TS	107.5 ± 7.5	0.51 ± 0.04	373 ± 6
2.55 g/g TS	81.1 ± 1.3	0.42 ± 0.02	353 ± 5
3.06 g/g TS	78.3 ± 1.5	0.42 ± 0.03	341 ± 5

^a Indicate standard deviations.

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590 **Fig. 1** - Schematic diagram of the continuously operated bench-scale anaerobic digesters.

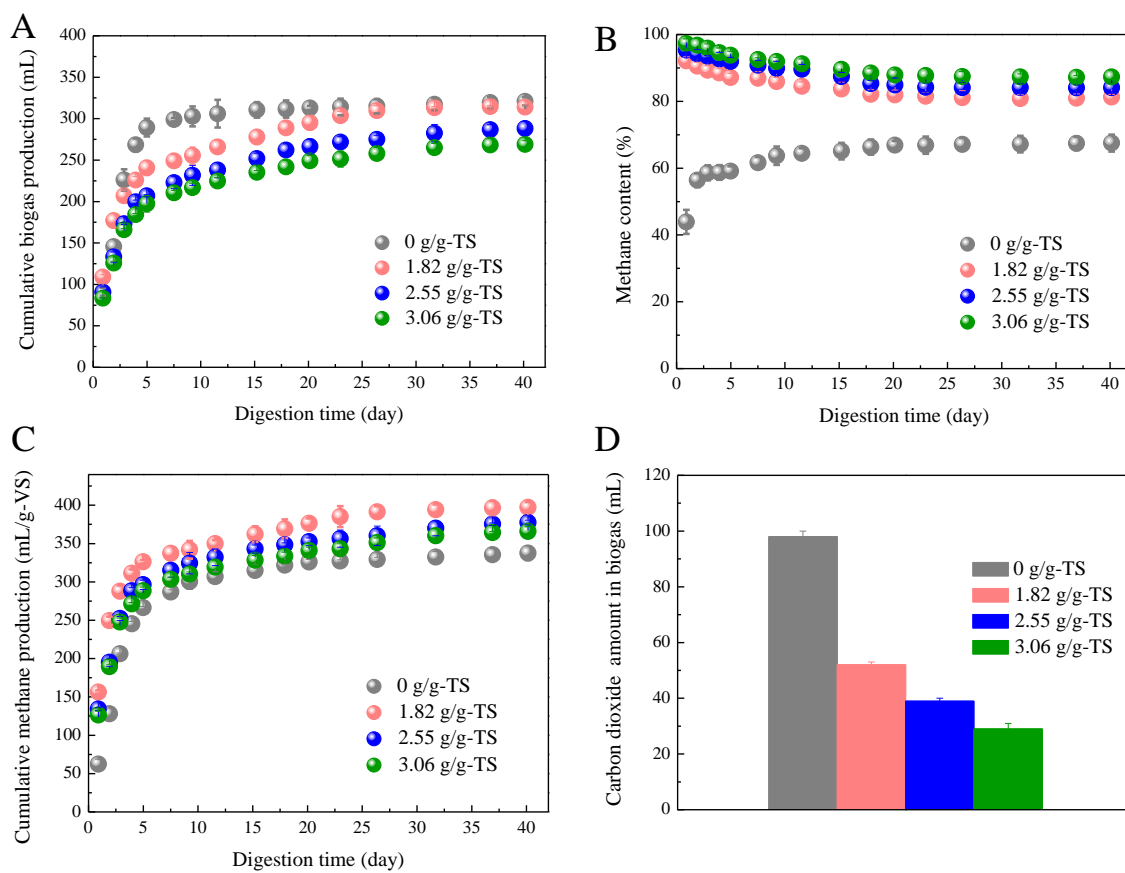


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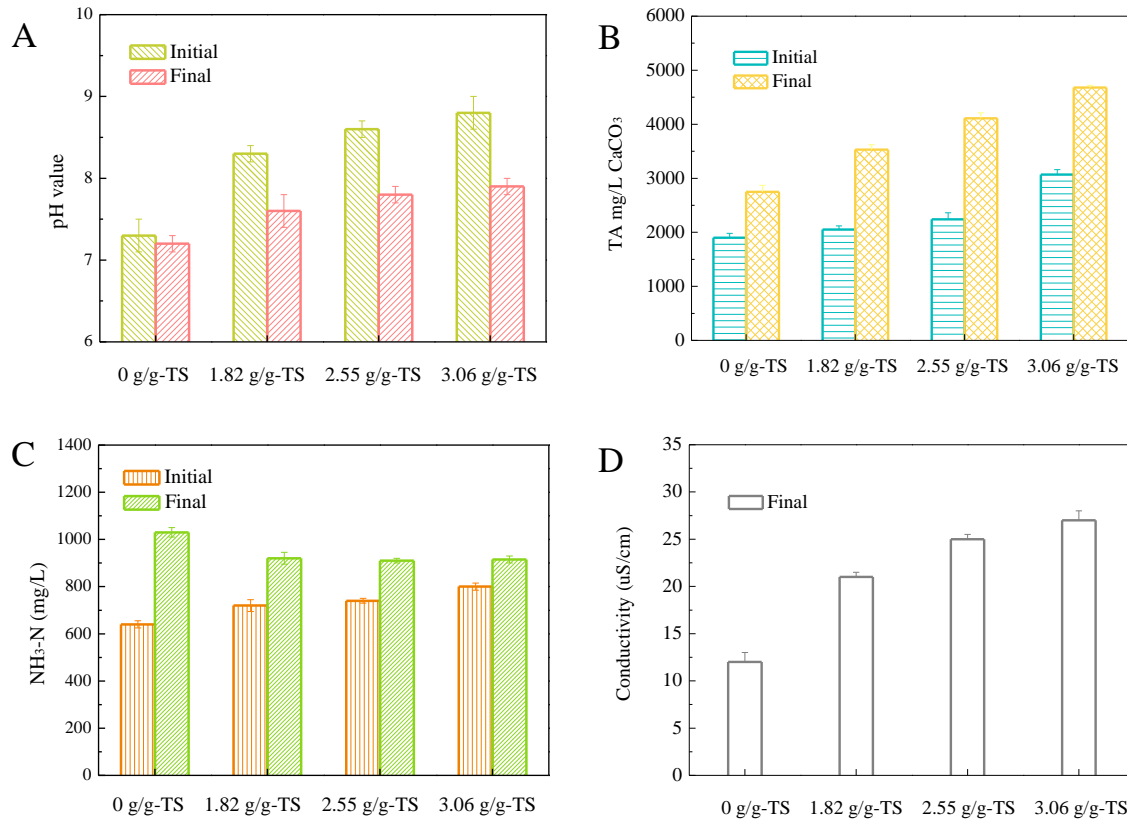


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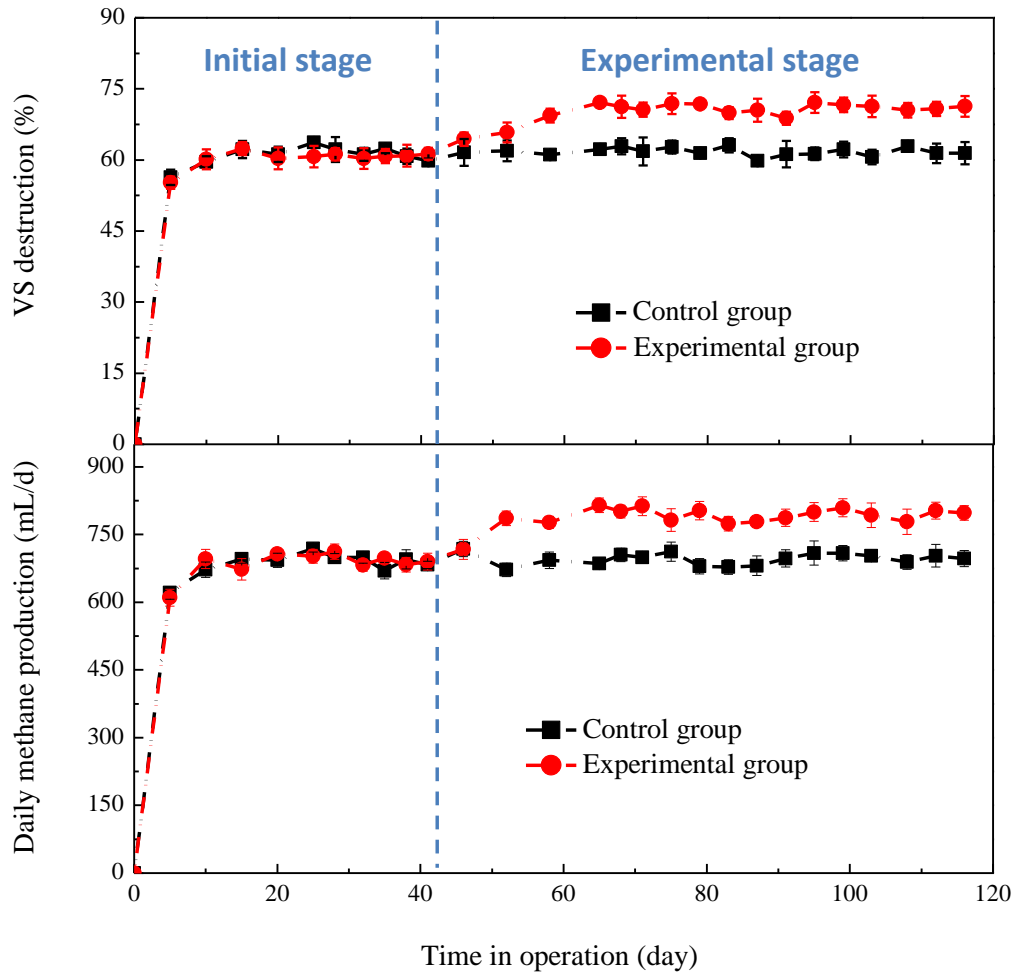


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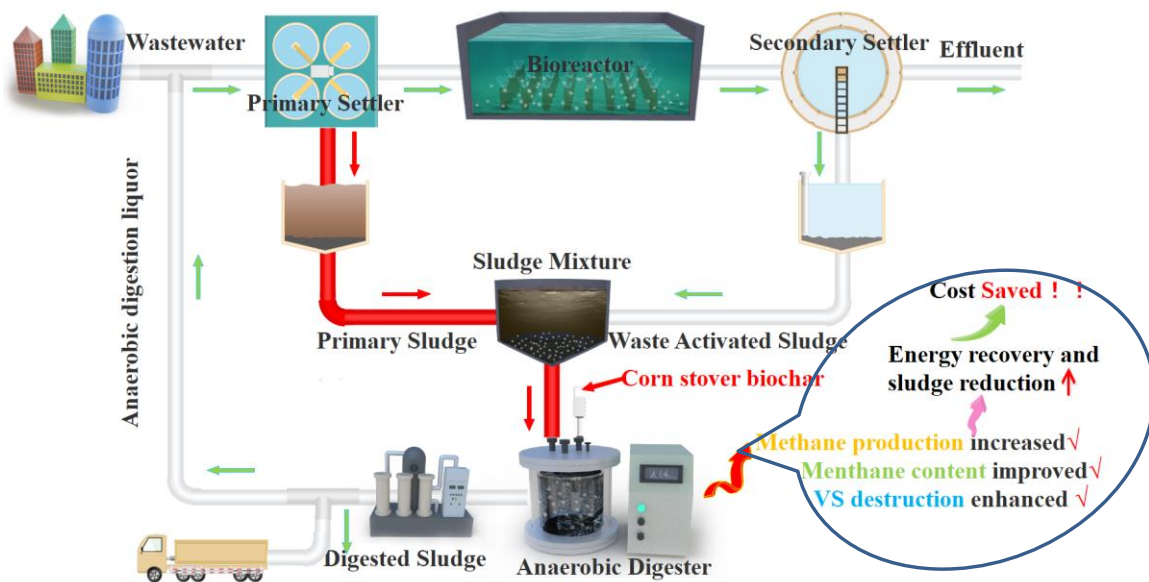


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