THERMOGRAVIMETRIC CHARACTERIZATION OF OIL REFINERY SLUDGE

Agustín G. Barneto,^{*1} Julia Moltó,² José Ariza,¹ Juan A. Conesa²

¹ Department of Chemical Engineering, Physical Chemistry and Organic Chemistry, University of Huelva (Campus de Excelencia Internacional Agroalimentario, ceiA3).

² Department of Chemical Engineering, University of Alicante.

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.

Keywords: oil, sludge, autocatalysis, thermogravimetry.

^{*} Corresponding author. Tel.: +34 959 219982; fax: +34 959 219983. Facultad de Ciencias Experimentales, Campus El Carmen, Universidad de Huelva, 21071 Huelva (Spain). *E-mail:* agustin.garcia@diq.uhu.es

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.

Thermogravimetric analysis (TGA) provides an effective alternative to chemical analysis for the characterization of fossil fuels [7]. 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 [7]. Karacan and Kok [8] 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 [9][10]. 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 [11].

Shishkin [12][13] 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. [14][15] 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.

Recently, thermal analysis coupled to mass spectrometry (TG/MS) with soft photoionization was used to characterize crude oils [16]. 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 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. 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 was ethanol–benzene extracted in Soxhlet equipment for 4 h to obtain extractives (E) and residues (R).

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 synthetic air (4:1 N₂:O₂) for gasification 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.

2.4. Gas chromatography coupled to mass spectrometry

Chemical composition of sludge extractives was obtained by using GC/MS. Runs were performed at 39.4 bar on an Agilent 5973 N Gas Chromatograph/Mass Spectrometer equipped with an HP1 column. The injector temperature was 250 °C and samples were heated from 35 to 325 °C at 5°C/min.

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. Figure 2 compares fresh sludge (S), extractives (E) and crude oil (C) thermal degradations. Sludge residue (R) has not been included in figure 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 figure 2), we qualitatively interpreted the sludge thermal degradation in accordance to Shishkin [12][13]. In their opinion, under thermogravimetric conditions, the heating of crude oil (see line C in figure 2) provides the following fractions: benzine–ligroin (BL, 180 °C), kerosene–gas oil (KG, 180–300 °C), paraffins-base oils (PB, 300–400 °C), condensed aromatics (resins) (CA, 400–550 °C) and asphaltenes (A, 550–600 °C).

As can be seen in figure 2, the mass loss rate for crude oil is higher than for sludge but lower than for extractive. This is because the volatile components content in oil crude is higher than in sludge but lower than in extractive. Fresh sludge (S) behaves like a reduced crude (crude oil after atmospheric distillation) with few volatile components but significant content of the heavy components and inorganic compounds which produce almost 30 wt% ash at 900 °C. On the other hand, based on the thermal degradation profile, sludge extractives (E) behaved like a very light crude oil enriched with light cuts that are degraded at low temperatures. According to Shishkin approach [12], the main cuts in sludge extract (E) must be BL and KG because 86 % of the overall mass loss accounts bellow 300 °C. In addition, extractives left virtually no residue upon heating at 900 °C.

Chemical analysis of sludge extractive supports this interpretation. According to GC/MS data, main components of extractives are hydrocarbons with carbon chains containing 6–35 carbon atoms, as well as aromatics and amines consisting of 14 and 16 carbon atoms. Most abundant hydrocarbons contain between 8 and 14 carbon atoms, with normal boiling point between 126 °C and 254 °C.

Figure 3 focus attention on fresh sludge and compares their thermal degradation in both inert (pyrolysis) and oxidant (combustion) atmospheres. As can be seen in this Figure 3, below 300 – 320 °C actual atmosphere do not influences thermal degradation because the mass loss happens due to vaporization of light components. In this first phase the loss of BL and KG cuts explains approximately 41.7% of the whole mass loss (peaks P2 and P3). Higher temperatures cause degradation of various heavy cuts, namely: PB (by 12% at 300–400 °C) and CA (by 7% at 400–500 °C). In this second phase does not occur volatilization but cracking. At very high temperature the heavy molecules are broken, yielding volatiles and char (carbonaceous residue) which remains in thermobalance in inert atmosphere but is fast oxidized in oxygen presence. For this reason, at temperatures between 400 and 500 °C the mass loss rate is higher in combustion than in pyrolysis. At these temperatures, in air atmosphere, char is rapidly transformed in carbon oxides. On the other hand, under inert atmosphere char is slowly volatilized because several reactions, including water shift reaction which yields hydrogen.

On this basis char production during cracking phase was monitored via TG/MS performed under inert atmosphere. As can be seen in figure 4, the intensity of hydrogen signal grows with temperature, leading a peak at 450 °C (see Fig. 4). Sharp rise in the hydrogen content between 400 and 500 °C proves an intense char production in this temperature interval [14]. At higher temperatures, over the temperature range 400–900 °C under inert atmosphere, char slowly volatilizes and gives a broad peak (P6 in figure

3); by contrast, if oxygen is present, char is rapidly oxidized and gave a sharp peak (P5) at ca. 400 °C (see Fig. 3).

On the other hand, thermogravimetric analysis reveals the presence of inorganic compounds in sludge. In oxidant atmosphere it causes the gradual mass loss observed between 600 and 900 °C after char combustion (see broad peak P6 in figure 3, combustion line). In inert atmosphere inorganic fraction degrades together char, leading broad peak with higher mass loss rate than in air atmosphere (see pyrolysis and combustion lines at high temperatures in figure 3). The presence of inorganic compounds with high degradation temperature is consistent with the nature of the sludge because it is obtained from the recovery of spills and rainwater from the drainage gutter.

Fig 2.

Fig 3.

Fig 4.

The following sections complete this qualitative approach introducing quantitative calculations which describe thermal degradation of sludge by means pseudo-mechanistic models based on pseudo-components (viz. sample fractions that are defined more accurately by their thermal degradation behavior than by their chemical composition) [8][12].

3.2. Pyrolysis model

According to Shishkin terminology [13], the pyrolysis of FQ sludge can be tentatively explained by using the following seven pseudo-components: water (W), benzine–ligroin (BL), light kerosene–gas oil (KG1), heavy kerosene–gas oil (KG2), paraffins and base oils (PBO), condensed aromatics (resins)–asphaltenes (RA) and char (Ch). In our thermal degradation model, in an inert atmosphere the first four (W, BL, KG1 and KG2) plus char (Ch) only undergo volatilization, whereas the other heavy components (PBO and RA) undergo cracking leading volatiles and char (carbonaceous

solid residue) while decomposing. In other words, our pyrolysis model assumes that the light cuts of sludge volatilize without residue production, whereas the heavy cuts undergo both volatilization and charring. Char remains on the thermobalance and subsequently volatilizes gradually at high temperatures. S_i in scheme 1 of Fig. 5 denotes the initial pseudo components; V_i and R_i represent volatiles and char, respectively; and subscript i denotes each individual pseudo-component.

Fig 5.

In our approach the thermal degradation of each pseudo component was represented in terms of nucleation kinetics, using a modified Prout–Tompkins equation (eq. 1) [17][18][19] where α is the actual reaction conversion, n the reaction order, m the nucleation order, k the kinetic constant [expressed as in the Arrhenius law, $k = k_0 \exp(E/RT)$, being k_0 the pre-exponential factor and E the activation energy], and s a constant usually taken to be 0.01 which ensures accuracy in the reaction rate at extreme reaction conversions (close to 0 or 1). This equation becomes the classical n th-order kinetic equation when the nucleation order is zero, that is, when autocatalysis is not significant.

Based on the nucleation concept, the reaction starts at various nuclei that react at an accelerating rate as their reaction interface grows until the reaction spheres coalesce when the reaction approaches completion. Consequently, the nucleation approach assumes thermal degradation to be the result of two consecutive processes, namely: nucleus formation and nucleus growth. As the significance of nucleation increases, so does the nucleation order, m . Roughly, peak position in a DTG profile is essentially dependent on the pre-exponential factor and activation energy. Peak shape also depends on reaction order and nucleation order: peaks sharpen with increase in m and decrease in n . However, these global tendencies overlap. Thus, a decrease in nucleation order leads to sharper peaks which, however, are also shifted to higher temperatures.

Nucleation kinetics is especially useful to describe reactions exhibiting an acceleratory period (autocatalysis). Autocatalysis, which sharpens broad DTG peaks in a manner inconsistent with any n th-order model, is more likely in an oxidative atmosphere or at high heating rates [16]. Under these conditions, DTG curves are sharper, and fitting models based on n th-order kinetics tend to reduce the reaction order or simultaneously change the activation energy and pre-exponential factor via a compensation effect. Nucleation kinetics allows these changes in the shape of DTG curves to be explained in terms of changes in nucleation order by effect of small variations in other kinetic parameters.

$$\frac{d\alpha_i}{dt} = k_i(1 - \alpha_i)^n (s + \alpha_i^m) \quad (1)$$

Substituting the mass of volatiles (V_i) for each pseudo component into eq. 1 converts it into

$$\frac{dV_i}{dt} = k_i V_{\infty i} \left(1 - \frac{V_i}{V_{\infty i}}\right)^{n_i} \left[s + \left(\frac{V_i}{V_{\infty i}}\right)^m\right] \quad (2)$$

Therefore, each component requires determining five parameters, namely: pre-exponential factor, activation energy, reaction order, nucleation order and mass of volatiles at infinite time.

Kinetic equations were integrated and optimized by using the Runge–Kutta and Gauss–Newton method, respectively. The objective function, which required minimization, was

$$OF = \sum_{i=1}^n \left(\frac{dm_{\text{exp}}}{dt} - \frac{dm_{\text{cal}}}{dt} \right)^2 \quad (3)$$

where $\frac{dm_{\text{exp}}}{dt}$ and $\frac{dm_{\text{cal}}}{dt}$ are the experimental and calculated mass loss rates, respectively, for the n points of each experiment. The model was validated in terms of the variation coefficient (VC):

$$VC(\%) = \frac{\sqrt{OF/(N - P)}}{\frac{dm_{\text{exp}}}{dt}} 100 \quad (4)$$

where N and P are the number of data points and parameters fitted, respectively; and $\frac{\overline{dm_{\text{exp}}}}{dt}$ is the average experimental mass loss rate.

3.3. Combustion model

The combustion model for the sludge thermal degradation was developed from the pyrolysis model because oxygen had little effect on the degradation profile of the pseudo-components below 400 °C. Higher temperatures required considering two differences, namely: (a) char was not gradually volatilized, but rapidly oxidized by oxygen, thereby resulting in an increased mass loss rate from 400 to 500 °C (see Fig. 3); and (b) a new inorganic pseudo component I appeared that was degraded at very high temperatures (see scheme 2 in Fig. 5).

3.4. Thermal degradation simulation

Modeling thermal degradation we can obtain a pseudo-component-based composition of samples. On this way, we can employ thermogravimetry as fast analytical method to characterize oil refinery sludge. Tables 1 and 2 show the kinetic parameters obtained by fitting the thermogravimetric data, and Figure 6 compares the experimental and calculated DTG curves, and shows the thermal degradation profile for each pseudo-component.

Thermal degradation of oil refinery sludge highlights the need for autocatalytic kinetics to explain thermogravimetric data. Figure 7 shows the DTG obtained in oxidative atmosphere at different heating rates. As can be seen, raising the heating rate from 5 °C/min to 10 °C/min had virtually no effect on the shape of the DTG curve for sludge combustion. However, further raising the rate to 20 °C/min significantly altered the DTG curve. This can be explained by an autocatalytic degradation between pseudo components. Based on the fitted thermogravimetric data (see Table 2), the nucleation order under a nitrogen atmosphere was always low, that is, none of the pseudo components exhibited significant autocatalysis (since $m \approx 0$, kinetics is similar to the n th-order equation). In the oxygen atmosphere, however, the nucleation orders for KG1,

KG2, PBO, RA and char degradation were high. For example, the m values for KG2 combustion at a heating rate of 5, 10 and 20 °C/min were 0.29, 0.29 and 0.94, respectively. As consequence, the average value and standard deviation for m were high between 5 and 20 °C/min (see table 2).

Activation energies obtained by thermogravimetric data fitting are coherent with experimental values of vaporization and cracking enthalpies of light and heavy components, respectively. During thermogravimetric runs, sludge samples are heated at a constant rate, which causes volatile compounds to evaporate according to volatility. In crude oil, this phenomenon affects hydrocarbons involving less than 18 carbon atoms (i.e. the naphtha, ligroin, kerosene and gas oil cuts) [12]. Approximately above 315 °C occurs cracking of heavy components (viz. long-chain compounds such as paraffins, base oils, resins and asphaltenes) [12].

The activation energy of vaporization is known be similar to the vaporization enthalpy. For example, for water vaporization in wet powders, Prado and Vyazovkin [20] obtained activation energies that were similar to those measured in bulk water (43.8 kJ/mol). This allows ascertain the accuracy of fitting by comparing vaporization enthalpies and activation energies for pseudo-components volatilization. As can be seen in tables 1 and 2, for the vaporization of the pseudo component Wat (water in sludge) a value of 44 kJ/ is calculated. Likewise, the activation energies calculated for the vaporization of BL (63.7 kJ/mol), KG1 (71.1 kJ/mol), KG2 (77 kJ/mol), and PBO (78 kJ/mol) in air were similar to the vaporization enthalpies for representative substances of these oil cuts (viz. undecane, tetradecane and hexadecane, with 60.0, 71.2 and 81.8 kJ/mol, respectively) [21]. As expected, the activation energies calculated for the cracking process were significantly higher than that for the vaporization process. For example, thermal degradation of the pseudo component RA (resins–asphaltene) was 108 kJ/mol under a nitrogen atmosphere and 99 kJ/mol in the air. These values are similar to that for char pyrolysis (117 kJ/mol, table 2).

In addition, fitting the thermogravimetric data allowed us to characterize the composition of the sludge in terms of pseudo components present in oil. Figure 8 compares the composition of refinery sludge (S) and its extractives (E). As can be seen, E was substantially rich in light cuts: BL, KG1 and KG2. On the other hand, as expected, the PBO and RA fractions were more abundant in fresh sludge than in extractives. Consequently, sludge extractives provide valuable fuel enriched in oil light cuts that can be used without char formation to improve the energy balance of oil refineries.

Fig 6

Fig 7

Fig 8

Table 1

Table 2

4. Conclusions

Fresh oil refinery sludge, obtained from wastewater subjected to physical separation treatments, has proven to be a blend of inorganic compounds and major crude oil cuts. Almost 40 % of fresh sludge can be recovered by Soxhlet extraction. The resulting extractives, which amount to ca. 400 ton/year in the studied refinery, consist mainly of a kerosene–gas oil mixture that can be used as fuel by the refinery itself.

Thermogravimetric analysis allows fast characterization of fresh sludge, being useful to monitor the performance of the liquid effluent treatment plant of an oil refinery. To do this it is sufficient, first, to model sludge on the basis of main components of crude oil and, secondly, to model their thermal degradation combining volatilization and cracking processes. Thereafter, accurately description of the thermal degradation of refinery sludge, which includes abundance of main components, was accomplished by using a Prout–Tompkins kinetic equation.

5. Acknowledgments

This work was funded by Junta de Andalucía, Spain (Project TEP-6688). CEPESA's "La Rábida" refinery and Research Center are gratefully acknowledged for kindly supplying the sludge samples and performing the GC/MS analyses, respectively.

6. References

- [1] Lise A, Jan B, Jan D, Raf D. Principles and potential of the anaerobic digestion of waste-activated sludge. *Prog. Energy Combust.* 2008; 34, 755–781.
- [2] Wang F, Wang Y, Ji M. Mechanisms and kinetics models for ultrasonic waste activated sludge disintegration. *J. Hazard. Mater.* 2005; 123, 145–150.
- [3] Bougrier C, Delgenes JP, Carrere H. Effects of thermal treatments on five different waste activated sludge samples solubilization, physical properties and anaerobic digestion. *Chem. Eng. J.* 2008; 139, 236–244.
- [4] Hossain M, Strezov V, Nelson P. Thermal characterisation of the products of wastewater sludge pyrolysis. *J. Anal. Appl. Pyrol.* 2009; 85 (1–2), 442–446
- [5] Monte M, Fuente E, Blanco A, Negro C. Waste management from pulp and paper production in the European Union. *Waste Manag.* 2009; 29, 293–308
- [6] Vieira G, Romeiro G, Sella S, Damasceno R, Pereira R. Low temperature conversion (LTC) – An alternative method to treat sludge generated in an industrial wastewater treatment station – Batch and continuous process comparison. *Biores. Technol.* 2009; 100 (4), 1544–1547
- [7] Kök M. Recent developments in the application of thermal analysis techniques in fossil fuels. *J. Therm. Anal. Calorim.* 2008; 91, 763–773
- [8] Karacan O, Kök M. Pyrolysis analysis of crude oils and their fractions. *Energy & Fuels* 1997; 11, 385–391
- [9] Kök M., Acar A. Kinetics of crude oil combustion. *J. Therm. Anal. Calorim.* 2006; 83, 445–449.
- [10] Kök M. Thermo-oxidative reactions of crude oils. *J. Therm. Anal. Calorim.* 2011; 105, 411–414

- [11] Herrington PR, Ball GF, Patrick JE. Determination of the relative oxidative stability of petroleum bitumens by thermogravimetry. *Thermochim. Acta*, 1992; 202, 201–213
- [12] Shishkin Y. A new quick method of determining the group hydrocarbon composition of crude oils and oil heavy residues based on their oxidative distillation (cracking) as monitored by differential scanning calorimetry and thermogravimetry. *Thermochim. Acta* 2006a; 440, 156–165
- [13] Shishkin Y. Fractional and component analysis of crude oils by the method of dynamic microdistillation – Differential scanning calorimetry coupled with thermogravimetry. *Thermochimica Acta* 2006b; 441, 162–167
- [14] Gonçalves ML, Ribeiro DA, da Mota DA, Teixeira AM, Teixeira MA. Thermal behavior of refinery atmospheric residue from some different oils. *J. Therm. Anal. Calorim.*, 2005; 80, 387–391
- [15] Gonçalves ML, Ribeiro DA, Mota DA, Cerqueira WV, André D, Saraiva LM, Coelho MI, Teixeira AM, Teixeira MA. *Fuel Process. Technol.* 2010; 91, 983–987
- [16] Barneto AG, Ariza J, Martín JE, Diaz J. Kinetic models based on biomass components for the combustion and pyrolysis of sewage sludge and its compost. *J. Anal. Appl. Pyrolysis* 2009; 86, 108–114
- [16] Geißler R, Saraji-Bozorgzad T, Streibel T, Kaisersberger E, Denner T, Zimmermann R. Investigation of different crude oils applying thermal analysis/mass spectrometry with soft photoionisation. *J. Therm. Anal. Calorim.* 2009; 96, 813–820.
- [17] Prout EG, Tompkins FC. The thermal decomposition of potassium permanganate. *Trans. Faraday Soc.* 1944; 40, 488–498
- [18] Prout EG, Tompkins FC, The thermal decomposition of silver permanganate. *Trans. Faraday Soc.* 1946; 42, 468–472
- [19] Burnham AK, Braun RL, Coburn TT, Sandvik EI, Curry DJ, Schmidt BJ, Noble RA. An Appropriate Kinetic Model for Well-Preserved Algal Kerogens. *Energy & Fuels.* 1996; 10(1), 49–59

- [20] Prado JR, Vyazovkin S. Activation energies of water vaporization from the bulk and from laponite, montmorillonite, and chitosan powders. *Thermochimica Acta* 2011; 524, 197–201
- [21] Chickos J, Acree W. Enthalpies of Vaporization of Organic and Organometallic Compounds. *J. Phys. Chem. Ref. Data*, 2003; 32 (2), 519–878

Figure captions

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

Fig 2. Thermal degradation profiles for refinery sludge (S), sludge extractives (E) and crude oil (C) as obtained under a nitrogen atmosphere at 10 °C/min. Mass loss rate was normalized to sample mass.

Fig 3. Thermal degradation profiles for refinery sludge (S) in the air and a nitrogen atmosphere at 10 °C/min. Mass loss rate was normalized to sample mass.

Fig 4. TG/MS profile for hydrogen during refinery sludge pyrolysis at 10 °C/min.

Fig 5. Thermal degradation models for refinery sludge: pyrolysis (scheme 1) and combustion (scheme 2).

Fig 6. Deconvolution of the thermal degradation profile for refinery sludge (*a*) in a nitrogen atmosphere (pyrolysis) and (*b*) air. TG analyses were performed at 10 °C/min. Mass loss rates on the y-axis are normalized to sample mass.

Fig 7. Influence of the heating rate on the thermal degradation profile for refinery sludge in the air (combustion).

Fig 8. Characterization of fresh sludge (S) and extractives (E) in terms of their contents in major oil cuts: BL benzine–ligroin, KG1 light kerosene–gas oil, KG2 heavy kerosene–gas oil, PBO paraffins–base oils, RA resins–asphaltene.

	Pyrolysis					Combustion				
	$\text{Ln } k_o$ (s ⁻¹)	E (kJ/mol)	n	m	V_∞ (%)	$\text{Ln } k_o$ (s ⁻¹)	E (kJ/mol)	n	m	V_∞ (%)
Wat	9.6 ± 0.3	43 ± 1	3.9 ± 0.1	0.01 ± 0.01	3.0 ± 0.1	9.6 ± 0.1	44 ± 1	4.0 ± 0.1	$10^{-4} \pm 10^{-4}$	2.9 ± 0.1
BL	12.5 ± 0.6	64 ± 2	1.7 ± 0.1	$10^{-4} \pm 10^{-4}$	7.5 ± 0.2	12.4 ± 0.1	63.7 ± 0.7	1.7 ± 0.1	$10^{-4} \pm 10^{-4}$	8.5 ± 0.7
KG1	12.4 ± 0.1	71 ± 1	1.0 ± 0.1	0.05 ± 0.04	12.8 ± 0.1	12.4 ± 0.1	71.1 ± 0.3	1.1 ± 0.1	0.10 ± 0.17	15 ± 1
KG2	12.5 ± 0.1	80 ± 1	1.2 ± 0.1	0.02 ± 0.03	19.1 ± 0.1	12.6 ± 0.1	77 ± 3	1.1 ± 0.1	0.5 ± 0.4	15 ± 1
PBO	10.8 ± 0.2	79 ± 1	1.8 ± 0.1	0.01 ± 0.01	8.6 ± 0.1	10.5 ± 0.1	78 ± 1	1.1 ± 0.1	0.27 ± 0.08	7.7 ± 0.4
RA	13.2 ± 0.4	108 ± 1	1.3 ± 0.1	0.01 ± 0.01	9.0 ± 0.1	13.2 ± 0.1	99 ± 1	1.2 ± 0.1	0.4 ± 0.1	7.6 ± 0.7
Char	8.6 ± 0.6	117 ± 2	4.7 ± 0.2	$10^{-4} \pm 10^{-4}$	11.5 ± 0.8	23.0 ± 0.1	160 ± 2	2.4 ± 0.1	0.10 ± 0.01	10.5 ± 0.7
I						17.9 ± 0.1	190 ± 0.3	4.4 ± 0.1	0.01 ± 0.01	3.3 ± 0.5
VC	0.42 %					1.0 %				

Table 1. Kinetic parameters for FQ sludge pyrolysis and combustion (average value and standard deviation for 3 runs performed at 5, 10 and 20 °C/min).

	Pyrolysis					Combustion				
	$\text{Ln } k_o$ (s ⁻¹)	E (kJ/mol)	n	m	V_∞ (%)	$\text{Ln } k_o$ (s ⁻¹)	E (kJ/mol)	n	m	V_∞ (%)
Wat	10.4 ± 0.4	47 ± 1	2.7 ± 0.1	0.01 ± 0.01	1.2 ± 0.1	9.1 ± 0.2	44 ± 1	3.0 ± 0.1	0.01 ± 0.01	1.7 ± 0.1
BL	11.9 ± 0.1	58 ± 2	2.1 ± 0.1	0.01 ± 0.01	17.8 ± 0.1	12.1 ± 0.1	59 ± 1	1.7 ± 0.1	$10^{-4} \pm 10^{-4}$	16.5 ± 0.4
KG1	12.5 ± 0.1	67.3 ± 0.7	1.6 ± 0.1	0.09 ± 0.03	34.1 ± 0.1	12.6 ± 0.1	67.5 ± 0.8	1.5 ± 0.1	0.16 ± 0.01	30.1 ± 0.2
KG2	12.3 ± 0.1	76 ± 2	1.1 ± 0.1	0.06 ± 0.04	29 ± 1	12.3 ± 0.1	76.2 ± 0.3	1.2 ± 0.1	0.02 ± 0.03	31.5 ± 0.2
PBO	11.2 ± 0.1	78.2 ± 0.2	1.7 ± 0.1	0.08 ± 0.02	7.8 ± 0.1	11.2 ± 0.2	76.7 ± 0.3	1.9 ± 0.1	0.01 ± 0.01	6.1 ± 0.7
RA	12.9 ± 0.1	101.4 ± 0.4	1.5 ± 0.1	0.02 ± 0.03	6.7 ± 0.1	12.7 ± 0.2	106 ± 2	1.6 ± 0.1	0.01 ± 0.01	8.6 ± 0.4
Char	10.1 ± 0.4	123.3 ± 0.3	3.1 ± 0.1	0.09 ± 0.01	4 ± 1	23.6 ± 0.3	166 ± 1	0.9 ± 0.1	0.50 ± 0.01	4.3 ± 0.4
VC	0.48%					0.71%				

Table 4. Kinetic parameters for the pyrolysis and combustion of refinery sludge extractives, E (average value and standard deviation for 3 runs performed at 5, 10 and 20 °C/min).