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Distribution and Identification of Some Sulfur Compounds in Rasco Light Gas Oil (Diesel Oil)

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Abstract: Sulfur compounds play an important factor in the specification of diesel oils. The identification of these compounds and their distribution in light gas oil (LGO) cut give useful information for refinery operation, production and instillation of hydrodesulphurization unit. In this study the isolation and characterization of sulfur compounds (0.043 wt %) in LGO produced by Ras Lanuf refinery (RASCO) were carried out. The LGO fraction was distilled from Messla + Sarir crude oil mixture at RASCO toping unit of temperature ranging from 200 to 340°C. LGO cut was separated into three fractions by atmospheric distillation (ASTM D86). The LGO fractions [F1 205-250 °C], [F2 250-290 °C], and [F3 290-336 °C] were fractionated by column chromatography in order to isolate the respective aromatic fraction and thiophenic compounds. Sulfur compounds in LGO fractions were characterized and identified by Gas chromatography mass spectrometry (GC-MS).

INTRODUCTION

Sulfur compounds play an important factor in the specification of diesel oils. A number of workers have successfully isolated sulfur compounds from petroleum by controlled oxidation of the sulfur compounds to sulfoxid with hydrogen peroxide[1]. The use of novel separation and analysis techniques (such as gas chromatography-mass spectrometry (GC-MS), high resolution gas chromatography, *etc*.) allowed recognition of several new classes of sulfur containing compounds [2-12].

The identification of these compounds and their distribution in light gas oil (LGO) cut give useful information for refinery operation, production and instillation of hydrodesulphurization unit. The organic sulfur exists either in aromatic rings or in aliphatic functional groups, usually categorized as mercaptans, aliphatic and aryl sulphides, disulfides and thiophenes[13]. Most thiol and disulfiedes decompose under 450 ^{0}C, alkyl-and aryl-sulfides lose H_2S between 440 and 630 ^{0}C and thiophenes lose H_2S above 600 ^{0}C[14, 15, 16].

Heteroatom organic compounds like sulfides, mercaptanes, thiophenes, pyrrols and indanes are known to be carcinogenic and mutagenic to animals and humans. Therefore, their presence in petroleum based products raises a health issue. In recent years, allowable sulfur levels in transportation fuels have been drastically lowered by many countries to combat air pollution. So the characterization of sulfur compounds in LGO has been and still is a major topic of interest, both from the point of view of environmental concerns with respect to the application of sulfur-rich petroleum fuels and their chemical significance. Different sulfur compounds have different structures and properties, which cause difficulties in the development of desulphurization technology. The knowledge of desulphurization reactants and products is useful for the optimization of sulfur removal processes. Therefore, analysis of sulfur compounds, especially the characterization of individual sulfur compounds in light gas oil, is fundamental for the production of ultra-low sulfur content diesel.

In this study the isolation and characterization of sulfur compounds (0.043 wt. %) in LGO produced by Ras Lanuf refinery (RASCO) were carried out. LGO cut was separated into three fractions by atmospheric distillation (ASTM D86). The LGO fractions [F1 205-250 ^{0}C], [F2 250-290 ^{0}C], and [F3 290-336 ^{0}C] were fractionated by column chromatography in order to isolate the respective aromatic fractions and thiophenic compounds. The sulfur compounds in LGO fractions were Characterized and identified by Gas Chromatography-Mass Spectrometry (GC-MS).

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EXPERIMENTAL AND RESULTS

The RASCO LGO cut was collected from refinery on 19-5-2006; Table (1) shows some physical properties of LGO. It was further separated by atmospheric distillation (ASTM D86) into three new fractions named LGOF1 (205-250^{0}C), LGOF2 (250-290^{0}C) and LGOF3 (290-336^{0}C). The four samples LGO, LGOF1, LGOF2 and LGOF3 were fractionated by column chromatography (CC), (Fig. 1), to isolate the respective aromatic fractions (LGOA, LGOF1A, LGOF2A and LGOF3A) and thiophenic compounds (LGOT, LGOF1T, LGOF2T and LGOF3T).

The chromatography was performed by diluting 5 g of LGO fraction in n-hexane and introducing the sample at the top of a 32 ×2.6 cm^2 (i.d) column packed with 100 g of silica gel (60-120 mesh, particle size 0.13-0.25 mm), which was previously activated for 12 h at 200 ^{0}C. Saturated compounds were eluted with 250 ml of n-hexane. The aromatic compounds were eluted with 250 ml of toluene. The UV- VIS spectrum (at 239 nm wavelength) of the hexane fraction confirmed that no aromatics were eluted with the saturated compounds. A second CC was carried out in a column packed with 110 g of SiO_2/Al_2O_3 (25/20, w/w) and performed for the previously concentrated aromatic fraction. The sample was eluted first with 250 ml of hexane to extract the possible remaining saturated compounds from the previous separation stage.

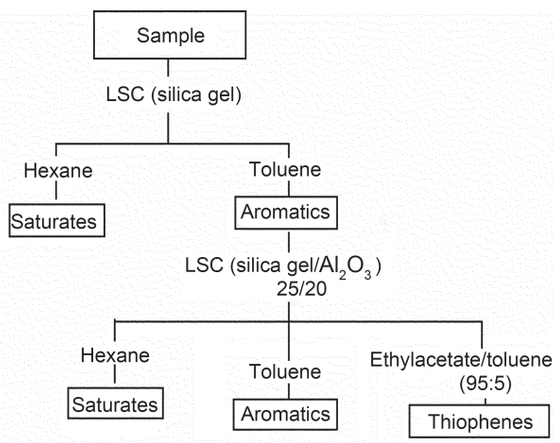


Fig. 1. Fractionating scheme for thiophenic compounds separation by CC.

The remaining aromatic compounds were eluted with 200 ml of toluene while the thiophenes were eluted with 250 ml of ethyl acetate/toluene (95:5) mixture[17] . All the fractions were evaporated to reduce the volume to about 1 ml.

Gas Chromatography-Mass Spectrometric (GC-MS) Analsis

The samples were injected into GC part (30 mm 0.25 mm id, 0.25 df, capillary column), held for 2 min at 80 ^{0}C, programmed at 2 ^{0}C / min to 160 ^{0}C, then programmed at 8 ^{0}C / min to 180 ^{0}C, where it is held for 20 min., the injector temperature was set at 100^{0}C, the split flow was at 100 ml/ min, mode CT splitless, the carrier gas was helium at constant flow rate of 1 ml/min, MS transfer line at 250 ^{0}C, ion source at 250 ^{0}C; 70 ev ionizing voltage, full scan (40-400) mass range.

The Distribution of the Sulfur Compounds in RASCO LGO

The distribution of the sulfur compounds in LGO were studied in the RASCO laboratory by distillation of LGO into three small fractions ranging between IBP 205 ^{0}C and FBP 336^{0}C of LGO (Fig. 2). The total sulfur content (weight %) of the fractions was obtained by an x-ray fluorescence method (ASTM-D2494).

Table 1. Physical properties of RASCO Light Gas Oil (LGO).

Method	Test	Unit	Result
ASTM D.1298	Specific gravity @15.6 ^{0}C	/	0.8185
ASTM D.1298	Density @15 ^{0}C	Kg/lit	0.8181
ASTM D.1298	API gravity	/	41.38
ASTM D.4294	Total sulfur	wt %	0.043
ASTM D.86	Distillation:- I.B.P F.B.P	^{0}C	 205 336
ASTM D.445	Viscosity at 37.8 ^{0}C	Cst	3.10
ASTM D.97	Pour point	^{0}C	-9
ASTM D.93	Flash point	^{0}C	86

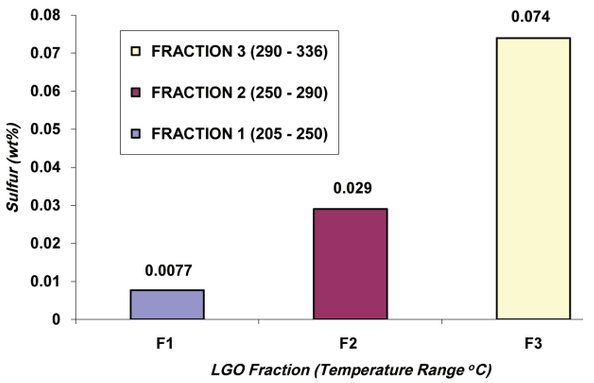


Fig. 2. The total weight % of sulfur compounds in LGO fractions.

DISCUSSION

Distribution of Sulfur in RASCO LGO

The high content of sulfur in the fuels is the main source for the air pollution. This forces the countries to set limitations for the total sulfur in the oil fractions specially diesel fuel. The recommended total sulfur in the diesel fuel for the European Countries in year 2009 is 10 ppm[18]. Figure 2 shows that the distribution of sulfur content is not linear, that means the amount of sulfur does not decrease gradually by decreasing the final boiling point of the fraction. Sulfur compounds may condense more in a specific boiling range of the fraction compared to other fraction of the same LGO cut, depending on the chemical composition of sulfur compounds and its boiling point temperature. Furthermore the percentage of some sulfur compounds increase with increasing the boiling point of the fraction which is depends on the type of crude oil. For example in sulphide and thiophene oils, the sulfur content increases with increasing boiling point of the fraction. In mercaptan oils the total sulfur content decreases with increasing boiling point of the fractions and dependent mainly on the thermal stability of the mercaptan compounds.

Identification of Sulfur Compounds in RASCO LGO

The GC-MS technique was used to identify all the sulfur compounds in LGO fractions Table 2. The sulfur compounds obtained was corresponding to Benzothiophene, alkyl Benzothiophene, dibenzothiophene, alkyl dibenzothiophene, thioxanthene and dimethylnaphtho [2,3-b]thiophene (Fig. 3). Because there were no available sulfur standards, we identified these compounds by two ways:

a) By comparing the mass spectra of the peaks

Table 2. Sulfur compounds identified in LGO cut.

Peak no.[a]	Molecular mass and major fragments[b]	Possible identity
A	176(70),161(100),159(35),128(15),115(15)	2,5,7-tri-methyl-benzo[b]thiophene
B	184(100), 152(15),139(20)	Dibenzothiophene
C,D	198 (100),197(50), 165(5),152(5),99(10)	Methyldibenzothiophene (2isomers)
E	198 (60),197(100), 165(15),152(10),99(5)	Thioxanthene
F,G,K	212(100), 211(50),197(15),105(35)	dimethyldibenzothiophene(3isomers)
H,L	212(100), 211(35),197(30),106(10)	dimethylnaphtho[2,3-b]thiophene(2isomers)
I	149(100),148(61),122(19), 104(18),77(15)	4-methylthieno[2,3-b] pyridine
J	149(100),148(25), 122 (10), 96(10), 77(5)	5-methylthieno[3,2-b] pyridine

[a] In Figure 3, [b] Figures in parentheses denote relative abundances in mass spectrum.

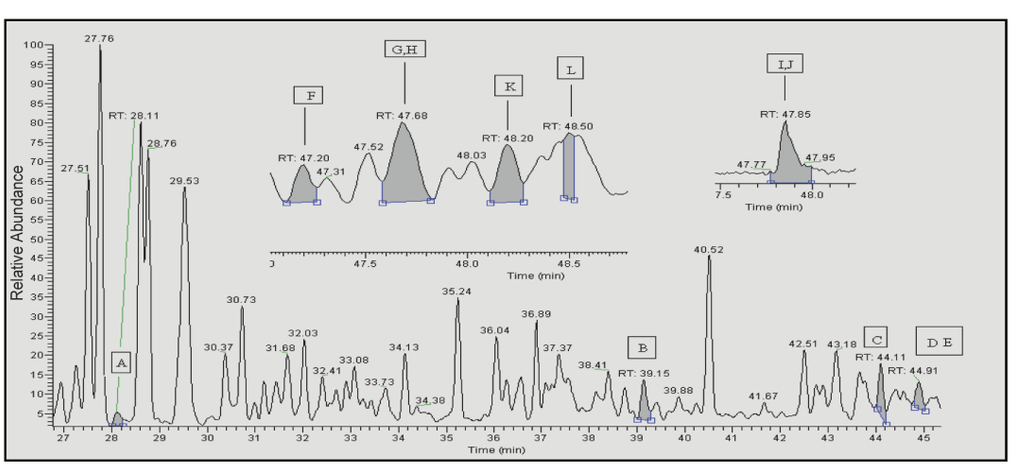


Fig. 3. Gas chromatographic and mass spectrometric data of LGO cut.

present in molecular ion mass fragmentograms with those of reference data (computerized library search) and characteristic fragmentation rules of thiophenic compounds [19,20,21,22] .

b) By using the chromatographically relationships between the retention time and the molecule weight for these compounds and their boiling points.

Fraction 1 (205-250 ^{0}C), contained 0.0077 wt% sulfur, which by GC-MS appears as 4-methylthino [2, 3-b] pyridine and 5- methylthino [3, 2-b] pyridine, while in fraction 2 (250-290 ^{0}C), 0.029 wt% sulfur, the major sulfur compound identified ,was dibenzothiophene and in addition to traces of methyl dibenzothiophene, di-methyldibenzothiophene.

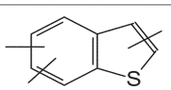
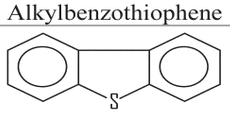
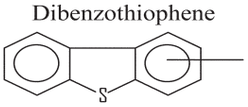
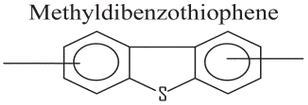
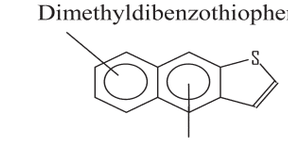
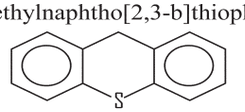
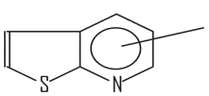
The sulfur content (0.074 wt.%) in fraction 3 (290-336^{0}C), appears as methyldibenzothiophene, dimethylbenzothiophene, thioxanthene, naphtho[2,3,b] thiophe-ne-dimethyl.

Benzo and dibenzothiophenes is the major compound present in the LGO, Table 3. Benzothiophenes and thiophenonaphthalenes would be easier to hydrodesulfurize than dibenzothiophenes. The large increase in alkylbenzenes in the product probably results from the hydrodesulfrurization of benzothiophenes. Similarly, the increase in the Tetralin and indane category may be a reflection of the hydrodesulfurization of dibenzothiophenes to yield a series of cyclohexylbenzenes which would contribute to this category. A dibenzothiophene desulfurization mechanisum to yield biphenyl, as some Russian works have claimed, would cause an increase in the acenaphthenes category[1].

CONCLUSIONS

The distribution of sulfur in distillates fractions of crude oil increases or decrease depending on the boiling point and the type of sulfur compound found in the crude oil. Benthothiophenes, dibenzothiophene, naphthanothiophenes and their alkyl analogous are major sulfur compound present in RASCO LGO.

Table 3. Probable Structures of Major and Minor Sulfur Compounds Represented by Significant Mass Series for LGO.

Empirical formula	Estimated percentage	Probable structures
$C_nH_{2n-10}S$	Minor	 Alkylbenzothiophene
	Minor	 Dibenzothiophene
	Minor	 Methyldibenzothiophene
	Major	 Dimethyldibenzothiophene
	Major	 Dimethylnaphtho[2,3-b]thiophene
	Minor	 Thioxanthene
$C_nH_{2n-9}SN$	Minor	 Methylthieno[2,3-b]pyridine

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