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CHARACTERIZATION OF ORGANIC MATTER IN PROCESS WATER ORIGINATING FROM CRUDE DISTILLATION UNITS OF LUKOIL NEFTOHIM BURGAS REFINERY

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Abstract

The distribution of organic matter in process waters originating from crude distillation units of LUKOIL Neftohim Burgas refinery were determined. The organic matter was identified by gas chromatography-mass spectrometry as the oxygen-containing compounds (naphthenic acids and phenols) and the sulfur-containing species mainly cyclic polysulfides. The levels of phenol compounds and naphthenic acids species were ranged between 0.05 to 24.4 mg/L and 0.05 to 3000 mg/L, respectively. This study showed that the sulphur species were varied between <0.05 to 24.6 mg/L. The result of this research can be generalizable as the deeper understanding of the substance composition in process wastewater and a theoretical basis for their control and reused. The identification of corrosion substances in refinery effluent will be useful for the protection of the technological equipment.

Keywords: *naphthenic acid species (alicyclic carboxylic acids); phenolic compounds; polysulphur components; refinery process waters; gas chromatography-mass spectrometry.*

1. Introduction

During the refining process, large volumes of wastewater are generated, as their quality varies widely, and usually, their volume is up to 1.6 times the volume of the oil being processed [1]. In recent decades, due to the growing importance of crude oil for industrial development, efforts have been made to improve the management of process waters from petrochemical facilities [2-3]. In this aspect of efforts, engineers continue to seek solutions for the characterization of production waters due to the occurrence of corrosive problems related to the technological equipment in the refineries. Studying the polar compounds that raise environmental and toxic issues in the petroleum refinery business, is a major challenge to analytical practice and analytical control.

Wastewater from oil refineries has a significant impact on the pollution of surface water systems because they contain different amounts of hazardous pollutants [4-5]. Among the polar components of petroleum, which contain heteroatoms, are naphthenic acids and phenolic compounds - the most common oxygen-containing classes of compounds. Additionally, naphthenic acids and phenolic components have been reported as one of the corrosive substances in the refinery [6-7]. The presence of naphthenic acids and sulfur compounds significantly increase the corrosion in high temperature process parts during the distillation of petroleum [6]. Corrosive problems in refinery equipment arise during the treatment of highly acidic types of oil. Corrosion mainly affects transmission pipelines between preheating furnaces and atmospheric and vacuum distillation units. Naphthenic acids may cause corrosion problems at temperatures between 220°C and 350°C in production equipment, storage, and transport facilities [8]. In the refining process, even the presence of small quantities of naphthenic acids in crude oil can cause operational problems such as foam formation in different production units. Traditionally, naphthenic acids are defined as mono carboxylic acids, which comprise one or more saturated cyclic ring structures in their molecule. In addition, linear carboxylic acids often refer to the

naphthenic acid class [9]. One of the most important environmental pollutants is phenol and alkyl phenol derivatives. The concentration range of phenolic compounds, naturally occurring organic chemicals, in the process water worldwide ranges from 0.6 to 23 mg/L [10]. They also have their presence in wastewater from the petrochemical industry and oil refineries [11-17]. In addition to its highly corrosive property, the phenol is also a serious agent in the poisoning of the nervous system of the living organism. Phenol causes harmful side effects such as acidity in the mouth, diarrhea, disturbed vision, etc. It is a highly toxic and dangerous agent for aquatic fauna [18]. Naphthenic acids are highly toxic for a num-ber of organisms. Low molecular weight naphthenic acids, in petroleum sands, are the most significant ecological and toxic pollutants [19-20,44].

Sulfur compounds are the most discussed and undesirable components of petroleum prod-ucts during technological refining processes. In general, sulfur occurs in the form of hydrogen sulphide, organic sulphides, disulfides, polysulfides, benzothiophene, dibenzothiophene and their derivatives [21]. These compounds cause corrosion in refinery process equipment at tem-peratures of 230°C to 425°C [22]. Heterocyclic polysulfide species are found in petroleum wastewater, with concentrations of these substances reaching 41 mg/L [23-24].

In each case, identification of corrosion substances in refinery effluent is required and an assessment of the degree of their negative environmental and technological impact. To this end, it is necessary to identify low molecular weight naphthenic acids, phenolic, and cyclic polysulfide compounds in order to select appropriate measures for the protection of the tech-nological equipment against possible corrosive processes and for the protection of the envi-ronment.

The characterization and structural determination of naphthenic acids from various sources have been investigated using a wide range of diverse analytical techniques and tools. The apparatus used is exclusively based on chromatographic separation by gas chromatography (GC) or high performance liquid chromatography (HPLC) methods, followed by detection by electron impact (EI) or electrospray ionization mass spectrometry (ESI) [5,26-27]. The ionization technique used depends on its compatibility with chromatographic eluates and assembled de-tectors, which may be high or low resolution mass spectrometers. Alternative ionization tech-niques for the analysis of naphthenic acids include fast atom bombardment (FAB-MS, which is used to a minor extent) or, more commonly, atmospheric chemical ionization (APCI) or pho-toionization (APPI) [8-15]. Many approaches for characterization of naphthenic acids include liquid extraction and reprocessing or fractionation of naphthenic acids prior to analysis, meth-ods such as solid phase extraction (SPE), silver ion chromatography (Ag-Ion) or ion exchange chromatography (IE). Most steps include preparative gas chromatography and supercritical fluid extraction (SFE). Modern chromatographic techniques include multiple gas chromatog-raphy-mass spectrometry (GC×GC-MS), gas chromatography coupled with Fourier transfor-mation-ionic cyclotron resonance mass spectrometry (e.g., GC-APCI FT-ICR MS and GC-TQ FT-ICR MS), liquid chromatography (HPLC) or supercritical liquid chromatography (SFC) ion-trap mass spectrometry (HPLC-or SFC-Orbitrap MS). The wide range of techniques including basic mass spectrometry is summarized in the numerous reviews and reports published over the past decade [9,25,28-34,43].

Numerous studies have demonstrated the application of gas chromatography-mass spec-trometry and high performance liquid chromatography for the analysis of phenolic compounds in wastewater [8-12].

A number of publications describe applications of the gas chromatography method with the various selective detectors-mass selective detector, sulfur-selective detector, a flame-photometric detector for the analysis of a number of organic sulfur compounds [28-30].

Many of the different methods for identifying and characterizing naphthenic acids, phenolic, and cyclic polysulfide compounds have respective advantages and disadvantages, but there is currently no universal method covering both quantitative and qualitative study of these polar components. Various information about them from various sources related to various extrac-

tion and preparation procedures, derivatization methods, ionization techniques, chromatographic conditions, mass spectral parameters, and even data representation are all factors that affect the actual and final composition of naphthenic acids, phenolic and cyclic polysulfide compounds in refinery effluent [31-40].

In this project, gas chromatography-mass spectrometry is applied in the chemical characterization of organic matter in process waters originating from crude distillation units of LU-KOIL Neftohim Burgas refinery. These organic matters are identified as the oxygen-containing compound (naphthenic acids and phenols), and the sulfur-containing species mainly cyclic polysulfides. The objective of the current study was also to determine the organic matter contents. The distribution of organic compounds in the process waters indicates a possible health risk to aquatic organisms. Our work will provide a deeper understanding of the substance composition in process wastewater and a theoretical basis for their control and reused.

2. Experimental

2.1. Materials, extraction

Analytical grade standard of the phenol is obtained from Merck (Bulgaria). Commercial naphthenic acids technical grade (a mixture of alkylated cyclopentane carboxic acids) is obtained from Sigma Aldrich (Buchs, Switzerland). Dichloromethane is purchased from Merck and is Uvasol grade solvent. The extraction procedure is described in details previously [36-37].

2.2. Wastewater samples

Wastewater samples are gathered from the technological facilities of atmospheric-vacuum distillation unit of LUKOIL Neftohim Burgas AD (LNB), Bulgaria. Three-distillation process facilities operate in LNB: AD-4– an atmospheric distillation of crude oil, AVD-1 integrated atmospheric and vacuum distillation of crude oil and VDM-2–vacuum distillation of atmospheric residue. The wastewaters from these units generally have different origins.

2.3. Instrumentation

The gas chromatography–mass spectrometry (CG-MS) analyses are performed in an Agilent Technologies 7890A model gas chromatograph connected to a 5975C Inert XL EI/CI Agilent Technologies mass selective detector (Agilent Technologies, Inc., USA). GC-MS system equipped with HP PONA 50 length m × 0.2 mm id × 0.5 μm film thickness capillary column. The helium carrier gas is kept at a constant flow rate of 0.8 mL/min, and a 1.0 μL extract was injected into a split/splitless injector at typically temperature 300°C. Temperature prog-ramming of the column oven: 80°C and ramp with 6°C min^{-1} to 250°C. The ion source and transference line temperatures are 225°C and 250°C, respectively. An ionization energy 70 eV is employed with mass scanning from *m/z* 15 to *m/z* 450.

The components identification is based on comparisons of the retention times and by interpretation of the mass spectra obtained from the NBS/NIST library (NIST Mass Spectral Library, 2002).

3. Results and discussion

The main quantities of process waters are generated during technological processes of crude oil preparation (desalting and dewatering) and rectification with water steam for stripping. Small quantities of wastewater are generated by the residual amount of water remaining in the crude oil after desalting. In accordance with the best refinery practices, the wash water rate vs. crude oil feed flow-rate varies between 3% and 7% depending on the quality of the processed oil [38]. Higher salt content supposes higher wash water rates in order to remove salts effectively. Effluent wastewater stream from desalting and dewatering section (E-109) goes to the water treatment facilities.

The other main source of wastewater from straight-run distillation units is processed condensates that are generated from the overhead streams of the rectification towers (atmospheric and vacuum). In LNB, these are the preflash tower (K-101), the main fractionators of the

atmospheric distillation units (K-102), and vacuum towers from the vacuum distillation units (K-1 in the vacuum section in AVD-1 and K-101 in VDM-2). Often these water streams are called sour water condensates because of its lower pH and hydrogen sulphide content. The process condensate from the preflash tower is formed only by the residual amount of water remaining in the crude oil after desalting section.

The process condensate from the main fractionator is formed predominantly from the water steam, which is injected to the bottom of the tower and side stripers for extracting middle distillates in order to reduce the partial pressure of the hydrocarbons and to improve the separation processes. Depending on the throughput of the unit, striping steam flow-rate could vary, but the rate vs. crude oil remains about 2.5%.

Process condensates in VDM-2 unit have the same origin such as the condensates from the main fractionators–stripping water steam. At this vacuum distillation process unit, water steam is injected not only for stripping but also as a turbulizer in the furnace passes. Both streams leave the system such as a process condensate from the overhead condensers drum.

The organic matter in process waters originating from crude distillation units depends on the crude oil composition and the process of oil production. Generally, extracts obtained from the wastewater samples have chemical compositions that differ significantly from one another. The extracts investigated are exhibited a relative wide molecule weight range compounds. They are arranged according to their dominant contents in the samples. Identification of the corresponding compounds is summarized in Table 1.

Table 1. Concentration of organic matter in process waters originating from crude distillation units of LUKOIL Neftohim Burgas refinery

| | Molecular formula | Concentration, mg/L | | | | | | | |
| | | AVD-1 | | | AD-4 | | | VDM-1 | VDM-2 |
		E-101	E-102	E-109	E-101	E-102	E-109	E-3	E-103
Phenol	C_6H_6O	3.5	2.8	7.1	0.6	3.6	3.4	1.2	7.1
Phenol, 2-methyl-	C_7H_8O	< 0.05	5.8	2.5	0.5	5.8	4.4	5.7	17.1
Phenol, 4-methyl-	C_7H_8O	4.0	6.8	3.2	0.6	9.1	5.6	6.3	24.4
Phenol, 2,4-dimethyl-	$C_8H_{10}O$	0.6	0.9	0.8	0.1	0.9	1.6	0.5	1.9
Phenol, 2,5-dimethyl-	$C_8H_{10}O$	1.9	0.8	0.4	0.1	1.0	0.9	1.7	4.9
Phenol, 2,3-dimethyl-	$C_8H_{10}O$	0.9	1.8	0.9	< 0.05	3.0	1.5	7.5	12.0
Phenol, 3,4-dimethyl-	$C_8H_{10}O$	0.6	0.6	0.7	< 0.05	1.2	2.0	3.7	11.0
Phenol, 2,6-dimethyl-	$C_8H_{10}O$	0.7	0.8	0.6	< 0.05	2.0	2.6	5.2	3.8
Phenol, 4-ethyl-	$C_8H_{10}O$	0.5	< 0.05	0.3	< 0.05	0.9	1.7	2.1	3.2
3-Isopropylphenol	$C_9H_{12}O$	0.2	< 0.05	0.5	< 0.05	0.4	1.4	2.5	3.4
3-n-Propylphenol	$C_9H_{12}O$	0.8	< 0.05	1.2	< 0.05	0.1	1.7	1.2	3.0
Phenol, 2-ethyl-6-methyl-	$C_9H_{12}O$	0.4	< 0.05	1.4	< 0.05	< 0.05	3.0	1.9	2.1
Phenol, 2,4,6-trimethyl-	$C_9H_{12}O$	0.4	< 0.05	0.9	< 0.05	< 0.05	2.2	2.2	1.5
Phenol, 3,4,5-trimethyl-	$C_9H_{12}O$	0.12	< 0.05	1.1	< 0.05	< 0.05	3.5	5.0	3.7
Formic acid	CH_2O_2	100	50	1000	13.0	2.0	6.0	< 0.05	< 0.05
Acetic acid	$C_2H_4O_2$	240	310	1500	14.0	1.8	12.0	< 0.05	< 0.05
Propanoic acid	$C_3H_6O_2$	25	47	2500	8.5	5.0	7.5	< 0.05	< 0.05
Butanoic acid	$C_4H_8O_2$	10	12	3000	1.8	< 0.05	3.4	< 0.05	< 0.05
Acetic acid, phenylthio-	$C_8H_8O_2S$	0.2	< 0.05	0.7	0.1	0.2	0.5	1.8	2.0
Propanoic acid, 3-phenylthio-	$C_9H_{10}O_2S$	0.4	1.9	1.1	< 0.05	2.8	0.5	1.8	0.8
Methylene bis-thioglycolic acid	$C_5H_8O_4S_2$	< 0.05	2.1	1.6	< 0.05	2.2	5.6	< 0.05	1.3
4,4´-Dithiobis-butanoic acid	$C_8H_{14}O_4S_2$	< 0.05	0.2	0.2	< 0.05	0.3	< 0.05	< 0.05	< 0.05
1,2,4-Trithiolane	$C_2H_4S_3$	8.9	0.7	1.0	< 0.05	0.7	0.5	< 0.05	< 0.05
1,3,5-Trithiane[40]	$C_3H_6S_3$	3.2	3.6	0.6	0.3	0.4	3.1	1.0	< 0.05
2,4,5-Trithiohexane	$C_3H_6S_3$	6.6	< 0.05	0.5	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
1,2,4,5-Tetrathiane	$C_2H_4S_4$	1.7	0.7	0.7	0.1	< 0.05	< 0.05	1.7	< 0.05
1,2,4,6-Tetrathiepane	$C_3H_6S_4$	0.2	< 0.05	< 0.05	< 0.05	0.7	1.2	1.1	< 0.05
1,2,5,6-Tetrathiocane	$C_4H_8S_4$	0.6	< 0.05	1.7	< 0.05	< 0.05	0.6	< 0.05	< 0.05
1,3,5,7,9-Pentathiecane	$C_5H_{10}S_5$	3.0	< 0.05	< 0.05	0.1	0.1	2.0	2.1	< 0.05
Lenthionine	$C_2H_4S_5$	0.4	< 0.05	3.2	0.2	< 0.05	2.2	4.0	< 0.05

In the tested samples, numerous methyl-, dimethyl- and trimethyl-phenol isomers are identified. The spectra of phenol and methyl-phenols are assigned from the strong molecular ions m/z 94 and m/z 108, while the spectra of dimethyl and trimethyl-phenol isomers are characterized by ионя of m/z 107 and m/z 121 connected with the loss of the methyl group. 2,4-Dimethyl-phenol is considered as the compound responsible for carcinogenic influence [41]. In this research, only four phenolic compounds are determined in all of the sampling sites (Table 1) while the other compounds are with different concentration even they were below detectable limits. The levels of individual phenolic compounds in the wastewater of AVD-1, AD-4, VDM-1, and VDM-2 samples range from detection limits to 7.1 mg/L, detection limits to 9.1 mg/L, from 0.5 to 7.5 mg/L and from 1.5 to 24.4 mg/L, respectively. The results indicate maximum content 24.4 mg/L of 4-methyl-phenol in the wastewater sample collected from E-103, VDM-2. The wastewater sample of VDM-2 shows higher total phenol content (99.1 mg/L) than wastewater sample of VDM-1 (46.7 mg/L) and wastewater sample of E-102, AD-4 (28.8 mg/L). Compared with the data in the literature, the contents of total phenol compounds are higher than the ones observed in the previous studies [42].

Naphthenic acid species analysis in all wastewater samples indicate a generally most abundant. Examination of the quantitative data confirms the more abundant presence of the naphthenic acid species in the AVD-1 wastewater compared to the other tested wastewater samples (Table I). The data show the level of individual naphthenic acid species is ranged between below detection limits to 3000 mg/L. The levels of naphthenic acid species are in agreement with earlier report data [42,45]. The highest concentrations of naphthenic acid species measured are in the E-109, AVD-1 wastewater.

S-containing hydroxy acids are also present of oil sands process water [9,28]. Analysis of the mass spectrum of acetic acid, phenylthio- revels significant ions at m/z 123 (loss of carboxylic group), m/z 168 (molecule ion) and a smaller ion at m/z 45 (carboxylic group). The mass spectrum of propanoic acid, 3-phenylthio- also has significant ions at m/z 123, m/z 182 (molecule ion) and m/z 45. Analysis of the mass spectrum of methylene bis-thioglycolic acid reveal to have an ion $M^{+\bullet}$ at m/z 196, and other significant ions are confirming the cleavage of the main chain (m/z 77 sulphur-carboxylic group cleavage). The formation of the fragment ion m/z 105 is associated with β-cleavage with respect to the sulphur atom. The abundance of m/z 137 results from the loss of methyl-carboxylic groups, cleaved from the thioglycolic acid main chain. Analysis of the mass spectrum of 4,4´-dithiobis-butanoic acid reveals that the significant ions exist at m/z 45 (carboxylic group) and m/z 87 (loss of the carboxylic group and hydrocarbon main chain). The presence of the fragment ion at m/z 134 indicates that the Sulphur atoms are present in the alkyl main chain of the 4,4´-dithiobis-butanoic acid. Total naphthenic acid contents and S-containing hydroxy acids the values range from 3.6 mg/L to 8000 mg/L.

High sulphur content in crude oils results in the significant generation of sulphur species, which are major environmental pollutants. In the present investigation, the spectrum of the 1,3,5-trithiane is characterized by abundant molecular ion m/z 138 and dominated ions by a peak ion of m/z 46, m/z 45 and m/z 92 due to heterocycle cleavage of the cyclic trimer and in losses of a C-S group. 1,2,4-trithiolane is identified by interpretation of the mass spectrum. Major fragment ion is m/z 45, and larges fragment ions are m/z 78, m/z 46 and m/z 124. The result of the sulphur analysis indicates a generally high level of sulphur species in wastewaters. Table I summarizes the mean concentrations of sulphur species in the wastewater samples. The most abundant is 1,2,4-trithiolane in the wastewater of E-101, AVD-1 with a concentration of 8.9 mg/L, accounting for 36.2% of the total sulphur species. Interestingly, sulphur species in the wastewater E-103, VDM-2 sample are not detected. The levels of total sulphur species content vary between a minimum of detection limits and maximum 24.6 mg/L, and this the value is less in previous studies reported [23]. In comparison, the results obtained of the different sulphur species in the wastewater sample of E-101, AVD-1 are higher than those of the other wastewater samples investigated.

One way to display the similarities or differences between phase distributions of organic matter in process wastewaters is to construct certain types of plots, such as plots of the percentage concentration of different classes of compounds. The distribution of single compounds varied among different wastewater samples. As can be seen from Figure 1 naphthenic species (4.0-99.6%) are predominant in the wastewaters investigated, and this may be attributed to their higher solubility. It is clear that the proportion of phenolic species in the wastewater is found to range from 0.3 to 96.9%. The proportion of sulphur species is in the range 0.1 to 12.0%.
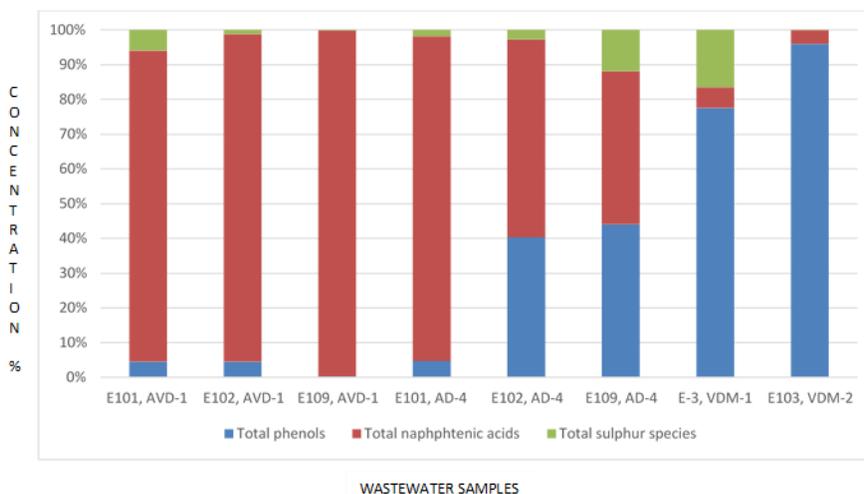

Figure 1. Composition of organic matter in process waters, originating from crude distillation units

4. Conclusion

By the use of gas chromatography-mass spectrometry the organic matter in process waters originating from crude distillation units are identified. The study herein shows the most abundant content of naphthenic acid species (alicyclic carboxylic acids) followed by phenolic compounds and polysulphur components.

By specifying organic matter contents, users can intake to describe the routing of water through the refinery or water can be additionally used before being assigned to one of the effluent streams.

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