Investigation on Characteristics of Liquid and Hydrochar Products from Hydrothermal Carbonization of Oily Scum at Different Temperatures

Shuanghui Deng (shdeng@xjtu.edu.cn)
Xi'an Jiaotong University https://orcid.org/0000-0001-7129-0509
Shilin Yu
Xi'an Jiaotong University
Houzhang Tan
Xi'an Jiaotong University
Xuebin Wang
Xi'an Jiaotong University
Xuchao Lu
Xi'an Jiaotong University

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Abstract

Hydrothermal carbonization (HTC) is a promising technology for upgrading organic substances with high moisture content. The characteristics of liquid and hydrochar products derived from oily scum at the different HTC temperatures were investigated in this study. The increase of HTC temperature resulted in a significant color shift of liquid from light yellow to strong yellow. The liquid uptake of hydrochar increased significantly with the increase of HTC temperature. SEM showed that there exhibited an irregular pit structure in hydrochars. Thermogravimetric analysis showed that high carbonization temperature of oily scum could improve the combustion characteristics of hydrochars. The comprehensive combustion properties were positively correlated with HTC temperature. The overall results of hydrochar combustion study showed that the activation energy of hydrochars decreased gradually with an increase in HTC temperature. This study provides a sustainable and promising treatment to reuse oily scum and suggests the possible fuel utilization of subsequent hydrochar product.

Statement Of Novelty

This work presents a comprehensive analysis of the characteristics of liquid and hydrochar products from hydrothermal carbonization (HTC) of oily scum at different temperatures. To our knowledge, the disposal and utilization of oily scum have been reported only by a few authors and in a partial way. This work may provide an efficient extraction method of value-added hydrochar from oily scum waste and present the high-efficient dewatering performance of oily scum via HTC. The obtained results allow researchers to see the potential application of oily scum in energy resource.

Introduction

A petroleum industry produces a large quantity of oily scum in oil-water separation process. Oily scum is a complicated and hazardous waste containing water with high content, crude oil and solid particles. It is a stable emulsion of oil in moisture and moisture in oil. Due to high moisture content as well as various toxic petroleum hydrocarbons and heavy metals [1, 2], oily scum is difficult to treat and apply. Improper disposal and utilization of oily scum contaminates groundwater or soil through leachate containing toxic petrochemical compounds and heavy metals. Additionally, the release and transform of volatile organic compounds in the disposal process of oily scum seriously pollutes the atmospheric environment. Hence, the disposal and utilization of oily scum is very urgent. A major disadvantage for oily scum disposal and application is its high moisture content. Therefore, drying and thermochemical conversion processes are often used to improve oily scum properties for easier disposal and utilization of such waste. Due to the high moisture content of oily scum, drying technology not only consumes more energy but also increases the costs of transport and treatment. If oily scum is directly burned as fuel, the combustion performance will be worse due to its higher moisture content and lower volatile components.

However, hydrothermal carbonization (HTC) decreases effectively the high moisture of fuel and avoids the consumption of costly energy resources associated with drying. One main advantages of HTC is that it can convert organic substances with high moisture content into carbonaceous solids at relatively high yields without the demand for an energy-consuming drying before or during the process [3]. HTC has been widely applied in the effective treatment of different types of biomass and wastes with high moisture. During the process of HTC, feedstock is heated in subcritical water at relatively low temperatures (180–250 ^{o}C) and under autogenous pressure that lower both the hydrogen and oxygen content of feedstock via dehydration, hydrolysis, polymerization and aromatization [4]. The products from HTC include a solid phase rich in carbon (the so-called hydrochar), a liquid by-product and a gas phase. It is regarded as combined dehydration and decarboxylation of feedstock to increase its carbon content and calorific value. Many studies have reported that HTC could simultaneously dehydrate feedstock with high moisture content, increase the energy density and reduce the pollutant elements contained in feedstock [5]. Additionally, hydrochar product from HTC of feedstock primarily results from a series of reactions such as hydrolysis, condensation, decarboxylation, and dehydration [6]. Compared with raw feedstock with high moisture content, the combustion performance and availability of hydrochar will be better [7]. HTC is used to upgrade high-moisture and low-value feedstock by improving hydrophobic properties, reducing oxygen and volatile contents and raising energy density. Especially for a hazardous solid waste with high moisture content, HTC could be used to convert this waste to hydrochar, thereby increasing effective utilization rate of energy and affording significant convenience in handing, storage and transport.

HTC will be a promising method to transform oily scum into value-added solid hydrochars if it is applied in oily scum. When oily scum is heated in hydrothermal environments, the physical and chemical properties of oily scum will be changed and improved through relevant reactions which include hydrolysis, dehydration, decarboxylation, aromatization and re-condensation [8]. Compared with pyrolysis, HTC process produces more water soluble organic compounds, higher hydrochar yields and fewer gases, comprised mainly of CO_2 [9]. Therefore, the organic components in oily scum will be easily decomposed and less stable in the hydrothermal environments, thus causing lower decomposition temperatures. Although it has been observed that processing parameters including reaction temperature and time can influence hydrothermal product properties of other types of fuels such as biomass and sludge, reaction temperature remains the most governing process parameter [10, 11]. HTC temperature is further limited to less than 260 ^{o}C to minimize liquefaction and gasification reactions thus maximizing solid recovery through HTC [12]. Overall, HTC is used in this study to dewater and carbonize oily scum, making hydrochar product with higher carbon contents and better combustion performance. It may contribute to a wider application of oily scum for waste disposal and energetic purposes.

Although HTC has been known on waste disposal and energy recovery for a long time, it has received little attention on current oily scum conversion application. Based on this background, the aim was to determine the effect and significance of reaction temperature on the properties of hydrochars produced from oily scum, thereby promoting disposal of oily scum and fuel utilization of hydrochars. The obtained hydrochars can be used as solid fuel in order to utilize oily scum waste. Investigating the effect of HTC temperature on the characteristics of hydrochars is of critical importance, which can enhance the disposal and utilization of oily scum. So this study primarily focused on the appearance characterization and combustion characteristics of the hydrochars derived from the HTC process of oily scum at increased temperature and attempted to supply comprehensive data for disposal and utilization of oily scum. The microscopic morphologies and microstructures of the hydrochars were also studied. Last, thermogravimetric analysis is used to investigate the combustion behaviors and kinetic of hydrochars because of its simplicity, rapidity and accuracy.

Samples And Methods

Preparation of hydrochar sample

The hazardous waste sample selected for conversion to hydrochar was oily scum provided by a petrochemical plant in Yulin, Shaanxin Province, China. The moisture content of the as-received oily scum reached 95%.

The design parameters and operation methods of the hydrothermal reactor used in this study have been described in detail elsewhere [13]. To investigate the effect of the HTC temperature on hydrochars, 120, 150, 210 and 240 ^{o}C were selected under the same reaction time of 1 hour. For each experiment, 140 g of oily scum feedstock was placed in the reactor, being continuously stirred at 100 rpm during the HTC process. The liquid and solid products after HTC were filtrated using filter paper with the big pore diameter. After the filtration, the solid hydrochars were obtained on the filter paper and then dried at 105 ^{o}C for more than 24 h to remain its quality unchanged. The dried hydrochars from different experimental conditions were stored in enclosed plastic bags before analysis and combustion test. When the HTC reaction was performed at the temperature of 120, 150, 210 and 240 ^{o}C, the obtained hydrochars were labeled as hydrochar-120, hydrochar-150, hydrochar-210 and hydrochar-240, respectively.

Sample analysis

Observations at high magnification

Representative photomicrographs were taken to characterize in detail and development of hydrochar samples at higher magnification and sensitivity by a super-resolution confocal microscope (Leica TCS SP8 STED 3X).

SEM-EDX

The morphological appearance and element contents of hydrochars before and after combustion were performed by a scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX, JEOL Co., Ltd, Japan).

Analysis of filtrates

The filtrates of the HTC process were collected in a small glass bottle after each experiment. A gas chromatography/mass spectrometry (GC-MS) (Shimadzu GCMS-QP2010 Ultra) equipped with a column (a Rxi-5Sil MS column (0.25 um film (thickness) × 0.25 mm (I.D.) × 30 m (length))) was used to analyze the main organic species in the filtrates.

Characteristic combustion parameters

Combustion tests of hydrochars were conducted in a thermogravimetric analyzer (TGA, NETZSCH STA 409 PC). Approximately 10 mg of hydrochars were placed on the bottom of a quartz crucible, which was placed on the support arm of the mass sensor in the furnace. Then, the furnace was heated at a heating rate of 20 ^{o}C/min. All the combustion experiments were carried out in a temperature range of 30-900 ^{o}C. The air was purged at the flow rate of 100 ml/min. The corresponding thermogravimetric (TG) and differential thermogravimetric (DTG) curves of each hydrochar sample were recorded continuously during the heating process.

Calculation

The comprehensive combustion index (S) [14], combustion stability index (R_w) [15] and ignition index (C_r) [16] were calculated by using Eq. (1),Eq. (2) and Eq. (3), respectively.

$$S = \frac{DTG_{max} \times DTG_{mean}}{T_i^2 \times T_b} \quad (1)$$

$$R_w = \frac{655}{T_i} \times \frac{763}{T_{max}} \times \frac{(dw/dt)_{max}}{8.73} \quad (2)$$

$$C_r = \frac{DTG_{max}}{T_i^2} \quad (3)$$

where T_i is the ignition temperature, ^oC; T_b is the burnout temperature, ^oC; T_{max} is the peak temperature at the maximum weight loss rate, ^oC; DTG_{max} and DTG_{mean} are the maximum and mean mass loss rate, respectively, %/min. S, R_w and C_r were used to evaluate the combustion performance of hydrochars. S indicates comprehensive effects of the combustion behaviors, and the higher the S is, the more complete and better the combustion of fuel is [17].

Results And Discussion

Characterization of liquid and hydrochars

Appearance characteristics of liquid

Temperature is the most important parameter which affects the moisture removal efficiency of oily scum during the HTC process. Therefore, its impacts on the present moisture removal process were studied on the four different HTC temperature levels (120, 150, 210 and 240 ^oC), and the illustrative results of these investigations are shown in Fig. 1.

As shown in Fig. 1, the liquid product obtained from the HTC process of oily scum at the different temperatures showed different shades of color. The increase of HTC temperature caused a significant color shift of liquid from light yellow to strong yellow, indicating an increase of dissolved organic compounds in produced liquid. At elevated temperatures, water solvent properties were significantly enhanced and some of organic compounds were dissolved in the liquid phase after oily scum HTC. This was because that the dehydration, decarboxylation, polymerization and aromatization reactions of petroleum hydrocarbons in oily scum occurred during the HTC process. In the subcritical conditions of HTC, the presence of water generally enhanced ion chemistry and suppressed free radical reactions. It was obvious that reaction extent of oily scum HTC was governed by temperature to a large extent. Higher HTC temperature generally increases reaction intensity. The liquid phase had a high load of organic compounds, many of which showed potentially valuable chemicals. This promoted bond cleavage of primarily hydrogen bonds, especially hydrolysis. Therefore, HTC temperature had an impact on the liquid components during the process of oily scum, especially produced dissolved organic compounds.

Photos analysis of hydrochars

After the HTC treatment of oily scum, the photographs of dried hydrochars obtained from the different temperatures are shown in Fig. 2.

From Fig. 2, the hydrochar products produced from oily scum through HTC at the different temperatures all displayed a dark brown color and appeared in a thick slimy morphology. HTC could mainly eliminate hydroxyl and carboxyl group of petroleum hydrocarbons in oily scum, resulting in solid product which had a lower moisture content and hydrophilicity than raw oily scum. So, this effect of reducing the amount of moisture and functional groups was effectively utilized via HTC treatment. However, the slimy appearance indicated that these hydrochar products might not be completely carbonized less than 240 ^oC in this study and still remained some parts of the original structure of oily scum. If the higher carbonized hydrochar products are needed, HTC is performed at more than 240 ^oC.

Observations at high magnification

The black and white as well as color display of hydrochars at high magnification are presented in Fig. 3 and 4, respectively.

In Fig. 3 (a), the surface of hydrochar-120 ^oC is granular, and the structure is dense. There are a large amount of carbon particles that formed on the surface. Fig. 3 (b) shows a granular structure of hydrochar-150 ^oC, and the amount of the carbon particles reduced due to the stronger hydrolysis and decarboxylation reactions. Also, there are more dissolved organic compounds in the liquid product in Fig. 2 and less carbon particles in the solid product at a relatively low HTC temperature in Fig. 3. From Fig. 3 (c), after the HTC treatment at 210 ^oC, there are less carbon particles. As seen in Fig. 3 (d), there are much smaller particles in the hydrochar-240. Meantime, there are some much bigger particles are located on the surface of hydrocha-240.

The hydrolysis reaction in the HTC process of oily scum was dominant at a relatively low HTC temperature (less than 220 ^{o}C), while the competition between hydrolysis and repolymerization was strong at 220-300 ^{o}C [18]. With the continuous increase in HTC temperature, repolymerization was predominant compared to hydrolysis [19]. Thus, the water-soluble products were decomposed and repolymerized into oily products. Meanwhile, the repolymerization occurred. These caused hydrochar-240 ^{o}C to obtain some much smaller particles and bigger polymer ones. The aggregates formed by partially deposited particles were finally detached from hydrochars, and the remaining structure was carbon microspheres. Those results indicated that higher HTC temperature facilitated the accumulation of carbon microspheres and other small molecule components. Besides, with the HTC conditions severer, the extent of the decomposition reactions of oily scum was increased, and the tendency of forming aggregates became more prominent. With the increase of HTC temperature, the aggregate structure became bigger, which might be that carbon microspheres and oil could be further aggregated on the surface of clusters simultaneously.

Analysis of the components in Liquid

Filtration performance

The experimental curves about the liquid percentage versus filtration time at the different HTC temperatures are shown in Fig. 5.

According to each curve in Fig. 5, the liquid percentage produced from oily scum HTC increases significantly with the filtration time. Liquid was removed in the first 15 min of filtration time with a high increasing rate, and then the liquid percentage increased slightly after 15 min, reaching the maximum at 30 min in this study. Additionally, as the HTC temperature increases from 120 to 240 ^{o}C, the maximum value of the liquid percentage gradually increases from 58.28 to 80.69% at 30 min filtration. This increase was attributed to the increase on the extent of dehydration, decarboxylation, and volatile matter decomposition reactions when the higher HTC temperatures were applied. Therefore, the liquid uptake of hydrochar significantly increased with the increase of HTC temperature. This suggested that the hydrochars with higher HTC temperature exhibited higher filtration ability and dewaterability. The hydrochar-120 ^{o}C presented the most hygroscopic behavior and lowest moisture uptake in this study. However, the liquid percentage at 240 ^{o}C is more than that at any other temperature. The higher liquid uptake of hydrochars produced at higher temperature was mainly ascribed to the bigger pore structure and higher surface area in comparison with hydrochars obtained at lower temperature. The dewatering and thermal decomposition of oily scum played a key role in causing the yield of liquid to increase with an increase in HTC temperature. Hence, HTC temperature was an important factor during the HTC treatment of oily scum when the liquid phase was recycled.

Compositions analysis

The water-soluble chemical components in the liquid product derived from the HTC process of oily scum were detected by GC-MS. Due to species and complexities of chemical components, the first hundred peaks with larger areas were applied to analysis the liquid product. The GC-MS curves and distributions of chemical components in the liquid product are shown in Fig. 6 (a) and (b), respectively.

The fifteen major peaks were observed in the different GC-MS curves in Fig. 6 (a), indicating that the fifteen main chemical components existed in the liquid product. As the HTC temperature increases, the value of Peak 1 (isovaleric acid, $C_5H_{10}O_2$), 3 (aniline, C_6H_7N), 5 (2,4,6-collidine, $C_8H_{11}N$), 6 (o-cresol, C_7H_8O), 7 (p-cresol, C_7H_8O) or 14 ((3S,6S)-3-Butyl-6-methylpiperazine-2,5-dione, $C_9H_{16}N_2O_2$) increases, while the value of Peak 8 (trans-2,5-Dimethyltetrahydro-4-thiopyrone, $C_7H_{12}OS$), 9 (2,4,6-trimethylaniline, $C_9H_{13}N$) or 10 (1-hydroxy-2,3-dimethylbenzene, $C_8H_{10}O$) decreases, and the value of Peak 11 (2,3,4,5,6-Pentamethylpyridine, $C_{10}H_{15}N$), 12 (2-(acetylthio) norbornane, $C_9H_{14}OS$) or 13 (3,5-di-tert-butylphenol, $C_{14}H_{22}O$) reduces or even disappears. In addition, the value of Peak 2 (2-methyl butyric acid, $C_5H_{10}O_2$) or 4 (phenol, C_6H_6O) first increases and then decreases with the increase of HTC temperature. During the HTC process of oily scum, a large quantity of dehydrated carbohydrate compounds were formed by bond breaking of petroleum hydrocarbons, which was further dehydrated and polymerized to form important intermediate substances and small-molecule organic compounds. Especially, these intermediates mainly underwent different reaction pathways to form different contents of gases, oil compounds and microsphere carbons.

According to the analysis of GC-MS curves, the main chemical compounds produced from the HTC process of oily scum were divided into the following six functional groups: ketone and aldehyde, ester and acid, heterocyclic compounds, phenyl amines, phenols, and others. Correspondingly, the relative proportions of the six functional groups were obtained on the basis of the area of each peak, and the results are presented in Fig. 6 (b). The liquid product from the HTC process at 120 ^{o}C contained higher amounts of phenyl amines than those from at other temperatures. There were a large amount of intermediate or final products produced in the course of HTC based on the diversity of process conditions and the reaction extent of the relevant mechanisms involved. Phenols increases as the increase of HTC reaction through the dehydration, decarboxylation and decarbonylation reactions which occurred during the HTC treatment of oily scum [20]. Many chemical reactions might appear during the HTC process of oily scum, including dehydration, hydrolysis, decarboxylation, condensation polymerization, and aromatization [21]. However, the HTC process was mainly governed by dehydration and decarboxylation, which meaned that it was exothermal. Simultaneously, functional groups were being eliminated to some extent. Dehydration during the HTC process of oily scum could cover both chemical reaction and physical processes. Chemical dehydration mainly significantly carbonized oily scum by lowering the O/C and H/C ratios, while physical dehydration removed water from oily scum without changing its chemical constitution [21]. Dehydration was generally explained by elimination of hydroxyl groups. Main decarboxylation only appeared after that specific amount of water was formed, but dehydration could be achieved without significant decarboxylation. Main decarboxylation appeared in the HTC process and caused a partial elimination of carboxyl groups. Carbonyl and carboxyl groups rapidly decomposed at more than 150 ^{o}C and produced CO and CO_2, respectively [22].

After oily scum HTC at 120 ^{o}C, the area percentage of phenyl amines in the liquid product accounts for 27.77%, followed by other chemical components (24.95%) and heterocyclic compounds (16.47%). However, when the HTC temperature was more than 120 ^{o}C, phenols accounts for a large proportion in the liquid. The change of the distribution of chemical components in the liquid product was mainly caused by the change of the chemical structure of hydrochars during the HTC process of oily scum. At 120 ^{o}C, the petroleum hydrocarbons of oily scum were transformed along the dehydration and even oxidation directions. The long-chain hydrocarbons or oil were decomposed and hydrolyzed, thereby improving the dewaterability. This was proved by the chemical components of the HTC liquid, which included many long chain organic species, such as 2,3,4,5,6-Pentamethylpyridine ($C_{10}H_{15}N$) and 3,5-di-tert-butylphenol ($C_{14}H_{22}O$).

SEM images before and after hydrochar combustion

SEM images before hydrochar combustion

The microscopic morphologies and microstructures of hydrochars derived from the HTC process of oily scum are measured by SEM images shown in Fig. 7. There was a very rough and heterogeneous surface structure presented on hydrochars. Moreover, the diameter of hydrochars with higher temperature (240 ^{o}C) was bigger than that of hydrochars with less than 240 ^{o}C (120, 150 and 210 ^{o}C). It was observed from Fig. 7 (a) that the surface of the hydrochar-120 ^{o}C displayed compact and dense in structure or arrangement. Additively, it exhibited an irregular crack structure. This was because that HTC produced myriad of tiny bubbles and enabled more vapor either enter the liquid phase or react on the gas-liquid/gas-solid interface. Meanwhile, the pit structure was also continually corroded and the residual organic structure in hydrochars was destroyed via decomposition reactions such as hydrothermal cracking and hydrolysis [23]. Therefore, with the effect of reaction temperature, petroleum hydrocarbons in oily scum took place a variety of reactions such as hydrothermal cracking, hydrolysis, depolymerization, oxidation, and rearrangement [24]. Finally, a pit structure formed which followed the previous research [13]. As the reaction temperature increased, the pit structure in hydrochars gradually became bigger.

Hydrochar formation was a series of very complex reactions under the hydrothermal conditions of oily scum, and many reactions including hydrolysis, dehydrations, condensations and polymerizations occurred at the same time. At 120 ^{o}C, the petroleum hydrocarbons in oily scum primitively decomposed, resulting in a rough surface of hydrochar matrix. Additionally, hydrochar-150, 210 and 240 ^{o}C all had the structure of hydrochar matrix. From Fig. 7 (a)~(d), the microsphere carbon particles were uniformly inserted into the hydrochar matrix whereas those particles were dispersed on the surface of the hydrochar matrix and prone to agglomerate. This was due to the fact that subcritical water raised vapor pressure, decreased surface tension and increased ionization constant, making the solid product formed in a sphere shape and distributed homogeneously [25]. As the HTC temperature increased, the size of the agglomerate became bigger. It may be attributed to the fact that severe hydrothermal conditions facilitated the formation of the inner-sphere surface complexes, while wet particles favored the appearance of outer-sphere surface complexes. Furthermore, as shown in Fig. 7 (d), the pore and crack structures of hydrochar-240 ^{o}C were more developed than those of hydrochar with less than 240 ^{o}C. These phenomenons showed that the HTC treatment under higher temperatures was a more effective way for the preparation of porous hydrochars. The porous of hydrochars was due to the decomposition and release of petroleum hydrocarbons in oily scum, which caused the blockage of many pores. The bigger pores and more irregular matrix of the hydrochar products demonstrated that the increase of HTC temperature could efficiently accelerate the dewaterability and decomposition process of oily scum. Hence, the hydrochar samples with higher degree of carbonization could be obtained.

Due to the improved hydrophobicity, the hydrochar products showed strong resistance against water immersion. Hydrochar-240 ^{o}C was consisted of scattered pieces combined with small particles, suggesting that a majority of petroleum hydrocarbons in oily scum was degraded. The pit structure of the hydrochars increased gradually with the increasing of HTC temperature, indicating that oily scum could be carbonized via HTC process. The increase of HTC temperature enhanced significantly the dehydration and decomposition of oily scum. However, since oily scum with high content of moisture was used directed as the initial reaction material during the HTC process, the larger quantity of moisture inside oily scum and the light organic molecules were separated from the oil-moisture structure and reacted with other matters. More sample particles with narrow dimensions were generated when higher temperature existed in the HTC condition, further evidencing that the chain rupture and degradation of petroleum hydrocarbons.

SEM images after hydrochar combustion

(1) SEM analysis

SEM images of the different ash samples after hydrochar combustion are presented in Fig. 8. From Fig. 8 (a)~(d), the microscopic characteristic of ashes after hydrochar combustion exhibited a comparatively rough and uneven surface with a large quantity of particles. After hydrochar-120 ^{o}C was oxidized in the air condition, the surface of ash-120 ^{o}C yielded large amounts of ash and slag particles with different sizes, but it still remained the hydrochar matrix before hydrochar combustion. When the HTC temperature increased to 150 ^{o}C, the surface of ash-150 ^{o}C began to appear fusion and slagging, which were spread over the surface in a sheet. When the HTC temperature continued to rise to 210 or 240 ^{o}C, the surface of ash-210 ^{o}C or ash-240 ^{o}C clumped and agglomerated to some extent. However, the fusion and slagging phenomena of hydrochar-150 ^{o}C were the most serious in this study. It could be seen that the degree of ash fusion and slagging after hydrochar combustion increased in varying degree with the extension of HTC temperature.

After HTC, hydrochars may have lower ash content than oily scum because the inorganic elements were released and dissolved in the liquid phase. Hydrochars with lower ash content would burn more cleanly and efficiently since the decrease of inorganic matters such as K, Na, S, Si, Cl and Ca caused easily fouling, slagging, and corrosion in combustors [26,27].

(2) EDX analysis

The slagging and fouling characteristics of solid fuels are important problems due the directly relation to the combustion performance in power plant boilers. To characterize hydrochars derived from different HTC temperatures in terms of their tendency to cause slagging and fouling on boiler heating surface, the ash composition after hydrochar combustion were analyzed. The EDX results of different ash samples after hydrochar combustion are shown in Fig. 9.

From Fig. 9, the ash compositions could be significantly changed after hydrochar combustion. The results of EDX analysis in Fig. 9 illustrated that the main elements of ashes were C (7.945~37.015%) and O (48.48~68.215%) after hydrochar combustion. There also were Na, Mg, Al, Si, Ca, Fe and P elements in ashes. It could be seen that the carbon content of ashes firstly decreased and then increased as the HTC temperature increased from 120 to 240 ^{o}C, reaching the minimum of 7.95% at ash-210 ^{o}C. However, the oxygen content was the opposite of the carbon content. On the whole, the increase of HTC temperature significantly changed the microstructures and compositions of hydrochars.

Combustion characteristics of hydrochars

Combustion behaviors

Thermogravimetric analysis data can be used to investigate the thermal degradation of different materials and kinetic parameters [28]. The TG and DTG curves from the combustion of hydrochars derived from the different HTC temperatures of oily scum are shown in Fig. 10. Also, the combustion characteristic parameters of hydrochars are listed in Table 1, 2 and 3. From Fig. 10, on the whole, the TG curve of hydrochar combustion shows an initial weight loss attributed to waster evaporation before 150 ^{o}C, followed by a flat region up to about 210 ^{o}C. Next, the three or four continue branches on each TG curve extend up to about 640 ^{o}C where the major weight loss rate was obtained. Last, the TG curve got flat until the combustion temperature reached 900 ^{o}C.

According to the weight loss rate in the DTC curve, the combustion process of hydrochars could be divided into four stages: (1) the evaporation stage of the moisture and low boiling point organic matters; (2) the devolatilization and combustion stage of volatile matters; (3) the burnout stage of fixed carbon; (4) the oxidation stage of inorganic compounds. The different temperature stages are shown in Table 1. Compared to hydrochar-120 ^{o}C and hydrochar-150 ^{o}C, the thermal decomposition temperature of hydrochar-210 ^{o}C and hydrochar-240 ^{o}C added a typical process of devolatilization in the temperature range of 360-410 ^{o}C and 370-410 ^{o}C, respectively. For hydrochar-120 ^{o}C and hydrochar-150 ^{o}C, the third weight loss rate peak was noticeable higher than the former two weight loss rate peaks because the volatile matters of oily scum were partly decomposed at a relatively low HTC temperature and were converted to thermally stable tar and hydrochars. However, for hydrochar-210 ^{o}C and hydrochar-240 ^{o}C, the first weight loss rate peak was higher than other three weight loss rate peaks. As expected, at a relative high HTC temperature most of the volatile matters in oily scum were decomposed with the increase of hydrothermal reactivity, and they were mostly in the form of easily crackable volatile and partly in the form of char. This caused the increase of volatile matters during the primary decomposition period of hydrochar combustion, bringing the increase of the first weight-loss rate peak. Also, the low proportion of organic matters and high proportion of ash decreased the fourth weight-loss rate peak of hydrochar-210 ^{o}C and hydrochar-240 ^{o}C.

Table 1 Combustion stages and characteristic temperatures of hydrochars

Samples	Evaporation stage	Weight loss at first stage/%	Devolatilization and combustion stage/^oC			Weight loss at second stage/%	Burnout stage/^oC	Weight loss at third stage/%	Oxidation stage	Weight loss at fourth stage/%
			Phase 1	Phase 2	Phase 3					
Hydrochar-120 ^oC	~185	1.58	185-370	-	370-498	-69.94	498-620	-24.62	620-900	0.07
Hydrochar-150 ^oC	~170	1.28	170-370	-	370-488	-69.66	488-610	-25.12	610-900	-0.54
Hydrochar-210 ^oC	~170	-0.31	170-360	360-410	410-502	-77.82	502-620	-23.80	620-900	-0.18
Hydrochar-240 ^oC	~170	0.05	170-370	370-410	410-495	-70.97	495-640	-27.00	640-900	-0.18

Table 2 summarized the characteristic temperatures and peak points of the combustion process of hydrochars. T_i and T_b of hydrochars first decreased and then increased with the increase of HTC temperature, both reaching the minimums at 150 ^oC. This was possible caused by the decomposition and repolymerization of organic matters in subcritical water. At 150 ^oC the decomposition reactions of the organic matters in hydrochars were dominant, causing T_i and T_b of hydrochars to the minimums. At 210 and 240 ^oC, the organic matters in hydrochars mainly occurred the repolymerization, leading T_i and T_b of hydrochars to increase [29]. So, HTC temperature is an important factor affecting the combustion characteristics of hydrochars.

Table 2 Combustion characteristic temperatures and indexes of hydrochars

Samples	T_i/^oC	T_{peak1}/^oC	T_{peak2}/^oC	T_{peak3}/^oC	T_{peak4}/^oC	T_b/^oC	T_{max}/^oC	S/ $10^{-7}$$^oC^{-3}$·$min^{-2}$	R_w/ -(%·min^{-1}·$^oC^{-2}$)	C_r -($10^{-5}$$^oC^{-2}$·$min^{-1}$)
Hydrochar-120 ^oC	260	317	466	533	-	618	533	8.34	6.29	22.51
Hydrochar-150 ^oC	248	303	461	527	-	610	527	6.78	4.74	17.59
Hydrochar-210 ^oC	262	328	401	459	546	619	328	7.40	8.37	18.30
Hydrochar-240 ^oC	273	327	400	460	562	639	327	5.76	7.32	15.32

Table 3 Combustion characteristic parameters of hydrochars

Samples	DTG_{peak1}/ %·min^{-1}	DTG_{peak2}/ %·min^{-1}	DTG_{peak3}/ %·min^{-1}	DTG_{peak4}/ %·min^{-1}	DTG_{max}/ %·min^{-1}	Mf/%
Hydrochar-120 ^oC	-9.51	-6.76	-15.22	-	-15.22	5.15
Hydrochar-150 ^oC	-9.98	-6.88	-10.82	-	-10.82	4.56
Hydrochar-210 ^oC	-12.56	-4.05	-9.03	-8.49	-12.56	-2.02
Hydrochar-240 ^oC	-11.42	-8.27	-8.62	-7.52	-11.42	1.22

Notes: T_i, T_{peaki} and T_b are the ignition temperature of each sample, the temperature according to the max combustion rate at the i peak, and the burnout temperature of each sample, respectively; DTG_{maxi} is the maximum mass loss rate at the i peak; M_f is residual mass at 900 ^oC.

As shown in Table 2, T_{max} was gradually shifted to a lower temperature as the HTC temperature increased. The hydrochar-120 ^oC or hydrochar-150 ^oC had higher T_{max} value as compared to hydrochar-210 ^oC or 240 ^oC, indicating that the increase of HTC temperature improved fuel quality of subsequently produced hydrochars. This improvement was mainly attributed to the decreased volatile matter content and increased fixed-carbon content in hydrochars with an increase of HTC temperature. From Table 2, the T_i value for hydrochar-120 ^oC or hydrochar-150 ^oC was lower than that of hydrochar-210 ^oC or 240 ^oC, indicating that hydrochar-120 ^oC or hydrochar-150 ^oC ignited easily. This was because that the HTC process of oily scum removed volatile matter to a certain extent, and hydrochars from low HTC temperature had more volatile matter than that from high HTC temperature. Hence, hydrochar-120 °C or hydrochar-150 °C with more volatile matters resulted in lower T_i value and had the performance of easy ignition and combustion. However, hydrochar-240 °C with the highest burnout temperature is safer than hydrochar-120 °C, hydrochar-150 °C and hydrochar-210 °C during handling, storage and transportation. Higher T_b value indicates thermally stable fuel with more prolonged combustion phase. Hydrochar-240 °C had the highest T_b value and thus took longer time to burnout, showing its thermal stability as fuel.

In order to further evaluate the combustion performance of the hydrochars as solid fuel, S, R_w and C_r were calculated according to Eq (1), (2) and (3), respectively. The results in Table 2 showed that as the HTC temperature increased from 120 to 240 °C, S, R_w and C_r decreased initially, followed by an increase, but then again decreased. The change trend of S, R_w or C_r was according with that of DTG_{max}. This was because that the increase in HTC temperature caused a higher combustion reactive of hydrochars; therefore, there was a higher combustion rate for organic matters, and at the same combustion stage, the reaction time was shorter and combustion temperature was higher when the hydrochars were decomposed and oxidized. Additionally, S and C_r both reached the maximum values at hydrochar-120 °C, while R_w got the maximum value at hydrochar-210 °C. This was mainly due to the removal of a large amount of inorganic metals from oily scum with an increase in HTC temperature, resulting in the decrease of the catalytic effect of inorganic metals on hydrochars [30,31] and the reduction of S, R_w and C_r. S, R_w or C_r at hydrochar-210 °C began slightly to increase because a higher HTC temperature could accelerate the degradation of petroleum hydrocarbons in oily scum and the formation of hydrochars with high carbon content, thereby improving the combustion performance of hydrochars and obtaining better S value. These observations may indicate that the combustion characteristics of hydrochar-120 °C were better than those at the other HTC temperatures.

The S value of hydrochar-120 °C was higher than that of other hydrochar samples. Hydrochar-120 °C performed the best S value with 8.34×10^{-7} °C^{-3}·min^{-2}, followed by 7.40-, 6.78- and 5.76×10^{-7} °C^{-3}·min^{-2} for hydrochar-210 °C, hydrochar-150 °C and hydrochar-240 °C, respectively. This suggested that the hydrochars had an optimal parameter to improve the combustion performance under appropriate HTC reaction temperature. The volatile matters of hydrochars decreased and the carbon content increased after the HTC treatment of oily scum, thus the combustion of hydrochars may be less violent and the flame was more stable. It could be found that the HTC reaction temperature had significant influences on combustion behaviors and characteristics of hydrochars. Generally, HTC could convert oily scum into solid fuel with an improved combustion performance.

Kinetic parameters

To date, there have been relatively few reports on evaluating the activation energy (E) change of hydrochars from the HTC process of oily scum. In order to confirm the combustion mechanism and E of hydrochars produced from the HTC treatment of oily scum, the kinetic parameters based on Arrhenius equation were applied for all hydrochar products in this study [32]. The first-order kinetic reaction model is typically used for the combustion process of solid fuel [33]. Therefore, the pre-exponential factor (A), E and correlation coefficient (R) associated with the combustion process of hydrochars were calculated according to the first-order reaction model equation [34]. The calculated results were shown in Table 4.

Table 4 Kinetic parameters of the different hydrochar samples

Samples	Combustion kinetic parameters		
	E/kJ•mol^{-1}	A/min^{-1}	R^2
Hydrochar-120 °C	40.03	178.59	0.8982
Hydrochar-150 °C	37.62	119.48	0.8797
Hydrochar-210 °C	34.58	58.49	0.9410
Hydrochar-240 °C	32.15	27.00	0.9372

A high correlation coefficient indicated that the first-order reaction model fitted well to explain the combustion process of hydrochars produced from oily scum. E provides important information in the minimum amount of energy needed to initiate a reaction. From Table 4, the E value of hydrochars varied with the HTC temperature of oily scum, indicating that temperature affected the thermal reaction. Also, as the HTC temperature increased, E showed a decreasing trend and reached its minimum value (32.15 kJ/mol) at hydrochar-240 °C. A presented the same downward trend as E upon increasing the HTC temperature. The hydrochar-120 °C showed relative higher E (40.03 kJ/mol) compared with other hydrochars. The decrease of activation energies of hydrochars at higher HTC temperatures (150, 210 and 240 °C) was mainly caused by the decomposition and destruction of complicated petroleum hydrocarbons structure of oily scum in HTC process. The combustion of hydrochars-240 °C is suggested to be easier because of its lower activation energy and pre-exponential factor.

According to the results above, it can be seen that HTC temperature has significant effects on appearance characteristics and combustion behaviors of hydrochars derived from oily scum. Table 4 presents the whole kinetics of weight loss occurred during the thermal reactions of hydrochars in TGA. The combustion characteristics and kinetic parameters obtained in this study could be used to predict the combustion behaviors of hydrochars during combustion in a fluidized bed boiler or other boilers. Overall, it is observed that HTC temperature of oily scum improves the properties of hydrochars. Therefore, the effective recovery and rational utilization of petroleum hydrocarbons of oily scum waste using HTC and combustion technology gives us a new opportunity.

Conclusions

Solid fuel was expected to be produced from oily scum with high-moisture content through hydrothermal carbonization (HTC). The appearance characteristics and fuel qualities of hydrochars produced from the HTC treatment of oily scum were evaluated in this study. At elevated temperatures, water solvent properties of oily scum were significantly enhanced and some of chemical components were dissolved in the liquid phase after HTC. Hydrochars produced at higher HTC temperature exhibited higher filtration ability and dewaterability. The microsphere carbon particles were uniformly inserted into the hydrochar matrix, while those particles were dispersed on the surface of the hydrochar matrix and prone to agglomerate. The microscopic characteristic of ashes after hydrochar combustion exhibited a comparatively rough and uneven surface with a large quantity of particles. The hydrochars had improved combustion characteristics at increased HTC temperatures: elevated comprehensive combustion reactivity, increased maximum weight loss rates and reduced residues. As the HTC temperature increased, activation energy showed a decreasing trend and reached its minimum value (32.15 kJ/mol) at the HTC temperature of 240 ^{o}C. The study provides a sustainable and promising treatment to reuse oily scum waste and suggests the possible utilization of its hydrochar product, which is expected to facilitate the disposal and utilization of oily scum waste.

Declarations

Acknowledgements

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Data Availability

The datasets used and/or analyzed during this study are available from the corresponding author on reasonable request.

Conflict of interest The authors declare no conflict of interest.

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Figures

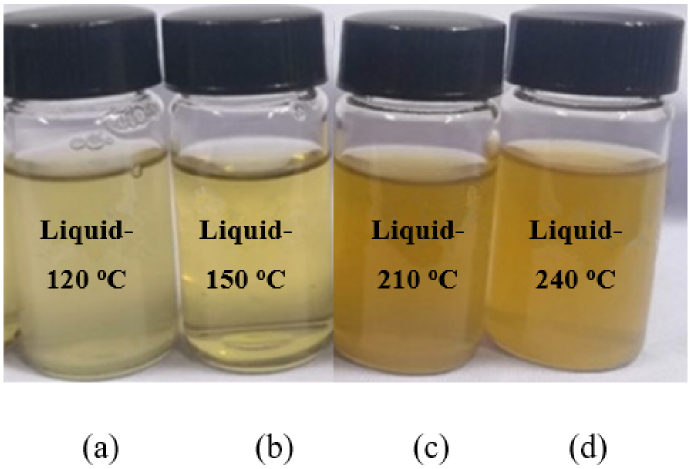


Figure 1

Photos of liquid at the different HTC temperatures

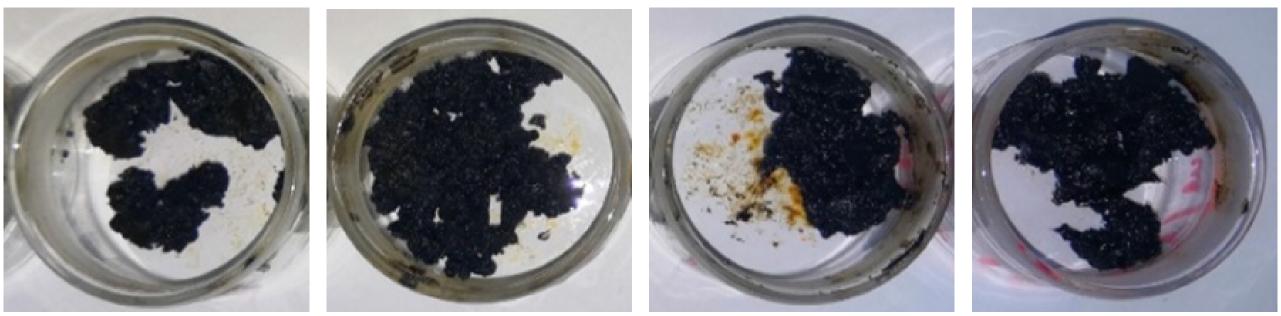


Figure 2

Photos of hydrochars at the different HTC temperatures

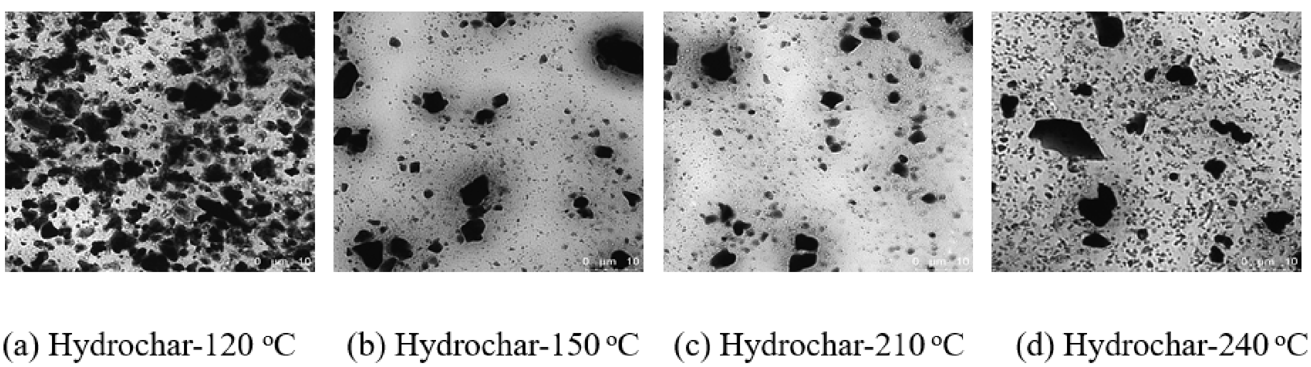
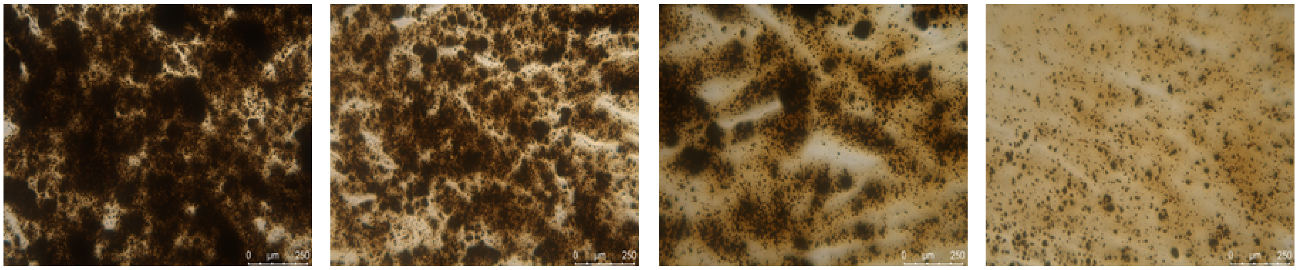


Figure 3

Black-and-white images of hydrochars at the different HTC temperatures



(a) Hydrochar-120 °C (b) Hydrochar-150 °C (c) Hydrochar-210 °C (d) Hydrochar-240 °C

Figure 4

Color images of hydrochars at the different HTC temperatures

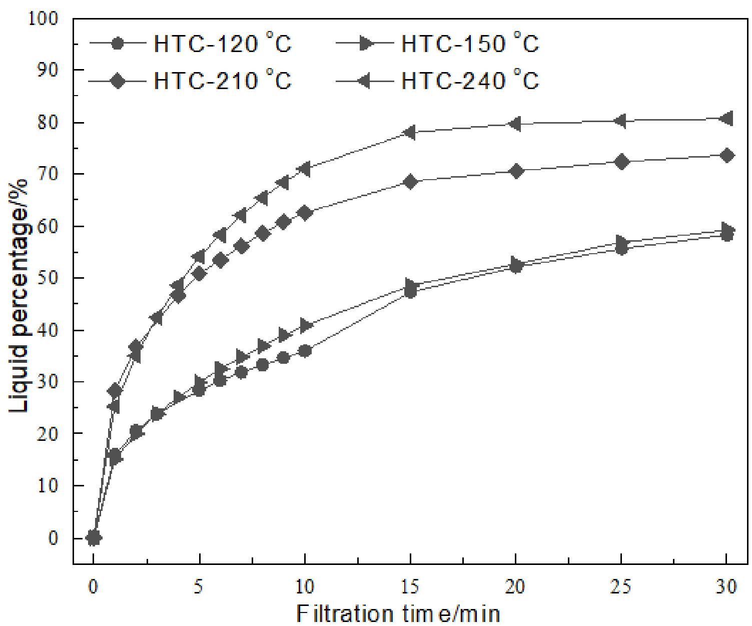
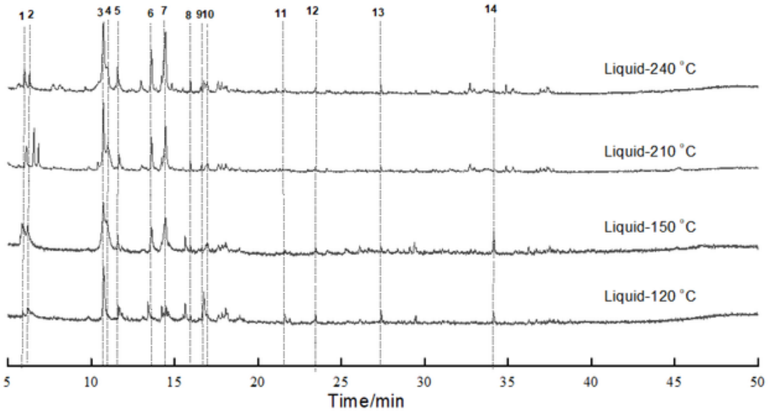
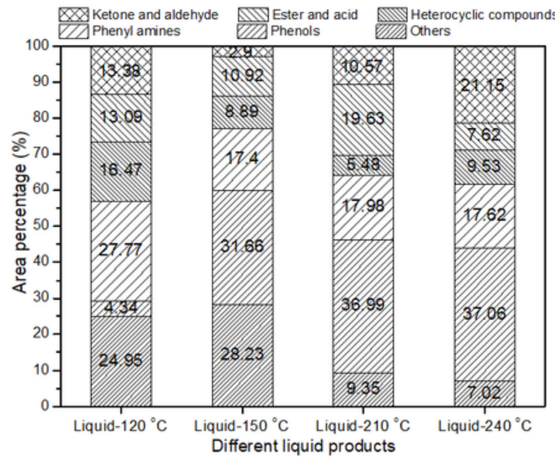


Figure 5

Filtration curves at the different HTC temperatures



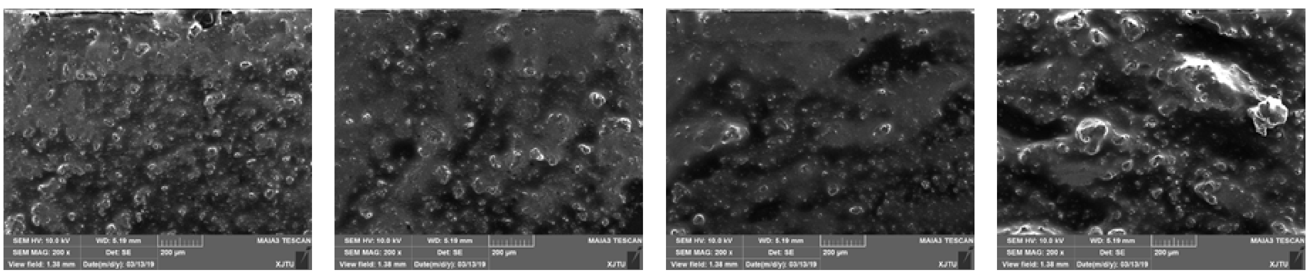
(a) GC-MS curves



(b) Chemical components in liquid

Figure 6

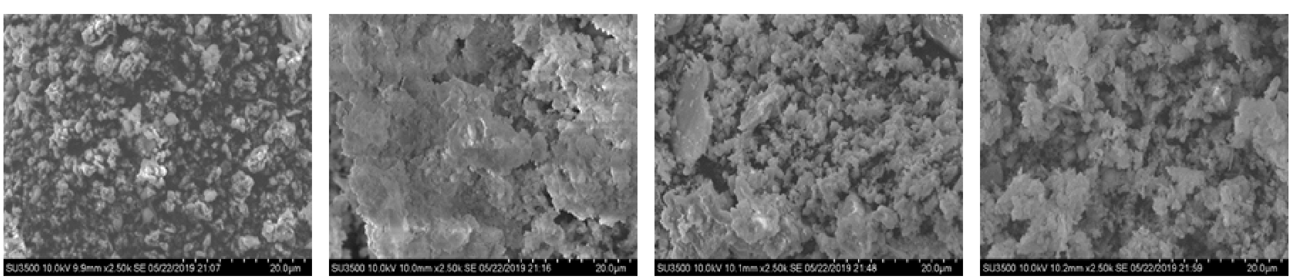
GC-MS curves and distributions of chemical components in the liquid product



(a) Hydrochar-120 °C (b) Hydrochar-150 °C (c) Hydrochar-210 °C (d) Hydrochar-240 °C

Figure 7

SEM images of hydrochars at the different HTC temperatures (200X)



(a) Ash-120 °C (b) Ash-150 °C (c) Ash-210 °C (d) Ash-240 °C

Figure 8

SEM images of different ash samples after hydrochar combustion (×2.5K, 20μm)

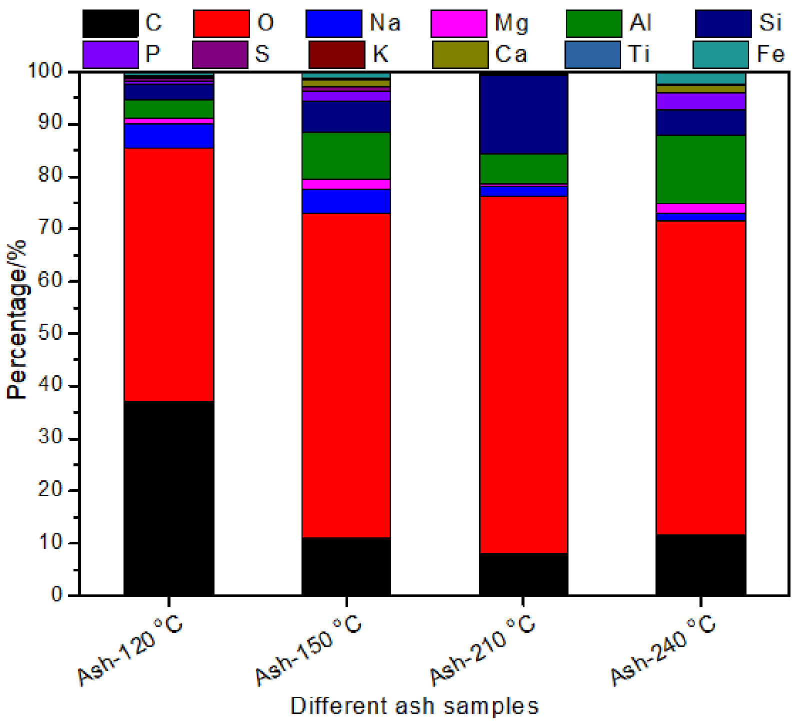


Figure 9

EDX results of different ash samples

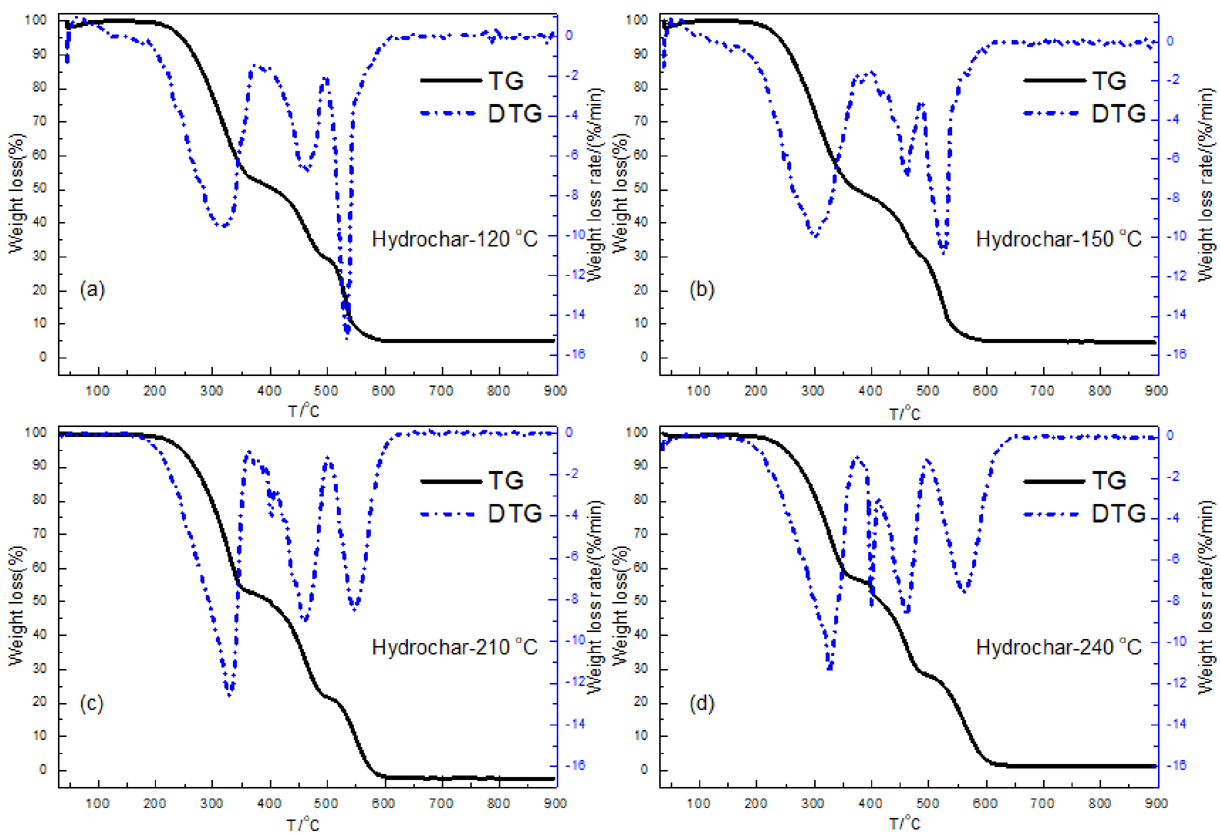


Figure 10

Combustion curves of hydrochars at the different HTC temperatures