Hydrothermal carbonization of sewage sludge: Multi-response optimization of hydrochar production and CO₂-assisted gasification performance

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Abstract

The harmful effects of improper sewage sludge (SS) treatment on the environment inspire the search for more benign sludge processing techniques such as hydrothermal carbonization (HTC); the abundant organic matter in SS is used for energy recovery. Herein, response surface methodology (RSM) was used to optimize the HTC-based preparation of SS hydrochar and its gasification performance. Specifically, the hydrochar yield, higher heating value (HHV), and gasification activity index were selected as optimization goals, while carbonization temperature (160–260°C), residence time (30–150 min), and acetic acid concentration (0–1.5 M) were selected as factors influencing the HTC process and CO₂-assisted gasification performance. Carbonization temperature was the dominant parameter determining hydrochar yield, HHV, and gasification activity. The hydrochar yield (82.69%) and calorific value (7820.99 kJ kg⁻¹) were maximized under comparatively mild conditions (160°C, 30 min, and 0.07 M acetic acid), whereas the gasification activity index (0.288 s⁻¹) was maximized under harsher conditions (211.34°C, 88.16 min, and 1.58 M acetic acid). The obtained results help to guide the HTC of SS intended for gasification, thus promoting the development of this promising waste-to-energy technology, and may facilitate the design and further optimization of thermochemical SS conversion.

1. Introduction

According to recent estimates, the amount of domestic and industrial wastewater generated worldwide each year is of the order of billions of tons and is expected to increase because of population growth and living standard improvement (Mateo-Sagasta et al. 2015; Bora et al. 2020), which in turn will cause serious pollution (Meng et al. 2016). Compared with the traditional methods of wastewater SS disposal (e.g., landfilling, incineration, and anaerobic digestion), which suffer from land shortage, secondary pollution, and long processing duration, the thermochemical conversion of SS by gasification offers the advantages of decreased pollutant emission and shorter processing duration, thus holding great promise (Zheng et al. 2020; Chen et al. 2020).

However, the gasification-based conversion of SS to valuable energy and fuels is hindered by its high moisture content. Currently, at least 50 million tons of SS with a moisture content of 80% are produced within the European Union annually (Kelessidis et al. 2012), and a similar value (40 million tons of SS with a moisture content of 80%) has been estimated for the United States and China (Venkatesan et al. 2015). Since most of the energy invested and released during the conventional heat treatment process is consumed to remove SS moisture, this has inspired the search for innovative and sustainable SS pre-drying technologies.

The main advantage of Hydrothermal carbonization (HTC) over other thermal conversion technologies, such as pyrolysis, gasification and incineration, is its ability to convert wet sludge to hydrochar with relatively high yields without preliminary dewatering and drying, which, consequently, requires less energy. Therefore, HTC has received much attention as a pretreatment technology allowing the effective conversion of wet biomass into solid fuel (hydrochar) (Yu et al. 2018; He et al. 2018), is a pressurized thermal conversion process that is achieved at a mild temperature (160–300°C) and self-generated pressure for various retention time (Sharma et al. 2020); it involves five principal reactions, namely hydrolysis, dehydration, decarboxylation, polymerization, and aromatization (Zhao et al. 2014; Reza et al. 2014). The feasibility of employing HTC to prepare solid fuel from biomass waste has therefore been extensively investigated (Park et al. 2018; Peng et al. 2016). Park et al. showed that the HTC of algal biomass affords hydrochar with improved carbon content, carbon recovery, energy recovery, and C/O and C/H atomic ratios (Park et al. 2018). Some researchers have observed a significant enhancement in SS dewaterability
after HTC (Peng et al. 2016; Escala et al. 2012; Kim et al. 2014; Wang et al. 2015). He et al. used HTC to convert SS into a clean solid fuel, achieving an 88% carbon recovery while removing 60% of nitrogen and sulfur (He et al. 2013). Atallah et al. found that with increasing reaction time and solid-to-liquid ratio, hydrochar yield decreased from 36 to 7%, while the carbon and energy contents increased to 76% and 36 MJ kg\(^{-1}\), respectively (Atallah et al. 2019). Lee et al. demonstrating that in terms of yield and higher heating value (HHV), the potential of hydrochar as a fuel increased at a relatively low HTC treatment temperature (180–200°C). (Lee et al. 2019). In addition to temperature and residence time, the type of acid catalyst is also an important factor affecting the performance of HTC-produced fuel. Liu et al. showing that acidic conditions favor hydrochar aromatization (Liua et al. 2020). Evcil et al. revealing that acid catalysis can reduce hydrochar yield and HHV and showed that although irregular carbon spheres formed at all temperatures tested in the catalytic runs, no such spheres were produced in non-catalytic runs (Evcil et al. 2020). Given that the acids produced during hydrothermal biomass processing catalyze HTC (Stemann et al. 2013), we herein considered the influence of the most abundant of these acids, namely acetic acid.

Numerous works show that HTC improves the fuel properties of sludge and provides raw materials more suitable for further thermochemical conversion (Park et al. 2018; Peng et al. 2016; Escala et al. 2012; Kim et al. 2014; Wang et al. 2015; He et al. 2013; Atallah et al. 2019; Lee et al. 2019). Gai et al. demonstrating that hydrochar contained more alkali and alkaline earth metals and featured higher gasification reactivity. In addition, the porous structure of hydrochar was claimed to result in higher gas yield and gasification efficiency (Gai et al. 2016). Zheng et al. found that higher hydrothermal reaction times and temperatures reduce H\(_2\) production (Zheng et al. 2019). Lin et al. demonstrating that after HTC the CO\(_2\)-assisted gasification of coke could be completed in a quite short time, and the reactivity of hydrochar was found to exceed that of the raw material (Lin et al. 2016). Wei et al. studied the characteristics of CO\(_2\)-assisted hydrochar gasification and found that the gasification activity could be enhanced by increasing the gasification temperature and hydrochar mixing ratio (Wei et al. 2017). Moon et al. showing that the amount and HHV of the gas produced by steam gasification increased after the hydrothermal treatment of SS (Moon et al. 2015). Mosqueda et al. probe the CO\(_2\)-assisted gasification behaviors of washed and non-washed banana leaf hydrochars, revealing that both hydrochars featured a decreased alkali content and thus had lower gasification reactivities than the raw materials (Mosqueda et al. 2019). Most existing reports on hydrochar gasification mainly employ steam as the gasification agent, whereas the use of CO\(_2\) for sludge hydrochar gasification remains underexplored. Given that the energy consumption as well as the emissions and costs related to the generation of superheated steam are not negligible, CO\(_2\)-assisted gasification has attracted much attention, allowing the simultaneous generation of energy and the reduction of overall CO\(_2\) emissions (Parvez et al. 2016). Therefore, in this study, we probed the gasification of SS hydrochar in an atmosphere of CO\(_2\).

The recent years have witnessed a surge of interest in the optimization of HTC conditions using the response surface methodology (RSM). A response surface model describing the relationship between the given factors and the response values is constructed by using appropriate functions, and the optimal process parameters are obtained by analyzing these relationships and dealing with multivariable problems (Franceschini et al. 2008). Oluwasola et al. used RSM to maximized the yield and HHV of hydrochar produced from coffee grounds. Under the optimal reaction conditions of 216°C and 1 h, the maximal hydrochar yield and HHV equaled 64% and 31.6 MJ kg\(^{-1}\), respectively (Afolabi et al. 2020). Kang et al. used RSM to optimize the microwave-assisted HTC of corn stalks. Statistical analysis showed that temperature is the main factor governing product quality and HHV. Under the optimal conditions of 181.9°C, 39.7 min, and 3.8 g/50 mL H\(_2\)O, the yield achieved 80.55%. Under the conditions of 230°C, 45 min, and 2 g/50 mL H\(_2\)O, the HHV equaled 22.82 MJ kg\(^{-1}\), exceeding the value of raw corn stalks by
41\% \text{ (Kang et al. 2019). These results indicate that RSM is a well-established and widely used technique for studying the joint interactions between independent (input) variables in the reaction process and is particularly useful for process optimization.}

Despite the great potential of HTC and subsequent hydrochar gasification, information on statistically optimized conditions for realizing best-quality hydrochar for energy applications is still scarce. Herein, RSM is used to establish the optimal HTC conditions for maximizing hydrochar yield and HHV as well as to determine the HTC conditions best suited to obtain hydrochar with maximal gasification activity.

2. Materials And Methods

2.1. Materials

Dewatered SS with a moisture content of \textasciitilde 80 wt\%, collected from a wastewater treatment plant in Jilin City, Jilin Province, China, was stored at 4 °C and used as the raw material for HTC. For characterization, SS was dried at 105 °C for 24 h, ground into fine powder, and sealed in a dry glass bottle for subsequent analysis. Table 1 lists the primary properties of raw SS. The high content volatiles were the main source of heat released during sludge thermochemical conversion, and the ash components were mainly SiO$_2$, Al$_2$O$_3$, and Fe$_2$O$_3$.

2.2. HTC experiments

HTC experiments were carried out in a 0.5-L stirred batch reactor (stainless steel 316 L, GCF-type, Dalian Controlled Plant, China). In each experiment, the reactor was charged with a mixture of SS (20 g) and deionized water (200 mL). In experiments involving acid catalysis, SS (20 g) was mixed with acetic acid solutions (200 mL) of different concentrations. The reactor was sealed, purged with N$_2$ to remove residual air, heated to the predetermined temperature (160, 210, or 260 °C) using an electric heater, and held at this temperature for a certain time (30, 90, or 150 min). The reaction pressure (that of water alone at the respective temperature) ranged from 1.6 to 4.7 MPa. After the reaction, the slurry samples were collected and separated into filtrates and hydrochar by filtration. After 24-h drying at 60 °C, hydrochar was ground into fine powder and stored in an enclosed plastic pipe until analysis. Hydrochar samples were denoted as “HC-A-B-C,” where $A$ is the HTC temperature, $B$ is the HTC residence time, and $C$ is the acetic acid concentration. Two indexes (hydrochar mass yield ($H_Y$) and HHV) were selected as dependent variables representing responses to HTC condition variation.

Table 1. Main characteristics of the employed sludge.

| Sample | Ultimate analysis (wt\%, db$^*$) | Proximate analysis (wt\%, db) | HHV (kJ kg$^{-1}$) |
|--------|---------------------------------|-------------------------------|--------------------|
|        | C      | H      | N      | S   | Volatiles | Fixed C | Ash |                |
| Sludge | 19.68  | 3.33   | 2.99   | 0.62| 32.88      | 5.78    | 61.34| 8200            |
| Ash (wt\%) | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | P$_2$O$_5$ | CaO        | MgO    | K$_2$O | SO$_3$ | Na$_2$O   |
|        | 41.90  | 18.10  | 10.40  | 7.03| 4.76       | 2.53    | 2.40 | 1.58 | 1.21      |

$db^*$ = dry basis.
Hy was estimated using Eq. (1), while HHV was estimated by bomb calorimetry (SDAC6000, Hunan Sundy Science and Technology Co., Ltd., China). The nitrogen, hydrogen, and carbon contents of hydrochar were determined by combustion at 950 °C employing an automatic elemental analyzer (EA3000, Euro Vector S.P.A., Italy).

\[ H_y (%) = 100\% \times \frac{\text{weight of dry hydrochar}}{\text{weight of dry raw material}} \] 

(1)

2.3. CO\textsubscript{2}-assisted gasification experiments

Hydrochar gasification was carried out in a micro-fluidized bed reaction analyzer coupled with a mass spectrometer (MFBRA-MS). The assembly mainly comprised a gas supply system, a gasification system, and an online gas monitoring and analysis system (Fig. 1).

Gasification was performed as follows. (1) The reactor was heated to 800 °C. (2) Hydrochar (10 mg) was placed into the feeding pipe. (3) The gasification agent (99.999 vol% CO\textsubscript{2}) was supplied to the reactor at a flow rate of 0.5 L min\textsuperscript{-1} to stabilize the gas baseline. (4) The pulse was turned on through the solenoid valve, and the sample was instantly sprayed into the reaction area. The gas was analyzed using an online mass spectrometer. (5) Procedures (2)–(4) were repeated until all experiments were completed.

The carbon conversion of hydrochar gasification (\(X\)) was calculated as

\[ X = \frac{\int_{t_0}^{t_d} \psi_i \times q_v \, dt}{\int_{t_0}^{t_d} \psi_i \times q_v \, dt}, \]

(2)

where \(t\) is the reaction time (s), \(t_0\) is the initial reaction time (s), \(t_d\) is the end reaction time, \(\psi_i\) is the volume fraction of component \(i\) in the produced gas (%), and \(q_v\) is the flow rate (mol min\textsuperscript{-1}).

To establish a relationship between HTC conditions and hydrochar gasification reactivity, we used RSM to optimize this reactivity and thus obtain optimal HTC conditions. The reaction index \(R_{0.9}\), employed to quantitatively characterize the overall gasification reactivity of hydrochar, was determined as

\[ R_{0.9} = \frac{0.9}{t_{X = 0.9}}, \]

(3)

where \(t_{X = 0.9}\) represents the gasification time (min) required for a carbon conversion of 0.9.

2.4. Experimental design for process optimization

RSM is a method of optimizing experimental conditions, which is suitable for solving the related problems of nonlinear data processing. By means of regression fitting and response surface drawing, the predicted optimal response value and corresponding experimental conditions can be found out.

Experiments were designed using the Box–Behnken method, a typical RSM technique that is usually used to optimize response-affecting process parameters.

To determine the optimum HTC conditions for hydrochar production, we investigated the effects of three factors (reaction temperature, residence time, and acetic acid concentration) and optimized them within the ranges of
160–260 °C, 30–150 min, and 0–3.0 M, respectively, to maximize the yield and HHV of SS hydrochar. The relationship between HTC conditions and gasification performance was investigated using the gasification activity index as the optimization goal under different HTC conditions.

The experimental design was carried out using Design-Expert.V8.0.6.1 data analysis software (Stat-Ease, Inc). The optimization conditions and objectives of HTC and gasification processes are presented in Tables 2 and 3.

**Table 2.** RSM design parameters and optimization objectives of HTC.

| Run | A: HTC temperature (°C) | B: Residence time (min) | C: Acetic acid concentration (M) |
|-----|------------------------|-------------------------|----------------------------------|
| 1   | 260                    | 90                      | 3                                |
| 2   | 210                    | 30                      | 0                                |
| 3   | 210                    | 90                      | 1.5                              |
| 4   | 160                    | 90                      | 0                                |
| 5   | 210                    | 90                      | 1.5                              |
| 6   | 260                    | 150                     | 1.5                              |
| 7   | 210                    | 150                     | 0                                |
| 8   | 160                    | 90                      | 3                                |
| 9   | 210                    | 90                      | 1.5                              |
| 10  | 210                    | 90                      | 1.5                              |
| 11  | 210                    | 150                     | 3                                |
| 12  | 160                    | 30                      | 1.5                              |
| 13  | 160                    | 150                     | 1.5                              |
| 14  | 260                    | 90                      | 0                                |
| 15  | 210                    | 90                      | 1.5                              |
| 16  | 260                    | 30                      | 1.5                              |
| 17  | 210                    | 30                      | 3                                |

**Table 3.** RSM design parameters and optimization objectives of SS hydrochar gasification.
### 3. Results And Discussion

#### 3.1. Analysis of hydrochar characteristics

Table 4 lists the fuel characteristics of hydrochar obtained under different HTC conditions. Compared with raw SS, hydrochar obtained at 160°C had a higher carbon content regardless of residence time and acetic acid concentration. Whereas carbon and hydrogen contents decreased with increasing HTC temperature and residence time, as observed by Zhang et al. (Zhang et al. 2019), the opposite trend was observed for nitrogen content (e.g., HC-260-90 was more nitrogen-rich than HC-210-30), which was ascribed to the occurrence of nitrogen absorption at higher temperatures and longer reaction times (He et al. 2013; Wang et al. 2020). The decrease in the contents of carbon, hydrogen, and nitrogen observed in the presence of acetic acid was ascribed to its promotional effect on hydrolysis. At high temperatures and long residence times, SS hydrolysis also produces organic (e.g., acetic, formic, levulinic, and glycolic) acids, the presence of which in the liquid phase catalyzed decarboxylation and dehydration reactions (Stemann et al. 2013). According to all the above analysis, different HTC conditions have different effects on the properties of hydrochar. To maximize the fuel performance of hydrochar, we optimized hydrochar yield and HHV by RSM.

| Run | A: HTC temperature (°C) | B: Residence time (min) | C: Acetic acid concentration (M) |
|-----|-------------------------|-------------------------|---------------------------------|
| 1   | 260                     | 90                      | 3                               |
| 2   | 210                     | 30                      | 0                               |
| 3   | 210                     | 90                      | 1.5                             |
| 4   | 160                     | 90                      | 0                               |
| 5   | 210                     | 90                      | 1.5                             |
| 6   | 260                     | 150                     | 1.5                             |
| 7   | 210                     | 150                     | 0                               |
| 8   | 160                     | 90                      | 3                               |
| 9   | 210                     | 90                      | 1.5                             |
| 10  | 210                     | 90                      | 1.5                             |
| 11  | 210                     | 150                     | 3                               |
| 12  | 160                     | 30                      | 1.5                             |
| 13  | 160                     | 150                     | 1.5                             |
| 14  | 260                     | 90                      | 0                               |
| 15  | 210                     | 90                      | 1.5                             |
| 16  | 260                     | 30                      | 1.5                             |
| 17  | 210                     | 30                      | 3                               |
### Table 4
Basic fuel characteristics of hydrochar.

| Run | C (ad %) | H (ad %) | N (ad %) | Hydrochar yield (wt%) | HHV (kJ kg\(^{-1}\)) |
|-----|----------|----------|----------|-----------------------|------------------------|
| 1   | 15.07    | 1.79     | 1.36     | 55                    | 5885.97                |
| 2   | 15.72    | 2.05     | 1.1      | 76                    | 6228.26                |
| 3   | 14.2     | 2.19     | 0.78     | 63                    | 6433.76                |
| 4   | 20.24    | 3.03     | 2.14     | 82.69                 | 7725.37                |
| 5   | 14.51    | 2.1      | 0.8      | 65                    | 6489.69                |
| 6   | 12.88    | 1.74     | 0.69     | 51.5                  | 5478.26                |
| 7   | 16.14    | 2.05     | 1.63     | 73.1                  | 6193.58                |
| 8   | 21.25    | 3.08     | 2.37     | 73.63                 | 8425.62                |
| 9   | 14.89    | 2.18     | 0.75     | 65                    | 6323.92                |
| 10  | 14.76    | 2.15     | 0.77     | 65                    | 6377.54                |
| 11  | 14.64    | 1.95     | 0.76     | 65                    | 6675.47                |
| 12  | 19.36    | 3.04     | 1.99     | 74.2                  | 8321.88                |
| 13  | 20.64    | 3.09     | 1.69     | 74.3                  | 8311.86                |
| 14  | 14.06    | 1.9      | 1.35     | 63.9                  | 5586.66                |
| 15  | 14.51    | 2.14     | 0.78     | 66                    | 6370.44                |
| 16  | 15       | 2.04     | 0.77     | 57                    | 6114.73                |
| 17  | 15.76    | 2.19     | 0.82     | 68                    | 6787.71                |

### 3.2. Optimization of hydrochar yield and HHV

#### 3.2.1 Analysis of variance (ANOVA) and model building

In the experimental process, only 17 groups of experimental conditions were selected, which could not intuitively obtain the optimal conditions. Through response surface analysis, the functional relationship between response target and factors can be established, and the response surface diagram can be used to display the functional relationship, and the optimal reaction condition can be obtained.

Firstly, regression analysis was carried out on the experimental results. The results of model variance analysis, presented in Tables 5 and 6, the \( F \)-values of the model equaled 168.2856 and 132.086, while the \( p \)-values were less than 0.05, and the lack of fit item is greater than 0.05, indicating that the model item is significant. Figs. 2a and 2b compare actual values with predicted values, revealing that the deviation between them was small and thus showing that the regression model could well predict the hydrochar HHV and yield.
Table 5
ANOVA of the regression model used to predict hydrochar mass yield.

| Source                          | SS    | df | MS       | F-value | p-value   |
|--------------------------------|-------|----|----------|---------|-----------|
| Model                          | 1035.21 | 9 | 115.0233 | 132.086 | < 0.0001  | significant |
| A: Temperature                 | 749.2321 | 1 | 749.2321 | 860.3739 | < 0.0001  |
| B: Residence time              | 15.96125 | 1 | 15.96125 | 18.32896 | 0.0036    |
| C: Acetic acid concentration   | 145.0105 | 1 | 145.0105 | 166.5215 | < 0.0001  |
| AB                              | 7.84   | 1 | 7.84     | 9.002994 | 0.0199    |
| AC                              | 0.0064 | 1 | 0.0064   | 0.007349 | 0.9341    |
| BC                              | 0.0025 | 1 | 0.0025   | 0.002871 | 0.9588    |
| A2                             | 5.424105 | 1 | 5.424105 | 6.228723 | 0.0412    |
| B2                             | 1.440947 | 1 | 1.440947 | 1.654699 | 0.2392    |
| C2                             | 111.2404 | 1 | 111.2404 | 127.7419 | < 0.0001  |
| Residual                       | 6.09575 | 7 | 0.870821 |          |           |
| Lack of fit                    | 1.29575 | 3 | 0.431917 | 0.359931 | 0.7862    | not significant |
| Pure error                     | 4.8    | 4 | 1.2      |         |           |
| total                          | 1041.306 | 16 |          |         |           |

df: degrees of freedom; SS: sum of squares (Total)=sum of squares(Model)+sum of squares(Residual); MS: mean squares=SS/df; F-value: Fisher test value= MS(Model)/MS(Residual); p-value: the probability when the value is bigger than F-value.
In general, the regression model of HHV and yield could be used for subsequent response surface analysis. The model formulated in terms of actual factors for $H_y$ (%) and HHV (kJ kg$^{-1}$) is given by Eqs. (4) and (5):

$$H_y (%) = 60.8 - 9.68A - 1.41B - 4.26C - 1.40AB + 0.04AC - 0.025BC - 1.14A^2 + 0.58B^2 + 5.14C^2,$$

$$HHV (%) = 6399.07 - 1214.89A - 99.18B + 255.11C - 156.61AB - 100.24AC - 19.39BC + 546.13A^2 + 111.48B^2 - 39.30C^2.$$ (5)

In the above and subsequent equations, $A$, $B$, and $C$ stand for HTC temperature (°C), residence time (min), and acetic acid concentration (M), respectively.

### 3.2.2 Response surface analysis of hydrochar yield

Hydrochar yield was negatively correlated with all three of these parameters, with the largest and smallest effects observed for temperature and residence time, respectively (Fig. 3). In particular, hydrochar yield decreased by 15, 10, and 5% as the reaction temperature, acetic acid concentration, and residence time increased from 160 to 260°C, 0 to 3 M, and 30 to 150 min, respectively.

The increase in the above three parameters promoted the thermal decomposition and dissolution of sludge macromolecules and thus decreased solid yield. The rise in temperature decreased the viscosity of water and thus facilitated its penetration into pores of hydrochar to promote biomass degradation (Funke et al. 2010; Wang et al., 2010).
2018). The largest decrease in hydrochar yield was observed when the reaction temperature increased from 210 to 260°C. According to Reza et al., this decrease was primarily due to the significant breakdown of hemicellulose and lignin in this temperature range and the large number of cellulose decomposition reactions above 210°C (Toufiq et al. 2016). Alternatively, the negative correlation between temperature and hydrochar yield was ascribed to the facts that (i) SS contains numerous nitrogen-containing compounds such as proteins, which, together with sugar hydrolysates, are dissolved in the aqueous phase (Wang et al. 2019) and (ii) hydrochar is difficult to produce by the thermal decomposition of proteins at ~250°C. Temperature also had a larger effect on mass yield than organic acids. Acetic acid is the main organic acid produced during HTC through the hydrolysis and dehydration of straight-chain polymers such as cellulose and hemicellulose or simple monomers in the presence of subcritical water (Liu et al. 2020). The presence of organic acids increases the concentration of protons or hydroxide ions, thus increasing the total ion concentration and promoting decarboxylation and dehydration (Reza et al. 2015). Acids also enhance dehydration, which is the main carbonization mechanism, and thus significantly decrease the oxygen content of hydrochar. It has been reported that hydrochar yield can be increased by decreasing the reaction time (Saetea et al. 2013), which is in line with our results. This behavior was ascribed to the depolymerization of macromolecules in SS and the further degradation of the resultant intermediates via cleavage, dehydration, decarboxylation, and deamination at long residence times.

3.2.3 Response surface analysis of hydrochar HHV

3.2.4 Results of process optimization

The optimization of HTC conditions is important for hydrochar recovery, especially from the perspective of process development. Ideally, maximal hydrochar yield and HHV should be obtained under mild conditions. The limiting conditions and results of hydrochar HHV and yield optimization are listed in Tables 7 and 8.

| Name                                | Goal          | Lower limit | Upper limit | Lower weight | Upper weight |
|-------------------------------------|---------------|-------------|-------------|--------------|--------------|
| A: Temperature                      | is in range   | 160         | 260         | 1            | 1            |
| B: Time                             | is in range   | 30          | 150         | 1            | 1            |
| C: Acetic acid concentration        | is in range   | 0           | 3           | 1            | 1            |
| HHV                                 | minimize      | 5478.26     | 8425.62     | 1            | 1            |
| Hydrochar yield                     | minimize      | 51.5        | 82.69       | 1            | 1            |
According to the prediction results, optimal conditions corresponded to an HTC temperature of 160°C, a residence time of 30 min, and an acetic acid concentration of 0.07 M, with the yield and HHV of hydrochar obtained under these conditions equaling 82.69% and 7820.99 kJ kg$^{-1}$, respectively. In the replication experiment conducted under these conditions, the hydrochar yield and HHV were determined as 83.07% and 7794.25 kJ kg$^{-1}$, respectively, deviating from the predicted values by 0.46 and 0.34%, respectively. The good agreement between simulated and experimental results confirmed the high reliability of our prediction.

The above results indicate that SS hydrochar can be used as a fuel for combustion, pyrolysis, and gasification. Among these applications, combustion is relatively simple but may produce gaseous pollutants. Therefore, the next section compares the release of gaseous pollutants in different combustion atmospheres.

### 3.3. Release of gaseous pollutants in different combustion atmospheres

The above analysis results show that SS hydrochar holds great promise as a combustion fuel. However, as gaseous pollutants are inevitably produced during conversion, alternatives featuring lower pollutant emissions are highly sought after. This section explores the release of nitrogen- and sulfur-containing gases during hydrochar combustion in O$_2$ (99.999 vol%) and CO$_2$ (99.999 vol%) atmospheres. As shown in Fig. 5, when hydrochar was burned in an O$_2$ atmosphere, the peaks of sulfur- and nitrogen-containing gases were more intense than those observed in a CO$_2$ atmosphere. In particular, almost no peak of sulfur-containing gas was observed in the latter case. Therefore, the gasification of hydrochar in a CO$_2$ atmosphere seems to be a promising thermal conversion method. The next section focuses on the gasification characteristics of hydrochar.

### 3.4 Analysis of CO$_2$ gasification characteristics

#### 3.4.1 CO$_2$ emission due to combustion of residual char obtained in different gasification atmospheres

Figure 6 shows the release of CO$_2$ upon the combustion of residual char obtained after the completion of hydrochar gasification in Ar and CO$_2$ atmospheres, revealing that more CO$_2$ (and hence, a lower carbon
conversion) was obtained in the former case. Therefore, the CO₂ atmosphere was concluded to be more suitable for gasification reactions than inert (e.g., Ar) atmospheres.

3.4.2 Analysis of gaseous product evolution

Figure 8. Effects of (a) temperature, (b) residence time, and (c) acetic acid concentration on the release of gaseous products during CO₂-assisted gasification.

With increasing HTC temperature and residence time, the amount of released gas decreased.

HTC temperature had the largest influence on gas release and was negatively correlated with the contents of CO, CH₄, and H₂ (Fig. 8a), as high temperatures aggravated sludge hydrolysis and increased the content of soluble carbon in the aqueous phase (Yu et al. 2018). Notably, the density and dielectric constant of water decreased with increasing temperature, whereas the ionic product significantly increased (Watanabe et al. 2004), which primarily contributed to the cleavage of hydrogen bonds and hydrolysis (Wang et al. 2019). In addition, high HTC temperatures favor the aromatization of hydrochar and thus make it more thermally stable and difficult to decompose during gasification. Residence time is an important parameter influencing hydrochar formation, and long times led to the polymerization of fragments dissolved in the liquid phase, which resulted in the formation of secondary hydrochar with a polyaromatic structure (Wüst et al. 2019; Kang et al. 2012). Therefore, it can be seen from Fig. 8b shows that with the increase of the hydrothermal residence time, the content of CO and CH₄ produced by gasification decreases, and the residence time has little effect on H₂. The addition of acetic acid reduced the amount of released gaseous products (Fig. 8c). Acidic environments favor the isomerization, dehydration, and cracking (open-loop and C–C bond breakage) of SS (Liua et al. 2020). During hydrothermal processing, the decomposition of intermediates produces a large number of organic acids and thus reduces the pH of the reaction medium, while the resulting acidic environment favors the further decomposition of intermediates and the formation of a more stable double bond structure, thus promoting hydrochar aromatization (Sevill et al. 2009).

3.4.3 Analysis of conversion during hydrochar gasification

Figure 9 shows the effect of time on conversion during CO₂-assisted hydrochar gasification, revealing that compared with raw SS, hydrochar required less time to reach a conversion of unity, i.e., the gasification activity of sludge increased after HTC. Moon et al. (Moon et al. 2015) showing that the rise in the lignin content of SS after HTC helped to increase the production of methane during gasification and allowed this gasification to be completed in a shorter time. At 160°C and 260°C, the conversion of hydrochar was lower than that of raw SS, but at the intermediate temperature (210°C), the conversion is higher. Moreover, hydrochar gasification reactivity increased with increasing residence time and acetic acid concentration.

3.4.4 Analysis of the gasification activity optimization of hydrochar

The ANOVA results for the regression model used to predict the gasification activity index are shown in Table 9. The p-value of the employed model was less than 0.05, and the model lack-of-fit (p > 0.05) was insignificant. Figure 10 compares the predicted results with the experimental results, and the adj. R² is 0.993, indicating that the difference between the two is small and the fitting degree is high. In the working condition 160-90-1.5, the value of
$R_{0.9}$ is the largest, so it is distributed in the upper right corner. The quadratic regression equation used to calculate this index is given below.

$$R_{0.9} (\text{s}^{-1}) = 0.2876 + 0.006A - 0.002B + 0.0061C + 0.0032AB - 0.0204AC - 0.0039BC - 0.086A^2 - 0.0367B^2 - 0.0503C^2. \ (6)$$

Table 9
ANOVA of the regression model used to predict the gasification activity index.

| Source                  | SS     | df | MS       | F-value | p-value |
|-------------------------|--------|----|----------|---------|---------|
| Model                   | 0.05454| 9  | 0.00606  | 991.2505| < 0.0001| significant |
| $A$: Temperature        | 0.000283| 1  | 0.000283 | 46.36046| 0.0003  |
| $B$: Time               | 3.66E-05| 1  | 3.66E-05 | 5.984332| 0.0443  |
| $C$: Acetic acid concen.| 0.000296| 1  | 0.000296 | 48.41328| 0.0002  |
| $AB$                    | 4.16E-05| 1  | 4.16E-05 | 6.809475| 0.0349  |
| $AC$                    | 0.00167 | 1  | 0.00167  | 273.1828| < 0.0001|
| $BC$                    | 6.22E-05| 1  | 6.22E-05 | 10.17782| 0.0153  |
| $A^2$                   | 0.031132| 1  | 0.031132 | 5092.356| < 0.0001|
| $B^2$                   | 0.005681| 1  | 0.005681 | 929.1869| < 0.0001|
| $C^2$                   | 0.010665| 1  | 0.010665 | 1744.561| < 0.0001|
| Residual                | 4.28E-05| 7  | 6.11E-06 |          |         |
| Lack of fit             | 3.2E-05 | 3  | 1.07E-05 | 3.949926| 0.1088  | not significant |
| Pure error              | 1.08E-05| 4  | 2.7E-06  |          |         |
| total                   | 0.054583| 16 |          |          |         |

Figure 11. Response surface maps (a, c, e) and contour maps (b, d, f) showing the effects of temperature, residence time, and acetic acid concentration on the gasification activity index of hydrochar.

Table 10
Limiting conditions for the optimization of the hydrochar gasification activity index.

| Name                      | Goal                   | Lower limit | Upper limit | Lower weight | Upper weight |
|---------------------------|------------------------|-------------|-------------|--------------|--------------|
| $A$: Temperature          | is in range            | 160         | 260         | 1            | 1            |
| $B$: Time                 | is in range            | 30          | 150         | 1            | 1            |
| $C$: Acetic acid concen.  | is in range            | 0           | 3           | 1            | 1            |
| Reactivity index          | maximize               | 0.12        | 0.29        | 1            | 1            |
### Table 11
Results of optimization of the hydrochar gasification activity index.

| Number | HTC temperature (°C) | Residence time (min) | Acetic acid concentration (M) | \( R_{0.9} \) (\( s^{-1} \)) | Desirability |
|--------|----------------------|----------------------|-------------------------------|-----------------------------|--------------|
| 1      | 211.34               | 88.16                | 1.58                          | 0.29                        | 0.99         | Selected  |

The results optimization of activity index listed in Tables 10 and 11. According to the predicted results, the highest gasification activity index (0.29 s\(^{-1}\)) was obtained at an HTC temperature of 211.34°C, a residence time of 88.16 min, and an acetic acid concentration of 1.58 M. When a replication experiment was conducted under the above conditions, \( R_{0.9} \) was obtained as 0.28 s\(^{-1}\), deviating from the predicted value by 2.19%, which was within the error range. Compared with those required to obtain high-quality hydrochar (160°C, 30 min, 0.07 M) as solid fuel in Section 3.2.3, the optimized conditions for hydrochar gasification (211.34°C, 88.16 min, 1.58 M) were more severe. Milder HTC conditions allowed hydrochar to retain more carbon and some soluble organic matter and thus maximize the HHV and yield, whereas harsher conditions favored hydrochar pore development and alkali metal retention, thus promoting catalytic gasification.

### 4. Conclusions

The main objective of this work is to convert the sludge into a usable bioenergy feedstock by hydrothermal carbonization. The main results are as follows.

1. With increasing HTC temperature, residence time, and acetic acid concentration, the carbon, hydrogen, and nitrogen contents of hydrochar decreased. The highest hydrochar yield and HHV were obtained under mild conditions.

2. The conditions affording maximal HHV and yield corresponded to 160°C, 30 min, and 0.07 M acetic acid. Under these conditions, the hydrochar yield and HHV were predicted to equal 82.69% and 7820.99 kJ kg\(^{-1}\), respectively. These values deviated from the experimentally determined ones by 0.34 and 0.46%, respectively, i.e., were within the acceptable error range.

3. HTC conditions strongly affected hydrochar gasification performance. As HTC conditions became more severe, the gasification activity index first increased and then decreased, i.e., was maximized under moderate conditions. The RSM-predicted optimal HTC conditions corresponded to 211.34°C, 88.16 min, and 1.58 M acetic acid. Under these conditions, the hydrochar gasification activity index equaled 0.29 s\(^{-1}\).

The results of this study provide a detailed observation of SS utilization by HTC coupled with gasification and providing referential information for the design, optimization, and even upscaling of thermochemical conversion processes. However, under the expected optimization conditions, extensive experiments on SS should be the future work. In addition, a comprehensive technical and economic analysis of SS HTC process is needed to prove its scalability.

### Declarations

**Authors' contributions** Chenchen Zhao and Shuai Guo had the idea for the article; Dandan Xu, Shuai Guo, and Xin Guo performed the literature search and data analysis; and Shuai Guo, Dandan Xu, Xin Guo, and Xingcan Li
drafted and/or critically revised the work. All authors read and approved the final manuscript.

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**Data availability** All data generated or analyzed during this study are included in this published article.

**Compliance with ethical standards**

**Conflict of interest** The authors declare that they have no conflict of interest.

**Ethical approval** The authors state that the research was conducted according to ethical standards.

**Consent to participate** Not applicable.

**Consent to publish** Not applicable.

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**Figures**

![Figure 1](image-url)
Schematic diagram of MFBRA-MS.

Figure 2

Comparison of actual and predicted (a) yields and (b) HHVs of hydrochar.
Figure 3

Response surface maps (a, c, e) and contour maps (b, d, f) showing the effects of temperature, residence time, and acetic acid concentration on hydrochar yield.
Figure 4

Response surface maps (a, c, e) and contour maps (b, d, f) showing the effects of temperature, residence time, and acetic acid concentration on hydrochar HHV.
Figure 5

Gaseous pollutant production during hydrochar combustion and gasification.
Figure 6

CO2 release during the combustion of residual char obtained after gasification in CO2 and Ar atmospheres.
Figure 7

Evolution of gaseous products during the gasification of raw SS and sludge hydrochar.
Figure 8

Effects of (a) temperature, (b) residence time, and (c) acetic acid concentration on the release of gaseous products during CO2-assisted gasification.
Figure 9

Effects of HTC conditions on the conversion of raw sludge and sludge hydrochar during gasification.

$$R_{0.9} \text{ (s}^{-1})$$

$$\text{Adj.} R^2 = 0.993$$

$$y = 1.02787x + 0.02006$$

Figure 10

Comparison between actual and predicted indexes of gasification reactivity.
Figure 11

Response surface maps (a, c, e) and contour maps (b, d, f) showing the effects of temperature, residence time, and acetic acid concentration on the gasification activity index of hydrochar.