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Full Length Article

Extraction of crude oil from petrochemical sludge: Characterization of products using thermogravimetric analysis

Jieqiong Hu [a], Jinhua Gan [b], Jinping Li [a,*], Ying Luo [a], Guangkun Wang [a], Liang Wu [a], Yimin Gong [a]

[a] School of Environmental Engineering, Wuhan Textile University, Wuhan, PR China
[b] Yangtze River Fisheries Research Institute Chinese Academy of Fishery Sciences, Wuhan, PR China

HIGHLIGHTS

- Study on the optimal conditions for the extraction of crude oil.
- At lower distillation temperature for recovery of organic solvent could not only save heating cost, but also prevent thermo degradation.
- The temperatures of weight loss of crude oil extraction were analyzed by TGA curves.
- With the heating rate increased, the time of pyrolysis was shortened, the total weight loss rate decreased and the stage of maximum weight loss rate moved towards higher temperature.

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ABSTRACT

In this study, solvent extraction was used to recover oil from petrochemical sludge. Three solvents were chosen to mix with petrochemical sludge to ensure adequate miscibility of crude oil in solvent under an appropriate condition. The petrochemical sludge, crude oil sample and residual petrochemical sludge were analyzed by thermogravimetric analysis (TGA). The experiments were performed at three different heating rates (10, 20, 30 °C/min) under nitrogen atmosphere. The aim of the study was to recover and evaluate crude oil from petrochemical sludge and assess the commercial potential of recycling the crude oil. Experimental results showed that the common temperature range of weight loss of the crude oil sample was about 200–550 °C. The residual petrochemical sludge still remained the partial characteristics of petrochemical sludge, which demonstrated that the residual petrochemical sludge still had the value of exploiting and utilizing for further research.

1. Introduction

An annual output of about one million ton of petrochemical sludge from a variety of sources, including crude oil tank bottoms, slop oil emulsions, oil/water separators, and on-site wastewater treatment pond have been generated by the petrochemical industry [1,2]. Owing to the petrochemical sludge is a complex mixture containing different quantities of waste oil, wastewater, sand, and mineral matter, most of its components such as benzene, phenol, anthracene, and pyrene are toxic, mutagenic, and carcinogenic [3]. Due to its adverse nature, a variety of methods have been developed to treat petrochemical sludge such as membrane filtration, ozonation, incineration and biodegradation [4–7]. However, most of them are expensive, requiring long time and even casing secondary pollution [7].

Compared with other treatment methods, solvent extraction is a simple process by mixing petrochemical sludge and solvent under an appropriate condition to ensure adequate miscibility of crude oil in solvent [8]. The residual petrochemical sludge gained by gravitational setting or centrifugation will be used for further research [1]. After extraction, the crude oil can be gained by distillation to be reused, and solvents that the boiling point is below 100 °C can be obtained for repeating the extraction cycle as well [9]. In addition, a lower distillation temperature can not only save heating cost, but also prevent thermo degradation [4]. The benefits would be twofold, firstly to improve crude oil utilization efficiency and secondly in reducing the environmental contamination associated with the petrochemical industry.

With the rapid development of the global economy, energy is the lifeblood of economic development. However, the conventional oil resources have been unable to meet the needs of mankind. For

* Corresponding author at: School of Environmental Engineering, Wuhan Textile University, Wuhan 430073, PR China.
E-mail address: 64421268@qq.com (J. Li).

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this reason, given the relatively high oil content in sludge, recovering and recycling of valuable crude oils not only attains the goal of the conservation of environment and energy resources [10,11] but also decreases the consumption of non-renewable energy resources [12].

2. Materials and methods

2.1. Experimental reagent and instruments

Petrochemical sludge is from a petrochemical refinery in Wuhan, Hubei Province. The characterize of petrochemical sludge is that the appearance is black and sticky, the flow performance is poor, and petrochemical sludge has the strong odor smell. In the pre-treatment process, petrochemical sludge is dried in an electric heating constant temperature air blast drying box at 105 °C for 24 h, and then dried petrochemical sludge is milled in a mortar to through 20 mesh screen for obtaining particles which is served as petrochemical sludge samples in this study.

The organic solvent used in this experiment respectively are trichloromethane, *sym*-dichloroethane, ethyl acetate. These are analytical reagent. DF-101s set heat type constant temperature heating magnetic mixer (YuZheng Company in Shanghai), 101-1electric heating air blast drying box (TianGuan Company in Henan), SXL-1700-3box type resistance furnace (HongLang Company in Zhengzhou), Vario Micro cube Elemental analyzer (Elementar company in Germany), STA7300 thermal gravimetric differential thermal synthesis analyzer (HITACHI company in Japan).

2.2. Experimental methods

2.2.1. Proximate analysis of petrochemical sludge

Water content (WC): The American Society for Testing and Materials (ASTM) standard method D95 was used for measuring the water content of the petrochemical sludge. The petrochemical sludge was heated with petroleum ether (solvent, boiling range 90–120 °C) which co-distilled with the water present in the sample in a fume cupboard. Condensed solvent and water were continuously separated in a trap, and the water settled as the bottom layer. The condensed liquid containing water and hydrocarbon was transferred to a graduated cylinder. A water layer with higher density was at the bottom of the cylinder. The volume of the water was then used to calculate the water content [7] (using the density of water of 1 g/cm^3).

Volatile hydrocarbon content (VHC): Sample with known mass was put in an oven (with ventilation) at 105 °C to constant weight. The reduction in mass indicated the moisture and light hydrocarbon content in the sludge [7]. As water content was measured previously, the light hydrocarbon content (in wt.%) was calculated as follows:

$$\mathrm{VHC} = \frac{\textit{reduced mass},\ \mathrm{g}}{\textit{mass}\ \text{of tested sample},\ \mathrm{g}} \times 100\% - \textit{WC}\ \text{wt.\%} \qquad (1)$$

Solid content (SC):Dried samples (105 °C) were placed in the box type resistance furnace at 800 °C for 120 min. The residue was weighed [7]. The solids content of the sludge was calculated in weight percent using the equation:

$$\mathrm{SC} = \frac{\textit{mass of residue remaining after burning},\ \mathrm{g}}{\textit{mass of tested sample},\ \mathrm{g}} \times 100\% \qquad (2)$$

Nonvolatile hydrocarbon content (NHC): After measuring the water content, light hydrocarbon content, solid content, and the nonvolatile hydrocarbon content can be calculated in weight percent as follows [7]:

$$\mathrm{NHC} = 1 - \mathrm{WC} - \textit{VHC} - \textit{SC} \qquad (3)$$

2.2.2. Elemental analysis of petrochemical sludge

The elemental analysis of petrochemical sludge was carried out by a Vario Micro cube elemental analyzer. Using the dynamic combustion method, the dried samples were oxidized in the high concentration of oxygen and helium, the gas that generated from oxidation would go into each adsorption system with helium to detect and analyze the carbon, hydrogen, oxygen, nitrogen and sulfur content. The results of elemental analysis of petrochemical sludge are given in Table 1. All analyses and measurements were performed by the Analysis and Testing Center of Huazhong University of Science and Technology.

2.2.3. The conditions of thermal gravimetric analysis of crude oil samples

The STA7300 thermal gravimetric differential thermal synthesis analyzer used in this experiment is produced by HITACHI company in Japan. In this experiment, the heating rate of 10, 20, 30 °C/min was applied to heat the petrochemical sludge, crude oil samples and residual petrochemical sludge from ambient temperature up to 800 °C. The gas flow rate of nitrogen was kept constant at 200 mL/min during the experiments. A sample size of ~10 mg was adjusted for each run conducted. The experiments were performed twice to test the repeatability and experiments showed good consistency with standard errors of ±0.1 °C. During the experiment, the system will automatically collect data, and get the weight loss rate curve, the thermal difference curve and the weight loss rate curve.

3. Results and discussion

3.1. Properties of the petrochemical sludge

Several key properties of the petrochemical sludge were analyzed in Table 1.

3.2. Operating conditions of extraction

3.2.1. Effect of several kinds of organic solvents on the extraction rate of crude oil

Divided twenty-one clean beakers into three groups. The purpose of the first group is using trichloromethane as extraction agent, the second one is serving *sym*-dichloroethane as extraction agent, and the last one is used ethyl acetate for extraction. 10 g petrochemical sludge samples are weighed in this twenty-one clean beakers respectively. As the first group, petrochemical sludge samples weighed in clean beakers are mixed with chloroform in

Table 1
The characteristics of petrochemical sludge.

Project	Petrochemical sludge
Proximate analysis (wt.%)	
Water content	6.8
Volatile hydrocarbon content	15.7
Non-volatile hydrocarbon content	73.1
Solid content	4.4
Elemental analysis (wt.% dry basis)	
C	75.09
H	5.35
O[a]	16.22
N	1.58
S	1.76
Calorific value (kJ/kg)	22,116

[a] Calculated by difference.