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Utilization of sewage sludge derived hydrochars towards efficient co-combustion with different rank coals: Effects of subcritical water conversion and blending scenarios

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Abstract

In the absence of prior drying, dewatered sewage sludge (DSS) was directly converted to hydrochars with superior fuel characteristics in subcritical water. Hydrochar derived under 320 °C and 12.0 MPa (SHC-320) was screened for systematical co-combustion with different rank coals. Results suggest that SHC-320 reduced activation energy of blends and altered main combustion profiles. Meanwhile, blending SHC-320 induced greater heat loss for higher rank coals, whereas higher portion of SHC-320 further improved ignition reactivity of high rank coal blends. In high temperature region, pre-exponential factor value increased with elevated Coal/SHC-320 ratios, resulting in more intense synergistic effects in blends. Under a low Coal/SHC-320 ratio (30:70), intense anti-synergistic effects occurred in co-combustion with low or high rank coals. Due to distinct synergistic interactions, co-combustion with moderate rank coal achieved the best combustion efficiency among blends. These findings benefit efficient utilization of DSS as hydrochar solid fuels in existing co-firing power plants.

Keywords: Hydrothermal treatment; Solid fuel; Co-combustion characteristics; Kinetics; Synergistic/anti-synergistic interaction

1. Introduction

With the rapid urbanization and increasingly stringent regulations on the quality of effluents, sewage sludge (SS) generation from wastewater treatment plants is soaring globally. In general, SS is rich in nutrients (nitrogen, phosphorus, and potassium) and organic matter which is mainly composed of proteins, carbohydrates,
small amount of lipids and lignin. Thus, SS could be considered as biomass with higher heating value (HHV) comparable to lignite. Nevertheless, pollutants present in SS, for instance, heavy metals, pathogens and persistent organic pollutants, may endanger environment and human health. Thus, appropriate treatment and efficient utilization of SS is imperative. Given the refractory pollutants and desirable calorific value in SS, thermochemical processes (i.e. pyrolysis, gasification and combustion) have been widely applied as efficient technologies for final disposal and energy recovery from SS. However, high moisture content (approximately 70–80 wt.%) in dewatered sewage sludge (DSS) hindered its further utilization as solid fuels. Because of a huge amount of vicinal and bound water therein and relatively high latent heat of water, conventional mechanical and thermal drying are energy-intensive. More recently, some novel energy-saving drying technologies have been developed, such as solvent aided dewatering, combined hydrothermal pretreatment and convective drying.

In order to reduce coal consumption by substituting certain amount of coal with SS, co-combustion of SS and coals has been explored. However, fuel characteristics between SS and coals are quite different and high volatile matter (VM) in SS could result in unstable flame. Thus, co-combustion performance of dried SS and coals may be considerably affected. The presence of high nitrogen and sulfur contents in SS may cause high emissions of NO\textsubscript{x} and SO\textsubscript{x}, which could increase the cost for flue gas cleaning. Hence, it is essential to upgrade fuel quality of SS to meet requirements for co-firing purpose based on current infrastructures. Hydrothermal carbonization of SS
has been applied to produce solid fuels of better quality, termed hydrochar, for energy
generation without prior drying.\textsuperscript{7, 9, 10} Apart from the upgraded HHV and fuel ratio for
hydrochar via dehydration and decarboxylation, it is also found that N and S
precursors in hydrochar could be significantly reduced during hydrothermal
carbonization.\textsuperscript{10} Moreover, quality of emissions from combustion of sewage sludge
derived hydrochars (SHCs) can be further improved. Parshetti et al.\textsuperscript{7} reported that
emissions of CO and CH\textsubscript{4} were mitigated through co-combustion of SHC and low
rank coal. During the combustion of hydrothermally pretreated sludge, as a result of
transformation of protein structure via hydrothermal treatment, interaction between
NO and NH\textsubscript{3} was facilitated and thus NO emissions could be reduced.\textsuperscript{9} These leading
research results suggest that there is a great potential to utilize SHC for existing
co-firing infrastructures towards lower coal consumption and better management of
SS.

Nonetheless, existence of interactions between different solid fuels during
co-combustion could lead to variations of fuel reactivity and burn out characteristics
since co-combustion performance may not necessarily demonstrate synergistic
interactions or simple additive behaviors as expected.\textsuperscript{11} Thus, extensive research
regarding interaction effects during co-combustion has been conducted, such as
co-combustion of SS and coals,\textsuperscript{5, 12} co-combustion of biomass or pretreated biomass
and coals.\textsuperscript{13, 14} In particular, Parshetti et al.\textsuperscript{7} studied co-combustion of low rank
Indonesian coal and SHC with a blending ratio ranging from 10\% to 30\%. Increasing
the amount of SHC addition improved combustion reactivity of blends. Besides, Liu
et al.\textsuperscript{15} concluded that synergistic interaction between hydrochar and low rank coals was more intense than that with high rank coals due to their similar fuel characteristics. But in order to enhance combustion reactivity, SHC of better fuel quality is desired. From the perspective of considerable coal consumption reduction, greater SHC blending ratio in co-firing is more economically viable. To date, limited information and systematic research is available pertaining to fuel characteristics and combustion behaviors evolutions of SHCs derived from different hydrothermal conditions and co-combustion performance with different rank coals.

Therefore, it is meaningful to screen SHC of good fuel quality for co-combustion with different coals at a wide range of blending ratio before designing co-combustion scenarios. To fill up this research gap, the main objectives of this study are to (1) investigate fuel characteristics and combustion behaviors of SHCs prepared under various hydrothermal conditions to screen the best SHC for co-combustion; (2) compare combustion behaviors of three different rank coals with SHCs; (3) analyze the co-combustion behaviors for selected SHC and three different rank coals with a wide range of Coal/SHC blending ratio; and (4) interpret interaction effects during co-combustion process.

2. Experimental section

2.1 Materials

Dewatered sewage sludge (DSS) was collected from Ulu Pandan Water Reclamation Plant in Singapore. After anaerobic digestion and dewatering process, the generated DSS possessed 82.5 wt.% of water. The DSS sample was stored in a 4
C cold room and used directly as feedstock to prepare hydrochar solid fuels using hydrothermal conversion (HTC). Three different rank coals (i.e. Hongshaquan coal, Shuicheng lignite, and Shaerhu coal) originated from China, which were designated as Coal-1, Coal-2, and Coal-3, respectively. Prior to characterization, all the DSS, hydrochars, and coal samples were oven dried at 105 °C overnight and ground into less than 0.5 mm fine powders using a rotary mill. These samples were sealed in dry polypropylene centrifuge tubes and stored in a dry cabinet.

2.2 HTC experiments

HTC of DSS was conducted in a 1.0 liter stainless steel (SS 316L) fixed-head batch reactor (Parr 4577 model) which was equipped with magnetic drive stirrer, external electric heating mantle and PID controller (Parr Instrument Co., USA). The reactor was designed to withstand a maximum operating temperature and pressure of 500 °C and 35 MPa, respectively. The temperature was precisely controlled by a J-type thermocouple. The pressure was autogenously generated by the water in DSS under corresponding temperature and shown both in analogue gauge and digital indicator. Based on records from preliminary experiments, 150 g of deionized water could generate a pressure of 22.0 MPa at 380 °C which reached near-critical water condition. In each batch experiment run, 182 g of DSS, which contained approximately 150 g of water, was loaded into the reactor vessel and sealed. Subsequently, the vessel was heated up to pre-set temperature and corresponding pressure using the electric heating mantle under a stirring speed of 500 rpm. Following the above procedure, six hydrothermal conversion conditions were applied,
i.e. 220 °C and 2.6 MPa, 260 °C and 5.0 MPa, 300 °C and 9.3 MPa, 320 °C and 12.0 MPa, 340 °C and 15.5 MPa, 380 °C and 22.0 MPa. After a reaction time of 20 min under desired temperatures and pressures, the heating mantle was removed. The vessel was firstly cooled by a standing fan. When the temperature was below 200 °C, an additional internal cooling coil was then employed to quench the vessel rapidly to room temperature via cooling water circulator.

After depressurization, the vessel was opened for solid and liquid products separation and collection. Liquid products were filtered through 0.45 µm PTFE membrane filters and kept in glass vials at 4 °C for further analysis. The solid residues were carefully collected and oven dried at 105 °C for 12 h. The dry solids were ground into less than 0.5 mm fine powders and termed hydrochars hereinafter. The SHCs were designated as SHC-220, SHC-260, SHC-300, SHC-320, SHC-340, and SHC-380, respectively. The number indicates the reaction temperature.

2.3 Characterization of samples

For proximate analysis, ash content determination was carried out based on ASTM D3174 and VM content was measured by STA 449 F3 Jupiter Simultaneous TG-DTA/DSC Apparatus (NETZSCH-Gerätebau GmbH) according to ASTM D7582-10. The fixed carbon (FC) percentage was then calculated by difference. Moreover, fuel ratio, which is expressed as the ratio of FC to VM, represents fuel properties of solid fuels and high rank coals generally exhibit high fuel ratio.\(^6\,^{16}\) In this study, the fuel ratio was used to present the evolution of FC and VM during HTC and reflect the solid fuel quality of derived hydrochars for co-firing applications.
Elemental compositions (i.e. carbon, hydrogen, nitrogen, and sulfur) of DSS, hydrochars, and coals were determined by vario EL CHNS elemental analyzer. The higher heating values (HHVs) of all the solid fuel samples were measured through IKA C2000 BASIC bomb calorimeter. Table 1 summarizes basic fuel characteristics of DSS, sewage sludge derived hydrochars, and three different rank coals.

2.4 Preparation of hydrochar and coal blends

Given the highest HHV (20.35 MJ/kg), greatest fuel ratio (3.66) and relatively low N and S contents in SHC-320, the hydrochar and coal blends were prepared by thoroughly mixing the hydrochars derived from sewage sludge under 320 °C and 12.0 MPa with the three Chinese coals. Different blending ratios of Coal:SHC-320, i.e. 30:70, 50:50 and 70:30, were selected. According to these blending ratios, coal and hydrochars were loaded into beakers and well dispersed in water using magnetic stirring bar at 650 rpm for 24 h under room temperature. Afterwards, the mixtures were oven dried at 105 °C for 24 h and ground into fine powders for subsequent combustion behavior analysis. In order to easily identify different blends, these hydrochar and coal blends were designated as 30C70HC-1, 50C50HC-1, 70C30HC-1, 30C70HC-2, 50C50HC-2, 70C30HC-2, 30C70HC-3, 50C50HC-3, and 70C30HC-3, respectively. Specifically, “C” represents coal sample and the number before “C” was the blending ratio (%) of coal, while “HC” represents SHC-320 sample and the number before “HC” was the blending ratio (%) of SHC-320. The number after “-” stands for different rank coals (i.e. “1” represents Coal-1, “2” represents Coal-2, and “3” represents Coal-3).
2.5 Combustion characteristics analyses

2.5.1 Thermogravimetric analysis (TGA)

In this study, combustion behaviors of solid fuel samples were analyzed by Perkin Elmer TGA7 Thermogravimetric Analyzer based on the widely used TGA method. Combustion experiments were performed according to the procedure described in our previous study. In each run, 9 mg of samples were loaded into TG pan and heated from 30 to 900 °C at a heating rate of 10 °C/min with a fixed air flow rate of 20 mL/min under an atmospheric pressure. The weight loss (TG) and the rate of weight loss (DTG) of each sample under the non-isothermal condition were recorded dynamically and used for evaluation of combustion performance and kinetics analysis of different solid fuel samples. Repeated combustion runs of samples were conducted to verify the reproducibility of experimental results and ensure that the deviations were less than 5%.

2.5.2 Kinetics analysis

In general, reaction kinetics during combustion process can be expressed according to the decomposition rate of solid fuels described previously:

\[ \frac{d\alpha}{dt} = kf(\alpha) \]  
\[ \alpha = \frac{(m_i - m)}{(m_i - m_f)} \]  
\[ f(\alpha) = (1 - \alpha)^n \]  
\[ k = A \exp\left(-\frac{E}{RT}\right) \]  
\[ \beta = \frac{dT}{dt} \]

where \( \alpha \) is the thermal conversion fraction of solid fuels at time \( t \); \( m_i \), \( m \), and \( m_f \) refer
to the initial, instantaneous, and final mass of solid fuels, respectively; \( f(\alpha) \) represents a general expression of the combustion mechanism; \( n \) is the order of reaction; \( k \) is the rate constant which can be derived by Arrhenius Eq. (4); \( E \) and \( A \) represent the activation energy (kJ mol\(^{-1}\)) and the pre-exponential factor (min\(^{-1}\)) of the reaction, respectively; \( R \) is the universal gas constant 8.314 J K\(^{-1}\) mol\(^{-1}\); \( T \) is the absolute temperature (K); \( \beta \) denotes a constant heating rate (10 °C/min) in the present non-isothermal combustion study.

A series of combination and rearrangement of Eqs. (1) – (5) gives:

\[
\frac{d\alpha}{f(\alpha)} = A \exp\left(-\frac{E}{RT}\right)dt = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right)dT
\]

Eq. (6) is integrated and becomes:

\[
G(\alpha) = \int_{0}^{\alpha} \frac{d\alpha}{f(\alpha)} = \int_{T_{i}}^{T_{f}} \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right)dT
\]

Eq. (7) is then transformed based on Coats-Redfern approximation method\(^{17}\) for kinetic parameters analysis in non-isothermal combustion process\(^{14}\), giving:

\[
\ln \left[ \frac{G(\alpha)}{T^{2}} \right] = \ln \frac{AR}{\beta E} \left(1 - \frac{2RT}{E}\right) - \frac{E}{RT}
\]

Since \( RT/E \ll 1 \) and \( 1 - RT/E \approx 1 \) in this study, the kinetic mechanism equation of combustion process can be described Eq. (9):\(^{10}\)

\[
\ln \left[ \frac{G(\alpha)}{T^{2}} \right] = \ln \frac{AR}{\beta E} - \frac{E}{RT}
\]

When an appropriate \( n \) is selected, a straight line can be obtained by plotting \( \ln [G(\alpha)/T^{2}] \) vs. \( 1/T \). Hence, \( E \) and \( A \) can be determined from the slope and intercept of this line, respectively.
2.5.3 Evaluation of combustion performance

Three characteristic temperatures, i.e. ignition temperature \((T_i, ^\circ C)\), maximum combustion rate temperature \((T_m, ^\circ C)\), and burn out temperature \((T_b, ^\circ C)\), were derived from TG-DTG data. Three points, i.e. point A, B, and C in all the figures, were identified following a previously described procedure.\(^{10, 15, 18}\)

According to characteristic temperatures and representative weight loss rates in combustion profiles, comprehensive combustibility index \((S)\) was calculated to evaluate overall combustion reactivity of solid fuels.\(^{10}\)

\[
S = \frac{(\frac{dw}{dt})_{\text{max}}(\frac{dw}{dt})_{\text{mean}}}{T_i^2 T_b} \tag{10}
\]

where \((\frac{dw}{dt})_{\text{max}}\) and \((\frac{dw}{dt})_{\text{mean}}\) are the maximum and mean rates of weight loss (wt.\%/min), respectively.

2.5.4 Deviation between experimental and theoretical combustion profiles

To investigate interaction phenomenon of hydrochars and coals during their co-combustion, theoretical TG and DTG curves were calculated by taking account of individual mass fraction, weight loss, and rate of weight loss of SHC-320 and coals as follows.\(^{19, 20}\)

\[
(TG)_{\text{cal}} = x_1 (TG)_{\text{hydrochar}} + x_2 (TG)_{\text{coal}} \tag{11}
\]

\[
(\frac{dw}{dt})_{\text{cal}} = x_1 (\frac{dw}{dt})_{\text{hydrochar}} + x_2 (\frac{dw}{dt})_{\text{coal}} \tag{12}
\]

where \((TG)_{\text{hydrochar}}\) and \((TG)_{\text{coal}}\) are normalized weight losses derived from TG curves of independent combustion of SHC-320 and coals, respectively; \((\frac{dw}{dt})_{\text{hydrochar}}\) and \((\frac{dw}{dt})_{\text{coal}}\) are normalized rates of weight loss derived from DTG curves of independent combustion of SHC-320 and coals, respectively; \(x_1\) and \(x_2\) are the mass
fractions of SHC-320 and coals in blends, respectively.

Deviations of maximum weight loss rates and residues between experimental and calculated curves can quantify whether synergistic interaction occurred after addition of hydrochars into coals. The deviations were determined according to Eq. (13).

\[
\text{Deviation (\%)} = \frac{(\text{Experimental value} - \text{Calculated value})}{\text{Calculated value}} \times 100 \quad (13)
\]

3. Results and discussion

3.1 Physicochemical properties of DSS, hydrochars, and coals

3.1.1 Effects of HTC on fuel characteristics of hydrochars

In Table 1, DSS consisted of 69.01% of VM, 9.19% of FC, and 21.80% of ash, leading to a low fuel ratio (FC/VM) of 0.13. The high N and S contents (6.04% and 5.62%, respectively) imply significant pollutants emissions when DSS is directly utilized as solid fuels. The high S content may originate from enriched alkyl surfactant and perfluorooctane sulfonate compounds in DSS. High O content (20.46%) could be detrimental to the calorific value of DSS. Consequently, HHV and lower heating value (LHV) of DSS were 17.97 MJ/kg and 16.61 MJ/kg, respectively.

The VM content of DSS decreased significantly after HTC. The DSS had a VM content of 69.01% which decreased to 12.86% in SHC-320 with the increased temperature and pressure. The loss of VM was converted into FC and gaseous products via dehydration and decarboxylation reactions,\textsuperscript{10} thus FC of hydrochars increased progressively from 9.19% in DSS to 47.03% in SHC-320. Due to increased generation and deposition of light volatile organic molecules on the surface of hydrochars,\textsuperscript{10,21} VM in hydrochars produced from severe hydrothermal treatment (i.e.
340 °C and 15.5 MPa, 380 °C and 22.0 MPa) was at least three times higher than that of SHC-320. However, further degradation and transformation of these volatile molecules in hydrochars tended to be obvious under even higher temperature and pressure. Compared with SHC-340, VM decreased from 42.03% to 38.25% in SHC-380 while slight increase (1.75%) of FC in SHC-380 may be associated with the partial conversion of VM. Furthermore, the excess loss of VM and retained minerals resulted in a constant increase of ash content (ca. 40%) in hydrochars during all the HTC conditions. Accordingly, fuel ratio increased from 0.13 for DSS to 3.66 for SHC-320 and decreased to around 0.40 afterwards.

Based on ultimate analysis results, H, N, S, and O contents in hydrochars declined as the temperature and pressure increased. Particularly, within a reaction time of 20 min under 380 °C and 22.0 MPa, the removal efficiency of N, S, and O contents reached 47%, 37%, and 87.4%, respectively. On the other hand, C content increased to around 43% to various extents. Due to the remarkable removal of O contents and increased C contents, calorific values of hydrochars were increased by 1.03 to 1.13 times. Taking into account of evolutions of three components (i.e. ash, VM, and FC) and elemental compositions in hydrochars, SHC-320 exhibited highest HHV and LHV of 20.35 MJ/kg and 19.28 MJ/kg, respectively. Hence, from the perspectives of superior fuel characteristics compared with DSS and other hydrochars, SHC-320 was selected as sewage sludge derived solid fuel for co-combustion with coals.
3.1.2 Fuel characteristics of different rank coals

Coal samples showed great difference in components and elemental compositions compared to DSS and hydrochars. As shown in Table 1, FC contents in coals were 3.68 to 7.13 times higher than that in DSS whereas VM contents were generally lower than 69.01% in DSS. Coal-1 and Coal-2 presented highest FC (65.54%) and VM (48.95%), respectively. Fuel ratios of the three different rank coals were 2.11, 0.69, and 1.76 for Coal-1, Coal-2, and Coal-3, respectively. Ash contents in coals were typically lower than 20% and Coal-1 contained only 3.36% ash. C contents (50.34–71.96%) in coals were much higher than 39.88% in DSS while H, N, and S contents were relatively lower. Especially, N and S contents in all coal samples were less than 1% and 3%, respectively. In addition, O content was around 20%, which was comparable to that in DSS but much higher than hydrochars. Because of higher C but lower ash contents, HHVs of coals were higher than 17.97 MJ/kg of DSS, which were 28.85 MJ/kg, 22.63 MJ/kg, and 24.37 MJ/kg for Coal-1, Coal-2, and Coal-3, respectively. Overall, coal rank followed the order of Coal-1 > Coal-3 > Coal-2 in terms of these fuel characteristics.

3.2 Effects of HTC on combustion profiles and characteristics of hydrochars

To investigate combustion behaviors of DSS and hydrochars, the entire decomposition profiles were characterized according to evident rates of weight loss in DTG curves. As described by He et al., combustion process generally consisted of dehydration stage D, devolatilization and combustion stage E, char combustion stage F, and burn out stage.
Previously, a two-stage decomposition kinetics was proposed to assess combustion of biomass.\textsuperscript{14,22} However, taking into account of delayed combustion of heavy VM and FC in solid fuels, a modified two-stage combustion scheme was employed to describe the combustion process in the present study as follows.

\[ V_1(\text{light volatile matter}) \xrightarrow{\text{First combustion stage}} C_1(\text{char}) + G_1(\text{gas}) \]
\[ V_2(\text{heavy volatile matter}) + C_1(\text{char}) + C_2(\text{fixed carbon}) \xrightarrow{\text{Second combustion stage}} G_2(\text{gas}) + R(\text{ash}) \]

where $E_1$ and $A_1$ represent activation energy and pre-exponential factor in the first combustion stage, respectively; $E_2$ and $A_2$ represent activation energy and pre-exponential factor in the second combustion stage, respectively.

Subsequently, the kinetics analysis of individual combustion stage was examined separately through Arrhenius equation by selecting an appropriate reaction order.

3.2.1 Combustion of DSS

As shown in Fig. 1, stage D (30 to 100 °C) was the initial water evaporation stage and two distinct decomposition stages (stage E and F) governed the intense combustion process of DSS. Unlike a single combustion profile (250 to 450 °C) of DSS in our previous study,\textsuperscript{10} the two-stage combustion profile was associated with noticeable FC content (9.19%) of DSS in this study. As summarized in Table 2, the first combustion stage E was extended from 150 to 370 °C while the second combustion stage F was from 390 to 550 °C, which was similar to main combustion process of microalgae under comparable conditions as reported by Tahmasebi et al.\textsuperscript{23} Two pronounced peaks were observed at 277.1 °C and 483.7 °C. Peak temperatures at 277.1 °C and 320.5 °C during stage E may be related to the step-wise decomposition of carbohydrates (180–270 °C), proteins and lipids (320–450 °C)\textsuperscript{23-25} while peak
temperature around 483.7 °C could be ascribed to residual lignin decomposition and char/FC oxidation.\textsuperscript{26,27} Moreover, weight loss in stage E (39.9\%) was higher than that in stage F (27.7\%), suggesting more light VM in DSS. $T_i$ is associated with release rate of heat from early combustion of light VM.\textsuperscript{26} As a result, $T_i$ was only 207.7 °C and maximum weight loss was at 278.8 °C, which were quite close. However, high $T_b$ (514.9 °C) led to a prolonged combustion process of 30.7 min. The water evolution and small amount releases of methane and carbon dioxide could be responsible for the first peak, whereas intensive decompositions of aromatic or heterocyclic hydrocarbons led to significant emissions of hydrogen, methane, and carbon dioxide in the second peak due to the abundant VM and O contents.\textsuperscript{24,25} Nevertheless, further investigations are necessary to gain more insights into gas evolutions.

3.2.2 Combustion of hydrochars

Fig. 2 illustrates combustion profiles of different hydrochars. Dehydration stage D of hydrochars was less obvious with the increases of temperature and pressure, which should be relevant to more hydrophobic characteristic of hydrochars.\textsuperscript{10} Besides, the peak of stage E became less intense while that of stage F tended to be sharper. Weight loss in stage E decreased to 22.5\% for SHC-220 but that in stage F increased to 37.0\%. The combustion kinetics of SHC-260 in Table 3 indicated there may be an overlap of stage E and F, causing a board stage F (200–550 °C) with a great mass loss of 57.6\%. As shown in Table 2, weight loss in stage F decreased from 49.2\% for SHC-300 to 40.9\% for SHC-380 due to accelerated de-polymerization and re-polymerization of heavy VM in subcritical water.\textsuperscript{28} On the other hand, during HTC
of sludge, formation of water soluble oil was favored at lower temperatures while increased temperature led to higher water insoluble heavy oil (HO) yield. \(^{29}\) HO was mainly composed of long-chain carboxylic acids, phenolic compounds and derivatives. Since the hydrochars in this study were not extracted with solvent, HO could be entrained. These small amounts of light volatile compounds contributed to slight increase of weight loss in stage E from 6.6\% for SHC-300 to 8.9\% for SHC-380. One apparent peak was observed around 200 °C. An increasing trend of residues agreed with previous discussion.

Because of reduced VM and elevated FC in hydrochars, \(T_i\) exhibited a remarkable increase of 70 to 108 °C as the temperature and pressure increased. Low \(T_i\) may cause potential fire hazard.\(^{15, 30}\) In this regard, hydrochars demonstrated advantages in safe handling and storage over DSS. Though VM contents in SHC-340 and SHC-380 were much higher than lowest VM in SHC-320, \(T_i\) values of the former hydrochars were even higher, suggesting that a high VM does not necessary give lower \(T_i\). Further, \(T_m\) also increased drastically to around 420 °C to different extents for hydrochars. There was a minor decrease of \(T_b\) within 10 °C for hydrochars derived under HTC temperature lower than 320 °C. On the contrary, \(T_b\) increased to 517.8 °C and 557.7 °C for SHC-340 and SHC-380, respectively. The noticeable decrease of FC and relatively high ash contents should be responsible for the difficult combustion. In particular, an evident shoulder in stage F for SHC-380 appeared at high temperature (470–550 °C). Main combustion was shortened to approximately 20 min. But combustion of SHC-380 lasted 24.2 min, which was the highest among SHCs.
Therefore, in terms of safer $T_n$, higher heat release in a higher temperature region, and slightly decreased $T_b$ during the shortened combustion profile, the performance of SHC-320 outweighed other SHCs.

### 3.3 Combustion profiles for different rank coals

As shown in Fig. 3, main combustion of coals was only characterized by stage F. This suggests that decomposition of VM during coal combustion requires a higher temperature as FC, resulting in a remarkable weight loss and simultaneous oxidation of heavy VM and FC$^{23,31}$ within a narrow stage F at high temperatures. Furthermore, higher rank coal exhibited narrower stage F and greater weight loss or heat release. In Table 2, the width of temperature range followed the order of Coal-1 (410–550 °C) < Coal-3 (350–520 °C) < Coal-2 (290–520 °C) while the weight loss was Coal-1 (75.2%) > Coal-3 (71.6%) > Coal-2 (68.5%). Overall, $T_n$, $T_m$ and $T_b$ increased as rank of coal became higher. The relatively lower rank Coal-2 showed $T_i$ and $T_m$ of 288.4 °C and 373.1 °C, respectively, which were more comparable to those of SHC-320. Typically, $t_b$ of coals was lower than DSS and hydrochars. Interestingly, $t_b$ of SHC-320 (20.5 min) and lower rank Coal-2 (19.9 min) was similar. Thus, a more compatible co-combustion of the two fuels was anticipated. Compared to DSS and hydrochars, burn out stage of the three coals presented some fluctuations, especially for Coal-2 which produced the highest residues (14.6%), which could be attributed to decomposition of inorganic salts or metal carbonates therein at 550 to 750 °C.
3.4 Effects of hydrochar on co-combustion with different rank coals

3.4.1 Effects of coal/hydrochar blending ratios and different characteristics of coals

3.4.1.1 Patterns of combustion profiles

According to co-combustion profiles in Fig. 4 and combustion kinetics data in Table 3, lower supplement coal of 30% and 50% resulted in a two-stage combustion (stage E and F) while there was only one distinct stage F at a high Coal/SHC-320 ratio (70:30). Nonetheless, weight loss in stage E was less than 5%. Except Coal-2, this mass loss was inclined to be slightly lower when Coal/SHC-320 ratio was elevated to 50:50. In contrast, weight loss in stage F showed an upward trend as Coal/SHC-320 blending ratio varied from 30:70 to 70:30. In addition, compared to weight loss in stage F for individual coal, this value for Coal/SHC-320 blended fuels declined drastically as the coal rank increased. Specifically, the value of Coal-2/SHC-320 retained 74.7 to 94.7% of weight loss value in lower rank Coal-2, which was higher than those of Coal-3/SHC-320 (70.9 to 80.0%) and Coal-1/SHC-320 (63.5 to 78.2%). This reveals that heat loss may be larger during co-combustion of SHC-320 with higher rank coals. Stage F in DTG curves for different coal bended fuels in Fig. 4 was closely examined. In Fig. 4a, d and e, in addition to the peak at $T_m$, there was at least one more sub-peak in stage F when low coal percentages of 30% and 50% were employed. This phenomenon may be attributed to less significant synergistic effects resulting from either apparently different or similar characteristics between two individual fuels. Since the proportion of coals was less, the combustions of coals cannot affect that of hydrochar too much. Meanwhile, though hydrochar made up of
the majority in blends, it may be inadequate to alter combustion patterns of coals. So components in Coal-1 or Coal-2 and SHC-320 may be combusted independently. Some combustibles may overlap, thereby exhibiting several sub-peaks in DTG curves. For the rest, especially Coal-3/SCH-320, VM and FC components may interact with each other, promoting a combined and short stage F. Yet Coal-3/SCH-320 at all blending ratios showed only one sharp peak in stage F, which may be associated with intense synergistic effects. In spite of this, there was a small shoulder at high temperatures. Besides, residues increased to approximately 30% when Coal/SHC-320 blending ratio decreased to 30:70.

3.4.1.2 Evolutions of characteristic temperatures

(i) Generally, $T_i$ increased with coal blending ratio. For low Coal:SHC-320 blending ratio (30:70), $T_i$ was 348.2 °C, 299.7 °C, 345.0 °C for 30C70HC-1, 30C70HC-2, 30C70HC-3, respectively, which fell between $T_i$ values of SCH-320 and individual coals. Because $T_i$ for Coal-2 was lower than that for SHC-320 and SHC-320 dominated the blends, $T_i$ for 30C70HC-2 was higher than lower rank Coal-2. Meanwhile, $T_i$ values for the other two blended fuels were lower compared to their respective coals due to their inherent relatively high $T_i (> 350 \, ^\circ C)$. On the other hand, high blending ratio resulted in a higher $T_i$ for their blends. Hence, when blended with higher rank coals, ignition performance could be improved in the presence of high proportion of SHC-320 but inhibited when smaller amount ($\leq 30\%$) of SHC-320 was introduced. (ii) With the increase of coal/hydrochar blending ratio, $T_m$ of blended fuels was shifted to lower temperature (ca. 350 °C) for lower rank Coal-2 due to higher VM
therein but was at higher temperature for higher rank Coal-1 (ca. 520 °C) and Coal-3 (ca. 425 °C). Interestingly, after introduction of 70% of SHC-320, $T_m$ displayed opposite evolutions, which was decreased to 439 °C for 30C70HC-1 but increased to 401.6 °C for 30C70HC-2. This was mainly related to the predominant role of SHC-320 in blends, resulting in a $T_m$ close to that of SHC-320. Due to prominent intrinsic characteristics of the two coals, their blends exhibited opposite behaviors. (iii) $T_b$ of all blends increased dramatically by ca. 20 to 50 °C to different extents, thereby extending $t_b$ up to 24.9 min for 30C70HC-1. Although Coal-2 and SHC-320 presented similar $t_b$, $t_b$ of their blends was obviously greater. Under the same blending ratio, it is worth noting that $t_b$ for combustion of SHC-320 with high rank Coal-1 and low rank Coal-2 was longer than that of moderate rank Coal-2. Thus, a shorter combustion process may be expected for blends of SHC-320 with moderate rank coals.

3.4.2 Kinetic parameters analysis and comparison

Two important kinetic parameters, i.e. activation energy ($E$) and pre-exponential factor ($A$), were determined to obtain in-depth insights into combustion behaviors of DSS, hydrochars, coals, and respective blends. Based on the two-stage combustion scheme proposed in Section 3.2 and different combustion stages in TG-DTG curves, data derived from individual stages were carefully screened and applied for kinetics analysis through linear regression by selecting the most suitable reaction order. As shown in Table 3, the first-order oxidative mechanism was the best fitting and reliable model with correlation coefficient ($R^2$) ranging from 0.9501 to 0.9973, which agreed with claims from combustions of DSS, hydrochars, and hydrochar-lignite blends.7,10,
Moreover, kinetic parameters derived from TG-DTG curves under constant heating rate and iso-conversional method were in good agreement in qualitative terms. Thus, kinetics data were interpreted for comparison below.

DSS showed lower $E_1$ and $A_1$ (18.12 kJ mol$^{-1}$ and 1.43 min$^{-1}$, respectively) under the first combustion stage but higher $E_2$ and $A_2$ (32.31 kJ mol$^{-1}$ and 26.14 min$^{-1}$, respectively) during the second combustion stage. After HTC, $E_1$ for hydrochars increased by 8.31–16.37 kJ mol$^{-1}$ to around 30 kJ mol$^{-1}$, confirming better reactivity of DSS than hydrochars at low temperatures. Particularly, $E_1$ for SHC-220 and SHC-320 was relatively lower (26.43 and 28.98 kJ mol$^{-1}$, respectively) while $E_1$ for SHC-340 was the highest (34.49 kJ mol$^{-1}$), which was in relation to their $T_i$ values. This reflects that SHC-220 and SHC-320 may be more reactive to ignite than other hydrochars. Interestingly, excluding SHC-380, $E_2$ values for all the other hydrochars were similar to that of DSS, suggesting comparable energies to oxidize char and FC. Compared with DSS, $A_1$ for hydrochars increased while $A_2$ decreased slightly due to compensation effects. The lowest $E_2$ (27.61 kJ mol$^{-1}$) and $A_2$ (6.60 min$^{-1}$) values for SHC-380 could be mainly attributed to the lower concentrations of heavy VM and FC therein as $A$ is closely related to concentrations of reactants based on Collision Theory.

Higher rank coal presented greater activation energy and pre-exponential factor, which followed the order of Coal-1 (87.60 kJ mol$^{-1}$ and 2.22E+05 min$^{-1}$) > Coal-3 (62.22 kJ mol$^{-1}$ and 5092.79 min$^{-1}$) > Coal-2 (39.07 kJ mol$^{-1}$ and 101.81 min$^{-1}$). However, $E$ values for coal blends in all combustion stages were lower than their...
respective coals. $E_1$ decreased with the elevated percentages of coals, suggesting the
decrease of activation energy to initiate decomposition of coal blended fuels.\(^{33}\) On the
other hand, $E_2$ gradually increased (37.69 to 61.74 kJ mol\(^{-1}\) for Coal-1/SHC-320; 38.69 to 45.84 kJ mol\(^{-1}\) for Coal-2/SHC-320; 40.11 to 58.35 kJ mol\(^{-1}\) for
Coal-3/SHC-320) as percentages of coals increased from 30% to 70%, pointing out
that higher energy was required to overcome barriers resulting from ring-opening,
depolymerization, recondensation and repolymerization.\(^{34}\) Similar trend was
observed for $A$ values. As percentages of coals were elevated to 70%, $A_2$ increased
drastically to 1653.08 min\(^{-1}\), 222.23 min\(^{-1}\) and 2114.05 min\(^{-1}\) for 70C30HC-1,
70C30HC-2 and 70C30HC-3, respectively, whereas $A_1$ was approaching 0.

3.4.3 Evaluation of combustion performance

Table 4 illustrates $(\text{dw/dt})_{\text{mean}}$, $(\text{dw/dt})_{\text{max}}$, and $S$ values for DSS, hydrochars,
coals, and Coal/SHC-320 blends. DSS exhibited greatest $S$ (11.63×10\(^{8}\)) among all
solid fuels, including three coals. This was primarily contributed by lowest $T_i$ as
$(\text{dw/dt})_{\text{mean}}$ (0.90 wt.%/min) and $(\text{dw/dt})_{\text{max}}$ (2.87 wt.%/min) for DSS were far lower
than $(\text{dw/dt})_{\text{mean}}$ (1.12 wt.%/min) and $(\text{dw/dt})_{\text{max}}$ (7.58 wt.%/min) for highest rank
Coal-1, respectively. Since low $T_i$ (< 220 °C) could pose fire hazard, especially during
co-milling of DSS and coals, it is not advisable to directly utilize DSS as solid fuels.
SHC-220 and SHC-320 presented higher $S$ value around $5\times10^{8}$ among hydrochars.
Similarly, despite relatively lower $(\text{dw/dt})_{\text{mean}}$ (0.98 wt.%/min) and $(\text{dw/dt})_{\text{max}}$ (4.54
wt.%/min), lower rank Coal-2 possessed a higher $S$ (10.98×10\(^{8}\)) than Coal-1
(9.30×10\(^{8}\)) and Coal-3 (10.85×10\(^{8}\)). With the increase of coal blending percentage,
(dw/dt)_mean, (dw/dt)_max, and S increased. Unexpectedly, 70C30HC-3 showed higher
(dw/dt)_max than 70C30HC-1 although this value for Coal-3 was much lower than that
for Coal-1, suggesting that more intense synergistic effects may occur during main
combustion. Overall, higher coal percentages of 50% and 70% provided higher S and
blends of SHC-320 with moderate rank Coal-3 gave the highest S value compared to
other blends.

3.5 Interactions between hydrochar and coals during their co-combustion

Fig. 5 depicts the comparisons of experimental and calculated TG and DTG
curves for co-combustion of SHC-320 and different rank coals. The experimental
curves always deviated from corresponding calculated curves. Compared with
calculated DTG curves, T_m in experimental DTG curves was shifted to higher
temperatures for SHC-320 blended with higher rank Coal-1 and Coal-3, but moved
towards to lower temperatures for blends with lower rank Coal-2. In addition, through
careful examinations on TG-DTG curves in Fig. 5, more remarkable interactions were
observed under high temperatures than low temperature region, which coincided with
previous findings.²⁰ In Table 5, corresponding characteristic parameters at high
temperatures, such as T_m, (dw/dt)_max and residues contents, were obtained from
experimental and calculated TG-DTG curves. Moreover, deviations between
experimental and calculated data were determined for quantitative comparisons.

Results in Table 5 suggest that both positive and negative interactions between
different coals and hydrochars took place during co-combustion. Briefly, “+”
(dw/dt)_max deviation implies that higher (dw/dt)_max can be expected and heat loss could
be less, while “+” residues deviation reveals that there are greater combustion
difficulties and thus more incomplete combustions occurs during co-combustion. In
this regard, “+” \((dw/dt)_{max}\) and “−” residues deviations present the most favorable
synergistic effects, which is desired during co-combustion of coal/hydrochar blends.
Conversely, “−” \((dw/dt)_{max}\) and “+” residues deviations indicate the highest
anti-synergistic effects, which should be avoided when designing co-combustion
scenarios. Synergistic effect index values were defined and marked accordingly.

On the whole, deviations for \((dw/dt)_{max}\) varied significantly while those for
residues were within ±7%. 50C50HC-1, 70C30HC-1 and 70C30HC-3 presented most
intense synergistic effects while 30C70HC-1, 30C70HC-2 and 50C50HC-2 showed
highest anti-synergistic effects. Compared with calculated values, experimental
\((dw/dt)_{max}\) for 30C70HC-2 decreased dramatically by 10.5% with an increase of 4.2%
in residues, indicating that high hydrochar blending ratio (70%) in low rank coal
inhibited co-combustion. Despite obvious enhancement in \((dw/dt)_{max}\) for 70C30HC-2,
30C70HC-3 and 50C50HC-3, incomplete co-combustion may lead to more residues.
Among these three blends, 70C30HC-2 was the most apparent one and demonstrated
+17.5% \((dw/dt)_{max}\) and +6.5% residues deviations. It is noted that the higher
synergistic effect index values were consistent with corresponding high \(A_2\) in high
temperature region, implying that synergistic interaction may be triggered increased
\(A_2\) as a result of high concentration of reactants.35

Based on the claims that more significant synergistic interactions occurred
between biomass/biomass derived hydrochars and low rank coals than high rank
coals, results in this study suggest both synergistic and anti-synergistic interactions can take place depending on blending ratios as well as intrinsic fuel characteristics of hydrochars and coals. Hence, coal rank and blending ratio are crucial criteria to be determined before co-combustion with SHC solid fuels. To conclude, for high rank coals, higher coal percentage (≥ 50%) in blends would achieve more synergistic interactions while low blending ratio (≤ 30%) may cause severe anti-synergistic interactions. For low rank coals, high coal percentage (≥ 70%) may induce positive interactions but more incomplete combustion, whereas coal percentage less than 50% may not benefit co-combustion. Introduction of moderate rank coals with a wide blending ratio range can facilitate synergistic interactions.

4. Conclusion

Dewatered sewage sludge (DSS) was directly converted to hydrochars under various subcritical water conditions. The fuel characteristics of hydrochar derived under 320 °C and 12.0 MPa (SHC-320) outweighed DSS and other hydrochars in terms of highest calorific value, safer $T_i$, higher heat release in a higher temperature region, and slightly decreased $T_b$ during the shortened combustion process. Introduction of SHC-320 lowered activation energy to initiate main decomposition of coal blends. Moreover, lower amount of SHC-320 led to a two-stage main co-combustion while large portion (≥ 70%) of SHC-320 improved ignition reactivity of high rank coal blends. During main co-combustion, blending SHC-320 resulted in higher heat loss to high rank coals. Intense synergistic effects were attributed to higher pre-exponential factor values in the second co-combustion stage. Under low
Coal/SHC-320 ratio (30:70), highest anti-synergistic effects occurred when blending SHC-320 with low or high rank coal, whereas co-combustion with moderate rank was impacted synergistically, thereby exhibiting highest combustion performance and burn out efficiency among blends.

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**Notes:**

The authors declare no competing financial interest.

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**References**


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Table 1
Characteristics of dewatered sewage sludge, sewage sludge derived hydrochars, and three different rank coals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Proximate analysis (wt.%, db)</th>
<th>Fuel ratio</th>
<th>Ultimate analysis (wt.%, db)</th>
<th>Calorific analysis ((MJ/kg, db))</th>
</tr>
</thead>
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<td></td>
<td>Ash</td>
<td>VM</td>
<td>FC</td>
<td>FC/VM</td>
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<td>9.19</td>
<td>0.13</td>
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<tr>
<td>SHC-220</td>
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<td>51.82</td>
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</tr>
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<td>2.36</td>
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<td>12.86</td>
<td>47.03</td>
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<td>42.03</td>
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<td>9.93</td>
<td>32.66</td>
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<td>1.76</td>
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</table>

db, dry basis.
VM, volatile matter; FC, fixed carbon; HHV, higher heating value; LHV, lower heating value.

<sup>a</sup> Calculated by difference on dry ash-free basis.
<sup>b</sup> Calculated by the formula: LHV<sub>dry</sub> (MJ/kg) = HHV<sub>dry</sub> (MJ/kg) – 2.4418 × (9 × H<sub>dry</sub>/100) (MJ/kg).
<table>
<thead>
<tr>
<th>Sample</th>
<th>Stage D</th>
<th>Stage E</th>
<th>Stage F</th>
<th>Weight loss (%)</th>
<th>Residues (%)</th>
<th>Characteristic temperatures</th>
<th>$t_b$ (min)</th>
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</thead>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Stage E</td>
<td>Stage F</td>
<td>$T_i$ ($^\circ$C)</td>
<td>$T_m$ ($^\circ$C)</td>
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<tr>
<td>DSS</td>
<td>~100</td>
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<td>390–550</td>
<td>39.9</td>
<td>27.7</td>
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<td>207.7</td>
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<td>350–550</td>
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<td>34.2</td>
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<td>47.8</td>
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<td>300–520</td>
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<td>375.7</td>
<td>427.3</td>
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$t_b$: burn out time, which initializes from the time corresponding to $T_i$ till the time corresponding to $T_b$. 
Table 3
Combustion kinetic parameters of DSS, hydrochars, three different rank coals and their respective blends with hydrochar derived under 320 °C and 12.0 MPa for 20 min.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature range (°C)</th>
<th>E (kJ mol⁻¹)</th>
<th>A (min⁻¹)</th>
<th>n</th>
<th>R²</th>
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<tr>
<td>DSS</td>
<td>150–370</td>
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<td>SHC-300</td>
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<td>30.53</td>
<td>18.11</td>
<td>1</td>
<td>0.9920</td>
</tr>
<tr>
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<td>1</td>
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</tr>
<tr>
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<td>14.50</td>
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</tr>
<tr>
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<td>300–550</td>
<td>32.60</td>
<td>22.70</td>
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<td>0.9927</td>
</tr>
<tr>
<td>SHC-340</td>
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<td>59.59</td>
<td>1</td>
<td>0.9899</td>
</tr>
<tr>
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<td>300–550</td>
<td>33.60</td>
<td>25.68</td>
<td>1</td>
<td>0.9894</td>
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<tr>
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<tr>
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<td>1</td>
<td>0.9973</td>
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<td>0.9911</td>
</tr>
<tr>
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<td>0.02</td>
<td>1</td>
<td>0.9923</td>
</tr>
<tr>
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<td>410–550</td>
<td>50.03</td>
<td>205.24</td>
<td>1</td>
<td>0.9809</td>
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<td>1653.08</td>
<td>1</td>
<td>0.9798</td>
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<td>101.81</td>
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<td>0.9919</td>
</tr>
<tr>
<td>30C70HC-2</td>
<td>200–270</td>
<td>42.82</td>
<td>218.33</td>
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<td>0.9942</td>
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<tr>
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<tr>
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<td>300–520</td>
<td>38.06</td>
<td>52.44</td>
<td>1</td>
<td>0.9963</td>
</tr>
<tr>
<td>70C30HC-2</td>
<td>250–520</td>
<td>45.84</td>
<td>222.23</td>
<td>1</td>
<td>0.9796</td>
</tr>
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<td>Coal-3</td>
<td>350–520</td>
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<td>5092.79</td>
<td>1</td>
<td>0.9893</td>
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<td>0.14</td>
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<td>340–550</td>
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<td>72.19</td>
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<td>0.9923</td>
</tr>
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<td>50C50HC-3</td>
<td>200–270</td>
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<td>340–550</td>
<td>44.37</td>
<td>140.07</td>
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<td>0.9860</td>
</tr>
<tr>
<td>70C30HC-3</td>
<td>370–520</td>
<td>58.35</td>
<td>2115.05</td>
<td>1</td>
<td>0.9909</td>
</tr>
</tbody>
</table>
Table 4

Comprehensive combustibility index for DSS, hydrochars, three different rank coals and their respective blends with hydrochar derived under 320 °C and 12.0 MPa for 20 min.

<table>
<thead>
<tr>
<th>Sample (dw/dt)</th>
<th>(dw/dt)mean</th>
<th>(dw/dt)max</th>
<th>S × 10^8</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSS</td>
<td>0.90</td>
<td>2.87</td>
<td>11.63</td>
</tr>
<tr>
<td>SHC-220</td>
<td>0.76</td>
<td>2.83</td>
<td>5.53</td>
</tr>
<tr>
<td>SHC-260</td>
<td>0.73</td>
<td>2.99</td>
<td>4.79</td>
</tr>
<tr>
<td>SHC-300</td>
<td>0.69</td>
<td>3.04</td>
<td>4.55</td>
</tr>
<tr>
<td>SHC-320</td>
<td>0.71</td>
<td>3.26</td>
<td>5.04</td>
</tr>
<tr>
<td>SHC-340</td>
<td>0.70</td>
<td>3.44</td>
<td>4.76</td>
</tr>
<tr>
<td>SHC-380</td>
<td>0.66</td>
<td>2.61</td>
<td>3.10</td>
</tr>
<tr>
<td>Coal-1</td>
<td>1.12</td>
<td>7.58</td>
<td>9.30</td>
</tr>
<tr>
<td>30C70HC-1</td>
<td>0.82</td>
<td>3.40</td>
<td>3.85</td>
</tr>
<tr>
<td>50C50HC-1</td>
<td>0.91</td>
<td>4.79</td>
<td>4.44</td>
</tr>
<tr>
<td>70C30HC-1</td>
<td>1.00</td>
<td>6.07</td>
<td>5.62</td>
</tr>
<tr>
<td>Coal-2</td>
<td>0.98</td>
<td>4.54</td>
<td>10.98</td>
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<td>30C70HC-2</td>
<td>0.77</td>
<td>3.07</td>
<td>4.91</td>
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<td>50C50HC-2</td>
<td>0.84</td>
<td>3.22</td>
<td>5.65</td>
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<td>70C30HC-2</td>
<td>0.88</td>
<td>4.50</td>
<td>7.85</td>
</tr>
<tr>
<td>Coal-3</td>
<td>1.08</td>
<td>6.80</td>
<td>10.85</td>
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<tr>
<td>30C70HC-3</td>
<td>0.81</td>
<td>4.53</td>
<td>5.71</td>
</tr>
<tr>
<td>50C50HC-3</td>
<td>0.89</td>
<td>5.29</td>
<td>6.15</td>
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<tr>
<td>70C30HC-3</td>
<td>0.97</td>
<td>6.24</td>
<td>8.27</td>
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</tbody>
</table>
Table 5
Deviations of maximum weight loss rates and residues of experimental curves from calculated curves and corresponding synergistic effect index values.

<table>
<thead>
<tr>
<th>Calculated sample</th>
<th>( T_m ) (°C)</th>
<th>((dw/dt)_{max})</th>
<th>Residues (%)</th>
<th>Deviation (%)</th>
<th>( (dw/dt)_{max} )(^{a}) Residues(^{b})</th>
<th>Synergistic effect index(^{c})</th>
</tr>
</thead>
<tbody>
<tr>
<td>30C70HC-1</td>
<td>450.0</td>
<td>3.51</td>
<td>27.71</td>
<td>−3.1</td>
<td>+1.8</td>
<td>1</td>
</tr>
<tr>
<td>50C50HC-1</td>
<td>460.0</td>
<td>4.59</td>
<td>20.56</td>
<td>+4.4</td>
<td>−0.3</td>
<td>4</td>
</tr>
<tr>
<td>70C30HC-1</td>
<td>470.0</td>
<td>5.76</td>
<td>13.4</td>
<td>+5.4</td>
<td>−3.7</td>
<td>4</td>
</tr>
<tr>
<td>30C70HC-2</td>
<td>410.0</td>
<td>3.43</td>
<td>31.3</td>
<td>−10.5</td>
<td>+4.2</td>
<td>1</td>
</tr>
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<td>410.0</td>
<td>3.56</td>
<td>26.5</td>
<td>−9.6</td>
<td>+0.4</td>
<td>1</td>
</tr>
<tr>
<td>70C30HC-2</td>
<td>370.0</td>
<td>3.83</td>
<td>21.7</td>
<td>+17.5</td>
<td>+6.5</td>
<td>3</td>
</tr>
<tr>
<td>30C70HC-3</td>
<td>410.0</td>
<td>4.26</td>
<td>28.6</td>
<td>+6.3</td>
<td>+2.1</td>
<td>3</td>
</tr>
<tr>
<td>50C50HC-3</td>
<td>410.0</td>
<td>4.95</td>
<td>22.1</td>
<td>+6.9</td>
<td>+3.2</td>
<td>3</td>
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<td>400.0</td>
<td>5.65</td>
<td>15.4</td>
<td>+10.4</td>
<td>−1.9</td>
<td>4</td>
</tr>
</tbody>
</table>

\(^{a}\)：“+” and “−” denote positive and negative interactions in co-combustion of blends, respectively.

\(^{b}\)：“+” and “−” denote negative and positive interactions in co-combustion of blends, respectively.

\(^{c}\): Higher index value denotes greater synergistic effect. Specifically, “4” and “1” indicate most intense synergistic and anti-synergistic effects, respectively.
Figure captions

**Fig. 1.** TG and DTG curves for combustion of DSS.

**Fig. 2.** TG and DTG curves for combustion of hydrochars derived under different temperatures and pressures.

**Fig. 3.** TG and DTG curves for combustion of three different rank coals.

**Fig. 4.** Co-combustion profiles of SHC-320 with different rank coals at three blending ratios.

**Fig. 5.** Comparisons of experimental and calculated TG and DTG curves for co-combustion of SHC-320 and different rank coals at three blending ratios. Coal-1 and SHC-320: (a) TG curves and (b) DTG curves; Coal-2 and SHC-320: (c) TG curves and (d) DTG curves; Coal-3 and SHC-320: (e) TG curves and (f) DTG curves.
Fig. 1.
Fig. 2.
Fig. 3.
Fig. 4.
Fig. 5.