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Review

Chromatographic and spectroscopic analysis of heavy crude oil mixtures with emphasis in nuclear magnetic resonance spectroscopy: A review

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ABSTRACT

The state of the art in the characterization of heavy crude oil mixtures is presented. This characterization can be done by different techniques, such as gas chromatography (GC), high performance liquid chromatography (HPLC), thin layer chromatography (TLC), infrared spectroscopy (IR), Raman spectroscopy, nuclear magnetic resonance (NMR) spectroscopy and mass spectrometry (MS). Nuclear magnetic resonance spectroscopy is the technique of choice due to its capability to provide information on the chemical nature of individual types of hydrogen and carbon atoms in different and complex mixtures of crude oils. The progress made in the interpretation of the NMR spectra with the development of new NMR techniques and different multivariate data analyses could give relevant information about the identification and characterization of hydrocarbons and their physical and chemical properties. These progresses can improve the refining industries operation as a result of the better knowledge on the crude composition that is fed in the refining process, as well as in the prediction of better operating conditions to obtain refined products with desired specifications and in quantities desirable to meet the market demands. The improvement in the refining operation conditions is reflected in economical benefits.

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1. Introduction

1.1. Petroleum industry

Nowadays, the great challenge for the crude oil refining industry is to refine large quantities of heavy crude oils and to transform them into specific sets of refined products to meet the market's demands [1]. This means that all the crude mixtures should be converted from heavy fractions to light distillate products in multiple complex refining steps, including distillation, catalytic cracking, hydrocracking, and coking [2]. The complex mixtures are composed by many compounds (Table 1), ranging in size from the smallest to large compounds where the quantity of carbon atoms varies, which has different quantities of various compounds and special properties depending on the geographical source. It is necessary to make periodic reviews and to characterize these substances in terms of chemical structure and their physical and chemical properties. The need of a specialised and exhaustive characterization is related to different compositions, namely different concentration of asphaltenes, sulfur, nitrogen and metal ions (normally heavy crude oils have high concentrations), and hence different chemical and physical properties that characterized heavy crude oils. Even heavy crude oils being such a complex mixture it is notable that due to the increase in the competitiveness of the markets, the demand and the high cost associated to the conventional oils, it is more notorious the need to process crude oil with a great variety of heavy components, sulfur and nitrogen. For these and to adjust the production to meet market demands, to obtain products with high quality and respect the environmental specifications most of the refineries around the world have the necessity to change and improve their refinery units and process aiming to make an accurate control and know very well the composition of the heavy crude oils.

Some examples showing the importance of knowing the composition of raw materials and currents in a refining unit are presented:

1.1.1. Composition of crude oil fractions

There are some compounds like polyaromatics, that are toxic or carcinogenic [3], sulfur and heavy metals in high concentrations, which have environmental implications and cause huge problems in the refining process due to the corrosion and poisoning of the catalysts [4], and asphaltenes which cause environmental problems as well as problems in the refining process, due to their tendency to flocculate and precipitate. The higher concentration of these compounds that can lead to a greater formation of coke and the possibility to increase the deactivation of catalysts [5], have a negative effect on the smoke point of a jet fuel [6] and also the risk of affecting the combustion process in various motors [7]. In addition, the presence of conjugated dienes can bring serious problems in the industry because their presence can decrease the quality of the final products, due to their tendency to polymerize, being important to remove them from the oil fractions [8].

1.1.2. Yield of heavy aromatic compounds

The presence of heavy aromatic compounds can have a negative effect on the smoke point of a jet fuel and on the cetane number of a diesel.

1.1.3. Paraffins in heavy crude oil

It is important to control the presence of paraffins due to the tendency of some of these structures to the crackability [5], and in the crude blending. The control of the paraffins is related to the prevention of some problems that may occur during the transport in the pipeline and the storage due to its high pour point. The crude blending can bring some advantages to the transportation, due to the flow properties that became better, to the value of the product that increase and also to the efficiency of the refining [9]. On the other hand it is possible, due to the blending, that instability (in the pre-heated train heat exchangers during processing) increases as well as some inconveniences in the refinery, *e.g.*, precipitation of the asphaltenes and fouling problems [9,10].

1.1.4. Feedstock properties [4,5]

It is important to know the feedstock properties since these properties depend on the source of crude oil. The knowledge of the properties of crude oil is very important in the industry for the right choice of the crude processing units [11]. The chemical and physical properties, such as the viscosity and the density, of the crude oil are important factors to control. For example, it is important to control the viscosity index since it is widely used to define the oil quality and due to the facility of knowing the effect of the

Nomenclature

NMR	nuclear magnetic resonance
GASPE	gated spin echo
PCSE	part-coupled spin echo
DEPT	distortionless enhancement by polarization transfer
QUAT	quaternary—only carbon spectra
DOSY	diffusion-ordered spectroscopy
INEPT	insensitive enhancement by polarization transfer
2D HETCOR	heteronuclear correlation spectroscopy
2D COSY	homonuclear correlation spectroscopy
2D TOCSY	homonuclear total correlation spectroscopy
HSQC	heteronuclear single quantum correlation
HMBC	heteronuclear multiple bond correlation
PFGSE	pulse field gradient spin-echo
RELAY	heteronuclear relayed coherence transfer
C_a	aromatic carbon
C_{ah}	aromatic carbon protonated
C_b	bridgehead aromatic carbons
C_S	substituted aromatic carbon
C_T	total relative number of carbons
A	aromatic ring protons (6.5–9.0) ppm
B	α-alkyl CH_2 to aromatic ring groups (2.0–2.4) ppm
C	α-alkyl CH_3 to aromatic ring groups (2.0–2.4) ppm
D	β-CH and CH_2 groups to aromatic rings and –CH and CH_2 groups of cycloalkanes and normal and isoparaffins (1.0–2.0) ppm
E	CH_3 to aromatic and other paraffinic CH_3 (0.5–1.0) ppm
A_{rb}	bridgehead carbons
C_q	quaternary aromatic carbons
Z	atomic H/C ratio for non-aromatic groups
H/C	hydrogen carbon relation
H_a	aromatic protons
$I_n(n = 1,2,\ldots)$	integral intensity of the respective region marked in the NMR spectrum
I_T	total integral intensity
I_d	integral intensity in the region 7.5–10.0 ppm
n	average of alkyl chain length of aromatic substituents
$I_{3.5–2.4}$	integral intensity of the 3.5–2.4 ppm region
$I_{2.0–1.0}$	integral intensity of the 2.0–1.0 ppm region
$I_{1.0–0.5}$	integral intensity of the 1.0–0.5 ppm region
T_A	number of total aromatic
A_W	molecular weight of the aromatics
T_W	total group molecular weight
M_A	estimation of mono-ring
P_A	global Di-Plus ring aromatics
f_a	aromaticity (^{13}C)
(Hau/C_a)	ratio non-bridgehead aromatic carbon to total carbon
σ	degree of aromatic ring substitution
NC	average number of carbons per molecule
BS	average number of branching sites per molecule
N_B	average number of branches per molecule
N_R	average number of rings per molecule
N_C	average n-alkane chain length
C	fraction of carbons atoms present as C groups
CH	fraction of carbons atoms present as CH groups
CH_3	fraction of carbons atoms present as CH_3 groups
$I(CH_n)$	total ^{13}C NMR intensity due to the groups in parentheses
NP	percentage of normal paraffin
IP	percentage of iso-paraffin
C^*	average alkyl chain length
(t-Me)	percentage of terminal methyl
(b-Me)	percentage of branched methyl
$I_{31.9}$	integral area due to CH_3
$I_{29.5–30.7}$	integral intensity in the region (29.5–30.7) ppm
C_p	percentage of paraffinic carbons
$N(CH_n)$	average number of CH_n groups
$f(CH_n)$	fraction of ^{13}C NMR intensity due to the various CH_n groups
$N(C^{ar})$	number of non-protonated aromatic carbons atom
$N(CH^{al})$	side chain that contain branches associated with aliphatic CH groups
$N(C^{al})$	side chain that contain branches associated with aliphatic C groups
$N(CH_3{}^{al})$	side chain that contain branches associated with aliphatic CH_3 groups
$f(CH^{ar})$	fraction of ^{13}C NMR intensity due to aromatic carbon atom
$f(CH_n)$	fraction of ^{13}C NMR intensity
H_{ar}	^1H NMR aromaticity
f_{am}	molar content of aromatic groups for any complex hydrocarbon mixture that falls within gasoline
Hα	number of α hydrogens
H_t	number of hydrogen atoms per average molecule
M	average molecular mass
(H/C)α	Aromatic α-hydrogen to α-carbon atom ratio
C_{ar}	number of aromatic rings
H_a	number of aromatic ring hydrogen
fH_a	fraction of aromatic ring hydrogen
$fH_n{}^{\circ}$	mole fraction of olefinic protons
$(H/C)_o$	hydrogen to carbon atom ratio of olefinic bond structure
$(H/C)_t$	total hydrogen to carbon atom ratio
NIP	average alkyl chain length of iso-paraffin
NNP	average alkyl chain length of normal paraffin
$C_{ali}^{(CH_3)T}$	number of methyl carbons
$C_{ali}^{(CH_3)t}$	number of terminal methyl carbons
$C_{ali}^{(CH_3)br}$	number of branched methyl carbons
$C_{ali}^{(CH_2)T}$	number of methylene carbon
$C_{ali}^{(CH)T}$	number of methane carbon
$C_{ali}^{(np)}$	number of normal paraffinic carbons
$C_{ali}^{(bp)}$	number of branched carbons
C_{ali}^{N}	number of naphthenic carbons
$^{10}\sigma_{ar}$	aromatic substitution index
$^{11}\gamma_{ar}$	aromatic condensation index
$^{12}\sigma_{ar}$	aliphatic substitution index
^{13}ACL	average length of paraffin chain
C_n	long-chain n-alkyl carbon
C_{ah}	aromatic carbon protonated
A_{rq}	number of substituted aromatic carbons
M_A	estimation of mono-ring
P_A	global Di-Plus ring aromatics
N_S	number side chains per molecule
L_S	average side chain length
N_{SB}	number of side chain branches per molecule
N_R	number of rings

temperature variation on the oil viscosity. High viscosity index means small changes of viscosity with the temperature and small viscosity index means big changes [12]. Controlling the density of the crude is also important because low densities mean a higher API degree [13] and a higher commercial value.

1.1.5. Controlling the composition of products in every process unit, controlling the quality and maximize the yield of the resulting products using different types of crudes [14], as well as designing the used refinery processes

The refinery design needs to know the chemistry of the crude, because it is essential to have units providing the conversion of many types of hydrocarbons into fractions. Units that chemically transform the separated hydrocarbons into more desirable products and units which remove the undesirable substances and produce products with higher purity [15].

1.1.6. Reducing the problems in the refining process operation

The change in the crude quality due to the change in the nature, in the transport and storage conditions can be responsible for some problems in the operation of refining processes.

In conclusion it is important to know in detail the composition, the physical and chemical properties, to evaluate the quality of crude oil and to know the capacity of refining, by evaluating the yield and the quality of the final products. The characterization is done through some tests being the most important the TBP (true boiling point) analyses that can be obtained at atmospheric pressure, ASTM D-86, or even by using simulated distillation based in gas chromatography. The TBP allows the evaluation and characterization of crude giving information on the composition, the properties, the behaviour during storage and use, the yield determination of the crude as well as provide important information for the optimization of refinery processes. Even being the TBP an excellent way to characterize heavy crude oil, the main problem associated with this analysis is the long time needed to make these studies and to obtain results. There are other analysis and tests that can be done [viscosity–gravity constant (VGO), correlation index, K-UOP factor and other ASTM and IP] which are not so time consuming but, on the other hand, they just give a generalist idea about the composition and properties of crude oil. In consequence, the purpose is to develop a better quantification analysis, using known technologies able to efficiently characterize the crude oil, and contribute to the time reduction of analyses, to the cost reduction and to give online information. The main technologies available are reviewed on the next section.

2. Some chromatographic and spectroscopic techniques used in the analysis of the heavy crude oil

There are different methods to classify the chemical compounds present in crude oil that allows to draw some conclusions concerning their properties. Until now most of the methods used to analyze petroleum fractions are chromatographic methods, like gas chromatography [16], high-performance liquid chromatography [17], thin-layer chromatography, and some spectroscopic techniques like infrared spectroscopy [18], Raman [19], and NMR spectroscopy and also mass spectrometry [20].

2.1. Gas chromatography (GC)

GC is used in the separation and analysis of complex mixtures of many components that can be vaporized without decomposition. In the GC technique the sample is carried through the column by the moving phase (a gas). The rate taken by the chemical

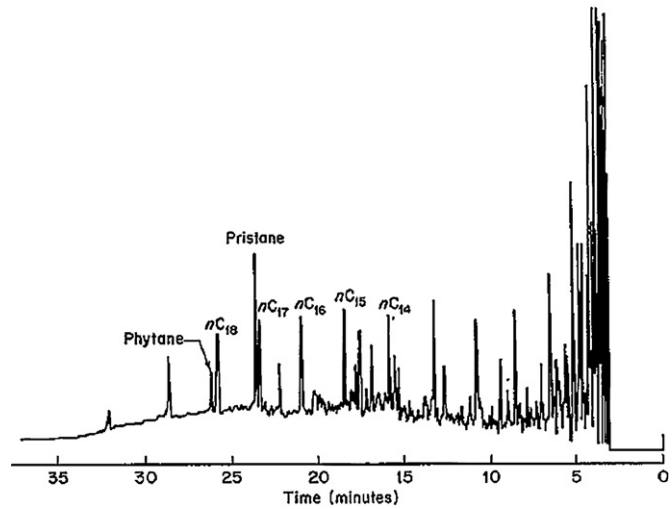


Fig. 1. Example of a GC spectrum of a light Nigerian crude (fraction with a boiling temperature smaller than 343 °C).
Reprinted with permission from [21].

constituents of the sample to pass through the column depends on their chemical and physical properties and on the interaction with the stationary phase (liquid or solid) of the column. The time taken for each compound to leave the column is called the retention time. The quantity of separated substances coming out of the column is detected and represented by an electronic signal. These signals are detected by some detectors as the flame photometric detector (FPD), flame ionization detector (FID) and the thermal conductivity detector (TCD), having different sensitivity (smallest quantity of compounds in analysis) and selectivity (type of compound). FID is very sensitive and selective just for some compounds, being used in the analysis of organic substances as benzene in gasoline according to the ASTM D3606 method [15]. The FPD is used in the identification of organic compounds containing sulfur or phosphorus as heavily biodegraded spill samples [21]. TCD is not very sensitive but very selective in detecting everything [22] being preferred in the analyses of crude oil fractions or products [15]. GC studies, using TCD detector, have proven that the mixture components are not destroyed during the analysis and just a small amount of the material is needed, while in the case of FID and FPD detectors the compounds are destroyed [22]. Beyond FID, FPD and TCD there are other detectors, as electron trap detector and nitrogen/phosphor thermo ionic detector, that can be used depending on the exactly compound under investigation. In spite of the advantages that can be achieved with the GC technique, due to the short time needed to make an analysis and the required small amount of sample, it is possible to conclude that this is not a very good method for the analysis of heavy crude fractions since all the compounds analyzed by GC must be in the gaseous phase and need to have a boiling temperature less than 350 °C [2,15]. The problem is that only the light fractions, as gasoline, kerosene and diesel, have a boiling point smaller than 350 °C. For the heaviest ones, as residue, the distillation temperatute is much higher, over 350 °C. The use of GC in the crude oil composition is limited or even inadequate due to the complex mixture of components, its composition in heavy compounds and the low volatility. This method is rather used when we have light [8] (Fig. 1) and middle distillates. Some examples on the application of GC for the crude oil characterization are the ASTM D2163 for the analysis of gaseous boiling range, ASTM D2427 method to gasoline boiling range, ASTM D3524 method for the analysis of diesel fuel and ASTM D3606 method for the aviation gasoline.

Table 1
Composition of crude oil.

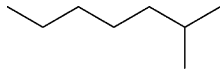
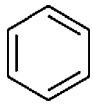
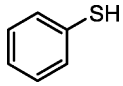
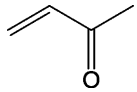
Hydrocarbons	Paraffins (*e.g. isooctane*)		Can present different structures, straight chain (normal paraffins) and branched chains (isoparaffins). Of these two different structures (straight and branched chains), the most frequently in the heavier fractions of crude oil are the branched chains [15]. The branched chains have a high octane index leading to a high quality of the gasoline.	
	Aromatics (*e.g. pyrene*)		The presence of aromatic compounds in heavy crude oils play an important role in the production of gasoline and in the production of aromatic compounds (ex.: toluene and benzene). It is possible to find heavy aromatic or light aromatic compounds depending on the petroleum fraction in analysis. The light ones have huge benefits for some units, as the platforming, once these compounds provide good octane indexes. The heaviest ones are responsible for some problems that may occur in some petroleum products, such as jet and diesel.	
	Naphthenes (*e.g. cyclohexane*)		Cycloalkanes, known as naphthenes in the petroleum chemistry, are cyclic saturated hydrocarbons defined by the number of rings, being mononaphthenes (monocyclic alkanes, C_nH_{2n}), dinaphthenes (dicyclic alkanes, C_nH_{2n-2}) and trinaphthenes (tricyclic alkanes, C_nH_{2n-4}). They are found in high quantities in most crude oils and are relatively stable.	
	Asphaltenes	(*)	Constitute the heaviest fraction of crude oil and are a complex mixture of molecules that contains significant quantities of heteroatoms (S, N, V, Ni, . . .), condensed aromatic rings, aliphatic chains and naphthenic rings.	**Drawbacks** They are responsible for the obstruction in flow lines, pipelines and petroleum wells and to the poisoning of the catalyst that are used in the cracking and hydrocracking [1].
Heterocompounds	Sulfur (*e.g. thiophenol*)		Sulfur may be present in the form of sulfites, thiophenols, cycloalkanethiols, thiophenes, benzothiophenes, alkylbenzothiophenes and as elemental sulfur. Crude can be classified as sour or sweet crude depending on the quantity of sulfur (values higher than 0.5% means sour crude and less than 0.5 means sweet crude).	They contribute to the development of corrosion, which damages the equipment, contributes to the air pollution due to the emission of SO_x in the atmosphere, to the catalyst contamination and are toxic. Sour crude cause many problems during the refining and its treatment is expensive and more difficult because needs specific equipments.
	Oxygen (*e.g. methyl vinyl ketone*)		These compounds may be present, for example, as carboxylic acids (ex: naphthenic acids), phenols, esters, amides and ketones.	They are responsible for the crude acidity. A high acidity means problems in the refineries as it aggravates the effect of corrosion in equipments and pipelines, make changes in the colour and odour and also in the costs associated with the equipments protection.

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Table 1 (*Continued*)

Nitrogen (*e.g. pyridine*)		These compounds may be present in the organic form, for example, in the form of pyridines, quinolines, pyrroles, polycyclic compounds with oxygen, sulfur and metals.	They contribute to the catalyst poisoning and are responsible for the change in the quality of the final products.
Metal ions		It is possible to distinguish nickel, vanadium, iron, zinc, mercury, boron, sodium, potassium, calcium and magnesium.	They are responsible for the catalyst poisoning.

(*) Asphaltenes do not have a chemical molecular structure. This is discussed in Section 4.

2.2. High performance liquid chromatography (HPLC)

HPLC is characterized by using high pressure to force chemical compounds to pass the column (metal tube) containing a stationary phase. HPLC is an important tool for the analysis of compounds that do not present enough volatility to be analyzed by GC. Besides the similarities between HPLC and GC, there are compounds analyzed by HPLC but not by GC. A crude with 80% of heavy fractions needs temperatures above 350 °C to vaporize, thus is more efficiently analyzed with HPLC than with GC. The possibility to obtain a good and efficient separation of heavy oil fractions and a very precise analysis in a very short time are the main advantages of HPLC. The main disadvantage of HPLC is that depending on the used detector [*e.g.* UV absorption (UV), refractive index (RI) or fluorescence (F)] there are some compounds which are impossible to distinguish. UV and F spectrophotometries only detect some species (F only detect fluorescent species), while RI has the ability to analyze all the compounds. However, the latter is not very sensitive and temperature variation can affect the output of the recorder [22]. HPLC is also a chromatography technique scarcely used in the analysis of crude oils since the objective is using one technique that provides precise analysis of every components and in a very short time, like minutes, if possible. When the objective is analysing group of compounds, such as paraffinic, naphthenic and aromatic compounds, HPLC continues to be a possibility, but to analyze individual compounds of crude oil the use of HPLC is inadequate. Besides that, HPLC does not give precise results when analysing hydrotreated and hydrocracked compounds which present identical boiling point range. However, HPLC was used in the identification of molecular types in non-volatile feedstocks, in the study of asphaltene fractions aiming to identify molecular species [23] and in the identification of aromatic groups (mono, di, tri- aromatics) [24]. HPLC is very important in fingerprinting oils being used in the identification of vanadyl compounds [25].

2.3. Thin layer chromatography (TLC)

TLC like the other chromatographic techniques, GC and HPLC, also have a stationary and a mobile phase. Here the stationary phase is silica or alumina placed on a glass, aluminum or plastic plate unlike the GC and HPLC where this phase is located in the column. The mobile phase is a solvent or a mixture of solvents that are needed to help in the separation of compounds. Hexane, tetrachloromethane, benzene, dichloromethane, trichlorometane, ethyl acetate, dioxane, acetone, isobutanol, isopropanol, ethanol and methanol are example of some used solvents. However, the use of mixture of solvents is desirable to ensure the properties needed for the chromatographic separation. TLC is an analytical method that can be used with other chromatographic and spectroscopic techniques to provide more information and analytical data on the isolated compounds. The TLC is used in the separation of mixtures and is proven to be faster and to provide better separations. It is also a simpler and an inexpensive technique, when compared with the HPLC and GC. It is recommended in the analysis of some organic substances. However, TLC is more often used in qualitative analysis, although other precise analyses are needed to analyze isolated substances. Until now, precise quantitative analysis was not obtained by TLC [15]. TLC is used in the analysis of heavy petroleum fractions being applied in the characterization of semi-volatile and non-volatile products and in the separation of compounds, such as asphaltenes, which present a high boiling point, proving to be simpler and quicker. Advances in TLC as TLC with flame-ionization detection (TLC-FID) has been used when the purpose was to make a distinction between hydrocarbon group, such as saturates, aromatics and polars ones in heavy oil (Fig. 2). Although, TLC presents some limitations as the impossibility to distinguish between diesel

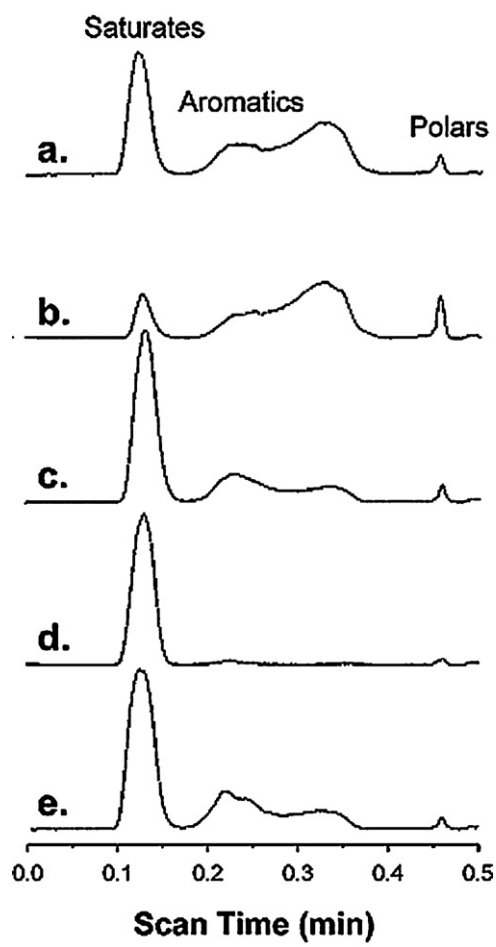

Fig. 2. Example of a TLC-Fid chromatograms of 500 N VGO cut and its fractions. Chromatogram (a) VGO, (b) extract, (c) raffinate, (d) wax and (e) base oil. Reprinted with permission from [26]. Copyright 2005.

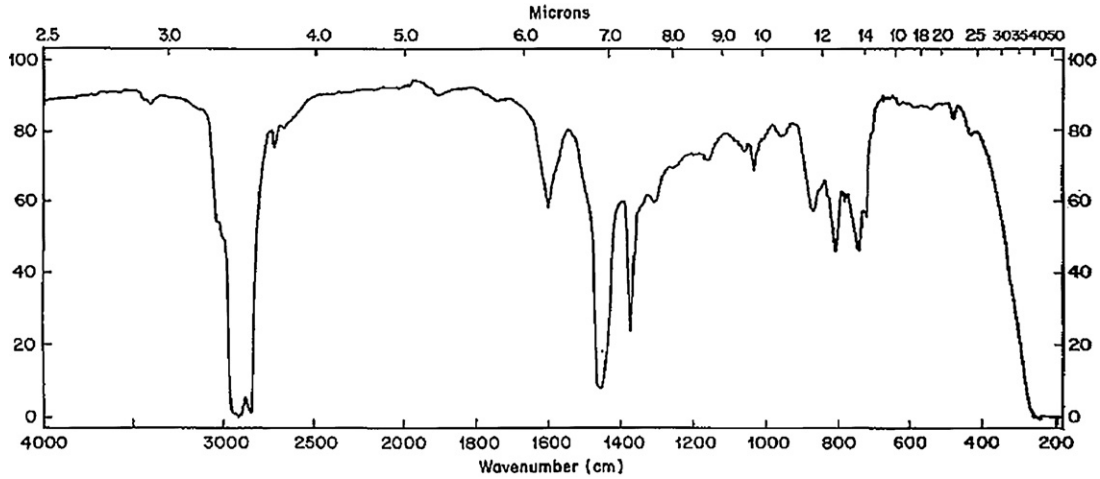

Fig. 3. Example of an IR spectrum of a heavy fuel oil.
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and jet fuel, two very similar products [11] and to give precise and accurate results.

2.4. Infrared spectroscopy (IR)

IR spectroscopy is one of the most important techniques that can provide miscellaneous information of complex mixtures of compounds, such as information about hydrocarbon skeleton and functional groups (*e.g.* hydroxyl and carbonyl groups). It allows to measure a great number of structural parameters like paraffinic and naphthenic character, aromatic hydrocarbons and methyl group content and gives information about functional features of various petroleum constituents, nature of polymethylene chains and the nature of polynuclear aromatic systems. It also contributes to the aging determination of oils related to the oxidation of carboxylic acids [27]. The main advantage of this technique is the possibility to analyze the hydrogen bonding in the crude oil mixture. It is possible to say that the IR can give more qualitative rather than quantitative information making impossible to detect some compounds. There is more limitations associate with this technique like the overlap that occurs between frequency ranges, which can be overcame by the use of NMR spectroscopy. There are some studies in the application of IR in the analysis of crude oil fractions (Fig. 3) but the implementation of this technique in more related with the study of middle distillates. An example is the determination of fatty methyl esters (FAME) content in middle distillates (EN 14078) and of benzene content in motor and aviation gasoline (ASTM D4053), the method of carbon type analysis in lubricating oils (EU AJ 051-01) and even the identification of chemical species as contaminated species (by comparison IR spectra). Another example is the use of IR in the study of spilled oils (derivatives from crude) but only in the definition of the chemical class to which they belong, since their use in the characterization and differentiation of different classes of hydrocarbons, from different heavy products, is difficult. In this case, once again, IR should be combined with other spectroscopic techniques [21]. On the other hand, it is possible to use multivariate techniques, such as the partial least squares regression (PLS) and principal component analysis (PCA) to predict properties of the sample in analysis [28] and with this establish correlations which could be an improvement for online IR.

2.5. Raman spectroscopy

Raman spectroscopy is used to obtain information about the vibrations of molecules bonds in the sample and to measure the energy needed to change the ground state of a chemical compound. The Raman effect occurs when there is a change in the molecular polarization, and can give more complete information than infrared spectroscopy. These two techniques are very similar in terms of results and can be used in combination to obtain more information about the analysis of petroleum samples [15]. Raman spectroscopy is used in the analysis of aromatic and olefinic compounds in hydrocarbon mixtures and it does not need a sample preparation and is quicker. This technique is not considered the best choice for the characterization of crude oil, fact which may be associated with the weak signal obtained in the Raman spectrum. Another disadvantage of using Raman spectroscopy in the analysis of crude oil may be related with the natural fluorescence, that leads to the impossibility of identifying any signals when hydrocarbon components are irradiated by visible lasers [15]. Details of these methods are mostly found when applied to light elements as gasoline (Fig. 4), gas oil, diesel, jet and kerosene and also when Raman is used in combination with Fourier transform. There are some studies on the use of

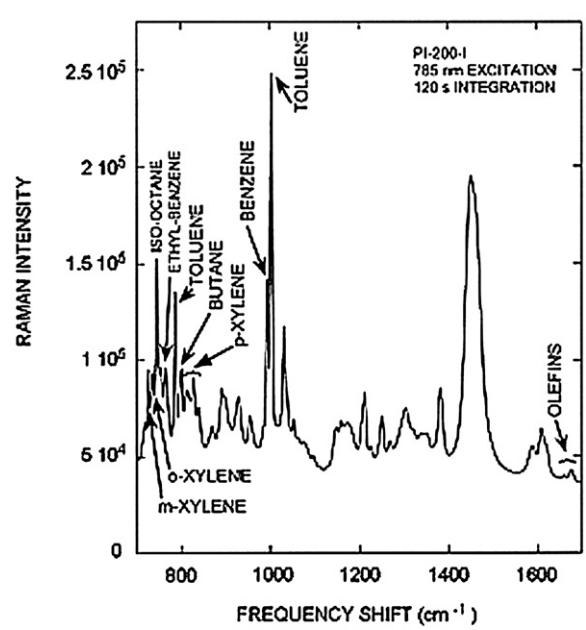

Fig. 4. Example of an Raman spectrum of a gasoline.
Reprinted with permission from [29].

FT-Raman spectroscopy in the determination of the octane number (RON), the motor octane number (MON), the pump octane number (pump) and the Reid vapour pressure (RVP) [30].

2.6. Mass spectrometry (MS)

MS can give information on the structure of some compounds, for example assigning their molecular formula based on the molecular weight, contributing to the identification of some compounds or to have an idea about new compounds. There are many different MS techniques that can be used, such as electron impact (EI), chemical ionization (CI), field ionization (FI), fast atom bombardment (FAB), among others. EI-MS is a technique of major importance and is characterized by the existent of a set of electrons with high energy that will contact with the molecules of compounds and will be responsible for the fragmentation of these molecules [22]. Normally each compound has a representative signal that results in the fragmentation of the molecule. For example, in alkyl chains the most pronounced fragments are caused by the loss of CH_3, C_2H_5 or C_2H_4. Fragments with four carbon atoms are an example of the most common ions of paraffinic chains. Other examples of fragments are those with C_3, C_2 and C_5. The monoalkylbenzenes are characterized by the fragment of C_6H_5. Besides these examples there are others related to monoalkylnaphthalenes, monoalkylphenanthrene, monocyclic alkanes and other molecules [2]. Being heavy petroleum fractions rich in thousand of compounds it is expected that due to such complexity and closely related compounds that the fragmentation patterns became crowded and impossible to distinguish. With this, EI-MS is not frequently used in the analysis of heavy petroleum fractions. Therefore, the most common type of MS techniques used in the analysis of heavy crude oil is the non-fragmenting (NF)-MS, also called, “soft ionization”. These techniques produce simpler spectra, when compared with the spectra resulting from the fragmentation [31]. For example, the hard fragmentation of aliphatic hydrocarbons does not follow a given pattern, making very difficult to identify these compounds. Sulfur and nitrogen compounds and species with the same chemical formula are also difficult to analyze, while other compounds like the aromatics has a good behaviour in the final spectra and are easy to identify, especially with “soft-ionization” techniques. Recently, the combination of some “soft-ionization” techniques as the low-voltage electron ionization, electrospray ionization (ESI), field desorption ionization (FDI) and atmospheric pressure photoionization (APPI) contributed to the development of FT-ICR-MS (Fourier transform ion cyclotron resonance mass spectrometry), which was used in the analysis of thousands of chemical constituents in heavy petroleum fractions. This new technique has already been used, for example, in the analysis of polycyclic aromatic sulfur heterocycles in different Arabian crude oils (Fig. 5) [32]. When the boiling point increases it becomes more difficult to use the MS in sample analysis due to the increase in the number of types of compound and the decrease in the concentration of these compounds [5]. Concluding, aromatic hydrocarbons, sulfur and nitrogen compounds are examples of compounds complicated to be analyzed by MS, and thus, to obtain information about all the heavy crude oil fractions it is necessary to use this technique conjugated with other complementary techniques. There is a possibility to use MS hyphenated techniques, like GC–MS or HPLC–MS, in other words a spectral method combine with chromatographic methods in order to exploit the advantages of both and obtain better information about the sample in analysis.

2.7. Nuclear magnetic resonance spectroscopy (NMR)

The NMR spectroscopy has been proven to be a very important technique in the study of heavy petroleum fractions and has

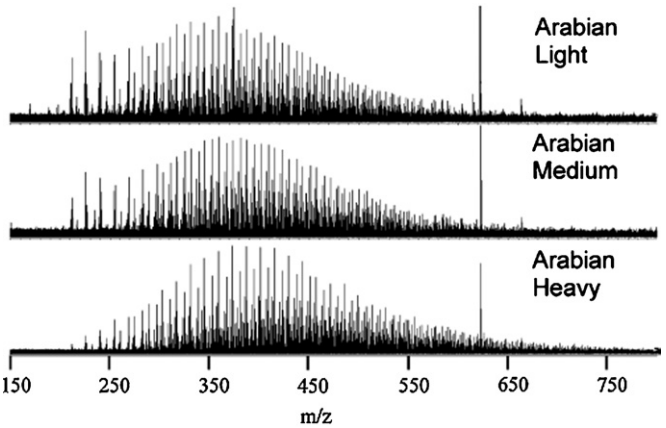

Fig. 5. Example of an ESI FT-ICR mass spectra of condensed thiophenes in different Arabian crude oil.
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became an alternative to the traditional methods used in laboratories. It has been applied in the study of the chemical composition of petroleum and in the characterization of petroleum fractions in a short time. It can provide an analysis in only a few minutes per stream, which can be performed in a continuous and online way and has the ability to analyze dark and opaque samples, such as crude. It is a rapid and non-invasive procedure, offering great analysis of the chemical nature of individual types of hydrogen and carbon atoms, in different and complex mixtures of petroleum and in the final products obtained by refining processes [27]. Even, the analysis of different types of carbon atoms and groups, like aliphatic, aromatic and other carbon-types [2] are possible. Besides the previously mentioned advantages there are other associate with this technique including the improvement in the analysis, reduction the number of analysis, reduction in maintenance costs and unique ability to provide all control properties with one analysis. As mentioned by the *Mesures Magazine* [33], the main advantages are the direct relation between the measured signal and the total proton concentration and the superior resolution of chemical information contained in the signals. In the NMR spectra the functional groups of aromatics, aliphatics and olefins are well distinguished, in consequence it is possible to distinguish a polynuclear aromatic from a mononuclear aromatic and to identify the fuel physical properties by the concentration of aromatics and the chain length of aliphatics. Besides these advantages there also exist commercial and operational benefits associated to the NMR spectroscopy. The commercial benefits are related to the optimization in the feed of refining processes to adjust the production taking into account the market necessity, to benefit the attractive price of some crudes and in saving money by using complete systems of acquisition analysis in a short time. The operational benefits are to improve higher value to product yields, maximize unit recovery of potential lost, throughput due to instability, and improve performance of downstream units [34]. On the other hand, there are some disadvantages associated with this spectroscopic technique like the high cost, the risk of magnetic disturbances, requiring magnetic shielding, and the overlap of frequency ranges. The overlap continues to make the analysis of the spectra a very difficult task. However, improvements have been made with the use of some techniques (DEPT, GASPE, COSY, etc.). Also the very complex information given by NMR spectroscopy requires a statistical approach to correlate the spectral data with the characterization of crude oil.

It is possible to conclude that there are some restrictions associated with all the present chromatographic and spectroscopic

techniques, making it unrealizable to analysis the heavy petroleum fractions. However, the NMR has been suggested as one of the most powerful methods for industrial analysis. Until now, NMR spectroscopy has been already used in some refinery laboratories with the purpose to determine the content in paraffinic and aromatic carbon contents of hydrocarbon oils [ASTM D5252-99(2009)] and also to determine the aromatic hydrogen and carbon content [IP 392/90], both by high resolution NMR. The hydrogen content of middle distillate petroleum products by low-resolution pulsed NMR [ASTM D7171-05], and the aromatic carbon content of lubricant mineral base oils and middle distillate petroleum fractions by ^{13}C NMR spectroscopy [IP 499] were also determined. Now, the great challenge is to use the online NMR once it can offer precise analysis in real-time and control the properties of the crude from the feed to the final product. Apart from the properties of crude oil it is possible to analyze the samples using the NMR spectroscopy, although, it is important to take in account, that the sample density and the viscosity affects the T_1 and T_2 relaxation times (*e.g.* high density and viscosity samples give spectra with broader signals and overlaps between different peaks difficult the NMR assignments). Analysis of heavy materials such as asphaltenes and residuals are also possible to be obtained.

3. NMR in the analysis of heavy crude oils

NMR has been used for a long time in the analysis of heavy petroleum fractions being first published by Friedel in 1959 [35], "*Absorption Spectra and Magnetic Resonance Spectra of Asphaltene*". Since then many researchers have been publishing the use of NMR in the analysis of heavy petroleum fractions. The main purpose was to help refineries to refine heavy crude oils with more efficient ways and at low processing costs.

This review has been prepared by the separation of the references into the following sections: ^{1}H NMR and ^{13}C NMR spectroscopy, ^{1}H and ^{13}C NMR spectra of crude samples, asphaltenes characterization, NMR techniques, NMR relaxation effects and multivariate data analysis of NMR spectra. All the equations used were summarized in Table 2.

Table 2
Equations used in the interpretation of the ^{1}H and ^{13}C NMR spectra.

Parameter	Expression	
C_a	$C_a = \left[(C_{ah} + C_S + C_b)/C_T\right] \times 100$	(6)
C_{ah}	$C_{ah} = I_1$	(7)
C_b	$C_b = 1.06 I_d$	(8)
	$C_b = 0.68 I_d$ [37]	(9)
C_S	$C_S = (B/2) + (C/3)$ [36, 37]	(10)
C_T	$C_T = (A/1) + (B/2) + (C/3) + (D/2) + (E/3) + A_{rb} + C_S$	(11)
A_{rb}	$\%A_{rb} = (0.68 I_d \times 100) C_T$	(12)
n	$n = [(I_{3.5-2.4}/2) + (I_{2.0-1.0}/2) + (I_{1.0-0.5}/3)/(I_{3.5-2.4}/2)]$	(13)
T_A	$T_A = (A_W/T_W) \times 100$	(14)
A_W	$A_W = 13A + 27B + 9C + 8.2 I_d$	(15)
T_W	$T_W = 13(A + B) + 9C + 7D + 5E + 8.2 I_d$	(16)
M_A	$M_A = T_A - P_A$	(17)
P_A	$P_A = (\%A_{rb} \times 100)/21.7$	(18)
f_a	$f_a = C_a/C_T$	(19)
(Hau/C_a)	$(Hau/C_a) = C_a - C_b/C_a$	(20)
σ	$\sigma = (C_S/C_a) - C_b$	(21)
NC	$NC = 6/f_a$	(22)
BS	$BS = NC(C + CH)$	(23)
	$BS = (b\text{-}Me \times C*)/IP$	(24)
N_B	$N_B = NC(2C + CH)$	(25)
N_R	$N_R = 0.5 \times NC(C + CH - CH_3) + 1$	(26)
	$N_R = 0.5(N_S + N(CH^{al}) + 2N(C^{al}) - N(CH_3^{al}))$	(27)
N_C	$N_C = (3I(CH_2) + 2I(CH_3)/I(CH_3))$	(28)
NP	$NP = 100 \times [(3I_{31.9} + I_{29.5-30.7})/I_T]$	(29)
IP	$IP = NP - C_P$	(30)
C^*	$C* = 2(C_p/t\text{-}Me)$	(31)
t-Me	$t\text{-}Me = 100 \times (I_{10.0-15.0}/I_T)$	(32)
b-Me	$b\text{-}Me = 100 \times [(I_{15.0-21.0} + I_{28.2})/I_T]$	(33)
$N(CH_n)$	$N(CH_n) = (f(CH_n)NC)$	(34)
H_{ar}	$H_{ar} = \left(f\left(CH^{ar}/\sum_{n=0}^{3} nf(CH_n)\right)\right)$	(35)
L_S	$L_S = (1 - f_a)N_C/NC$	(36)
N_S	$N_S = N(C^{ar})$	(37)
N_{SB}	$N_{SB} = N(CH^{al}) + 2N(C^{al})$	(38)

3.1. ^{1}H NMR spectroscopy of crude samples

^{1}H NMR spectroscopy has been successfully applied in the characterization and identification of crude oil fractions. It is a way to predict the total hydrogen content as well as the distribution of hydrogen among functional groups present in the crude. It contributes to obtain information about the structural characteristics, to estimate the molecular weight and to analyze the effects in several refining processes.

Sarpal et al. [36] developed an interesting work with the objective to create a new method to estimate the aromatic content (C_a) of base oils using ^{1}H NMR spectroscopy. Due to the interpretation of the ^{1}H NMR spectra and the use of two-dimensional heteronuclear correlation (2D HETCOR) technique it was possible to calculate the aromatic carbon content by changing the Brown–Ladner equation (1), as well as to estimate the bridgehead carbons (C_b) and the quaternary aromatic carbons (C_q) content. The objective for modifying the Brown–Ladner equation was due to the quantity of factors needed to determine the aromatic content, like the elemental H and C content, the average number of hydrogen per α-alkyl substituents, the atomic H/C ratio for non-aromatic groups (Z), the aromatic protons (H_a), among others. The new C_a Eq. (2) does not need the determination of such factors but just the directly use of one and two-dimensional NMR spectra. This method gives similar results than the Eq. (1) being more advantageous due to the possibility to be used in all types of base oils as well as to the quickness that the results are obtained. With that, the authors also developed other equations such as C_b Eq. (8) and C_S (substituted aromatic carbon) Eq. (10).

$$C_a = 100 - [(100 - H_a)(H/C)/Z] \quad (1)$$

$$C_a = [(C_{ah} + C_S + C_b)/C_T] \times 100 \quad (2)$$

Being the reduction of the aromatics content one of the future objectives of the refineries it is important to quantify the total amount of aromatics in the petroleum fractions. Bansal et al. [37] started to use ^{1}H NMR spectroscopy to estimate the content of total aromatics and their distribution as mono and polynuclear aromatics. These authors [37] started to analyze the ^{1}H NMR spectra and the 2D HETCOR (^{13}C–^{1}H) NMR spectra of a representative diesel sample and of the aromatic fraction of a diesel sample, respectively. They estimated some structural parameters like the number of substituted aromatic carbons (C_S) (10), the average of alkyl chain length (n) of aromatic substituents (13), the number of bridgehead carbons (C_b) (9), the number of total aromatics (T_A) (14) and also the estimation of mono-ring (M_A) (17) and global di-plus-ring aromatics (P_A) (18). 2D HETCOR spectra were used to improve the analysis and the signals assignment in the ^{1}H NMR spectra, due to the overlapping. It allowed to conclude that only exist –CH_3 groups between 0.5 and 1.0 ppm and did not exist any overlap; while some α-CH_3 (α-substitution in aromatic carbons) groups were found between 2.4 and 2.6 ppm. It was possible, as well, to find a relationship between the –CH_2 carbons, 25–40 ppm, and the protons that exist in the 2.4–3.5 ppm region. With these data, it was concluded that some α-CH_2, α-CH_3 substituents on the aromatics and also some α-CH protons in the range 2.4–3.5 ppm exist. In the ^{13}C NMR spectra, the overlap achieved between 18 and 20 ppm may be due to the methyl substituents of the aromatic carbons.

Table 3
Chemical shift regions of various types of protons.

	Chemical shift range (ppm)	Type of protons
Aromatic region	6–9	Total aromatic proton
	6–7.2	Mono-aromatics proton
	7.2–7.6	Di-aromatic molecules
	7.2–8.0 or >8.0	Poly-aromatics molecules
Aliphatic region	2.05–4.5	H-α to aromatic ring
	1.1–2.05	H-β to aromatic ring in paraffinic CH and CH_2
	0.4–1.1	H-γ to aromatic ring/terminal CH_3
	1.3	CH_2 in long alkyl chains
	0.5–4.5	Total aliphatic proton
	0.9	CH_3 in long alkyl chains
	2.1	CH_2 in aromatic rings
	2.6	CH_3 in aromatic rings

From the ^{1}H NMR spectra interpretation of heavy crude oil developed by Durand et al. [38], Behera et al. [5], Bansal et al. [37], and Ali et al. [39] it is possible to assign a range of chemical shifts to different protons (Table 3).

3.2. ^{13}C NMR spectroscopy of crude samples

The information given by the ^{13}C NMR spectra is generically similar to that of ^{1}H NMR spectra. The ^{13}C NMR gives information related to the molecular carbon skeleton, being also an important method for the structure elucidation and chemical composition of a sample. In addition, it detects the existence of quaternary carbons of many functional groups (C≡N, C=O, C=NR, etc.) [40] and produces spectra with well-resolved features. For this reason ^{13}C NMR spectra has become one of the methods of choice in the analysis of crude oil fractions, even though crude is a very rich complex mixture of a large number of constituents. When comparing ^{1}H and ^{13}C NMR spectra it is possible to identify many differences between them. For example, ^{13}C NMR spectra have much larger chemical shifts scale (more than 220 ppm) that produces less overlapping between peaks. The ^{13}C NMR is less sensitive than ^{1}H NMR due to their lower natural abundance (1.1%) and magnetogyric ratio of the ^{13}C nucleus, but in the case of the ^{1}H decoupled ^{13}C NMR spectra it is much simpler once there is no peak splitting.

Yoshida et al. [41] developed a work on some characteristics compounds in the ^{13}C NMR spectra of the ring-type fractions of coal-derived oil aiming to determine the chemical shift ranges of protonated, bridgehead, and substituted carbons of this type of sample and with that determine the equation for structural parameters. From the results of the Yoshida work [41] it was established that usually, aromatic carbons appear in the order of protonated, bridgehead, and substituted carbons from low to high frequency values. Normally, the chemical shifts of the protonated carbon appear at 115.0–129.2 ppm, the bridgehead carbons at 129.2–132.5 ppm, and the substituted carbons at 132.5–149.2 ppm. However, the presence of the phenolic OH and the amino groups influence the chemical shift of the neighbor protonated carbon shifting them to lower frequency values. Some of the bridgehead carbons were extended to a field lower than 132.5 ppm and others continued to appear in the range of 129.2–132.5 ppm, depending if these carbons were naphthalene and methylated or just naphthenonaphthalene, respectively. On the other hand, the chemical shift of the substituted carbons depends on the type of aliphatic carbons bonded to aromatic rings. In the subsequent ^{13}C NMR spectra analysis it was possible to assign some signals to chemical shifts of model compounds, for example, the signals at 132.5–137.2 ppm were due to substituted aromatic carbons bonded to methyl groups or to cycloparaffinic α-CH_2. The signals at 137.2–149.2 ppm corresponded to the resonance of substituted aromatic carbons bonded to some of alkyl groups (not include methyl and methylene bridge between aromatic rings) and that at 149.2–158 ppm to C_a–OH groups. Other important aspects established in the Yoshida work [41] were that the coal-derived oil contains a lot of alkyl substituents and naphthenic rings. It was also possible to reach this conclusion through the analysis of some structural parameters like the aromaticity (f_a) (19), the ratio of non-bridgehead aromatic carbon to total carbon (Hau/C_a) (20), and the degree of aromatic ring substitution (σ) (21).

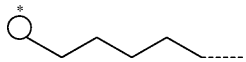
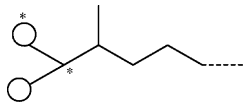
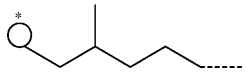
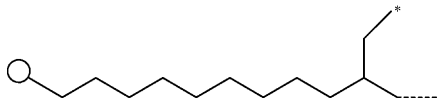
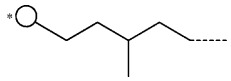
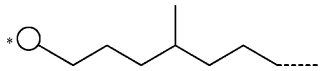
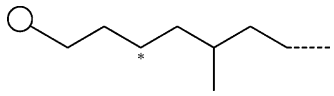
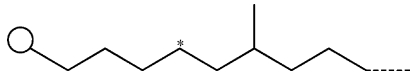
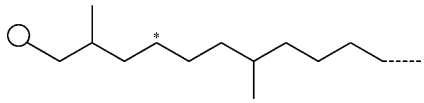
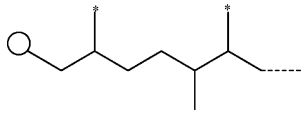
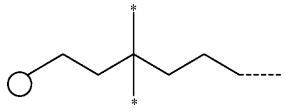
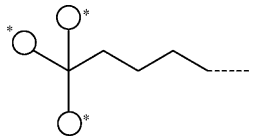
Cookson and Smith [42] studied a total of nine diesel samples, six of which were petroleum and three of them were synfuels, with two kerosene samples, aiming to obtain a better understanding on the differences in the composition, structural characteristics, and in the properties of each fuel using the ^{13}C NMR spectroscopy. They have used the gated spin echo technique (GASPE) with the objective to minimize the overlap of resonances due to C, CH, CH_2 and CH_3 groups that usually occurred in a ^{13}C NMR spectrum of complex mixtures. From the analysis of the resonances appearing in the spectra, they could identify a possible structure of n-alkane, $(\alpha CH_3)_2(\beta CH_2)_2(\gamma CH_2)_2(\delta CH_2)_2(\varepsilon CH_2)_2$, and therefore calculate some parameters as the N_C (average n-alkane chain length) (28), BS (average number of branching sites per molecule) (23), N_B (average number of branches per molecule) (25) and N_R (average number of rings per molecule) (26). It was also demonstrated that all the diesel samples have an average chain length of 15–16 carbons while the kerosene examined has about 12 carbons chain length. However, firstly it is necessary to estimate the average number of carbons per molecule (NC) that depends on the sample used. NC is not always equal to the average n-alkane chain length (N_C), once n-alkanes, branched saturated and cyclic saturated structures may have different average number of carbons atoms.

The same authors, Cookson and Smith [6], compared 50 jet and diesel fuels using ^{13}C NMR spectroscopy, to understand some fuel properties and to define its composition (like aromaticity information as well as n-alkane abundance). The main objective of this analysis was to provide better information about the composition of this type of samples needed for the preparation of better quality refining products. Using earlier published works [42,43], Cookson and Smith [6] developed a new approach (3) that listed a fraction relation of the total ^{13}C NMR spectral intensity due to a long-chain n-alkyl carbon (C_n) atoms with the fraction of the total ^{13}C NMR spectral intensity due to aromatic carbon (C_a) atoms. In this Eq. (3) b_1, b_2 and c were determined by a multiple linear regression and P was the property value. Cookson and Smith [6] only considered the ^{13}C NMR spectroscopy to determine the samples composition, since it was considered a good technique to provide aromatic carbons identification. They had also proven that this approach was more efficient than other complex equations, better to distinguish a large quantity of fuels from different sources and available to determine their properties.

$$P = b_1 C_n + b_2 C_a + c \quad (3)$$

Sarpal et al. [44] began to develop some experiments with some base oils aiming to estimate the content of some structural parameters, like the normal (NP) and isoparaffin (IP) contents, the number of branching sites (BS) and the average alkyl chain length (C^*). These base oils, produced from different treatments like hydrocracking and wax isomerisation, were hydrofinished-solvent-refined oils (HF) of high viscosity index (HVI), hydrofinished (SHF) oils of very high viscosity index (VHVI) and hydrotreated base oils (HT). It was verified that although the similarity between the types of branched structures produced by the hydrocracking and wax isomerisation, there were some differences especially in the obtained quantities.

Table 4
Some branched structures identified in base oils and their characteristic ^{13}C NMR chemical shifts. P = $-CH_3$, S = $-CH_2$ and * = carbons for which chemical shifts are reported [44].

Structure	Identification	Δ (ppm)
	S-1	14.0 (P)
	S-2	22.7 (P), 28.2 (S)
	S-3	11.4 (P)
	S-3′	10.7 (P)
	S-4	14.2 (P)
	S-5	14.3 (P)
	S-6	27.0 (S)
	S-7	27.0 (S)
	S-8	24.0–25.6 (S)
	S-9	16.2 (P)
	S-10	28.6, 27.4
	S-11	30.8 (P)

For example, the HT base oils presented more branched structures bearing methyl groups located at the fifth (or higher) carbon away from the end of the chain, but it did not have the contribution of some branched structures, like the S-8, and had a greater amount of S-3, S-4 and S-5 structures (Table 4). The HF and the SHF have more S-8 type branched structures and reduced amounts of S-3, S-4 and S-5 (Table 4). From the analysis of the ^{13}C NMR spectra, Sarpal et al. [44] could estimate the percentage of normal (29) and isoparaffin (30) contents. They concluded that the HT and SHF base oils presented an IP of 45–60% whereas the HF base oils presented a smaller amount of isoparaffins (30–40%). As it was intended, other structure parameters were also calculated such as the C^* (31), BS (24), t-Me (percentage of terminal methyl) (32) and the b-Me (percentage of branched methyl) (33). From these results it was possible to conclude that the HT and SHF base oils have a less average number of branching sites (BS) (3.0–3.5) compared with the HF base oil (3.5–5.5). It was also found that the HT base oils presented more branched paraffin structures than branching near terminal methyl groups (S-2, S-3 and S-4) compared with other oils (Table 4). It also had more predominance of S-6 and S-7 and less quantity of S-8 structures (Table 4). These last structures were found in a higher percentage in the HF and SHF oils. HT oils presented high quantity of branched structures, high quantity of isoparaffins, low quantity of BS, a lower pour point and a higher viscosity index. These results allowed to conclude that oils having structures with higher quantity of branching near the end of the chain present a lower pour point. It was also concluded that the HVI and VHVI base oils presented a higher quantity of branched structures near (S-2, S-3) and far (S-6, S-7) from the terminal carbon (Table 4). The VHVI oils had high quantity of NP and more S-6 and S-7 structures (Table 4) that contribute to the higher viscosity index. The LVI base oils presented a high number of branching sites, a high pour point and a lower viscosity index.

Very recently, Verdier et al. [12] used the ^{13}C NMR data of a broad variety of samples produced from different vacuum gas oils to analyze the molecules with high viscosity indexes (VI). They concluded that oils presenting molecules with long alkyl chains, low aromatic contents, ethyl branching and tertiary carbons presented high VI. Theoretically, the VI has been considered an important way to predict the influence of the temperature on the viscosity; being

Table 5
Assignment of ^{13}C NMR chemical shifts to different types of carbon atoms.

Chemical shift range (ppm)	Type of carbon atoms
202–220	Ketone carbonyl
182–170	Acid carboxyl
175–165	Ester or amide carboxyl
100–160	Aromatic carbon
149.2–158	Aromatic carbons attached to heteroatoms
137.2–149.2	Substituted carbons bonded to some alkyl groups (not include methyl and methylene bridge between aromatic rings)
128.5–160	Quaternary aromatic carbons without triple-bridged aromatic carbons
100–128.5	Tertiary aromatic and triple-bridged aromatic carbons
132.5–137.2	Substituted carbons bonded to methyl group or to cycloparaffinic α-CH_2
132.5	Naphthalene derivatives and methylated derivatives
129.2–132.5	Bridgehead aromatic carbons
115.0–129.2	Protonated aromatic carbon
5–10	Total Aliphatic carbon
25–60	Naphthenic carbon
29.1–31.5	Carbons in alkyl chains ($n > 6$)
27.6–28.6	Carbons in branching position of a terminal *iso*-propyl group
17.6–20.4	Carbons in CH_3 branches
13.7–15.5	Carbons in terminal position of n-alkyl chains ($n > 6$)
0–20.5	Total carbon in CH_3 groups

the viscosity of oils with a high VI slightly influenced by temperature. However, these authors [12] also indicate that it is not always correct to correlate the viscosity index with the influence of the temperature on the oils viscosity, being also important to analyze the effect of the activation energy. They had also announced that it is preferred to use the flow activation energy rather then the viscosity index to analyze the influence of the temperature on the oils viscosity.

Based on the results obtained by Yoshida et al. [41] and Behera et al. [5] it was possible to assign a range of chemical shifts to resonances of different carbon signals in the ^{13}C NMR spectra of crude oils (Table 5).

3.3. ^{1}H and ^{13}C NMR spectra of crude samples

Woods et al. [45] used NMR spectroscopy to characterized the SARA fractions (saturated, aromatics, resins and asphaltenes) separated from different Canadian crude oils. The assignment of different types of proton and carbon atoms in the ^{1}H and ^{13}C NMR spectra (Fig. 6) of SARA fractions led the authors [45] to conclude that the aromaticity region (110–150 ppm) increases from saturated to asphaltenes fractions. This was confirmed by the H/C ratio decreasing with the increasing of aromaticity. On the other hand the saturated fraction was characterized by an aliphatic nature represented with a high H/C ratio. It was also concluded that the aliphatic chain length increases from saturated < aromatics < resins < asphaltenes; becoming the asphaltenes rich in long chain aliphatic compounds.

Cookson and Smith [43] studied the monoaromatic fractions obtained from petroleum, coal and shale-derived distillate fuels with the purpose to get new structure information. With the obtained data it was possible to analyze some average structure parameters, such as NC (22), $N(CH_n)$ (average number of CH_n groups) (34), N_S (number side chains per molecule) (37), L_S (average side chain length) (36), N_{SB} (number of side chain per molecule) (38), N_R (number of rings) (27), H_{ar} (^{1}H NMR aromaticity) (35), and then conclude that all the analyzed diesel fuel had an average of 13–15 carbons atoms per molecule whereas the kerosene aromatics had a lower value (11–12 carbons atoms). Other similarities between all the seven diesel fractions were seen, such as the same number of side chains per molecule ($N_S = 3$), the same average side chain length ($L_S \approx 2.8$) (in only six of the samples) and the absence of quaternary carbon branching sites. One of the main differences between the samples was related to the number of ring structures involving aliphatic carbon atoms. The number of rings (N_R) observed for a specific fraction depends of the original sample; when a fraction is a product of hydro-treatment it has a large quantity of saturated ring structures. Kerosene samples compared with the diesel fractions presented a lower number of saturated rings per molecule and lower number of carbon atoms per molecule (NC). This could be due to the lower number of side chains and to the lower side chain length. From the ^{1}H and ^{13}C NMR spectra it was also possible to determine the average number of specific CH_m groups (α-CH_3 and γ-CH_3) per molecule. The assignment of proton resonances indicated that normally the intensity near 2.25 ppm region was due to α-CH_3, while for some samples that signal could be at 2.1–2.4 ppm. The intensity of these signals generally yields 0.1 or 0.14 α-CH_3 groups per molecule, depending on the spectra and on the occurring overlapping. In the ^{1}H NMR spectra, the signal at around 1 ppm was assumed to be due to the γ-CH_3 groups. In this work [43] it was also possible to identify some structures, like methyl, ethyl, propyl and butyl groups, tetralin, indane and 1-methylindane ring side chains in the analyzed samples of shale oil diesel.

Unlike the work of Cookson and Smith [43] and Bansal et al. [37], Lee and Glavincevski [7] decided to analyze the content of aromatics in middle distillate oils and have developed a NMR method for the determination of the molar content of aromatics. A new expression (4) was developed to estimate the number or mole fractions of carbons and protons of aromatic rings, α-CH_n protons, and the aromatic α-hydrogen to α-carbon ratio. However, these authors [7] have concluded that the presence of olefinic protons should be taken into account, therefore another expression (5) was used in the aromaticity calculation.

$$fA_m = \frac{1}{3}\left[\frac{H_\alpha}{(H/C)_\alpha} - 0.5C_{ar} + H_a\right] \quad (4)$$

$$f_a(\text{corrected}) = f_a - \frac{fH_n{}^\circ(H/C)_t}{(H/C)_o} \quad (5)$$

Sergeant et al. [46] used ^{1}H and ^{13}C NMR spectroscopy to analyze different products from shale deposits in Australia; being possible to obtained information about the diversity of structures composition of lubricating oils, of maltenes and of Rundle distillate. From the differences between these products, it is noteworthy that lubricating oils were characterized by the absence of olefinic structures, the Rundle distillate samples by the presence of monoaromatic with some polyaromatic and naphthenic structures, while the maltenes where characterized by the existences of some olefinic structures and aliphatic chains that were less substituted.

Recently, Andrade et al. [8] presented a review with 62 references on the determination of conjugated dienes in petroleum products using different chemical and instrumental techniques, including NMR spectroscopy. Among the implementation of different techniques analysis, these authors [8] indicated NMR as one of the chosen to characterized naphtha or gasoline samples with alcohol and to characterize conjugated dienes in the samples. NMR was considered one of the techniques which contributed to obtained rapid answers and information about the conjugated dienes composition.

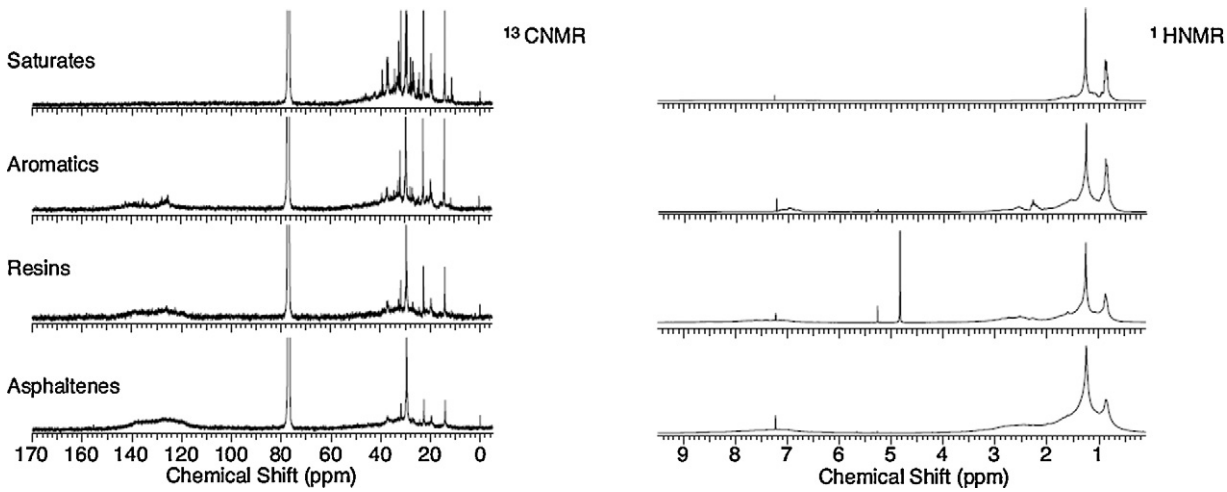


Fig. 6. Typical ^{13}C and ^{1}H NMR spectra for SARA fractions, obtained in a Varian Unity Inova 400 MHZ spectrometer with a 5 mm 4 nucleus probe. Reproduced with permission of Oil&Gas Science and Technology-Revue *d'IFP* Energies nouvelles.

3.4. Asphaltenes characterization

Asphaltenes present a dark colour and are defined as the fraction from crude oil that is soluble in toluene and insoluble in heptane. They are known to be the most complicated compounds in crude oil and are very difficult to analyze due to their tendency to associate, to the high molecular weight (approximately 1000 g mol^{-1}) [28] and to the paramagnetism [15]. Due to the their complex nature it has not been found a specific molecular structure or a specific family compounds of asphaltenes [13], however, there are different ideas relatively to their composition. Asphaltenes are characterized to be complex mixtures containing high quantity of heteroatoms (like nitrogen, oxygen and sulfur, and metals such as vanadium, nickel or iron) and condensed aromatic rings, aliphatic chains and naphthenic rings (Table 1).

The objective of several research groups is to gain more information about asphaltenes and to further understand their influence in thermal and catalytic processes.

Calemma et al. [47] compared the content of asphaltenes present in heavy crude oils of seven different sources and reported structural characterization of asphaltenes using NMR and other spectroscopic techniques. NMR techniques (^{13}C GASPE) allowed the identification of some CH groups in the aliphatic chains, some condensed alicyclic structures, especially in the more aliphatic asphaltene molecules, and the aliphatic CH_3/CH ratio. Furthermore it was possible to characterize the maturity of asphaltenes that is related to their capability to aggregate through π–π aromatic interactions. With the analysis of some molecular parameters from the NMR spectra, like the aromatic carbon fraction (f_a), an average number of carbon per alkyl side chain (n) and the percentage of aromatic rings substitution (C_S) it was possible to draw some conclusions. Almost all the analyzed asphaltenes presented comparable average aromatic condensations and average numbers of polycondensed aromatic rings in the range of 5–7. It was also possible to observe that asphaltenes presented different behaviours with the increase in the carbon content. As consequence, when the carbon content of the asphaltene samples increases, the aromaticity and the average aromatic core size increase, the average length of alkyl side chains decrease and the heteroatom content and the average molecular weights also decrease. Asphaltenes with smaller molecular weight presented more aromatic carbons, less heteroatoms, slightly sulfur, and smaller aliphatic side chains.

In the same path, Sheremata et al. [48] described a quantitative molecular representation of Athabasca asphaltenes where ^{1}H and ^{13}C NMR spectroscopy was used to provide data from elemental analysis. These authors [48] have pointed out that the combination of ^{1}H and ^{13}C NMR spectroscopy were very useful in the analysis of asphaltene chemistry and for an additional and better chemical detailed molecular structure description of these compounds. This study provided more information about aromatic and aliphatic primary structures, the concentration of quaternary and

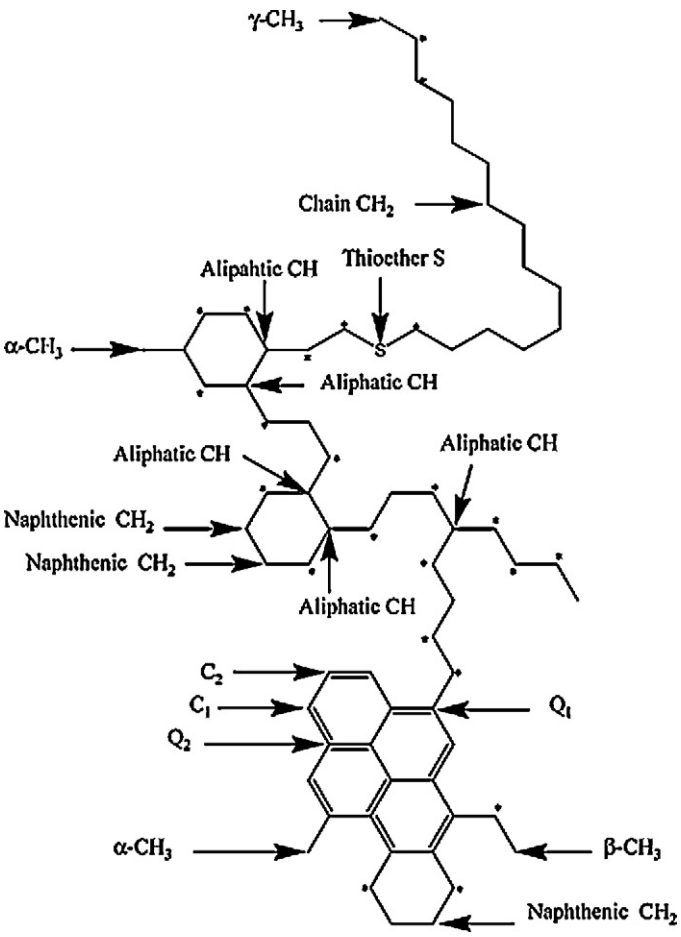


Fig. 7. Various aliphatic and aromatic carbons present in the asphaltene representation [48]. Q_1 = alkyl-substituted aromatic quaternary carbon. Q_2 = bridgehead aromatic quaternary carbon. C_1 = aromatic CH beside a Q_2 carbon. C_2 = all aromatic CH's that are not a C_1 carbon. * = other aliphatic carbons.

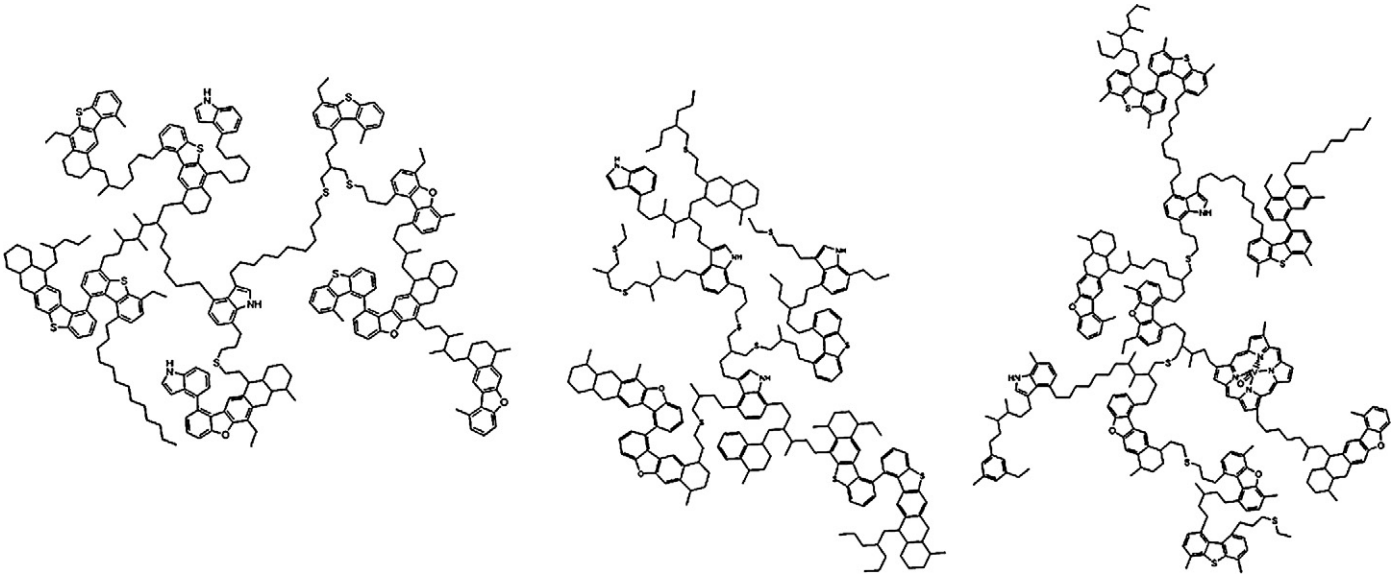


Fig. 8. Example of some asphaltene structures generated by using Monte Carlo method [48].

protonated aromatic carbons, the naphthenic content and the concentration of aliphatic CH and β-CH_3 groups (Fig. 7). Finally, three possible structures of asphaltenes, with multiple bridges between aromatic group were represented (Fig. 8). However, it was stated that these structures, as well as those denominated asphaltenes as archipelago structures, were not rigid and some changes can occur depending on the solvent environment. It is possible to exist interactions between the porous surface of asphaltenes and the surrounding solvent which has the capacity to entrain in the reticulated asphaltenes microstructure and change its geometry.

Douda et al. [49] analyze some asphaltene mixtures by comparing the asphaltenes fraction obtained after pyrolysis (at different temperatures) with the original ones, by using solution-state ^{1}H and ^{13}C NMR spectroscopy. The large bands of aromatic and saturated regions in the ^{1}H and ^{13}C NMR spectra were thought to be due to the high values of different structures of asphaltene compounds. From the obtained results it was concluded that pyrolysis processes at high temperatures were responsible for a higher formation of asphaltenes. This knowledge that temperature contributed to the asphaltenes modification are very important to the prevention of some problems during the crude oil refining, like the deposition of asphaltenes in cooking, cracking and in the distillation.

Durand et al. [38] presented for the first time a ^{1}H DOSY NMR spectrum of asphaltenes (Fig. 9), from which it was possible to concluded that asphaltenes have more aliphatic than aromatic structures. Although in this spectrum no aromatic protons were detected due to the influence of the toluene signals that have a high signal-to-noise ratio compared to the sample aromatic protons. However, a separation in the aromatic region exists and there are some aromatic protons, although these aromatic rings are very substituted by alkyl chains. Furthermore, it was calculated the diffusion coefficient of asphaltenes and toluene using the modified Stokes–Einstein equation and then compared them with the sample concentration. The intention was to analyze the intermolecular interactions between solvent and solute and their dependence with the solute concentration and also to analyze the behaviour of the diffusion coefficients, while increasing the sample concentration, which can give some information about the nature of the mixture constituents. The separation in the diffusion coefficient between residual heptane and asphaltenes was demonstrated (Fig. 9), and it was concluded that the diffusion coefficient remains constant at low concentrations, probably due to the predominance of the solute–solvent interactions. However, when the sample

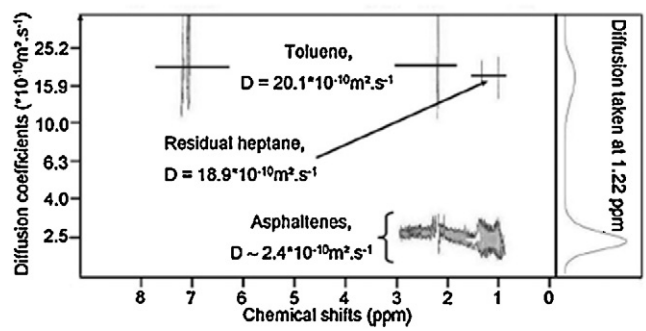


Fig. 9. ^{1}H DOSY NMR spectrum of asphaltenes in toluene and the projection of a diffusion spectrum taken at 1.22 ppm. A Varian INOVA Unity 600 narrow bore spectrometer with a Performa II gradient pulse amplifier and a triple resonance (HCN) proble was used. For the diffusion measurements the Doneshot sequence was used with a gradient pulse strength of 50 linear steps between 0 and 60 G cm^{-1}, with a 1.5–3.5 ms for gradient pulse duration and 0.08–0.5 s for the diffusion delay. A 90° pulse duration of 6.30 μs and a relaxation delay of 30 s were used. Reprinted with permission from [29].

concentration increased (more than 10 wt% in toluene) the self-diffusion coefficient decreased, showing that the solute–solvent interactions are not limited and more intermolecular interactions are involved. From the signals in the spectrum it was concluded that terminal CH_3 of long alkyl chains were represented by signals at 0.9 ppm while at 1–2 ppm some CH_2 groups were found and peaks at 2.1–3 ppm correspond to CH, CH_2 and CH_3 in polycyclic aromatic hydrocarbons. It was also calculated the average molecular weight of asphaltenes ($M \approx 3450$ g mol^{-1}), being this result higher than expected when comparing with the published value (approximately 1000 g mol^{-1}) [28].

3.5. NMR techniques

Being crude oil a complex mixture of compounds it is important to use different techniques to improve the quality of the NMR spectra and to obtain better quantitative information about the sample in analysis. For this, beyond the use of 1D NMR spectroscopy, the typical ^{1}H and ^{13}C NMR spectra, it is beneficial to use the "spectral editing" techniques and the 2D NMR experiments (Table 6). In the literature, depending on the object of the research, there are many works where 1D and 2D NMR spectra are used in

Table 6
Spectral editing NMR techniques.

		Advantages/Drawbacks	
GASPE	Gated spin echo	Information about carbon type distribution, distinguishing and isolating C, CH, CH_2 and CH_3 sub-spectra.	
PCSE	Part-coupled spin echo	Information about carbon type distribution, distinguishing and isolating C, CH, CH_2 and CH_3 sub-spectra.	
DEPT	Distortionless enhancement by polarization transfer	Better than GASPE and PCSE due to a precise and quick analysis of the CH and CH_3 sub-spectra. Quantifies CH, CH_2 and CH_3 carbons but not quaternary carbons.	
QUAT	Quaternary—only carbon spectra	Used to determine quaternary carbons.	
DOSY	Diffusion-ordered spectroscopy	One of the most commonly employed methods for identifying compounds in complex mixtures of petroleum fractions depending on different diffusion coefficients. Allows a better resolution of the signals and a better structure elucidation in both ^{1}H and ^{13}C NMR spectra. Although, when comparing with a ^{1}H–^{13}C HSQC or HMBC it presents very low resolution in the diffusion axis being for this an inferior method.	
INEPT	Insensitive enhancement by polarization transfer	Results of the excitation of ^{1}H and polarization transfer to ^{13}C by H–^{13}C coupling which contributes to the identification of CH_n groups but quaternary carbons are not identify in the INEPT spectra. The principal drawback is that the signal from each carbon is spread with many components resulting in the overlap of other carbon nuclei [63].	
2D HETCOR	Heteronuclear correlation spectroscopy	Correlation of the ^{1}H and ^{13}C NMR spectra, allowing a better interpretation of these spectra due to the identification of peak position. Is called a "direct" experiment because it is a way of doing ^{1}H–^{13}C correlation by direct detection of ^{13}C [64].	
2D COSY	Homonuclear correlation spectroscopy	Correlation between coupled protons NMR spectrum, allowing a better interpretation of the proton NMR spectrum due to the identification of peak position.	
2D TOCSY	Homonuclear total correlation spectroscopy	Allows to assign a whole spin system and contributes to the structure characterization of a molecule even in such complex mixtures as crude oils.	
HSQC	Heteronuclear single quantum correlation	Technique similar to HETCOR, called an "inverse" experiment due to ^{1}H being directly detected and ^{13}C being indirectly detected. It is used to detected carbon nuclei indirectly from more sensitive protons, to assigned side chain structures to aromatics [40] and to locate the position of a functional group within a known carbon skeleton [64].	The combination of HSQC and HMBC is, today, a powerful method used in tracing the carbon skeleton of a compound [64].
HMBC	Heteronuclear multiple quantum correlation	Technique also called an "inverse" experiment. It is used to detect indirectly quaternary and protonated carbons coupled to protons and providing unique information about the skeleton of a molecule [64].	
PFGSE	Pulse field gradient spin-echo	Characterized by introducing a perturbation in the magnetic field that propagates to the nearby protons. This perturbation only leaves the peak of interest and the rest of the peaks are destroyed [64]. This technique allows the measurement of asphaltenes diffusion coefficients.	
RELAY	Heteronuclear relayed coherence transfer	Gives information about coupled H_n–H_m groups and relates ^{13}C resonances associated with the CH_n and CH_m groups [43].	

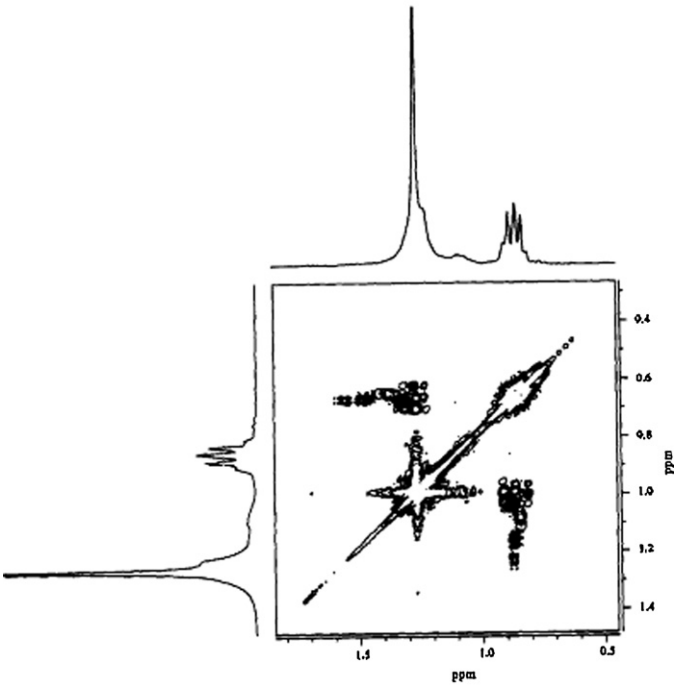


Fig. 10. Example of a COSY spectrum of a Base oil. Obtained using a 300 MHz spectrometer with a sweep width of 3016 Hz and 4 K data points.
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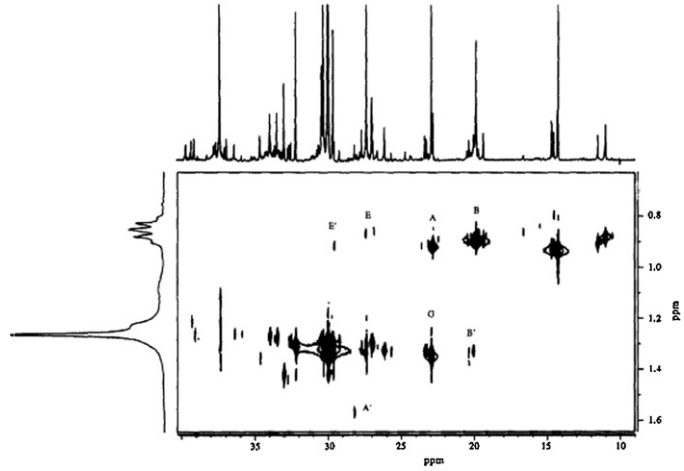

Fig. 11. Example of an HETCOR spectrum of a Base Oil, obtained in spectrometer operating a 300 MHz for ^{1}H and 75.4 MHz for ^{13}C. Main characteristic peaks: A and G = isopropyl methyl (δ 22.7 and 0.93 ppm) and β-methylene groups (δ 22.4 and 1.3 ppm) of S-2 of S-1 and S-2 structures, respectively. A′ = –CH resonance (S-2) at δ 28.2 ppm with a clear correlation peak. B and B′ = –CH_2 of S-4 at δ 20.3 ppm merged with the methyl groups (δ 19–21 ppm), well resolved in the second dimension. E (δ 28.6, 27.4 and 0.9 ppm) and E′ (δ 30.2 and 0.99 ppm) = branched methyls of structures S-10 and S-11. With S-1, S-2, S-4 and S-10 from Table 4.
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combination; not referring only to studies about heavy crude oil but in other different areas such as the Organic Chemistry and Biochemistry in mixture analysis of natural products [50–52] where the use of 2D NMR spectroscopy have demonstrated great potentialities in structural elucidation and quantification of complex mixtures.

The "spectral editing" [2] techniques can be used to improve the analysis of the ^{1}H and ^{13}C NMR spectra due to the overlapping of the signals, which make difficult the identification of some structures. The aim of these "spectral editing" techniques is to contribute to the separation of primary (CH_3), secondary (CH_2), tertiary (CH) and quaternary carbons (C_q) and to a sensitivity improvement. Examples of "spectral editing" techniques are the INEPT (insensitive enhancement by polarization transfer), DEPT (distortionless enhancement by polarization transfer), GASPE (gated spin echo), PCSE (part-coupled spin echo) and QUAT (quaternary—only carbon spectra). INEPT and DEPT are examples of methods also known as polarization transfer methods. The aim of these methods is to transfer the large excess population (polarization) of the ^{1}H to the insensitive nuclei before its perturbation (in the present case to ^{13}C nuclei). On the other hand, the 2D NMR spectra depend on the coupling between two nuclei. It is possible to have a 2D homonuclear spectra that result from the coupling between nuclei from the same type and the 2D heteronuclear spectra between nuclei from a different type. 2D COSY is an example of a homonuclear spectra (Fig. 10). In this spectra it is correlated one proton to another proton, depending on the coupling constant value, which leads to identify resonances that are coupled each other. Cookson and Smith [43], Sarpal et al. [53], and Behera et al. [5] are example of works, presented below, where this technique was used in the analysis of crude oils.

TOCSY (total correlation spectroscopy), another 2D homonuclear spectra, is very useful in the analysis of complex mixtures helping in the characterization of the molecule structure. In this case it is establish a correlation between all the spins in a set of coupled spins in a molecule. Doan et al. [3] has used these technique in the analysis of polyaromatics in crude gas oil mixtures.

HETCOR is a 2D heteronuclear spectrum (Fig. 11) where it is possible to obtain a correlation between coupled heteronuclear spins across a single bond. Cookson and Smith [43], Sarpal et al. [53] and Behera et al. [5] are examples of some works using the HETCOR technique in their research.

Besides the referred homo- and heteronuclear spectra there are the 2D inverse detected homo–heteronuclear experiments, although we will only describe the used in crude oil area, the heteronuclear ones [HSQC (heteronuclear single quantum correlation) and HMBC (heteronuclear multiple bond correlation) spectra (Fig. 12)]. In these techniques the ^{1}H magnetization is directly detected while the ^{13}C magnetization is indirectly detected being for this reason know as the "inverse" experiment. While the HETCOR, also a heteronuclear experiment, it is the "normal" one because in this case the ^{1}H magnetizations is indirectly detected and the ^{13}C directly. The "inverse" experiments are preferable over HETCOR, since the latter has lower sensitivity due to the detection of the lower nuclide, typically ^{13}C. HSQC correlates coupled heteronuclear spins across a single bond while HMBC correlates coupled spins across multiple bonds. Some workers have demonstrated that using HSQC and HMBC in combination is a very good choice when information about carbon skeleton is desirable. Kontogianni et al. [51], Exarchou et al. [52] and Behera et al. [5] are example of works using these techniques in the analysis of crude oils.

The DOSY (Diffusion Ordered Spectroscopy) spectrum (Fig. 9) is very useful to analyze the composition of mixtures based on the differences in diffusion coefficients of the individual components. This technique contributes to identify signals from one molecular species, to differentiate these signals from those of another molecular and with that analyze complex mixtures of petroleum fractions. Additionally, this separation can contribute to differentiate molecules taking into account the size, shape and even the physical properties of the surrounding environment [38,54].

It is not frequently to find researches where ^{14}N, ^{15}N, ^{33}S and ^{17}O NMR spectroscopy are used in the analysis of crude oil derivatives. Most of the investigations are done via ^{1}H and ^{13}C NMR,

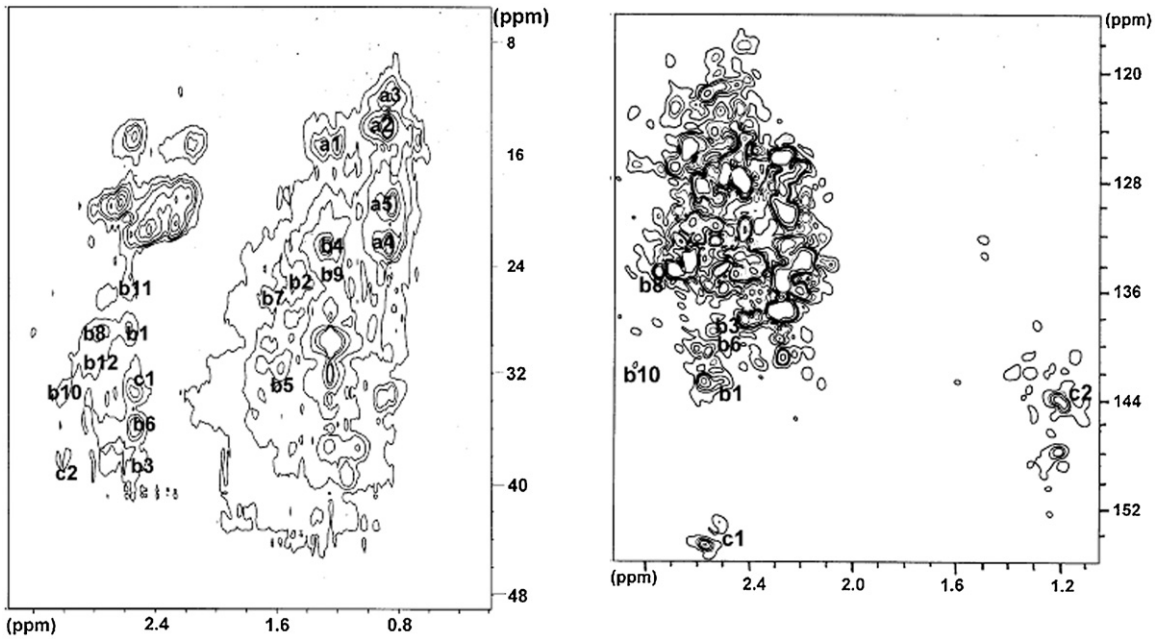

Fig. 12. Example of an (a) HSQC and an (b) HMBC spectra of an high boiling fraction VGO, identifying CH_3 (a), CH_2 (b) and CH (c) groups in different side chains – ethyl (a_1,b_1), propyl (a_2,b_2b_3), butyl (a_3,$b_4b_5b_6$), iso-propyl (a_4, c_1), tetraline (b_7b_8), indane (b_9b_{10}) and 1-methylindane (a_5,$b_{11}b_{12}c_2$). Obtained in a Bruker Avance 400 MHz equipped with an inverse detecting probe, using a $\pi/2$ pulses of 13.3 and 9.6 μs for ^{1}H and ^{13}C, respectively, a recycle delay of 2 s and 3 sine gradients of 1.5 ms with 8:3:2 ratio for HSQC and 5:3:4 ratio for HMBC.

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however, the use of different nuclides (nitrogen, sulfur and oxygen) may be a good choice when the concentration of acidic OH and basic N groups are desirable. It will be possible to identify some compounds as ethers, furans, secondary amines, thioethers and thiophenes [55]. Ethers are a way to identify oxygen bonds that may have some impact in some processes, such as desulfurization and denitrogenation.

In 1987, Cookson and Smith [43] used homonuclear 2D COSY spectra, coupled and decoupled 2D HETCOR spectra, and a RELAY 2D NMR method to provide a better analysis of the ^{1}H and ^{13}C NMR spectra and thus making a better structures assignment.

Sarpal et al. [53], in 1996, used GASPE, PCSE, INEPT, DEPT, QUAT, 2D COSY and HETCOR to classify the composition of some different base oils into the hydrocarbon types, especially the isoparaffins. 2D COSY and HETCOR helped to specifically improve the identification of some branching structures, because these spectra allow to clarify the existing information inside the overlapping signals. The use of DEPT also contributed to the improvement to solve the signals overlapping, especially in the region 28–40 ppm, as well as contributing to the separation of some carbons of normal paraffins, but did not give any idea about the existence of quaternary carbons, which could be due to the size of these structures. The use of 2D COSY and HETCOR contributed to the improvement in the identification and quantification of some types of branched structures (about eleven types of different branched structures).

Besides the techniques used by Sarpal et al. [53] it was already demonstrated that other techniques could contributed to the separation, assignment and identification of various signals in a crowded spectrum. Kapur et al. [54] showed, for the first time, that the 2D DOSY NMR spectroscopy is very useful in the interpretation of the ^{1}H and ^{13}C NMR spectra of such complex mixtures such as crude oil, which are characterized by a great signals overlapping making difficult the identification of some components. In the ^{1}H NMR spectra the overlapping occurs in the 0.5–2.0 ppm range due to the saturated components, whereas in the ^{13}C NMR the overlapping was stronger in the 10–45 ppm range. Using the DOSY spectra the characteristic overlapping of both ^{1}H and ^{13}C NMR spectra was reduced allowing a better resolution of the signals and a better structure elucidation, being this technique very helpful in the analysis of heavy petroleum fractions.

After Kapur et al. [54] used a DOSY technique in the analysis of an aromatic petroleum fraction, in the distillate boiling range, Durand et al. [38] presented a DOSY spectrum of a diesel sample and for the first time a ^{1}H DOSY spectrum of asphaltenes. These authors [38] confirmed that DOSY NMR technique is very important in the analysis of complex samples, such as crude oil, that could provided information on size, molecular weight, aggregation state and the composition of the mixture. The main advantage of this technique was the potential to give physical and chemical information all at once when compared to the pulse field gradient spin-echo NMR diffusion sequences (PFGSE NMR).

More recently, Behera et al. [5] used some NMR techniques, such as the gated-decoupled ^{13}C, DEPT, 2D (^{1}H–^{13}C) HETCOR and other 2D NMR methods for better identification of some structures in the very crowded NMR spectra of heavy petroleum fractions. For example, these authors [5] showed that HSQC and HMBC spectra were proven to be a better identification of side chain structures of aromatics.

3.6. NMR relaxation effects

The spin nuclear relaxation parameters are a very important way to obtain information about stereochemistry and molecular dynamics. This nuclear relaxation phenomenon is related with the structure, flexibility and molecular mobility that is responsible for the existent of different magnetic fields. The relaxation rate can be determined experimentally using the relationship between the relaxation times, T_1 and T_2, and the correlation time for molecular tumbling. The NMR techniques based on the analysis of T_1 (*longitudinal or spin-lattice relaxation time*) and T_2 (*transverse relaxation time*) decay curves can be obtained using the low-field ^{1}H NMR spectroscopy and correlate and supplemented with information taken with the high-field nuclear magnetic resonance.

The relaxation times are an important tool in the comprehension of the molecular structure; for example, when comparing two molecules if the relaxation time decreases it can be due to the existence of intramolecular hydrogen bonds that decrease the mobility. The low field ^{1}H NMR relaxation method has been used for a long time especially in petrophysical analysis and well logging in petroleum exploration [56]. Since 1990s, this method has been used in the characterization of reservoir properties (porosity, permeability, viscosity and saturation of oil and gas) [56].

The correlation of relaxation times (T_1 and T_2) with viscosity/temperature and Larmor frequency was analyzed by Hirasaki et al. [57]. These authors demonstrate that relaxation times T_1 and T_2 are equal, in crude oils, at low viscosity and can be correlated with the ratio of viscosity/temperature. However, for high viscosity crude oils T_1 and T_2 are different. T_1 is a function of the Larmor frequency while T_2 follow the viscosity/temperature correlation. They concluded that the temperature influences the viscosity as well as the relaxation time of heavy oils. In this work NMR was used to analyze the presence of water, oil and gas in the reservoirs of petroleum, taking into account the relationship between diffusivity and relaxation time. From the interpretation of the NMR logs it was concluded that water presented a large relaxation time, the fluids presented different diffusivity while crude oil presented a huge relaxation time and a large diffusivity distribution.

Ramos et al. [58] used T_2 of protons in the viscosity prediction of crude oils. The analysis of the expansion of the ^{1}H raw T_2 relaxation curves of four Brazilian crude oil samples with different viscosities has demonstrated that there was a decrease in the relaxation decay curve when the oil viscosity increased. Therefore, a shorter T_2 was produced for the sample with high viscosity. As a result, more viscous oil represents a lower relaxation time and less viscous oil has a larger relaxation time. In the crude oil, saturated fractions and resins are responsible for a higher contribution to the T_2 spectra, aromatics are responsible for a lower contribution while the asphaltene protons are less expressive in the T_2 spectra.

Yao et al. [56] used the low field NMR relaxation method to study the petrophysical properties of coals, such as the pore types, pore structures, porosity and permeability of coals. The interpretation of the spectra resulting from the decomposition of the dipole moment time evolution in the longitudinal (T_1) and relaxation (T_2) time distributions indicated that T_2 is faster and usually provide similar distribution to T_1 [56,59]. However, pore information could be obtained from T_1 and T_2 especially for low resonance frequency, pulse spacing and in the presence of relaxation mechanism as the bulk, diffusion and surface relaxations. The identification of pore types with the T_2 distribution indicated its relationship; smaller pores are associated with shorter relaxation times and larger pores are associated with longer relaxation time. NMR data of cores with 100% water-saturated and reduced water conditions were used to determinate the porosity. The permeability could not be directly measured by NMR, but can be estimated based on the porosity and the pore size distribution. Since the classic models (free fluid model or Coates and mean T_2 model or SDR), originally developed for sandstones, do not work well for low permeable coal, new NMR-based models has been proposed to estimate the permeability and the pore size distribution of coals. These new models prove that NMR is an important tool in the petrophysical characterization especially because it does not destroy the original pore structure.

3.7. Multivariate data analysis of a NMR spectra

Principal component analysis (PCA), partial least squares (PLS) and artificial neural networks (ANN) are important multivariate data analysis of several types of spectra and are very useful in the reliability, characterization, classification and prediction of the most important information contained in a data set. These techniques allow the construction of models that can predict macroscopic properties of mixtures of crude oil from NMR measurements [28].

Very briefly, PCA is a method of data analysis applied in contexts where there are several variables collected in each observation. The idea is to transform all these correlated variables into a reduced set of variables called the principal components. The main objectives of PCA are to reduce the size of the data and analyze the structure relationship between the variables and observations. PLS regression generates and combines characteristics from principal component analysis and multiple regression. PLS seeks to estimate the subspace that best explains the variability in the *Y*-axis, also describing the variability in the *X*-axis. The interpretation of PLS model allows the analysis of the relative importance of variables *X* in predicting *Y*. ANN regression is a mathematical model that contributes to simulate the structure and/or the functional aspects of the sample. They are usually associated with nodes or processing units and responsible to establish relationships between other units receiving inputs and sending outputs, finding some patterns in complex data sets.

Molina et al. [60,61] developed a new PLS based method contributing to the yield analysis and the principal physicochemical properties of a crude mixture. Taking into account some studied physicochemical properties, like the gravity values (°API), K_{UOP} factor, wax content, and correlation index (IC) it was confirmed the composition of the crudes study (paraffinic or aromatic) [60]. For example, the crude classified as the most paraffinic was characterized as presenting the highest value of °API and K_{UOP} factor, while the most aromatic one was characterized for having low values of °API and K_{UOP} factor. It was also observed that when the paraffinic hydrocarbons content decreased and the aromatic resins and asphaltenes contents increased, other properties' values increase such as the sulfur, nitrogen, vanadium and nickel content, the percentage of insolubles in nC_7 and nC_5 (% mass) and the percentage of micro-carbon residue (MCR). The studied crude, most naphthenic, has presented the lowest pour point and the highest acid number. The authors justified the achieved correlation between ^{1}H NMR spectrum and the content of vanadium and nickel by the PLS method probably due to the presence of paramagnetic metallic centers (for example vanadyl-porphyrins). These paramagnetic metallic centers in the molecules affect the chemical shifts of the entire ^{1}H NMR spectrum, the area of the spectrum of more distant protons and also the protons closest to the molecules, being the perturbation extended further than the molecules containing metallic centers. Using the PLS regression method and the ^{1}H NMR spectra of different crudes it was possible to meet the physicochemical properties and the refining product yields with a high precision.

Nielsen et al. [14] used multivariate data analysis in the study of different heavy crude oil fractions, aiming to identify physical and chemical properties. The physiochemical parameters analyzed were the carbon aromaticity index (CCAI), density at 15 °C, gross (GCV) and net calorific values (NCV), viscosity at 50 °C, ash content (ASH), total sediment accelerated (TSA), micro-carbon residue (MCR) plus aluminum, silicon, zinc and water contents. The obtained results, especially of density, showed that high aromatic content is associated with a high density while a high fraction of aliphatic compounds normally has a lower density. A higher aromatic content means a higher value of carbon aromaticity index (CCAI) of the sample. Relatively to the GCV, NCV and water content, which are very important parameters in the oil quality analysis, it was verified that they have a positive contribution for the signals at 1.5, 0.7 and 0.5 ppm and a negative contribution for the signal at 2.5 ppm in the ^{1}H NMR spectra. The MCR parameter, related with the oil stability, can be determined in the ^{1}H NMR spectrum by the signals at 4.7–6.2 ppm, having therefore a slighter contribution for the signals at 3.2–3.7 ppm and a negative effect for that at 1 ppm. The sulfur content can be determined by taking into account

the region between 2.1 and 3.0 ppm, while the water content is predicted near 4.5 ppm. The combination of the PLS and PCA techniques with the NMR spectroscopy have demonstrated, once again, to be very important in the analysis of physical and chemical properties on the heavy crude oil due to the facility, fast and reliable way to obtain this type of information.

Peinder et al. [4] analyzed the potential of PLS to predict long residue properties of crude oils, such as yield long-on-crude (YLC), density (D_{LR}), viscosity (V_{LR}), sulfur content (S), pour point (PP), asphaltenes (Asph) and carbon residue (CR). The results obtained with the multivariate analysis and the traditional methods like the ASTM and IP demonstrated the importance of the PLS modeling that gave valuable and fast results. In this research [4] ^{1}H and ^{13}C NMR spectra and also other spectroscopy technique (IR) were used, primary to the analysis of each single technique and then associated together, to determine the properties previously described. It was verified that a single spectrum from different techniques did not lead to any improvement in the results concerning the crude oil properties. The combination of the two techniques did not present additional information once the sample in the analysis was the same crude oil. However, each single spectrum was modeled by PCA model and then compared with the results of the PLS models with the single spectrum of each technique without the PCA method. With that it was concluded that modeling PCA scores instead of a spectra only contribute to a better results if the ^{13}C NMR spectroscopy was used.

In 1985, Kvalheim et al. [62] used PCA to help in the NMR interpretation of the crude oil naphtha fraction. The main idea was to analyzed samples of the same geographical area aiming to identify correlations between samples from the same source. It was found a dependence between the samples especially in the composition, for example in long chain versus short chain alkanes, branching, cyclization, and aromatization; being the main differences in the quantities of the different structures.

4. Conclusions

The preference of a method to analyze heavy crude oil depends especially on the nature of the sample and on the analysis purpose. In this review, NMR was chosen as the main technique to be used in crude oil refining industries that want to characterize the "messy" that describe the crude oil fractions and the obtained refined products. With all the references analyzed NMR in combination with multivariate data analysis has been proven to be a challenge technique in providing information about the physical and chemical properties and of the structure and chemical composition of crude oils in a short time. This information helped in the reduction of the transient periods of the units face to the disruption of the feeds, due to the variation of the crude, and to contribute to a rapid action in the downstream processes of the analyzed chains.

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