Sludge char-to-fuel approaches based on the hydrothermal fueling IV: fermentation

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ABSTRACT

Sewage sludge was subjected to hydrothermal fueling (HTF) (330 °C for 40 min), obtaining hydrochar at 13.5 MJ kg⁻¹. The higher heating value (HHV) of the raw sludge was related to its fatty acid content. The results showed that although the higher heating value (HHV) of the raw sludge was related to its fatty acid content, with the intensification of HTF, the increase in aliphatic/cyclic amino acids determined the production of HHV in the hydrochar. In order to increase the content of fatty acids and amino acids, the sludge was fermented. However, the Bacteroidetes consumed the organic matter too early, which was detrimental to the production of HHV. Therefore, appropriate sludge fermentation is recommended to restrict excessive Bacteroidetes proliferation, decompose lipids to saturated fatty acids, and convert proteins to aliphatic/cyclic amino acids to increase the efficiency of converting sludge to fuel.

Key words: amino acids, Bacteroidetes, fatty acids, HHV, hydrothermal fueling

HIGHLIGHTS

- Hydrochar of 13.5 MJ/kg produced at 330 °C for 40 min can be used as fuel.
- HHV of sludge relates to fatty acids, while HHV of hydrochar relates to amino acids.
- Saturated fatty acids, aliphatic & cyclic amino acids play a role in HHV production.
- Over-proliferation of Bacteroidetes harmful to HHV production is to be controlled.

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**INTRODUCTION**

With increasing urbanization of cities and the development of municipal sewage systems, sewage sludge disposal has attracted increasing concern. To reutilize sludge resources, a preliminary study on pyrolysis was carried out. First, blended pyrolysis could effectively increase the fatty acid content in the product and increase its higher heating value (HHV) (Qin et al. 2019b). Second, when the moisture content of the sludge reached 20–40%, the HHV of the product obtained via catalytic pyrolysis increased up to 50.61 MJ kg\(^{-1}\) (Qin et al. 2018). Recently, it was discovered that the primary heat-producing matter in sludge was the cell phase and protein. On the premise that the sludge is not dehydrated, increasing the cell phase and protein content can significantly increase the HHV of pyrolysis products (Qin et al. 2019a). A series of studies have shown that the macromolecular components in sludge are the key factors affecting its use as fuel. The role of different macromolecular components in the cell phase, such as lipids and proteins, needs to be further studied.

Although proper heat treatment gives the sludge the potential to be used as fuel, the high moisture content requires mechanical dewatering and drying, which consumes energy. Therefore, it is not a cost-effective solution (Wang et al. 2019). Hydrothermal treatment is performed at relatively low temperatures (180–350 °C) and under autogenous pressure (2–10 MPa). The hydrothermal product is hydrochar with high hydrophobicity which is easily dehydrated (Wang et al. 2018). After subsequent mechanical dewatering, the moisture content of the sludge can be reduced to approximately 30% (Wang et al. 2014), which allows the hydrochar to be used directly as fuel without the need for auxiliary materials to support combustion. In addition, the operating cost of hydrothermal treatment combined with mechanical dewatering was significantly lower than that of thermal drying (Zhao et al. 2014). The calorific value of hydrochar is close to that of lignite and can be burned to recover residual energy (Fytili & Zabaniotou 2008). Based on these priorities, hydrothermal fueling (HTF) has become the most cost-effective and promising method for sludge reuse.

The HTF process includes depolymerization and polymerization of sludge. Almost 90% of the volatile organic compounds in the sludge were proteins, lipids, and polysaccharides (Yuan et al. 2006). During the HTF process, proteins were more susceptible to the hydrothermal temperature, making them decompose faster than polysaccharides (Wang & Li 2015), followed by lipids (Hii et al. 2014). These compounds were decomposed into amino acids and fatty acids. Amino acids have relatively low activation energy and undergo deamination and decarboxylation, and can be then further decomposed (Abdelmoez et al. 2007; Peterson et al. 2008) to short-chain volatile fatty acids and hydrocarbons (Klingler et al. 2007). The active intermediates produced in the hydrothermal process can be polymerized and recombined (Yuan et al. 2006; Wang et al. 2019), while some
insoluble components produce high-carbon solid fuel (Kruse et al. 2013; Wang et al. 2019). All of these changes ultimately allow for the conversion of sludge into fuel. Sludge is often not transported and disposed in time, and biological fermentation occurs naturally as it accumulates. It is unclear how HTF is carried out after sludge fermentation. In order to maximize the conversion of sludge into fuel, this research attempts to combine the effects of anaerobic fermentation followed by hydrothermal fueling.

In order to improve the conversion efficiency of macromolecular organic matter to fuel, the temperature, time and stirring speed in the HTF process were changed, and HCl was added to accelerate the hydrolysis of macromolecular organic matter. Compare the difference in HHV produced by HTF processing fermented/ raw sludge, it is to analyze the influence of various factors on fuel conversion efficiency. In addition, the changes in the content of fatty acids and amino acids during the HFT process were measured. The relationship between organic matter and the HHV produced was analyzed to determine their impact on energy conversion. Finally, bio-fermentation was used to decompose proteins and lipids to study the influence of microbial communities on the HTF of sludge. The purpose of this study is to convert fermented sludge into fuel, which seems to be the most promising method of sludge reuse.

MATERIALS AND METHODS

Materials
Municipal sludge was collected from the centrifugal dewatering workshop of the Xi’an Fourth Municipal Wastewater Treatment Plant from August to December 2019. The wastewater treatment used the A²O process, and sludge was collected from a combination of primary and secondary treatment. All sludge samples were stored at 4 °C before use. The characteristics of the sludge are listed in Table 1.

Hydrothermal fueling experiment
The sludge samples collected in August were packed in a 1 L anaerobic fermentation reactor to complete the anaerobic fermentation process. The anaerobic fermentation was controlled at 30 ± 1 °C for 60 days. In addition, hydrochloric acid (0.5 mol L⁻¹) was manually added to the same batch of sludge to artificially control its hydrolysis. HTF was carried out in a 500 mL reactor (MC500, Senlang, China). A 100 g of sludge was placed in the reactor and filled with inert gas for 5 min to remove residual air in the reactor. When the residual air in the reactor was completely removed, the reactor was sealed. During the experiment, the reaction temperatures (310, 330, 350, 370, and 390 °C), running times (20, 30, 40, 50, and 60 min), and stirring speeds (0, 100, and 200 rpm) were controlled. After the reaction, the reactor was cooled to room temperature, and the hydrochar was removed. Figure 1 displays the experimental flowchart. To determine the content of amino acids and fatty acids, the hydrochar was then dried in an oven at 105 °C for 12 h, ground, and passed through a 150 μm sieve for storage. The HHV of combustion was measured using an automatic calorimeter (HYHW-8A, Huayu, China). The types and contents of fatty acids and amino acids were analyzed using gas chromatography-mass spectrometry (GC-MS) and high performance liquid chromatography (HPLC). All experiments were repeated three times.

Analysis of raw sludge and hydrochar
After saponification and methylation of 0.5 g of sludge/hydrochar, 1 mL of premixed solvent (n-hexane: methyl tertbutyl ether = 1:1) was added for extraction. The upper organic phase was extracted and used for GC-MS. The injection port and flame ionization detector temperatures were 250 °C and 300 °C, respectively. The GC oven program was as follows: 40 °C with a linear temperature gradient of 50 °C min⁻¹ to 280 °C and held for 2 min. 1 μL of sample was injected with a split ratio of 45:1. The analysis of fatty acids was as previously described (Qin et al. 2018).

A total of 0.1 g of sludge/hydrochar was added to a 20 mL hydrolysis tube, which was then filled with hydrochloric acid extract, vented with nitrogen, heated at 150 °C for 8 h, and finally centrifuged to extract 1 mL of supernatant. After

Table 1 | Characteristics of sewage sludgea used in the experiments

| Sample | pH     | MC (%)  | VM (%)   | Ash (%)  | FC (%)  | HHV (MJ kg⁻¹) |
|--------|--------|---------|----------|----------|---------|---------------|
| SSa    | 7.07 ± 0.28 | 80.1 ± 1.40 | 45.4 ± 0.32 | 51.9 ± 0.41 | 2.7 ± 0.12 | 10.2 ± 0.45   |

aMC, moisture content; VM, volatile matter; FC, fix carbon; HHV, higher heating value.
derivatization with phenyl isothiocyanate, the extract was measured using HPLC (C₁₈ column, elution system was acetonitrile: water = 8:2) (NS4201, Hanbang, China).

Phenyl isothiocyanate, triethylamine, methanol, and acetonitrile were purchased from Sigma-Aldrich (MO, USA). All reagents were analytical reagent grade. The purity of the gas used in the experiment was approximately 99.9%. Gene sequencing reagents were purchased from Life (Thermo Fisher, USA). The DNA of the microbial community in the sludge was extracted and amplicons were sequenced using the PGM platform. Bacterial 16S rRNA genes were PCR-amplified with forward primer 338F (5′-ACTCCTACGGGAGGCAGCA-3′) and reverse primer 806R (5′-GGACTACHVGGGTWTCTAAT), targeting the V3 and V4 regions. Water was prepared using a MilliQ apparatus (Millipore, USA).

Statistical analysis
Redundancy analysis (RDA) of the fatty acids and HHV patterns was conducted using Canoco for Windows 4.5. Values are reported as the means of replicates.

RESULTS AND DISCUSSION

Optimized process for hydrothermal fueling
Different operating temperatures and times will affect the conversion of sludge into fuel. Determination of the optimal working temperature and times can effectively control costs and improve the practicability of the technology. In addition, the uniformity of the sludge heating must be considered.

As shown in Figure 2(a), the temperature increased from 310 to 390 °C, while Figure 2(b) shows that the internal temperature rose from 50 to 230 °C, which had a significant impact on the generation and storage of HHV. The generated HHV first increased with temperature, reaching a peak of 13.5 MJ kg⁻¹ at 330 °C, and then decreased (see Figure 2(a)). The increase in internal temperature ruptured the cells and released the macromolecular organic matter, then broke the water–hydrogen bond to produce H⁺ and OH⁻, decomposing the macromolecule into small units of molecular organic matter (Wang et al. 2019). Subsequent dehydrogenation and deamination reactions of small molecular organic material increased the relative carbon content in hydrochar (Wang et al. 2018). The atomic ratios of O/C and H/C decreased accordingly (Sevilla & Fuertes 2009; Wang et al. 2019), increasing HHV production.

For a set temperature of 330 °C, it took 53 min for the internal temperature to reach 170 °C. When the set temperature was 390 °C, the time to reach 170 °C was shortened to 37 min. It was reported that above 170 °C, the decomposition of lipids leads to the production of large amounts of fatty acids (Wilson & Novak 2009). When the set temperature was 310 °C, the internal temperature reached 180 °C in 60 min, but when the set temperature was 390 °C, it exceeded this temperature in 40 min. Once it exceeded 180 °C, the protein attached protons to the nitrogen atom of the peptide bond and broke it (Brunner 2009). Hydroxide ions from water molecules attached to the carbocation to form carboxy (Zhu et al. 2011), and the protein was hydrolyzed into amino acids (Peterson et al. 2008). The increase in fatty acids and amino acids improved the production of HHV in the hydrochar. However, the external temperature was set too high, causing the internal temperature to continue to rise. When the temperature exceeded 180 °C for an extended period, secondary cracking occurred, converting organic matter into CO₂, CO, and other gases, thereby reducing the total content of organic matter and limiting the production of HHV.

Figure 1 | Experimental flowchart.
Along the time axis, it can be seen from Figure 2(a) that the HHV increased to the maximum value of 13.5 MJ kg\textsuperscript{−1} with the time from 20 to 40 min, and then decreased with the rest of the time. This phenomenon shown that different reaction times play an important role in the energy conversion of raw sludge during HTF. In a short residence time, amino acids are decarboxylated and deaminated to form volatile fatty acids, which is beneficial for the production of HHV (Klingler et al. 2007). A longer running time was likely responsible for causing the dissolved organics to polymerize, forming hydrochar with a polyaromatic structure (Kang et al. 2012; He et al. 2013). This increased the char yield (Funke & Ziegler 2010) and was beneficial to the fuel ratio (volatile matter/fixed carbon) (He et al. 2013). However, long-term thermal hydrolysis will cause organic matter to decompose and allow gas to escape, thereby affecting the production of HHV. Therefore, the running time controls the characteristic of hydrochar by determining various reactions in HTF.

Different temperatures and running times change the level of carbonization of sludge (Wang et al. 2018) and change the production of HHV. This also indicated that the quality of hydrochar can be controlled by adjusting the reaction temperatures and running times to achieve the goal of hydrochar as a fuel. As the stirring rate increased from 0 to 200 rpm, there was no distinct HHV change (see supplementary material Fig. S2). The stirring speed had little effect on the HHV output as the sludge was evenly heated during the HTF process due to the small reactor capacity.

**Fatty acids and HHV in hydrochar**

Among the saturated fatty acids, palmitic acid (C\textsubscript{16:0}), palmitoleic acid (C\textsubscript{16:1}), stearic acid (C\textsubscript{18:0}), oleic acid (C\textsubscript{18:1}), and oleic acid (C\textsubscript{18:2}) were the main components in the sewage sludge (Dufreche et al. 2007). Its carbon length was between C\textsubscript{16} and C\textsubscript{18}, and its caloric value was approximately 40 MJ kg\textsuperscript{−1}, which was higher than that of other organic matter. Therefore, the amount of fatty acids was directly related to the level of hydrothermal conversion of sludge to fuel. Figure 3(a) shows the change in the fatty acid content of the hydrochar obtained from HTF treatment of raw and fermented sludge with reaction time.

After 20 min of HTF treatment, the fatty acid content in the fermented sludge reached its maximum at 16.86 mg g\textsuperscript{−1}. For the raw sludge, the peak of fatty acid content appeared at 40 min. The reason for the increase in fatty acid content may be that the cells ruptured in the first stage of the hydrothermal reaction. Intracellular substances, such as proteins and lipids (Garcia et al. 2017) were released into the extracellular space. The lipids were hydrolyzed to generate long-chain fatty acids (Shanableh & Jomaa 2001) and then these long-chain fatty acids were stored in the hydrochar. Therefore, the fatty acid content increased. However, long-chain fatty acids that have long been present at high temperatures will be broken down into low-molecular fatty acids. These low-molecular organics were not within the detection range of the target fuel, and were easily degraded into CO\textsubscript{2} and discharged into the gas phase (Bougrier et al. 2008). Thus, the measured fatty acid content was low.

The development trends of HHV and fatty acid content were consistent, indicating that the fatty acid content was positively correlated with the HHV generated. For the raw sludge, HHV increased by 1.61 MJ kg\textsuperscript{−1} between 0 and 40 min. Based on the difference in fatty acid content, the Knothe formula (Fassinou 2012) calculated that its contribution to HHV was 0.51
MJ kg\(^{-1}\), which was much less than 1.61 MJ kg\(^{-1}\). Hence, it is concluded that changes in fatty acid content are not the only factors that may affect HHV production.

Since 39% of the protein and 52% of the carbohydrates in the sludge will be degraded by anaerobic fermentation (Carberry & Henshaw 1988), the decomposition of the proteins and lipids in the sludge will last 21 days (Yang et al. 2015). Sludge fermentation reduced the fatty acid content from an initial value of 8.47 mg g\(^{-1}\) to 7.63 mg g\(^{-1}\). Lipids and proteins were released from the cell in advance, and the time was decreased from 40 to 20 min. Although this simplified the process of HTF rupturing the cell wall, the peak time of HHV in the hydrochar was still 40 min. Since the energy storage substances in the product were not only fatty acids, the increase in fatty acid content was not synchronized with the change in HHV, which shows that other energy content involved in hydrochar may affect the correlation between fatty acids and HHV.

The experiment shown in Figure 4 attempted to increase the rate of lipid hydrolysis in HTF by adding hydrochloric acid. Compared with raw and fermented sludge, it was found that the fatty acid content in the hydrochar increased from 8.24 to 25.06 mg g\(^{-1}\) after the addition of HCl to the raw sludge followed by HTF treatment. This is because the product of the hydrothermal process was conducive to production of fatty substances (Liu et al. 2020). In order to eliminate the influence of the acid produced by sludge fermentation on the energy conversion in the HTF process, the sludge was artificially hydrolyzed by adding acid. Compared with the HHV produced by the hydrolysis-HTF treatment, the research focus was still on the HHV produced by the fermentation-HTF. In contrast, the generated HHV decreased from 11.62 to 10.64 MJ kg\(^{-1}\). Therefore, catalytic hydrolysis is not expected to increase the efficiency of the HTF process.

**Correlation between fatty acids, amino acids, and stored HHV**

Figure 5(a) shows that the HHV of raw sludge had a linear relationship with the content of fatty acids, while the HHV of the hydrochar had a linear relationship with the content of amino acids (Figure 5(b)). Since the fatty acids in the raw sludge
accounted for most of the total biomass (Tunlid & White 1992), the higher fatty acid content implied the higher HHV production. Based on the above statement, other energy storage substances were also produced during the HTF process. It was found that when fatty acids underwent secondary cracking, the amino acids released by protein decomposition became the main energy source in hydrochar (Liu et al. 2016).

The protein content of raw sludge accounted for 50–60% of the total biomass (Yuan et al. 2006; Tan et al. 2010), but the quantity of free amino acids was minimal. In the process of HTF, proteins are thermally hydrolyzed into free amino acids, peptide bonds are gradually broken, and an endothermic reaction occurs, storing energy in the hydrochar. As evidence, the concentration of amino acids in hydrochar ranged from 130–200 mg g\(^{-1}\), higher than 6–21 mg g\(^{-1}\) of fatty acids, so amino acids clearly dominated the production level of HHV.

**Correlation between fatty acids, amino acids, and the generated HHV in the hydrochar**

Different types of fatty acids and amino acids have different molecular structures and exhibit different exothermic capabilities. Studying the changes in different species in the reaction process will provide new ideas for increasing HHV production. The

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**Figure 4** | Changes in fatty acid content and generated HHV in hydrolyzed sludge + HTF, raw sludge + HTF, and fermented sludge + HTF.
redundancy analysis was used to explore the correlation between fatty acids, amino acids, and the generated HHV in raw sludge and hydrochar, respectively.

As shown in Figure 6, compared with unsaturated fatty acids (UFA), the angle between saturated fatty acids (SFA) and the HHV of the raw sludge was smaller. Specifically, the correlation between C15:0 iso, C14:0, C12:0, and the HHV was higher than that between C18:1 w7c, C18:1 w9c, and C16:1 w7c. The results indicated that SFA plays an important role in the energy storage ability of fuel, which may be due to the fact that SFA generally has a higher HHV than UFA (Fassinou 2012). When the temperature increased, the UFA was usually reduced by hydrogenation, and the proportion of SFA increased accordingly (Qin et al. 2019b). SFA had a greater impact on the direct use of raw sludge as fuel. However, as shown in Figure 6(b), although SFA was highly correlated with HHV production in raw sludge, it was very poorly correlated with HHV production in hydrochar. The angle between SFA and HHV changed from 3° in the raw sludge to 65° in the hydrochar. This may be because the total content of fatty acids could not support the main energy source of the hydrochar, and thus was replaced by an increasing number of amino acids.

Figure 5 | Correlation between fatty acids (a), free amino acids (b), and HHV stored in raw sludge (square) and hydrochar (circle, 330 °C for 40 min).

Figure 6 | Redundancy analysis between fatty acids and HHV stored in raw sludge (a) and hydrochar (b) over five months (August–December) (UFA is unsaturated fatty acids, and SFA is saturated fatty acids).
The free amino acid content in the raw sludge was below the detection limit. Therefore, Figure 7(a) shows the total amino acid content after proteolysis. However, this is not the case with the generated HHV. This may be due to the fact that amino acids were stored in the sludge in the form of protein. Amino acids produced by protein hydrolysis can contribute to the hydrothermal carbonization to produce HHV. Figure 7(b) shows that His, Ala, Arg, Thr, Pro, and Lys in the hydrochar were highly correlated with HHV, indicating that these six amino acids play an important role in energy production.

Considering the carbon yields of amino acids (Wei et al. 2018), they can be divided into aliphatic amino acids (AAA) and cyclic amino acids (CAA). Ala, Arg, and Lys were representative of AAA. Ala contains a methyl group, which is conducive to the occurrence of deamination. Arg and Lys had redundant amino groups on the alkyl substituent. These amino groups were easy to detach, and their NH$_3$ yield was higher than that of Ala. Due to this characteristic, AAA was easily deaminated during thermal treatment to generate NH$_3$ and other gases (Li et al. 2006) and was easily completely decomposed. The combustion of low-N-containing hydrochar can release greater heat energy (Channiwala & Parikh 2002). The His and Pro of CAA promoted the production of nitrogen-containing heterocyclic compounds during the heating process and inhibited the formation of aromatic hydrocarbons during the sludge cracking process, which was conducive to the occurrence of condensation reactions. The nitrogen-containing heterocyclic organic compound produced by CAA was a high-energy product that tended to increase HHV production.

**Microbial community structure and HHV production**

Microorganisms tend to secrete a large amount of protein, polysaccharides, and other extracellular products, which form an extracellular polymeric substance (EPS) structure. We found that EPS may contain substances that inhibit heat release (Qin et al. 2019a). In the field, microorganisms involved in sludge fermentation will selectively degrade some types of proteins and lipids in the cell phase and EPS, which terminally affects HHV production. Therefore, it is meaningful to study the microbial community in sludge for the field application of fermented HTF.

Figure 8 showed that the relative abundance of *Proteobacteria* and *Bacteroidetes* was the largest, and the sum of the two exceeded 50%. These microbes commonly occur in sewage sludge (Riviere et al. 2009). Redundancy analysis was used to analyze the correlation between the main strains and HHV production, and the results are shown in Fig. S1 (see supplementary material).

As shown in Fig. S1, the angle between the *Bacteroidetes* in raw sludge and the HHV in hydrochar was close to 180°, indicating a significant negative correlation between them. It should be noted that *Bacteroidetes* are common in anaerobic fermented sludge (Li et al. 2014; Cho et al. 2015), and *Bacteroidetes* can hydrolyze proteins in an anaerobic environment, thereby reducing organic content (Xue et al. 2016). Although the relative abundance of *Proteobacteria* in the biological

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**Figure 7** | Redundancy analysis between free amino acids and HHV stored in hydrolyzed sludge (a) and hydrochar (b) over five months (August–December) (AAA is aliphatic amino acids, and CAA is cyclic amino acids).

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community of the sludge was higher, it was not correlated with the HHV of the hydrochar. Since most Proteobacteria use carbon dioxide or carbonate in the environment as carbon sources, they cannot directly use the proteins, polysaccharides, or lipids in sewage sludge for heterotrophic growth (Kersters et al. 2006); hence, they had little effect on the organic components in the sludge.

Bacteroidetes are suitable for heterotrophic growth in an anoxic/anaerobic atmosphere, degrading lipids and proteins into fatty acids and amino acids. In the anoxic/anaerobic digestion process, amino acids can be oxidized and degraded into volatile fatty acids (Finstein 1989), and fatty acids finally release gases such as CH₄ and CO₂. In brief, Bacteroidetes can assimilate the main active organic matter, especially protein, thereby decreasing the energy storage in sludge. The propagation of these microorganisms and the fermentation in the sludge are not conducive to the subsequent increase in the level of HHV produced by HTF.

In practical application, the environment in the secondary settling tank is anaerobic, while the environment in the accumulation of dewatered sludge is anoxic. The species and abundance of bacteria in it should be analyzed first, and the retention time of the sludge should be considered to obtain the desired fermentation level. In this way, the highest HHV produced by HTF processing of fermented sludge can be optimally predicted, and the sludge can be converted into fuel more effectively.

**CONCLUSIONS**

The hydrothermal fuel of sewage sludge was introduced at a lower temperature than before, and the lower temperature-HTF reached the same HHV level as the high temperature reaction. Although sludge fermentation can effectively increase lipid hydrolysis and release fatty acids 20 min earlier, the peak of HHV still appears at 40 min. Therefore, the composition of hydrochar in the process needs to be studied further.

HHV was positively correlated with the fatty acid content before the sludge was hydrothermally fueled. An increase in HTF levels produced more free amino acids in the product. AAA was completely decomposed and CAA produced high-energy products; both tended to increase the HHV of hydrochar. The experiment was originally designed for sludge fermentation to enable internal bacteria to selectively degrade lipids and proteins to produce different kinds of energy substances. Notably, on analyzing the correlation between changes in the microbial community and the HHV produced, it was found that Bacteroidetes degraded organic matter, thereby affecting the production of HHV in hydrochar.

Overall, it is recommended that sewage sludge be handled promptly after it is discharged from the sewage treatment plant. By controlling the anoxic/anaerobic environment, the excessive proliferation of Bacteroidetes can be restricted, the
decomposition of lipids into saturated fatty acids should be increased, and the hydrolysis of proteins into AAA/CAA should be advanced. This is likely the only way to effectively increase the HHV of hydrochar and reduce the operating costs of HTF.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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