

## Detailed Characterization of Light Cycle Oil for BTX Production Purposes

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**Abstract:** *Samples of Mexican light cycle oils were characterized by several techniques. Physical and chemical characteristics are presented. Besides the usual American Standard Test Methods (ASTM) a gas chromatography – mass spectrometry (GC-MS) technique was presented. Based on the GC-MS technique a detailed chemical characterization method was proposed by considering the retention times and sorting out the compounds as hydrocarbon-type derivatives such as benzene, naphthalene, phenanthrene and alkanes derivatives. This procedure is a useful tool for assessing the feasibility and potential of LCO samples as feedstocks for petrochemical or gasoline production. A sample was also distilled in fractions and characterized for the ASTM and GC-MS methods to define the optimum final boiling point for attaining a certain upgrading method.*

**Keywords:** *Light cycle oil; BTX, gasoline, chemical characterization, chromatography, mass spectrometry*

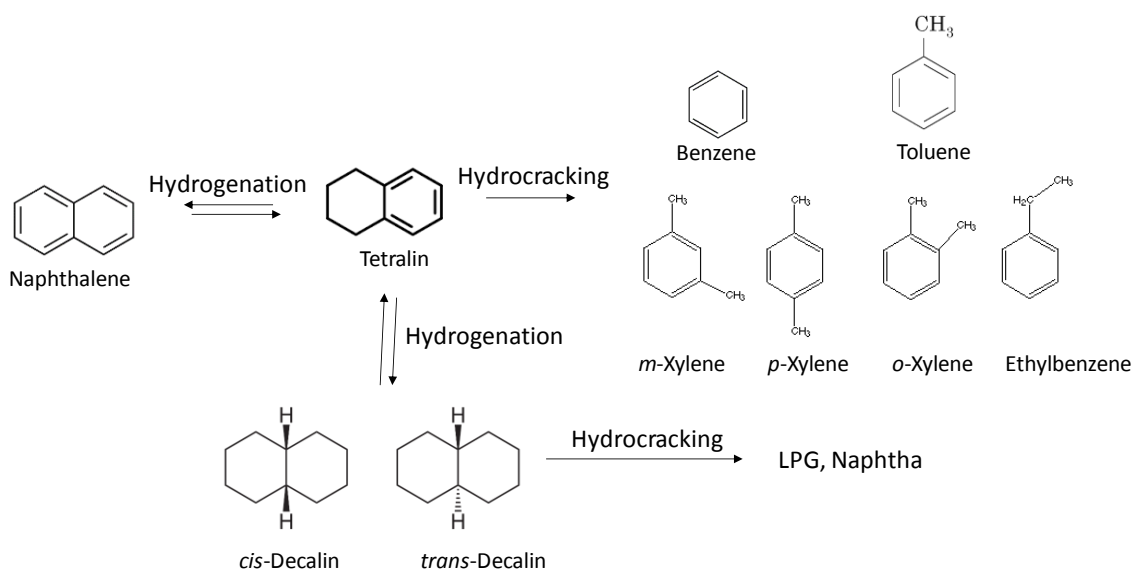
### 1. INTRODUCTION

Light cycle oil (LCO) is a middle distillate from FCC (fluid catalytic cracking) units with high sulfur (up to 4 wt.%), nitrogen (up to 400 mg/kg), and aromatic contents (up to nearly 90 wt.%) [1, 2], which make the processing of this middle distillate very difficult and suitable to comply with the environmental legislation [3, 4].

There have been several technological alternatives for producing diesel from LCO and SRGO/LCO mixtures that includes:

- LCO fractionation into light fractions (final boiling point lower than 340 °C) to avoid the strong inhibition of aromatics due to competing hydrogenation of those species with that of highly refractory organo-sulfur compounds [5, 6].
- Utilization of more active catalysts [7-10]
- Newer and revamped technologies [11-13]

A remarkably interesting alternative for LCO upgrading is obtaining a benzene, toluene, and xylenes (BTX) enriched fraction after hydrogenation/hydrotreating (HYD/HDT) and hydrocracking (HCK) from LCO feedstock. Reaction pathways from LCO (naphthalene as model compound representing diaromatics present in that middle distillate) to a BTX enriched fraction is shown in Figure 1 [14]. After HYD/HDT, the naphthalene derivatives produced 1,2,3,4-tetrahydronaphthalenes (tetralins). In the case of real feedstocks, HDT is required to decrease the amount of sulfur- and nitrogen-bearing contaminants that could act as poison for further processes. Then, the tetralin derivatives were subjected to HCK for BTX production.



**Figure 1.** Reaction scheme for obtaining BTX and LPG (liquefied petroleum gas) and naphtha from LCO [15]

Physical and chemical characterization of the feedstocks and corresponding products of different processes is crucial to face future refining challenges. Characterization by ASTM D-5186 method [15] provides approximated values of mono-, di- and tri-aromatic compounds in the LCO. However, it was designed for middle distillates with less than 50 wt.% of aromatic content and it does not describe the chemical structures involved (i.e., benzene or tetralin derivatives in the case of mono-aromatics) or the type of naphthalene derivatives which are present or remain after HYD/HDT and HCK processes. This type of characterization is crucial because each type of species could provide different product slates.

Regarding the corresponding state of the art, detailed chromatograms of fractionated LCO were presented by Choi et al. [16] although no detailed characterization of the crucial compounds was attempted. LCO characterization by using two-dimensional high-resolution gas chromatography and time-of-flight mass spectrometry (TD-GC-HRMS) followed by enhanced software processing has been presented by Bisht and Petri [13] and Alonso et al. [17]. Vendevre et al. [18] revealed that by using a comprehensive two-dimensional gas chromatography (GC x GC) combined with the boiling range distribution of complex mixtures allowed them to obtain the group type separation of a gas oil. Ruiz-Guerrero et al [19] studied straight run gas oils (SRGOs), and LCOs and demonstrated the effectiveness of two-dimensional gas chromatography coupled to sulfur chemiluminescence detection (SCD) as a powerful tool for improving characterization and identification of sulfur compounds. Adam et al [20] reported the use of supercritical fluid chromatography (SFC) coupled to a twin comprehensive two-dimensional gas chromatography allowed the detailed characterization of middle distillates avoiding the risk of misidentifications. The extended PIONA analysis of middle distillates in one single injection was for the first time reported. Jennerwein et al [21] established a two-dimensional GC x GC-time-of-flight mass spectrometric (TOFMS) method the complete group-type quantification of petroleum middle distillates. The combination of these two techniques offered the possibility to distinguish between compounds groups based on their fragmentation patterns where exact retention time information is missing. This method needed the application of Visual Basic Scripting as an analytical tool for the analysis of mass spectral data. Alvarez-Majmutov et al. [22]. reported a technology based on trends followed by the different hydrocarbon families against their boiling point, allowing the chemical characterization of middle distillates. Although the technology is not always reliable due to the presence of different hydrocarbons families of the LCO that does not always follow the predicted normal configuration provided by that authors. The LCO is not a natural occurring mixture and its composition depends highly in the FCC procedure i.e. crudes oils source, HDT or not HDT involvement before FCC, FCC catalyst and configuration. Additionally, the hydrocarbon differentiation is not as carefully as required for the purposes described in this paper.

The main purpose of this work is to provide an accessible method using a GC-MS technique to characterize different LCOs to assess the suitability of each one either for production of valuable petrochemicals or gasoline.

## 2. EXPERIMENTAL

### 2.1. Materials

LCO samples were kindly provided by PEMEX. The samples were named LCO 1 to 8.

Distillated fractions: The LCO sample No. 6 was fractionated into nine 20 °C-cuts by using an Older-Shaw distillation equipment following the ASTM D86 [15].

### 2.2. ASTM Characterization of LCO Samples and Distillation Fractions

LCO samples were chemically characterized using the ASTM standards shown in Table 1 [15].

**Table1.** ASTM and UOP characterization methods used for middle distillates and their hydrotreated products [26]

Characteristic	Method		Description
Sulfur, wt%	ASTM	D4294	Standard Test Method for Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry
Nitrogen, mg/kg	ASTM	D4629	Standard Test Method for Nitrogen in Petroleum and Petroleum Products by Boat-Inlet Chemiluminescence Standard Test Method for Trace Nitrogen in Liquid Petroleum Hydrocarbons by Syringe/Inlet Oxidative Combustion and Chemiluminescence Detection
Basic nitrogen, mg/kg	UOP	269	Nitrogen Bases in Hydrocarbons by Potentiometric Titration
Bromine number, gBr/100g	ASTM	D1159	Standard Test Method for Bromine Numbers of Petroleum Distillates and Commercial Aliphatic Olefins by Electrometric Titration
Refraction index	ASTM	D1218	Standard Test Method for Refractive Index and Refractive Dispersion of Hydrocarbon Liquids
Chemical composition	ASTM	D5186	Standard Test Method for Determination of the Aromatic Content and Polynuclear Aromatic Content of Diesel Fuels By Supercritical Fluid Chromatography
Cetane index	ASTM	D 976	Standard Test Method for Calculated Cetane Index of Distillate Fuels
Specific gravity	ASTM	D1298	Standard Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method
API gravity	ASTM	D287	Standard Test Method for API Gravity of Crude Petroleum and Petroleum Products (Hydrometer Method)
Atmospheric distillation, °C	ASTM	D86	Standard Test Method for Distillation of Petroleum Products and Liquid Fuels at Atmospheric Pressure

### 2.3. Gas Chromatograph Coupled to Mass Spectrometry Detector (GC-MS)

LCO samples and distillated fractions were characterized with an Agilent Technologies 6890N gas chromatograph coupled to a 5973N mass spectrophotometer (GC-MS) was used by following the EPA method 8270D [23] through SIM mode (quantitative analysis) for naphthalene and phenanthrene derivatives and SCAN mode (qualitative analysis) for the alkanes and iso-alkanes, 1,2,3,4-tetrahydronaphthalene (tetralin, T) and decahydronaphthalene (decalin, D). Table 2 shows the retention times of the several compounds found: benzene, naphthalene, phenanthrene, alkenes and (1,2,3,4-tetrahydronaphthalenes/Tetralins) derivatives respectively.

**Table2.** Retention times ( $t_R$ ) obtained by the GC-MS method

Compound	$t_R$ (min)	Compound	$t_R$ (min)
<i>Benzene derivatives</i> [24]		<i>Naphthalene derivatives</i>	100.9
Benzene	48.5	Naphthalene	100.9
Toluene	66.9	1-Methylnaphthalene	113.5
Ethylbenzene	80.2	2-Methyl-naphthalene	119.0
<i>p</i> -Xylene	80.4	2,6/2,7-Dimethyl-naphthalene	130.8
<i>m</i> -Xylene	81.5	1,3/1,7-Dimethyl-naphthalene	132.7

<i>o</i> -Xylene	83.9	1,6-Dimethyl-naphthalene	133.3
1,3-Dimethyl-benzene	86.7	1,4/2,3-Dimethyl-naphthalene	135.3
Mesitylene	92.5	1,5-Dimethyl-naphthalene	135.6
1-Ethyl-2-methyl-benzene	93.1	1,2-Dimethyl-naphthalene	137.0
1,2,3-Trimethyl-benzene	95.6	1,3,7-Trimethyl-naphthalene	145.1
1-Methyl-3-propyl-benzene	97.0	1,3,6-Trimethyl-naphthalene	146.0
2-Ethyl-1,4-dimethyl-benzene	97.4	1,3,5/1,4,6-Trimethyl-naphthalene	147.6
1-Methyl-2-propyl-benzene	97.9	2,3,6-Trimethyl-naphthalene	148.2
1-Ethyl-2,4-dimethyl-benzene	98.4	1,2,7/1,6,7/1,2,6-Trimethyl-naphthalene	149.6
2-Ethyl-1,4-dimethyl-benzene	98.8	1,2,4-Trimethyl-naphthalene	151.5
1,2,3,4-Tetramethyl-benzene	99.9	1,2,5-Trimethyl-naphthalene	152.5
1,2,4,5-Tetramethyl-benzene	100.5	1,3,5,7-Tetramethyl-naphthalene	161.2
1-Methyl-4-butyl-benzene	102.2	1,3,6,7-Tetramethyl-naphthalene	162.9
1-Ethyl-2,4-dimethyl-benzene	102.3	1,2,4,6/1,2,4,7/1,4,6,7-Tetramethyl-naphthalene	163.4
(1-Methyl-2-cyclopropen-1-yl)-benzene	102.5	1,2,5,7-Tetramethyl-naphthalene	164.3
1-Methyl-4-(1-methylpropyl)-benzene	102.8	2,3,6,7-Tetramethyl-naphthalene	165.2
1-Methyl-4-(2-methylpropyl)-benzene	103.3	1,2,3,7-Tetramethyl-naphthalene	165.7
Pentamethyl-benzene	104.4	1,2,3,6-Tetramethyl-naphthalene	166.4
(1,3-Dimethylbutyl)-benzene	104.9	1,2,5,6/1,2,3,5-Tetramethyl-naphthalene	168.0
2,4-Dimethyl-1-(1-methylpropyl)-benzene	105.7	Phenanthrene	174.1
1,4-Dimethyl-2-(2-methylpropyl)-benzene	106.5	1-Methyl-phenantrene	185.1
1,3,5-Trimethyl propyl-benzene	107.1	2-Methyl-phenantrene	185.7
		3-Methyl-phenantrene	188.0

### 3. RESULTS AND DISCUSSION

#### 3.1. LCO Characterization by the ASTM Standards [15]

Sulfur concentration of LCO samples varied from 2.07 to 3.34 wt.% (Table 3). Due to high content of heterocyclic sulfur compounds LCO HDT requires moderate temperature and high hydrogen partial pressures because sulfur removal reaction pathways via hydrogenated intermediaries are inhibited at high temperature and low pressure due to low equilibrium concentrations of the latter species [9]. Distribution of various organo-sulfur compounds in LCO depends on the origin of the processed crude blend, the catalyst type, feed quality and operating conditions used in the FCC units where that middle distillates come from. Benzothiophenes with alkyl substituents containing 1-7 carbon atoms are concentrated in fractions having boiling points below 300 °C whereas dibenzothiophenes with alkyl substituents containing 1-5 carbon atoms belongs to fractions with boiling points above 300 °C. The three-ring sulfur compounds are one order of magnitude less reactive than the two-ring sulfur species [9].

The total and basic nitrogen concentrations were from 132 to 545 mg/kg and from 27 to 71 mg/kg, respectively (Table 3). Based on average values, the basic nitrogen represented 15.8 % of the total nitrogen. Nitrogen-rich feedstocks are harmful for the LCO hydrocracking because they have to be processed at higher hydrogen partial pressure and/or lower LHSV in the HDT reactors in order to efficiently reduce the nitrogen content of the effluent to levels acceptable for hydrocracking. Besides, ammonia poisons the acid sites of HCK catalysts resulting in weakened catalyst cracking function and, consequently, in loss of the catalytic activity [10].

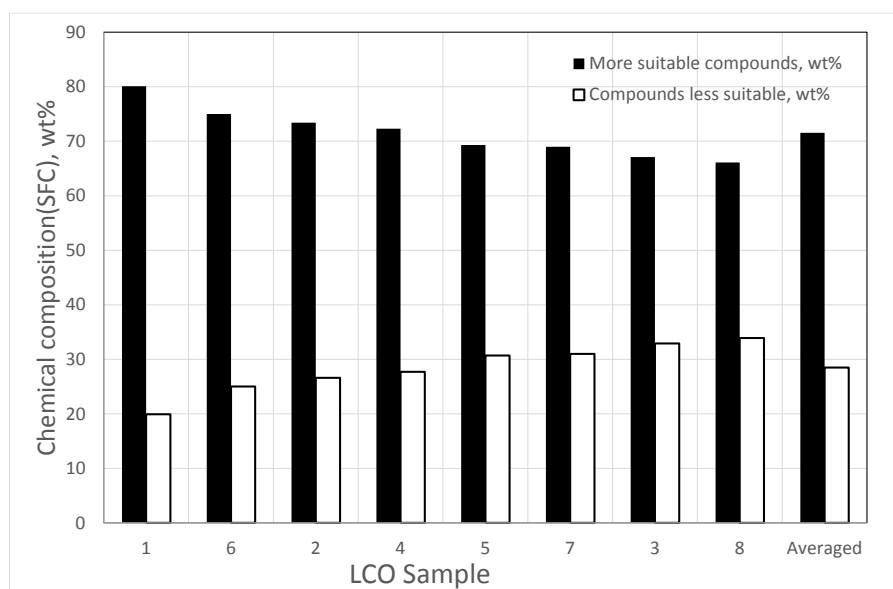
**Table 3.** Chemical characterization of LCO samples 1 to 8 by ASTM D5186 method

LCO simple	1	2	3	4	5	6	7	8	Averaged
Sulfur, wt%	3.22	2.4	3.34	2.68	3.3	2.94	2.28	2.07	2.78
Nitrogen, mg/kg	337	269	544.8	253.6	346	132	224	319	303.2
Basic nitrogen, mg/kg	71.3	40	57.3	48.2	38.1	54.3	45	27.3	47.7

Bromine number, g <sub>Br</sub> /100g	10.24	18.97	19.4	13.15	14.39	11.6	15.48	28.04	16.41
Chemical Composition									
Mono-Aromatics	9.40	23.60	12.70	19.80	14.70	29.30	22.00	11.10	17.83
Di-Aromatics	70.70	51.40	56.30	52.50	54.60	44.10	45.10	55.00	53.71
Tri-Aromatics	7.10	8.60	14.40	6.10	6.70	2.00	5.40	5.60	6.99
Total Aromatics	87.20	83.60	83.40	78.40	76.00	75.40	72.50	71.70	78.53
Aliphatics	12.80	16.40	16.60	21.60	24.00	24.60	27.50	28.30	21.48
Cetane Index	17.9	20.7	21.08	23.62	24.8	23.7	28.7	28.3	23.60
Specific gravity	0.91	0.97	0.98	0.94	0.96	0.9	0.92	0.965	0.94
API gravity	23.99	14.38	12.89	19.03	15.90	25.72	22.30	15.13	18.67
Atmospheric distillation, °C									
IBP	236.9	173.5	225.2	214.8	200.3	173.4	151.5	178.8	194.3
5 vol.%	248.2	210.7	242.6	230.7	239.7	199.6	214.5	240.7	228.3
10 vol.%	250.5	221.1	246.5	236.2	249.7	207.2	221.9	257.5	236.3
30 vol.%	257.3	235.7	261.7	251.6	265.2	228.3	252.5	265	252.2
50 vol.%	264.2	259.2	279.1	264.5	275	248.5	268.2	277.8	267.1
70 vol.%	274.6	277.3	302.9	275.1	288.1	266.8	284.8	298.8	283.6
90 vol.%	285.5	316.3	349	288.3	310.7	288.9	310.5	329.5	309.8
95 vol.%	310.2	330.6	365.8	314.3	323.9	299.9	321.6	337.3	325.5
FBP	326.9	344.2	392.3	335.6	345.8	315.5	334.5	350.5	343.2

Aromatics concentrations in LCO samples were in the following intervals (Table 3): mono-aromatics: 9.4-29.3 wt.%; di-aromatics: 44.1-70.7 wt.%; tri-aromatics: 2.0-14.4 wt.%; total aromatics: 71.7-87.2 wt.%, respectively. According to the average values, the ratio of mono-/di-/tri- aromatics (i.e. 2.6/7.7/1.0), showed a predominant presence of di-aromatics (i.e., 68.4% of the total aromatics content), which were followed by the mono-aromatic compounds (i.e. 22.7% of the total aromatics content). Due to the greater stabilization by resonance of mono-aromatic species those compounds are generally an order of magnitude less reactive than di-aromatics [9]. HYD of aromatics is sequential and cracking of the saturated outer ring of tri-aromatics occurs above 427 °C [9]. HCK of aromatic feeds needs catalysts with good saturation function and moderate-to-high acidity because those species could be cracked only after HYD and show tendency to deposit coke on the catalyst surface [24]. HYD of aromatics are exothermic and reversible reactions with lower equilibrium conversions under practical processing conditions of industrial interest. Thus, increasing temperature to achieve higher saturation reaction rates often results in lower equilibrium conversions, especially at lower pressures. In this line, during LCO HDT at high hydrogen partial pressure (7.8 MPa) in batch reactor over a CoMo/Al<sub>2</sub>O<sub>3</sub> sulfided catalyst [25] the minimum concentration of di-aromatics was found when operating at 360 °C. At higher temperatures (400 °C) thermodynamically favored dehydrogenation reactions resulted in mono-aromatics transformation back to corresponding di-aromatics which they came from. Summing up, operating at high hydrogen partial pressure, moderate temperature, low LHSV and using active dual-function catalysts is recommended to hydrogenate aromatics to an appreciable extent.

High concentration of mono- and di-aromatics could be valuable for BTX production [26]. Following that criterion, in Figure 2 various LCO samples are shown ordered from the most valuable to the least one. Tri-aromatics and alkanes are considered as not suitable for that particular purpose. After processing, poly-aromatics provided an array of hydrogenated hydrocarbons not particularly suitable to produce BTX as shown in reaction pathways of Figure 1. For example, phenanthrene hydrogenation demands for higher temperature and pressure, and enhanced hydrogen consumption as well, producing among other compounds: octahydrophenanthrene (OHP), octahydroanthracene (OHA), tetrahydrophenanthrene (THP) and dihydrophenanthrene (DHP) at 9.07%, 34.84%, 18.36% and 32.85% [27]. During the hydrocracking procedure, aliphatic compounds are converted to LPG gases [24]. Alternatively, a low presence of all kinds of aromatics and a high presence of long chain alkanes and iso-alkanes can be very suitable for diesel fuel production, as it is known that long linear hydrocarbons increased the quality of the diesel produced [28].



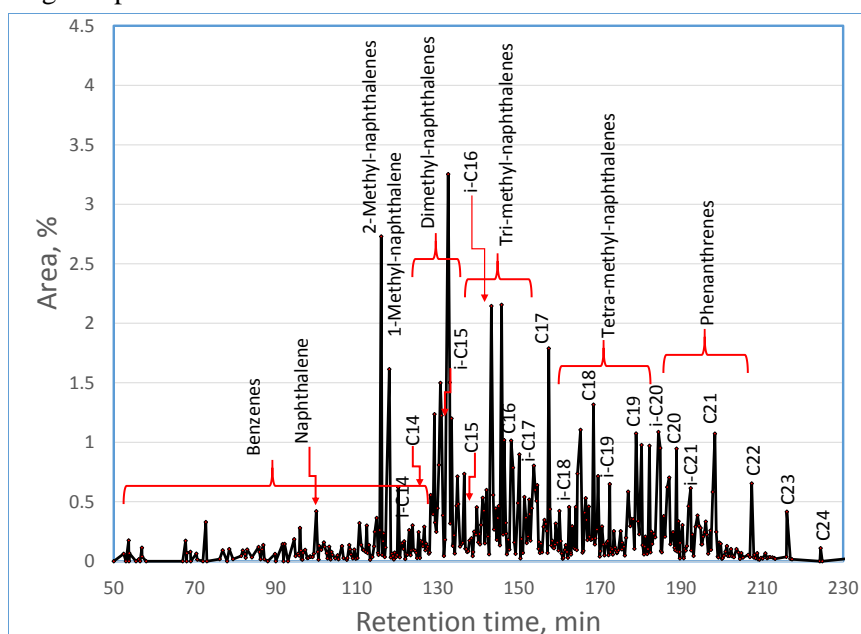
**Figure 2.** Chemical composition of various LCO samples by the ASTM D5183 method, from the most to the least suitable hydrocarbon type distribution for BTX production

Cetane index varied from 17.9 to 28.7 (Table 3), accordingly to the aromatics content. That is, the lowest value of the cetane index (i.e. 17.9) corresponded to the sample of the highest content of both di-aromatics (i.e., 70.7 wt.%) and total aromatics (i.e., 87.2 wt.%).

API gravities varied from 12.9 to 25.7 °API. Boiling point ranged from IBP: 151.5-236.9 °C, to FBP: 315.5-392.3 °C. Higher FBP means higher amounts of heavy aromatics not suitable for BTX production [26].

### 3.2. Identification of the LCO Composition by Lumps Using the GC-MS Technique.

Using mass spectrometry, the samples were analyzed. The retention times ( $T_R$ ) obtained compared successfully with the values presented by Alonso et. al. [17]. The identified compounds from Table 2 were grouped into lumps according to their chemical type as: alkanes and iso-alkanes, benzene and tetralin derivatives, naphthalene, mono-, di-, tri- and tetra-methylnaphthalenes (MN, DMN, TMN, TMN and TTMN respectively) and phenanthrene derivatives. This type of chemical characterization based on GC-MS chromatography technique of the sample 6 is shown in Figure 3. This characterization represents a fingerprint of a middle distillate and goes beyond the usual characterization of mono-, di- and tri-aromatics by the ASTM D5186 method (supercritical fluid chromatography with flame ionization detection, SFC-FID) and it could provide information on the potential of a sample to be used as feedstock in a given process.



**Figure 3.** Detailed GC-MS analysis of the LCO sample 6

**Table 2.** Retention times ( $t_R$ ) obtained by the GC-MS method (continuation)

Compound		$t_R$ (min)
<i>Alkanes</i>		
Tetradecane		126.0
Pentadecane		137.7
Hexadecane		148.9
Heptadecane		159.2
Octadecane		169.1
Nonadecane		178.6
Eicosane		187.6
<i>1,2,3,4-Tetrahydronaphthalenes /Tetralins) derivatives (only the HDT sample)</i>		
Naphthalene, 1,2,3,4-tetrahydro	Tetralin	97.2
Naphthalene, 1,2,3,4-tetrahydro-2-methyl-	2-Methyl-tetralin	104.9
Naphthalene, 1,2,3,4-tetrahydro-1-methyl-	1-Methyl-tetralin	106.0
Naphthalene, 1,2,3,4-tetrahydro-5-methyl-	5-Methyl-tetralin	111.7
Naphthalene, 1,2,3,4-tetrahydro-1,4-dimethyl-	1,4-Dimethyl-tetralin	113.0
Naphthalene, 1,2,3,4-tetrahydro-6-methyl-	6-Methyl-tetralin	115.1
Naphthalene, 1,2,3,4-tetrahydro-1,8-dimethyl-	1,8-Dimethyl-tetralin	119.6
Naphthalene, 2-ethyl-1,2,3,4-tetrahydro-	2-Ethyl-tetralin	120.2
Naphthalene, 1,2,3,4-tetrahydro-2,6-dimethyl-	2,6-Dimethyl-tetralin	121.3
Naphthalene, 1,2,3,4-tetrahydro-2,7-dimethyl-	2,7-Dimethyl-tetralin	121.9
Naphthalene, 1,2,3,4-tetrahydro-1,5-dimethyl-	1,5-Dimethyl-tetraline	123.0
Naphthalene, 5-ethyl-1,2,3,4-tetrahydro-	5-Ethyl-tetralin	123.6
Naphthalene, 1,2,3,4-tetrahydro-1,1,6-trimethyl-	1,1,6-Trimethyl-tetralin	124.6
Naphthalene, 1,2,3,4-tetrahydro-1,4,6-trimethyl-	1,4,6-Trimethyl-tetralin	125.2
Naphthalene, 1,2,3,4-tetrahydro-5,7-dimethyl-	5,7-Dimethyl-tetralin	127.8
Naphthalene, 1,2,3,4-tetrahydro-5,6-dimethyl-	5,6-Dimethyl-tetralin	128.3
Naphthalene, 1,2,3,4-tetrahydro-1,5,7-trimethyl-	1,5,7-Trimethyl-tetralin	129.4
Naphthalene, 1,2,3,4-tetrahydro- 2,5,8-trimethyl-	2,5,8-Trimethyl-tetralin	133.5

A comparison between LCO samples 1 and 7 in Figure 4, shows some differences between LCOs. SIM in the GC-MS technique demonstrated the presence of naphthalene derivatives. However, when using the SCAN mode, tetralin derivatives could be observed.

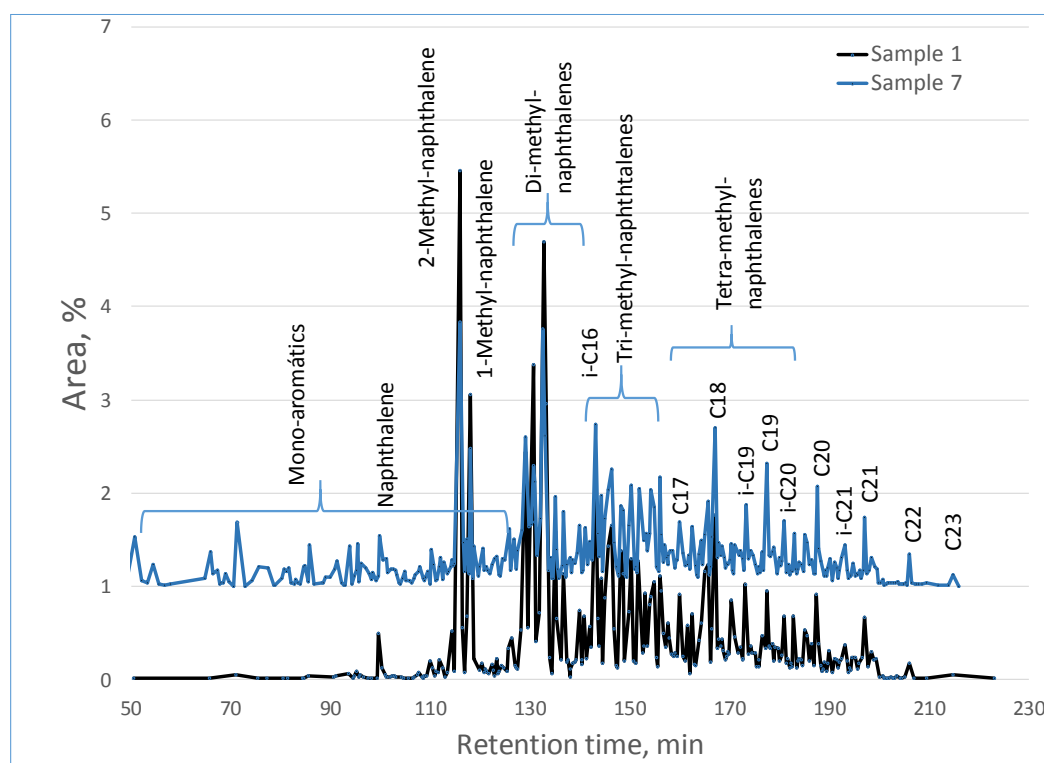
**Figure 4.** Comparison of GC-MS chromatograms of LCO samples 1 and 7.

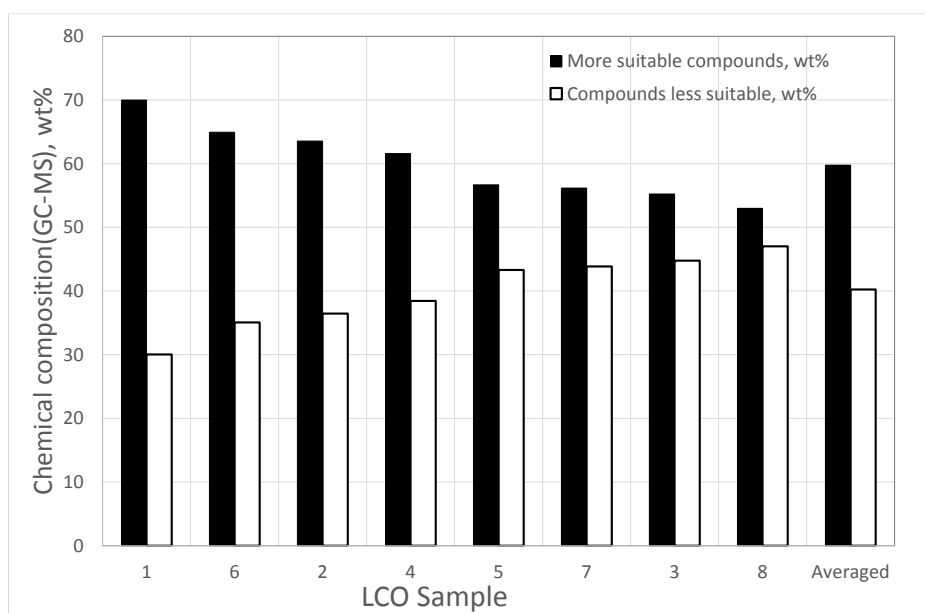
Table 4 shows the characterization of the LCO samples according the lump separation depicted before. The presence of methyl-naphthalene (MN), di-methyl-naphthalene (DMN), tri-methyl-naphthalene (TMN) and tetra-methyl-naphthalene (TTMN) derivatives in the LCO samples were from 4.3 to 10.0, 12.1 to 28.5, 13.8 to 20.3 and 10.1 to 14.8 wt.%, respectively. It is quite clear that, DMN and TMN derivatives were predominant in almost all studied samples, being the percentages of the average ratios 11.6, 31.4, 32.5, and 23.5.

**Table4.** GC-MS characterization by lumps of LCO samples 1 to 8

LCO sample	1	2	3	4	5	6	7	8	Averaged
n-Alkanes, wt%	6.23	6.70	8.01	8.75	9.55	8.53	9.74	8.96	8.31
I-Alkanes, wt%	6.09	10.24	8.94	12.31	13.32	14.30	15.38	17.69	12.28
Benzene der. , wt%	9.48	24.54	12.85	20.47	16.89	28.00	21.08	13.04	18.29
Naphthalene, wt%	0.48	0.32	0.45	0.79	0.42	1.14	0.54	0.20	0.54
MN, wt%	8.26	9.99	6.47	6.74	4.39	5.11	4.33	4.86	6.27
DMN, wt%	28.46	14.90	19.06	16.30	18.24	13.74	12.15	14.94	17.22
TMN, wt%	20.31	13.79	16.41	17.28	16.74	16.95	18.06	19.94	17.44
TTMN, wt%	13.70	10.91	13.40	11.37	13.54	10.14	13.33	14.80	12.65
Phenanthrene der. , wt%	7.00	8.60	14.41	6.00	6.90	2.10	5.40	5.56	7.00

It is noteworthy to remember that heavily alkylated naphthalenes, phenanthrene derivatives and aliphatic hydrocarbons are not suitable as feedstock for BTX production, and the presence of the tetra-methylated aromatics are going to face difficulties during HYD for any upgrading purpose due to the steric hindrance exerted by these groups. Furthermore, it has been reported [16, 26] that as the number of methyl moieties attached to aromatic rings in naphthalene derivatives increases so does the difficulty for their hydrogenation to tetralin derivatives. Therefore, presence of large amounts of highly branched naphthalenes could affect the yield towards BTX fraction from a given LCO sample.

For the BTX production a term was defined as most suitable compounds for BTX production or MSCB, by summing up benzene, mono-, di- and tri-methylnaphthalene derivatives. In Figure 5 the LCO samples were ordered from the most to the least suitable.



**Figure5.** Chemical composition of various LCO samples by the GC-MS method, from the most to the least suitable hydrocarbon type distribution for BTX production.

### 3.3. Characterization of the Fractionated LCO Sample 6 by ASTM Methods.

The results of some ASTM standards of the fractionated LCO sample 6 is shown on Table 5. Sulfur compounds presented the usual bimodal distribution where benzothiophenes appeared before 300 °C



boiling point whereas dibenzothiophenes were identified after that temperature, as already disclosed in previous publications [1]. The nitrogen compounds increased as the boiling point of the fraction [1]. Carbazole type compounds are expected to be the main nitrogen compounds present [1].

**Table5.** Characterization of the 20 °C-boiling point fractions of LCO sample 6 according to used ASTM methods

Boiling point interval (°C)		175-195	195-215	215-235	235-255	255-275	275-295	295-315	315-335	>335
Distillated amount (wt.%)	AST M	1.82	1.87	8.53	15.98	19.88	19.98	11.87	10.54	9.52
Sulfur (wt%)	D4294	0.90	1.42	2.95	4.41	4.39	3.20	2.58	3.45	3.82
Nitrogen (mg/kg)	D4629	138	179	139	189	351	343	199	522	1451
Chemical composition (wt.%)	D5183									
Mono-aromatics		63.9	60.7	48.9	17.8	8.9	6.2	4.8	4.2	4.4
Di-aromatics		15.3	22.3	35.8	69.1	78.2	76.8	60.4	36.8	19.9
Tri-aromatics		0.1	0.2	0.3	1.5	2.1	4.6	18.7	40.1	50.5
Total aromatics		79.3	83.2	85.0	88.4	89.2	87.6	83.9	81.1	74.8
Aliphatic		20.7	16.8	15.0	11.6	10.8	12.4	16.1	18.9	25.2

The chemical composition obtained by using the ASTM D5186 followed the tendency reported previously [1, 2]. As it was already discussed, both aliphatic and tri-aromatic hydrocarbons are not desirable when intending to use LCO as feedstock for BTX petrochemicals production [24, 27] although aliphatic hydrocarbons would be suitable for diesel [28]. Aliphatic compounds appeared all along the boiling point intervals from 10.8 to 25.2 wt%. Clearly, higher heavy aliphatic concentration was registered at the upper end of the distillation curve and mostly of them were long n-alkane hydrocarbons. Tri-aromatics showed up in the 295-315 °C boiling point interval their amount increasing in heavier fractions. Evidently, final boiling point temperature should be lower than 295 °C to eliminate that type of compounds in each LCO sample.

### 3.4. Chemical Characterization of the Fractionated LCO Sample 6 by the GC-MS Method.

The chemical characterization of 20 °C-boiling point fractions from LCO sample 6 according to the detailed GC-MS method previously described, is shown in Table 6 Phenanthrene (tri-aromatic) derivatives appeared in very low concentration in the 275-295 °C fraction notably increasing their amount in the subsequent heavier cuts. TTMN which did not show good reactivity towards hydrogenation aiming to tetralin formation [16, 26], were the main components exactly in the 295-315 °C fraction, and it is convenient to avoid them.

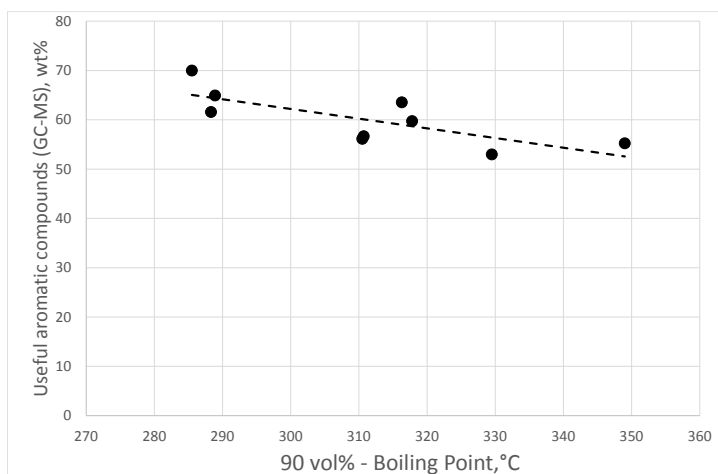
**Table6.** Characterization of the 20 °C-boiling point fractions of LCO sample 6 according to the detailed GC-MS technique.

Boiling point interval (°C)	175-195	195-215	215-235	235-255	255-275	275-295	295-315	315-335	>335
Distillation (wt.%)	1.82	1.87	8.53	15.98	19.88	19.98	11.87	10.54	9.52
n-Alkanes	8.60	6.17	6.82	4.52	8.55	6.07	5.50	9.55	16.88
iso-Alkanes	12.31	11.03	9.07	6.22	9.21	8.43	10.72	7.63	9.43
Benzene der.	62.21	65.50	40.52	6.54	0.00	0.00	0.04	0.00	0.00
Naphthalene	6.61	6.93	2.42	0.07	0.00	0.00	0.00	0.00	0.00
MN	5.83	6.04	31.04	7.50	43.76	0.00	0.00	0.00	0.00
DMN	3.63	4.10	10.05	73.76	37.96	8.27	0.00	0.00	0.00
TMN	0.59	0.18	0.06	1.33	0.34	57.30	16.36	1.16	0.00
TTMN	0.05	0.06	0.04	0.06	0.18	19.33	58.50	37.87	13.15
Phenanthrene der.	0.16	0.00	0.00	0.00	0.00	0.60	8.88	43.79	60.53

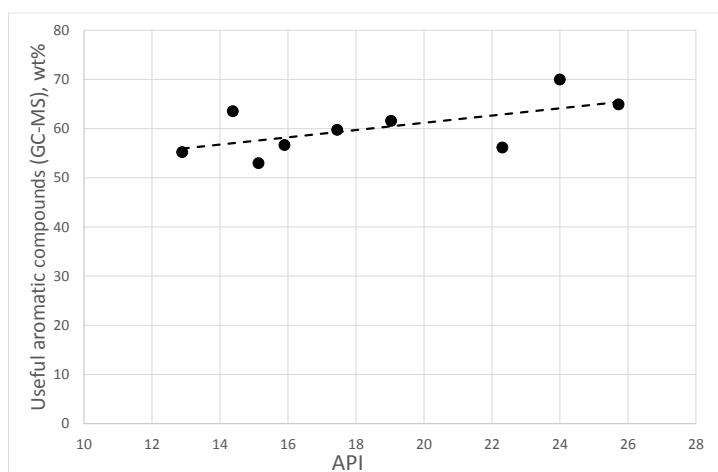
### 3.5. Practical Relations to Apply for Selecting a Suitable LCO Feedstock for Upgrading.

A better LCO for upgradeability purposes to BTX must possess a low value of FBP, to avoid highly methylated naphthalene and phenanthrenes derivatives as is shown in Figure 6. The lowest the value of

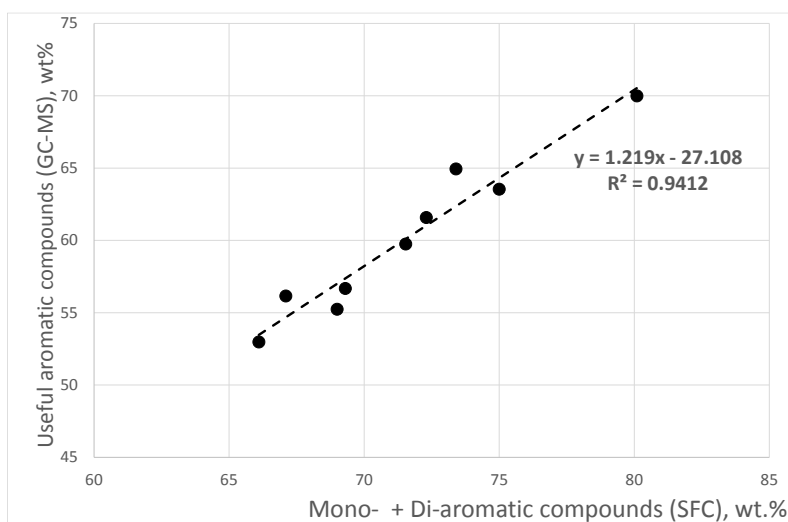
the 90 vol% distillation boiling point was, the higher the more suitable hydrocarbons presence was. It is convenient that the LCO presented a high API value (Figure 7). A rapid suitability analysis may be carried out graphically after summing the mono- and di-aromatic compounds values obtained from the ASTM D5186 test versus the most suitable compounds for BTX (MSCB) and calculate according to Figure 8.



**Figure6.** Effect of the 90 vol% distillation boiling point on the amount of the more suitable compounds for BTX production.



**Figure7.** Effect of the API on the amount of the more suitable compounds for BTX production



**Figure8.** Effect of the mono- + di-aromatic content on the amount of the more suitable compounds for BTX production

### 4. CONCLUSION

A detailed chemical characterization of samples of LCO was presented. The method could be useful for decision-making regarding the suitability of certain distillate as feedstock for valuable petrochemicals (like benzene, toluene and xylene) production or gasoline. Detailed characterization allowed not just the usual separation as mono-, di- and tri-aromatic compounds, obtained by the ASTM D5186 method (supercritical fluid chromatography with flame ionization detection) but also provided information regarding the complexity of the naphthalene derivatives (mono-, di-, tri- or tetra-methyl-naphthalenes) which could have different reactivities during the hydrogenation-hydrocracking processes required when aiming to valuable petrochemicals or diesel production.

By using the provided data, the amount of the more suitable compounds for upgrading to BTX (MSCB) production was defined by summing up benzene, mono-, di- and tri-methylnaphthalene derivatives. This value presented an inverse relation with 90 vol% boiling point and a direct relation with API. An equation relating the amount of mono- and di-aromatic compounds obtained by ASTM D55186 with the most suitable compounds for BTX (MSCB) value, is also provided.

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### REFERENCES

- [1] Laredo G.C., Leyva S., Álvarez R., Mares M.T., Castillo J., Cano J.L. Nitrogen compounds characterization in atmospheric gas oil and light cycle oil from a blend of Mexican crudes. *Fuel* 81(10) 1341 (2002);
- [2] Laredo G.C., Figueroa Y., Cano J.L., Mares M.T., Castillo J. Chemical composition of LCO obtained from Mexican crudes. *Rev. Soc. Quím. Mex.*, 46(2), 115 (2002).
- [3] Norma Oficial Mexicana de Emergencia NOM-EM-005-CRE-2015, Especificaciones de calidad de los petrolíferos. *Diario Oficial de la Federación*. 30/10/2015.
- [4] <https://www.epa.gov/diesel-fuel-standards/diesel-fuel-standards-rulemakings>.
- [5] Choi K.-H., Sano Y., Korai Y., Mochida I. An approach of deep desulfurization of light cycle oil. *Appl. Catal. B*. 53 (4), 275 (2004).
- [6] Laredo G.C., Saint-Martin R., Martínez M.C., Castillo J., Cano J.L. High quality diesel by hydrotreating of atmospheric gas oil/light cycle oil blends. *Fuel*;83(10), 1381 (2004).
- [7] Turaga U.T., Song C. MCM-41 support Co-Mo catalyst for deep hydrodesulfurization of light cycle oil. *Catal. Today*; 6 (1-4), 129 (2003).
- [8] Yao S., Zheng Y., Ding L., Ng S., Yang H. Co-promotion of fluorine and boron on NiMo/Al<sub>2</sub>O<sub>3</sub> for hydrotreating light cycle oil. *Catal. Sci. Technol.* 2(9),1925 (2012).
- [9] Azizi N., Ali S.A., Alhooshani K., Kim T., Lee Y., Park J-I., Miyawaki J., Yoon S-H., Mochida I. Hydrotreating of light cycle oil over NiMo and CoMo catalysts with different supports. *Fuel Process. Technol.* 109, 172 (2013).
- [10] Yun G-N., Lee Y-K. Dispersion effects on Ni<sub>2</sub>P catalysts on hydrotreating of light cycle oil. *Appl. Catal. B*. 150-151 (May), 647 (2014).
- [11] <http://www.mustangeng.com/NewsandIndustryEvents/Publications/Publications/MUSTANGPTQ.pdf>.
- [12] Lee C.K., McGovern S. J., Zagorsk J. A. Refiners have many options to convert high-aromatic streams into ULSD. *Oil & Gas J.* (05/15/2006).
- [13] Bisht D., Petri J. Considerations regarding light cycle oil upgrading with hydroprocessing technologies. *Ind. Chem. Eng.* 56 (4), 321 (2014).
- [14] Laredo G.C.; Perez Romo P., Escobar J., Garcia-Gutierrez J.L. Vega-Merino P. Light Cycle Oil Upgrading to Benzene, Toluene and Xylenes by Hydrocracking: Studies Using Model Mixtures. *Ind. Eng. Chem. Res.* 56 (39), 10939 (2017).
- [15] <https://www.astm.org/>.
- [16] Choi Y., Lee J., Shin J., Lee S., Kim D., Lee J.K. Selective hydroconversion of naphthalenes into light aromatics. *Appl. Catal.* 492 (Feb),140 (2015);
- [17] Alonso D.E., Klitzke C. Blinkey J. Light and Middle Petroleum Distillate Characterization Using Two-Dimensional Gas Chromatography–High-Resolution Time-of-Flight Mass Spectrometry and Enhanced Software Processing. *Spectrometry*. 14 (1), 21 (2016).

- [18] Vendevre C., Ruiz-Guerrero R., Bertoncini F., Duval L., Thiébaud D., Hennion M-Cl. Characterization of middle-distillates by comprehensive two-dimensional gas chromatography (GC x GC): A powerful alternative for performing various standard analysis of middle-distillates. *J. Chromatogr. A.*; 10861-2), 21 (2005).
- [19] Ruiz-Guerrero R., Vendevre C., Thiébaud D., Bertoncini F., Espinat D. Comparison of comprehensive two-dimensional gas chromatography coupled with sulfur chemiluminescence detector to standard methods for speciation of sulfur-containing compounds in middle distillates. *J. Chromatogr. Sci.* 44(9), 566 (2006).
- [20] Adam F., Thiébaud D., Bertoncini F., Mourtiade M., Hennion M-Cl., Supercritical fluid chromatography hyphenated with twin comprehensive two-dimensional gas chromatography for ultimate analysis of middle distillates. *J Chromatogr. A*, 1217 (8), 1386 (2010).
- [21] Jennerwein M.K., Eschner M., Gröger Th., Wilharm Th., Zimmermann R. Complete group-type quantification of petroleum middle distillates based on comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry (GCxGC-TOFMS) and visual basic scripting. *Energy Fuels*. 28 (9), 5670 (2014),
- [22] Alvarez-Majmutov A., Gieleciak R., Chen J. Deriving the Molecular Composition of Vacuum Distillates by Integrating Statistical Modeling and Detailed Hydrocarbon Characterization. *Energy Fuels* 29(12). 7931 (2015).
- [23] EPA. 1998. "Method 8270D (SW-846): Semivolatile Organic Compounds by Gas Chromatography/ Mass Spectrometry (GC/MS), Revision 4.
- [24] Sahu R., Song B.J., Jeon Y-P., Lee C.W. A review of recent advances in catalytic hydrocracking of heavy residues. *J. Ind. Eng. Chem.* 27(July), 12 (2015).
- [25] Palos R., Gutiérrez A., Arandes J.M., Bilbao J. Upgrading of High-Density Polyethylene and Light Cycle Oil Mixtures to Fuels via Hydroprocessing. *Catal. Today* 305 (May), 212 (2018).
- [26] Kim Y.S., Yun G.N., Lee Y.K. Novel NiP/zeolite catalyst for hydrocracking of naphthalene to BTX. *Chem. Commun.* 45(Feb), 133 (2014);
- [27] Zhang D., Zhao J., Zhang Y., Lu X. Catalytic hydrogenation of phenanthrene over NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts as hydrogen storage intermediate. *Int. J. Hydrogen Energ.* 41 (27), 11675 (2016);
- [28] Stanislaus A., Marafi A., Rana MS. Recent advances in the science and technology of ultra low sulfur diesel (ULSD) production. *Catal. Today* 153 (1-2), 1 (2010).

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