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Thermogravimetric monitoring of oil refinery sludge

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ABSTRACT

The present work has two dimensions: analytical and environmental. On the one hand we proved that thermogravimetric analysis can be used to perform fast characterization of oil refinery sludge. To this end, thermogravimetric curves were deconvoluted by using autocatalytic kinetics to take into account acceleratory phases in a thermal degradation performed in oxygen-containing atmosphere or at high heating rates. Based on thermogravimetric results, oil refinery sludge was modeled in terms of various fractions (pseudo-components) which degrade as major oil cuts. On the other hand, as an alternative to landfill, we have seen that Soxhlet extraction allows recovery almost half of the weight of sludge as a mixture of hydrocarbons, similar to gas–oil, which burns without residue. This ensures both, waste inerting and significant reduction in sludge volume.

1. Introduction

Crude oil is a complex mixture of substances including linear and cyclic saturated hydrocarbons, aromatics, and oxygen, nitrogen and sulfur derivatives. Obtaining useful products from it requires its separation into fractions (cuts) for subsequent processing. Crude oil is most often refined by atmospheric or vacuum distillation, and its products are given an added value by chemical means, i.e., catalytic reforming and cracking.

Oil refinery wastes can be processed to recover aqueous and oil fractions which are usually recycled. Also, the liquid effluent treatment plant (LETP) of a refinery produces sludge that requires appropriate disposal (usually by landfilling). However, oil enriched sludge may be a potential source of energy for improving the energy balance of oil refineries. Sludge is typically converted into usable energy by anaerobic digestion [1]; however, the pretreatment needed to facilitate digestion of organic matter makes it somewhat complex [2,3]. Alternatively, thermal treatments such as gasification and pyrolysis have proven to be effective to obtain biogas, bio-oil and char from industrial sludge [4,5]. According to Vieira et al. [6], bio-oil obtained by low-temperature pyrolysis of oil refinery sludge is useful for energy production purposes.

Due to the extreme complexity of petroleum and its residues (i.e. oil sludge), this substances are usually characterized by standardized ASTM methods which measure API gravity, elemental composition (C, H, N and S), SARA (saturated, aromatic, resins and asphaltenes) composition or boiling point, among other properties [7].

Thermogravimetric analysis (TGA) provides an effective alternative to chemical analysis for the characterization of fossil fuels [8]. TGA measures the mass loss of a sample subjected to a heating program under specific conditions in an inert (pyrolysis) or oxidative (combustion) atmosphere. This technique has been extensively used to examine thermal degradation in petroleum and its cuts, and also for analytical purposes. A review of the uses of thermal analysis for characterizing fossil fuels was recently published [8]. Karacan and Kok [9] showed that major SARA (saturates, aromatics, resin, and asphaltene) fractions of crude oil are thermally degraded via independent reactions and also that TGA is useful to calculate kinetic parameters such as the activation energy to characterize their thermal degradation [10,11]. Thus, TGA has been used to assess relative oxidative stabilities for a number of bitumens and exposed a correlation between activation energy and lifetime in the field [12].

Shishkin [13,14] used TGA and differential scanning calorimetry (DSC) in combination to study the main processes occurring during oil heating in the air, namely: distillation of the liquid constituents and oxidative cracking of the solid residue. According to this author, the distillation step affects benzine, ligroin, kerosene and gas oil cuts, whereas the cracking step affects paraffins, base oils, condensed aromatics (resins) and asphaltenes. Gonçalves et al. [15,16] used TGA to study asphaltenes contained in residues from oil atmospheric distillation and found light and heavy oils to differ markedly in their contents in asphaltenes, which, however, were the greatest sources of char in both cases.

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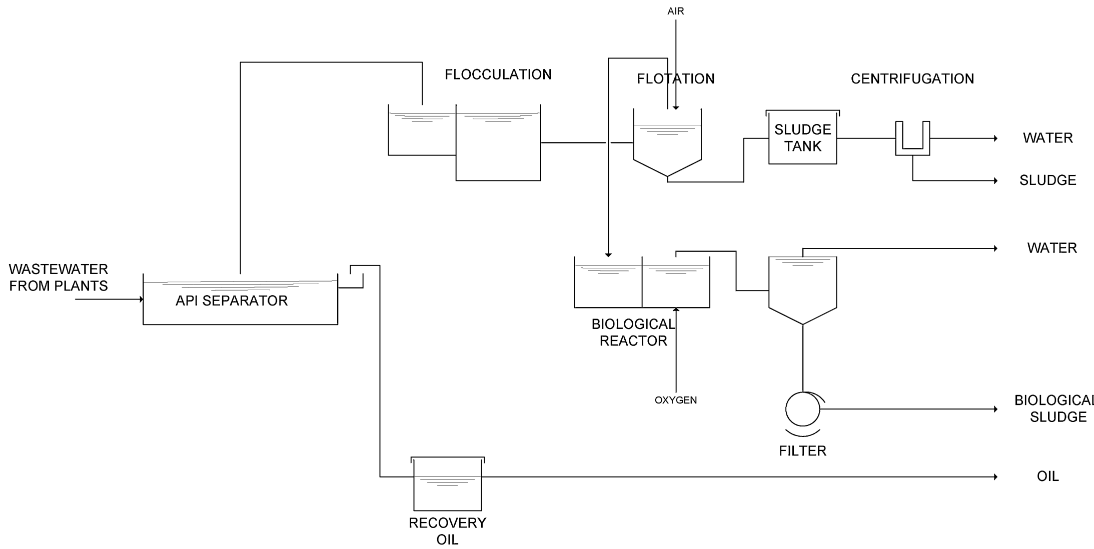

Fig. 1. Scheme of the liquid effluent treatment plant (LETP) in the studied oil refinery.

Recently, thermal analysis coupled to mass spectrometry (TG/MS) with soft photoionization was used to characterize crude oils [17]. The single photon ionization (SPI) mode has the advantage that it causes little fragmentation of aliphatic hydrocarbons in the oil and hence facilitates their detection from their molecular ion signals.

In the present work fresh sludge (as obtained in the liquid effluent treatment plant) was subjected to Soxhlet extraction to separate extractives and residues. Thermal degradation for all sludge fractions and crude oils was monitored by using thermogravimetric analysis (TGA). In addition, thermogravimetry coupled to mass spectrometry (TG/MS) was used to assess char formation by controlling intensity of hydrogen signal (hydrogen is obtained from char and water at high temperature). Furthermore, gas chromatography coupled to mass spectrometry was used to obtain chemical composition of sludge extractives.

2. Materials and methods

2.1. Samples

Sludge and crude oil samples were supplied by La Rábida-CEPSA Refinery (Huelva, Spain). The sludge, S, was obtained by flocculation, flotation and centrifugation of wastewater from an API separator used to collect residues from several plants. S (approximately 1000 ton/year) was ethanol–benzene extracted in Soxhlet equipment for 4 h to obtain extractives (E) and residues (R). Approximately, extractives represent almost 40%wt of fresh sludge (Fig. 1).

2.2. Thermogravimetric analysis

For all samples TG runs were performed on a Mettler Toledo TGA/SDTA851e/LF1600 balance, using a sample mass of ca. 5 mg under nitrogen (pyrolysis) and mixture of nitrogen and oxygen (4:1 N_2:O_2) for combustion runs. The temperature was raised from 25 to 900 °C at three different rates (5, 10, and 20 °C/min).

2.3. Thermogravimetric analysis coupled to mass spectrometry

TGA/MS runs of fresh sludge were performed with a Mettler Toledo TGA/SDTA851e/LF1600 balance, using an amount of sample of ca. 5 mg. In this case, pyrolysis runs were conducted in a helium atmosphere in order to see m/z 28 (carbon monoxide) with no nitrogen interference. The temperature was raised from 25 to 900 °C at 10 °C/min. A portion of the volatile products obtained was introduced into the mass spectrometer through a heated line. The quadrupole mass spectrometer used was a Thermostar GSD301T model from Pfeiffer Vacuum. Mass intensities were normalized with respect to the helium signal in order to avoid errors associated with differences in MS sensitivity. Hydrogen signal was used to monitor char production during sludge pyrolysis. At high temperature carbon and water react to yield hydrogen.

2.4. Gas chromatography coupled to mass spectrometry

Qualitative chemical composition of sludge extractives was obtained by using GC/MS. Runs were performed at 39.4 bar on an Agilent 5973N Gas Chromatograph/Mass Spectrometer equipped with an Agilent J&W HP-1 column with 0.20 mm I.D., 25 m length and 0.33 μm thick film. The injector temperature was 250 °C and samples were heated from 35 to 325 °C at 5 °C/min. Mass spectrometer was operated in the electron impact mode using 70 eV ionization voltage. Scan detection mode was used to identify compounds in the samples. The m/z range was 25–450 amu at a rate of three scans per second.

3. Results and discussion

3.1. Thermal degradation of oil refinery sludge

Fresh sludge of oil refinery is a complex mixture and their chemical characterization has little meaning and utility for us. On the contrary, in the present work we have chosen to focus attention on the thermal behavior of sludge component because in comparison to oil thermal degradation we can obtain their oil-based composition. In addition, in order to improve understanding of sludge nature, fresh sludge (S) was Soxhlet extracted obtaining two fractions: extractive (E) and residue (R). On average, extractive represent almost 40%wt of fresh sludge. All fractions were thermally characterized by using thermogravimetric analysis. Fig. 2 compares fresh sludge (S), extractives (E) and crude oil (C) thermal degradations. Sludge residue (R) has not been included in Fig. 2 because almost not volatilize, being thermally inert and not significant as potential fuel.

Based on the similarity of thermogravimetric curves of both sludge and crude oil (see Fig. 2), we qualitatively interpreted the