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Low Temperature Pyrolysis Characteristics of Oil Sludge under Various Heating Conditions

Zhiqi Wang, Qingjie Guo,* Xinmin Liu, and Changqing Cao

College of Chemical Engineering, Qingdao University of Science and Technology,
Qingdao, Shandong 266042, China

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Pyrolysis of oil sludge first by thermogravimetry/mass spectroscopy (TG/MS) and then in a horizontal quartz reactor with an electrical laboratory furnace under different pyrolysis conditions was carried out. The influence of heating rate from 5 to 20 °C·min⁻¹, final pyrolysis temperature from 400 to 700 °C, various interval holding stage, and catalyst on the products were investigated in detail. The TG/MS results show that pyrolysis reaction of oil sludge starts at a low temperature of about 200 °C, and the maximum evolution rate is observed between the temperatures of 350–500 °C. A higher final pyrolysis temperature, an interval holding stage, and adding catalyst can promote the pyrolysis conversion (in terms of less solid residue production). In all parameters, an interval holding stage for 20 min near the peak temperature of 400 °C can enhance the yield of oil and improve its quality. Three additives used in this work as catalysts do not improve oil product quality markedly in spite of increasing pyrolysis conversion greatly.

Introduction

In the petroleum refineries, a considerable quantity of oil sludge accumulates from refining processes. The oil sludge contains various amounts of solids, water, and oil. The major sources of oil sludge include oil storage tank sludge, biological sludge, and dissolved air flotation (DAF) scum. Most of the oil sludge waste is conventionally disposed by landfills or incineration. The disposal by landfills requires much space, and the soil has to be sealed adequately to prevent the leaching of harmful compounds. Oil sludge contains mainly heavy organic compounds and a large amount of combustible matters with high heating values, so there exists an approach to convert this stored energy into a usable energy source such as for heating or perhaps as a liquid fuel substitute and the production of specialty chemicals.

Thermal disposal methods including incineration and pyrolysis, which offer some benefits over landfills, mean: energy recovery and reduction of the volume and quantity of waste. Incineration reduces a large volume of sewage or oil sludge and improves thermal efficiency. However, the scrubbing costs for air pollution control are usually very high due to the treatment of larger flue gas volume. With its unique characteristics to break down large molecules into smaller ones, pyrolysis has been proven to be an alternative to the disposal of many wastes such as plastic waste, biomass, municipal solid waste, and other solid wastes.^{1–5} The benefit of using such a process not only minimizes or disposes the volume of solid waste but also yields valuable products. Compared with incineration, a

number of studies have demonstrated that emission of poisonous matters by suitable pyrolysis methods might be less than that of direct incineration.^{4–8} Emission controls are easier for pyrolysis than for incineration due to the reduced air flow rate and lower temperature.

There are a number of papers on the pyrolysis of sewage sludge or oil sludge.^{9–26} However, most of them have focused on the basic behavior of thermal conversion and thermal reaction

* Author to whom correspondence should be addressed. Tel.: 86-532-84022506. Fax: 86-532-84022757. E-mail: qj_guo@yahoo.com.

(1) Miller, S. J.; Shah, N.; Huffman, G. P. *Energy Fuels* **2005**, *19*, 1580–1586.

(2) Hall, W. J.; Williams, P. T. *Energy Fuels* **2006**, *20*, 1536–1549.

(3) Czernik, S.; Bridgwater, A. V. *Energy Fuels* **2004**, *18*, 590–598.

(4) Whitely, N.; Ozao, R.; Cao, Y.; Pan, W.-P. *Energy Fuels* **2006**, *20*, 2666–2671.

(5) Wang, Z.; Huang, H.; Li, H.; Wu, C.; Chen, Y.; Li, B. *Energy Fuels* **2002**, *16*, 136–142.

(6) Zevenhoven, R.; Axelsen, E. P.; Hupa, M. *Fuel* **2002**, *81*, 507–510.
(7) Matsuzawa, Y.; Ayabe, M.; Nishino, J.; Kubota, N.; Motegi, M. *Fuel* **2004**, *83*, 1675–1687.

(8) Balabanovich, A. I.; Hornung, A.; Luda, M. P.; Koch, W.; Tumiat, V. *Environ. Sci. Technol.* **2005**, *39*, 5469–5474.

(9) Shen, L.; Zhang, D.-k. *Fuel* **2005**, *84*, 809–815.

(10) Dominguez, A.; Menendez, J. A.; Inganzo, M.; Bernad, P. L.; Pis, J. J. *J. Chromatogr., A* **2003**, *1012*, 193–206.

(11) Domínguez, A.; Menéndez, J. A.; Inganzo, M.; Pis, J. J. *Fuel Process. Technol.* **2005**, *86*, 1007–1020.

(12) Doshi, V. A.; Vuthaluru, H. B.; Bastow, T. *Fuel Process. Technol.* **2005**, *86*, 885–897.

(13) Lutz, H.; Romeiro, G. A.; Damasceno, R. N.; Kutubuddin, M.; Bayer, E. *Bioresour. Technol.* **2000**, *74*, 103–107.

(14) Scott, S. A.; Dennis, J. S.; Davidson, J. F.; Hayhurst, A. N. *Fuel* **2006**, *85*, 1248–1253.

(15) Punnarattanakun, P.; Meeyoo, V.; Kalambaheti, C.; Rangsunvigit, P.; Rirkomboon, T.; Kitiyanan, B. *J. Anal. Appl. Pyrolysis* **2003**, *68*–69, 547–560.

(16) Shie, J. L.; Chang, C. Y.; Lin, J. P.; Wu, C. H.; Lee, D. J. *J. Chem. Technol. Biotechnol.* **2000**, *75*, 1–8.

(17) Chang, C.-Y.; Shie, J.-L.; Lin, J.-P.; Wu, C.-H.; Lee, D.-J.; Chang, C.-F. *Energy Fuels* **2000**, *14*, 1176–1183.

(18) Shie, J.-L.; Chang, C.-Y.; Lin, J.-P.; Lee, D.-J.; Wu, C.-H. *Energy Fuels* **2002**, *16*, 102–108.

(19) Shie, J.-L.; Lin, J.-P.; Chang, C.-Y.; Wu, C.-H.; Lee, D.-J.; Chang, C.-F.; Chen, Y.-H. *Energy Fuels* **2004**, *18*, 1272–1281.

(20) Shie, J.-L.; Lin, J.-P.; Chang, C.-Y.; Lee, D.-J.; Wu, C.-H. *Resour. Conserv. Recycl.* **2003**, *39*, 51–64.

(21) Shie, J.-L.; Lin, J.-P.; Chang, C.-Y.; Shih, S.-M.; Lee, D.-J.; Wu, C.-H. *J. Anal. Appl. Pyrolysis* **2004**, *71*, 695–707.

(22) Schmidt, H.; Kaminsky, W. *Chemosphere* **2001**, *45*, 285–290.

(23) Shen, L.; Zhang, D.-K. *Fuel* **2003**, *82*, 465–472.

(24) Inganzo, M.; Domínguez, A.; Menéndez, J. A.; Blanco, C. G.; Pis, J. J. *J. Anal. Appl. Pyrolysis* **2002**, *63*, 209–222.

(25) Karayildirim, T.; Yanik, J.; Yuksel, M.; Bockhorn, H. *Fuel* **2006**, *85*, 1498–1508.

kinetics by means of thermogravimetric analysis (TGA). Pun-naruttanakun et al.¹⁵ have studied the kinetic and thermal conversion behaviors of API separator oil sludge pyrolysis at different heating rates by TGA, and a deduced pseudo-bicomponent model can be represent the TG curve relatively well. A series of studies on the pyrolysis of oil sludge using TGA has been carried out by Shie and his colleague.^{16–21} They have investigated the major products obtained from the pyrolysis of oil sludge and the pyrolysis properties of oil sludge with catalytic additives by TGA. Furthermore, they found that all the additives improved the qualities of liquid oils.

Some investigations of pyrolysis of oil sludge or sewage sludge in laboratory-scale reactors have been presented. Schmidt and Kaminsky²² have pyrolyzed oil sludge in a fluidized bed at temperatures from 460 to 650 °C. They found that about 70–84% of the oil could be separated from the solids. Shen and Zhang²³ have studied the effects of temperature and gas residence time on the product distribution and composition of pyrolysis of activated sewage sludge in a fluidized bed reactor. Their results indicated that a maximum of 30% oil yield (wt% daf of sludge fed) was achieved at a pyrolysis temperature of 525 °C and a gas residence time of 1.5 s.

Inguanzo et al.²⁴ performed the influence of pyrolysis conditions (temperature and heating rate) on solid, liquid, and gas fractions during the pyrolysis of sewage sludge. Little of the literature has reported the effects of operating parameters such as temperature, heating rate, and interval residence time on product distribution by the low temperature pyrolysis of oil sludge. The present study aims to evaluate the feasibility of the oil recovery and product distribution in the low-temperature pyrolysis process under different heating conditions by a tube furnace and seek an optimum pyrolysis parameter for maximum oil recovery. Using a chromatographic simulation distillation method, the recovered oil from oil sludge pyrolysis was divided into three parts: gasoline, diesel oil, and heavy oil. And, the effects of heating rate, final pyrolysis temperature, catalysts, and interval retention time on the product distribution, specifically the oil composition such as gasoline (C_{8–12}), diesel oil (C_{13–18}), and heavy oil (C_{>18}) of the oil sludge pyrolysis process, were investigated.

Experimental Section

Samples. The oil sludge used in this study was sampled from the crude oil storage tank of a typical petroleum refinery plant located in Shandong province, northern China. The received samples appear as black, viscous slurry, which are 80.7% water by weight. To remove the water of oil sludge, samples were first filtered by an air suction filter to remove most of the water and the filter cakes were dried by air for 2 days. These samples were then used as pyrolysis samples in a horizontal quartz reactor. Meanwhile, thermogravimetric experiments were carried out using dried samples at 105 °C for 6 h in a drying oven again. The samples obtained were as the pyrolysis feedstocks and underwent the proximate analysis according to ASTM D3172-89. A bomb calorimeter was employed to measure the heating value of the sample. The properties of oil sludge were listed in Table 1.

Pyrolysis of Oil Sludge. Thermogravimetric analyses were carried out with a thermobalance (STA 409 PC Luxx, NETZSCH GmbH, Germany) coupled to a quadrupole mass spectrometer. The TG experimental conditions were as follows: oil sludge sample weight, 80 mg; gas atmosphere, Ar; pressure, 0.1 MPa; heating rate, 10 °C·min⁻¹; final temperature, 900 °C.

Table 1. Analysis of Oil Sludge Properties

proximate analysis (wt %)				ultimate analysis (wt %)					heating value (kJ·kg ⁻¹)
moisture	ash	volatile	fix carbon	C	H	O ^a	N	S	
26.89	18.51	44.97	9.63	81.84	13.61	1.56	0.75	2.24	35170

^a By difference.

The pyrolysis experiments of the oil sludge were carried out in a horizontal quartz reactor, which was placed in an electrical laboratory furnace equipped with an intellectualized program-rising temperature instrument and temperature controller. In order to ensure an inert environment during the experiments, a 100 mL/min flow rate of N₂ was maintained to flow through the reactor. In a typical pyrolysis experiment, 150 g of oil sludge was loaded, N₂ with a 100 mL/min flow rate was passed through the reactor for purging the air for 30 min, and then the reactor temperature was increased at a desired heating rate up to a final temperature and held at this temperature for 1 h. In some cases, the reactor temperature was increased to the desired temperature and kept for an interval time, then increased to a final temperature, and held for 1 h.

The pyrolysis products were swept out of the reactor and passed through a glass condenser immersed in a mixture of ice and water, whose condensable liquid fractions were collected. The noncondensable volatiles passed through a glass ampule filled with water. As the gases entered, the water was displaced, and then, the remaining gases were collected in gas bags. The connecting glass line between the pyrolysis furnace and condensing tube was wrapped with a thermal belt at 150 °C. After the reaction, the aqueous phase in the condensate was separated from the organic phase (pyrolysis oil) by centrifugation. For each experiment, solid residues, pyrolysis oil (oil) and aqueous (water) fraction yields were determined by weight and the gas fraction yield was calculated by weight difference.

Products Analysis. A Balzers MS Omnistare 200 quadrupole mass spectrometer linked to the thermobalance (TG/MS) was employed to record the gas evolution profiles. The evolved gases were analyzed by a Balzers Omnistare mass spectrometer, and the operation conditions of MS were as follows: ionizing voltage, 40 V; input gas volume, 2 mL; mass range, 1–300 amu.

Pyrolysis gases collected in gas bags were analyzed by gas chromatography using an HP model 5890 series II with a thermal conductivity detector. A stainless steel packed column was used. The separations of C_{1–6} hydrocarbons were achieved by the Propack Q column.

An Agilent Technologies 6890N gas chromatograph (GC) with an injector port and a flame ionization detector (FID) was used for the quantitative analyses of pyrolysis liquid oils. The chromatographic column was a stainless steel capillary column (0.5 m, 2.1 mm id, 3.3 mm od; stationary phase 10% UCW-982/chromasorb PAW 80–100 mesh). The operating conditions for the simulation distillation of oil products were set as follows: injector temperature 150 °C, detector temperature 350 °C, column temperature following the sampling injection being held at for 1 min, programmed from 30 to 350 °C at 10 °C/min, and finally held at 350 °C for 20 min, nitrogen carrier gas flow rate 30 mL/min, hydrogen as burning gas flow rate 30 mL/min, clean air as combustion-supporting gas flow rate 400 mL/min, sample volume 0.1 µL. The oil products consist of gasoline, diesel oil, and heavy oil by the mentioned method.

Results and Discussion

TG/MS Results. Figure 1 shows the TG/DTG results of oil sludge. As Figure 1 illustrated, the main decomposition peak was observed between 100 and 500 °C. The reason is that oil sludge consisted of petroleum hydrocarbons with a wide range in boiling point. The sharp peak at 200 °C in the differential thermogravimetry (DTG) curve might due to evolution of water and volatilization of small hydrocarbon components in the

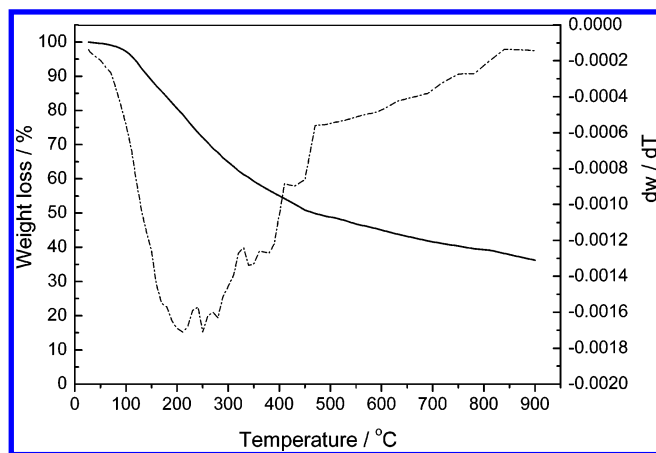


Figure 1. TG and DTG curves of the oil sludge at the heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$.

sludge. Note that two or three main reactions from the conversion observed in the other articles^{15,26} are not very distinct at the temperature from 100 to 500 $^{\circ}\text{C}$. So, the oil sludge pyrolysis can be divided into two main reaction region combining TG and DTG curves. One reaction region is at a temperature from 150 to 500 $^{\circ}\text{C}$, and the other is at a temperature from 500 to 850 $^{\circ}\text{C}$. The first region might be due to decomposition and devolatilization of petroleum hydrocarbons which is a larger fraction in the oil sludge. In the second stage of sludge pyrolysis, main decomposition reactions of a small fraction of more complex organic structures and inorganic materials (such as CaCO_3 , MgCO_3 , etc.) took place.

The coupling of thermogravimetry with mass spectrometry presents an insight into the course of the characterization of gaseous products during different materials pyrolysis. Therefore, the coupled configuration (TG/MS) allowed us (a) to analyze mass spectra recorded vs time, i.e., vs pyrolysis temperature,

(b) to reveal the presence of the evolved gaseous species, and (c) to follow the ion current of a single proper m/z value, which may represent the evolution, as a function of the temperature, of a particular molecular species.

To identify the degradation products from pyrolysis of the oil sludge by TGA, thermogravimetric experiments were carried out with a thermobalance coupled to a quadrupole mass spectrometer. Figure 2 shows some of the most relevant peaks obtained in the TGA degradation of the oil sludge. All evolution of light gas products, including H_2 , CH_4 , C_2H_6 , C_3H_8 , C_4H_{10} , CO_2 , start at low temperature of about 200 $^{\circ}\text{C}$. With increasing temperature, the evolution of light gas products gradually increases, the maximum evolution rate is observed between the temperatures of 350–500 $^{\circ}\text{C}$ except H_2 and CO_2 , and then, it decreases. H_2 and CO_2 evolution rates do not decrease after 500 $^{\circ}\text{C}$, the reason may be that H_2 and CO_2 formation are not only from the decomposition of petroleum hydrocarbons at lower temperature but also from the following reactions at higher temperature:

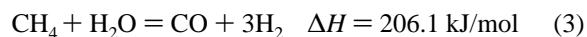
Water gas reaction



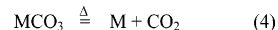
Water gas shift reaction



Methane gasification



Inorganic carbonate degradation reaction:



The two peaks in the CO_2 evolution curve at about 650 and

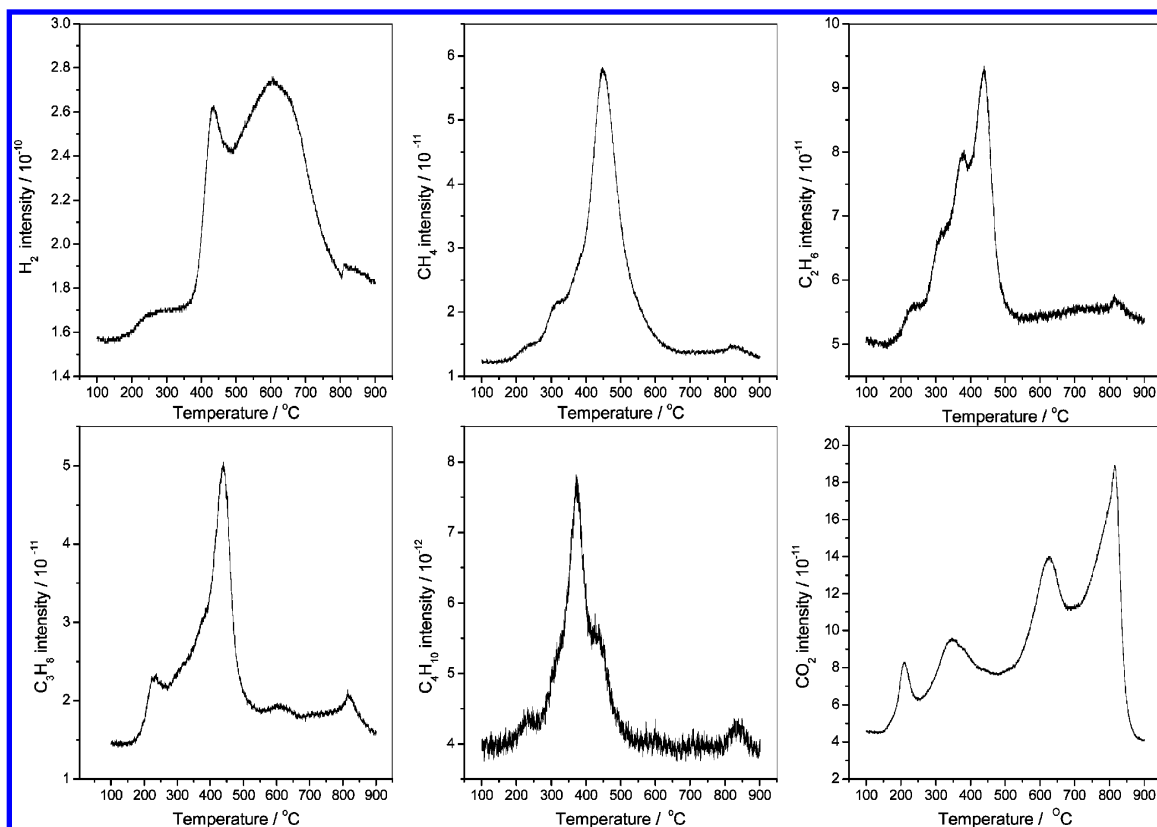


Figure 2. Evolution curves of low-molecular-weight gas products from MS during pyrolysis of oil sludge.

Table 2. Distributions of Solid, Liquid, and Gas Fractions under Different Pyrolysis Conditions

gas	products (wt %)			heating rate (°C/min)	final temperature (°C)	retention time at 400 °C (min)
	water	oil	solid			
15.3 ± 0.8	20.2 ± 1.3	33.1 ± 1.0	31.4 ± 0.9	2.5	500	
17.6 ± 1.1	20.4 ± 1.0	31.8 ± 0.9	30.2 ± 0.9	5	500	
17.8 ± 0.9	20.6 ± 0.7	31.5 ± 0.6	30.1 ± 1.2	10	500	
16.9 ± 0.5	20.8 ± 0.8	32.8 ± 0.7	29.5 ± 1.0	20	500	
18.7 ± 0.7	20.6 ± 0.6	31.9 ± 0.8	28.8 ± 0.7	10	600	
20.1 ± 1.0	20.1 ± 0.8	32.6 ± 0.9	27.2 ± 0.8	10	700	
16.6 ± 1.1	20.2 ± 0.7	34.3 ± 1.0	28.9 ± 1.0	10	500	20
17.5 ± 1.0	20.7 ± 0.9	33.5 ± 0.8	28.3 ± 1.1	10	500	40
15.6 ± 0.9	21.1 ± 1.1	29.8 ± 1.2	33.5 ± 0.9	10	400	60

850 °C might be attributed to the degradation of inorganic carbonate such as MgCO_3 and CaCO_3 according to eq 4. The evolution of CH_4 , C_2H_6 , C_3H_8 , and C_4H_{10} continues over 500 °C because of the breaking of terminal C—C bonds or branch C—C bonds in the condensed organic structure in coke, but the evolution rates are very small. On the basis of the TG/MS results, one can find that the pyrolysis reaction temperature of the oil sludge pyrolysis mainly occurs between the temperatures of 350–500 °C.

Effect of Pyrolysis Conditions on the Solid, Liquid, and Gas Fractions. Table 2 shows the solid, liquid (water and oil), and gas yield resulting from the pyrolysis of oil sludge under different pyrolysis conditions. The results presented in the table are the mean values of at least three pyrolysis runs carried out under the same condition. From the data shown in Table 2, we can see that the heating rate has a different influence on the gas, liquid, and gas yield fractions when the final pyrolysis temperature is 500 °C. The heating rate has almost no effect on the solid yield fraction but has a relative influence on the gas and liquid yield fractions obviously. According to the known mechanism of pyrolysis, high heating rates, which would produce more free radicals, benefit the gas and liquid yields especially for oil product. As shown in Table 2, the heating rate increase from 5 to 20 °C·min⁻¹ displays the tendency that more oil would be formed. However, the heating rate of 2.5 °C·min⁻¹ exhibits a maximum oil yield. The very slow heating rate might be favorable for oil recovery, though the economic efficiency of industrial operation would decrease due to needing the very long heating time.

In order to decrease the vaporization of the heavy metals, Stambach et al.²⁶ have proposed that the pyrolysis temperature should not be much higher than 600 °C for pyrolysis of sewage sludge in a fluidized bed. As TG/MS results have shown, the oil sludge underwent the mainly pyrolysis at approximately 400 °C; therefore, an interval holding process at 400 °C with different interval holding times, under a heating rate of 10 °C·min⁻¹ and a final temperature of 500 °C, was designed as shown in Table 2 for increasing the conversion of oil sludge and oil recovery. Compared with a no holding process, the interval holding processes can improve the pyrolysis conversion and more oil yield fractions are obtained. Pyrolysis is an endothermic reaction, so large molecule products may further crack into small molecule products such as hydrogen and methane while the temperature further increases. And also, a higher final pyrolysis temperature leads to faster decomposition reactions and more gas and oil production. In the holding stage at 400 °C, more large hydrocarbons would be decomposed, the holding temperatures are relatively lower, and the degrees of further decomposition of large molecule products are much less. Therefore, the oil yields are higher. The longer the interval retention time lasts, the more fractions of gas and oil form. The results of different holding time at 400 °C suggest that holding

for 20 min is more favorable for oil recovery than other longer holding times.

It can be found that an increase in the final pyrolysis temperature led to a decrease in the solid fraction and to an increase the gas and liquid fractions. The amounts of the water fraction of the oil sludge pyrolysis are less than the moisture content of the oil sludge feedstock. The possible reason is that the steam cannot condense to liquid water entirely while flowing through the condenser immersed in a mixture of ice and water.

Effect of Heating Rate on the Oil Product Compositions. Both the yields and the compositions of the pyrolysis products depend on the operation conditions. In order to gain more the nature of the oil products, a simulation distillation analysis of the oil samples obtained under different heating rate pyrolysis conditions was performed. The effect of heating rate on the gasoline, diesel oil, and heavy oil distributions of the oil products under the same final pyrolysis temperature of 500 °C is shown in Figure 3. It can be observed that the gasoline content decreases with the heating rate increased; the much slower heating rate of 2.5 °C·min⁻¹ causes the lowest gasoline content in the oil product. A much higher fraction of gasoline is obtained when the heating rate is increased from 2.5 to 5, 10, and 20 °C·min⁻¹. Nevertheless, the contents of diesel oil and heavy oil decline slightly with increasing the heating rate from 2.5 to 10 °C·min⁻¹. Although a lower heating rate can increase the oil yield, the lighter fractions such as gasoline and diesel oil in the oil products decrease.

Effect of Final Pyrolysis Temperature. The pyrolysis process is where larger molecular matter breaks up to small molecular matter at certain high temperatures under the inert conditions. The higher the temperature, the easier the process and the more cracking of the hydrocarbon. So, the solid fraction of 700 °C is less, and the gas and oil fractions are higher than that of 500 °C, which means the conversion at a final temperature of 700 °C is higher than that at 500 °C. However, the yields of oil do not increase markedly when elevating the final temperature from 500 to 700 °C as shown in Table 2. Figure 4 shows the composition distribution of the oil product

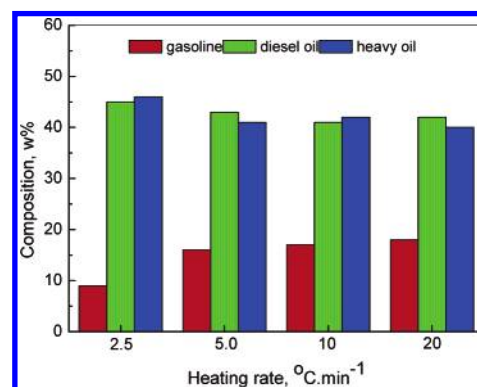


Figure 3. Effect of heating rate on the oil product compositions.

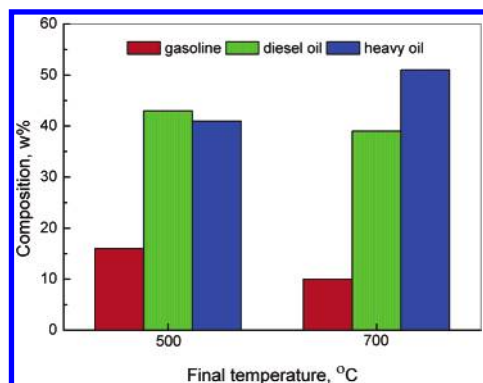


Figure 4. Effect of final pyrolysis temperature on the oil product compositions.

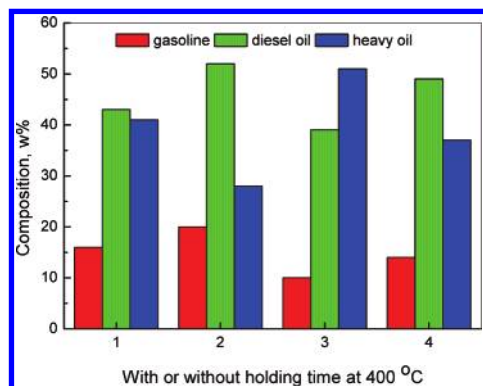


Figure 5. Oil product compositions with or without holding stage at 400 °C examined under four processes: (1) without interval holding at a final temperature of 500 °C; (2) with interval holding at a final temperature of 500 °C; (3) without interval holding at a final temperature of 700 °C; (4) with interval holding at a final temperature of 700 °C.

at different final temperatures without holding at 400 °C. From Figure 4, one can find that the three oil fractions show a difference when elevating the end temperature. The fractions of gasoline, diesel oil, and heavy oil are 16 wt %, 43 wt %, and 41 wt % at 500 °C and 10 wt %, 39 wt %, and 51 wt % at 700 °C, respectively. It seems that the final temperature has a great effect on the gasoline and heavy oil fractions. A decrease in the gasoline fraction and an increase in the heavy oil fraction are found to occur when increasing the final temperature from 500 to 700 °C. The value of decrease in the gasoline fraction is 6 wt %; the value of increase in the heavy oil fraction is 10 wt %. This result suggests that a higher final temperature favors heavy oil formation but does not favor gasoline formation. However, the diesel oil fraction changes little while increasing the final temperature from 500 to 700 °C. It is generally considered that a higher final temperature would produce much gasoline and less heavy oil, but Figure 4 shows a reversed result. In the present work, the reactor was heated to the desired final temperature and then held for 1 h, but the gas and oil products were swept off by N₂. Thus, the possible reason is owing to the nature of the oil structure in the sludge. It should be pointed out that the reason that a higher final temperature increases the heavy oil fraction could not be ascertained.

Effect of Interval Holding on the Oil Compositions. Figure 5 exhibits the change of the three oil fractions when a holding at 400 °C for 20 min was performed at the final temperatures of 500 and 700 °C. The operation of an interval holding at 400 °C can decrease the amount of heavy oil product, but increase the amounts of gasoline, especially diesel oil product whether the final pyrolysis temperature is 500 or 700 °C. This finding

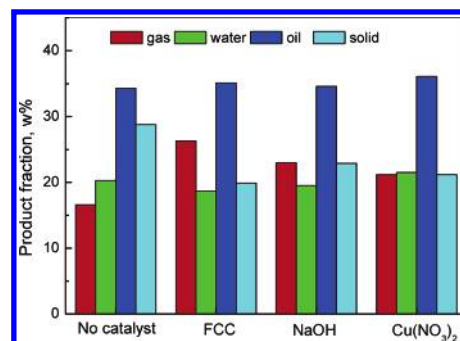


Figure 6. Effect of additives on the pyrolysis product fractions.

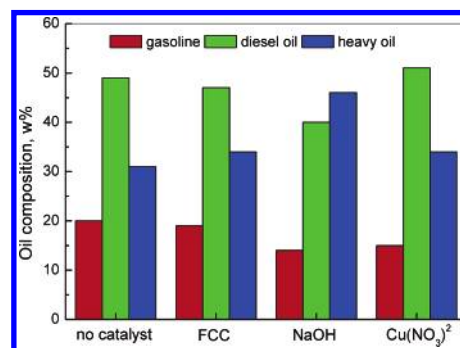


Figure 7. Effect of additives on the oil product composition.

suggests that the holding at the mild temperature of 400 °C would produce more free radicals and the free radicals prefer to form light oil molecular. Moreover, the lower holding temperature also can restrain secondary cracking reactions comparing to the higher final pyrolysis temperature. As Figure 5 and Table 2 have shown, an operation of holding at 400 °C can not only increase the oil fraction but also improve the quality of oil product (in terms of the sum of gasoline and diesel oil). Since the demands for light hydrocarbons such as gasoline and diesel oil are increasing, the operation with an interval holding at mild temperature is beneficial for the oil consumption.

Effect of Additives on the Oil Product Compositions. Studies^{21,22} have indicated that some additives could promote the pyrolysis conversion ratio (in terms of a decrease of the solid fraction). In this test, three additives including FCC (a fluid catalytic cracking catalyst), NaOH, and Cu(NO₃)₂·3H₂O were employed as the catalyst for promoting oil sludge pyrolysis. The amount of additives was 3 wt % of the oil sludge sample weight. The additives were mixed with the oil sludge sample entirely, and then, the mixture samples were pyrolyzed in the reactor with an interval holding of 20 min at 400 °C and a final temperature of 500 °C. In essence, CuO is the catalyst while adding Cu(NO₃)₂·3H₂O to the oil sludge because cupric nitrate decomposed into cupric oxide below 300 °C.

Figures 6 and 7 reveal the effect of additives on the pyrolysis product fraction and oil product composition, respectively. The solid product fractions in Figure 6 have deducted the weight of additives. Pyrolysis of oil sludge with three additives results in a higher production of gas and a decrease in solid residue markedly, but a negligible change of oil production as shown in Figure 6. Adding additives can promote the pyrolysis efficiency due to less solid production, but most oil sludge converts into gas product. If the efficiency of oil sludge pyrolysis was evaluated only by oil production, three additives used in the present study were not optimal catalysts because they do not increase the oil production. Furthermore, from Figure 7, one can find that the three catalysts decrease the percentage of gasoline and diesel oil components, except for Cu(NO₃)₂ whose

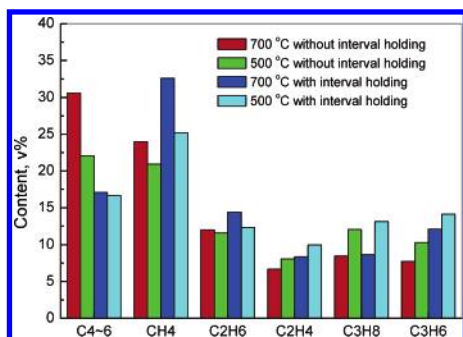


Figure 8. Gas product compositions under different pyrolysis conditions.

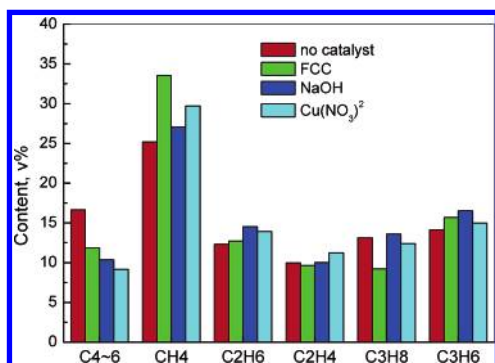


Figure 9. Effect of additives on the gas product compositions.

addition resulted in a slight increase of diesel oil production. On the basis of the above discussions, three additives employed in this work can improve the oil sludge pyrolysis conversion but decrease the quality of the oil product with a slightly quantity increase.

Effect of Pyrolysis Condition on the Gas Product. The gas product of oil sludge pyrolysis includes a lot of components such as CO₂, CO, H₂, and a series of light hydrocarbons. The effect of different pyrolysis parameters on the gas product component distribution was comparatively irregular. In this paper, the gas product component was mainly focused on the C₁₋₆ hydrocarbons. Figures 8 and 9 display the gas product composition under different pyrolysis conditions such as different final temperatures, with or without an interval holding stage, and different catalysts.

As shown in Figure 8, the contents of C₄₋₆ hydrocarbons and CH₄ at the pyrolysis final temperature of 700 °C are higher than those at 500 °C, but the contents of C₂H₄, C₃H₈, and C₃H₆ are lower than those at 500 °C. From the result of Figure 8, it is found that the yields of C₄₋₆ hydrocarbons are higher than those of CH₄. This suggests that the content of the -CH₃ side

chain in the oil sludge, which is mainly responsible for the formation of CH₄, is less. Figure 8 also shows the changes of C₁₋₆ hydrocarbons' content with an interval holding at 400 °C for 20 min under the final temperatures of 500 and 700 °C. The contents of C₄₋₆ hydrocarbons with an interval holding operation have a great decrease, but the CH₄ contents have a comparative increase, whether at the pyrolysis final temperature of 500 or 700 °C. The contents of C₂ and C₃ hydrocarbons have an increase to some extent after being held at 400 °C for 20 min. This suggests that the holding stage at 400 °C does make new chemical bonds in the original oil sludge and some products cleave with more free radicals formed.

Figure 9 shows the effect of different additives on the C₁₋₆ hydrocarbons' distributions with an interval holding at 400 °C for 20 min under the final temperature of 500 °C. The result displayed in Figure 9 shows that a higher content of C₁₋₃ hydrocarbons is obtained when the three additives were mixed with oil sludge samples as catalysts. However, the contents of C₄₋₆ hydrocarbons with an interval holding operation and catalysts decrease greatly. The results also imply that the three additives are favorable to induce the formation of very small free radicals; thus, the increase in the gas production and light hydrocarbons' content during an interval holding operation is reasonable.

Conclusion

Pyrolysis of oil sludge under different pyrolysis conditions was carried out. The influence of heating rate, final pyrolysis temperature, interval holding stage, and catalyst on the products were investigated in detail. The TG/MS results show that pyrolysis reaction of oil sludge starts at a low temperature of about 200 °C and the maximum evolution rate is observed between the temperatures of 350–500 °C. A higher final pyrolysis temperature, an interval holding stage, and adding catalyst can promote the pyrolysis conversion (in terms of less solid residue production). In all parameters, an interval holding stage near the peak temperature of 400 °C for 20 min can not only enhance the yield of oil but also improve the quality of oil product. The three additives used in this work as catalyst do not improve oil product quality markedly in spite of promoting pyrolysis conversion greatly.

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