



ORIGINAL ARTICLE

Sulfur speciation of Kuwaiti crude oils fractions using two-dimensional gas chromatography



Hassan Al-Rabiah*, Latifa Al-Ostad, Tahani Al-Shamary, Abdullwahab Al-Hendi, Hisham Al-Henayyan, Roaya Khazemi

Petroleum Research Center, Kuwait Institute for Scientific Research, Kuwait

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Abstract The main objective of this study is to develop a methodology for sulfur compounds speciation using two-dimensional gas chromatography coupled with a flame ionization detector and sulfur chemiluminescence detectors. The methodology enhances the ability to detect and quantify the refractory sulfur in petroleum distillates, and it was utilized to screen the molecular differences between distillates of two Kuwaiti heavy crude oils from different reservoirs but with similar physical properties. Despite the similarity in the physical properties, the detailed comparative analysis indicated significant differences in molecular composition, which suggests substantial differences in crude oil processability based on the reactivity of the detected compounds. The distillates that have been considered in this study include heavy naphtha, kerosene, and gas oil. The compositional differences between the distillates were observed using the two-dimensional gas chromatography system with an in-house developed method. This method groups the sulfur compounds into thiols, benzothiophenes (BTs), and dibenzothiophene (DBTs), and it can handle any atmospheric distillate up to 365 °C. Furthermore, the method includes the possibility of identifying and quantifying a total number of 44 sulfur species, which covers the previously mentioned sulfur groups.

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1. Introduction

Crude oils are playing an essential role in securing the world's growing needs for fuels and petroleum products. Heavy crude

* Corresponding author at: Petroleum Research Center, Kuwait Institute for Scientific Research, P.O. Box 24885, 13109 Safat, Kuwait.
E-mail address: hrabiah@kisir.edu.kw (H. Al-Rabiah).

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oils are expected to play an essential role in securing the world's growing demand for energy in the near future, considering the depletion of conventional light crude oils and the increase in demand for petroleum products. Variation in refinery feedstock specifications can result in difficulties in refining processes, which consequently affect the consistency of product quality. Therefore, the refiners should not only rely on crude oil basic properties, such as API gravity and total sulfur, but rather on advanced characterization. This advanced characterization of crude oils will give an in-depth compositional information to understand the chemistry of the crude oil and its impact on the refining processes. Sulfur content in the

feedstock is an important criterion for selecting the most suitable refining process and operating parameters. However, the total sulfur content might be a misleading element since the refractory nature, and the reactivity of the sulfuric compounds differs significantly between crude oils. Some sulfur compounds are very reactive, while others are more stable or even inert towards catalytic reactions. Thus, it is essential, from the processor point of view, to identify and quantify the different species of sulfur that exists in various petroleum fractions and to understand their impact on catalytic processes. Such detailed information on sulfur species in feedstock can substantially improve the desulfurization processes in terms of catalyst selection and operating parameters. Furthermore, the understanding of the chemical nature of the sulfur compounds can also help in assessing the corrosive nature of crude oils, which can help in selecting the proper preventive measures to mitigate the risk of corrosion in both up and down-stream industries (Pollo et al., 2018).

There are many techniques to measure sulfur in petroleum products. Some methods can be used to determine the total sulfur concentration (ASTM-D2622, 2016; ASTM-D4294, 2016; ASTM-D5453, 2019) while other methods are able to analyze the sulfur compounds as chemical groups (UOP163, 2010). Moreover, some methods can further identify individual sulfur compounds, which require a reasonable degree of separation with efficient detection. Individual sulfur compounds can be analyzed by different techniques (Han et al., 2018) such as High Performance Liquid Chromatography (Beens and Tijssen, 1997; Panda et al., 2019), single dimensional Gas Chromatography (1D-GC) with nonselective detectors (Hegazi and Andersson, 2007; Nishioka et al., 1986a; Zhao, 2007) or with sulfur-selective detector (Andari et al., 1996; Andersson and Schmid, 1995; ASTM-D5623, 2019; Chawla and Di Sanzo, 1992; Moustafa and Andersson, 2011; Nishioka, 1988; Nishioka et al., 1986a; Nishioka et al., 1986b). Nevertheless, each of the previously stated methods has its limitations in term of its ability to separate the ever-increasing number of sulfur compounds as the sample boiling range increases. To effectively resolve this difficulty, a more efficient sulfur speciation methodology is needed. Comprehensive two-dimensional Gas Chromatography (GCxGC) methodology achieved an excellent multidimensional partition resulting in superior resolution and improved sensitivity. Hydrocarbons in petroleum streams have been efficiently analyzed using GCxGC with a flame ionization detector (FID) (Blomberg et al., 1997; von Muhlen et al., 2006). Similar approach was used to investigate the sulfur-containing compounds in petroleum distillates using GCxGC with Sulfur Chemiluminescence Detectors (SCD) (Chawla and Di Sanzo, 1992; Gieleciak et al., 2016; Hua et al., 2003, 2004; Ruiz et al., 2006; Wang et al., 2003). SCD selectivity towards sulfur compound helps in resolving the problems associated with detecting co-eluted hydrocarbon compounds in petroleum product analysis (Dijkmans et al., 2015).

In this study, a GCxGC system equipped with both FID and SCD detectors in series were used to further enhance the ability to analyze petroleum products, in term resolution, sensitivity, and selectivity. The GCxGC/FID-SCD arrangement has the ability to overcome the difficulties associated with co-eluting unresolved sulfur peaks in petroleum distillates (Beens et al., 2000; Bertsch, 1999, 2000). In this work, an in-house developed analytical procedure for GCxGC/FID-SCD

has been used to identify and quantify the nature of sulfur species in Kuwaiti heavy crude oil distillates. The sulfur compounds in the developed method were categorized as groups that include thiols, benzothiophenes (BTs), and dibenzothiophenes (DBTs). This method can be used to analyze sulfur species in distillates on a molecular level, which is essential for downstream desulfurization processes.

2. Experiments

2.1. Sample preparation

Samples from two Kuwaiti heavy crude oils, namely Lower Fars and Eocene, were analyzed for their physico-chemical properties. The general properties and compositions of the two crude oils are shown in Table 1. The analysis clearly indicates that the two heavy crude oils have very comparable physico-chemical properties. The two Kuwaiti heavy crude oils were distilled using a 30 L capacity distillation unit from Gecil Process with a 15 theoretical plates column working with a 5:1 reflux ratio. All distillation process temperature control and other operation parameters were computerized according to (ASTM-D2892, 2018). The atmospheric distillation method involves several steps to collect the following fractions: Gases up to butane; Light Naphtha (LN; IBP-80 °C); Heavy Naphtha (HN; 80–180 °C); Kerosene (Kero; 180–240 °C); Gas Oil (GO; 240–355 °C) and Atmospheric Residue (AR; +355 °C). The collected liquid fractions were analyzed for their composition and physico-chemical properties, as shown in Table 2. The current study mainly focuses on three fractions, namely, heavy naphtha, kerosene, and gas oil. The light naphtha cannot be analyzed due to limitations in ZX2 – Closed Cycle Refrigerated Loop Modulator, which is only capable of analyzing C7+. The atmospheric residue, on the other hand, is too heavy to be processed by the GCxGC system.

2.2. Two-dimensional gas chromatograph system

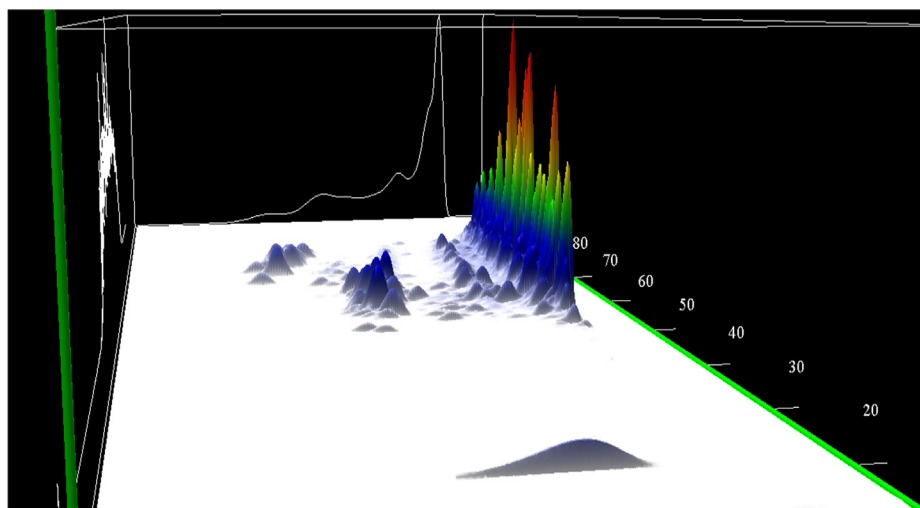
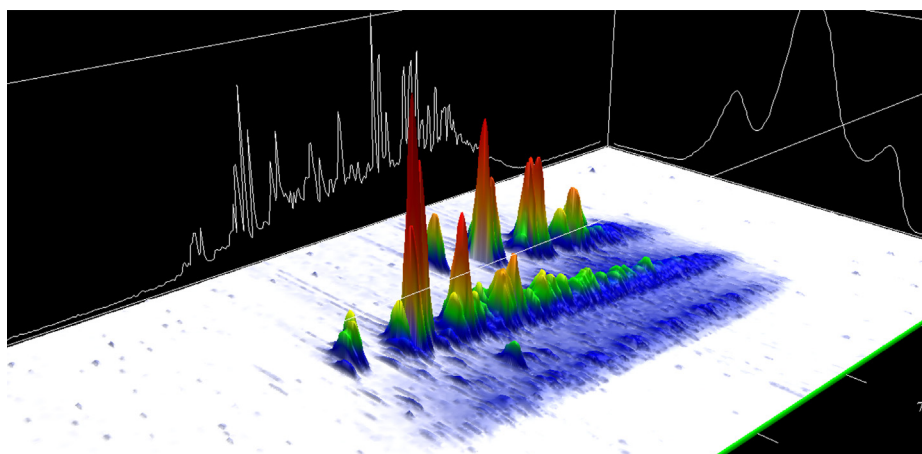
GCxGC system was used to analyze and identify the sulfur species in three distilled fractions. The Comprehensive GCxGC system from Agilent model number 7890 GC with ZX2 – Closed Cycle Refrigerated jet cooled loop thermal

Table 1 Physico-chemical properties of crude oils.

Parameter	Reference no.	Lower fares	Eocene
Density at 15 °C, g/ml	D5002/IP365	0.9643	0.9632
Gravity, °API	D1250/IP200	15.09	15.25
Elemental Composition,	D5291		
Sulfur, % wt	D4294	5.05	4.82
Nitrogen, ppmw	D5762	1562	1541
Acid number, mgKOH/g	D664/IP177	1.03	0.26
Micro carbon residue, % wt	D4530	10.6	11.8
Asphaltenes, % wt	Cosmo Analyzer	5.3	7.0
Metals,	D5708		
Nickel, mg/kg		0.55	0.50
Vanadium, mg/kg		113.26	61.03

Table 2 Physico-chemical properties of distillates.

Parameter	LN		HN		Kero		GO		AR	
	LF	EOC	LF	EOC	LF	EOC	LF	EOC	LF	EOC
Yield % wt	2.11	1.80	6.57	5.61	7.59	5.59	8.32	15.04	74.91	71.81
Yield % vol.	3.14	2.63	8.65	7.30	9.09	6.79	9.31	17.13	73.15	71.45
Density at 15 °C D4052 g/ml	0.6725	0.6836	0.7598	0.7685	0.8357	0.8232	0.8938	0.8781	1.024	1.005
Gravity D1250 °API	78.70	75.28	54.55	52.44	37.65	40.20	26.65	29.48	6.54	9.09
Sulfur D5453 ppmw	159	284	1362	1822	5982	3517	21,223	15,636	44,309	36,822

**Fig. 1** 3D-Chromatogram of hydrocarbon distribution in gas oil sample using GCxGC-FID.**Fig. 2** 3D-Chromatogram of sulfur compounds distribution in gas oil sample using GCxGC-SCD.

modulator from Zoex/JSB was used for the compositional analysis of samples using an in-house developed method. The chromatographic data were acquired using OpenLab software from Agilent. The acquired chromatographic data were transformed into 3-D dimensional chromatograms using GCImage software from Zoex Corporation. Fig. 1 is a 3-D representation of hydrocarbon distribution in gas oil sample, showing the concentrations of the different hydrocarbon com-

pounds. Similarly Fig. 2 illustrates the 3D-Chromatogram of sulfur compounds distribution in gas oil sample. Both figures demonstrate the ability of the method to separate the molecules of complex petroleum fraction and clearly showing the difference's in their concentrations. The data analysis and quantitation were processed using GC project software from Zoex Corporation. The main column was Restek, Rxi-5Sil MS, low polarity phase; Crossbond 1,4-bis(dimethylsiloxy)

Table 3 Operational conditions for GCxGC system.

Injection volume	0.1 μ L (neat samples)
Inlet mode	Split 50:1
Carrier gas type	Hydrogen
Column gas flow	0.75 ml/min in constant flow mode
Inlet temperature program	300 °C Hold 0.05 min Ramp 1: @ 250 °C/min to 400 °C. Hold 0.4 min Ramp 2: 50 °C/min to 250 °C Hold to the end of the run.
Temperature program for the main oven (non-polar column)	Initial temperature: 40 °C Hold 5 min Ramp 1: 2 °C/min to 60 °C. Hold 0.1 min Ramp 2: 3 °C/min to 300 °C Hold to the end
Temperature program for the secondary oven (polar column)	Initial temperature: 45 °C Hold 5 min Ramp 1: 2.5 °C/min to 60 °C. Hold 0.1 min Ramp 2: 3.2 °C/min to 320 °C Hold to the end
Hot jet temperature program	Initial temperature: 250 °C Hold 1 min Ramp: 4 °C/min to 400 °C. Hold to the end Hot jet duration: 500 ms
Cold jet flow	12 L/min
Modulation time	6.5 s

phenylene dimethyl polysiloxane, length 30 m, 0.25 mm ID, 0.25 μ m Film (non-polar column). The Secondary column was SGE, BPX50, polar 50% Phenyl Polysilphenylene-, length 2.7 m, 0.1 mm ID, 0.1 μ m Film (polar column). The columns were connected to two detectors in series; flame ionization detector and Agilent sulfur chemiluminescence detector model 355. Individual neat sulfur compounds from PASH standard solutions and Sigma-Aldrich were used to create sulfur compounds template. The standard sulfur samples were selected to cover thiols, sulfides, disulfides, thiophenes, benzothiophenes, and dibenzothiophenes groups. The sulfur standards were diluted in toluene to prepare calibration standards of 1 ppm, 10 ppm, 100 ppm, and 1000 ppm. The diluted standards were analyzed according to ASTM D5453 to verify their sulfur concentrations. A certified single hydrocarbon standards and multi concentration hydrocarbon premix standards from Chiron, and AccuStandard, covering paraffins,

monoaromatics, di-aromatics, tri-aromatics, were used to create the hydrocarbon template. The developed method for this study applied the conditions indicated in Table 3.

3. Results and discussion

3.1. Method development

The molecular analysis of distillates was carried out using a comprehensive GC \times GC system, equipped with a non-polar column followed by a polar column. The usage of two columns led to a substantial improvement in peak capacity of chromatographic separation, where the 1st dimension separation (non-polar column) is based on the molecular size of hydrocarbon (i.e., boiling point) while the 2nd dimension separation (polar column) is based on polarity (i.e., chemical groups).

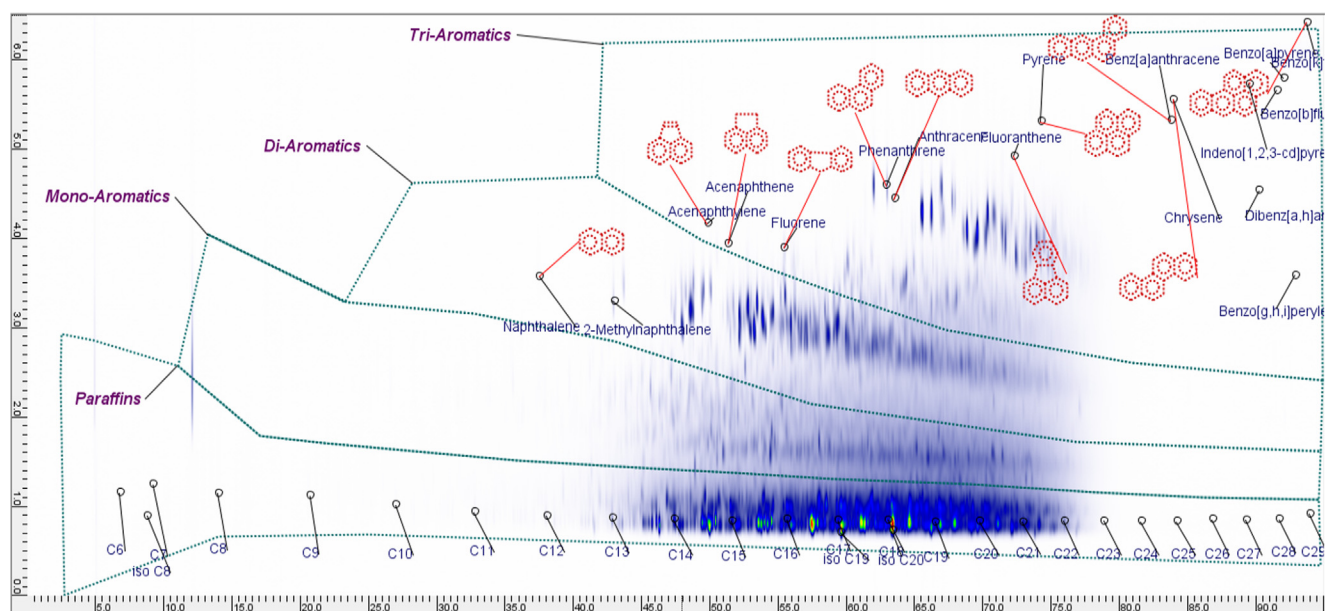


Fig. 3 Distribution template of hydrocarbon groups for gas oil sample using the GCxGC-FID.

The operating conditions of the system were optimized using the approached reported by Mostafa et al. (2012) to obtain the best possible chromatographic separation on the two dimensions of the chromatogram. The standard sulfur and hydrocarbon materials were injected individually to create the analytical templates. The multi-level concentration standards injections were used to measure the equimolar response from the respective detector.

Fig. 3 illustrates the identification template for hydrocarbon compounds and groups, while Fig. 4 represents the identification template of sulfur compounds and groups. The ability of the sulfur identification template is exemplified in Fig. 5, which is a zoomed view on the DBTs of Fig. 4. The ana-

lytical template, system configuration file, chromatograms of the standards, and chromatograms of crude oil fractions samples were processed and analyzed as a batch using GC Project software to create the quantity table based on the volume of their respective peaks. The total amount of detectable sulfur compounds was verified using ASTM D5453.

3.2. Application of the developed methodology on crude oil distillates

The developed method was utilized to compare the distillate fractions of Lower Fars and Eocene. Fig. 6 illustrates the hydrocarbon group distribution in the crude oil distillates,

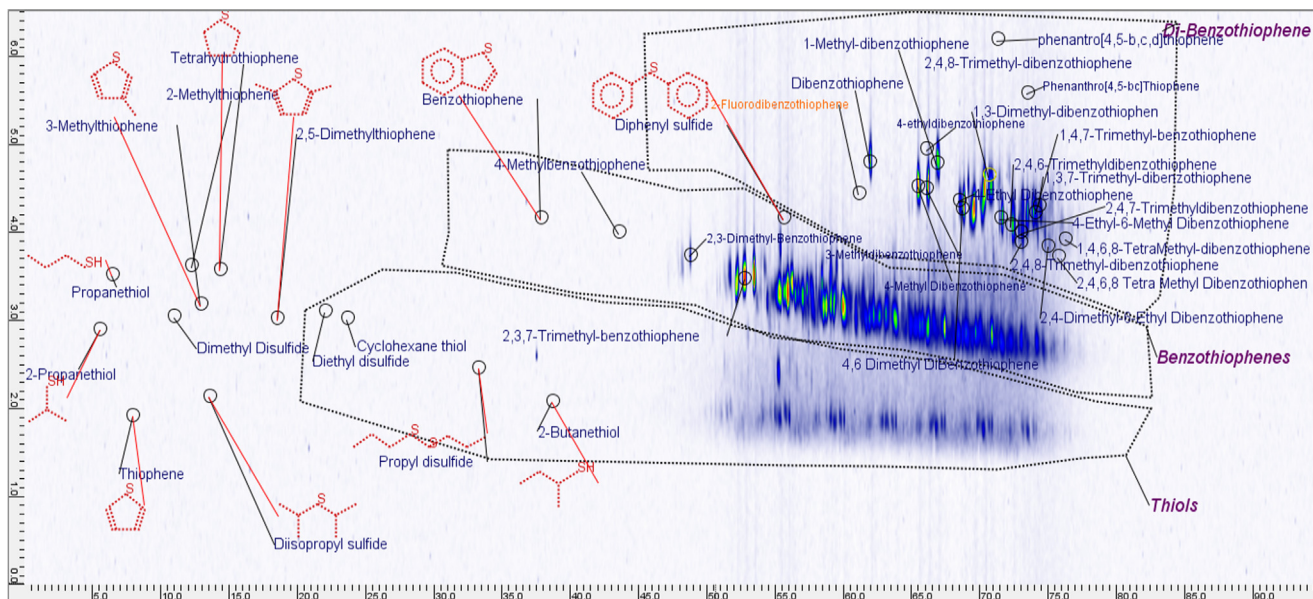


Fig. 4 Distribution template of sulfur groups for gas oil sample using GCxGC-SCD.

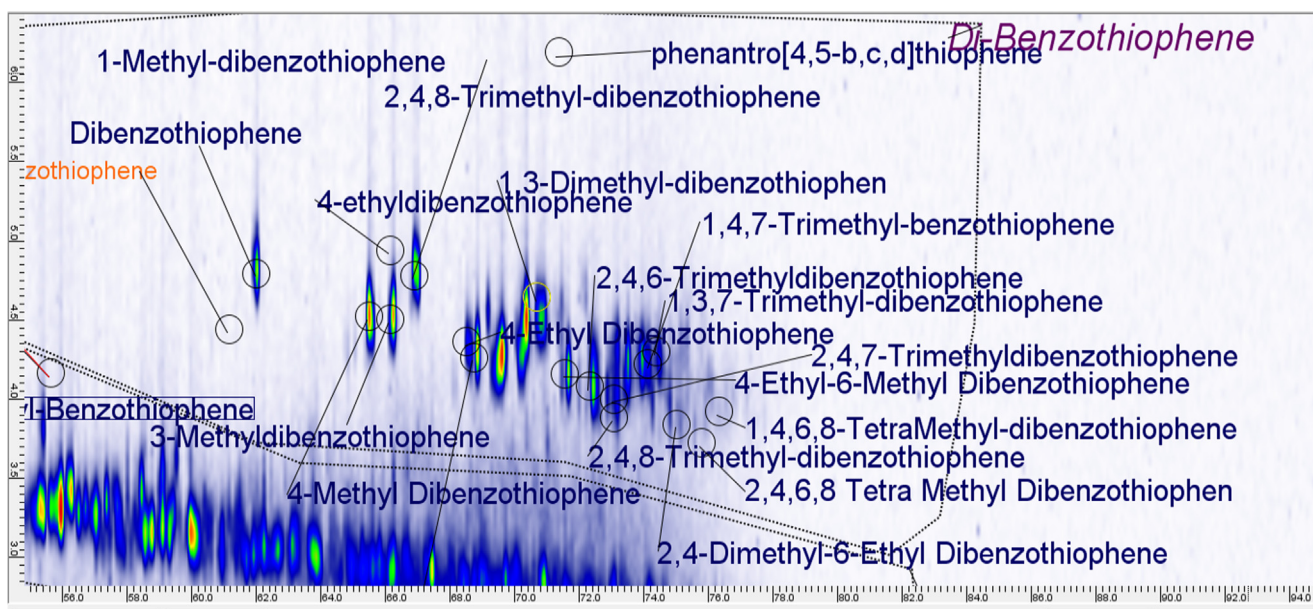


Fig. 5 Zoomed view on the dibenzothiophenes sulfur compounds from Fig. 2.

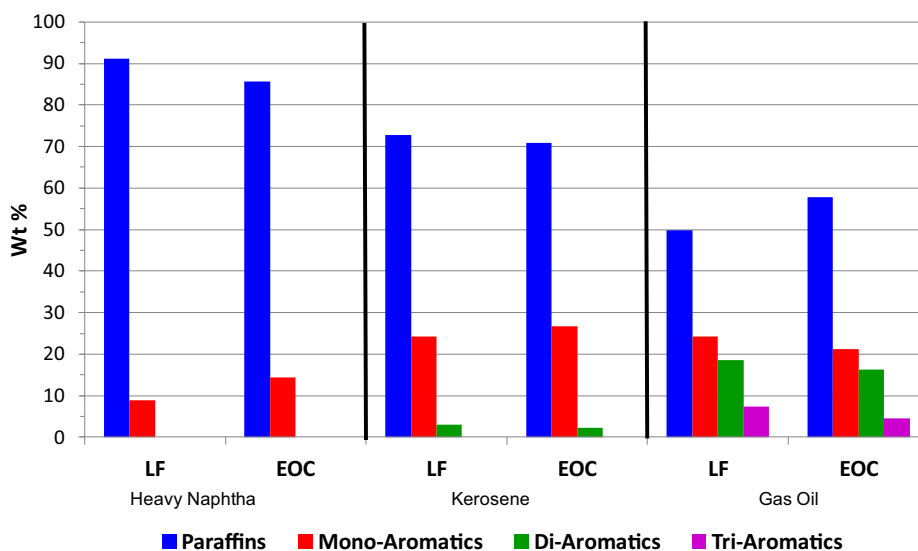


Fig. 6 Hydrocarbon groups distribution of crude oil distillates.

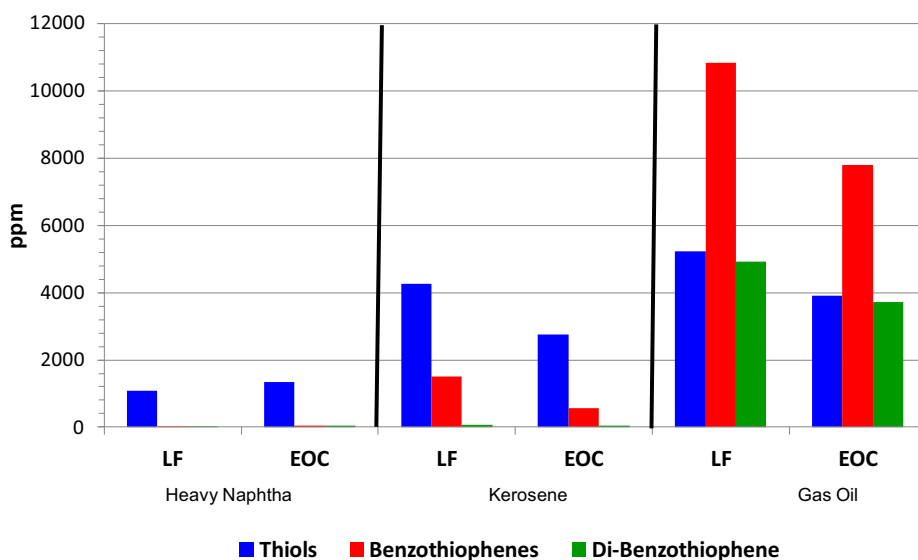


Fig. 7 Sulfur compound groups distribution in two Kuwaiti crude oil fractions.

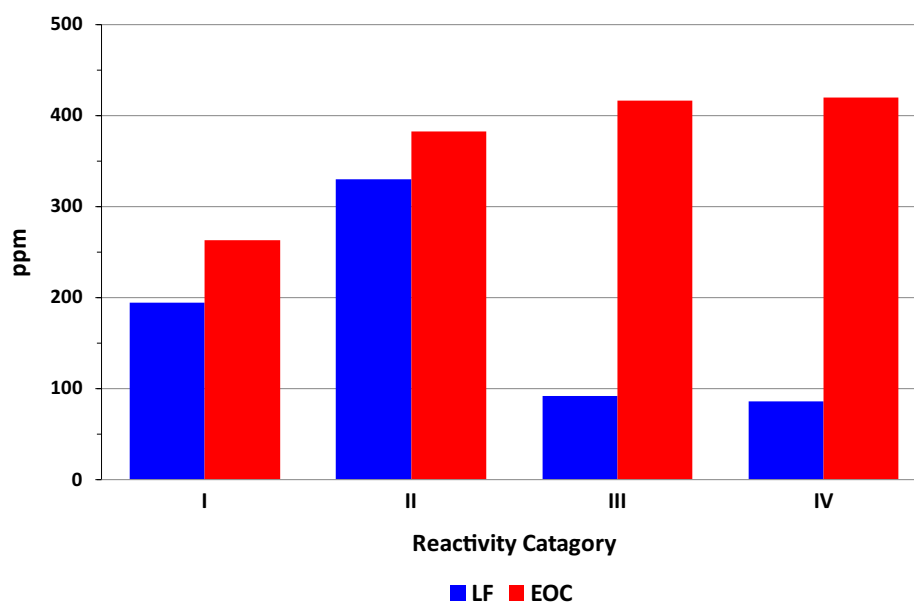
while Fig. 7 shows the distribution of sulfur groups in the same respective fractions. Fig. 6 suggests that the kerosene fractions from both crudes were very comparable in terms of hydrocarbon composition, whereas the heavy naphtha from Lower Fars is more paraffinic than that of Eocene. Conversely, the gas oil fraction of Lower Fars is more aromatic compared to the one obtained from Eocene. The sulfur group distribution (Fig. 7), on the other hand, indicates that the naphtha fractions from both crudes oils only contain thiols, where no detection of BTs and DBTs was noted. This finding is expected for the naphtha fraction considering its low boiling range. The comparison between the kerosene fractions clearly shows that Lower Fars kerosene has much higher thiols and BTs than the one obtained from Eocene. Similarly, the gas oil fraction from Lower Fars has more thiols, BTs, and DBTs than the gas oil from Eocene. In spite of that, the detailed analysis for sulfur species shows that Eocene gas oil has higher concen-

trations of refractory sulfur compounds than Lower Fars gas oil, which will be thoroughly discussed in the following paragraph.

The gas oil fraction is a complex mixture of hydrocarbon that contains various sulfur compounds with different reactivity. Those sulfur compounds are usually removed from gas oil to meet the environmental regulations through refining processes such as hydrodesulfurization (HDS). The HDS reactivity of various sulfur compounds in gas oil was investigated by Ma et al. (1994). They thoroughly examined the HDS reactivities of BTs and DBTs and classified the sulfur compounds in diesel into four categories. The first category has most of the alkyl BTs, whereas the second category contains the DBT and alkyl DBT without substituents at the 4- and 6- positions. The third category, on the other hand, comprises alkyl DBTs with only one substituent either at 4- or 6-position. The sulfur compounds of the third category are relatively more challeng-

Table 4 List of detected sulfur compounds in gas oil fractions and their reactivities.

Reactivity category	Sulfur compound	EOC (ppm)	LF (ppm)
I	4-Methyl-benzothiophene	3.09	2.11
I	2,3-Dimethyl-benzothiophene	58.99	0.43
I	2,3,7-Trimethyl-benzothiophene	198.31	12.91
I	2,4,7-Trimethyl-benzothiophene	1.95	178.75
II	Dibenzothiophene	79.59	0.41
II	1-Methyl-dibenzothiophene	89.14	1.18
II	3-Methyl-dibenzothiophene	118.52	1.61
II	1,3-Dimethyl-dibenzothiophene	8.57	229.58
II	1,3,7-Trimethyl-dibenzothiophene	87.10	97.39
III	4-Methyl-dibenzothiophene	154.559	9.55
III	4-Ethyl-dibenzothiophene	43.86	69.62
III	2,4,7-Trimethyl-dibenzothiophene	71.97	2.89
III	2,4,8-Trimethyl-dibenzothiophene	2.39	3.11
III	1,4,7-Trimethyl-dibenzothiophene	144.08	6.52
IV	4,6-Dimethyl-dibenzothiophene	100.94	13.74
IV	2,4,6-Trimethyl-dibenzothiophene	141.59	28.44
IV	4-Ethyl-6-methyl-dibenzothiophene	63.75	24.67
IV	6-ethyl,2,4-dimethyl-dibenzothiophene	54.14	10.96
IV	1,4,6,8-TetraMethyl-dibenzothiophene	29.86	7.18
IV	2,4,6,8-TetraMethyl-dibenzothiophene	29.26	1.13

**Fig. 8** Reactivity category of the Gas oil sulfur compounds based on their structure.

ing to desulfurize than the ones from the first and second categories. The fourth category, which is the most refractory, has the alkyl DBTs with two alkyl substituents at the 4- and 6-positions. The sulfur compounds in this category are difficult to desulfurize even at severe operating conditions (i.e., high operating pressure and temperature with long reaction time). For this study, the detailed qualitative and quantitative analyses of the sulfur compounds from the gas oils are shown in Table 4 and Fig. 8. The figure clearly indicates that Eocene's gas oil has more refractory sulfur compounds than the gas oil from Lower Fars. Table 4, on the other hand, specifies the refractory sulfur compounds that exist in Eocene's gas oil, which make it more difficult to process than gas oil from Lower Fars, in spite of the fact that the latter has more sulfur

content as shown in Fig. 7. As a consequence of that, the processing of Eocene gas oil should require more severe operating conditions and more efficient HDS catalyst than that of Lower Fars.

4. Conclusions

Coupling comprehensive two-dimensional gas chromatography with flame ionization detector and sulfur chemiluminescence detector has definitely shown advantages in the separation, identification, and quantification of sulfur species in petroleum products. The developed method in this study was set to analyze samples from heavy naphtha to gas oil by

directly injecting neat samples and obtaining all the desired information on the importantly selected hydrocarbons and sulfur compounds and their groups. The sulfur speciation methodology was utilized to illustrate the importance of such detailed analysis for enhancing the desulfurization processes in the refining industry, where distillates from different crude oils were compared. The comparison between the gas oil fractions from Lower Fars and Eocene has shown a very interesting finding. The gas oil from Lower Fars has shown a higher total sulfur content than that from Eocene; however, the detailed molecular analysis clearly indicates that the nature of sulfur compounds in Eocene gas oil is more refractory, which consequently makes it more difficult to desulfurize. Such valuable information of detailed analysis will surely have an impact on selecting proper feedstock and optimizing operating conditions in refining processes.

Declaration of Competing Interest

The authors declared that there is no conflict of interest.

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