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Effects of potassium hydroxide on the catalytic pyrolysis of oily sludge for high-quality oil product

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ABSTRACT

Oily sludge has received increasing attention for its hazardousness as well as its high potential as an energy resource. Previous studies have developed many methods for oil recovery from oily sludge. In this paper, the effect of KOH on improving the quality of oil product from different oily sludge through pyrolysis was studied. Gel permeation chromatography (GPC), rheometer and gas chromatography–mass spectrometry (GC–MS) were applied to characterize the pyrolysis oil products. The product yields along with possible reaction mechanisms and kinetic characteristics were discussed. It was found that the oil yield decreased while the gaseous yield and solid residues increased with the addition of KOH. The GPC results showed that hydrocarbon species in the pyrolysis oil were more pure and the average molecular weight could be reduced by 53% for the used sample when KOH was added, which could be possibly explained by the cracking reaction of heavy oil into light species. The viscosity of the oil product also showed a significant reduction while the heating value increased in the case of adding KOH. Additionally, SARA fractions were extracted from oil to obtain the asphaltenes content and to identify the detailed components of saturated compounds. Results showed that the concentration of asphaltenes was declined by half and more saturate hydrocarbons (such as $C_{14}H_{30}$ to $C_{17}H_{36}$) were produced when KOH ratio reached up to 10%. It revealed that quality of oil product was improved in terms of smaller average molecular weight, lower viscosity, higher heating value, less asphaltenes and more straight chain hydrocarbons.

1. Introduction

In China, million tons [1] of oily sludge accumulates during the processes of drilling, petroleum production, transportation, storage and refining annually. The oily sludge is a complex mixture generally consisting of 30–50% water, 30–80% oil and 10–20% solids by mass [2,3]. It exists as emulsion stabilized by asphaltenes, resins, solid particles and chemical surfactants [4]. Oily sludge is regarded as a hazardous solid waste in many countries for its considerable concentration of hydrocarbons and other recalcitrant components [3]. As many of these compounds are toxic, improper disposal of oily sludge may cause serious environmental and human health problems. On the other hand, it is also a potential energy resource. The recycling of oily sludge is receiving increasing attention in recent years and the most desirable option is recovering valuable oil.

Many methods have been developed for the oil recovery from oily sludge. Among them, centrifugation treatment is the most common approach. The performance of centrifugation strongly depends on the viscosity of oily sludge. After centrifugation, the separated oil must be given further treatment to obtain valuable oil [5]. Solvent extraction is another attractive solution that is also simple but effective method to recover oil from oily sludge. However, when it comes to industrial application, a large volume of organic solvents are consumed and the recovered oil usually requires further purification for commercial use [6]. This could result in significant energy cost and possible secondary pollution. Other developing methods include microwave irradiation [7] and ultrasonic irradiation [8], both of them can decrease the stability of W/O emulsion within a short time and make the separation more efficient. In spite of their high efficiency of oil recovery, the industrial application of microwave irradiation and ultrasonic irradiation to large-scale oil recovery is limited by their high operating costs.

Pyrolysis is a promising method for obtaining fuels from oily sludge compared with other methods [9]. Previous studies have

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investigated the characteristics of pyrolysis of oily sludge. Chang et al. [10] have studied the major products obtained from pyrolysis of oil tank sludge in the temperature range 103–600 °C and found the distillation characteristics of liquid product was close to diesel oil. Liu et al. [11] have investigated the effect of heating rate on the pyrolysis of tank bottom oil sludge and studied the kinetics behavior of pyrolysis by applying a model-free *iso*-conversional method. Pyrolysis reaction can be affected by a number of factors. Wang et al. [12] found a higher pyrolysis temperature, an interval holding stage and the addition of catalyst can promote the pyrolysis conversion rate. A pyrolysis experiment conducted in a fluidized bed at temperatures from 460 °C to 650 °C by Schmidt and Kaminsky [13] indicates that at higher temperature, more oil was cracked into low boiling compounds.

Catalytic pyrolysis is also a popular topic in the petroleum industry. Pánek et al. [14] have researched the pyrolysis of lagoon oil sludge with the presence of calcium oxide and obtained a large amount of oil riched in saturate compounds with low sulfur content. Wang et al. [15] have reported that the rate of oil recovery from oily sludge pyrolysis could reach up to 85.52% with the addition of catalysts such as molecular sieve. A series of pyrolysis experiments were carried out by Shie et al. [16–18] to investigate the effects of inexpensive additives (such as sodium, potassium, aluminum and iron compounds) and catalytic solid wastes (such as fly ash, DAY-zeolite and PVA) on the liquid product. It appeared that the addition of $Fe_2(SO_4)_3\ nH_2O$ can increase the liquid product yield as well as improve the quality of oil product (in terms of sum of light and heavy naphtha and light gas oil).

Most previous studies were focused on the product yield through catalytic pyrolysis and there was no systematic analysis of oil product. Though a few works have been conducted to upgrade liquid fuel from various wastes in recent years [19–21], little attention has been paid to improve the oil product quality which is relative poor due to its high viscosity and low calorific value [22] and the direct utilization of the oil fuel may be limited. It has been proposed that the combustion properties of fuel oil are closely related to its chemical composition [23], which means lighter fractions are more favorable.

In this study, a catalytic pyrolysis experiment of different oily sludge samples with the presence of potassium hydroxide, aiming at improving the quality of oil product (in terms of smaller average molecular weight, lower viscosity, higher heating value, less asphaltenes and more straight chain hydrocarbons), has been carried out in a laboratory-scale reactor. The pyrolysis characteristics of the oily sludge samples and the catalytic effect of KOH on the product yields were discussed. Oil products were subjected to a series of characterization methods to identify the quality of the pyrolysis oil. The results of this research will contribute to the utilization of oily sludge.

2. Materials and methods

2.1. Oily sludge samples

Two different oily sludge samples were discussed in this paper. GL (Guolian oily sludge) was collected directly from a refined oil storage reservoir at Sinopec Petroleum Refinery Plant located in Zhejiang. XZ (Xingzhong oily sludge), supplied by Sinochem Xingzhong Oil Staging (Zhoushan) Co., Ltd, was obtained from the bottom of crude oil tanks [24].

The proximate, ultimate analysis and primary components of the sludge samples were analyzed before pyrolysis tests. Total hydrocarbon content was determined by soxhlet extraction using petroleum ether as solvent and water content was obtained according to ASTM-D95-05.

2.2. Experimental setups

The pyrolysis experiment of oily sludge was carried out in a horizontal quartz tube fixed-bed reactor, which was placed in an electrical furnace equipped with temperature-programmed device and thermocouple. According to previous studies [13], the pyrolysis temperature was set at 600 °C and the environment in the quartz tube was maintained with inert carrying gas at a flow rate of 200 ml min^{-1}.

During the test, the sample held in a ceramic crucible was loaded into the reactor at 600 °C and the pyrolysis volatiles were swept out through a condenser filled with cold water, where the condensable liquid was collected for further analysis. The non-condensed gas was scrubbed before release. Duplicate experiments were performed and average results were discussed.

KOH (analytical reagent with more than 85% purity, white uniform granular solid) was directly added into the ceramic crucible with oily sludge. For comparison, 8 g of untreated oily sludge without and with 0.4/0.8 g of KOH (mass ratio 5/10 wt% of the oily sludge, respectively) was used.

2.3. Analysis methods

After the reaction, the water phase was removed from the liquid products by centrifugation at 3000 rpm/min for 10 min. Then the oil products were analyzed for molecular weight by gel permeation chromatography (GPC, Waters 1525/2414, Waters) performed using RI detector (Water 2414), three columns in series (PLgel 10 μm 10E3A, 10E4A, 500A) and THF mobile phase (1 ml min^{-1}). The column temperature was maintained at 34 °C and the pressure of the system was stabilized at 612 psi. Data were acquired and analyzed by Empower software.

SARA (saturates, aromatics, resins, asphaltenes) contents of oil product were first separated by precipitation of asphaltenes with *n*-hexane, followed by further separation through a chromatographic column filled with silica gel and neutral alumina according to Chinese Standard SY/T 5119-2008. The saturates compounds were identified using GC–MS (Trace ISQ, Thermo Fisher) equipped with a chromatographic column (TR-5MS, 30 m × 0.25 mm inner diameter, 0.25 μm film thickness). The column oven temperature was programmed from 50 °C (hold 5 min) to 240 °C at a rate of 10 °C min^{-1} and held for 10 min. Samples were dissolved in *n*-hexane and the injection temperature was 270 °C. The injector was operated in splitless mode and helium was the carrier gas at a constant flow of 1.0 ml min^{-1}. Mass spectrometer ionization was operated in EI mode. The ion source and transfer line temperatures were 250 °C. The scan range was 35–600 amu. Data were obtained and analyzed by Xcalibur software.

3. Results and discussion

3.1. Properties of the oily sludge samples

The primary composition and SARA contents of the two oily sludge samples are shown in Table 1. It can be seen that the main components of the two oily sludge samples were different. The solid particles content in Xingzhong sample was extremely low, and the quantity of oil contained in Guolian sludge was low compared with that of Xingzhong sludge. The reason is that part of the oil phase in Guolian sludge was recovered during the refining process. The heating value and volatiles of Xingzhong sample was much higher due to its high oil content. There were not obvious differences in SARA concentrations between Guolian and Xingzhong samples except for saturates and asphaltenes contents, which