Study of the fast pyrolysis of oilfield sludge with solid heat carrier in a rotary kiln for pyrolytic oil production

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In this work, an experimental study of flash pyrolysis of oilfield sludge in different operation conditions was carried out under inert condition in a rotary kiln reactor. The effects of pyrolysis temperature, mixture ratio (MR) of sludge and solid heat carrier on the characteristics of product distribution were investigated. The composition of oils obtained from extraction and pyrolysis process were analyzed by Fourier transform infrared spectroscopy (FT-IR) and gas chromatography–mass spectrometry (GC–MS), respectively. The results indicated that, the maximum oil yield was achieved at temperature of 550 °C and MR of 1:2, which was 28.98% (wt% of sludge oil) and oil recovery rate was 87.9% basing on the oil content in the sludge. High fraction of saturates (72.5%) was obtained at 550 °C. The increasing temperature and solid heat carrier favor of pyrolysis gases increase. FT-IR analysis of pyrolytic oils shows that the oils have similar IR features as extraction oils. The pyrolytic oil was also found to contain the major linear chain hydrocarbons in the range of C11–C25.

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1. Introduction

The oil industry unavoidably generates large quantities of oily and viscous residue called oilfield sludge, which is formed during crude oil exploitation and development of various productions in oilfields, transportation, and refining processes. The oilfield sludge is a complex mixture of petroleum hydrocarbons and water with solid mineral admixtures, such as soil and sand, adversely affecting human health and posing environmental problems. The major sources of oil sludge include oilfield sludge, petrol storage tank sludge, and residue derived from the crude oil refining processes. In China, it is estimated that more than 3 million tones of oilfield sludge discharged by the petrochemical industry [1]. Most of them were disposed in landfills and drains from the treatment process of oil storage tank cleanup which may pollute the groundwater and cause health problems. Although oilfield sludge is listed in the China National Hazardous Waste List because of its toxicity and harmful compounds, only a minor amount of oilfield sludge was disposed in a safe manner. The conditional disposals of oilfield sludge involve aerobic biodegradation [2] and ultrasound oil recovery [3,4]. Nevertheless, it has been found that such methods cause secondary pollution. As oil sludge is a useful recycling resource based on its high heating value and organic volatiles, to retrieve the energy or to convert into fuels from oilfield sludge is a promising method. The technology of thermal–chemical [5,6] can reduce the volume of the waste oilfield sludge and recover energy. However, pyrolysis treatment is one of the important thermal–chemical technologies which were used widely in the field of solid waste treatment. As the unique characteristics to crack large molecules into smaller ones, pyrolysis has been proven to be an alternative to handle the oilfield sludge for energy utilizing.

Pyrolysis has been applied to recover oil from waste oilfield sludge. Schmidt and Kaminsky [7] have investigated the separation of oil from the sludge and distribution of the oil products in a fluidized bed at temperatures from 460 to 650 °C. They found that between 70% and 84% of the oil could be separated from the solids. Wang et al. [1] reported that the pyrolysis reaction of oilfield sludge under heating rate from 5 to 20 °C/min starts at a low temperature of about 200 °C and the maximum evolution rate was observed between the temperatures of 350 and 500 °C by using TG/MS. Some researchers had focused on the behavior of thermal conversion and pyrolysis kinetics by means of thermogravimetric analysis (TGA). Punnarutatanakun et al. [8] showed that typical derivative curves of the sludge consist of two major peaks. The first peak was found between 230 and 270 °C while the other was found between 415 and 400 °C. A series of studies on the pyrolysis of oilfield sludge using TGA has been carried out by Shie et al. [9–14]. It was reported the major products obtained from the pyrolysis characteristics of oilfield sludge with and without catalytic additives by TGA. Liu et al. [15] had investigated the change of mass loss and

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pyrolysis gas composition in heating process by TGA and fixed bed reactor. The conclusion showed that higher heating rate causes the peak intensity of C-H evolution to increase and the C-H evolution to move toward a high-temperature region.

As the high heat rate is one of the necessary factors for pyrolysis oil conversion, to acquire the high heat rate of oilfield sludge might be an effective method to oil production. Quartz sand has the properties of large heat capacity, and the high heat rate and strong mass and heat transfer can occur between oilfield sludge and heat sand. It is an alternative to be chosen as solid heat carrier for oilfield sludge pyrolysis medium. As rotary kiln pyrolyzer offers some unique advantages comparing to other types of reactors, for example, the slow rotation of rotary kiln enables well mixing of oilfield sludge, and the residence time of oilfield sludge can be easily adjusted to provide optimum conditions for pyrolysis reaction [16], it is might be an attractive reactor for oilfield sludge decomposition with solid heat carrier. The rotary kiln with solid heat carrier was different from the traditional one. The rotary kiln was filled with quartz sand as solid heat carrier which was preheated to a desired temperature. Once the oil sludge was fed into the rotary kiln, it mixed immediately with the hot quartz sand, and the temperature of oilfield sludge sharply increased. By this way, an extremely high heating rate was achieved, and the flash pyrolysis occurred in the rotary kiln. In order to recover oil effectively from the oilfield sludge, flash or fast pyrolysis [17] was employed in this study to investigate the product distribution of oilfield sludge decomposition, the GC–MS is applied to detect the molecular distribution and structure of the oil and FT-IR is used to verify the GC–MS results.

2. Experimental

2.1. Sample

The oilfield sludge used as the feedstock in this study was obtained from Shengli Oil Field, China. From the appearance, the received samples are black and viscous slurry. The results of proximate analysis and ultimate analysis of the oilfield sludge are listed in Table 1. The carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) analyses of sample were performed on a CHNS/O analyzer (Elementar, VarioEL III). Because oxygen cannot be determined by any suitable method, its estimation is carried out by subtracting the sum of other constituents (ash, C, H, N, S) from 100. The moisture, ashes and volatile matter were measured according to the ASTM standard test method no. E871, D1102 and E872. The fixed carbon was calculated by difference to 100%. The bomb calorimeter was employed to measure the heating value of the sample which is also given in Table 1. The proximate analysis indicates the oilfield sludge has moderate moisture, high volatile matter, high ash content and very low fixed carbon.

2.2. Experimental apparatus

The bench-scale plant of the rotary kiln reactor is shown in Fig. 1. This plant consist of a feed hopper with a screw conveyor, a tubular reactor with a removable overflow weir, an electric heater, an oil condenser and reservoir, a gas sampling device and a residue receiver. The rotational kiln speed was selected as a manipulated variable to provide a mean for the control of the residence time of the oilfield sludge in the kiln. The rotary kiln reactor is made of stainless steel cylindrical tubular (855 mm long and 90 mm i.d.), and it was placed in an external electrical furnaces (3.3 kW, 220 V, 15A) which provided the heat for pyrolysis reaction. Four K-type thermocouples with a diameter of 10 mm were mounted through the wall of the reactor and measured the temperatures at the reactor centerline. All experiments were carried out at atmospheric pressure.

To clean the gas and separate it from the condensable fraction, two stages of traps were set up. First, the product gases leaving the rotary kiln contact directly with a countercurrent ice-cooled heat exchanger, and the pyrolytic oil condensed from product gas was collected in oil reservoirs. Second, the product gas pass through a tube filled with CaCl₂ for the sake of steam removal and gas purity.

2.3. Pyrolysis procedure

Pyrolysis reaction procedure was conducted on the system given in Fig. 1. The air of the reactor was removed by purging with nitrogen at a flow rate of 0.3 m³/h. And then the rotation bed loaded the particle of 1–2 mm quartz sand as the solid heat carrier. The sand in the rotary kiln was heated from ambient temperature to an

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Table 1
Proximate and ultimate analysis of the oil sludge.

<table>
<thead>
<tr>
<th>Ash (%)</th>
<th>Volatile matter (%)</th>
<th>Fixed carbon (%)</th>
<th>Moisture (%)</th>
<th>Ultimate analysis (wt% daf)</th>
<th>HHV (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>53.92</td>
<td>29.63</td>
<td>1.14</td>
<td>15.31</td>
<td>C: 23.28</td>
<td>H: 3.54</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N: 0.19</td>
<td>S: 1.29</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>O*: 3.47</td>
<td></td>
</tr>
</tbody>
</table>

* By difference.
adjusted temperature with the rotating of the kiln at a step of 5 rpm. The operating pyrolysis temperature varied from 480 to 650 °C in the mixture ratio of 1:1. When the sand temperature reached to the desired experimental temperature, the screw conveyor was switched on and the oilfield sludge was fed to the reactor. The rotary kiln run continuously until no further volatile matters was produced. In the solid heat carrier experiments, the amount of the sand used was varying from none to three times of the oilfield sludge at 550 °C. In the experimental process, the initial temperature of solid heat carrier was 550 °C. When the oil sludge was injected to the kiln with the hot solid carriers, the temperature of the mixed material dropped from 550 °C (solid heat carrier) to about 530 °C within seconds. The profile of temperature variation implied the heating rate was extremely fast in the kiln with the solid heat carrier. Mass balances were taken of sludge consumed and pyrolytic oil collected, while the gas yields were calculated through the measured volume and mole mass of mixed gaseous products.

2.4. Products analysis

The separation method of chemical organic materials composition in the pyrolytic oil is shown in Fig. 2. First, 50 mg of pyrolytic oil and 5 ml of HPLC grade n-hexane were transferred into the beaker which was heated at 90 °C on the steam bath with continuous stirring for about 2 h in order to maximize the solubility of oil in n-hexane. And then the solution was cool to room temperature for about 24 h. The cooling time produced efficient precipitation of asphaltites. The solution was filtered using a filtration apparatus with 0.8 μm pore size filter paper. The insoluble material was regard as asphaltites. The soluble solution was poured into the chromatography column. Saturates were leached by n-hexane three times and aromatics was leached by toluene twice. At last, the resins were eluted by the mixture of methanol, toluene and CHCl3.

The pyrolytic oil composition was determined using the gas chromatography mass spectrometry. GC–MS analysis was carried out on HP 6890N with an Agilent auto sampler and coupled to HP 5975 series detector. The oven was raised from 80 to 300 °C at a rate of 4 °C/min and held for 10 min. Helium was used as a carrier gas at a rate of 60 ml/min in splitless. The injector temperature was held at 280 °C with a volume of 1 μL. The compounds were identified using NIST mass spectra library. The samples were diluted with chloroform to a ratio of 1:100. The pyrolytic oil was applied as a cast film between two KBr windows using Nicolet 6700 Flex FT-IR Spectrometer.

The product gas was collected periodically through a gas syringe and analyzed off-line by gas chromatography (GC). The gas products (H2, CO, CH4, CO2 and C6H6 (C8H8, C12H8, C16H8, C20H8)), was identified using GC with a thermal conductivity detector and a double injector connected to three 5 m lengths, 3 mm diameter columns. Helium was used as a carrier gas for equipment.

3. Results and discussion

3.1. Effect of temperature on the yield of pyrolysis products

The effect on the pyrolysis temperatures of the solid heat carrier on the yield of the products (oil, char and NCG (non-condensable gas)) obtained from the pyrolysis of oilfield sludge are presented in Fig. 3. Reactions were performed at four reaction temperatures from 480 to 650 °C and the rotating speed was 5 rpm. It can be observed from Fig. 3 that the oil yield increased from 8.73% to 22.09% in the temperature range of 480–550 °C, and then decreased to 14.95% from 550 to 650 °C. The decrease is considered to be the secondary decomposition reactions which break the volatile oil into lighter, gaseous hydrocarbons [18]. The char yield decreased steadily from 86.03% to 51.41% between 480 and 650 °C. Char yields were expected to decline as the releasing of more volatiles. More char was consumed more oil and gases produced. The NCG yield, however, increased continuously from 5.24% to 33.64% as the temperature increases. But the gas yields remained fairly constant under 550 °C and above this temperature a significant increase was observed. It was caused by the secondary decomposition reactions. The yield of NCG appears to increase with increasing temperature, presumably as a result of the intensification of polycondensation reactions to form a more stable char [1].

The effect on the chemical composition of organic materials distributions of the pyrolytic oil under the different solid heat carrier temperatures is shown in Fig. 4. The pyrolysis temperature had a great effect on saturates and asphaltites. But the variance of aromatics and resins content were inconspicuous. It can be observed that saturates were the main composition of the oil product. The maximum concentration of the saturates (72.5%) was obtained at 550 °C and the lowest asphaltites content (9.8%) in oil also observed in the temperature range of 480–650 °C. Nevertheless, the concentration of saturates showed a decrease trend between 580 and 650 °C. While the concentration of asphaltites showed an inverse trend in this temperature range. This result indicated that the asphaltites are favored by the increase in the pyrolysis temperature while saturates are favored by low temperature. It
can be deduced that asphaltenes were desorbed from the oilfield sludge, and then the large structural asphaltenes cracked into small molecules compositions such as n-alkanes, n-alkenes, etc. As higher temperature caused more volatile matters broken from the oilfield sludge, saturates occurred secondary decomposition reactions easier than asphaltenes. This might be the reasons that the content of saturates dropped at higher temperature.

Fig. 5 exhibits the NCG concentration of the oilfield sludge pyrolysis products with a constant rotating speed of 5 rpm at different temperatures. The gas compositions including H₂, CH₄, C₆H₆, CO and CO₂ were identified by GC. The concentration of H₂ and CH₄ increased steadily from 13.46% to 34.33% and from 11.14% to 29.99% in the temperature range of 500–650 °C, respectively. However, the release of C₆H₆ exhibits a decreasing trend with temperature. The high concentration of C₆H₆ was mainly due to the dissociation or depolymerization of asphaltenes into lighter, gaseous hydrocarbons at relatively low temperature conditions. Higher temperature led C₆H₆ breaking to small molecular species such as H₂ and CH₄. Higher temperature favors to convert the larger molar organic materials into NCG as well as for the purposes of getting rid of the harmful organic contents existing in pyrolysis oil. At high temperature stage, the CH₄ increase might to be attributed to secondary decomposition of the −CH₃ side chain in the volatile in the kiln [1]. The concentration of CO increased from 27.16% at the temperature of 500 °C, and then reached the maximum concentration of 39.11% at 550 °C. From 550 to 650 °C, the content of CO declined to 23.97%. The contents of CO₂ are low in all temperatures might be caused by the low oxygen content in the oilfield sludge. To sum up, the 550 °C of pyrolysis temperature was selected as optimum and the solid heat carrier experiments were performed at this temperature from the point of oil yield.

3.2. Effect of mixture ratio of oilfield sludge and solid heat carrier on pyrolysis products

The effect of mixture ratio oilfield sludge and solid heat carrier has been studied between 1:0 and 1:3 at the pyrolysis temperature of 550 °C. The product yields of oilfield sludge pyrolysis were shown in Fig. 6.

The production of chars decreased from 80.48% to 55.92% in the MR range of 1:0–1:3. The yield of NCG showed an increase trend with MR from 2.89% under pure sludge pyrolysis to 28.25% at the MR of 1:3, respectively. Oil yields increased from 16.63 at the MR value of 1:0 to the maximum yield of 28.87% at MR of 1:2, which oil recovery rate achieved 87.9% based on the oil content in the sludge, and then declined to 15.83% under MR value of 1:3. This due to the heat transfer coefficient of solid heat carrier is greater than the coefficient of thermal radiation. The oilfield sludge contacts the solid heat carrier directly, and the temperature of sludge increased in a short time caused by high heating rate. Large amount volatile matter was evolved rapidly. In addition, the oilfield sludge was grated into small pieces in the sand which can promote the heat transfer effectively. However, a decrease of pyrolytic oil product appeared under the condition of the excessive solid heat carrier. This might be associated with secondary decomposition by the escape of volatile oil fraction through the carrier.

Fig. 7 represents the concentration of the NCG released at 550 °C with the sludge and solid heat carrier mixture ratio of 1:2. H₂ has the largest gaseous product in pyrolysis process. The H₂ evolution is significantly in the first 10 min of residence time and reaches peak concentration at 10 min. And the quantities of the evolved H₂ decreased with the following 5 min. After 15 min, however, more and more H₂ are released with the time increase. The C₆H₆ evolution curve is against that of H₂. The evolution of CH₄ has a
similar behavior of CsH8 but with relatively weak release intensity. The time increase would produce a marked lowering of CsH8 conversion. This may be associated with secondary decomposition in lighter hydrocarbons itself. And the CsH8 release trend to be steady till pyrolysis reaction finish. But, the evolved CsH4 has a minor raise at the latter part of experiment process. Compared to the H2 and CsH2, the maximum evolving of CO lagged with reaction time. During the first 15 min, the evolution of CO level fluctuates in the range of 5–10%. The maximum concentration of CO appears at 25 min, the residence time present an important influence on the conversion of CO. The CO2 shows a slight percentage in the total pyrolysis.

### 3.3. FT-IR analysis results

IR spectroscopy proved to be a very useful technique in analyzing structural changes in oil products [19]. FT-IR spectra of produced oils from soxhlet extraction and pyrolysis of oilfield sludge at 550 °C was presented in Fig. 8. The IR patterns of oils obtained from extraction (EO) and pyrolysis (PO) were similar. This result revealed that the two kinds of oil have similar corresponding functional group distribution. Pokorna et al. [17] also observed the same result. The most prominent IR vibrations were C–H modes of vibrations. Most of the functional groups observed in the IR spectra of both oils were related to –CH2, –CH3 and C=C groups.

In the IR spectra of EO, the present of bonds of O–H stretching vibration at 3420 cm−1, this can be assigned to carboxylic group or hydroxyl functionalities. But the absence of absorbance peak of the C=O band between 1725 and 1700 cm−1 indicated that there were no carboxylic acids in EO [20]. The IR spectra of PO displayed a C=O stretch absorption at 1703 cm−1 due to carbonyl or carboxyl groups. No O–H and stretching vibrations were observed in the region 3500–3100 cm−1 in case of PO. The peak differences between EO and PO show that these structural properties are related to the chemical conversion or reactions occurred in oilfield sludge on pyrolysis. This trend shows that there was dehydrogenation reaction with ketone and olefins formation on pyrolysis of oil. The region 800–600 cm−1 found to contain impurities and was ignored (Table 2).
the composition of oil from the soxhlet extraction of the oilfield sludge was also investigated. The total ion count (TIC) of evolved gases from crude oil derived from oilfield sludge extraction and the oil produced from oilfield sludge pyrolysis are depicted in Figs. 9 and 10, respectively. The total of 8 and 26 main compounds were identified from the two kinds of oil, and the peaks of TIC are characterized in Tables 3 and 4. From the extracted oil, the main compounds with the corresponding % area identified were C_{20}H_{32}O (28.33%), C_{30}H_{52} (20.53%), C_{30}H_{50}O_2 (15.39%), C_{20}H_{52} (10.53%), C_{27}H_{48} (7.87%), C_{28}H_{46}O (7.26%). While most chemical compounds of pyrolysis oil were long-chain olefinic or alkane. The oil extracted from oilfield sludge had a most complicated composition, which were made up of long-chain aliphatic compounds with a number of carbons ranging from C_{10}–C_{30} and cyclic hydrocarbons. Other oxygenated compounds detected by GC–MS in the crude oil derived from extraction are alcohols and phenolics, while in the pyrolytic oil are ketones. The crude oil was centered on a number of polymeric structures with a large molecular weight. Comparatively, the pyrolytic oil composed of straight chain hydrocarbons, as these had a high heating value and lower viscosity. The crude oil contained polyhydric alcohols, alicyclic systems and aromatic rings bearing long aliphatic substituents. Table 4 shows that the concentrations of long chain n-alkanes and 1-alkenes increased through pyrolysis. In order to determine the distribution of these hydrocarbons in the oil fraction, a semi-quantitative study was made by means of the percentage of area of the chromatographic peaks [20]. It

<table>
<thead>
<tr>
<th>Peak no.</th>
<th>Rt (min)</th>
<th>Area (%)</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>47.449</td>
<td>7.87</td>
<td>C_{27}H_{48}</td>
</tr>
<tr>
<td>2</td>
<td>47.775</td>
<td>7.26</td>
<td>C_{28}H_{40}O</td>
</tr>
<tr>
<td>3</td>
<td>48.986</td>
<td>10.53</td>
<td>C_{29}H_{52}</td>
</tr>
<tr>
<td>4</td>
<td>51.159</td>
<td>20.53</td>
<td>C_{30}H_{52}</td>
</tr>
<tr>
<td>5</td>
<td>52.513</td>
<td>28.33</td>
<td>C_{30}H_{50}O_2</td>
</tr>
<tr>
<td>6</td>
<td>54.086</td>
<td>15.39</td>
<td>C_{30}H_{52}O_2</td>
</tr>
<tr>
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<td>55.335</td>
<td>4.41</td>
<td>C_{29}H_{52}O_2</td>
</tr>
<tr>
<td>8</td>
<td>57.389</td>
<td>2.84</td>
<td>C_{17}H_{36}O</td>
</tr>
</tbody>
</table>

Fig. 9. GC–MS chromatograms of crude oils from soxhlet extraction.

Fig. 10. GC–MS chromatograms of produced oils from 550 °C pyrolysis of oil sludge.
was observed from the pyrolysis oil that major long chain hydrocarbons were distributed in the range C_{13}–C_{25} mainly including heptadecanamide and eicosanamide. It indicated that the pyrolysis caused to an improved amount of chain structures, while a considerable reduction was observed in the amount of the cyclic structures. The reason for this degradation might be radical formation at high temperatures [21].

The complex reactions may be involved in the pyrolysis of oil sludge, according to the Koufopoulos et al. [22] mechanism, the following pyrolysis mechanism for describing the kinetics is shown in Fig. 11. The oilfield sludge decomposes to volatiles (volatile 1), gases (CH_{4}, CO, CO_{2}, H_{2}, etc.) and char (char 1). The volatiles and gases may further react with char to produce different types of volatiles (volatile 2), gases (gases 2) and char (char 2) where the compositions are different. Therefore, the primary pyrolysis products participate in secondary interactions (Reaction 3), resulting in a modified final product distribution.

4. Conclusion

Pyrolysis of the oilfield sludge in the rotary kiln reactor was investigated in this study with and without solid heat carrier. Under the experimental conditions, it was possible to recover up to 87.9% at 550 °C of the solid heat carrier temperature and the mixture ratio of 1:2. The experimental results revealed that moderate solid heat carrier loading could promote the recovery of oil from the sludge. The analysis of chemical composition of organic materials distributions in the recovered oil samples indicated that a much higher fraction of saturates (72.5%) was obtained at 550 °C and the lowest asphaltene content (9.8%). FT-IR analysis of pyrolytic oils shows that the oils have similar IR features as extraction oils. Comparing to the crude oil which was extracted from oilfield sludge and the pyrolytic oils, the pyrolysis process favors to long chain n-alkanes and 1-alkenes forming. The pyrolytic oil was also found to contain the major linear chain hydrocarbons in the range C_{13}–C_{25}. The flash pyrolysis process could represent an environmentally friendly and economically competitive alternative for the effective treatment of oilfield sludge.

Acknowledgments

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