Enhanced Biogas Yield of Chinese Herbal Medicine Extraction Residue by Hydrothermal Pretreatment

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Chinese herbal medicine extraction residue (CHER) is a special organic waste produced in China. Because of the high content of lignocelluloses, CHER have a weak bioconversion efficiency for bio-products production. This study investigates the effect of a hydrothermal pretreatment (HTP, 140 to 220 °C, 15 min) on the organic matter solubilisation, biochemical methane potential, and methanation kinetics of CHER during anaerobic digestion (AD). The AD test was conducted with 5 g/L total solid at 35 °C for 30 d. The results showed that the HTP clearly improved the solubilisation of CHER, and the obtained soluble COD (%) reached over 30% (only 4.5% in untreated). Acetic acid, xylose, and glucose were found to be the main products in the hydrolysate. The methane yield and methanation speed of the treated CHER were also enhanced. The highest methane yield of 306 mL/g volatile solid was achieved at a HTP temperature of 180 °C, while the untreated control was only 175 mL/g VS. Moreover, a carbonisation phenomenon was observed at HTP temperatures over 200 °C, which resulted in a loss of organic matter and methane yield.

Keywords: Chinese herb-extraction residue; Hydrothermal pretreatment; Anaerobic digestion; Methanation kinetics; Biogas

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INTRODUCTION

Because of the contribution of modern advanced research methods in recent years, traditional Chinese medicine (TCM) science is rapidly progressing (Wang *et al*. 2014). Meanwhile, the industry and market of TCM has also been developing and growing in China and other Asian countries, such as Japan and South Korea. Moreover, many patents about TCM products used in relation to human health have been registered in the European or United States Patent Office. Although there is still a gap between TCM and compound medicine to confirm the pharmacological action, ingredients, and standardisation, TCM is on its way to developing internationalised drugs and health food for people globally (Teschke *et al*. 2014).

Chinese herb-extraction residue (CHER) is the main solid waste produced from the TCM production. According to statistics, approximately 1.5 million tons of CHER are being produced each year in China (Wang *et al*. 2010). The disposal of the waste has been a tricky problem for producers of TCM. Although some traditional methods have been proven to be effective for the disposal of CHER, such as sanitary landfills and incineration, these methods would easily cause a secondary pollution to groundwater, soil, or air if not operated strictly. The CHER has become one of the main organic solid wastes in China and could potentially be troublesome for other countries in the near future.

Due to the specific principle of TCM, one finished TCM is usually comprised of several or dozens herbal materials obtained from the plant root, stem, leaf, or fruit. The collected plant materials are firstly chopped and mixed, then they are extracted by hot water or water-ethanol, and the obtained soluble section is concentrated to produce medicine, while the extraction residue is usually treated as solid waste. At present, more than 200 types of herbal materials are being used to produce various TCM medicines in China. Different TCM factories often produce different kinds of medicines, which leads to the organic composition of CHER produced from different factories also being very different, which has been problematic for the disposal of CHER. An investigation focused on the organic composition and biogas production of six CHERs collected from different sites was studied in a previous assay (Wang *et al.* 2013). The result showed that the content of total lignocelluloses in those CHERs ranged from 46% to 55%, which is similar to the straw biomass, besides, the protein, fat, and total sugar contents, which varied with different degrees.

Organic wastes, such as farm manure, energy crops, and crop straw, can be used as materials to produce biogas though a bioconversion process *via* anaerobic digestion (AD), which has been widely reported and applied in recent decades (Mao *et al.* 2015; Horváth *et al*. 2016). However, there is minimal literature focused on the AD treatment of CHER until currently because CHER is a special waste that primarily exists in China and has a weaker biodegradability. A previous study by the authors found that CHER has a weaker methane yield due to its high lignocelluloses content (Wang *et al.* 2013). It had been demonstrated that lignocelluloses have a complex and rigid structure in biomass, and they are considered to be recalcitrant to biodegradability for biogas or ethanol production (Taherzadeh and Karimi 2008; Zheng *et al.* 2014).

Many pretreatment methods have been employed to improve the biodegradability of lignocellulosic biomass, such as mechanical (*e.g.*, milling), thermal (*e.g.*, liquid hot-water and steam explosion), chemical (*i.e.*, acid or alkaline), and biological (*e.g.*, white rot fungi and enzymatic) treatments (Taherzadeh and Karimi 2008; Shafiei *et al*. 2013). In some instances, the combination of different treatments can achieve a good efficiency, especially when the biomass has a high lignocellulosic crystallinity degree (Zheng *et al*. 2014; Matsakas *et al*. 2016). Although pretreatment methods have been demonstrated to be effective in improving the biodegradability of biomass, a universal optimal method for all types of biomass materials has not yet been developed. This can be attributed to the diversity of biomass, which can lead to varied feedstock characteristics, such as an organic composition, the complexity of cell-wall constituents, and the crystallinity degree of lignocellulose. Thus, it is hard to determine which method should be used as the pretreatment of biomass solely depending on its characteristics.

Among those pretreatment methods, sole hydrothermal pretreatment (HTP) is the most commonly used, with a temperature ranging from 160 to 260 °C, for the duration of a few minutes to upwards of a few hours (Chandra *et al*. 2012a; Barlage *et al.* 2014). HTP not only can avoid the consumption of chemical reagents, but also it can recover its own thermal energy to warm the material or the fermented tank (Zheng *et al.* 2014). Chandra *et al*. (2012a) studied the effect of HTP (200 °C, 10 min) on the methane production of rice straw, and the result showed that the hydrothermal pretreated substrate had resulted in a 222.0% increase of methane production relative to untreated rice straw substrate. The same pretreatment conditions were employed to enhance the methane yield of wheat straw, leading to 20% more methane yield compared to the untreated wheat straw (Chandra *et al.* 2012b). Kim *et al.* (2015) found that the HTP (180 to 210 °C) can increase the COD solubilization (30 to 37%) and soluble COD (sCOD) levels of waste activated sludge, in addition, while it reduced volatile solids (VS), and improved final methane yields. However, studies on the HTP pretreatment of CHER for improving biogas production have not been reported. Therefore, a series of HTP experiments without extra chemical reagents and instant explosion to CHER were performed in this study to investigate the effect of HTP on the organic matter solubilisation, biochemical methane potential (BMP), and methanation kinetics. The results of this study can also serve as a reference for exploring other possible combined treatments of CHER.

EXPERIMENTAL

Materials

The CHER used in this assay was collected from a TCM workshop located in the Hongshan district, Wuhan, China, and it was comprised of Dangshen (*Codonopsis pilosula* (Franch.) Nannf.), Huangqi (*Astragalus membranaceus* (Fisch.) Bunge.), Baizhu (*Atractylodes macrocephala* Koidz.), Gancao (*Glycyrrhiza uralensis* Fisch.), Shanyao (*Dioscorea opposita*), Danggui (*Angelica sinensis*), and Yinyanghuo (*Epimedium brevicornum* Maxim). The fresh CHER with a water content of 40 to 60% was primarily dried at 105 °C and then milled to 50- to 80-mesh powder prior to storage. The anaerobic sludge used as inocula was collected from an anaerobic digester for cattle manure at 35 °C (working volume: 500 L; pH: 7.52 ± 0.07; HRT: 20 days; total solids (TS): 45.5 ± 1.3 g/L), and was stored at 4 °C until use. The characteristics of the CHER and inocula are shown in Table 1.

Table 1. Characteristics of CHER and Inocula

Parameter	CHER	Inocula
Total solids (TS)	35.4	4.6
Volatile solids (VS)*	88.3	81.1
Total organic carbon (TOC)*	43.2	34.8
Total Kjeldahl nitrogen (TKN)*	1.8	2.1
Carbon-nitrogen ratio (C/N)	24.0	16.6
Hemicelluloses*	37.8	-
Cellulose*	20.1	-
Lignin*	5.8	-
Total protein*	11.3	-
Total fat*	6.4	-
Note: * based on dry matter		

Pretreatment

The HTP test was performed in a laboratory-scale autoclave (5 L, Zhaoyang Chemical Macinery Co., Ltd., Weihai, China). The CHER was diluted to a TS of 5% with tap water before pretreatment; specifically, 50 g of oven-dry matter was mixed with 950 g of water. An electric jacket was used to heat the autoclave, and a thermostat based on a

Fuzzy Algorithm was employed to control the reaction temperature. A magnetic stirring apparatus was installed on the top cover of the autoclave and connected to a stirring paddle within the autoclave; its stirring rate was set to 120 rpm during the HTP process. The reaction temperature ranged from 140 to 220 °C with an interval of 20 °C, and the top temperature was maintained for 15 min in the HTP process. When the duration time for each treatment reached the scheduled value, tap water was then run to cool the thermal sample *via* a stainless steel coil in the autoclave. Untreated CHER was used as the control.

BMP Experiment

An automated methane potential test system (AMPTS, Bioprocess Control, Lund, Sweden) was employed to investigate the BMP of the CHER samples. The AD test was conducted at 35 °C ± 1 °C in 500-mL glass bottles at approximately 50 g/L of total solids (TS) loading for 30 days. The inocula and sample were mixed in a 1/1 (V/V) ratio with a total working volume of 400 mL in each bottle. Each treatment was performed in triplicate, and two extra bottles were loaded with only inocula (200 mL) and fermented simultaneously to determine the effects of chemical oxygen demand (COD), VS, and methane yield produced from the inocula. The pH of all of the digesters was set to neutral using NaOH (2 mol/L), and each digester was flushed with N_2 for 3 min to remove the oxygen inside the bottle before beginning the test.

Calculations

The pretreatment severity was calculated according to Eq. 1, as described by Overend *et al.* (1987),

$$SF = \log(t \times \exp(T - 100)/14.75) \qquad (1)$$

where *SF* is the severity factor of HTP, *t* is the residence time (min), and *T* is the pretreatment temperature (°C).

The sCOD ratio (%) in the hydrolysate was calculated according to Eq. 2,

$$sCOD\text{ratio}(\%) = sCOD/total\ COD \times 100\% \qquad (2)$$

where *sCOD* is the amount of soluble COD in the hydrolystate after pretreatment and the *total COD* is detected using the untreated CHER sample. The first-order kinetic model expressed as Eq. 3 simulated a kinetic model of biogas production, and the fitted process was conducted according to the method introduced by Budiyono and Sumardiono (2013),

$$y(t) = y_m(1 - \exp(-kt)) \qquad (3)$$

where $y(t)$ represents the fitted methane yield (mL/g VS) at a given time, y_m is the actual ultimate methane yield (mL/g VS), *k* stands for the first-order rate constant (d^{-1}), also called the methanation rate constant (d^{-1}), and *t* represents the anaerobic digestion time (d).

The theoretical methane potential (y_{th}, mL/g VS) of untreated substrate was calculated based on the stoichiometric conversion of organic matter (Giuseppe *et al.* 2013),

$$y_{th} = 415 \times carbohydrates + 496 \times protein + 1014 \times fat \qquad (4)$$

where carbohydrates represent the total carbohydrates content calculated as VS subtracted by the content of protein and fat.

Substrate biodegradability (BD) was determined by comparing the cumulated methane yield at the end of the test with the theoretical potential (Giuseppe *et al.* 2013),

$$BD(\%) = \frac{y_m}{y_{th}} \times 100 \tag{5}$$

where y_m is the actual ultimate methane yield (mL/g VS) and y_{th} is the theoretical methane potential (mL/g VS).

Methods

Analytical

The methane and carbon dioxide concentrations in the biogas were determined with a gas chromatograph (GC-6890N, Agilent Inc., Santa Clara, USA) equipped with a stainless steel column (1.5 m × 3 mm I.D. carbon molecular sieve TDX-01: 1.5 nm to 2.0 nm) and a thermal conductivity detector (TCD) that used argon as the carrier gas. The volatile fatty acids (VFAs) were determined by the same instrument equipped with a flame ionisation detector (FID) and a capillary column (30 m × 0.25 mm) (Agilent 1909/N-133, Agilent Inc., Santa Clara, USA) with nitrogen used as the carrier gas. The TS, VS, COD, soluble COD (sCOD), pH (Sartorius basic pH meter PB-10, Gottingen, Germany), total organic carbon (TOC), and total Kjeldahl nitrogen (TKN) were determined according to standard methods (APHA 2004). Soluble sugars (glucose, xylose, and arabinose) were determined by a high efficiency liquid chromatography (Agilent 1200; column, Aminex HPX-87H, 7.8 mm × 100 mm, 65 °C; mobile phase 5 mmol/L H_2SO_4; flow rate, 0.6 mL/min) equipped with a refractive index detector at 45 °C. Moreover, 5-hydroxymethyl furfural (HMF) and furfural were measured by UV-detector after HPLC determination at the same conditions. Total fat was measured as the weight of the dried ethyl ether extract obtained by prolonged extraction at 45°C for 12 h using a Soxhlet apparatus (Luque-García and Castro 2004), and total protein was calculated as TKN×6.25 (Giuseppe *et al.* 2013). The contents of hemicelluloses, cellulose, and lignin were determined with an automatic fiber analyzer (ANKOM A2000i, US) according to the method previously reported (Soest *et al.* 1991). All reagents (Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) used were of analytical grade. All of the measurements were conducted in triplicate, and the averaged data with a standard deviation lower than 5% are presented.

Statistical analysis

All of the experimental data were statistically analysed using a one-way analysis of variance (ANOVA) using the software SPSS 19.0 (IBM, Armonk, USA). The Student-Newman-Keuls (SNK) test at $P \leq 0.05$ was used as the separate means of statistically significant traits. The graph and data were processed *via* Originpro 8.0 (Originlab, Northampton, USA).

RESULTS AND DISCUSSION

Organic Matter Solubilisation

The main purpose of the pretreatment was to improve the solubilisation of the organic matter in the biomass, such as the starch, fats, proteins, and the amorphous part of lignocellulose (hemicellulose and cellulose). Generally, the released sCOD is used to evaluate the solubility of the organic matters in biomass where more solubility represented more bioavailability. For the AD process, the sCOD is determined as the substance that could be readily used to produce methane during anaerobic digestion (Kim *et al*. 2015). As shown in Table 2, all the sCOD values after HTP were significantly higher than the untreated sample, and the highest sCOD of 496.7 mg/L was observed at T3 (180 °C) with a ratio of 33.9% in the total COD of the untreated sample. However, the sCOD clearly declined at the temperatures of 200 and 220 °C. During the actual experiment, large amounts of dark brown powders were found in the treated samples of T4 and T5. This could be interpreted by the phenomenon of hydrothermal carbonization. In hydrothermal processes, the solid material is surrounded by water during the reaction, which is kept in a liquid state by allowing the pressure to rise with the steam pressure in (high)-pressure reactors. With process temperatures of up to 220°C and corresponding pressures up to approximately 20 bar, the organic matter in the biomass began to be thermochemically decomposed in the absence of oxygen, very little gas (1 to 5%) is generated, and most organics remain as or are transformed into solids (charcoal) (Libra *et al*. 2011). This was also reflected from the difference of the total COD values (Table 2), in which the total CODs of T4 and T5 were significantly lower than the other treatments ($P \leq 0.05$), which also indicated that some organic matter was lost in the HTP process at temperatures over 200 °C.

Table 2. Characteristics of Untreated Control and Treated Samples *via* HTP

Treatments	Temp. (°C)	Severity Factor	Total COD (mg/L)	sCOD (mg/L)	sCOD ratio (%)	pH
Untreated	-	-	1466.2^a	65.8^a	4.5	7.45
T1	140	2.4	1449.7^a	475.1^b	32.4	6.84
T2	160	2.9	1455.5^a	478.6^b	32.6	6.77
T3	180	3.5	1392.4^a	496.7^c	33.9	6.49
T4	200	4.1	1184.0^b	452.1^d	30.8	6.53
T5	220	4.7	1043.1^c	332.1^e	22.7	6.68

Note: Top temperature is maintained for 15 min, heating rate and cooling rate are 5-10 °C/min and 20-30 °C/min, respectively. Different letters represent the difference is significant ($P \leq 0.05$).

Hydrolysate Composition

Volatile fatty acids

As illustrated in Fig. 1, acetic acid was the predominant VFA produced during the HTP, while all of the other VFAs were minimal, and pentanoic acid was only found in treatments at temperatures above 200 °C. This result was consistent with the previous relative findings reported by Ahring *et al.* (2014) and Di Girolamo *et al.* (2013). The acetic acid produced in the pretreatment was positively correlated with the hemicellulose content in the biomass, which was due to the release of the acetyl groups bonded to the chains of hemicellulose (Kaparaju *et al*. 2009). Compared with cellulose, the hemicellulose was more amorphous, random, and branched heterogenic polysaccharides of various pentoses; thus, it is very sensitive to heat, acid, or alkali (Zheng *et al*. 2014). In the present study, a high acetic acid content was observed in the hydrolysate of CHER, which indicated that the HTP could effectively remove the acetyl groups from the hemicellulose of CHER. Moreover, the acetic acid content increased as the temperature increased, while it decreased as the temperature reached 220 °C (Fig. 1). Previous studies also reported that the hydrolysis of hemicellulose started to happen at 150 °C, and the temperature was a critical parameter in the thermo-chemical hydrolysis of hemicellulose (Bobleter 1994; Garrote 1999).

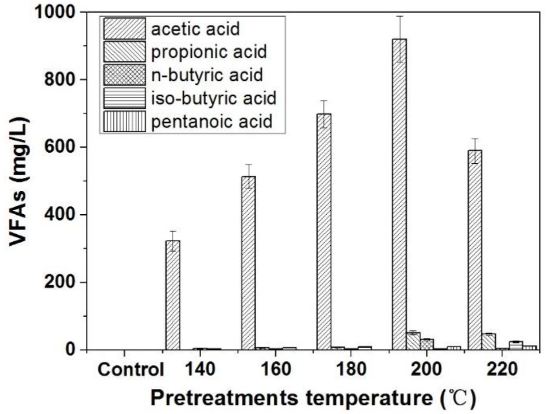

Fig. 1. The VFAs produced from the different HTP treatments

Sugars and inhibitors

Generally, three soluble sugars are produced in the hydrolysis of carbohydrates: glucose comes from starch and cellulose, and xylose or arabinose are obtained from hemicellulose. Table 3 shows that the sugars in the hydrolysate of CHER were primarily composed of glucose and xylose, while the content of arabinose was negligible. The highest total sugars yield of 38.1 g/kg TS was observed in the HTP at 180 °C, followed by 160 and 200 °C; the lowest total sugars content was found at 140 and 220 °C. Because of their crystalline and thermo-resistant structure, glucose polymers are very difficult to degrade into mono-sugars at temperatures below 200 °C without the addition of catalysts (Zhao *et al*. 2012). In contrast, hemicellulose can be readily dissolved at temperatures above 150 °C because of the special structure of amorphous heteropolymers (Zhao *et al*. 2012). Hence, the obtained glucose was clearly less than that of the xylose in the hydrolysate of CHER (Table 3). This was consistent with the results reported in previous studies (Bari *et al*. 2013; Di Girolamo *et al*. 2013).

Table 3. Characteristics of the Hydrolysate of CHER

Pretreatment	Glucose	Xylose	Arabinose	Total Sugars	HMF	Furfural
	(% TS)				(g/kg TS)	
Untreated	0	0	0	0	0	0
140	5.2^a	15.4^a	2.2^a	22.8^a	0	0
160	7.8^b	24.0^b	1.7^b	33.5^b	0	0
180	9.2^c	28.9^c	2.4^a	40.5^c	0.05^a	0
200	7.5^b	24.8^b	1.2^b	33.5^b	0.15^c	0.07^a
220	5.4^a	18.5^d	1.6^b	25.5^d	0.17^c	0.10^b
Note: Different letters indicate significant difference ($P \leq 0.05$); HMF, 5-hydroxymethyl furfural.						

HMF and furfural are the main two fermentation inhibitors that have been seen to originate from the degradation of glucose and xylose following pretreatment under severe conditions (Shafiei *et al.* 2015). In present assay, the two noxious compounds were not found in the pretreatments below 180 °C, and only slight HMF was detected in the pretreatment of 180 °C, while both HMF and furfural simultaneously appeared when the treatment temperature rose to 200 °C and 220 °C (Table 3). The HMF and furfural yields shown in Table 3 are much less than that (HMF: 0.22–0.36 g/kg; furfural: 0.14–0.32 g/kg) of acid H_2SO_4 pre-soaking (2% w/w) treated Giant reed (Di Girolamo *et al.* 2013). These findings are in accordance with the previous report that the HTP added acid catalyst will be easier to produce inhibitors than that without acid addition (Mood *et al.* 2013).

BMP Test

Batches of AD tests were performed over 30 days to evaluate the BMP of the CHER samples. The results showed that all of the treatments except for T5 (220 °C) enhanced the trait with respect to the untreated CHER (Fig. 2 and Table 4).

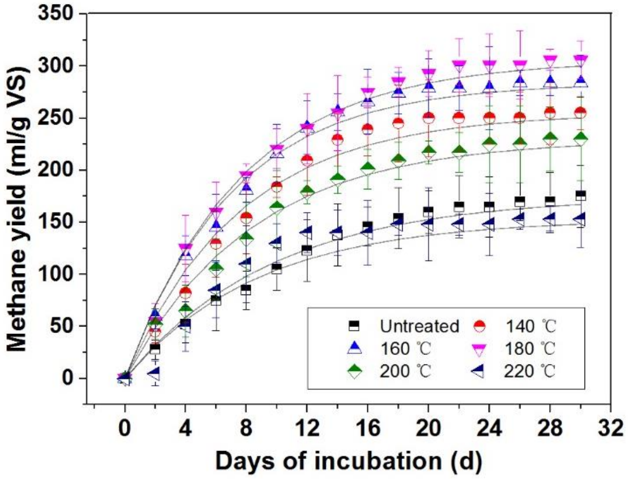

Fig. 2. Cumulative methane yield during the anaerobic digestion of the untreated control and HTP treatments, and the fitted functions (lines, equation parameters, and regression coefficients are shown in Table 4.)

Table 4. Equation Parameters and Regression Coefficients of the Functions Fitted in Fig. 4

Treatments	y_m (CH_4, mL/g VS)	*k* (d^{-1})	R^2_{adj}	*BD* (%)
Untreated	175	0.103 (0.004)	0.9854	42
140 °C	255	0.132 (0.006)	0.9811	62
160 °C	284	0.143 (0.005)	0.9889	69
180 °C	306	0.131 (0.003)	0.9942	74
200 °C	230	0.119 (0.004)	0.9858	56
220 °C	153	0.115 (0.004)	0.9861	37

Notes: y_m, potential methane yield; *k*, methanation rate constant; and VS, volatile solids; *BD* (%) is the substrate biodegradability calculated by Eq. (5) (y_m/y_{th}*100, y_{th} is 413 mL/g VS calculated by Eq. (4)).

The methane production was initiated after two days of incubation, and the cumulated methane yield followed a similar pattern in these four pretreatments, although different final levels were attained (Fig. 2). As shown in Table 4, the exponential rise to the max function of all treatments explained a very high share of total variation ($R^2 > 0.98$). The minimum methane yield of 153 mL/g VS was found in T5, which was lower than the untreated control's 175 mL/g VS (- 13%). The samples T1, T2, T3, and T4 achieved significant gain in the potential methane yield (+46%, +62%, +75%, and +31% *vs.* the untreated, respectively). According to previous literature, the increases of methane yield are usually different for different materials and pretreatment conditions; the growth rates of methane yield resulted from sole HTP are usually at the range of 0 to 250%, mainly concentrated in 10 to 100%. Di *et al.* (2013) studied the effects of HTP on the methane production of Giant reed, and the result showed that four HTP treatments without acid catalyst achieved a 10%, 7%, 23% and 4% yield gain in different conditions (150 to 180 °C, 10 to 20 min). Chandra *et al.* (2012a,b) reported that the methane growth rates of rice straw and wheat straw were 222% and 20% in same pretreatment condition (200 °C, 10 min). O-Thong *et al.* (2012) reported that an increase of 29% (from 161 to 208 mL/g VS) was found on the methane yield of oil palm empty fruit bunches treated by HTP. Thus, a growth of 31 to 75% was found in the present assay, which suggested the HTP was effective in improving the methane yield of CHER. In addition, all of the treatments showed faster kinetics than the untreated control (Table 4), which also indicated that the HTP process could clearly improve the bioconversion efficiency of CHER.

CONCLUSIONS

1. Hydrothermal pretreatment (HTP) was found to be effective for improving the solubilisation of Chinese herbal medicine extraction residue (CHER), and the highest sCOD (%) of the hydrolysate reached 34% (only 4.5% in the untreated).
2. The HTP performed at 140 to 200 °C was found to contribute to the biochemical methane potential (BMP) of the CHER, and the highest methane yield of 306 mL/g volatile solids (VS) was obtained from the treatment at 180 °C.
3. The BMP decreased as the HTP temperature increased up to 200 and 220 °C, which indicated that HTP at an excessively high temperature would be disadvantageous to the bioavailability of CHER. Therefore, it might be necessary to combine HTP with other methods (*e.g.*, dilute acid or alkaline) for further improvement of the BMP of CHER.
4. The regression analysis of the fitted functions of BMP indicated that the kinetics was also accelerated greatly by the HTP, and the top kinetics value of 0.143 (k, d^{-1}) was obtained in the HTP at 160 °C.

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