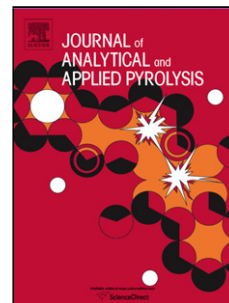


Accepted Manuscript

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PII: S0165-2370(14)00033-3
DOI: <http://dx.doi.org/doi:10.1016/j.jaap.2014.02.009>
Reference: JAAP 3147

To appear in: *J. Anal. Appl. Pyrolysis*

Received date: 24-9-2013
Revised date: 3-2-2014
Accepted date: 7-2-2014

Please cite this article as: Juan A. Conesa Julia Moltó José Ariza María Ariza Agustín García-Barneto Study of the thermal decomposition of petrochemical sludge in a pilot plant reactor (2014), <http://dx.doi.org/10.1016/j.jaap.2014.02.009>

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HIGHLIGHTS

- Pyrolysis of oil refinery sludge has been studied in a pilot plant reactor.
- Temperatures in the range 350-530 °C were used in a nitrogen atmosphere.
- Gas, liquid and char fractions were characterized.
- An increase of liquid fraction is observed when increasing the temperature.
- Light hydrocarbon yields increase with temperature.

Accepted Manuscript

Prepared for submission to J. Anal. Appl. Pyrol.

STUDY OF THE THERMAL DECOMPOSITION OF PETROCHEMICAL SLUDGE IN A PILOT PLANT REACTOR

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ABSTRACT

The pyrolysis of a sludge produced in the waste water 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) are 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 analysed, finding a material that reacts rapidly with oxygen regardless of the conditions it is formed.

KEYWORDS

Petroleum sludge, oil refinery, thermogravimetry, pyrolysis, char reactivity

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 & EQUIPMENT

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

- a) Extraction of physicochemical sludge in a Soxhlet with ethanol-benzene to give a refined (inorganic) and a fraction consisting of water and hydrocarbons.
- b) Water separation from the oils by vacuum distillation on a rotary evaporator.
- c) Elemental analysis of the hydrocarbon fraction (extract) by Perkin-Elmer CHNS analyzer.

d) 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.

{Table 1}

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.

{Figure 1}

An scaled scheme of the reactor and condensation system is shown in Figure 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, were 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 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.

The system also disposes of a cooling and condensation system (see Figure 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 minutes (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 switched off and after cooling, the solid char was recovered from the reactor. The tars condensed in the cold zone are removed by opening the corresponding valves (see Figure 1), and the condensation system is cleaned with acetone; the acetone with the rests of tars are also collected and later the acetone is evaporated at vacuum and low temperature (< 40 °C); the tars of this fraction are analyzed separately.

2.1. Analytical methods

The gas fraction was analyzed by gas chromatography. The analysis is performed by injecting a sample of the gas collected in the Tedlar bag. Shimadzu GC-14A gas chromatograph with a TCD detector was used for the quantification of H₂, N₂, O₂, CO₂ and CO. The light hydrocarbons C₁-C₆ were analysed in Shimadzu GC-17A chromatograph with a FID detector. Although methane is measured both by FID and TCD, the later is more sensitive and will be preferably used. A total of six different gas patterns containing known amount of hydrocarbons C₁-C₆ together with CO₂ and CO, with the balance completed with N₂, were used to calibrate the gas chromatographs. Hydrogen calibration is done by injecting different amounts of pure hydrogen in the chromatographic system (TCD detector), in such a way that we used an external calibration method. The injection in the GC was done three times, and the values shown in the present work are average values.

A characterization of the oil has been performed by analyzing the main components. This analysis was performed in a low resolution mass spectrometer (Scan mode, m/z from 50 to 500) connected to a gas chromatograph. For the analysis the used equipment was a gas chromatograph Agilent 6890 N with a mass spectroscopy detector Agilent 5973N. The column used was a DB-5 MS of length 30 m and an intern diameter of 0.25 mm. For identifying and quantifying the liquids, the sample was diluted with dichloromethane and injected to a chromatograph with a MS Scan mode detector. The identification of the detected compounds was made by comparing their mass spectras to ones found in the software library. The detection limit of this method has been estimated to be 10 ppm [17]. Products have been lumped into three groups: non aromatic hydrocarbons (HC) with a number of carbons between 1 and 14 (C_1 - C_{14}), no aromatic HC with more than 15 carbons ($> C_{15}$) and aromatic HC. Note that only a semi-quantitative analysis of the liquid/tar fraction is given, because the different compounds should exhibit different response factors.

For the characterization of the solid residue after pyrolysis, a thermobalance has been used. Runs for the TG analysis were carried out on a Mettler Toledo thermobalance model TGA/SDTA851e/LF/1600. This apparatus has a horizontal furnace and a parallel-guided balance. In this way, positioning of the sample has no influence in the measurement, and flow gas perturbation and thermal buoyancy are minimized. Two different atmospheres were used in the thermobalance: helium with a flow rate of 100 mL min^{-1} for the pyrolysis runs and a mixture of helium and oxygen 4:1 for combustion of solid residue, while the total flow rate was kept constant at 100 mL min^{-1} . The sample temperature was measured with a thermocouple directly attached to the sample holder. Dynamic experiments were carried out at heating rates of 5, 10 and 20 K min^{-1} , from the room temperature up to 1000 K.

3. RESULTS AND DISCUSSION

3.1. Yield of the different fractions

Figure 2 shows the percentages (in weight basis respect to the original petrochemical sludge) of the different fractions collected. An estimated error of 5 % in the determination of these results has been included in the plot.⁷

{ Figure 2 }

As can be seen, at low temperatures the fraction not decomposed (char) is high and decreases as the pyrolysis temperature increases. Also a clear increase of liquid fraction (condensated in the condensation system) is observed when increasing the temperature. Meanwhile, the gas fraction seems to be approximately constant in the temperature interval studied. Note that the total volatile fraction does increase with temperature, as expected, although in the range of temperatures studied, the effect is not very much clear.

This behavior should be explained by the nature of the petrochemical sludge: at low temperatures, the pyrolysis process is more a boiling process than decomposition. In this way, the decomposition does not form craked species of low molecular weight (gas). In any case, the volatile (liquid+gas) fraction does increase with increasing temperature, as expected, whereas solid-char fraction decreases.

A good correlation is found (with correlation coefficient higher 0.95) between logarithm of temperature and the percentage of fraction observed, with the following equations (T in K):

$$(\% \text{ liquid}) = -68.754 \cdot \ln(1/T) - 407.91$$

$$(\% \text{ solid}) = +58.12 \cdot \ln(T) + 403.35$$

$$(\% \text{ gas}) = 100 - (\% \text{ solid}) - (\% \text{ liquid}) = 104.56 + 10.634 \cdot \ln(T)$$

These correlation lines are also shown in Figure 2 (note that the lines shown in the figure are not linear fits). *According to these tendency lines*, a temperature around 1000 K (727 °C) would totally decompose the petrochemical sludge, with a liquid fraction of about 65 %, if same tendencies are followed.

3.2. Analysis of the gas fraction

A clear variation of the composition of the gas produced was not observed in the temperature range studied (350-530 °C). Samples were taken at different times in each run, and an average representative composition of the gas is as follows (yields expressed in % wt. of tire fed): 0.15 CO₂, 0.17 H₂, 3.51 methane, 0.50 ethane, 0.74 ethylene, 0.42 propane, 0.64 propylene, 0.16 isobutane, 0.27 n-butane, 0.29 1-butene, 0.10 isobutene, 0.15 n-pentane. Other compounds are found, but their yield is lower than 0.05 %. As can be seen, a very important amount of non aromatic HC is obtained in the gas at the different temperatures. Analysis of the gas fraction has been already reported in other conditions[6] where high ratios H₂/CO are found (close to 3.5) in the pyrolysis at low heating rate.

3.3. Analysis of the liquid (tar) fraction

The composition of the oil has been analysed by chromatography, as commented before. Figure 3 resumes the results. As can be seen, a slight increase of non aromatic HC C₁-C₁₄ and a decrease of aromatic HC are observed as the temperature increases. This should be related with the evaporation of heavier compounds as the temperature increases, because the maximum temperature (530 °C) is not enough to break the stable aromatic rings.

{Figure 3}

The composition and yield of the liquid fraction indicates that it is possible to obtain, at the conditions studied in the present research, approximately a 30 wt. % yield of non aromatic hydrocarbons at the higher temperature.

3.4. Properties of the solid residue

Decomposition characteristics of the produced solid residue (char) have been analysed by means of a thermobalance. Both pyrolysis (in Helium) and combustion (in a mixture He:O₂=4:1) at different heating rates are discussed.

Figures 4 to 7 show the pyrolysis and combustion of the different chars obtained at the reactor.

{Figures 4-7}

In the Figures it can be seen both the effect of heating rate for the same process and for the species in question and the comparison the effect of heat and mass loss for different processes, pyrolysis and combustion. Each of the graphs shows the weight loss as the fraction $w = m / m_0$ where m is the actual mass of the sample and m_0 is the initial mass. In the previous graphs we can see the effect of the heating rate on TG curves. It can be appreciated that increasing heating rate curves are shifted to the right, i.e. that the weight losses occur at increasing temperatures. This behavior has been described by several researchers and can be explained by the mathematical form of the kinetic laws [18-20], which can provide a shift of the curves at higher temperatures with increasing reaction rate.

In our particular case, the decomposition of the char produced in the pyrolysis of the petrochemical sludge presents a behavior quite different depending on the temperature it was produced:

- The combustion of the chars obtained at low temperatures (350 and 400 °C) is similar to its pyrolysis in the first stages, with decomposition curves that overlap at low temperature. This indicates that the char combustion proceeds through the pyrolysis of the char and later combustion of the residue formed [21,22].
- Nevertheless, the combustion of the chars obtained at higher temperatures (470 and 530 °C) is delayed respect to the pyrolysis (the presence of oxygen produces partial oxygenation of solid material, causing the apparent delay in the decomposition of the solid) [23]. The incorporation of oxygen is so important in this case that it can be observed even an increase of the weight at intermediate temperatures, by incorporation of oxygen into the structure forming intermediate species that lately are decomposed at higher temperatures. This has been observed in other materials [24-26] and is related to the presence of inorganic species in the char.
- Other important aspect to be considered is that the pyrolysis of the char formed is more easy to produce (at lower temperature) for chars formed at lower temperature, i.e., a char formed at 350 °C decomposes at approximately 450 °C (Figure 4) whereas a char formed at 530 °C

decomposed at >700 °C (Figure 7). Remarkably, this is not true for combustion of the chars, that is produced at $T < 450$ °C in any case (Figures 4-7). This indicates that the reactivity of the chars vs. the oxygen is very high despiteless of the conditions they are produced.

4. CONCLUSIONS

The pyrolysis of a sludge produced in the waste water treatment plant of an oil refinery was studied in a pilot plant reactor at 350-530 °C. At low temperatures the fraction not decomposed (char) is high and decreases as the pyrolysis temperature increases, while the liquid fraction increased. The analysis of the gas produced reveals a slight variation in this temperature range, being methane, ethane, ethylene, propane and propylene the most important compounds. In the liquids, the light hydrocarbon yield increases with increasing temperature, whereas the aromatic compounds diminish. The decomposition of the solid fraction proceeds through the pyrolysis of the char and later combustion of the residue formed. Furthermore, the reactivity of the chars vs. the oxygen is very high despiteless of the conditions they are produced.

5. Acknowledgements

TEP-6686 project funded by the Operational Program FEDER and FSE of Andalusia 2007-2013. Ministry of Education and Science (Spain): CTQ2008-05520. Valencian Community Government (Spain): PROMETEO/2009/043 and ACOMP2011/224.

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Figure 5. Thermal decomposition of the char produced at 400 °C in the absence (pyrolysis) and in the presence of oxygen (combustion) at three different heating rates.

Figure 6. Thermal decomposition of the char produced at 470 °C in the absence (pyrolysis) and in the presence of oxygen (combustion) at three different heating rates.

Figure 7. Thermal decomposition of the char produced at 530 °C in the absence (pyrolysis) and in the presence of oxygen (combustion) at three different heating rates.

FIGURES

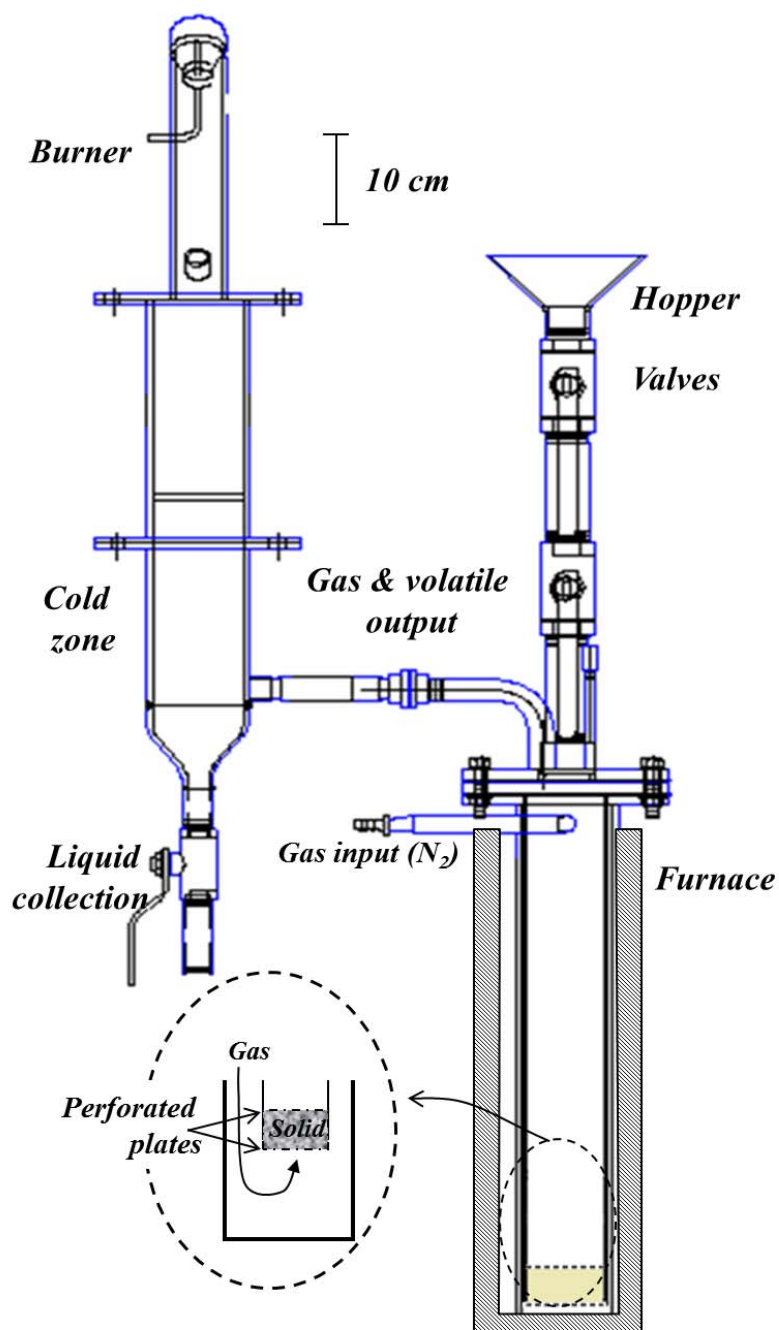


Figure 1. Schematic of the reactor system.

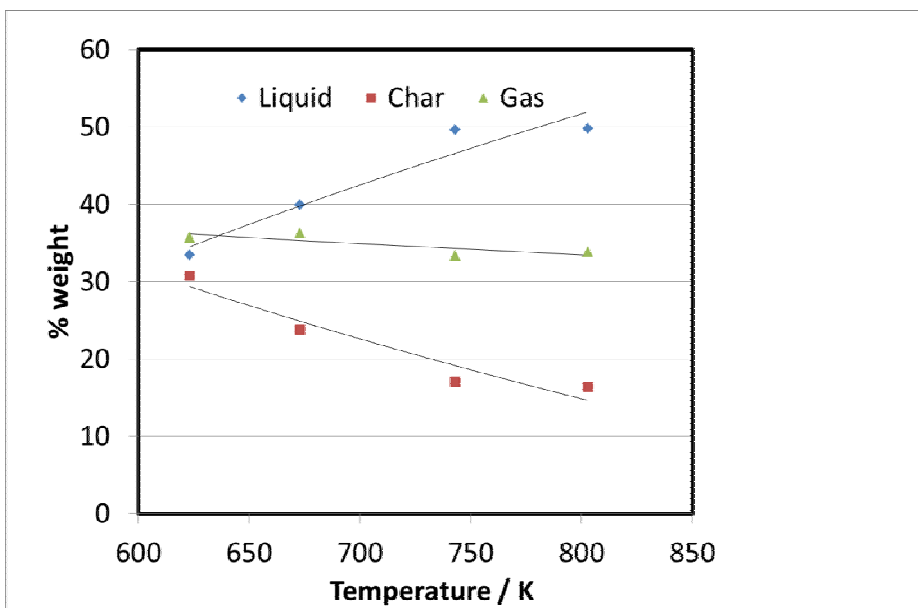


Figure 2. Yield of the different fractions in the runs performed together with tendency lines (presented in the text).

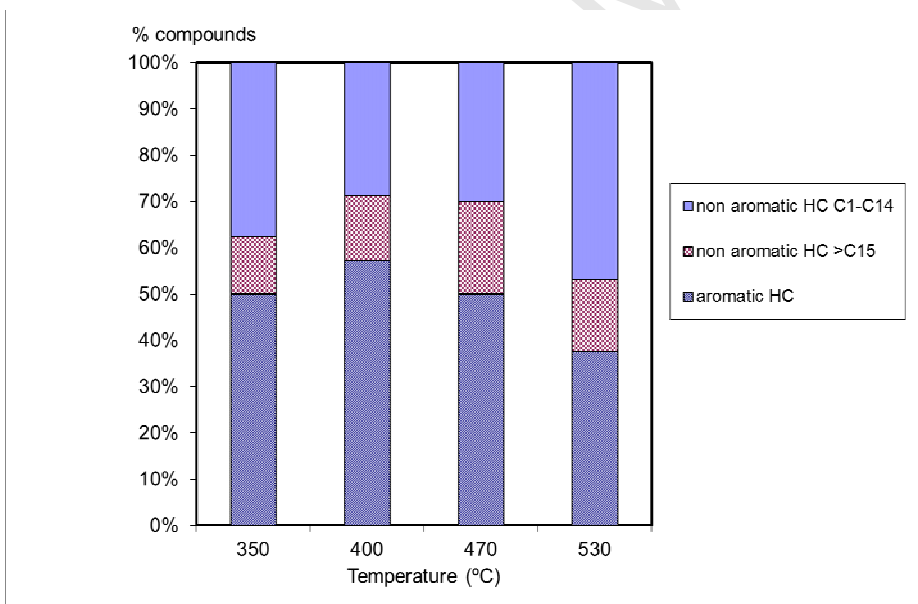


Figure 3. Evolution of the composition of liquid oil fraction as a function of temperature.

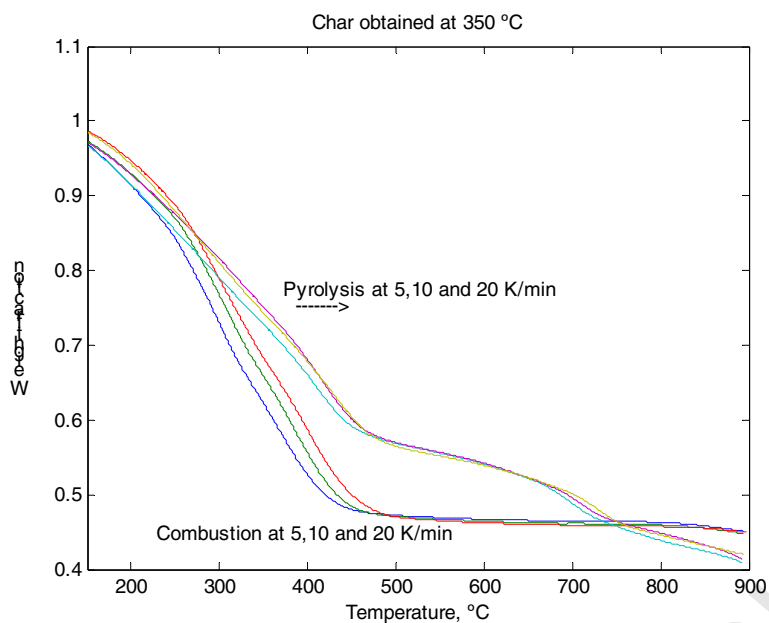


Figure 4. Thermal decomposition of the char produced at 350 °C in the absence (pyrolysis) and in the presence of oxygen (combustion) at three different heating rates.

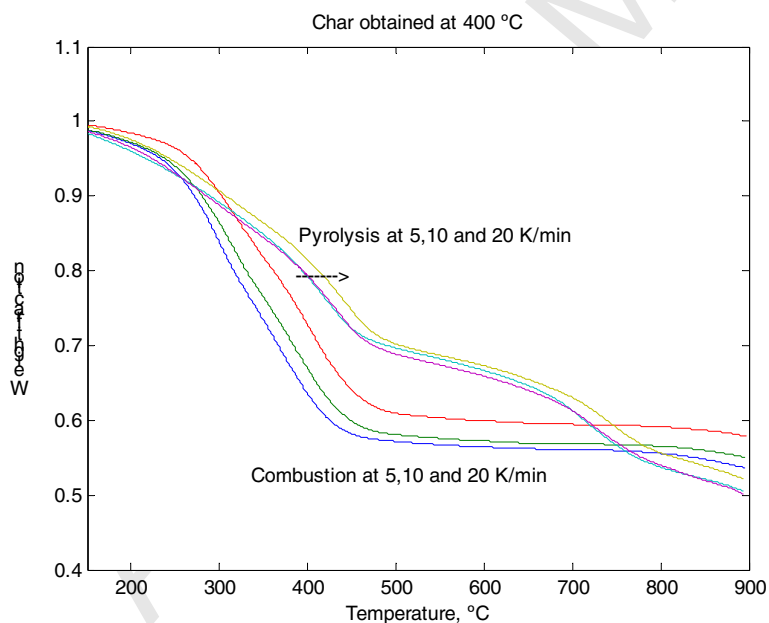


Figure 5. Thermal decomposition of the char produced at 400 °C in the absence (pyrolysis) and in the presence of oxygen (combustion) at three different heating rates.

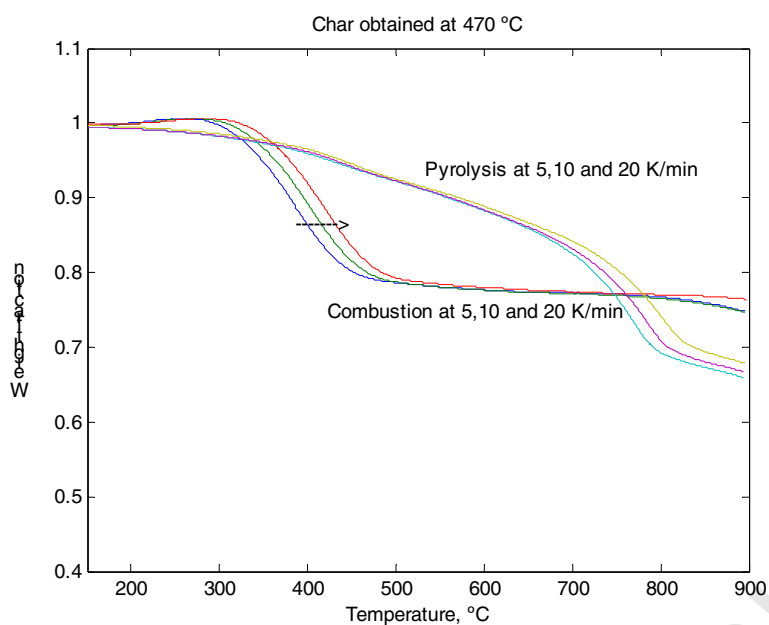


Figure 6. Thermal decomposition of the char produced at 470 °C in the absence (pyrolysis) and in the presence of oxygen (combustion) at three different heating rates.

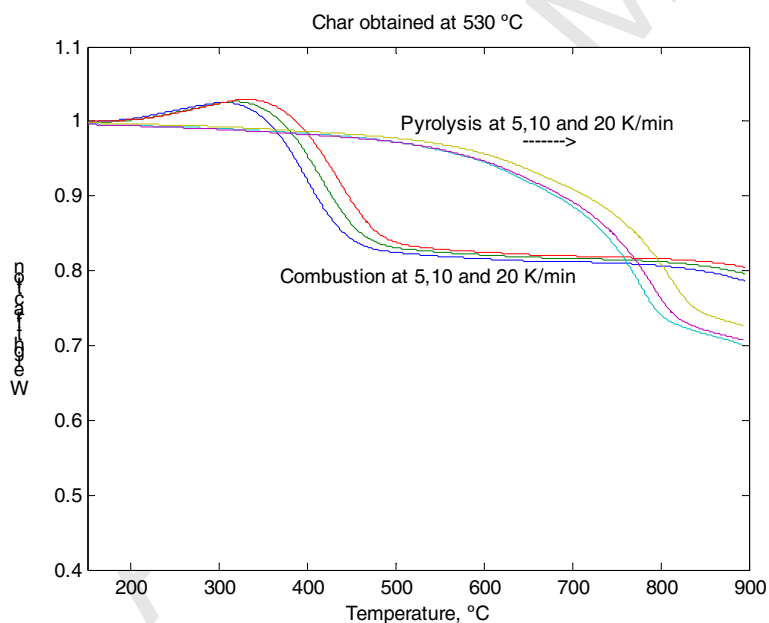


Figure 7. Thermal decomposition of the char produced at 530 °C in the absence (pyrolysis) and in the presence of oxygen (combustion) at three different heating rates.

TABLE

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)	18110

Table 1. Proximate and ultimate analysis of the petrochemical sludge.