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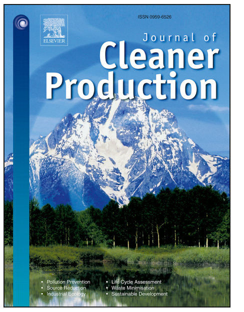

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CRediT roles

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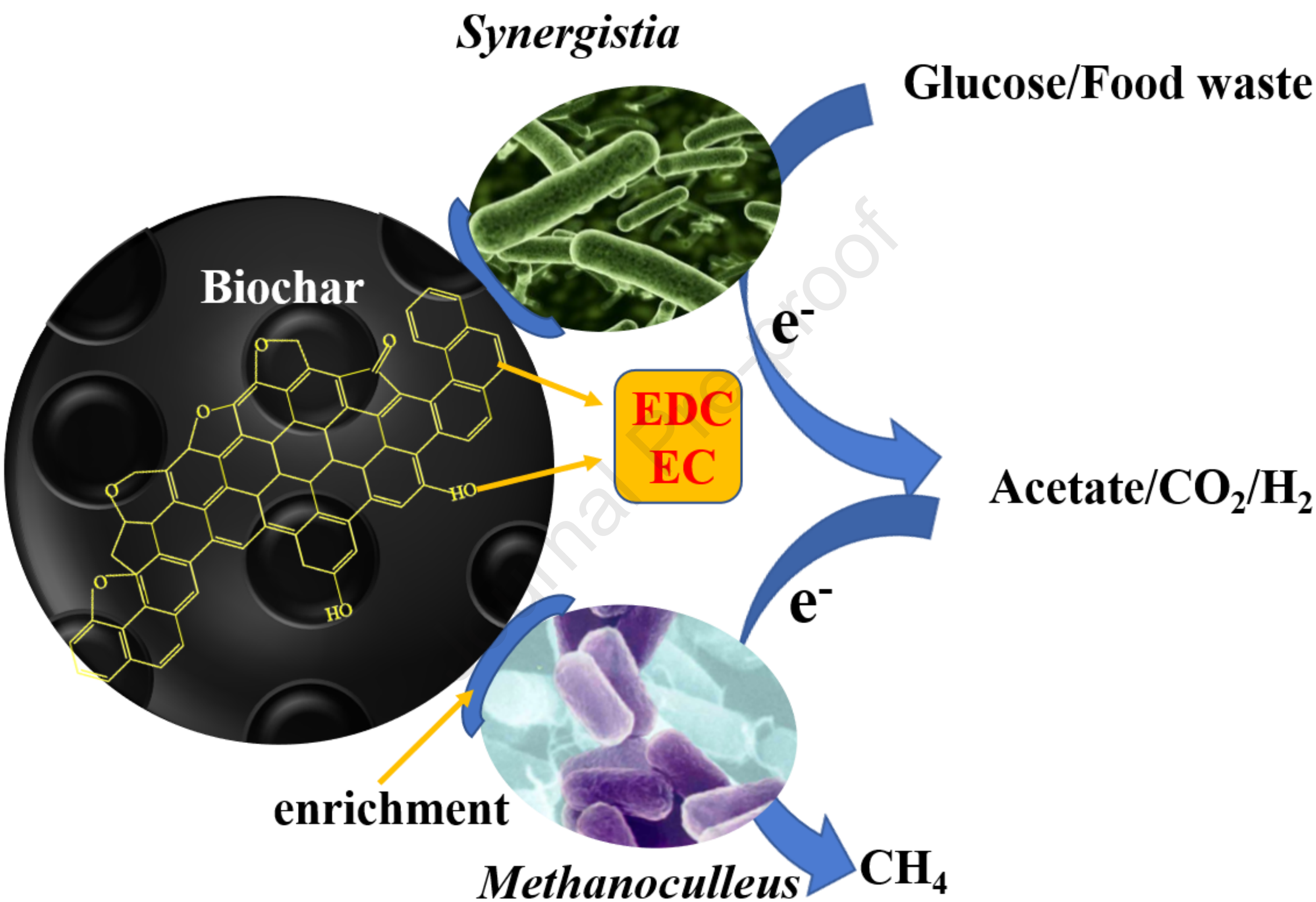
Yongming Han: Supervision, Writing – review & editing.

Hongjun Zhou: Supervision, Writing – review & editing.

Junting Pan: Supervision, Writing – review & editing.

Graphical abstract:



The role of electrochemical properties of biochar to promote methane production in anaerobic digestion

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Abstract

The electrochemical properties of biochar may be the key factor to promote anaerobic digestion, which has attracted extensive attention. However, the mechanism and the role of the electrochemical properties of biochar are remaining unclear. In this study, biochar with different electrochemical properties was prepared by pyrolysis at different temperatures (BC300/600/900) and oxidation or reduction modification (O/RBC300/600/900). The biochar was added as an additive to promote methanogenic performance of anaerobic digesters of glucose and food waste anaerobic. In both anaerobic digestion systems, the cumulative methane production of food waste increased by 42.07% and the maximum methane production of glucose enhanced by 17.80% after BC900 treatment. RBC600 was inferior to BC900, but superior to BC600. Microbiological analysis suggests that biochar enriched the relative abundant *Synergistia* and *Methanoculleus*. This is conducive to the establishment of the direct interspecies electrons transfer (DIET). Results from correlation analysis, principal component analysis and machine learning confirmed that both of the electron donating capacities (EDC) and electrical conductivity (EC) are dominated factors affecting the cumulative methane yield. Through the analysis of electrochemical properties and preparation process of biochar, the results showed that the pyrolysis temperature increases and the content of phenolic hydroxyl decreases under moderate temperature of biochar, which was beneficial to the methane production. This study found the key factors of the electrochemical properties of biochar in anaerobic digestion, provided new insights for the mechanism of biochar promoting anaerobic digestion and proposed novel directions for the preparation of biochar.

Keywords: Anaerobic digestion; Biochar; Electron donating capacities; Electrical conductivity; Oxidation and reduction modification.

Abbreviations	
BC	biochar
OBC	oxidation modified biochar
RBC	reduction modified biochar
DIET	direct interspecies electrons transfer
CMs	conductive materials
OCFGs	oxygen-containing functional groups
EDC	electron donating capacities
EC	electrical conductivity
VFAs	volatile fatty acids
EAC	electron accepting capacities
TS	total solid
VS	volatile solid
MEO	mediated electrochemical oxidation
MER	mediated electrochemical reduction
FTIR	fourier to transform infrared spectroscopy
XGBoost	Extreme Gradient Boosting
AI	aromaticity index
DBE	double bond equivalent

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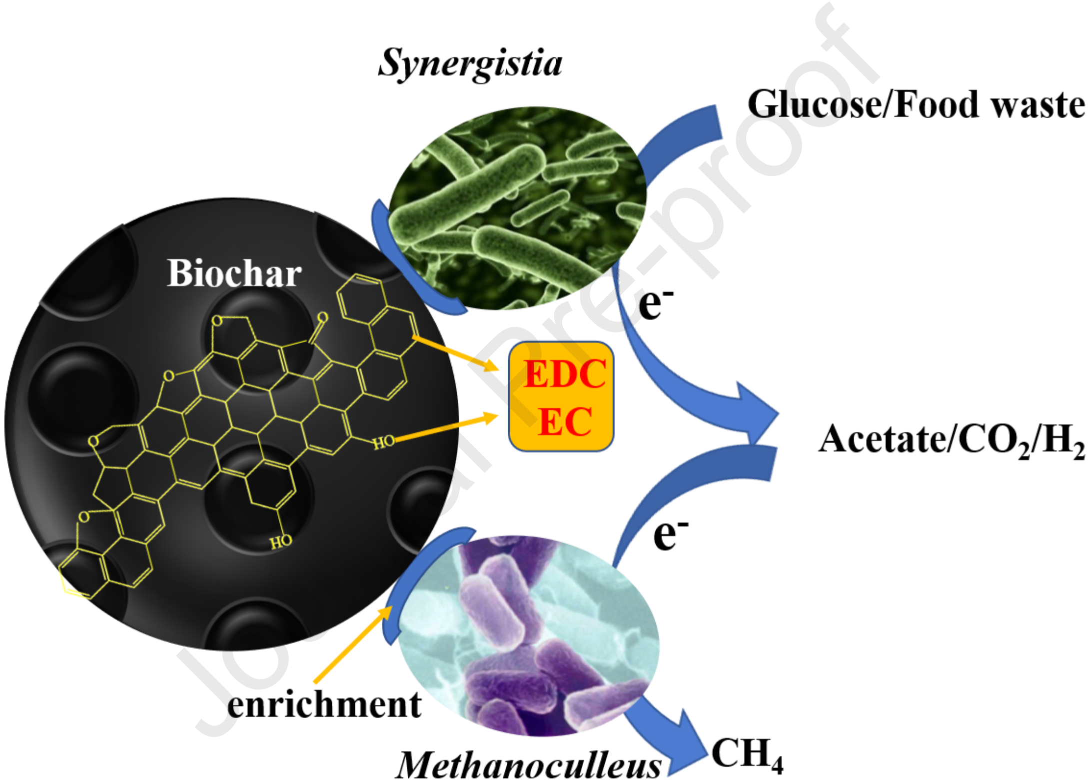
Highlights:

- BC900 increased the cumulative methane production of food waste by 42.07%;
- BC900 increased the maximum methane production rate of glucose by 17.80%;
- RBC600 was inferior to BC900, but superior to BC600 in anaerobic methanation;
- Electron donating capacities and electrical conductivity of biochar are keys factors;
- Higher pyrolysis temperature and lower phenolic hydroxyl of biochar are beneficial.

Graphical abstract:



1. Introduction

Anaerobic digestion is a well-developed method for treating residues as it could both generate bioenergy as the form of biogas and recovery nutrients as bio-fertilizer(Satchwell et al., 2018). It consists of four stages, hydrolysis, acidogenesis, acetogenesis and methanogenesis, while each of which is performed by a unique set of functional microorganisms(Lv et al., 2010). Methanogens is sensitive to environmental variation and the activity of methanogens could be inhibited by various factors including (1) accumulation of volatile fatty acids (VFAs); (2) accumulation of molecular hydrogen; and (3) accumulation of formate(Gahlot et al., 2020). Recent studies suggested that some bacteria can transfer electrons directly to methanogenic archaea, so called DIET methanogens pathway(Rotaru et al., 2014). DIET achieves rapid transformation from wastes to energy(Cheng and Call, 2016).

The efficiency of DIET directly relies on conductivity, while addition of conductive materials (CMs) can be used as the electronic channel to realize the direct exchange of electrons(Barua and Dhar, 2017). Among these CMs, biochar has advantages of low cost, wide range of raw materials, large specific surface area, abundant surface functional groups(Zhao et al., 2021), which is therefore considered as the most promising CMs to accelerate DIET and enhance the efficiency of anaerobic digestion(Zhao et al., 2021 , Khalid et al., 2021).

Recent years, implementation of biochar to improve DIET and the mechanism were widely reported. For instance, Quintana-Najer (Quintana-Najera et al., 2021) reported that the most critical characteristics for biochar to improve the anaerobic digestion performance is surface oxygen functionality. Results from Qi (Qi et al., 2021) showed that biochar with more aromatic groups and condensed carbon structure is more favorable to DIET, while the specific surface area and EDC were found to be the key properties that biochar could enhance anaerobic digestion by Qin (Qin et al., 2020). However, the role of electrochemical properties of biochar on anaerobic digestion is yet fully recognized and the understanding on the impact of electrochemical properties limited. Moreover, it has been well-recognized that the electrochemical performance of biochar is also affected by the preparation conditions of biochar. However, there is a lack of in-depth research to reveal these internal links. The electrochemical properties of biochar mainly include: pseudocapacitance, EC and capacitance(Chacón et al., 2017). Pseudocapacitance of biochar is mainly related to the oxidation and reduction capacity of oxygen-containing functional groups（OCFGs） (Chacón et al., 2017 , Klupfel et al., 2014). The EC of biochar depends greatly on the degree of carbonization(Gabhi et al., 2017). Capacitance is an ability to store energy electrostatically in the way of electric charges
(Chacón et al., 2017). Based on our best knowledge, there is very limited study reported the internal relationship between electrochemical properties and preparation process of biochar to explore the mechanism of biochar acting on anaerobic system. In addition, most of the current studies focused on using single substrate or co-substrate for

anaerobic digestion. Because of different substrate, anaerobic digestion performance is different(Xu et al., 2020). This may hinder the understanding of the role and mechanism of biochar addition in anaerobic digestion. Implementation of simple substrates may help to understand the mechanism, but complex substrates are closer to reality.

In this study, biochar with different electrochemical properties was prepared by changing pyrolysis temperatures or processed by oxidation/reduction modification. Both the most common simple and complicated substrate (e. g. glucose and food waste) were used as to research the mechanism of biochar on promotion of the anaerobic digestion process. Therefore,the purposes of this study were as follows: (1) compare the effects of biochar on promoting methane production of different anaerobic substrates; (2) explore the mechanism of biochar electrochemical properties promoting methane production; and (3) reveal the internal relationship between the preparation process, electrochemical properties of biochar and promoting methanogenesis.

2. Materials and methods

2.1 Materials

Dried corn straws collected from Beijing were used for biochar preparation. The corn straws were firstly grinded to 20 mesh and stored in sealed bag. Food waste was taken from the canteen of China University of Petroleum (Beijing), which was firstly removed the large particles, for instance bones, and impurities, following homogeneous protocols including grinding and sufficient mixing. Inoculum was collected from stably operated biogas plant treating mainly food waste. Total solids (TS) and volatile solids (VS) were determined following the APHA (2005). Main characteristics of corn straws, food waste and inoculum are shown in Table 1.

Table 1 Characteristics of corn straws, food waste and inoculum.

Substrate	TS (%)	VS (%)	C (%)	H (%)	O (%)	N (%)
Corn straws	91.26±3.16	82.59±0.91	49.14	6.62	36.93	0.51
Food waste	27.18±0.22	25.50±0.30	55.47	7.24	33.80	1.80
Inoculum	2.52±0.01	1.02±0.03	-	-	-	-

2.2 Biochar preparation and modification

Biochar is prepared in a tubular furnace. 10g corn straws powder was put into tubular furnace within nitrogen atmosphere and heated to 300, 600 and 900 ºC, named BC300, BC600, and BC900, respectively. The temperature was maintained at the target temperature for 1 hour. The obtained biochar was filtered and washed with deionized water and ethanol. The cleaned biochar was dried at 80 ºC for 12 hours, grounded to 80 mesh, and kept in a centrifugal tube for sealing preservation.

Oxidation:10 g biochar from the first step with 10mL hydrogen peroxide (H_2O_2, 30%*w/w*) stirred at 120 rpm for10 hours. The biochar was then cleaned with deionized water. The cleaned biochar was dried at 80 ºC for 12 hours, namely OBC 300, OBC600, and OBC900, respectively, and stored in a sealed centrifugal tube.

Reduction:10g biochar from the first step was placed in 250mL 2mol/ L sodium hydroxide (NaOH) solution, stirred at 120 rpm and 10 hours. The biochar was cleaned with deionized water. The cleaned biochar was placed in an oven, dried at 80 ºC for 12 hours, namely RBC300, RBC600 and RBC900, and stored in a sealed centrifugal tube.

2.3 Anaerobic digestion experiment

Glucose and food waste were used as substrates. Batch assay was conducted using both 10gVS/L of substrates and inoculum, with addition of 10g/L of biochar. The incubation temperature was 37 ºC, the rotation speed was 80rpm. Nitrogen was flushed into the system for 3-5 minutes to create anaerobic condition. Each group was carried out duplicate. Methane production was recorded by Automatic Methane Potential Test System II (AMPTSII) (Bioprocess Control, Sweden). Preparation of biochar and experiment set-up are shown in Fig.1(a).

2.4 Analysis methods of biochar

Biochar yield is determined by the mass percentage of biochar to the raw material. The moisture, ash content, volatile matter and fixed carbon of biochar were determined according to GBT212-2008 coal industrial analysis method. The element content of biochar was performed by elemental analyzer (EA3000, EuroVector, Italy), and the O content was calculated by difference. The EDC and electron accepting capacities (EAC) of biochar were quantitatively determined by means of mediated electrochemical oxidation (MEO)/reduction (MER) method. The details regarding the specific methods are reported by Klupfel(Klupfel et al., 2014). The OCFGs of obtained biochar were quantitatively analyzed by Boehm titration method. The detailed methods were described in the method S1. Other physical and chemical properties of biochar and microbial community analysis methods refer to previous studies of our research group(Li et al., 2022b).

2.5 Data processing and analysis

The modified Gompertz model is used to describe the gas dynamic characteristics of each treatment, as shown in Equation (1):

$$P = P_0 \times \exp\left\{-\exp\left[\frac{R \times e}{P_0} \times (\lambda - t) + 1\right]\right\} \qquad (1)$$

Among them, t is fermentation time (d), P represents the cumulative methane production (mLCH_4/g VS), P_0 is the methane production potential (mLCH_4/g VS), R is the maximum methane production rate (mLCH_4/g VS·d), and λ is the lag period (d).

Microsoft Office Excel (2019) and Origin Pro 2018 (Origin Lab, MA 01060, U.S.A) were used for graphing and data treatment. IBM SPSS Statistics 21 (IBM, NY 10504, U.S.A) was used to ANOVA on the significance of results, when $p < 0.05$ was considered to be statistically significan.

3. Results and discussion

3.1 Physicochemical properties of biochar

As shown in Fig.S1, the surface becomes rough and the pore wall becomes thinner of biochar with the increase of pyrolysis temperature. After oxidation or reduction modification, the pore surface becomes smooth and the disorder degree decreases. In terms of the elemental composition, biochar treated with higher pyrolysis temperature had lower nitrogen, hydrogen, and oxygen contents (no nitrogen was detected at 900°C) in Fig.1(b). However, there is a opposite trend observed for carbon, which could be explained as the dehydration and decarboxylation reaction occurs at higher temperature and that reduces functional groups(Qi et al., 2021). Moreover, modification of biochar has limited impact on the nitrogen and hydrogen content but has huge impact on the content of carbon and oxygen. Carbon from oxidation modified biochar decreased dramatically, accompanying with significantly higher oxygen content. Biochar treated with reduction process, however, presented oppositely. These results indicated that OCFGs were successfully introduced to the surface of biochar modified by H_2O_2, while the reducibility of biochar modified by NaOH increased.

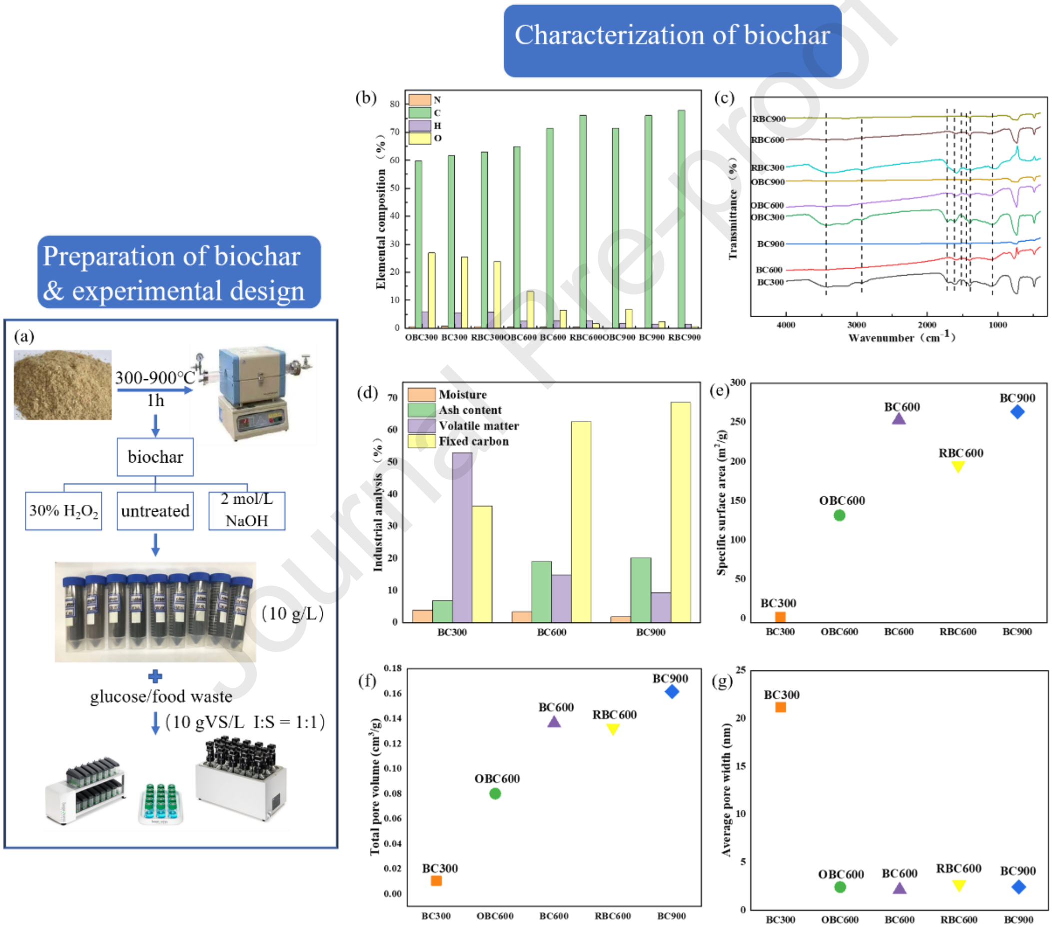


Fig.1. Schematic diagram of the experimental set-up and characterization of biochar: (a) preparation of biochar and the experiment design, (b-g) characterization results of biochar.

The functional groups of biochar can be determined by FTIR (Fig. 1(c)). The absorption peaks at 3600-3200cm^{-1} are caused by vibration of hydroxyl groups of polymers, such as alcohol, phenol and carboxylic acids; the characteristic peaks of 2900-2800cm^{-1} indicate the presence of aliphatic C-H; the absorption peak at 1700cm^{-1} is caused by C=O stretching vibration of carbonyl, quinone, ester and carboxyl group;

the absorption peaks of 1650-1450cm^{-1} are caused by stretching vibrations of C=C bonds in aromatic or benzene ring structures; the absorption peak at 1650 cm^{-1} indicates the presence of C=O (Bhushan et al., 2020 , Wang et al., 2018). The FTIR spectra shown that the characteristic peaks decreased as the increased pyrolysis temperature. It indicates that decarboxylation and carbonylation reactions occurred during high temperature pyrolysis, while most OCFGs were removed. OCFGs were found more abundant as only cellulose was pyrolyzed but not lignin at 300 ºC (Zhang et al., 2019b). Lignin started to be pyrolyzed when the temperature rising to 600 ºC, resulting the large loss of OCFGs. C-O-C bond was also observed, which is probably sourced from the un-pyrolyzed lignin. There is almost no characteristic peak observed at 900℃, indicating that biochar has been graphitized at that temperature (Wan et al., 2019).

As shown in Fig.(d), both the moisture and volatile content decreased as a result of increased pyrolysis temperature, while ash content and fixed carbon content increased. The results showed that the components of straw were decomposed and gradually converted from aliphatic carbon to aromatic carbon with the increase of pyrolysis temperature. During the pyrolysis process, lignocellulosic biomass is first depolymerize into oligosaccharides, and then generated to biochar, bio-oil, and pyrolysis gas through dehydration, decarboxylation, aromatization, intramolecular condensation, and other reactions(Kambo and Dutta, 2015). The ash consists of mainly silicon, alkali metal, and alkali earth metal element, while the pyrolysis process has very limited impact on the absolute content(Li et al., 2017b). Organic matter such as C, H and O is decomposed, and minerals are accumulated at the end of pyrolysis(Enders et al., 2012). Fixed carbon content represents the carbon sequestration capacity of biochar itself. Fixed carbon content was significantly increased from 36.39 to 62.70% as the pyrolysis temperature increased from 300 to 600 ºC. However, the fixed carbon content didn't change significantly with pyrolysis temperature up to 900 ºC, indicating that the biochar was stabilized as most of the organic substances have been converted(Yang et al., 2020).

The specific surface area characteristics of biochar are considered to be a key factor that may affect the efficiency of anaerobic digestion as the high specific surface area and porous structure can promote the loading and immobilization of microorganisms(Jaafar et al., 2015). The higher the pyrolysis temperature of biochar, the higher the specific surface area. After oxidation and reduction modification, the specific surface area of biochar decreased slightly in Fig.(e). The specific surface area of BC300 is 1.99 (m^2/g), that is significantly lower comparing to BC600 (252.97 m^2/g) and BC900 (263.24 m^2/g). This may be explained by the larger amount of not pyrolysis straw existed in BC300. Based on the results of previous tests, the specific surface area of raw straw was significantly lower than that of biochar(Qu et al., 2021). Pyrolysis temperature was found positively affected the pore volume, while modification of biochar via reduction decreased the pore volume while oxidation had only limited impact on that in Fig.(f). The pore size of biochar is about 2 nm, with the only exception of BC 300 in Fig.(g). Both oxidation and reduction modification enlarged the pore size of biochar, which could be conducive to microbial attachment.

3.2 Effect of biochar addition on anaerobic digestion of different substrates

3.2.1 Anaerobic digestion of glucose- as simple substrate

Different substrates have different degradability and the addition of biochar may also have different effects on anaerobic digestion(Xu et al., 2020). At present, most studies use a substrate, but the research on the influence of substrate is not enough. Therefore, it is necessary to research the influence of biochar on anaerobic digestion of different substrate types. In this study, both glucoses (as simple substrate) and food waste (as complex substrate) were utilized to better explain the role and mechanism of biochar addition on anaerobic digestion.

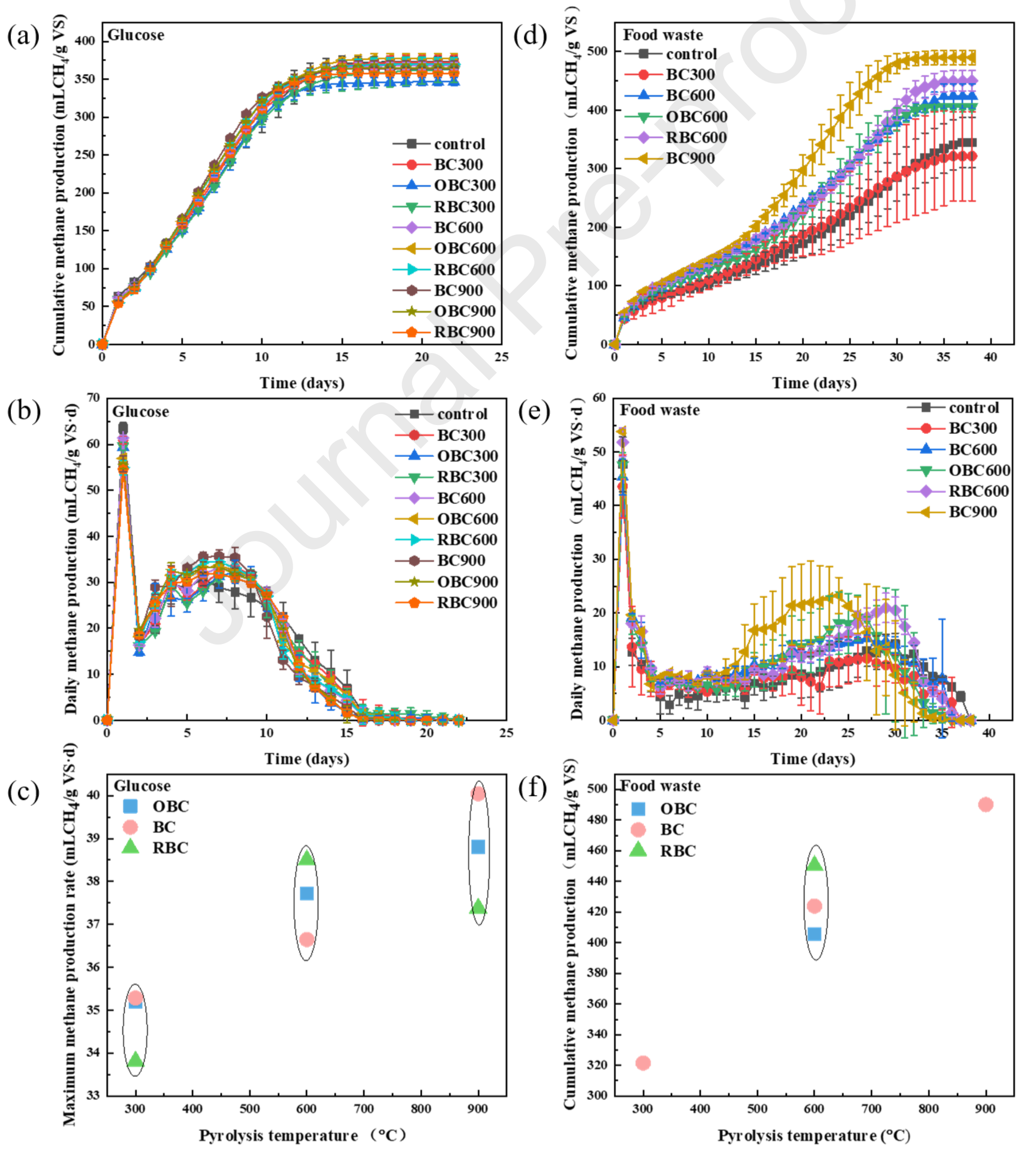


Fig.2. Cumulative methane production, daily methane and effect of pyrolysis temperature and modification of biochar on gas production performance:(a-c) glucose

as a substrate; (d-f) food waste as a substrate.

There was no significant difference between the experimental group with biochar addition and the control group without biochar addition except OBC300 (p=0.01) and RBC900 (p=0.029) groups in Fig 2 (a). The control group achieves up to 99.8% of theoretical methane production (373.4 $mLCH_4$/g VS). Glucose, the most common simple substrate, is almost completely degraded. During anaerobic digestion, glucose could be directly used to produce methane and there no inhibitory intermediates such as ammonia is released. Therefore, the addition of biochar has very limited effect on promoting of methane production. This is in accordance with Ren and Li. Ren(Ren et al., 2020) added four types of hydrochar to glucose anaerobic digestion system but failed on promoting methane production. Li(Li et al., 2022b) added biochar and hydrochar to ethanol anaerobic digestion system, respectively. The results also failed to increase cumulative methane production.

According to Fig. 2 (b) and Table 2, although the addition of biochar failed to promote the cumulative methane production from glucose, it promoted the methane production rate (RBC 300 is the only exception). The addition of BC900 achieves the highest methane production rate, which is 17.80% higher than control. The maximum methane production rate of RBC600 was 5.47% higher than BC600 and 13.27% higher than control group. As shown in Fig. 2 (c), the increase of pyrolysis temperature and reduction modification at medium temperature of biochar both have beneficial effects for the methane production rate. However, addition of biochar has no impact on shorten the lag time.

Table 2 The modified Gompertz model anaerobic digestion with glucose as substrate.

Group	P_0 ($mLCH_4$/g VS)	R ($mLCH_4$/g VS·d)	λ (d)	R^2
Control	389.06	33.99	0.11	0.993
BC300	386.88	35.28	0.34	0.993
OBC300	359.00	35.20	0.37	0.990
RBC300	375.72	33.81	0.32	0.993
BC600	381.09	36.64	0.40	0.991
OBC600	390.00	37.72	0.47	0.994
RBC600	380.76	38.50	0.57	0.994
BC900	374.44	40.04	0.56	0.993
OBC900	376.49	38.80	0.52	0.993
RBC900	369.83	37.38	0.52	0.992

3.2.2 Anaerobic digestion of food waste- as complex substrate

When food waste as substrate, the cumulative methane production of the control group was not significantly different with BC300 (p=0.458) and OBC600 (p=0.07), but was significantly different with BC600 (p=0.024), RBC600 (p=0.005) and BC900 (p=0) in Fig.2(d). Compared with glucose as substrate, the addition of biochar significantly promoted the cumulative methane production when food waste was used as substrate. The contents of protein and lipids in food waste are high, and it is easy to produce inhibitors such as ammonia, hydrogen sulfide and long-chain fatty acids, which reduces the stability of the system and leads to the decrease of methane production(Xu et al., 2018). The addition of biochar improves the buffering capacity of the system, reduces the ammonia concentration, and promotes the stability of the reactor and methane production (Pan et al., 2019 , Giwa et al., 2019). The cumulative methane production increases with the increase of pyrolysis temperature of biochar and the effect of reducing modified biochar on promoting methane production was better than that of unmodified biochar at the medium pyrolysis temperature in Fig. 2 (f). Compared to the control group, the cumulative methane production of BC900 increased by 42.07%; BC600 raised by 22.90%; and RBC600 enhanced by 30.55%.

Fig.2(e) presents two gas production peaks of each gas curve; first peak appears on day 1 and the second is observed between day 24-30. In the first peak, the results were similar between the control and the experimental groups. The experimental group with biochar added reached the second peak gas production earlier than the control group. Except BC300, the peak of gas production of biochar group was higher than control group. Biochar also has a positive effect for the methane production rate.

In conclusion, the influence of biochar on anaerobic digestion of different substrates is indeed different. For simple substrates, the addition of biochar can promote the rate of methane production. For complex substrates, biochar can also increase cumulative methane production. The increase of pyrolysis temperature and reduction modification at the middle pyrolysis temperature of biochar are conducive to promoting cumulative methane production. As we all know, the higher the pyrolysis temperature of biochar, the lower the yield, and the higher the safety requirements for equipment. Therefore, biochar modified with reduction could achieve reasonable yield under moderate temperature and therefore is more feasible.

3.2.3 Microbial community analysis

To research the diversity of microorganisms in the environment, the species abundance and diversity of environmental microbial community can be understood through single sample Alpha diversity analysis, including Coverage, Sobs, ACE, Chao, Shannon and Simpson statistical analysis index, as shown in Table 3. Sobs index reflects the actual number of observed species in the sample. As shown in Table 3, the number of species from the experimental group with biochar addition was larger than that in the control group except for the BC300 in archaea. It showed that the addition of biochar increased the number of microorganisms. Coverage index represents the coverage of the sample library, the higher value represents the higher probability of sequence detection in the sample (Li et al., 2018). The coverage index of 12 samples in this test was all greater than 0.99, indicating that the detection results can reflect the real situation of most of the bacteria and archaea in the samples.

Ace and Chao1 index reflected microbial community richness, Shannon and

Simpson index reflected microbial community diversity(Zhang et al., 2020). Among them, Shannon, ACE and Chao 1 index were used as ecological indicators(Li et al., 2018). The ecological index values of bacterial sequences were large, indicating that the diversity and richness of bacteria were much higher than archaea. The results showed higher value of Shannon, Chao1 and Ace index were higher, but the Simpson index is lower, which had a positive influence to methane production(Li et al., 2017c). In this study, the parameters of the biochar group (except BC300) meet the above rules.

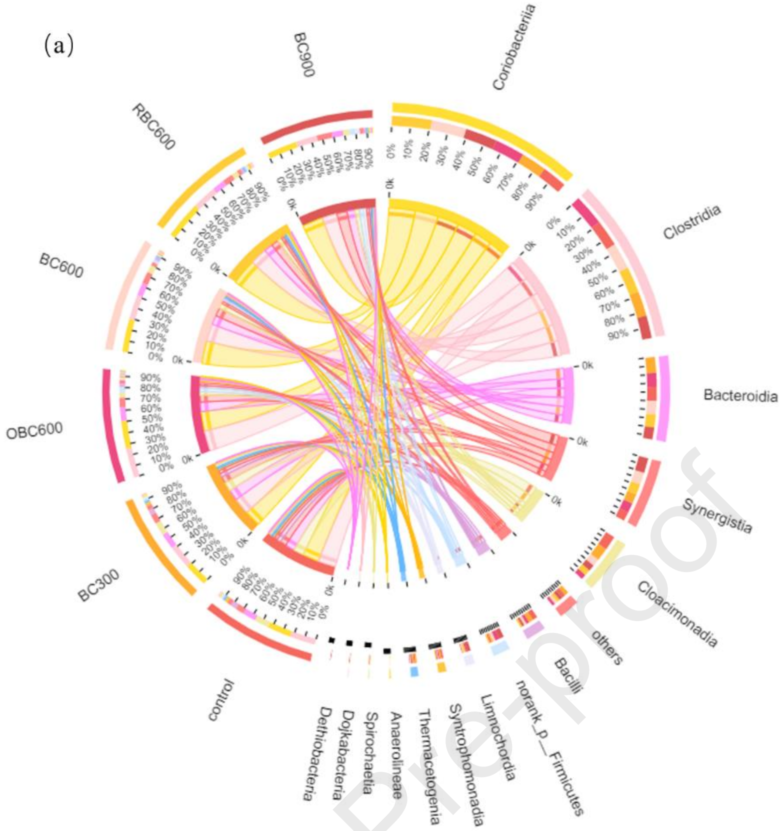
Table 3 Alpha diversity of the bacteria and archaea.

	Sample	Coverage	Sobs	Ace	Chao1	Shannon	Simpson
Bacteria	control	0.998	478.00	561.178	573.509	3.775	0.066
	BC300	0.999	529.00	594.659	612.720	3.791	0.067
	OBC600	0.999	529.00	592.953	587.043	3.767	0.081
	BC600	0.998	494.00	563.623	555.119	3.536	0.105
	RBC600	0.998	494.00	594.378	611.283	3.333	0.133
	BC900	0.999	486.00	551.638	552.455	3.641	0.091
Archaea	control	1.000	88.00	105.951	98.059	0.989	0.600
	BC300	1.000	86.00	91.265	87.800	1.287	0.466
	OBC600	1.000	93.00	105.355	100.059	1.380	0.418
	BC600	1.000	98.00	128.544	116.455	1.349	0.445
	RBC600	1.000	101.00	189.561	151.214	1.249	0.490
	BC900	1.000	111.00	148.325	137.714	1.126	0.468

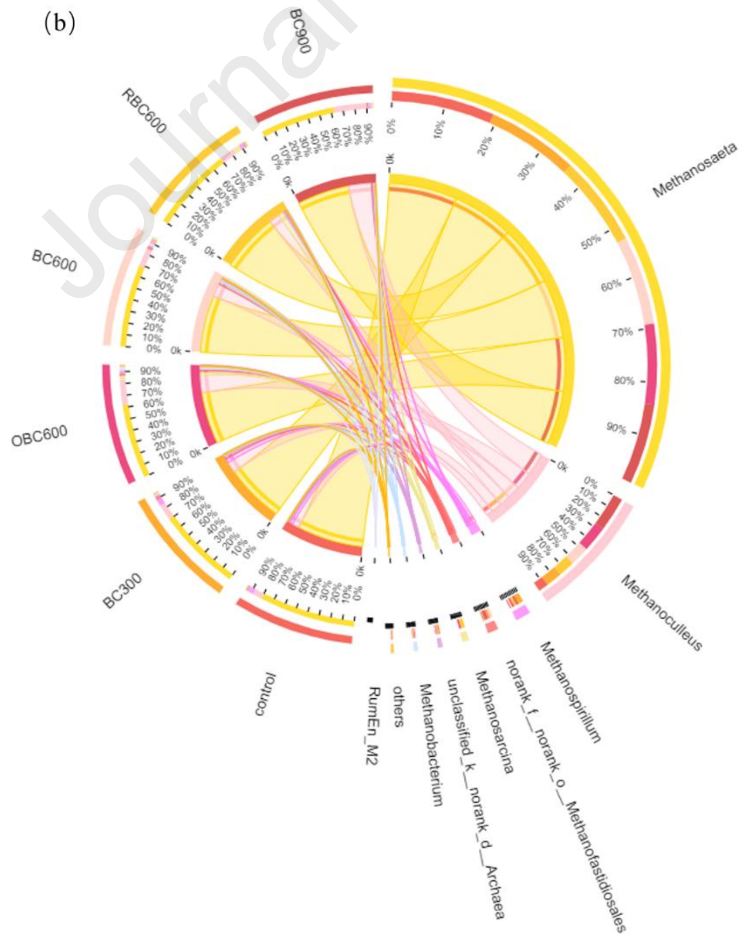
Fig.3 (a) and (b) reflects the distribution proportion of dominant species in each sample and the distribution proportion of dominant species in different samples through the visual circle diagram. In Fig.3(a), the class level bacterial community is dominated by *Coriobacteriia* (13-21%), *Clostridia* (14-17%), *Bacteroidia* (15-19%), *Synergistia* (14-23%) and *Cloacimonadia* (9.9-28%). The addition of biochar enhanced the relative abundance of *Coriobacteriia* and *Synergistia,* decreased the abundance of *Cloacimonadia*, but had little effect on the abundance of *Clostridia* and *Bacteroidia.* RBC600 had the highest *Coriobacteriia* (21%). BC900 had the highest *Synergistia* (23%). *Coriobacteriia* is associated with the production of formic, lactic and acetic acids(Li et al., 2022a). The increase of relative abundance of *Coriobacteriia* indicated that the addition of biochar promoted the formation of formic acid, lactic acid and acetic acid. The abundance of *Coriobacteriia* of RBC600 was 10.53% higher than BC600, indicated that reduction modification of biochar was more conducive to the occurrence of this process. Addition of biochar enriched methanogens that can only use monocarbon, acetic acid and hydrogen/carbon dioxide as substrates directly(Demirel and Scherer, 2008). Biochar effectively enriched *Coriobacteriia*, which has positive impact on methane generation. The control group has the most abundant *Cloacimonadia*. Some genera in *Cloacimonadia* convert amino acid, sugars or alcohols to VFAs(Ni et al., 2020). The addition of biochar reduced the relative abundance of *Cloacimonadia*, which possible be related to the enhancement of buffering capacity of anaerobic system by biochar. *Synergistia* is a typical symbiotic fermentation bacterium, usually symbiosis with hydrotrophic methanogenic archaea to overcome thermodynamic energy barrier and promote the degradation and metabolism of VFAs to generate methane(Świątczak et al., 2017). The addition of biochar effectively enriched *Synergistia*. The relative abundance of *Synergistia* is 14% (control), 15% (BC300), 15% (OBC600), 18% (BC600), 16% (RBC600) and 23% (BC900), respectively, corresponding to an increment of 7.14% (BC300), 7.14 (OBC600), 28.57 (BC600), 14.28% (RBC600) and 64.28% (BC900), respectively.

Methanosaeta and *Methanoculleus* are main archaeal genus in Fig.3(b). *Methanosaeta* is an obligate acetic acid nutritive methanogenic archaeon(Vavilin et al., 2008 , Zhang et al., 2018a). *Methanoculleus* is hydrogenotrophic methanogen. The relative abundance of *Methanosaeta* was similar in each group. However, the addition of biochar effectively enriched *Methanoculleus*. The relative abundance of *Methanoculleus* increased from 8.3% (control) to 13% (BC300), 21% (OBC600), 16% (BC600), 13% (RBC600) and 28% (BC900), respectively. Addition of BC 900 had the most abundant *Methanoculleus,* which was 3.37 times that of the control group. *Methanoculleus* is a typical syntrophic methanogenic Archaea(Wang et al., 2020). The addition of biochar can effectively enrich *Methanoculleus*, which may be related to the establishment of DIET(Lim et al., 2020).Because the addition of biochar effectively enriched *Synergistia* and *Methanoculleus.* Therefore, the addition of biochar may promote the establishment of DIET between anaerobic fermentation bacteria and methanogenic archaea.

(a)


Coriobacteriia
Clostridia
Bacteroidia
Synergistia
Cloacimonadia
others
Bacilli
norank_p__Firmicutes
Limnochordia
Syntrophomonadia
Thermacetogenia
Anaerolineae
Spirochaetia
Dojkabacteria
Dethiobacteria
control
BC300
OBC600
BC600
RBC600
BC900

(b)


Methanosaeta
Methanoculleus
Methanospirillum
norank_f__norank_o__Methanofastidiosales
Methanosarcina
unclassified_k__norank_d__Archaea
Methanobacterium
others
RumEn_M2
control
BC300
OBC600
BC600
RBC600
BC900

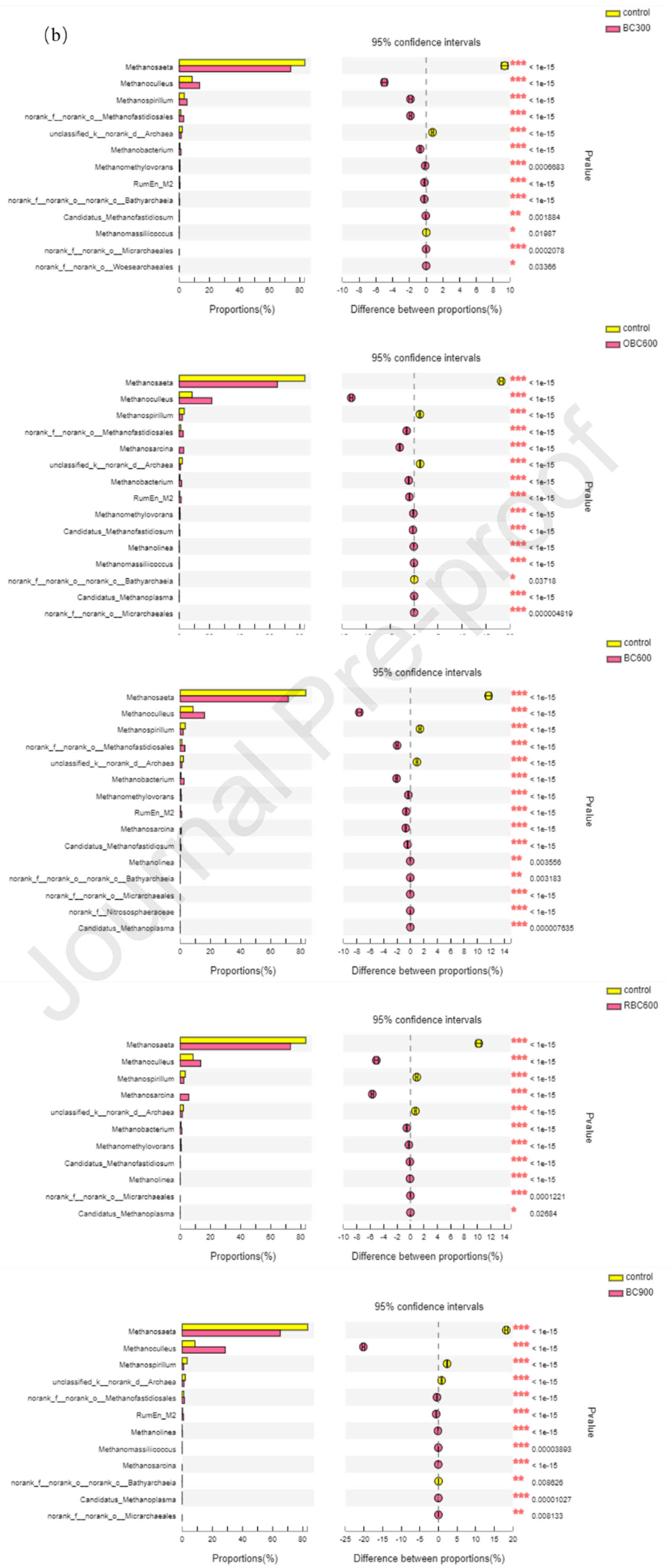
393

Fig. 3. Sample and species relationships diagrams of bacteria and archaea: (a) bacteria at class level; (b) archaea in genus level.

According to the abundance data of microbial communities obtained from the test samples, Fisher′ exact test was used to compare the differences of microbial abundance between two samples. Significant differences of bacteria and archaea between the control and add biochar group samples were obtained in Fig.4, respectively. Fig.4 (a) and (b) show the distribution histogram of microorganisms and the abundance difference between the species in two samples, within 95% confidence interval, as well as the markers of significance difference (the more marks represent the higher significance level) and the size of *p* value. There is a clear difference observed between biochar added group and the control, which correlated to the increased pyrolysis temperature.

(a)


control
BC300
95% confidence intervals
Clostridia
Bacteroidia
Cloacimonadia
Synergistia
Bacilli
Limnochordia
Spirochaetia
Desulfotomaculia
Thermotogae
Caldatribacteriia
Gammaproteobacteria
unclassified_k__norank_d__Bacteria
Leptospirae
Thermovenabulia
unclassified_p__Patescibacteria
Proportions(%)
Difference between proportions(%)
Pvalue
control
OBC600
95% confidence intervals
Clostridia
Coriobacteriia
Cloacimonadia
Synergistia
Bacilli
norank_p__Firmicutes
Syntrophomonadia
Limnochordia
Thermacetogenia
Dojkabacteria
Spirochaetia
Dethiobacteria
unclassified_k__norank_d__Bacteria
Gammaproteobacteria
Leptospirae
Pvalue
control
BC600
95% confidence intervals
Coriobacteriia
Cloacimonadia
Synergistia
Bacilli
norank_p__Firmicutes
Syntrophomonadia
Thermacetogenia
Limnochordia
Dojkabacteria
Desulfotomaculia
Spirochaetia
Dethiobacteria
Caldatribacteriia
Thermotogae
Leptospirae
Proportions(%)
Difference between proportions(%)
Pvalue
control
RBC600
95% confidence intervals
Coriobacteriia
Clostridia
Bacteroidia
Cloacimonadia
Synergistia
Bacilli
Syntrophomonadia
Limnochordia
Anaerolineae
Dojkabacteria
Desulfotomaculia
Dethiobacteria
Caldatribacteriia
unclassified_k__norank_d__Bacteria
D8A-2
Proportions(%)
Difference between proportions(%)
Pvalue
control
BC900
95% confidence intervals
Coriobacteriia
Clostridia
Bacteroidia
Synergistia
Cloacimonadia
Bacilli
norank_p__Firmicutes
Limnochordia
Syntrophomonadia
Thermacetogenia
Spirochaetia
Anaerolineae
Dethiobacteria
Dojkabacteria
Desulfotomaculia
Proportions(%)
Difference between proportions(%)
Pvalue


(b)
control
BC300
95% confidence intervals
Methanosaeta
Methanoculleus
Methanospirillum
norank_f__norank_o__Methanofastidiosales
unclassified_k__norank_d__Archaea
Methanobacterium
Methanomethylovorans
RumEn_M2
norank_f__norank_o__norank_c__Bathyarchaeia
Candidatus_Methanofastidiosum
Methanomassiliicoccus
norank_f__norank_o__Micrarchaeales
norank_f__norank_o__Woesearchaeales
Proportions(%)
Difference between proportions(%)
P-value
control
OBC600
Methanosarcina
Methanolinea
Candidatus_Methanoplasma
control
BC600
norank_f__Nitrososphaeraceae
control
RBC600
control
BC900

(*: $0.01<p\leq0.05$; **: $0.001<p\leq0.01$; ***: $p\leq0.001$)
Fig. 4. Analysis diagram of significant difference diagram of bacterial and archaea abundance between the control group and add different biochar: (a) bacterial in class level; (b) archaea in genus level.

3.3 Mechanism of biochar electrochemical properties on anaerobic digestion

The test results of EDC, EAC, EC and Zeta of biochar are shown in Fig.5 (a)-(d). The electrochemical properties are affected by oxidation and reduction modification. EDC and EAC are mainly related to the ability of gaining and losing electrons of OCFGs of biochar(Chacón et al., 2017). Tan (Tan et al., 2020)found that Zeta of biochar was also related to OCFGs. However, the conductivity of biochar mainly depends on the degree of carbonization(Gabhi et al., 2017). Its relationship with oxygen-containing functions has rarely been reported.

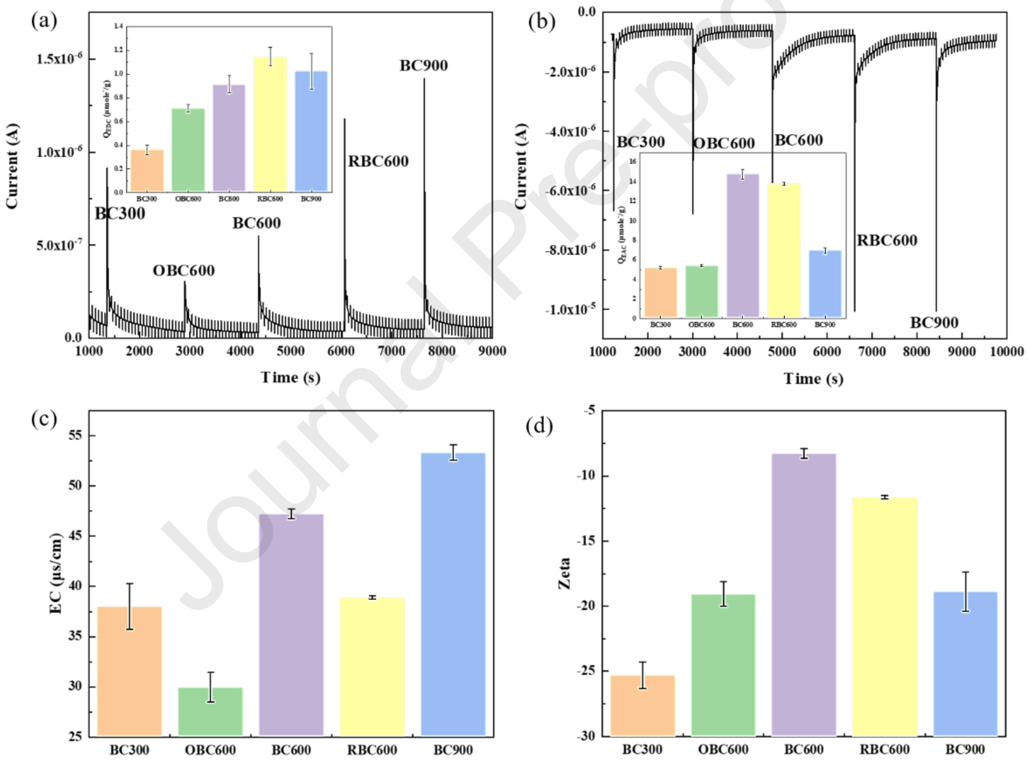


Fig.5. Electrochemical properties of biochar: (a) EDC; (b) EAC; (c) EC; (d) Zeta.

Three analytical methods, linear correlation, principal component analysis and machine learning, were accustomed to analyze the relationship between cumulative methane production and four electrochemical properties with different mathematical perspectives. Linear correlation is the most common analysis of the relationship between two variables in anaerobic digestion(Yu et al., 2018 , Liew et al., 2012). According to Fig.6 (a), the cumulative methane production is positively correlated with EDC, EAC, EC and Zeta potential, while the EDC is the most relevant factor (strongly correlated) following with EC (moderately correlated), EAC and Zeta potential (weakly correlated). Principal component analysis is a multivariate statistical method for dimensionality reduction and is widely accustomed to analyze the interaction between different factors(Li et al., 2021). Analyses using principal component analysis show that cumulative methane production has a stronger correlation with EC and EDC (Fig.6 (b)). Extreme Gradient Boosting (XGBoost) in machine learning algorithms has the advantage of fast learning speed and high prediction accuracy(Xu et al., 2021). XGBoost shows that EDC and EC are the main feature importance factors affecting cumulative methane production in Fig.6(c). However, there are different opinions on the contribution of electrical conductivity to methane production. Ye(Ye et al., 2018) found that higher conductivity promoted electron transfer between the syntrophic bacteria and methanogens and promoted methane generation. Baek (Baek et al., 2021) believes that the conductivity of the material itself does not improve anaerobic digestion performance. In this study, the conclusion based on three analytical methods revealed that both EDC and EC are the main factors affecting cumulative methane production. Multiple regression analysis was performed on them. The fitting equation: CMP=171.289[EDC]+1.331[EC]+220.651 (R^2=0.768). The coefficient of EDC is much larger than that of EC, indicating that EDC is the most dominant factor affecting the cumulative methane production.

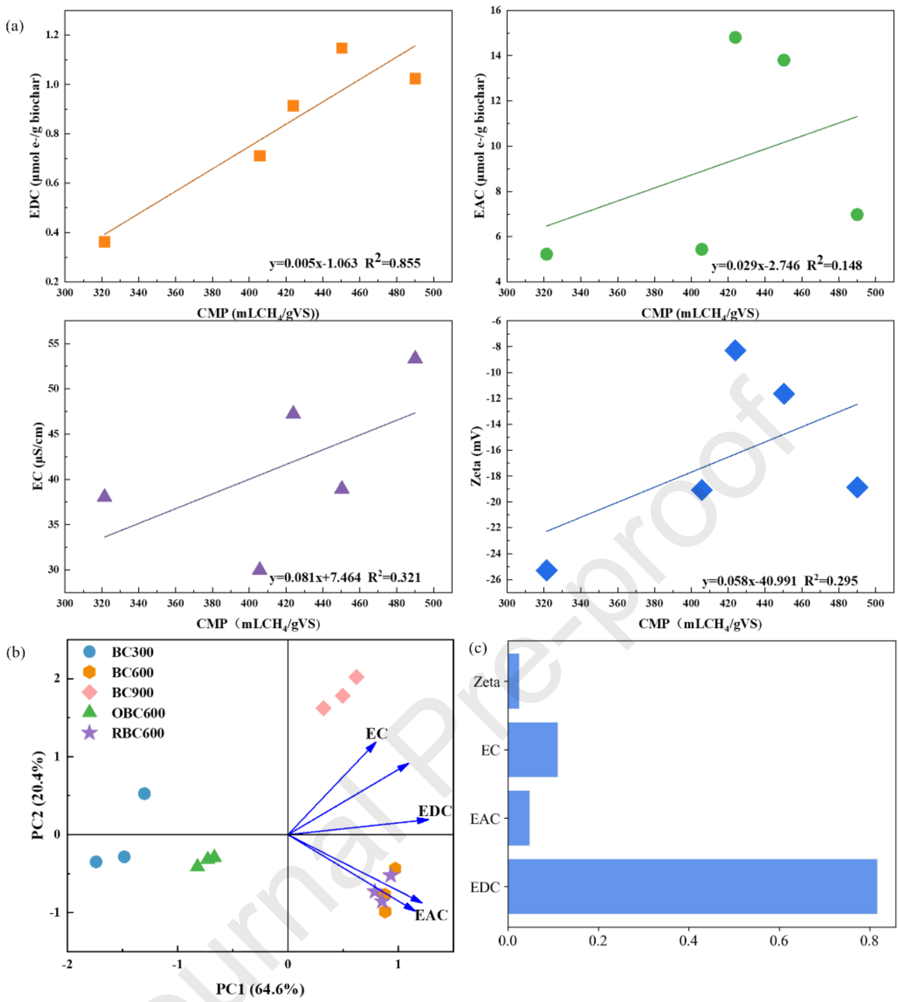


Fig. 6. The relationship between cumulative methane production and four electrochemical properties of biochar: (a) linear correlation; (b) principal component analysis; (c) XGBoost feature importance of cumulative methane production.

3.4 Relationship between electrochemical properties of biochar and its preparation process

Results from 3.3 reflected that the cumulative methane production were mainly depended on EDC and EC. According to previous studies, EDC is related to OCFGs and carbon structure(Zhang et al., 2018b). Below 650 °C, the EDC of biochar is mainly attributed to phenolic hydroxyl groups. Above 650 °C, the conjugated p-electron system associated aromatic structure became dominated (Zhang et al., 2018b). EC is related to the degree of carbonization. However, in this study, EC is also affected by oxidation and reduction modification. Suliman (Suliman et al., 2016) reported irregular fluctuations of conductivity with addition of biochar modified with air oxidation. Therefore, it is necessary to deeply research the relationship between the preparation process of biochar and EDC and EC, for purpose of finding the best preparation process of biochar.

The OCFGs of biochar were analyzed by XPS and Boehm titration. XPS is used to quantitatively characterize the element content and form of materials (XPS results are shown in Fig. S2). The C1s spectrum is divided into three peaks: the peak at 284.6-284.8eV belongs to aromatic or aliphatic carbon (C-C/C-H); the peak at 285.2-285.8eV is the phenolic and alcohol carbon (C-O); the peaks at 287.3-288.2eV are attributed to C=O. O1s spectrum is divided into two peaks: the peak at 530.8-531.2eV belongs to C=O; The peak at 533.2-533.8eV is attributed to C-O(Singh et al., 2014 , Quintana-Najera et al., 2021).

Table 4 XPS oxygen and carbon peaks of biochar.

Biochar	C spectrum	O spectrum
Biochar	C-O/C=O	C-O/C=O
BC300	3.29	3.50
OBC600	1.08	1.28
BC600	1.18	1.85
RBC600	0.90	1.13
BC900	0.55	0.73

Functional groups containing C-O bonds are mostly reductive groups with electron donating capacities, such as phenolic hydroxyl groups. Functional groups containing C=O bonds are mostly oxidizing groups with electron accepting capacities, such as carbonyl quinone groups. In Table 4, the ratio of C-O/C=O decreases with the raise of pyrolysis temperature, while that from RBC600 is lower than BC600 probably due to the NaOH neutralizes hydroxyl groups (Zhang et al., 2019a , Li et al., 2017a). The ratio from OBC600 was also lower than BC600, which could be explained by the successful introduction of C=O functional groups on the surface of biochar (Shen et al., 2019 , Wu et al., 2017).

Boehm titration was implemented for qualitative and quantitative analysis of oxygen-containing functions with different reaction capacities of alkali with different strengths and acid OCFGs on the surface of carbon (Fig. S3)(Fidel et al., 2013). It was obtained the specific contents of four OCFGs in biochar. The content of OCFGs decreases with the raise of pyrolysis temperature. After reduction modification, RBC600 contains only phenolic hydroxyl groups which is lower than BC600.

Elemental analyzer can quantitate the specific content of each element from biochar, while the ratios of different elements could reflect the properties of biochar. For example, H/C represents the degree of carbonization and aromatization of biochar; lower H/C value indicates high degree of aromatization and carbonization. O/C represents the oxidation of biochar while the higher O/C reveals stronger oxidation. It is well known that increasing of pyrolysis temperature could enhance the carbonization and aromatization of biochar. Koch (Koch and Dittmar, 2006) proposed the general aromaticity index (AI) and two thresholds, $AI > 0.5$ aromatic compounds were found in organic matter, and $AI \geq 0.67$ condensed aromatic compounds were found in organic matter. The higher AI indicates higher the degree of condensation. The unsaturation of carbon-carbon double bonds in the molecule should be evaluated before calculating AI. The double bond equivalent (DBE) represents the sum of unsaturated rings and double bonds in the molecule. DBE and AI are calculated by the Equation (2) and (3), respectively:

$$DBE = \frac{1 + [\mathrm{C}] - 0.5[\mathrm{H}] + 0.5[\mathrm{N}]}{[C]} \quad (2)$$

$$AI = \frac{1 + [C] - [O] - 0.5[H]}{[\mathrm{C}] - [\mathrm{O}] - [\mathrm{N}]} \quad (3)$$

As shown in Table 5, the degree of carbonization and aromatic properties are increased as a results of higher pyrolysis temperature. AI>0.67 of BC600 indicates that condensed aromatic compounds started to appear at with pyrolysis temperature above 600℃.

Table 5 Ratio of characteristic elements of biochar.

biochar	Mass fraction ratio		molar ratio	
	O/C	H/C	DBE	AI
BC300	0.411	0.089	0.491	0.26
OBC600	0.202	0.039	0.786	0.75
BC600	0.091	0.038	0.792	0.78
RBC600	0.021	0.036	0.800	0.80
BC900	0.030	0.021	0.892	0.89

Correlation analysis between EDC and phenolic hydroxyl groups and AI of biochar are shown in Fig.7 (a, b). EDC was found strongly correlated with phenolic hydroxyl groups (R^2=0.798) and AI (R^2=0.804), in which EDC was negatively correlated with phenolic hydroxyl groups and positively correlated with AI. Multiple regression analysis was performed on EDC and phenolic hydroxyl groups and AI that obtained the fitting equation as following: EDC=-0.909[Ar-OH] +0.624[AI]+0.539 (R^2=0.630). The coefficients of phenolic hydroxyl and AI were similar, indicating that phenolic hydroxyl groups and AI contributed equally to EDC. EC has a good correlation with BC300, BC600, and BC900 (R^2=0.942) (Fig. 7(d)), which is consistent with most conclusions: the conductivity of biochar depends on its carbonization degree(Gabhi et al., 2017). However, when OBC600 and RBC600 are added, the correlation becomes significantly worse (R^2=0.143), indicating that EC is greatly affected by oxidation and reduction modification (Fig. 7 (c)).

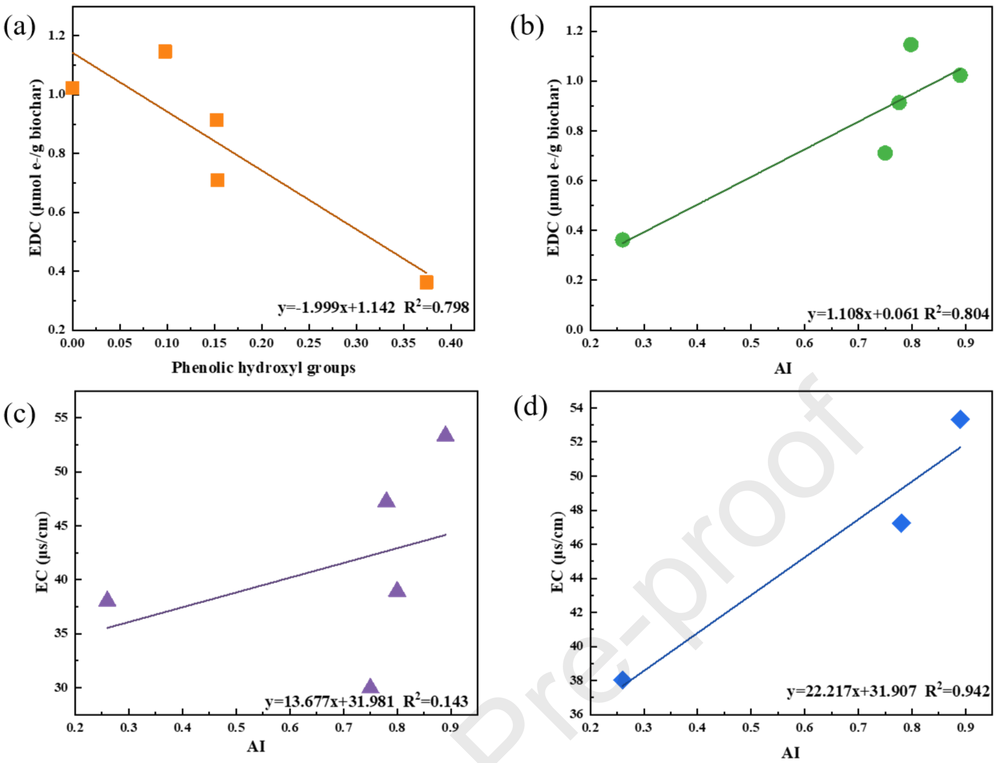


Fig. 7. Correlation analysis: (a) EDC and phenolic hydroxyl groups, (b) EDC and AI, (c) EC and AI, (d) EC and AI (onlyBC300, BC600, BC900).

In short, the increased pyrolysis temperature improved the carbonization of biochar, which further both enhance EDC and EC. After reduction modification, the phenolic hydroxyl content of biochar decreased, which had positive impact on EDC but unfavorable to EC. Since EC contributes less to methane production, the overall results are favorable for promoting anaerobic digestion.

4. Conclusions

In this study, the influence of biochar with different electrochemical properties on the methanogenic performance of anaerobic digesters of different substrates were compared. The results indicated that the addition of biochar to simple substrate-glucose can promote the methane production rate, while for complex substrate-food waste, the cumulative methane production was promoted. In the two anaerobic digestion systems, BC900 has the best effect on methanation. The effect of RBC600 is lower than BC900, but better than BC600, better than the control group. After BC900 was added, the cumulative methane production of food waste and the maximum methane production rate of glucose increased by 42.07% and 17.80%, respectively. The addition of biochar can effectively enhance the relative abundance of *Synergistia* (7.14-64.28%) and *Methanoculleus* (1.57-3.37 times), which is conducive to the establishment of DIET system. The ability of biochar to enhance anaerobic digestion largely depends on mainly EDC and EC. It was found that EDC and EC could be affected by changing the pyrolysis temperature and OCFGs of biochar. The enhance of pyrolysis temperature or the decrease of phenolic hydroxyl content under moderate temperature of biochar is beneficial to methane production. A new direction was pointed out for the preparation and improving the methanation promoting effect of biochar. The effect of oxidation and reduction modification on EC and EDC of biochar can be further studied in order to optimize the preparation process of biochar.

CRediT authorship contribution statement

Ziyan Sun: Experiment, Data curation, Methodology, Resources, Software, Writing - original draft. Lu Feng: Supervision, Writing – review & editing. Yeqing Li: Funding acquisition, Investigation, Methodology, Software, Writing - original draft. Yongming Han: Supervision, Writing – review & editing. Hongjun Zhou: Supervision, Writing – review & editing. Junting Pan: Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

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Highlights:

• BC900 increased the cumulative methane production of food waste by 42.07%;

• BC900 increased the maximum methane production rate of glucose by 17.80%;

• RBC600 was inferior to BC900, but superior to BC600 in anaerobic methanation;

• Electron donating capacities and electrical conductivity of biochar are keys factors;

• Higher pyrolysis temperature and lower phenolic hydroxyl of biochar are beneficial.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: