Journal of Analytical and Applied Pyrolysis 105 (2014) 183–190

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

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

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ARTICLE INFO

Article history:
Received 2 May 2013
Accepted 8 November 2013
Available online 18 November 2013

Keywords:
Oilfield sludge
Flash pyrolysis
Solid heat carrier
Pyrolytic oil

ABSTRACT

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 C_{13}–C_{25}.

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). Punnaruttanakun 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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0165-2370/$ – see front matter
http://dx.doi.org/10.1016/j.jaap.2013.11.003

Table 1
Proximate and ultimate analysis of the oil sludge.

Proximate analysis (wt% wet basis)				Ultimate analysis (wt% daf)					HHV (MJ/kg)
Ash	Volatile matter	Fixed carbon	Moisture	C	H	N	S	O[a]	
53.92	29.63	1.14	15.31	23.28	3.54	0.19	1.29	3.47	14.02

[a] By difference.

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_xH_y evolution to increase and the C_xH_y 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, 15 A) 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 $CaCl_2$ 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 m^3/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

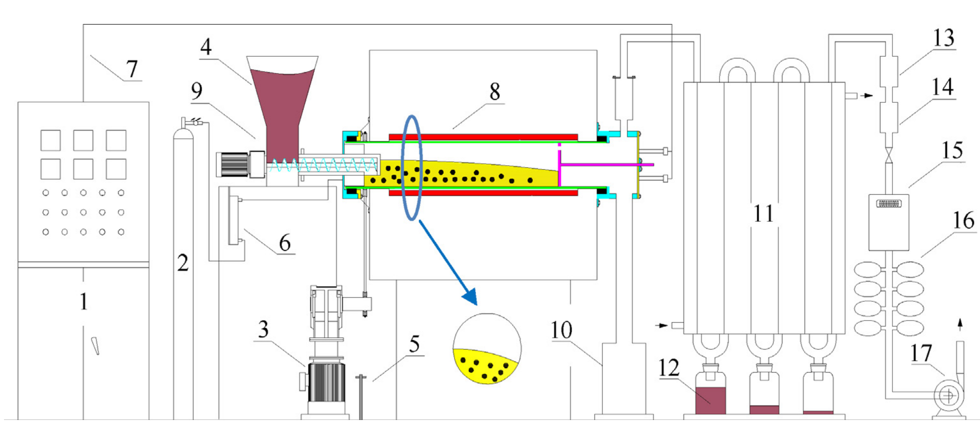

Fig. 1. Diagram of the bench-scale plant solid heat carrier rotary kiln system.