1 **Producing pipeline-quality biomethane via anaerobic digestion of sludge amended**
2 **with corn stover biochar with in-situ CO₂ removal**

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8

9 **Abstract**

10 This study presents a novel process for producing pipeline-quality biomethane by
11 anaerobic digestion (AD) of sludge with *in-situ* biogas cleanup and upgrading using corn
12 stover biochar. The biochar has high surface area (105 m²/g), high ash content (45.2%
13 dry weight) and high concentrations of potassium, calcium and magnesium (14.2% K₂O,
14 3.9% CaO and 4.2% MgO of the ash content, respectively). The biochar-amended
15 digesters produced near pipeline-quality biomethane (>90% CH₄ and <5 ppb H₂S),
16 facilitated CO₂ removal by up to 86.3%, boosted average CH₄ content in biogas by up to
17 42.4% compared to the control digester, close to fungibility of natural gas. The biochar
18 addition enhanced the methane yield, biomethanation rate constant and maximum
19 methane production rate by up to 7.0%, 8.1% and 27.6%, respectively. The biochar
20 addition also increased alkalinity and mitigated ammonia inhibition, providing
21 sustainable process stability for thermophilic sludge AD. The biochar-amended digestate
22 is enriched with nutrients such as potassium, nitrogen and phosphorus, and therefore has
23 great potential for soil applications.

24
25 **Keywords:**

26 Biomethane, sewage sludge, anaerobic digestion, CO₂ removal, biochar

1. Introduction

Municipal wastewater treatment plants (WWTPs) in the United States produce approximately 6.5 million metric ton (dry weight) of sewage sludge annually [1]. This generates a total energy potential of nearly 10^5 MJ (10^8 million BTU) annually [2].

Anaerobic digestion (AD) is a widespread proven technology adopted by US WWTPs for sludge stabilization and biogas production. Biogas is a renewable energy source with great potential to reduce dependence on fossil energy and decrease greenhouse gas emissions. In July 2014, the US Environmental Protection Agency (USEPA) qualified biogas from landfills and anaerobic digesters as a cellulosic transportation biofuel under the new Renewable Fuel Standards (RFS2). Biogas generates D3 Renewable Identification Number (RIN) credits for the producer. The USEPA's ruling creates market opportunity for biogas utilization at a large scale and triggers development of a sustainable and affordable process for biogas production at WWTPs. Biogas derived from sludge AD typically contains 50~70% methane (CH_4), 30~50% carbon dioxide (CO_2) and trace amounts of hydrogen sulfide (H_2S), ammonia (NH_3), siloxanes, hydrogen (H_2), nitrogen (N_2) and oxygen (O_2). Onsite utilization of biogas for combined heat and power (CHP) generation requires upgrading and cleanup (i.e. removal of CO_2 , H_2S , water and other contaminants) to achieve pipeline quality biomethane (CH_4 content >96%, heating value > 37 MJ/m³) [3]. The costly and energy-intensive biogas upgrading process is one of the technical barriers limiting use of biogas in US WWTPs [2].

Commercially available biogas upgrading technologies include water/solvent/amine absorption, pressure- or temperature-swing adsorption and membrane separation [4], while new technologies, such as metal-organic framework materials-based adsorption,

51 are emerging to increase the process energy efficiency and economic viability [5].

52 Pressure swing adsorption (PSA) (Figure 1) is a most applied technology for biogas

53 cleanup and upgrading [4]. Activated carbon is a common material used in the PSA unit.

54 Agricultural byproducts such as coconut shells have been used extensively to produce

55 activated carbon with KOH activation [6]. The resultant activated carbon products have

56 high specific surface area and hierarchical pore structure with high CO₂ adsorption

57 capacity and fast adsorption kinetics [7]. However, this process usually requires elevated

58 temperature and pressure to achieve high CO₂ selectivity and efficient CO₂ capture [8].

59 Biochar is the carbonaceous solid residue produced from thermochemical processing,

60 such as gasification and pyrolysis, of lignocellulosic biomass under oxygen-starved

61 conditions [9]. The composition and property of biochar vary considerably depending on

62 the biomass feedstock and processing conditions [10]. Corn stover-derived biochar

63 contains high ash content [10, 11] with high potassium (K) concentration mainly because

64 K-rich fertilizer is commonly applied for corn cultivation [12]. Hence using corn stover

65 biochar as an adsorbent eliminates the need for KOH activation for manufacturing of

66 activated carbon. Corn stover biochar also provides supplemental nutrients including

67 calcium, magnesium and iron for AD of sludge.

68 In nature, CO₂ is captured directly from the atmosphere by its reaction with magnesium

69 and calcium rich-silicate minerals to form carbonates as rocks weather. Typical half-lives

70 of natural weathering process are 100 - 1,000 years since the atmospheric CO₂

71 concentration is low and silicate rocks have small surface area. This reaction is mediated

72 first by CO₂ dissolution in surface waters, second by carbonate contact with the rock

73 surfaces containing calcium and magnesium, third conversion into CaCO₃/MgCO₃, and

then slow ablation of the latter [13]. High monovalent and divalent cation concentrations in biochar can stimulate accelerated carbonation reaction. Furthermore, biochar's highly porous nature provides a large surface area for CO₂ removal [8, 14]. Biochar has been also used as a potential soil amendment with the carbon capture and storage capability as well the nutrient source for plants [15]. Although biochar has been investigated as an additive to alleviate NH₃ inhibition in AD processes [16] and to enhance methane yield [17], no systematic research has been conducted on their potential capabilities to achieve *in-situ* biogas cleanup and upgrading. The objective of this study is to develop a simple and efficient *in-situ* process for biogas upgrading and cleanup. This is a novel concept in AD where both biogas production and *in-situ* removal of CO₂ and H₂S take place in the same reactor at atmospheric pressure (Figure 1) [18]. Practicality of implementing this process will significantly reduce costs for upgrading biogas to meet fuel use specifications. This process could generate improved economic benefits for WWTPs, farms and all other waste digestion industry. Moreover, the resultant nutrient rich digestate can be used locally for soil application due to its high fertilizer value, and therefore reduces the transportation and tipping cost for sludge disposal. The present study initiates a new paradigm for improving performance of AD of WWTP sludge, facilitating *in-situ* biogas cleanup and upgrading and generating nutrient-enriched digestate for soil application.

2. Material and methods

2.1 Sewage sludge and biochar

The sludge for AD experiments was provided by Woodridge Greene Valley Wastewater Facility located in Woodridge, IL. The facility operates a temperature-phased anaerobic digester system for sludge treatment, consisting of two digesters in sequence in order to separate acid and methane formation stages of the AD process. The first digester (acid phase) is operated at mesophilic temperature ($\sim 37^{\circ}\text{C}$) with hydraulic retention time (HRT) of 1.2 days, and the second (methane phase) digester is operated at thermophilic temperature ($\sim 53^{\circ}\text{C}$) with HRT of 12 days. The inoculum was obtained from the methane-phase digester, while the substrate sludge was obtained from the acid-phase digester inlet stream.

The biochar was provided by National Renewable Energy Laboratory (NREL) located in Golden, CO. It was derived from pyrolysis of corn stover using NREL's pilot-scale Thermochemical Process Development Unit [19]. Unless otherwise indicated herein, the "biochar" refers to the corn stover biochar in this study.

2.2 Anaerobic digestion experiments design

The AD experiments were conducted in 600-mL digesters at thermophilic temperature ($55^{\circ}\text{C} \pm 1^{\circ}\text{C}$) with working volume of 550 mL. Positive control (PC) and digesters amended with biochar at four different dosages (1.82, 2.55, 3.06 and 3.64 g/g TS of sludge) were investigated (Table 1). Each experimental condition was conducted in triplicate, with one digester placed in an MPA-200 Biomethane Potential Analyzer system (Challenge Technology, Springdale, AR) and two digesters placed in a New Brunswick's model I24 benchtop incubating shaker (Eppendorf, Hauppauge, NY), otherwise identical continuously stirred digesters. The MPA-200 system (Figure 2) consists of an eight-position water bath providing temperature control and agitation, an

eight-channel respirometry-based unit for gas measurement, and a computer with pre-installed software for automated data recording. Each digester in incubating shaker was attached to a multi-layer foil gas sampling bag (Restek, Bellefonte, PA) for gas collection and the volume of biogas produced was measured using a 100-mL high-performance gastight syringe (Hamilton, Reno, NV) manually on daily basis. The gas volume was adjusted to standard conditions (20 °C, 1 atm) [20]. Each digester contained inoculum (4.70 g dry matter), substrate sludge (2.35 g dry matter), biochar (depends on the experimental condition) and deionized water as the makeup water, and was sparged with helium gas (99.999% purity, Airgas, IL) for 2.5 min before AD experiments began. All the experiments were operated in batch mode and at 50 rpm agitation.

2.3 Analyses

2.3.1 Biochar characterization

Particle size distribution was determined by sieving the pre-weighed (10 g) biochar using a micro sieve set (Scienceware, Wayne, NJ), where one standard mesh screen is inserted in each segment. After sieving the biochar on an analog vortex mixer for 30 seconds, the biochar was separated by particle sizes using 8 mesh sizes (25, 35, 45, 60, 80, 120, 170 and 230). The material retained in each segment was collected and weighed to find out the size distribution of the biochar samples. Brunauer-Emmet-Teller (BET) surface area, total pore volume and pore size were determined utilizing argon or nitrogen gas adsorption analysis at 77.35 K [10].

Proximate, ultimate and ash elemental analyses were conducted in triplicate. Moisture, ash content, volatile matter and fixed carbon were analyzed using ASTM D3172-89.

Carbon, hydrogen, nitrogen and oxygen contents were analyzed using ASTM D3176-89.

Sulfur content was analyzed using ASTM D4239-08. Elements (Si, Al, Fe, Ti, P, Ca, Mg, Na, K and S) in ash were analyzed using ASTM D2795-86, ASTM D3682-01 and ASTM D5016-08. The ash was calcined at 600 °C prior to analysis. Chlorine in ash was analyzed using ASTM D2361-95.

2.3.2 Sludge characterization

Total solids (TS) and volatile solids (VS) contents were determined according to Standard Methods [21]. Chemical oxygen demand (COD), total organic carbon (TOC), total alkalinity (TA), total phosphorus (TP), total nitrogen (TN) and ammonia nitrogen (NH₃-N) were determined using Hach test kits (Hach, Loveland, CO).

Total metal (aluminum, calcium, iron, magnesium, manganese, potassium, silicon, sodium) concentrations were analyzed using USEPA Method 200.7 and 200.8.

2.3.3 Biogas sampling and analysis

Periodically 10 mL of biogas sample was withdrawn from the headspace of each digester and stored in a glass vial (Agilent Technologies, Santa Clara, CA) by using a 10-mL gastight syringe (Hamilton, Reno, NV). Each glass vial was pre-flushed with helium under standard conditions. Biogas was then analyzed for methane (CH₄) and carbon dioxide (CO₂) concentrations by using a Shimadzu GC-2014 gas chromatograph equipped with a thermal conductivity detector (TCD) and a Supelco 80/100 Porapak Q packed column (5 m × 1/8 inch × 2.1 mm) (Sigma-Aldrich, St. Louis, MO). Helium (99.999% purity, Airgas, IL) was used as the carrier gas. The column temperature was set at 100 °C isothermally and the TCD temperature was set at 170 °C. The biogas was also analyzed for hydrogen sulfide (H₂S) concentration using a gas chromatograph equipped with a sulfur chemiluminescence detector (SCD) according to ASTM D 5504-12.

3. Results and discussion

3.1 Biochar characteristics

The particle size distribution of the biochar is shown in Figure 3. Approximately 78.5 wt% of the particles are smaller than 707 μm and the majority of them fall into size range of 250-354 μm (16.12 wt%), 177-250 μm (13.30 wt%) and less than 63 μm (13.43 wt%).

The BET surface area, total pore volume and pore size are shown in Table 2. The BET surface area of the biochar (315.3 m^2/g) in this study is remarkably higher than the corn stover biochar obtained by fast pyrolysis (0.76 – 12 m^2/g) [10, 11, 22-24], slow pyrolysis (20.9 m^2/g) [10] or gasification (23.9 – 29 m^2/g) [10, 24]. According to Type I or Langmuir isotherm, the limiting uptake of adsorbate is governed by the accessible volume of micropores rather than the internal surface area [25]. BET surface area of biochar is dependent on the processing temperature and the activation procedure [26]. For example, the BET surface area of corn stover biochar could be increased to over 1000 m^2/g by CO_2 activation at 800 $^\circ\text{C}$ with continuous CO_2 purge for 2 hours [27].

Table 2 also presents the results of proximate, ultimate and ash elemental analyses of the biochar. The biochar has high ash content (45.2 wt%), as compared to wood-derived biochar (ash content < 5 wt%) at similar conversion temperature [28]. This is expected because of the high ash content in the corn stover feedstock (10.7 wt%, data not shown), which has been identified as the primary determinant of the resultant biochar [10].

Moreover, the biochar is relatively low in carbon content (52.8%). It appears that carbon content is less concentrated in the biochar derived from corn stover than from woody biomass such as oak and pine [10, 28-30], regardless of gasification or pyrolysis operative temperature. Hydrogen and oxygen concentrations of the biochar in this study

are much lower than the biochar derived from corn stover gasification as reported previously [10, 24]. The extremely low atomic H:C (0.075) and O:C ratios (0.004) reflect highly efficient aromatic condensation and dehydration during gasification [31, 32], and more importantly, they indicate superior soil stability of this corn stover biochar with respect to the longevity of captured and stored carbon [30, 33]. The biochar contains high sulfur (520 ppm), but the concentration is significantly ($p < 0.01$) lower than that in the corn stover feedstock (800 pm, data not shown). This indicates that the biochar lacks sulfur enrichment, which is possibly attributed to the high silica content [29]. Silicates bind alkali and alkaline earth metals (K, Ca and Mg) during thermochemical process, which favors release of sulfur into syngas rather than formation of sulfate in biochar [34]. The biochar ash predominantly contains silica (60.6%), which is probably due to the sand and/or soil contamination during biomass collection [10]. Surface-rich basic sites in the biochar, in particular, high K concentration (14.2 ash% K₂O) promote *in-situ* CO₂ removal in the digester. Potassium carbonate (K₂CO₃) has been widely used for CO₂ absorption in industry as a viable commercial process [35]. Additionally, various amino acids produced from sludge hydrolysis in the digester may promote potassium-mediated CO₂ absorption [36].

In summary, the biochar used in this study shows favorable characteristics for CO₂ and H₂S capture based on the highly porous structure, large surface area and the unique chemical composition.

3.2 Anaerobic digestion experiments

The AD experiments were conducted under batch operation at thermophilic temperature. Thermophilic AD has many inherent advantages over mesophilic AD, including faster

reaction rate, higher biogas production, less foaming occurrence and enhanced pathogen reduction [37]. The elevated temperature will also enhance the leaching and dissolution of the alkali and alkaline earth metals (K, Ca and Mg) from biochar [38, 39]. Furthermore, conducting AD under alkaline condition at thermophilic temperature would also improve the digestibility of sludge [40].

3.2.1 Biogas and methane production

The AD experiments were conducted for approximately 26 days. The experiments were terminated when the daily biogas production was less than 1% of the total biogas production [41]. Figure 4 shows the time course of cumulative biogas production, methane content of biogas, cumulative methane production and methane production rate for the tested conditions compared to the positive control. Cumulative biogas production decreased with the increase of biochar dosage (Figure 4A). Biogas production of all biochar-amended digesters was significantly lower than that of the PC ($p < 0.01$ for all conditions). The methane content in the biogas from all biochar-amended digesters started from above 95% on day 1 and decreased gradually, while the methane content in biogas of the PC increased from 64.0% to 69.6% and thereafter was steady (Figure 4B). The 26 days' average methane content in biogas of CS25, CS35, CS42 and CS50 was 88.5%, 93.5%, 94.9% and 96.7%, respectively, as compared to that of the PC (avg. 67.9%). The methane content in biogas of all biochar-amended digesters was significantly higher than that of the PC ($p < 0.001$ for all conditions). Contrary to the trend of biogas production, CS25, CS35 and CS42 produced significantly more methane than the PC ($p < 0.0001$ for three conditions), whereas CS50 produced comparable amount of methane with the PC ($p > 0.05$) (Figure 4C). The above results indicated that

methane production from sludge AD is not inhibited by biochar addition with dosage up to 3.64 g/g TS under thermophilic operations, and that the decreased cumulative biogas production from digesters amended with biochar results from the CO₂ adsorption and mineralization.

Methane yield and production rate were evaluated to further investigate the impacts of biochar on AD performance. First-order reaction kinetics were assumed [42, 43] for fitting the methane production rate curves (Figure 4D) since sewage sludge is heterogeneous substrate. Methane production data fitted appropriately into a simple exponential equation ($R^2 > 0.9$ for all three replicates). The biochar addition enhanced both reaction rate constant (k -value) and maximum potential methane production rate ($P_{CH_4, \max}$) of AD process by up to 8.1% and 27.6%, respectively (Table 3). Statistical analysis results show that k -value of CS35 was very significantly ($p = 0.005$) higher than that of the PC; $P_{CH_4, \max}$ values of CS25 ($p = 0.018$), CS35 ($p = 0.028$) and CS42 ($p = 0.029$) were all significantly higher than that of the PC; Y_{CH_4} (mL CH₄/g COD degraded) values of CS25 ($p = 0.028$) and CS35 ($p = 0.007$) were significantly higher than that of the PC. Table 3 also shows that the k -value and $P_{CH_4, \max}$ decreased with the increase of biochar dosage. While high biochar dosage increases methane content in the biogas, it results in toxicity in the CS42 and CS50 digesters. Potassium and calcium concentrations in the digesters increased up to 2600 mg/L and 800 mg/L, respectively (Figure 7B, as discussed later), which may have the adverse effects on the AD performance (Chen et al., 2008). Therefore, biochar dosage is an important parameter for this novel process where sludge AD and *in-situ* biogas cleanup and upgrading occur simultaneously. Based on the performance results, we will evaluate pathways to piloting and scale-up of this process.

Biochar addition increased both biogas CH₄ concentration and production rates in the digester. The high alkali and alkaline earth metals (K, Ca and Mg) content of the biochar results in the slightly alkaline pH in the biochar-amended digesters, which converts CO₂ to bicarbonate/carbonate. This would contribute to the accelerated carbonation reaction and hence provide high alkalinity (Figure 6B, as discussed in 3.2.2). The improved buffering capacity would prevent pH drop resulting from the organic acids produced during AD, which could enhance the process stability. Furthermore, maintaining CO₂ in the bicarbonate/carbonate form in the liquid phase facilitates the methane formation via CO₂ reduction by hydrogenotrophic methanogens [44]. It should be noted that this reaction relies on the syntrophic relationship between organic acid-oxidizing acetogenic bacteria and CO₂-reducing methanogenic archaea, where interspecies electron transfer efficiency plays a crucial role [44]. A recent study reported that electrically-conductive materials stimulate methane production by establishing the extracellular direct interspecies electron transfer (DIET) between the syntrophic microorganisms [45]. Considering the high electrical conductivity observed in the biochar-amended digesters (Figure 5D, as discussed in 3.2.2), the biochar will probably promote DIET to improve methane production. However, further research is needed to address the impact of biochar on electron transfer mechanism among the complex microbial communities in the sludge digester. Moreover, biochar addition reduced NH₃ inhibition (Figure 6C, as discussed in 3.2.2) in favor of methane production.

In summary, the increased methane production in the biochar-amended digesters compared to the control digester could be attributed to the enhanced process stability provided by high alkalinity (buffering capacity), improved sludge digestibility provided

280 by alkaline pH, alleviated NH_3 inhibition, improved CO_2 reduction by hydrogenotrophic
281 methanogens and higher electrical conductivity (Figure 5D, as discussed in 3.2.2) which
282 probably promoted interspecies electron transfer efficiency.

283 Overall, the biochar-amended digesters achieved CO_2 removal of 54.9% - 86.3%. The
284 kinetics of CO_2 removal in the biochar-amended digesters with different dosages is
285 provided in Figure S1-S5 in the Supplementary Material. The CO_2 sorption/desorption
286 reached equilibrium after day 7 for CS25, while the equilibrium was not achieved until
287 day 18 for CS35, CS42 and CS50 (Figure S1 and S2). There were two phases of CO_2
288 removal rate in the biochar-amended digesters (Figure S3). The initial 7-day CO_2
289 removal rates with respect to time were well characterized with the first-order kinetics
290 (Figure S4), whereas pseudo-second-order kinetics model is applicable for the length of
291 the experiment (Figure S5) [46]. There are various mechanisms for CO_2 removal in the
292 digester, including but not limited to electrostatic interaction, adsorption/partition and
293 polarity attraction [47]. As discussed before, the high porosity of the biochar provides a
294 large surface area of carbonized and non-carbonized sites for CO_2 adsorption/partition.
295 The activation energy (E_a) of CO_2 sorption process based on pseudo-second-order
296 kinetics ranges from 5.2 to 22.8 kJ/mol, indicating physical adsorption, a weak bonding
297 between adsorbate and adsorbent, is involved in the removal of CO_2 [48]. The low O:C
298 molar ratio (0.004, Table 2) suggests the minimal polarity and highly hydrophobicity for
299 the biochar [49]. The absence of the O-containing functional groups on the biochar
300 surface prevents the formation of water clusters via H-bonding [50]. This would facilitate
301 the hydrophobic sites on biochar surface to attract CO_2 as a non-polar compound.

Additionally, the biogas samples taken from the biochar-amended digester contained H₂S concentration below method detection limit (<5 ppb), compared to the PC (H₂S 90 ppm). The H₂S concentration is significantly lower than the US EPA's specification for pipeline-quality natural gas (40CFR72.2) (H₂S < 4 ppm). Therefore, the biochar amendment could be a promising method for sulfur removal to reduce the cost and energy demand of biogas upgrading.

3.2.2 Sludge and digestate characteristics

Sludge characteristics were compared before and after thermophilic AD for all tested conditions (Figure 5 and 6). Both TS and VS increased with biochar addition (Figure 5A, 5B), as expected. All biochar-dosed digesters had higher pH than the PC (Figure 5C), with pH values ranging from 8.64 to 8.99 before AD. Alkaline pH treatment has been utilized to facilitate hydrolysis of WWTP sludge and to improve production of volatile fatty acids (VFAs) during anaerobic fermentation [51]. It was also demonstrated that alkaline pretreatment (pH >8) at thermophilic temperature could maximize VFAs yields during sludge AD with faster reaction kinetics and enrichment of VFA producer bacteria [52]. The final pH values of all biochar-amended digesters were lower than the initial pH but still in a slightly alkaline range (pH > 7.5), indicating the strong buffering capacity. This would maintain the desirable process stability for the AD process.

The electrical conductivity (EC) of all digesters increased after AD (Figure 5D). EC increased by 48.9% - 56.7% after AD in biochar-dosed digesters and are higher than in the PC (37.0%) which can largely be attributed to cation release from the biochar. The high EC resulting from biochar may enhance extracellular electron transfer to enhance

324 methanogenesis via CO₂ reduction even in the absence of conductive-pili-associated
325 bacteria [53].

326 The biochar addition caused a TOC increase in the sludge (Figure 6A), which probably
327 resulted from the volatile matter in the biochar. Nevertheless, it should be noted that
328 biochar stores the organic carbon in a recalcitrant form [54] which is resistant to
329 microbial degradation [55]. With extremely low O:C molar ratio (0.004), the carbon
330 decay half-life of the biochar is estimated to exceed 1,000 years [33, 56]. Hence, the
331 biochar addition hardly increases bioavailable organic matter concentration in the
332 digester. The biochar addition also increased total alkalinity (Figure 6B). Total alkalinity
333 concentrations of CS25 and CS35 were slightly higher than the PC, whereas those of
334 CS42 and CS50 were significantly higher than the PC. It was also noted that total
335 alkalinity of all digesters increased after AD, mainly resulting from cation release and
336 ammonium formation during the AD process. Total alkalinity concentrations are in the
337 desirable range (2000-5000 mg/L) for a successful AD process in all digesters [57].

338 The NH₃-N concentration increased by 41.5% in the PC digester after AD (Figure 6C),
339 which is expected due to degradation of organic nitrogen-compounds to ammonia. In
340 spite of the slightly higher NH₃-N concentration in biochar-dosed digesters after AD, the
341 increment of NH₃-N ranged from 0.2% to 18.1%, much lower than that of PC. This is
342 unexpected because the biochar-amended digesters had higher pH than the PC (Figure
343 5C). The inhibitory effect of free ammonia (NH₃) is greater than ammonium (NH₄⁺) in
344 the digesters [57]. It was at first assumed that biochar addition would aggravate ammonia
345 inhibition in the digesters, since pH increase would shift the NH₃-NH₄⁺ equilibrium
346 towards NH₃ formation. However, the experimental results showed that the [NH₃-N] is

negatively correlated with biochar addition (Figure 6C), indicating that biochar is capable of mitigating ammonia inhibition because the large biochar surface area promotes NH_3 adsorption [58]. The mitigation of NH_3 inhibition by the biochar enhances CH_4 production, in a manner similar to how activated carbon alleviates NH_3 inhibition during thermophilic AD of swine manure [59]. AD did not impact total nitrogen (N) (Figure 6D) or total phosphorus (P) (Figure 6E). This is because AD process only partially hydrolyzes organic and particulate N and P into inorganic forms, namely ammonia and orthophosphate, respectively [60]. It was also noted that biochar addition did not cause any evident increase of total N or P in the sludge stream, probably due to the relatively low concentrations of the two elements in the biochar (Table 2).

Figure 7 shows the metal composition of the sludge stream for all test conditions in comparison to PC. No significant changes were observed before or after AD treatment, except that minimal amounts of sodium (54.0-79.3 mg/L) were detected after AD in the sludge supplemented with biochar. The concentrations of total Al, Ca, Fe, Mg and Mn were higher in the sludge stream supplemented with biochar than the PC, regardless of biochar dosage.

The total Ca, Fe, Mg and K in the biochar-amended digesters increased by 60-134%, 43-95%, 82-183% and 2051-4435%, respectively. The increase in metal concentration (i.e. total concentration in the test condition in comparison to the PC) was proportional to the biochar dosage. Potassium (K) exhibited the highest concentration in the sludge supplemented with biochar among all the elements, which is consistent with the biochar characterization results (Table 2). An increase in K content enhances the value of the resultant digestate: improves soil fertility, reduces nutrients losses in run-off, enhances

the water-retention capacity of soils and enables carbon capture and storage [54]. This efficient nutrient recycle approach could reduce of energy and water consumption and decrease GHG emissions in comparison to synthetic fertilizer production.

In summary, this study conveys the concept of an Integrated Waste to Energy and Nutrient Recycle System (IWENRS) to enhance the sustainability of AD. IWENRS paves a path towards a new paradigm to produce renewable natural gas (i.e. biomethane), generate fertilizer-grade digestate for soil application and reduce greenhouse gas emissions and waste disposal, as illustrated in Figure 8. In IWENRS, the water, energy, nutrients and environmental sectors are considered as components of a single system and previous environmental liabilities are transformed into renewable resources for biomethane production. Our aim is to fully integrate the agro-renewable-carbon cycle for CO₂ removal and produce renewable natural gas and value-added digestate fertilizer.

4. Conclusions

This study presented a potentially revolutionary process utilizing mineral-rich porous corn stover biochar for AD of WWTP sludge with efficient *in-situ* removal of CO₂ and H₂S in the biogas. This process provides a new path towards efficient and economical biomethane production for the AD industry. The method increased methane yield, enhanced CO₂ removal, improved process stability and substantially reduced energy/cost intensive biogas cleanup and upgrading. Moreover, this process generates digestate enriched with nutrients including potassium, calcium, iron and sulfur, which can be applied as fertilizer for crop cultivation. Taken together, this novel IWENRS could foster

utilization of renewable natural gas, reduce fugitive methane emissions, and displace synthetic fertilizer.

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408 **Table 1. Experimental conditions**

Condition	Ingredients
PC ^[a]	Inoculum + Substrate
CS25	Inoculum + Substrate + Biochar (1.82 g/g TS of sludge)
CS35	Inoculum + Substrate + Biochar (2.55 g/g TS of sludge)
CS42	Inoculum + Substrate + Biochar (3.06 g/g TS of sludge)
CS50	Inoculum + Substrate + Biochar (3.64 g/g TS of sludge)

409 [a] Positive control

410

411 **Table 2. Physical properties and chemical composition of corn stover biochar**

Analysis	Parameter	Value ^[a]
Physisorption Isotherm	BET surface area (m ² /g)	315.30
	Total volume of pores (cm ³ /g)	0.09
	Average diameter of pores (nm)	6.50
Proximate	Moisture	0.97 ± 0.05
	Ash	45.18 ± 0.40
	Volatile matter	7.18 ± 0.58
	Fixed carbon	46.66 ± 0.86
Ultimate	Moisture	0.97 ± 0.05
	Ash	45.18 ± 0.40
	C	52.78 ± 0.41
	H	0.33 ± 0.03
	N	0.50 ± 0.02
	O	0.25 ± 0.04
	S	520 ± 50 ppm
Atomic Ratio ^[b]	H:C molar	0.075 ± 0.007
	O:C molar	0.004 ± 0.001
	C:N molar	122.4 ± 2.8
Ash Elemental ^[c]	SiO ₂	60.58 ± 0.58
	Al ₂ O ₃	5.65 ± 0.10
	TiO ₂	0.27 ± 0.01
	Fe ₂ O ₃	1.93 ± 0.05
	CaO	3.87 ± 0.11
	MgO	4.23 ± 0.13
	Na ₂ O	0.74 ± 0.03
	K ₂ O	14.17 ± 0.15
	P ₂ O ₅	2.19 ± 0.12
	SO ₃	0.22 ± 0.06
	Cl	1.01 ± 0.02
	CO ₂	1.17 ± 0.13

412 [a] Unit of all data is weight percentage (wt %) unless otherwise stated; data are shown in average
413 values based on triplicate measurements ± standard deviations.

414 [b] Molar ratio calculated from ultimate analysis results

415 [c] Weight percentage on ash basis

416 **Table 3. Methane yield (Y_{CH_4}), maximum methane production rate ($P_{CH_4,max}$) and reaction rate constant (k) for different AD**
417 **conditions**

AD condition	Y_{CH_4}		$P_{CH_4,max}$	k
	(mL CH ₄ /g VS degraded)	(mL CH ₄ /g COD degraded)	(mL CH ₄ /day)	(day ⁻¹)
PC	488.9 ± 19.6	290.6 ± 10.5	125.5 ± 3.6	0.161 ± 0.004
CS25	494.3 ± 10.8	310.8 ± 6.8	160.1 ± 11.1	0.174 ± 0.010
CS35	494.9 ± 16.0	302.9 ± 9.8	144.5 ± 3.9	0.171 ± 0.004
CS42	495.2 ± 11.6	299.9 ± 7.0	143.6 ± 2.2	0.169 ± 0.010
CS50	494.5 ± 21.7	296.6 ± 13.0	131.5 ± 8.9	0.163 ± 0.007

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560

FIGURES

Figure 1. Conventional multi-step biogas upgrading technology versus novel *in situ* biogas upgrading process with biochar amendment

Figure 2. Challenge Technology's Biomethane Potential Analyzer MPA-200

Figure 3. Particle size distribution of corn stover biochar

(B)

Figure 4. Time-course profiles of anaerobic digestion experiments: (A) cumulative biogas production; (B) methane content of biogas; (C) cumulative methane production; (D)

Methane production rate (mL/day). Data are means of triplicates and error bars show standard deviations.

Figure 5. Sludge characteristics before and after anaerobic digestion: (A) total solids; (B) volatile solids; (C) pH value; (D) electrical conductivity. Data are means of triplicates and error bars show standard deviations.

Figure 6. Sludge characteristics before and after anaerobic digestion: (A) total organic carbon (TOC); (B) total alkalinity (TA); (C) ammonia nitrogen (NH₃-N); (D) total nitrogen (Total N); (E) total phosphorus (Total P). Data are means of triplicates and error bars show standard deviations.

Figure 7. Metal concentration of sludge samples (A) before and (B) after anaerobic digestion

Figure 8. Concept of the Integrated Waste to Energy and Nutrient Recycle System (IWENRS)