

DEVELOPING CHARACTERISATION METHODS FOR FOULANTS DEPOSITED IN REFINERY HEAT EXCHANGERS

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ABSTRACT

This paper discusses several characterisation methods used in combination to examine the properties of crude oil deposits in oil refinery heat exchanger trains. The ultimate objective of the work is to correlate the sources of refinery solid foulants with results of the deposits characterization.

Due to the complexity of the samples a combination of analytical techniques is required. Initially, deposit samples were extracted by a series of solvents (acetone, chloroform, 1-methyl-2-pyrrolidinone (NMP) and toluene) to determine their solubility properties. The extracted materials were examined by size exclusion chromatography (SEC) using a mixture of NMP with chloroform (6:1 volumes) as eluent and synchronous UV-fluorescence spectroscopy. Both techniques indicated the presence of progressively larger aromatic ring systems with the diminishing solubility of the fractions.

These results were combined with results from examining the insoluble material and samples of the “whole” deposit. Thermo-gravimetric analysis (TGA) allowed the estimation of volatiles, ash content and fixed carbon in the deposits and their extracted fractions. Elemental analysis (EA) provided information about heteroatom contents. ATR-IR was used to examine the structural features of the deposits.

The work has shown that useful insights on the nature of the deposits can be gained by characterising them after fractionation using different solvents. The relatively low solubilities of these samples require analyses in solution to be combined with techniques for characterizing solids. Results indicate that this is a promising method for the study of crude oil deposits and complex carbonaceous materials.

INTRODUCTION

Fouling in oil refineries affects the operation of crude oil pre-distillation heat exchanger trains. It is costly in terms of energy, maintenance costs and lost production – due to unit shutdowns for cleaning. Although petroleum fouling has been the subject of study for decades, there is a lack of fundamental understanding of the chemical transformations leading to fouling.

The premise of the present study is that characterizing heat exchanger deposits may provide a key to

understanding organic and inorganic fouling in these heat exchangers.

The peculiarities of recovered deposit samples raise a number of unusual difficulties. Heat exchanger deposits are usually collected from the refinery after a long running time. This implies that a large number of different crudes would have travelled through pipelines, making it impossible to relate deposit chemistry with the properties of the feed material. Chemical and physical properties of heat exchanger deposits also change with temperature and aging. At higher temperatures, deposit structures become more graphitic with aging (Marsh et al, 1982). An additional issue is related to the deposit recovery procedure. It should be designed so that the recovered deposit is a representative sample of the foulant present in the unit.

On the other hand, the limitation of the characterization methods arises in part from the limitation of the analytical techniques themselves and from the complexity of the samples. The first aspect is related to technical parameters such as resolution of the technique, limits of detection, the capability to use certain solvents, etc. Another aspect is the commonly low solubility of these deposits. This last feature is one of the most important and difficult to avoid and/or control.

Therefore, an approach combining solvent solubility based fractionation to separate sub-samples and identification of the insoluble foulants was developed. Brons et al. (2006) have suggested the characterisation of the trapped-feed free (toluene insoluble) fraction of the deposits in order to identify the type of chemical species present in the foulants.

This approach should include the use of different analytical techniques combined with data related to the actual feedstock, the location and collection of the deposits and the operating conditions in the heat exchangers.

This paper outlines the development of a combination of techniques used for the characterization of heat exchanger deposits. The approach takes into account the solubility properties of the samples. The method attempts to obtain information about molecular weight, chemical structure and composition of the deposits. The analytical work was performed using size exclusion chromatography (SEC) with NMP/CHCl₃ (6:1) ratio v/v as eluent, synchronous UV-fluorescence spectroscopy, elemental analysis and thermal gravimetric analysis (TGA). ATR-IR

was used to examine the functional groups of the deposits and to calculate the aromaticity index. Due to the high ash content, a better understanding of inorganic components in the deposits is required in some of these samples. SEM/EDX and XRD have been used for this purpose.

Despite the limitations, the results suggest this is a promising approach for the study of crude oil deposits and complex carbonaceous materials.

EXPERIMENTAL

Samples

To aid the interpretation of the results it is important to obtain as much information as possible about the operating conditions, configuration of the flow and details about the design of the heat exchanger. Table 1 lists the four heat-exchanger deposits analysed in this work. The origin of the samples is confidential.

All the samples originate from tube side locations with exception of the sample DA (shell side) and were collected by oil refinery operators, following standard cleaning protocols. Contamination due to chemicals or additives used during the cleaning operation is unlikely. In addition, the samples have different cleaning histories. PHTD and KPHTD correspond to two heat exchangers cleaned after 6 months. In terms of efficiency, this is a not desirable result; ideally the time between cleaning should be 1-2 years.

Table 1: list of heat-exchanger deposits samples

Sample	Unit Type	Temperature	Feed processed
PHTD	Pre-heat train	T _{in} = 158°C, T _{out} = 166°C	Desalted crude oil
KPHTD	Kero pre-heat train	T _{out} = 240-260 °C	Kerosene
DA	Desulfurizer train	Reactor inlet (tube) = 315°C max	VGO*
DB	Resid. Processing	Shell side = up to 370°C	Crude oil resid.

*VGO= Coker mid-distillate, light cycle oil and vacuum gas oil

Solubility test

Similar amounts (2 mg) of sample were mixed with the same volume of three different solvents (chloroform, 1-methyl-2-pyrrolidinone and toluene). The mixtures were shaken (vortex mixer) for around 1.5 hour. The solution was then filtered, using a syringe filter with a pore diameter of 1 µm, to separate the insoluble particles. When chloroform was used as solvent, vacuum filtration was used with a sinter Grade 4 (pore diameter between 5-15 µ) due to the behaviour of the insoluble material which remains suspended in the solution. Next, both fractions were dried and weighed, and the solubility was calculated using the equation:

$$S = \frac{B - I}{B} \times 100, \quad (1)$$

where B is the weight of the initial sample and I is the weight of the insoluble material. When NMP is used as solvent, a special procedure is needed to recover the samples. Fractions soluble and insoluble in this solvent were dried under a N₂ flow and gentle heating to avoid any contamination with NMP oxidation products during drying (Berruoco et al., 2009). The solubility tests were repeated three times; the standard deviation was calculated to have a maximum value of 5%.

Size exclusion chromatography

A 30 cm long, 7.5 mm o.d. column, packed with 5 µm polystyrene-divinylbenzene polymer particles ('Mixed-D' column, Polymer Laboratories Ltd, UK) was operated at 80 °C at an eluent flow rate of 0.50 ml min⁻¹. The eluent was a solution of NMP/CHCl₃ (ratio 6:1). Detection was carried out using a Perkin-Elmer LC290 variable wavelength UV absorbance detector. Calibration and operating conditions have been previously described (Berruoco et al. 2008).

UV-fluorescence

The procedure has been described elsewhere (Morgan et al. 2005). The Perkin-Elmer LS51 luminescence spectrometer was set with a slit width of 25 nm, to scan at 240 nm min⁻¹; synchronous spectra were acquired at a constant wavelength difference of 20 nm. A quartz cell with 1 cm path length was used. The spectrometer featured automatic correction for changes in source intensity as a function of wavelength. Emission, excitation and synchronous spectra of the sample were obtained in NMP/CHCl₃ (6:1 v/v ratio) solutions; only synchronous spectra are shown. All spectra were height normalized to clarify the positions of the peaks and facilitate the comparison.

Elemental analysis

The carbon, hydrogen, sulphur and nitrogen contents of the samples were determined with a LECO-CHNS-932 micro-analyzer. The oxygen content was obtained directly using a LECO-VTF-900 furnace coupled to the micro-analyzer. The analyses were performed with 1 mg of sample ground and sieved to < 0.2 mm. The results were quoted as the mean of values from four determinations. In all cases, the experimental error was < 0.5% of the absolute value.

In some of the cases, oxygen content was calculated by difference.

Thermal Gravimetric Analysis

In order to evaluate the ash content of heat exchanger deposits and their toluene-insoluble fractions a Perkin-Elmer thermogravimetric analyzer (TGA) has been used. The sample (4-5 mg) was heated to 50 °C and held for 5 minutes under an inert atmosphere (N₂ 40 mL/min). Afterwards the temperature was increased in two steps. The first one up to 105 °C (20°C/min and held for 35 min) and the second one up to 900 °C (100°C/min and held for 30 min). In this way moisture content and volatiles are determined. The difference in the weight loss from the initial sample to 105 °C is related to the moisture present in

the sample, while the weight loss up to 370 °C is defined as volatile content. Next, the temperature is reduced to 850 °C (10°C/min) and once the weigh and temperate are stable the gas supply was switched to air (40 mL/min) to burn out the fixed carbon. The fixed carbon is calculated as the weight loss in this last step. The final weight equates to the ash content of the sample.

SEM-EDX

The EDS spectra were recorded with a spectrometer attached to the SEM microscope. It is important to indicate that, normally, the atomic % of the light elements obtained from such analysis is not directly proportional to the real content of the studied samples because such elements are in the lowest range of X-ray beam excitation.

X-ray diffraction (XRD)

A X'Pert Pro diffractometer (from PAN analytical) was used to obtain the diffraction patterns of all the samples (XRD). Semi-quantitative analyses were performed on these sets of data using PANalytical X'Pert HighScore, which compared peaks present in the data collected with reference patterns from the International Centre for Diffraction Data Powder Diffraction File 4 (ICDD PDF-4). Ash samples were prepared by heating the toluene insoluble fractions of the samples in a muffle furnace at 800 °C for 4 hours.

ATR-IR

All the FTIR spectra were measured using a Spectrum 100 FTIR spectrometer (PerkinElmer) with a Pike Miracle detector. The solid samples were deposited on a modified attenuated total reflection (ATR) accessory (ZnSe crystal). Spectra were obtained with a spectral resolution of 2 cm⁻¹ and 8 scans in the 4000-800 cm⁻¹ wavenumber range. Spectra were corrected from scattering using 'Baseline' (Software version 6.2.0.0055).

RESULTS

Low solubility in common solvents is a usual problem faced when characterizing deposit samples. Thus the first step of the characterization procedure was to test the solubility of the samples in some common solvents. The results for the four deposits are listed in Table 2. Standard deviation has been estimated from ± 0.6 to ± 5 %.

Table 2: Solubility results

Solvent	Solubility (%)			
	PHTD	KPHTD	DA	DB
Acetone	4±3.1	39±2.1	32±3.6	31±1.6
Chloroform	45±4.9	80±5.0	61±5.0	58±5.0
NMP	35±0.7	38±2.1	37±0.6	32±1.8
NMP/CHCl ₃ (6:1)	39±5.0	42±0.4	39±1.1	34±2.3
Toluene	43±1.2	46±0.3	33±1.2	34±2.1

The differences in solubility obtained for the KPHTD, compared to the other deposits, could be related with the

original feed material. DA and DB were less soluble in the solvents used, compared to PHTD and KPHTD. This appears related to their exposure to higher temperatures, which contributed to the formation of coke-like material. The solvent with the highest capacity to dissolve the samples was chloroform; PHTD was the least soluble in this solvent (~45%).

Figure 1 presents size exclusion chromatograms of the deposit samples. It is important to note that only the fraction of the samples that were soluble in NMP/CHCl₃ (ratio 6:1) could be analysed (~40 %). Clear differences were observed between the samples. First, the retained peak (longer elution times - lower masses) was observed to shift to shorter elution times (higher masses) from KPHTD (20.5 min) to DA (23.7 min). This suggests the presence of larger molecules in KPHTD compared to DA. The maximum intensity of the KPHTD retained peak corresponds to 250 u according to a calibration based on polystyrene (PS) and polyaromatic hydrocarbon (PAH) standards (Berruenco et al, 2008). The DB chromatogram shows a bimodal retained peak with a maximum intensity for the second peak around 23 minutes. In terms of distribution, PHTD and KPHTD chromatograms showed the presence of larger molecules in comparison with DB, whereas DA contained the lightest distribution of molecular masses.

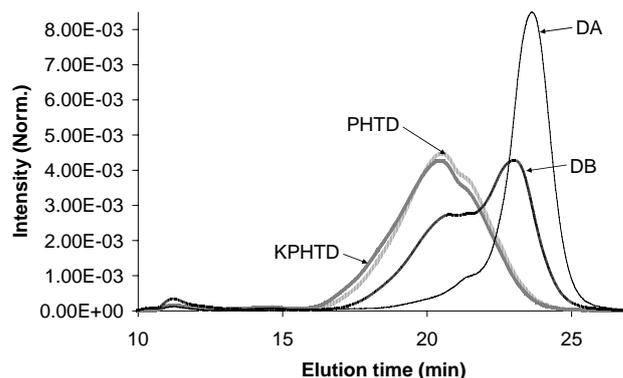


Figure 1: Size exclusion chromatograms of heat exchanger deposits. Mixed D column, 300 nm detection.

An excluded peak was observed between 10 – 13 min, for all samples. The relative size of this peak increased from DA to PHTD and KPHTD with DB having the largest excluded peak. At the levels of dilution prevalent in SEC systems (< 0.001 mg mL⁻¹), these excluded peaks are unlikely to result from the aggregation of smaller molecules (Karaca et al, 2004) and all attempts to disaggregate these materials have given no tangible results. However, it is still possible that existing elution time calibrations (based principally on PS standards) overestimate the molecular masses of material showing signal in the excluded range.

We have previously suggested that the overestimation could be due to changes in conformation from relatively planar to bending shapes, acquiring nearly 3-dimensional forms (Berruenco et al, 2008). The issue remains to be resolved definitively. Mass estimations based on SEC elution time calibrations have therefore been presented (Table 3) only for the retained (i.e. later eluting) peak,

according to the PS and PAHs calibration (Berruoco et al, 2008).

Table 3: Elution time and mass estimates from SEC of heat exchanger deposits

Samples	Retained Peak Max.	
	Time/mins	Mass/u
PHTD	20.6	245
KPHTD	20.5	250
DA	23.7	120
DB	(20.8) , 23	(250) , 150

Intensity-normalized synchronous UV-fluorescence spectra of the deposits are presented in Figure 2. These results show that DA contains the smallest aromatic chromophores of the four deposits and can be related to the SEC results (DA had the lowest average mass / size). The spectra display a red-shift towards longer wavelengths, from KPHTD to DB and to PHTD, suggesting that larger aromatic cores are concentrated in the PHTD sample.

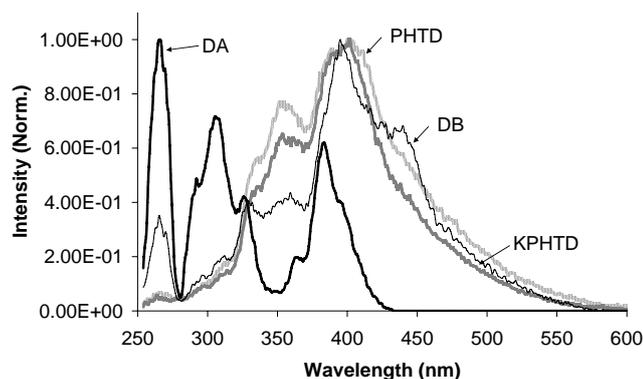


Figure 2: Synchronous UV-f spectra of heat exchanger deposits.

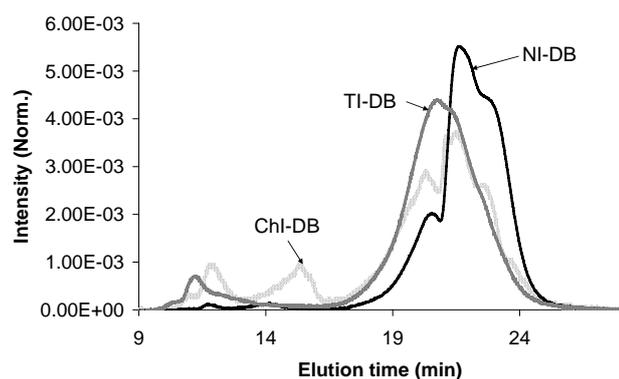


Figure 3: Size exclusion chromatograms of DB fractions. Mixed D column, 300 nm detection.

The characterisation of the bulk deposits does not provide conclusive information due to the wide polydispersity and complexity of the samples. Therefore, fractionating the samples based on solubility helps in their characterization. As an example, the characterisation of DB

sub-fractionations is discussed below. DB is a vacuum residue sample and therefore, probably, the most asphaltenic and thermally degraded (up to 370°C) sample.

Figure 3 presents size exclusion chromatograms of the DB insoluble fractions in toluene (TI-DB), insoluble in NMP (NI-DB) and insoluble in chloroform (ChI-DB). These samples are soluble in the (NMP/CHCl₃) mixed SEC eluent at the low concentrations required. The main feature that can be observed is the presence of larger molecules in the toluene insoluble and CHCl₃ insoluble fractions than in the NMP insoluble fraction. The TI-DB retained peak was observed to shift to shorter elution times (higher masses) compared to ChI-DB and NI-DB, with maximum intensity at 20.8 minutes (~250 u).

Figure 4 shows synchronous UV-fluorescence spectra of DB insoluble fractions. There was a shift towards longer wavelengths, from the NMP-insoluble to the chloroform-insoluble fractions, which suggests an increase in the size of the aromatic chromophores in the same order. The ability of chloroform to dissolve large aromatic compounds seems to be lower than those of NMP and toluene. This can explain the shift to longer wavelength of the chloroform insoluble material.

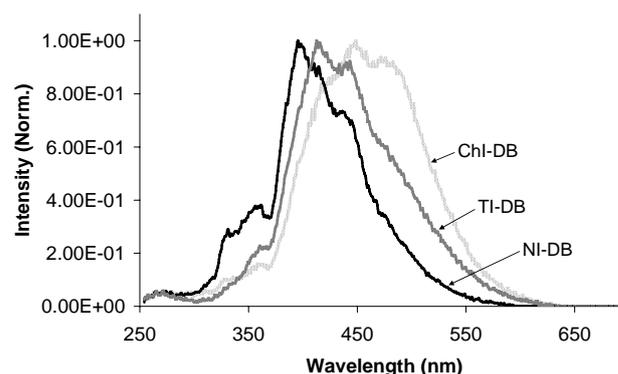


Figure 4: Synchronous UV-f spectra of DB fractions.

Heat exchanger deposits and their toluene-insoluble fractions were analysed by TGA. The results are shown in Figure 5 and summarized in Table 4 together with elemental analysis. C and H contents decreased in the toluene-insoluble fractions in comparison with the whole samples. This result can be explained taking in account that toluene washes all trapped feed during the extraction. The evolution of the other elements is not that evident. On the one hand, N content decreases in PHTD-TI and KPHTD-TI but not in DA-TI and DB-TI, for which a slight increase can be observed compared to the whole samples. On the other hand, S content increases in all the toluene-insoluble fractions.

For PHTD, KPHTD, DA-TI and DB-TI the oxygen content is calculated by difference assuming a very low concentration of other elements (metals, salts, corrosion products, etc). However, the high values of oxygen calculated for PHTD and KPHTD and their fractions are possibly artefacts, suggesting a significant presence of inorganics in these samples. Notice that due to the high ash

contents of some of the samples (KPHTD-TI and PHTD-TI) the errors in the elemental analysis become significant.

C/H/N was used to determine the approximate organic content. Total C, H and N content of these samples ranged from 78 to 89 and from 52 to 83 wt% for whole and toluene-insoluble fractions respectively. Lower values were observed for PHTD and KPHTD toluene-insoluble fractions suggesting the presence of inorganic foulants.

These results were integrated with those obtained by TGA (ash content) which yielded a 1.8 – 2.7 % weight lost upon heating to 370°C and approximately from 42 to 57 % involatile inorganic material (ash content) for PHTD and KPHTD toluene-insoluble fractions.

Other researchers (Brons et al. 2006, Asomaning et al. 2000) recommended H/C values as an indicator of the aging of deposits. For example, the lower H/C ratio of DB-TI compared to DA-TI (0.7 vs 0.9) could indicate that DB-TI is more thermally degraded. This fact agrees with the higher operation temperature for DB (up to 370°C), and matches their solubility behaviours. PHTD and KPHTD have been exposed at medium temperatures and their H/C values do not indicate significant thermal cracking (values higher than 1), in accordance with the literature (Brons et al., 2006).

Considering the high ash contents of KPHTD and PHTD, further characterisation is required to identify the inorganic foulants present.

Thus, qualitative information about composition was obtained from SEM-EDX (Figure 6). The XRD analyses of the ash samples were then performed to complement the SEM-EDX test (cf. Table 5). XRD is useful to identify crystalline phases of inorganic components such as the type of iron sulphide present in corrosion scale. As the toluene-insoluble fraction is regarded to be the main foulant component of the deposit, only those fractions were analysed. High levels of iron and sulfur are present in all of the samples, especially in PHTD-TI and KPHTD-TI. The high ash, iron and sulphur contents may indicate corrosion fouling as the main issue for PHTD and KPHTD.

For these samples, the presence of acids and salts was also relevant. High levels of sodium were observed (from 2.7 to 3.8 % wt. in KPHTD-TI and PHTD-TI respectively), with the presence of sodium chloride confirmed by XRD analysis. This result was somewhat unexpected considering that the feed processed in the PHTD's unit type was desalted crude. The deposition appears related to incomplete desalting.

Analysis of the KPHTD-TI sample also suggested the presence of magnesium silicate. A possible source of this is the reservoir and/or organic acid salts added during the production process. The results suggest that DA and DB were mainly related to thermal decomposition due to the high operating temperature. In both cases, corrosion fouling was also observed. Sulfates and sulphides were detected, especially in DB-TI.

The presence of Ni and V in this last sample suggests a more asphaltenic nature. The DA ash content was found to be lower than that in DB. DA is probably made up of lighter material, coming from a vacuum gas oil feed, which would

explain the small differences between values for the DA sample and its toluene insoluble fraction.

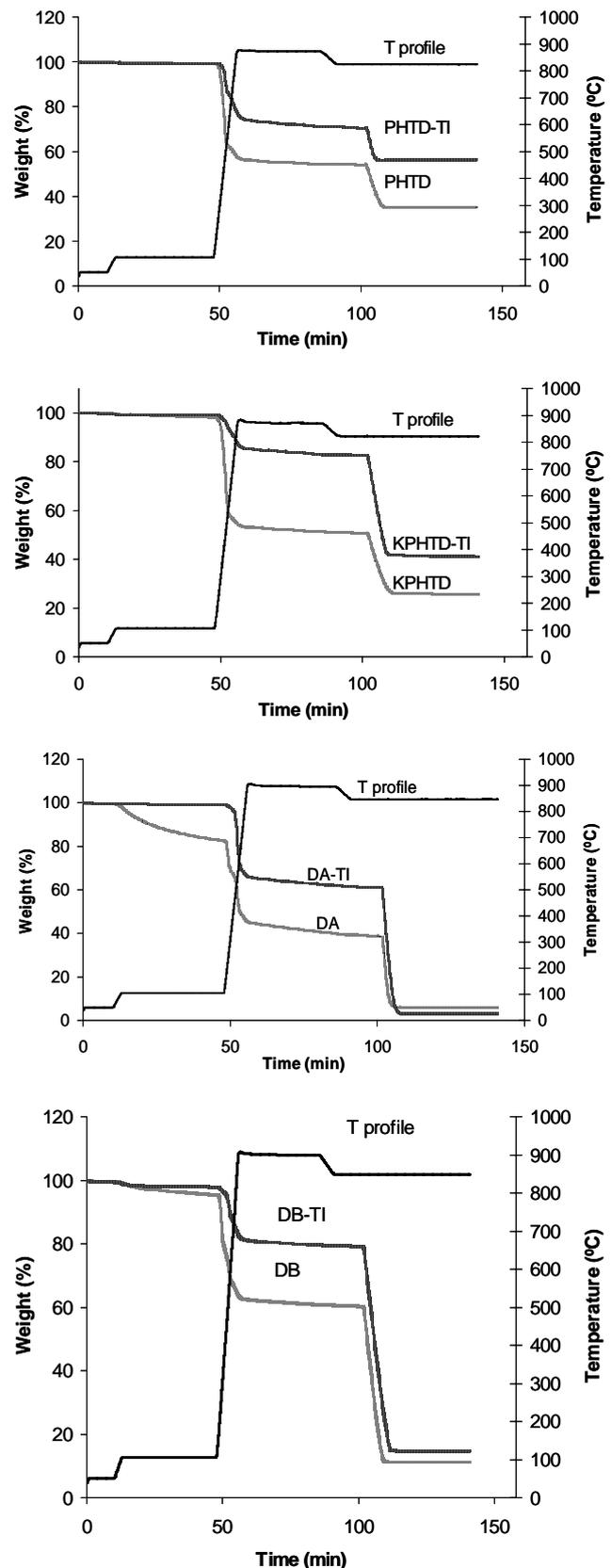


Figure 5: TGA analysis of heat exchanger deposits and their insoluble fractions

Table 4: Summary of analytical results

	PHTD	PHTD-TI	KPHTD	KPHTD-TI	DA	DA-TI	DB	DB-TI
<i>Elemental analysis</i>								
C (% wt.)	79.4	62.9	71.4	49.2	81.9	77.5	77.9	73.5
H (% wt.)	8.2	4.3	6.0	2.5	6.9	5.8	5.7	4.3
N (% wt.)	1.6	0.7	1.1	0.7	0.1	<0.5	0.4	0.7
S _{tot} (% wt.)	1.8	6.3	1.8	3.3	2.2	2.3	2.0	3.8
O (% wt.)	9.0*	11.2	19.7*	18.9	1.9	13.9*	5.1	17.7*
H/C ¹	1.2	0.8	1.0	0.6	1.0	0.9	0.9	0.7
C/S ²	119.6	26.6	108.3	39.8	101.2	89.9	104.5	51.6
C/H/N _{tot} (% wt.)	89.2	67.9	78.6	52.3	88.9	83.8	84.0	78.5
<i>TGA results</i>								
Ash (% wt.)	35.2	56.4	25.6	41.2	5.9	3.1	11.4	15.0
Volatiles lost by 370°C (% wt.)	16.8	1.8	7.4	2.7	27.0	1.0	14.0	4.0
Fixed carbon	18.0	13.8	24.1	39.9	33.0	57.0	47.9	63.6

¹H/C atomic ratio²C/S atomic ratio

*Oxygen calculated by difference

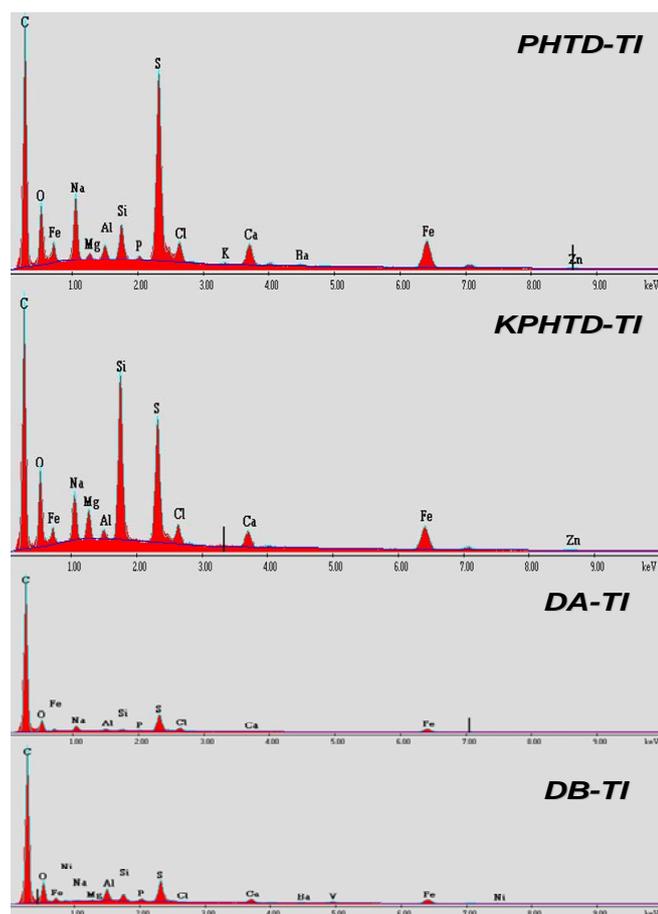


Figure 6: EDX analysis of toluene-insoluble fractions of heat exchanger deposits

Table 5: Measured composition for toluene insolubles

	PHTD-TI	KPHTD-TI	DA-TI	DB-TI
<i>Major metals from SEM-EDX</i>				
Na	3.8	2.7	0.1	0.2
Mg	0.3	1.3	-	0.1
Al	0.7	0.5	0.3	1.7
Si	1.5	7.2	0.2	1
K	0.2	-	-	-
P	0.2	-	0.1	0.5
Ca	2.2	1.7	0.2	1.1
V	-	-	-	0.8
Ba	0.9	-	-	1
Fe	10.4	8.8	5.3	4.9
Ni	-	-	0.2	0.7
Zn	1	1.4	-	-
<i>Inorganic presents from XRD</i>				
Iron sulphide	X	X	X	X
NaCl	X	X	X	
SiO ₂				X
BaSO ₄				X
CaSO ₄				X
FePO ₄	X			
VS				X
MgAlSiO		X		
AlSiO		X		
ZnS		X		
CaCO ₃	X			

Figure 7 presents the ATR-IR spectra of the set of heat exchanger deposits. This techniques was used to study the different functional groups present in the samples. The

analyses of the toluene-insoluble fractions were also performed by ATR-IR (not shown in this work). Due to their graphitic coke-like structures, IR spectra showed weak signal making the functional groups identification complicated. Thus, the whole deposit samples were considered.

The results showed that no bands in the 3900 to 3100 cm^{-1} region, indicating low concentrations of OH or NH groups. The region 3000-2800 cm^{-1} is related to the aromaticity of the samples and depict peaks with high intensity. However, since the foulant (defined as toluene insoluble fraction of the whole sample) showed a C-H stretching vibration in aromatics 3050 cm^{-1} weaker with aging time, this band can be attributed to the presence of trapped feed material.

In the 1750-1600 cm^{-1} region, all samples showed a peak about 1700 cm^{-1} corresponding to carboxylic acids with low intensity. The 1600 cm^{-1} band is known as the coke band and shifted to a lower wavelength for longer aged deposit (Fan and Watkinson, 2006). These results indicate that the aged deposits have a more typical condensed polyaromatic structure. However, a direct comparison of these peaks is not possible because of the different aging history of the samples.

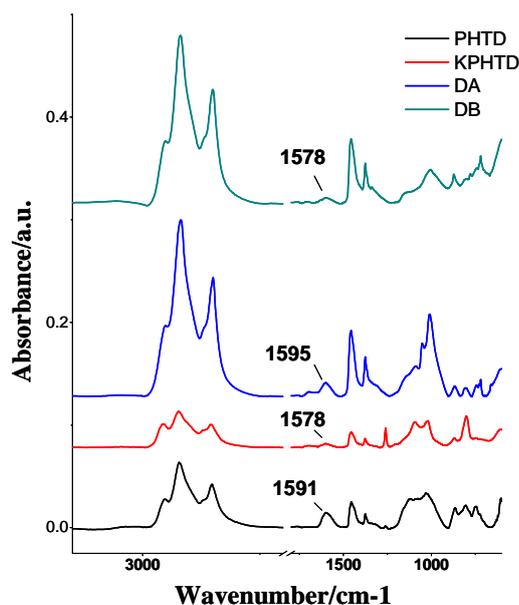


Figure 7: ATR-IR of heat exchanger deposits

The band assignment in the 1300-1500 cm^{-1} region corresponds to CH_3 and CH_2 alkyl chains bending mode. More intense signal in this region was observed in the cases of PHTD and KPHTD.

The band at 1100-950 cm^{-1} is assigned to ethers, alcohols and sulfoxides. The presence of C=S (1026 cm^{-1}) was observed in all four samples. However, the signal in this band is more evident for the DB and KPHTD samples. This result evidences the corrosion due to sulphides and is in agreement with data from elemental analysis, SEM-EDX and XRD.

The 900-700 cm^{-1} region shows the aromatic out-of-plane vibrations of aromatic C-H bonds. Three main peaks are observed in all the spectra, being more important for the DB sample. The band at about 865 cm^{-1} corresponds to isolated aromatic hydrogen. The band in the range 850-800 cm^{-1} may be attributed to systems containing two and/or three adjacent hydrogen. The peak at 750 cm^{-1} is due to the ortho-substitution of the aromatic rings (Guillen et al., 1992).

Combining the information obtained through the different analytical techniques, some possible causes of fouling are proposed for each case.

The pre-heat train deposit (PHTD) seems to be mainly formed through sulphide corrosion with coking. The deposit was made up of a large amount of toluene insoluble material (57 %) and high ash content (35 %). EDX and EA of PHTD-TI sample confirmed the presence of high values of Fe and S (10.4 % and 6.3 % respectively) as iron sulphide (XRD results). Despite PHTD coming from a desalted crude oil, there is evidence of salts and relatively high contents of Na and Ca.

Similar conclusions were reached for KPHTD (kerosene feed material). This deposit was found to be low in asphaltenes, yet with high ash content (25.62 %). The toluene insoluble fraction contained 8.8% Fe and 3.3 % S, respectively. XRD indicated the presence of iron sulphide, NaCl and other salts. The sample was rich in magnesium and other silicates. These findings suggest forms of corrosion fouling associated with the presence of various salts.

DA was different from the other samples. It comes from a VGO, a relatively light fraction. SEC and UV-fluorescence spectroscopy confirmed the presence of small molecules (120 u) and small aromatic chromophores. The sample also had low ash content (6 %). Metal and salt contents are low. Thermal degradation appeared to be the main cause for fouling. Additionally, the H/C ratio obtained for DA-TI (lower than one) suggests that these deposits are thermally degraded, although to a lesser extent than DB-TI (H/C ratio 0.7).

The results suggest that DB deposit also had its origins in thermal degradation at the high temperatures of exposure - up to 370°C. The toluene insolubles content was high (76 %) and the H/C ratio (~0.86) was low. The relatively low ash content appears due to the presence of iron sulphides. The higher levels of organic material in these deposits, compared to the PHTD and KPHTD deposits, seems consistent with exposure of DA and DB to higher temperatures. The presence of Ni and V appears consistent with the more asphaltenic nature of the samples. Indeed, DB was produced from a vacuum residue.

DB and KPHTD shows some similarities in terms of aromaticity index and C=C aromatic double bond (ATR spectra). Evidence of sulphide corrosion comes from the more evident signal in the band at 1100-950 cm^{-1} observed for these two samples. These findings are in agreement with EA, EDX and XRD results.

SUMMARY & CONCLUSIONS

Different analytical techniques have been used to examine the chemical/structural properties of heat exchanger deposits. The aim of the present work was to identify the sources of refinery solid foulants.

Samples were extracted by a series of solvents to aid their analysis. Size exclusion chromatography in NMP/CHCl₃ (6:1) eluent was used to examine the molecular size distributions. Taking into account their different solubility in the SEC eluent, it was observed that the toluene-insoluble fraction contains larger molecular mass material, compared to the NMP-insoluble and chloroform-insoluble fractions. Furthermore, larger chromophores were observed in the chloroform insoluble fraction as suggested by UV-fluorescence results. As an example, the characterization of the DB-deposit (from a resid. processing unit) after sub-fractionation has been described in detail.

The developed analytical procedure combines analysis in solution with techniques for characterizing solids, including TGA, ATR-IR, SEM/EDX and XRD. This method allows to propose some of the possible fouling causes for each of the studied samples.

Despite limitations arising from the complex nature of the sample, the results suggest this is a promising approach for the study of crude oil deposits and complex carbonaceous materials.

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