Journal of Chromatography Open 2 (2022) 100068

Contents lists available at ScienceDirect

Journal of Chromatography Open

journal homepage: www.elsevier.com/locate/jcoa

Comparison of gas and kerosene oils chemical composition before and after hydrotreating using comprehensive two-dimensional gas chromatography

Lucie Šindelářová[a,b], Estella Ngoc Luu[c], Petr Vozka[c,*]

[a] ORLEN UniCRE a.s., Revoluční 1521/84, 400 01 Ústí nad Labem, Czech Republic
[b] Department of Petroleum Technology and Alternative Fuels, University of Chemistry and Technology, Prague 616628, Czech Republic
[c] Department of Chemistry and Biochemistry, Complex Chemical Composition Analysis Lab (C^3AL), California State University, Los Angeles, CA 90032, United States

ARTICLE INFO

Keywords:
GC×GC
Hydrotreating
Diesel fuel
Sulfur
Dibenzothiophenes

ABSTRACT

Information on the detailed composition of the feedstock and product from the hydrotreating is essential for a better understanding of the reactions, possible optimization of the process conditions, development of new catalysts, and achieving a better overall performance of the diesel fuel, especially in terms of environmental impact. This work aims to determine the detailed composition of the gas and kerosene oils before and after hydrotreating to validate the performance of the hydrotreating. Comprehensive two-dimensional gas chromatography (GC×GC) was chosen as an effective analytical characterization tool for supporting such initiatives. The quantitative group hydrocarbon and sulfur compounds compositions were determined using GC×GC with flame ionization detector (FID) and selective chemiluminescence detector (SCD), respectively.

1. Introduction

Despite the COVID-19 pandemic, diesel demand is still immense. Simultaneously, a great emphasis is placed on diesel chemical composition, mainly regarding environmental impacts. Diesel is a mixture of many middle distillate streams from refinery processes. Primarily, it is produced by fractional distillation of crude oil between 150 and 350 °C at atmospheric pressure [1]. Yet, due to the high diesel consumption, it is also necessary to produce middle distillates by secondary processes, such as thermal and catalytic cracking of heavier oil fractions and residues. However, these secondary products have far worse properties making them less suitable as diesel blends [2]. In particular, they contain higher amounts of heteroatoms, mainly sulfur, which act as catalytic poisons, cause equipment corrosion, and their combustion generates sulfur oxide emissions [3]. They also consist of more polyaromatic hydrocarbons, whose combustion causes particulate matter emissions.

All middle distillate streams must undergo hydrogenation refining (hydrotreating) prior to mixing, so the resulting diesel meets the requirements set by the standards [4,5]. Hydrotreating is carried out under hydrogen pressure and catalysts, mostly Co-Mo/Al_2O_3 or Ni-Mo/Al_2O_3, with a primary goal of removing sulfur compounds and hydrogenating polyaromatic hydrocarbons [6]. It is necessary to know the detailed composition of middle distillates to optimize the hydrotreating, develop better catalytic systems tailored according to the detailed composition of the sulfur species, understand the reaction kinetics, maximize engine power, and minimize emissions from diesel combustion.

Middle distillates (150–430 °C) are complex chemical mixtures containing over a thousand compounds [2]. One-dimensional gas chromatography (1D GC) is an insufficient analytical tool for separation. In 1991, comprehensive two-dimensional gas chromatography (GC×GC) began to develop. In GC×GC, the middle distillate sample is separated into individual components (if optimized properly) using two capillary columns with different phases [2–7]. The separation occurs by continuous re-injection of the eluent from the first column to the second column using a modulator, allowing far better separation and a more detailed determination of the compounds [8]. Currently, GC×GC hyphenated to a time-of-flight mass spectrometry (TOFMS) detector and a flame ionization detector (FID) is a state-of-the-art technique for quantitative and qualitative analysis of middle distillates, respectively. Many researchers have already addressed this topic [2,9,10]. TOFMS detector with unit mass resolution can acquire 100+ mass spectra per second, which is particularly suitable in conjunction with the GC×GC as its high data acquisition rate corresponds to the high separation rate in the second dimension [10,11]. Additionally, FID is a universal detector with a linear response to the hydrocarbon content [12].

The sulfur content before and after the hydrotreating is a critical factor indicating the proper functioning of the process. The total sulfur content can be determined in many ways, such as UV or XRF fluores-

* Corresponding author.
E-mail address: pvozka@calsatatela.edu (P. Vozka).

https://doi.org/10.1016/j.jcoa.2022.100068
Received 15 September 2022; Received in revised form 1 November 2022; Accepted 1 November 2022

cence [13,14]. Gas chromatography with a selective sulfur detector is the most suitable technique for a detailed analysis and identification of sulfur compounds [15]. However, the amount of different sulfur compounds in the non-desulfurized middle distillates is so large that there is a vast coelution between the peaks in 1D GC. Therefore, in recent years, GC×GC combined with a sulfur chemiluminescent detector (SCD) has become more widely used [16]. SCD is suitable due to its linearity and equimolar response to all types of sulfur compounds, has excellent sensitivity (0.5 pg S/s) and selectivity (S/C = 10^7), and its interaction with the hydrocarbon matrix is minimal [15]. An alternative to the SCD detector is the flame photometric detector (FPD). FPD is cheaper and has a higher sampling frequency, which is advantageous for GC×GC. However, the response is nonlinear and additionally reduced due to the coelution of sulfur compounds with hydrocarbons [8]. Sulfur compounds can also be identified using GC×GC/TOFMS; however, the sensitivity of the TOFMS detector to sulfur compounds is lower when compared to selective detectors [3].

This work aimed to characterize and compare the composition of different components of diesel fuel, gas and kerosene oils, as feedstock and products from different hydrotreating units. Two-dimensional gas chromatography in combination with a flame ionization detector (GC×GC-FID) was chosen to determine the group composition of hydrocarbons in the samples. Detailed determination of the group composition of sulfur compounds was performed by GC×GC-SCD, which allowed for identifying individual poorly desulfurized compounds in the samples after hydrotreating. Possible options for reducing the content of sulfur and polyaromatic compounds in the produced diesel fuel are also discussed in this work. These solutions will be necessary in the case of further reduction of the limit content of these substances in diesel fuel, mainly in the context of environmental protection.

2. Experimental

2.1. Materials

Two samples of gas oil and two samples of kerosene oil before and after hydrotreating from different refinery hydrotreating units were analyzed. The gas oil (GO) was the feedstock for hydrotreating units 1 and 2, and will be referred to as GO 1 and GO 2, respectively. GO 1 contained 9 wt% of light cycle oil (product of fluid catalytic cracking), 9.5 wt% of visbreaking gas oil, 75 wt% of straight gas oil, and 6.5 wt% of straight kerosene. GO 2 comprised 6 wt% of cracked pyrolysis material, 47 wt% of straight gas oil, and 47 wt% of straight kerosene. The product from the hydrotreating unit is called hydrotreated gas oil (HGO) and was further used as a diesel fuel component. HGO from hydrotreating units 1 and 2 will be designated as HGO 1 and HGO 2, respectively. For instance, HGO 1 is a product from hydrotreating unit 1, where GO 1 was used as a feedstock.

Kerosene was the feedstock for hydrotreating units 3 and 4 and will be referred to as KO 3 and KO 4, in both cases, it was 100 wt% straight kerosene. The products of hydrotreating units 3 and 4 will be referred to as HKO 3 and HKO 4, respectively.

The following Table 1 describes the conditions for each commercial hydrotreating units.

2.3. GC×GC instrumentation

Two GC×GC systems were used for analyzing the samples. GC×GC-FID system (LECO's QuadJet^{TM} SD) was composed of an Agilent 8890 GC, secondary oven, and liquid nitrogen-cooled QuadJet Thermal Modulator. The classification was developed following the procedure in the previous paper [17]. Each sample composition was reported as wt% for each carbon number (C_5 to C_{27}) from each hydrocarbon class (*n*-paraffins, isoparaffins, cycloparaffins (mono-, di-, tri-), and aromatics (alkylbenzenes, cycloaromatics, alkylnaphthalenes, and biphenyls)). GC×GC-SCD system consisted of an Agilent 7890B GC equipped with a secondary oven and QuadJet Thermal Modulator (LECO Corporation, St. Joseph, MI), with cryogenic cooling. The SCD was an 8355 S (Agilent Technologies) with a dual plasma burner, in which sulfur compounds are burned to form sulfur oxide (SO). SO is further oxidized by ozone to SO_2^*. Once these high-energy species return to the ground state (chemiluminiscence), the emitted light is detected by a photomultiplier tube. The data were analyzed and integrally quantified by the LECO's ChromaTOF software (version 4.72.0.0 optimized for GC×GC-FID). GC×GC-SCD classification was built and validated using 42 standard compounds (see Supplementary Table S1), roof tile effect [18], and other findings from the literature, such as the elution order of sulfur compounds and their retention indices [15,19,20]. For hydrocarbon analysis of petroleum products via GC×GC-FID, the reverse column configuration was used as a better separation of the alkane and cycloalkane groups is achieved. On the other hand, for the analysis of sulfur compounds by GC×GC-SCD, the normal column configuration was used because the sulfur-containing compounds are mostly aromatics. Thus, better separation is achieved when this column configuration is used. Other GC×GC parameters can be seen in Table 2.

2.4. Other instrumentation

The total sulfur content was determined using the X-ray fluorescence method using the Sindie +CI sulfur analyzer (XOS, East Greenbush, NY). This test method covers the determination of total sulfur by monochromatic, wavelength-dispersive X-ray fluorescence spectrometry in diesel fuels [21].

3. Results and discussion

3.1. GC×GC-FID

The total contents of the main hydrocarbon classes obtained from GC×GC-FID for all samples are shown in Fig. 1. Each sample comprised all main hydrocarbon classes (alkanes, mono-, di- and tri-cycloalkanes, mono-, di-, tri- and tetra-aromatics hydrocarbons). This GC×GC-FID method cannot distinguish between olefins and cycloparaffins; thus, they were grouped and referred to as "cycloparaffins." During hydrotreating, the double bonds of alkenes and aromatic hydrocarbons are saturated. Alkenes are not present in crude oil; they are formed during secondary processes of oil residue processing. In our case, they were present in the feedstock GO 1 from light cycle oil and visbreaking gas oil and GO 2 from cacked pyrolysis material. For these two gas oils, it was evident that hydrogenation of alkenes to alkanes occurred; therefore, the alkane content increased in the products. Although the main objective of hydrotreating is to remove heteroatoms, the reduction of aromatic hydrocarbons is also desired. The content of polyaromatics (i.e., hydrocarbons with three and more aromatic rings) in diesel fuel is limited by the standard [4], these substances are carcinogenic and mutagenic, and their increase has a negative impact on emissions [22]. The highest content of aromatics was in sample GO1, namely 32.08 wt.%, this sample showed the highest loss of these aromatics by 11.51 wt.% due to the use of higher pressure and mainly NiMo catalyst, which has higher hydrogenation activity than CoMo catalyst [23]. For GO2, the initial aromatic content was 22.97 wt% and decreased by only 3.57 wt%. The results clearly show that the hydrogenation of alkylbenzenes to monocycloalkanes and cycloaromatics to dicycloalkanes occurs. In the case of diaromatic and polyaromatic compounds, a saturation of the aromatic rings occurred; for example, all the products had a higher content of cycloaromatics when compared to their feedstocks, which is the result of saturation of relevant compounds (i.e., diaromatics). The saturation is not random but primarily affects one of the aromatic rings of diaromatics. For kerosene, the compositional changes after hydrotreating are not as noticeable as for gas oils. Still, the saturation of diaromatics can be seen, and thus, their loss in the products and increased cycloaromatics content. Fig. 2 shows the GC×GC-FID chromatograms of GO 1 and HGO

Table 1
Conditions used for each commercial hydrogenation unit.

Number of Units	1	2	3	4
Location	Litvinov	Litvinov	Litvinov	Kralupy
Crude Oil	80% REB, 20% CPC*	80% REB, 20% CPC*	80% REB, 20% CPC*	80% Azeri light, 20% CPC*
Feedstock	GO 1	GO 2	KO 3	KO 4
Products	HGO 1	HGO 2	HKO 3	HKO 4
Catalysts	$NiMo/Al_2O_3$	$CoMo/Al_2O_3$	$CoMo/Al_2O_3$	$CoMo/Al_2O_3$
Injection rate (Nm^3/m^3)	320	275	–	–
Pressure (MPa)	6.0	3.5	2.9	3.0
Purity of hydrogen (vol.%)	99	99	88	97.4
WHSV (h^{-1})	1.0	1.4	–	–

*REB – Russian Export Blend, CPC – Caspian Pipeline Consortium.

Table 2
Experimental conditions of GC×GC analysis.

Instrument	GC×GC-FID	GC×GC-SCD
Columns	Rxi-17SilMS (30 *m* × 0.25 mm × 0.25 µm) Rxi-1MS (0.85 *m* × 0.18 mm × 0.18 µm) Deactivated (0.3 *m* × 0.25 mm)	Rxi-5SilMS (30 *m* × 0.25 mm × 0.25 µm) Rxi-17SilMS (1.7 *m* × 0.15 mm × 0.15 µm) Deactivated (1.6 *m* × 0.10 mm)
Injection	Split/Splitless, 0.3 µl, 100:1, 280 °C	Split/Splitless, 1 µl, 100:1, 250 °C
Carrier gas	He, 1.5 mL/min	
Oven program	40 °C (1.5 min) 40–300 °C, ramp rate 4 °C/min 300 °C (5 min)	300 °C (10 min)
Offsets	Secondary oven: 5 °C Modulator: 15 °C	
Modulation	10 s, hot pulse 2.5 s	12 s, hot pulse 3.6 s
Detector	FID, 320 °C	SCD, 300 °C
Acquisition rate	200 Hz	

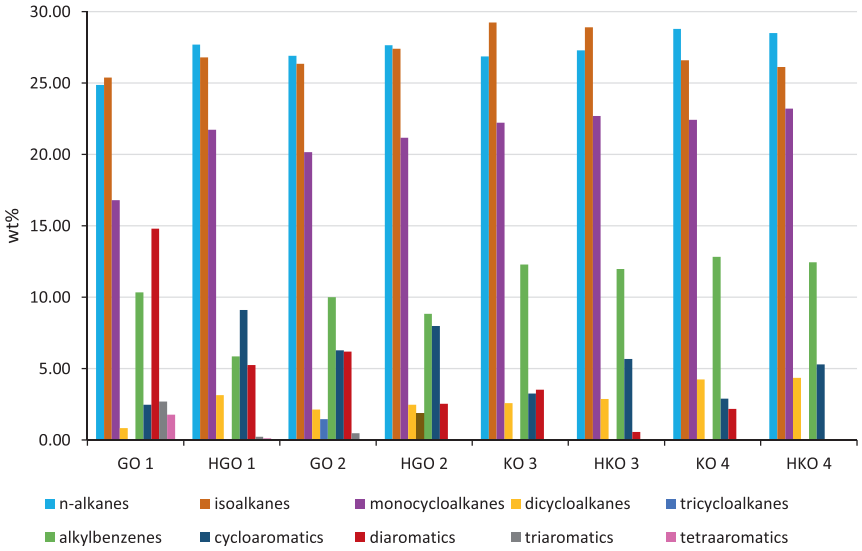

Fig. 1. Total contents (wt%) of each hydrocarbon class in the samples.

1 samples. More detailed chemical compositional results can be found in Supplementary Table S2.

3.2. GC×GC-SCD

Samples from hydrotreating 1 contained the most sulfur compounds before and after hydrotreating. The resulting chromatograms of samples GO 1 and HGO 1 analyzed by GC×GC-SCD, including the classification distribution, are presented in Fig. 3. The GO 1 sample (before hydrotreatment) contained many sulfur compounds, such as thiophenes, benzothiophenes, dibenzothiophenes, as well as polyaromatics sulfur compounds - benzonaphthothiophene. The reactivity during desulfurization decreases in the following order: thiophenes > benzothiophenes > benzonaphthothiophene > dibenzothiophenes [24]. The least reactive and, therefore, hard to desulfurize substances are dibenzothiophenes, which remained in the HGO 1 sample after hydrotreatment (Fig. 4). The individual reactivity of dibenzothiophenes varies greatly according to the position of the attached alkyl group. When the alkyl group is bonded in the beta position relative to the sulfur atom (Fig. 5), this sulfur atom is overshadowed by the alkyl, and the ability to desulfurize is low. The alkyl groups in both beta positions sterically hinder the desulfurization process. In contrast, dibenzothiophene with a substituent in a position other than beta (relative to the sulfur atom) is slightly reactive and, thus, more easily desulfurized [25].

The total sulfur content was also determined using the X-ray fluorescence (XRF) method in all samples. The results of the determination of

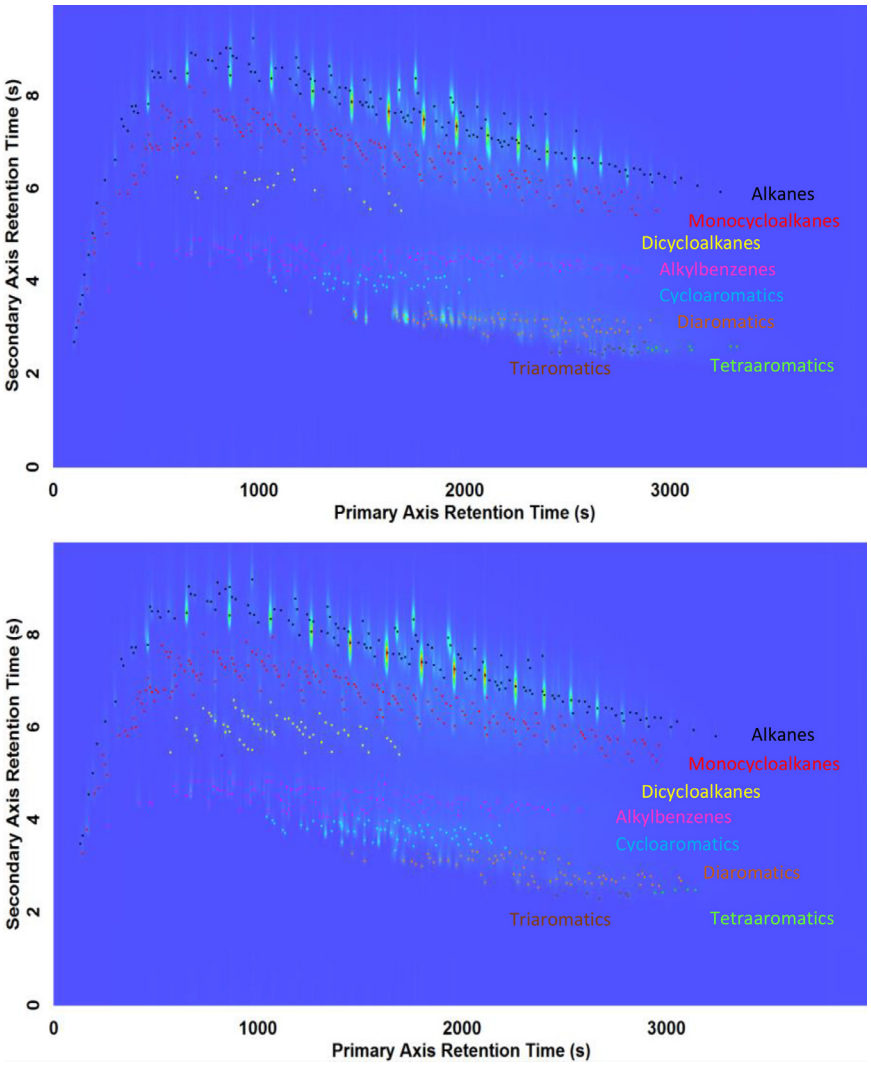

Fig. 2. GC×GC-FID chromatogram of GO 1 (top) and HGO 1 (bottom).

total sulfur by XRF and the results of the determination of the sulfur content (mg/kg) of the individual groups by GCxGC-SCD are presented in Table 3 (kerosene oils) and Table 4 (gas oils). These tables also indicate the desulphurization efficiency of the individual sulfur groups.

Due to its lower boiling point, kerosene does not contain as much sulfur as gas oils. In HKO 3, only 4,6-dimethyldibenzothiophene (2,1 mg/kg S) remains after desulphurization, and in HKO 4, the desulphurization reached 100%; however, KO 4 contains only non-aromatic sulfur substances and C1-C3-alkylbenzothiophenes.

As shown in Table 4, HGO 2 has a lower total sulfur content than HGO 1. Specifically, there were fewer hard-to-desulfurized alkyldibenzothiophenes in HGO 2, resulting in better desulfurization with an efficiency of 99.96%. In the HGO 2 sample, only two sulfur species remained after hydrotreating - 4,6-dimethyldibenzothiophene (1.5 mg/kg S) and unidentified C3-alkyl dibenzothiophene (1.0 mg/kg S). The hydrotreating of GO 1 reduced the sulfur content by 99.82%. Although most of the sulfur substances were removed, some dibenzothiophenes remained in the sample, and the total sulfur content exceeded 10 mg/kg (ppm), which is the maximum allowed sulfur content in diesel in the EU [4]. In the USA, the limit for sulfur content in ultra-low-sulfur diesel is 15 ppm [5], but this may also be reduced in light of tightening environmental measures.

Additionally, more stringent regulations worldwide may be expected in the future. HGO 1, as the dominant component of diesel fuel, significantly influences the total sulfur content of the resulting diesel fuel mixture. The production processes in the refineries are set up to ensure that the final products meet the requirements set by the standard at the lowest possible cost. The knowledge of the chemical composition of the un-desulfurized compounds can help to improve hydrotreating and achieve better desulfurization by developing and testing new catalysts and modifying the conditions of the hydrotreating where necessary. The following Table 5 presents the contents (mg/kg S) of alkyl dibenzothiophenes before and after hydrotreating GO 1 and the identification of some of the compounds.

The hydrodesulfurization of thiophenes, benzothiophenes, dibenzothiophenes, and other complex sulfur compounds occurs via two pathways. The first pathway is hydrogenation, and the second pathway is direct desulfurization. The formation of intermediates and final products depends on the catalyst used and the process conditions. For example, CoMo catalyst favors the direct desulfurization route, while NiMo catalysts hydrodesulfurize predominantly via the hydrogenation route [27]. The final product of thiophene desulfurization is an alkane. Hydrodesulfurization of benzothiophene produces dihydrobenzothiophene via the hydrogenation pathway, followed by further hydrogenation to produce ethylbenzene as the final product, while the direct desulfurization pathway produces styrene [27]. The hydrodesulfurization reaction of alkyl-substituted dibenzothiophene is more complex, the direct desulfurization pathway is sterically hindered, and thus, hydrogenation becomes the main reaction pathway [24]. The final product of the hydrodesulfurization of 4,6-dimethyldibenzothiophene by direct desulfu-

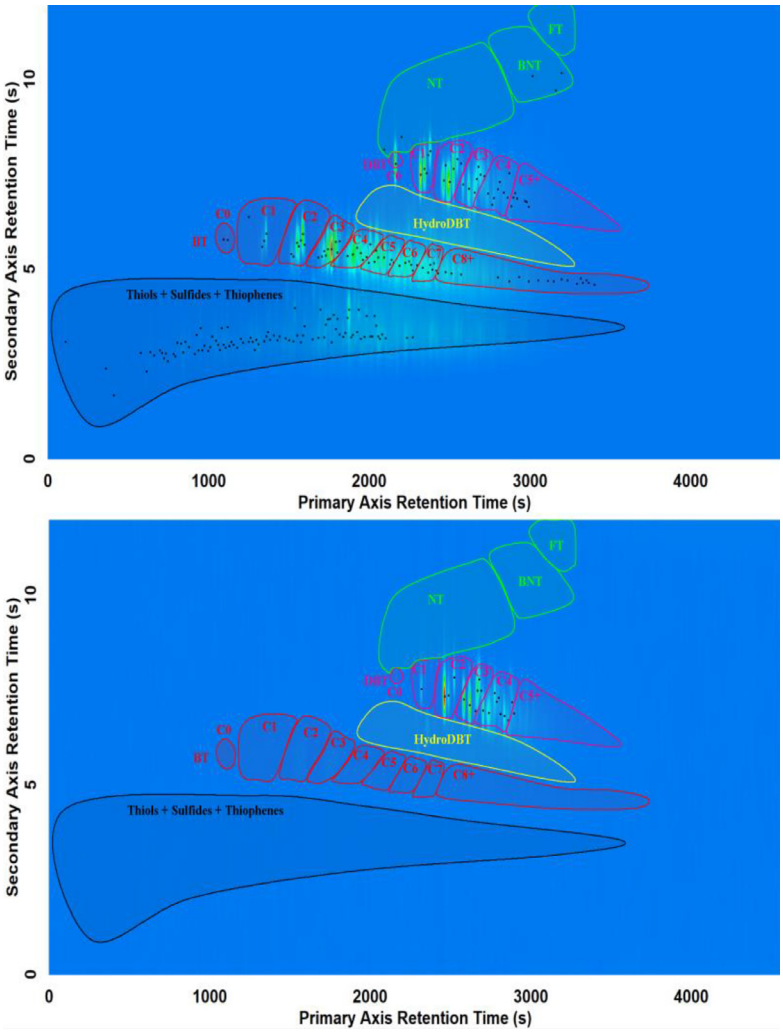

Fig. 3. Distribution of sulfur-containing compounds in GO 1 (top) and HGO 1 (bottom) obtained from GC×GC-SCD. (BT - benzothiophenes, HydroDBT – hydrodibenzothiophene, DBT - dibenzothiophenes, NT – napthothiophenes, BNT – benzonapthothiophenes, FT – phenanthrothiophenes).

rization is dimethylbiphenyl, while hydrogenation proceeds with the ingress of dimethylbicyclohexyl and dimethylcyclohexylbenzene [27]. The increase in monoaromatics and dicycloalkanes can also be seen in the GC×GC-FID results.

The only methyl-dibenzothiophene present in HGO 1 after desulphurization was 4-methyldibenzothiophene, the least reactive, among all methyl-dibenzothiophenes, due to the alkyl bound at position 4. HGO 1 also contained C2-, C3-, C4-, and one C5+ alkylated dibenzothiophene. The dibenzothiophenes remaining in the HGO 1 in the most significant amounts are those alkylated at the 4th and 6th positions (Fig. 5), such as 4,6-dimethyldibenzothiophene, 4-ethyl-6-methyldibenzothiophene, 2,4,6-trimethyldibenzothiophene, and 2,4-dimethyl-6-ethyldibenzothiophene. This confirms that dibenzothiophenes alkylated at these two positions are the most difficult to desulfurize. They can be eliminated, for example, by increasing the process temperature. However, the increase in temperature results in higher coke formation and, thus, faster deactivation of the catalyst. These problems can also be solved by increasing the hydrogen partial pressure, low-

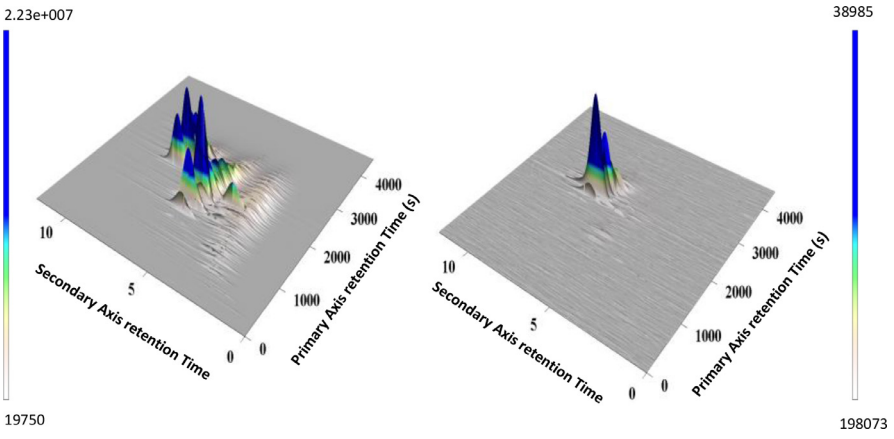

Fig. 4. 3-D plot of sulfur-containing compounds in GO 1 (left) and HGO 1 (right), showing successful desulfurization during hydrotreating.

Table 3
Group composition of sulfur compounds presented as sulfur content (mg/kg S) of each group in kerosene oils and desulphurization efficiency in the group.

Classification groups	mg/kg S		%	mg/kg S		%
	KO 3	HKO 3	Efficiency	KO 4	HKO 4	Efficiency
Thiols+Sulfides+Thiophenes	2686.9	0.0	100.0	890.8	0.0	100.0
Benzothiophene	0.0	0.0	n/a	4.8	0.0	100.0
C1-Alkyl benzothiophenes	44.8	0.0	100.0	29.7	0.0	100.0
C2-Alkyl benzothiophenes	273.3	0.0	100.0	55.2	0.0	100.0
C3-Alkyl benzothiophenes	479.9	0.0	100.0	16.3	0.0	100.0
C4-Alkyl benzothiophenes	334.5	0.0	100.0	0.0	0.0	n/a
C5-Alkyl benzothiophenes	183.1	0.0	100.0	0.0	0.0	n/a
C6-Alkyl benzothiophenes	90.0	0.0	100.0	0.0	0.0	n/a
C7-Alkyl benzothiophenes	19.4	0.0	100.0	0.0	0.0	n/a
C8+-Alkyl benzothiophenes	0.0	0.0	n/a	0.0	0.0	n/a
Hydrodibenzothiophenes	5.6	0.0	100.0	0.0	0.0	n/a
Dibenzothiophene	13.7	0.0	100.0	0.0	0.0	n/a
C1-Alkyl dibenzothiophenes	18.3	0.0	100.0	0.0	0.0	n/a
C2-Alkyl dibenzothiophenes	5.0	2.1	57.7	0.0	0.0	n/a
Napthothiophenes	4.4	0.0	100.0	0.0	0.0	n/a
TOTAL SCD	4158.7	2.1	99.95	996.9	0.0	100.00
TOTAL XRF	4673.0	2.0	–	1055.0	0.0	–

Table 4
Group composition of sulfur compounds presented as sulfur content (mg/kg S) of each group in gas oils and desulphurization efficiency.

Classification groups	mg/kg S		%	mg/kg S		%
	GO 1	HGO 1	Efficiency	GO 2	HGO 2	Efficiency
Thiophenes	2207.0	0.0	100.0	2358.6	0.0	100.0
Benzothiophene	7.0	0.0	100.0	0.0	0.0	n/a
C1-Alkyl benzothiophenes	68.2	0.0	100.0	30.6	0.0	100.0
C2-Alkyl benzothiophenes	322.1	0.0	100.0	217.4	0.0	100.0
C3-Alkyl benzothiophenes	639.3	0.0	100.0	463.4	0.0	100.0
C4-Alkyl benzothiophenes	771.9	0.0	100.0	509.4	0.0	100.0
C5-Alkyl benzothiophenes	958.5	0.0	100.0	515.8	0.0	100.0
C6-Alkyl benzothiophenes	837.8	0.0	100.0	438.2	0.0	100.0
C7-Alkyl benzothiophenes	538.7	0.0	100.0	269.0	0.0	100.0
C8+-Alkyl benzothiophenes	1045.0	0.0	100.0	590.8	0.0	100.0
Hydrodibenzothiophenes	0.0	0.0	n/a	0.0	0.0	n/a
Dibenzothiophene	101.7	0.0	100.0	47.6	0.0	100.0
C1-Alkyl dibenzothiophenes	362.5	0.3	99.9	135.3	0.0	100.0
C2-Alkyl dibenzothiophenes	457.3	3.9	99.2	172.9	1.5	99.1
C3-Alkyl dibenzothiophenes	517.8	5.6	98.9	124.0	1.0	99.2
C4-Alkyl dibenzothiophenes	272.1	6.3	97.7	76.5	0.0	100,0
C5+-Alkyl dibenzothiophenes	177.8	0.4	99.8	0.0	0.0	n/a
Napthothiophenes	15.5	0.0	100.0	3.5	0.0	100.0
Benzonapthothiophenes	7.6	0.0	100.0	0.0	0.0	n/a
TOTAL SCD	9308.2	16.5	99.82	5953.0	2.5	99.96
TOTAL XRF	9410.0	14.7	–	6813.0	2.0	–

Table 5
The sulfur content (mg/kg S) of individual alkyl dibenzothiophenes present in HGO 1 and their comparison with GO 1.

Classification	Identification	R.T. (s)	GO 1	HGO 1
C1-Alkyl dibenzothiophenes	4-MDBT	2316, 7.545	143.2	0.3
C2-Alkyl dibenzothiophenes	4,6-diMDBT	2460, 7.355	112.2	2.5
C2-Alkyl dibenzothiophenes	2,6-diMDBT	2484, 7.375	98.5	0.7
C2-Alkyl dibenzothiophenes	1,4-diMDBT	2520, 7.845	138.7	0.6
C3-Alkyl dibenzothiophenes	4-E-6-MDBT*	2580, 7.275	42.7	1.4
C3-Alkyl dibenzothiophenes	2,4,6-triMDBT	2616, 7.120	70.9	1.6
C3-Alkyl dibenzothiophenes	–	2652, 6.965	95.3	0.6
C3-Alkyl dibenzothiophenes	–	2664, 7.510	41.6	1.1
C3-Alkyl dibenzothiophenes	–	2676, 7.795	40.0	0.7
C3-Alkyl dibenzothiophenes	1,4,7-triMDBT	2688, 7.510	83.6	0.4
C4-Alkyl dibenzothiophenes	4,6-diEDBT	2700, 6.980	78.2	0.8
C4-Alkyl dibenzothiophenes	2,4-diM-6-EDBT*	2736, 6.915	77.8	1.7
C4-Alkyl dibenzothiophenes	–	2772, 7.440	39.4	0.7
C4-Alkyl dibenzothiophenes	1,4,6,8-tetraMDBT	2784, 7.215	22.5	0.3
C4-Alkyl dibenzothiophenes	–	2796, 7.310	25.6	0.4
C4-Alkyl dibenzothiophenes	–	2808, 6.895	24.4	0.3
C4-Alkyl dibenzothiophenes	–	2832, 6.835	26.6	0.9
C4-Alkyl dibenzothiophenes	–	2856, 6.725	23.9	0.7
C4-Alkyl dibenzothiophenes	–	2880, 7.200	24.3	0.5
C5+-Alkyl dibenzothiophenes	–	2892, 6.900	19.6	0.4

*Identified using literature [20–26].

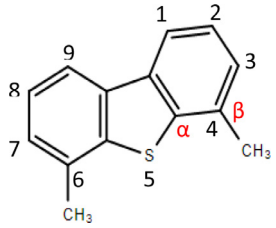

Fig. 5. Structure of 4,6-dimethyldibenzothiophene.

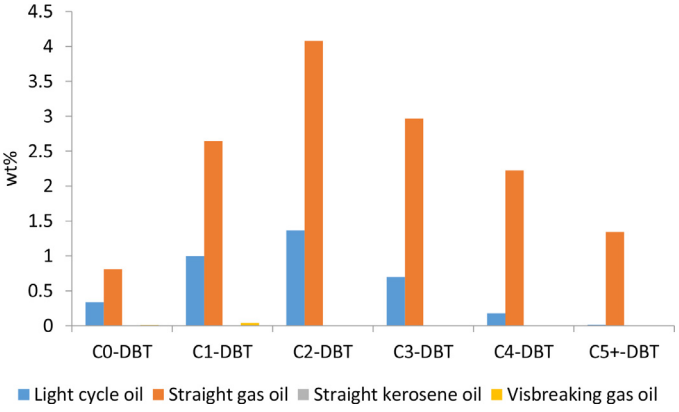

Fig. 6. Contributions of dibenzothiophenes (wt%) from individual feed middle distillates of feedstock GO1.

ering the LHSV, or increasing the reactor volume [24]. Another possible solution is to start using more efficient catalysts to remove these less-reactive sulfur substances, but this might be a costly solution. Some researchers have already begun to address this issue, mainly using 4,6-dimethyldibenzothiophene as a model feedstock [28–33]. Another last resort for refiners in the event of a significant reduction in the limiting sulfur content of diesel is to reduce the distillation fraction of the most problematic diesel components to remove the unwanted dibenzothiophenes. In this case, GO 1 was the most problematic feedstock. After desulphurization, it contained the highest number of hard desulphurized dibenzothiophenes.

Moreover, HGO 1 is the main component of diesel fuel, so its dibenzothiophenes contribution was the highest in the final diesel fuel. GO 1 comprises four feedstocks: 9 wt% of light cycle oil (LCO), 9.5 wt% of visbreaking gas oil (VGO), 75 wt% of straight gas oil (SGO), and 6.5 wt% of straight kerosene oil (SKO). GC×GC-SCD analysis was performed on these middle distillates to determine the dibenzothiophene content, which was then converted to the percentage of dibenzothiophenes from each middle distillate in the feedstock. The individual contributions of dibenzothiophenes from these feedstocks are shown in Fig. 6. Most of the dibenzothiophenes come from straight gas oil and light cycle oil, so the solution would be to reduce the distillation fraction for these two feedstocks. However, this will reduce the amount of diesel produced, which is undesirable. At present, this would probably be the fastest and most effective solution in the case of reducing the sulfur limit to zero.

4. Conclusions

The use of comprehensive two-dimensional gas chromatography (GC×GC) combined with FID and SCD detectors is a very effective tool for obtaining detailed information on the composition of gas and kerosene oil samples before and after hydrotreating. Using GC×GC-FID, the detailed chemical composition of individual hydrocarbons was obtained. The results show hydrogenation of alkenes to alkanes, monoaromatics to monocycloalkanes, and saturation of higher aromatic compounds to (mainly) compounds with one aromatic ring. This results in a desirable reduction of polyaromatics. Hydrogenation was carried out to the greatest extent on hydrotreating unit 1, where a higher pressure was used than on the other hydrotreating units. A NiMo catalyst was also used, which is more efficient in hydrogenation than a CoMo catalyst.

Furthermore, the sulfur content in these samples was determined by GC×GC-SCD. For kerosene oils, which contain less sulfur than gas oils, desulphurization was carried out with an efficiency of approximately 100%. For gas oils, dibenzothiophenes were a significant problem as they have low reactivity and were not fully desulfurized. The most problematic sample was HGO 1, where only 99.82 wt% of the sample was desulfurized. With the knowledge of this newly obtained information on the composition of these samples, it should be much easier to optimize the process and assess the performance of the newly developed catalysts when it is necessary to achieve a better-quality diesel fuel. There are several possible solutions; the question is which one will be the least costly for refineries.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

CRediT authorship contribution statement

Lucie Šindelářová: Project administration, Conceptualization, Methodology, Data curation, Formal analysis, Writing – original draft, Writing – review & editing. **Estella Ngoc Luu:** Data curation, Formal analysis, Writing – review & editing. **Petr Vozka:** Methodology, Validation, Writing – original draft, Writing – review & editing, Supervision, Funding acquisition.

Acknowledgments

This work has been supported by the Center of Research Excellence in Science and Technology (CREST) Center for Energy and Sustainability (CEaS) NSF HRD-1547723. We thank Mr. Josef Peška for his help troubleshooting GC×GC-FID. The publication is a result of the project carried out with the financial support of the Ministry of Industry and Trade of the Czech Republic with institutional support for the long-term conceptual development of the research organization.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jcoa.2022.100068.

References

[1] J.G. Speight, Production, properties and environmental impact of hydrocarbon fuel conversion, Adv Clean Hydrocarb Fuel Process Sci Technol (2011) 54–82 Jan. https://doi.org/10.1533/9780857093783.1.54.
[2] F.C.Y. Wang, Comprehensive three-dimensional gas chromatography mass spectrometry separation of diesel, J Chromatogr A 1489 (2017) 126–133 Mar. https://doi.org/10.1016/J.CHROMA.2017.01.091.
[3] B.M.F. Ávila, V.B. Pereira, A.O. Gomes, D.A. Azevedo, Speciation of organic sulfur compounds using comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry: a powerful tool for petroleum refining, Fuel 126 (2014) 188–193 Jun. https://doi.org/10.1016/J.FUEL.2014.02.055.
[4] E.N. "ČSN 590+A1 Motorová paliva - Motorové nafty - Technické požadavky a metody zkoušení". 2018.
[5] "D975-21 standard specification for diesel fuel". 2018.
[6] P. Vozka, D. Orazgaliyeva, P. Šimáček, J. Blažek, G. Kilaz, Activity comparison of Ni-Mo/Al2O3 and Ni-Mo/TiO2 catalysts in hydroprocessing of middle petroleum distillates and their blend with rapeseed oil, Fuel Process Technol 167 (2017) 684–694 Dec. https://doi.org/10.1016/J.FUPROC.2017.08.019.
[7] Z. Liu, J.B. Phillips, Comprehensive two-dimensional gas chromatography using an on-column thermal modulator interface, J Chromatogr Sci 29 (6) (1991) 227–231 Jun. https://doi.org/10.1093/chromsci/29.6.227.
[8] C. Lorentz, D. Laurenti, J.L. Zotin, C. Geantet, Comprehensive GC × GC chromatography for the characterization of sulfur compound in fuels: a review, Catal Today 292 (2017) 26–37 Sep. https://doi.org/10.1016/J.CATTOD.2017.04.052.

[9] J. Mommers, E. Ritzen, T. Dutriez, S. van der Wal, A procedure for comprehensive two-dimensional gas chromatography retention time locked dual detection, J Chromatogr A 1461 (2016) 153–160 Aug. https://doi.org/10.1016/J.CHROMA.2016.07.052.

[10] W. Genuit, H. Chaabani, Comprehensive two-dimensional gas chromatography-field ionization time-of-flight mass spectrometry (GCxGC-FI-TOFMS) for detailed hydrocarbon middle distillate analysis, Int J Mass Spectrom 413 (2017) 27–32 Feb. https://doi.org/10.1016/J.IJMS.2016.12.001.

[11] M.Z. Özel, M.W. Ward, J.F. Hamilton, A.C. Lewis, T. Raventós-Duran, R.M. Harrison, Analysis of organic nitrogen compounds in urban aerosol samples using GCxGC-TOF/MS, Aerosol Sci Technol 44 (2) (2010) 109–116 Feb. https://doi.org/10.1080/02786820903410105.

[12] P. Vozka, H. Mo, P. Šimáček, G. Kilaz, Middle distillates hydrogen content via GC×GC-FID, Talanta 186 (2018) 140–146 Aug. https://doi.org/10.1016/J.TALANTA.2018.04.059.

[13] M. Doğan, Determining the lowest sulfur detection limit in diesel fuel by ultraviolet fluorescence, Phosphorus Sulfur Silicon Relat Elem 196 (1) (2021) 47–53 Jan. https://doi.org/10.1080/10426507.2020.1800701.

[14] T.A. Saleh, Characterization, determination and elimination technologies for sulfur from petroleum: toward cleaner fuel and a safe environment, Trends Environ Anal Chem 25 (2020) e00080 Mar. https://doi.org/10.1016/J.TEAC.2020.E00080.

[15] R. Ruiz-Guerrero, C. Vendeuvre, D. Thiébaut, F. Bertoncini, D. Espinat, (2006). Comparison of comprehensive two-dimensional gas chromatography coupled with sulfur-chemiluminescence detector to standard methods for speciation of sulfur-containing compounds in middle distillates. Available Online: https://academic.oup.com/chromsci/article/44/9/566/286299.

[16] F.C.-Y. Wang, W.K. Robbins, F.P. Di Sanzo, F.C. McElroy, (2003). Speciation of sulfur-containing compounds in diesel by comprehensive two-dimensional gas chromatography. Available Online: https://academic.oup.com/chromsci/article/41/10/519/372126.

[17] P. Vozka, G. Kilaz, How to obtain a detailed chemical composition for middle distillates via GC × GC-FID without the need of GC × GC-TOF/MS, Fuel 247 (2019) 368–377. https://doi.org/10.1016/j.fuel.2019.03.009.

[18] G.P. da Silva Maciel et al., "Comprehensive two-dimensional gas chromatography and its application to the investigation of pyrolytic liquids", in Pyrolysis, M. S, Ed. Rijeka: IntechOpen, 2017. doi: 10.5772/68077.

[19] G.A. Depauw, G.F. Froment, Molecular analysis of the sulphur components in a light cycle oil of a catalytic cracking unit by gas chromatography with mass spectrometric and atomic emission detection, J Chromatogr A 761 (1–2) (1997) 231–247 Feb. https://doi.org/10.1016/S0021-9673(96)00819-9.

[20] R. Gieleciak, D. Hager, N.E. Heshka, Application of a quantitative structure retention relationship approach for the prediction of the two-dimensional gas chromatography retention times of polycyclic aromatic sulfur heterocycle compounds, J Chromatogr A 1437 (2016) 191–202 Mar. https://doi.org/10.1016/J.CHROMA.2016.02.006.

[21] "ASTM D7039", Standard test method for sulfur in gasoline, diesel fuel, jet fuel, kerosine, biodiesel, biodiesel blends, and gasoline-ethanol blends by monochromatic wavelength dispersive x-ray fluorescence spectrometry. 2015.

[22] C.V. de Souza, S.M. Corrêa, Polycyclic aromatic hydrocarbons in diesel emission, diesel fuel and lubricant oil, Fuel 185 (2016) 925–931 Dec. https://doi.org/10.1016/J.FUEL.2016.08.054.

[23] R. Shafi, G.J. Hutchings, Hydrodesulfurization of hindered dibenzothiophenes: an overview, Catal Today 59 (3–4) (2000) 423–442 Jun. https://doi.org/10.1016/S0920-5861(00)00308-4.

[24] X. Weng, et al., Ultradeep hydrodesulfurization of diesel: mechanisms, catalyst design strategies, and challenges, Ind Eng Chem Res 59 (49) (2020) 21261–21274 Dec. https://doi.org/10.1021/acs.iecr.0c04049.

[25] J. Blomberg, T. Riemersma, M. van Zuijlen, H. Chaabani, Comprehensive two-dimensional gas chromatography coupled with fast sulphur-chemiluminescence detection: implications of detector electronics, J Chromatogr A 1050 (1) (2004) 77–84 Sep. https://doi.org/10.1016/J.CHROMA.2004.07.105.

[26] G.A. Depauw, G.F. Froment, Molecular analysis of the sulphur components in a light cycle oil of a catalytic cracking unit by gas chromatography with mass spectrometric and atomic emission detection, J Chromatogr A 761 (1–2) (1997) 231–247 Feb. https://doi.org/10.1016/S0021-9673(96)00819-9.

[27] S.S. Bello, et al., A review on the reaction mechanism of hydrodesulfurization and hydrodenitrogenation in heavy oil upgrading, Energy Fuels 35 (14) (2021) 10998–11016 Jul. https://doi.org/10.1021/acs.energyfuels.1c01015.

[28] A.D. Delgado, L. Alvarez-Contreras, K.A. Beltrán, C. Leyva-Porras, A. Aguilar-Elguezabal, Comparison of three-dimensional versus two-dimensional structure of mesoporous alumina as support of (Ni)MoS2 catalysts for HDS, Catal Today 360 (2021) 165–175 Jan. https://doi.org/10.1016/J.CATTOD.2019.06.012.

[29] M. Nikulshina, et al., Enhancing the hydrodesulfurization of 4,6-dimethyldibenzothiophene through the use of mixed MoWS2 phase evidenced by HAADF, Catal Today 329 (2019) 24–34 Jun. https://doi.org/10.1016/J.CATTOD.2018.11.051.

[30] W. Zhou, Q. Wei, Y. Zhou, M. Liu, S. Ding, Q. Yang, Hydrodesulfurization of 4,6-dimethyldibenzothiophene over NiMo sulfide catalysts supported on mesomicroporous Y zeolite with different mesopore sizes, Appl Catal B 238 (2018) 212–224 Dec. https://doi.org/10.1016/J.APCATB.2018.07.042.

[31] D. Zhang, X.M. Liu, Y.X. Liu, Z.F. Yan, Impact of γ-alumina pore structure on structure and performance of Ni–Mo/γ-Al2O3 catalyst for 4,6-dimethyldibenzothiophene desulfurization", Microporous Mesoporous Mater 310 (2021) 110637 Jan. https://doi.org/10.1016/J.MICROMESO.2020.110637.

[32] Q. Wei, et al., Rhenium modification on NiMo/Al2O3 catalyst and effects on the hydrodesulfurization reaction route selectivity of 4,6-dimethyldibenzothiophene, Catal Today (2021) Jul. https://doi.org/10.1016/J.CATTOD.2021.07.021.

[33] B.D. Radhi, W.T. Mohammed, Novel nanocomposite adsorbent for desulfurization of 4,6-dimethyldibenzothiophene from model fuel, Mater Today Proc 42 (2021) 2880–2886 Jan. https://doi.org/10.1016/J.MATPR.2020.12.738.