



Study of the thermal decomposition of petrochemical sludge in a pilot plant reactor



Juan A. Conesa^{a,*}, Julia Moltó^a, José Ariza^b, María Ariza^b, Agustín García-Barneto^b

^a Dept. Chemical Engineering, University of Alicante, Ap. 99, E-03080 Alicante, Spain

^b Dept. Chemical Engineering, University of Huelva, Spain

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ABSTRACT

The pyrolysis of a sludge produced in the wastewater treatment plant of an oil refinery was studied in a pilot plant reactor provided with a system for condensation of semivolatile matter. The study comprises experiments at 350, 400, 470 and 530 °C in nitrogen atmosphere. Analysis of all the products obtained (gases, liquids and chars) is presented, with a thermogravimetric study of the char produced and analysis of main components of the liquid. In the temperature range studied, the composition of the gas fraction does not appreciably vary. In the liquids, the light hydrocarbon yield increases with increasing temperature, whereas the aromatic compounds diminish. The decomposition of the solid fraction has been analyzed, finding a material that reacts rapidly with oxygen regardless of the conditions it is formed.

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1. Introduction

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 gas, oil and char can be obtained from industrial sludge [4–6]. According to Vieira et al. [7] the oil obtained from pyrolysis of oil refinery sludge at low temperature is a very interesting fuel for energy recovering purposes. During the incineration of these kind of sludges, different types of reactors have been used, such as fluidized bed combustors, circulating fluidized bed combustors (CFBC), and kiln, rotary, rack, and step-type furnaces with combustion temperatures of 1073–1173 K [8–13].

Sankaran et al. [12] studied the decomposition of three different oil sludge wastes in a fluidised bed reactor at oxidizing conditions. The flue gas composition at the stack location, the scrubber sludge generated at the alkali wash water tank and the ash collected at the post combustion chamber were analyzed. The results of the

analysis conclude that fluidized bed incineration technique is a safe and effective way of treating these wastes.

The influences of using inexpensive and nonharmful additives on the possible improvement of the pyrolysis of oil sludge were also investigated. The most active additive with the greatest conversion is $\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$, which improves the liquid qualities of pyrolysis oils (in terms of the total light and heavy naphtha and light gas oil) [14–16].

In a previous work [6] an analysis of the gas evolved in the pyrolysis and gasification of this kind of sludges in different conditions was performed. This was done in order to optimize the thermal treatment of oily sludges from the CEPESA refinery and gain better insight the origin and evolution of the main volatiles obtained. The heating rate, the presence of oxygen, the contact time and the nature of the sludge were studied and showed a great influence on the composition of the gas produced. The presence of oxygen produced a reduction of the content of hydrogen, while decreasing also the CO production.

The objective of the present study is to investigate the pyrolysis of refinery sludge in pilot plant equipment at different temperatures. An exhaustive analysis of the products evolved is done, including the quantification and analysis of the gas, liquid and solid fractions.

2. Materials and equipment

The sample comes from a liquid effluents treatment plant of the CEPESA refinery in Huelva (Spain). In this plant the process is as follows: the oily waters flow through American Petroleum Institute

* Corresponding author. Tel.: +34 965903400; fax: +34 965903826.

E-mail address: ja.conesa@ua.es (J.A. Conesa).

Table 1
Proximate and ultimate analysis of the petrochemical sludge.

C (wt.%)	51.2
H (wt.%)	7.54
N (wt.%)	0.52
S (wt.%)	1.69
O (by difference)	4.05
Ash content (wt.%)	35.0
Net calorific value (kJ/kg)	18,110

(API) separators, where some oil is recovered and sent to the main input of the refinery to be reprocessed. After the separation, water passes through a coagulation–flocculation system that eliminates part of the pollutant content as sludge. This sludge, named physico-chemical sludge (PC) is later centrifuged. An estimated production of about 2500 tons/year of this PC sludge is considered. In this study physico-chemical sludge has been employed. A subsequent treatment is given to the wastewater from this PC treatment.

Elemental analysis of the sludge was previously published [6], where a total content of 33% of carbon and 22% oxygen is indicated. Nevertheless, maybe these figures are not correct because a drying was done prior to the elemental analysis. During drying a portion of hydrocarbons can be lost, especially the more volatile fractions (benzene–ligroin fractions and kerosene–diesel), so that the conventional oven-drying is not suitable. Therefore, for elemental analysis the following procedure was applied:

- Extraction of physicochemical sludge in a Soxhlet with ethanol–benzene to give a refined (inorganic) and a fraction consisting of water and hydrocarbons.
- Water separation from the oils by vacuum distillation on a rotary evaporator.
- Elemental analysis of the hydrocarbon fraction (extract) by Perkin-Elmer CHNS analyzer.
- Determination of the elemental composition of sludge dry basis from the extract elemental analysis, assuming that all C, H, N and S comes from this hydrocarbons fraction.

The result of such procedure is shown in Table 1, where a more believable 51.2% of carbon and 4% of oxygen is found. The calorific value was obtained with a Leco Corporation calorimetric bomb AC-350 model. Ash content was obtained by calcination at 850 °C.

It is expected that wastewater from refinery plants contains a very high amount of hydrocarbons. After the physico-chemical step, the organic content in wastewater must be drastically reduced. Consequently, the PC sludge should be a complex mixture where hydrocarbons are the main substances. PC-sludge presents an important content in sulphur, as this compound is one of the different types of products obtained in the CEPESA refinery.

A scaled scheme of the reactor and condensation system is shown in Fig. 1; the length of the reactor that is inside the furnace is 654 mm. The system comprises a feeding zone consisting in a two-valve manual system, but in the present study it has not been used for security reasons. Instead of this, a specific amount of the sludge (approximately 700 g) is initially introduced in the furnace, before heating.

The carrier gas is preheated by circulating vertically between two cylindrical tubes: the outer one is the calandria and the inner one is the reactor itself, where the solids are fed. The nitrogen flow rate was 1.5 L/min approximately (measured at room temperature and pressure).

The reactor is inside the vertical electric furnace. The nominal temperatures used in the runs have been 350, 400, 470 and 530 °C. The temperature is controlled by a type-K thermocouple sited inside the furnace near to the reactor that is introduced by

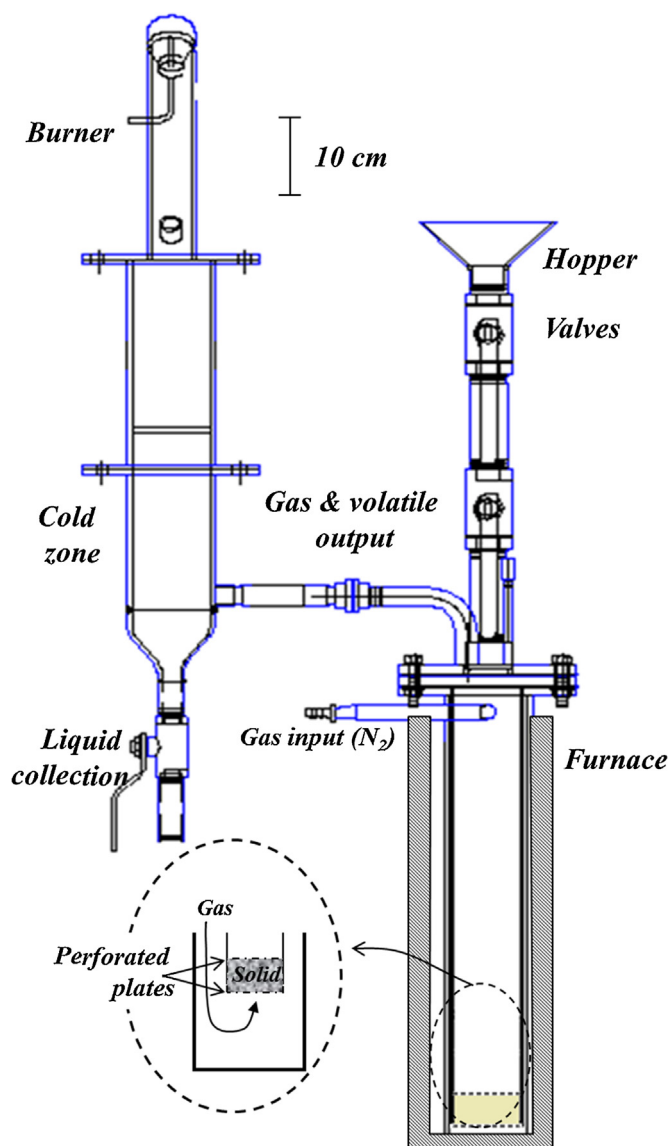


Fig. 1. Schematic of the reactor system.

its upper side; measure of the temperature inside the reactor was performed during the runs in order to account for the possible endothermic processes taking place in the reactor. The measurements at different positions show a maximum difference of 20 °C between the furnace and the inner part of the reactor. The average heating rate of the runs performed in the present study is ca. 15 K min^{−1}.

The system also disposes of a cooling and condensation system (see Fig. 1) that consists in a jacket filled with solid CO₂ (−78 °C), approximately 300 g in each run. The temperature inside the system in this zone is lower than 13 °C in all the runs, so a very good condensation of semivolatile species is expected.

At different times, gas samples are taken directly from the upper part of the reactor. The gas sample is collected throughout 5 min (approx. 1 L of gas sample) in a Tedlar® bag. Note that there is no possibility of any oxygen in the reactor during gas sampling, since no depression is produced in the reactor in any way.

The furnace is maintained at the reaction temperature for two more hours, in order to get a solid completely reacted. The carrier gas flow rate is also maintained during this time. The furnace is then

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